

QUALITY ASSURANCE PROJECT PLAN

**Former Willow Run Assembly Plant
Ypsilanti, Michigan**

**OCTOBER 13, 2006
REF. NO. 17303 (11)**

QUALITY ASSURANCE PROJECT PLAN (QAPP)

FORMER WILLOW RUN ASSEMBLY PLANT
(CURRENTLY WILLOW RUN BUSINESS CENTER AND COMPANY VEHICLE
OPERATIONS)
YPSILANTI, MICHIGAN

REVISION NUMBER 0
OCTOBER 13, 2006

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Prepared For: General Motors Corporation (GM)

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QUALITY ASSURANCE PROJECT PLAN (QAPP)

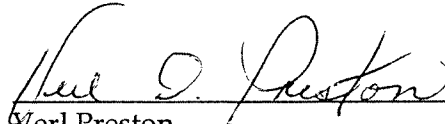
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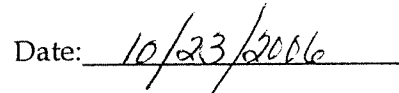


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1.0 PROJECT DESCRIPTION

The following outlines the scope of the continuing remedial investigation (RI) to be performed in accordance with the requirements of Conestoga-Rovers & Associates, Inc. (CRA) and General Motors Corporation (GM) for the Former Willow Run Assembly Plant (Site). The Site currently houses the Willow Run Business Center (WRBC) and Company Vehicle Operations (CVO).

This Quality Assurance Project Plan (QAPP) presents the organization, objectives, planned activities, and specific quality assurance / quality control (QA/QC) procedures associated with the RI for the Site. Protocols for sample collection, sample handling and storage, chain-of-custody procedures, and laboratory and field analyses are described or specifically referenced to related investigation documents.

This QAPP addresses the QA/QC elements in the U.S. EPA Region 5 QAPP policy presented in the "U. S. EPA RCRA QAPP Instructions" dated April 1998 and other relevant guidance documents. The QA/QC procedures described in this QAPP are generally consistent with U.S. EPA guidance.

1.1 INTRODUCTION

This QAPP has been prepared on behalf of GM by CRA in support of the RI activities at the Site.

1.1.1 PROJECT OBJECTIVES AND DECISION STATEMENT

The primary objectives for data collection activities include:

- i) Define the nature and extent of releases of hazardous wastes and/or hazardous constituents in environmental media (soil, sediment, groundwater, and/or surface water) at the Site; and
- ii) Collect sufficient data and information to evaluate the risk to human health and the environment, if any, associated with any releases of hazardous waste and/or hazardous constituents.

The Decision Statement for the investigation is as follows:

- i) Determine whether additional interim remedial actions are necessary to control current unacceptable risks, if any, to human health or the environment; and
- ii) Provide data for the development of a study of appropriate remedial actions (if warranted) to control current and future unacceptable risks to human health and the environment.

Associated specific objectives for field and laboratory data collection are discussed in Section 1.4 of this plan.

1.1.2 PROJECT STATUS/PHASE

The project status and investigation approach for CVO and WRBC are presented in various work plans associated with each portion of the Site. Additional work plans will be prepared as the preliminary site reconnaissance of the WRBC is completed. Section 1.2 summarizes the Site background, describes the potential areas of concern (PAOCs) to be investigated, and gives a brief description of each area and the proposed investigation for each PAOC at the Site (known/planned at the time this QAPP was prepared).

1.1.3 QAPP PREPARATION GUIDELINES

As previously noted, this QAPP has been prepared to present the project specific QA/QC elements in the "U.S. EPA Region 5 QAPP Instructions" dated April 1998.

1.2 SITE DESCRIPTION

The general Site description is provided and is incorporated here by reference to the following documents.

Documents of Existing Conditions (BBL, 1997)
Phase III EOC Work Plan and associated addenda (CRA, 2003 -2005)

1.3 SITE INVESTIGATION BACKGROUND

The Site investigation background is provided in the following documents and incorporated here by reference.

Documents of Existing Conditions (BBL, 1997)
Phase III EOC Work Plan and associated addenda (CRA, 2003 -2005)

1.4 PROJECT OBJECTIVES AND INTENDED DATA USE

1.4.1 TARGET PARAMETER LIST

The investigative program includes the sampling and analysis of environmental media for the presence of organic and inorganic constituents based on historical operations and previous investigations at the Site. The field and laboratory parameters are summarized below and presented in Table 1.1.

1.4.1.1 FIELD PARAMETERS

Concurrent with sample collection, several field parameters will be determined by the field sampling personnel. For soils and solid matrices, these field parameters will include visual observations, odor identification, and VOC screening using handheld monitoring equipment such as photo-ionization detectors (PID). For aqueous samples (surface water and groundwater), at a minimum, the following parameters will be determined with field testing equipment: pH, specific conductivity, and temperature. The low-flow purging techniques utilized for groundwater sampling, will include additional field parameters including turbidity, dissolved oxygen (DO), and oxidation/reduction potential (ORP).

1.4.1.2 LABORATORY PARAMETERS

The laboratory parameters for the investigative soil and groundwater samples will vary depending on the area and prior investigative results and may include target compound list (TCL) volatile organic compounds (VOCs), TCL semi-volatile organic compounds (SVOC),

TCL polychlorinated biphenyls (PCBs), and target analyte list (TAL) metals excluding earth metals (aluminum, calcium, iron, magnesium, potassium, and sodium). In addition to the TCL/TAL parameters, select samples may be analyzed for total and amenable cyanide, petroleum fingerprinting, hexavalent-chromium, fine/coarse grain lead, pH, and hardness. Non-aqueous phase liquid (NAPL) samples may also include analysis for petroleum fingerprinting, viscosity, specific gravity, and heating value. Waste samples will be analyzed for toxic characteristic leachate procedure (TCLP) VOC, TCLP SVOC, TCLP Metals, PCBs, ignitability and corrosivity. Groundwater wells monitored for natural attenuation may include sample analysis for total and dissolved manganese and iron, alkalinity, biochemical oxygen demand, chemical oxygen demand, nitrate-nitrogen, nitrite-nitrogen, sulfate, sulfide, total organic carbon and dissolved gases (methane, ethane, and ethene).

The estimated quantitation limits (EQL) and method detection limits (MDL) for each compound or analyte are presented in Table 1.2 – TCL/TAL and associated investigative parameters, Table 1.3 – waste characterization and NAPL parameters, Table 1.4 – air monitoring parameters, and Table 1.5 – natural attenuation monitoring parameters. The MDL studies have been performed by Severn Trent Laboratories, Inc. (STL) in accordance with the procedures established in the Federal Register, Volume 49, number 209, October 26, 1984 pp. 198-199, the results of these MDL studies are presented in Appendix D.

1.5 SAMPLING LOCATIONS

The work plans for CVO and WRBC provide summaries and rationale for the location of soil and groundwater samples within each PAOC at the Site. It is possible, however, that depending on the nature of encountered field conditions, sampling locations will vary. The person responsible for making such decisions will be the Field Quality Assurance (QA) Officer whose responsibilities are described in Section 2.0 of this QAPP. Any change of the sampling strategy will only be implemented after approval from the GM Project Manager.

1.6 PROJECT SCHEDULE

The schedule is presented in the work plans for CVO and WRBC.

2.0 **PROJECT ORGANIZATION AND RESPONSIBILITIES**

The CRA Project Manager will have the primary responsibility for the implementation and organization of the Phase III EOC Work Plan at the discretion of the GM Project Manager. STL will perform the analyses of environmental samples collected at the Site. This section defines the roles and responsibilities of the individuals who will perform the RI activities.

2.1 **MANAGEMENT RESPONSIBILITIES**

Management responsibilities are as follows:

Ken Richards – GM Project Manager

The GM Project Manager is responsible for authorizing the project, and has the authority to commit the resources necessary to meet project objectives and requirements. The GM Project Manager's primary function is to ensure that technical, financial, and scheduling objectives are achieved successfully. The GM Project Manager will provide the major point of contact and control matters concerning the project and represent the project team at regulatory agency meetings and public hearings. The Project Manager will define project objectives and develop a detailed project schedule in conjunction with the CRA Project Manager. The GM Project Manager will establish project policy and procedures to address the specific needs of the project as a whole, as well as the objectives of each task.

Frederick Blickle – CRA Project Manager

The CRA Project Manager is responsible for managing the implementation of the Site work plans and coordinating the collection of data pertaining to the investigation. The CRA Project Manager is responsible for technical quality control and project oversight. The CRA Project Manager also provides approval of the QAPP.

The CRA Project Manager will:

- i) Acquire and apply technical and other resources as needed to ensure performance within budget and schedule restraints;
- ii) Review work performed on each task to ensure quality, responsiveness, and timeliness;
- iii) Be responsible for the preparation and quality of interim and final reports; and
- iv) Communicate with GM/ENCORE about the progress of the project.

Beth Landale - CRA Project Coordinator

The CRA Project Coordinator will assist the Project Manager in day-to-day project management. The CRA Project Coordinator is responsible for coordinating all field activities and the procurement of project subcontractors. Additional responsibilities include:

- i) Assisting in monitoring the RI progress and quality;
- ii) Preparing and reviewing RI reports; and
- iii) Providing technical support of project activities.

2.2 QUALITY ASSURANCE RESPONSIBILITIES

The Quality Assurance team will consist of a Quality Assurance Officer and the Project Manager. Quality Assurance responsibilities are described as follows:

Paul Wiseman - CRA Quality Assurance (QA) Officer

The CRA QA Officer reports directly to the CRA Project Manager and will be responsible for ensuring that all QA/QC procedures are being followed. The CRA QA Officer will be responsible for overseeing the review of all field and laboratory data. Additional responsibilities include:

- i) Assuring the application and effectiveness of the QAPP by the analytical laboratory and the project staff;
- ii) Conducting internal QA/QC of the investigation activities;

- iii) Providing input to the CRA Project Manager and CRA Project Coordinator as to corrective actions required resulting from the above-mentioned evaluations;
- iv) Preparation and review of data validation and audit reports; and
- v) Approval of the QAPP.

The CRA QA Officer will be assisted by the data validation staff in the evaluation and validation of field and laboratory generated data. The CRA QA Officer will monitor the performance of the laboratory to ensure that the Data Quality Objectives for the project are met.

2.3 LABORATORY RESPONSIBILITIES

STL's North Canton, Ohio Laboratory (STL-North Canton) will provide laboratory services in support of the Site work plans with support from their facilities in Buffalo, New York (STL-Buffalo) and Knoxville, Tennessee (STL-Knoxville).

Denise Heckler - STL Project Manager

The Laboratory Project Manager will report directly to the CRA QA Officer and will be responsible for ensuring all resources of the laboratory are available on an as-required basis through coordination with the Operations Manager. The Laboratory Project Manager will also be responsible for the approval of the final analytical reports and approval of the laboratory's ability to adhere to the QAPP.

Ray Ridsen - STLNorth Canton Operations Manager**Robyn Wagner - STL-Knoxville Operations Manager**

John Schove - STL-Buffalo Operations Manager

The Laboratory Operations Manager will report to the Laboratory Project Manager and will be responsible for coordinating laboratory analysis, supervising in-house chain-of-custody reports, scheduling sample analyses, overseeing data review, and overseeing preparation of analytical reports.

Dorothy Leeson - STL-North Canton QA Officer**Chris Rigell - STL-Knoxville QA Officer**
Verl Preston - STL-Buffalo QA Officer

The Laboratory QA Officer is responsible for coordination and oversight of the laboratories quality assurance program which includes:

- i) Coordinate and oversee laboratory system audits;
- ii) Overview of QA/QC documentation;
- iii) Conduct detailed data review upon request;
- iv) Implement and document laboratory corrective actions, if required;
- v) Technical representation of laboratory QA procedures;
- vi) Oversee preparation of laboratory SOPs; and
- vii) Approval of the QAPP.

John McFadden - STL-North Canton Sample Custodian
Bryan Dameron - STL-Knoxville Sample Receiving Group Leader
Ken Kinecki - STL-Buffalo Sample Receiving Group Leader

The Laboratory Sample Receiving Group Leader will report to the Laboratory Operations Manager and will be responsible for the following:

- i) Receiving and inspecting the incoming sample containers;
- ii) Recording the condition of the incoming sample containers;
- iii) Signing appropriate documents;
- iv) Verifying chain-of-custody and its correctness;
- v) Notifying the Project Manager and Operations Manager of sample receipt and inspection;
- vi) Assigning a unique identification number and customer number, and entering each into the sample receiving log; and
- vii) Controlling and monitoring access/storage of samples and extracts.

Laboratory Technical Personnel

The laboratory technical staff will have the primary responsibility in the performance of sample analysis and the execution of the QA procedures developed to determine the data quality. These activities will include the proper preparation and analysis of the project

samples in accordance with the contract laboratory's Quality Assurance Manual and associated Standard Operating Procedures.

Data Validation Staff

The data validation staff will be independent of the laboratory and familiar with the analytical procedures performed. The validation will include a review of each validation criterion as prescribed by the guidelines presented in Section 9.2.2 of this document and be presented in a formal written report for submittal to the CRA Project Manager.

2.4 FIELD RESPONSIBILITIES

Beth Landale – CRA Field QA Officer

The Field QA Officer is responsible for the overall operation of the field team and reports directly to the and Project Manager. The Field QA Officer works with the project Health & Safety Officer to conduct operations in compliance with the project Health & Safety Plan. The Field QA Officer will facilitate communication and coordinate efforts between the Project Manager and the field team members. Other responsibilities include:

- i) Developing and implementing field-related work plans, ensuring schedule compliance, and adhering to management-developed project requirements;
- ii) Coordinating and managing field staff, including sampling and drilling;
- iii) Performing field system audits;
- iv) Overseeing quality control for technical data provided by the field staff;
- v) Preparing, and approving of text and graphics required for field team efforts;
- vi) Coordinating and overseeing technical efforts of subcontractors assisting the field team;
- vii) Identifying problems in the field, resolving difficulties in consultation with the CRA QA Officer and CRA Project Manager, implementing and documenting corrective action procedures;
- viii) Approving the QAPP; and
- ix) Participating in preparation of the final reports.

Field Team Personnel

Field Team Personnel involved in the RI will be responsible for:

- i) Performance of field activities as detailed in the Site work plans and in compliance with this QAPP; and
- ii) Immediately reporting any accidents and/or unsafe conditions to the Site Health & Safety Officer and taking all reasonable precautions to prevent injury.

3.0 QUALITY ASSURANCE OBJECTIVES FOR MEASUREMENT DATA

The Site work plans and associated QAPP are designed to produce data of the quality necessary to achieve the project objectives and meet or exceed the minimum standard requirements for field and analytical methods. The overall QA objective for measurement data is to develop and implement procedures for field sampling, chain-of-custody, lab analyses, and reporting that will provide results which are adequate for supporting the RI objectives and legally defensible in a court of law. The QAPP program will include:

- i) A mechanism for ongoing control of measurements and evaluation of data quality.
- ii) A measure of data quality in terms of precision, accuracy, representativeness, completeness, and comparability.

The following section is a general discussion of the criteria used to measure the field and laboratory analytical data quality. The laboratory reference data and standard operating procedures (SOPs) provided in Attachments 2 and 3, present the performance criteria for laboratory QC objectives.

3.1 PRECISION

3.1.1 DEFINITION

Precision is defined as a quantitative measure of the degree to which two or more measurements are in agreement. Precision will be stated in terms of relative percent difference (RPD). The overall precision of measurement data is a mixture of sampling and analytical factors. Precision will be determined by collecting and analyzing field duplicate samples and by creating and analyzing laboratory duplicates from one or more of the field samples. The analytical results from the field duplicate samples will provide data on sampling precision. The results from the laboratory created duplicate samples will provide data on analytical precision.

3.1.2 FIELD PRECISION SAMPLE OBJECTIVES

Field precision will be assessed through collection and measurement of field duplicates at a rate of 1 duplicate per 20 investigative samples.

3.1.3 LABORATORY PRECISION SAMPLE OBJECTIVES

Laboratory duplicate analyses will be performed through the use of matrix spike/matrix spike duplicates (MS/MSD) for organic parameters and matrix duplicate (MD) analyses for certain inorganic parameters. The analytical data will be presented in summary table format. The precision criteria for laboratory MS/MSD/MD analyses are provided in the laboratory reference data provided in Attachment 3.

3.2 ACCURACY

3.2.1 DEFINITION

Accuracy relates to the bias in a measurement system. Bias is the difference between the observed and the "true" value. Sources of error are the sampling process, field contamination, preservation techniques, sample handling, sample matrix, sample preparation and analytical procedure limitations.

3.2.2 FIELD ACCURACY OBJECTIVES

Sampling bias will be assessed by evaluating the results of field equipment rinsate and trip blanks. Field equipment rinsate and trip blanks will be collected as appropriate for each sampling effort.

Field equipment rinsate blanks will be collected by passing laboratory purified water over and/or through the respective field equipment utilized during each sampling effort. One rinsate blank will be collected every 20 investigative samples. However, at a minimum one equipment rinsate blank sample will be collected per day for each type of field equipment used for the sampling effort. Field rinsate blanks will be analyzed for each target parameter for the respective sampling effort for which environmental media have been collected.

(Note: If dedicated or disposable sampling equipment is used, equipment rinsate samples are not required as part of that field effort.)

Trip blank samples will be supplied by the laboratory and provided with each cooler that includes volatile organic compound (VOC) analysis containers. Trip blank samples will be analyzed for each VOC for which environmental media have been collected for analysis.

3.2.3 LABORATORY ACCURACY SAMPLE OBJECTIVES

Analytical bias will be assessed through the use of known laboratory control samples and site specific matrix spike sample analyses. Laboratory control samples (LCS) and MS/MSD sample analysis will be performed as prescribed by the analytical method SOPs. LCS analyses will be performed with each analytical batch of project samples to determine the accuracy of the analytical system.

One (1) set of MS/MSD analyses will be performed with each batch of 20 project samples to assess the accuracy of identification and quantification of analytes within the site-specific sample matrices. Additional sample volume will be collected at sample locations selected for MS/MSD analyses so that MDLs and EQLs can be met.

The results of the LCS and MS/MSD analyses will be presented in a summary table reporting format and evaluated versus the acceptance criteria presented in the laboratory analytical reports. Current acceptance criteria are presented in the laboratory reference data provided in Attachment 3.

The accuracy of organic parameter analyses is also monitored through the analysis of system monitoring or surrogate compounds. Surrogate compounds are added to each sample, standard, blank, and QC samples prior to the sample preparation and analysis. Surrogate compound percent recoveries provide information on the effect of the sample matrix on the accuracy of the analyses and are evaluated against the acceptance criteria presented in laboratory analytical reports. Current acceptance criteria are presented in the laboratory reference data provided in Attachment 3.

3.3 REPRESENTATIVENESS

3.3.1 DEFINITION

Representativeness expresses the degree to which sample data accurately and precisely represents a characteristic of a population, a parameter variation at a sampling point, or an environmental condition. Representativeness is a qualitative parameter that is dependent upon the design of the sampling program. The representativeness criterion is satisfied by proper selection of sampling locations and quantity of samples collected.

3.3.2 MEASURES TO ENSURE REPRESENTATIVENESS OF FIELD DATA

Representativeness will be addressed by describing sampling techniques and the rationale used to select sampling locations. Sampling locations may be biased (based on existing data, instrument surveys, observations, etc.) or unbiased (completely random or stratified-random approaches).

For this project, sampling will be biased; that is, sampling associated with the soil and groundwater will be based on the observed presence/absence of site specific contaminants, and/or site knowledge. Specific sampling technique descriptions, which allow consistency, repetitiveness and thus representativeness, are provided in ENCORE Field Method Guidelines (FMG).

3.3.3 MEASURES TO ENSURE REPRESENTATIVENESS OF LABORATORY DATA

Representativeness in the laboratory is ensured by using proper analytical procedures, and analyzing field duplicate samples. By definition, field duplicate samples are collected to be representative of a given point in space and time. Thus, sample duplicates provide both precision and representativeness information.

3.4 COMPLETENESS

3.4.1 DEFINITION

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

3.4.2 FIELD COMPLETENESS OBJECTIVES

Completeness is a measure of the amount of valid measurements obtained from all measurements taken in this project. Field completeness objective for this project will be 90 percent.

3.4.3 LABORATORY COMPLETENESS OBJECTIVES

Laboratory data completeness objective is a measure of the amount of valid data obtained from all laboratory measurements. The evaluation of the data completeness will be performed at the conclusion of each sampling and analysis effort. Corrective actions such as revised sample handling procedures will be implemented if problems are noted.

The completeness of the data generated will be determined by comparing the amount of valid data, based on independent validation, with the total data set. The completeness objective will be 90 percent.

3.5 COMPARABILITY

3.5.1 DEFINITION

Comparability is a qualitative parameter expressing the confidence with which one data set can be compared with another.

3.5.2 MEASURES TO ENSURE COMPARABILITY OF FIELD DATA

Sample data should be comparable with other measurement data for similar samples and sample conditions. This goal is achieved through using standard operating procedures to collect, preserve, store, and analyze representative samples and the reporting of analytical results. The ENCORE FMG for the various activities to be conducted during this investigation provide guidelines to generate reproducible results.

3.5.3 MEASURES TO ENSURE COMPARABILITY OF LABORATORY DATA

Comparability of laboratory data will also be measured with the results from the analysis of reference materials traceable to standards from accredited suppliers for instrument initial and continuing calibration verification. The reported analytical data will be presented in standard units of mass of contaminant within a known volume or mass of environmental media.

- i) Solid Matrices - micrograms (μg) contaminant per kilogram (kg) for organic analyses, and milligrams (mg) contaminant per kilogram (kg) for inorganic analyses of media (Dry Weight).
- ii) Aqueous Matrices - micrograms (μg) contaminant per liter (L) of media for organic analyses, and milligrams (mg) per liter (L) for inorganic analyses.
- iii) Non-Aqueous Phase Liquids - (NAPL) - micrograms (μg) contaminant per kilogram (kg) of media.
- iv) Gaseous Matrices - micrograms (μg) contaminant per cubic meter (M^3) of media

Additional guidance on analytical data reporting is contained in the laboratory SOPs.

3.6 LEVEL OF QUALITY CONTROL EFFORT

Equipment rinsate, trip, and method blanks samples, field duplicate samples, laboratory control and MS/MSD samples will be prepared and analyzed to determine the data quality provided by the sampling and analysis activities conducted during the execution of the RI program.

Equipment rinsate blanks will be prepared by field personnel and submitted for analysis of target parameters. Equipment rinsate blanks will provide the means to assess the quality of data resulting from the field program. Equipment rinsate blank samples will be analyzed to check for contamination of equipment introduced during sampling at the Site. One equipment rinsate blank will be collected for every 20 investigative samples. However, a minimum of one will be collected each day of sampling activities for each type of non-dedicated or non-disposable equipment.

Trip blanks are used to assess the potential for contamination during sample storage and shipment. The trip blank consists of laboratory purified water (water samples) or methanol (soil samples) provided with the sample containers to be used for the sampling of VOCs. Trip blanks will be preserved and handled in the same manner as the investigation samples. One trip blank will be included along with each shipment cooler containing project samples to be analyzed for VOCs.

Method blank samples will be prepared by the laboratory and analyzed concurrently with all project samples to assess potential contamination introduced during the analytical process.

Field duplicate samples are analyzed to check for sampling and analytical reproducibility. One field duplicate will be collected for every 20 or fewer investigative samples collected per day of sampling activities.

Matrix spikes will provide information to assess the precision and accuracy of the analysis of the target parameters within the environmental media collected at the Site. Matrix spikes will be performed in duplicate for all TCL/TAL parameters. One MS/MSD will be collected for every 20 or fewer investigative samples per sample matrix (i.e. soil, groundwater). Soil MS/MSD samples requires a triple sample volume for VOCs only. Aqueous MS/MSD samples require triple the normal sample volume for VOCs analysis and double the volume for the remaining parameters.

4.0 SAMPLING PROCEDURES

Samples of groundwater, surface water, soil, soil gas and sediment will be obtained during the RI program. The sampling procedures for the RI will be consistent for the objectives of the project. The Site work plans describe each of the sampling tasks and objectives.

Refer to the FMGs for the field investigation standard operating procedures.

4.1 SAMPLE CONTAINERS

Sample containers for each sampling task will be provided by the project laboratory. The containers will be cleaned by the manufacturer to meet or exceed the analyte specifications established in the U.S. EPA, "Specifications and Guidance for Obtaining Contaminant-Free Sample Containers", April 1992, OSWER Directive #9240.0-0.5A. Certificates of analysis for each lot of sample containers used during the RI will be maintained by the laboratory and will be available upon request.

The appropriate sample containers, preservation method, maximum holding times, and shipping information for each target parameter and sampling task are provided in Table 4.1.

4.2 SAMPLE LABELING

Each sample will be labeled with a unique sample number that will facilitate tracking and cross-referencing of sample information. Field blank and field duplicate samples also will be numbered with a unique sample number to prevent analytical bias of field QC samples.

Refer to the FMGs for the sample labeling procedures.

4.3 FIELD QC SAMPLE COLLECTION

4.3.1 EQUIPMENT RINSATE BLANK SAMPLE COLLECTION

Equipment rinsate blank samples will be collected when non-dedicated or non-disposable sampling equipment is used to collect samples. Equipment rinsate blanks consist of

laboratory purified water that has been routed through decontaminated sampling equipment and collected into the appropriate containers. The containers will be filled in order of decreasing analyte volatility (i.e., VOCs first, SVOCs second, which are followed by the containers for the remaining analyses).

4.3.2 FIELD DUPLICATE SAMPLE COLLECTION

4.3.2.1 WATER SAMPLES

Field duplicate samples will be collected concurrently with the investigative sample alternating the filling of each sample container using the procedures identified in the FMGs.

4.3.2.2 SOIL AND SEDIMENT SAMPLES

Soil and sediment field duplicates will be collected concurrently with the investigative sample using the procedures identified in the FMGs.

4.3.3 MS/MSD SAMPLE COLLECTION

MS/MSD sample collection for aqueous samples requires triple the sample volume for VOC analysis and double the volume for all remaining parameters. The sampling procedure specified in Section 4.3.2.1 is used to collect aqueous samples. Soil MS/MSD samples require triple volume for VOC analyses. No additional volume is required for remaining soil parameters. Section 4.3.2.2 describes the sampling procedures for soil sample collection.

5.0 **CUSTODY PROCEDURES**

Custody is one of several factors necessary for the admissibility of environmental data as evidence in a court of law. Custody procedures help to satisfy the two major requirements for admissibility: relevance and authenticity. Sample custody is addressed in three parts: field sample collection, laboratory analysis, and final evidence files. Final evidence files, including all originals of laboratory reports, are maintained under document control in a secure area.

Custody of a sample begins when it is collected by or transferred to an individual and ends when that individual relinquishes or disposes of the sample. A sample or evidence file is under your custody if:

1. the item is in actual possession of a person;
2. the item is in the view of the person after being in actual possession of the person;
3. the item was in actual possession but is stored to prevent tampering; or
4. the item is in a designated and identified secure area.

5.1 **FIELD CUSTODY PROCEDURES**

Field personnel will be required to keep written records of field activities on applicable preprinted field forms or in a bound field notebook. The logbooks provide the means of recording data collecting activities. These records will be written legibly in ink and will contain pertinent field data and observations. Entry errors or changes will be crossed out with a single line, dated and initialed by the person making the correction. Field forms and notebooks will be periodically reviewed by the Field QA Officer. Each member of the field team will be assigned a logbook. Each logbook title page should include field team member's name, project name, project start date, project end date, and unique logbook number.

The beginning of each entry in the logbook will contain the following information:

- i) Date,

- ii) Start ,time
- iii) Weather,
- iv) Names of field personnel (including subcontractors),
- v) Level of personal protection used at the Site, and
- vi) Names of all visitors and the purpose of their visit.

For each measurement and sample collected the following will be recorded:

- i) Detailed description of sample point,
- ii) Equipment used to collect sample or make measurement and the date equipment was last calibrated,
- iii) Time sample was collected,
- iv) Sample description,
- v) Depth sample was collected,
- vi) Volume and number of containers, and
- vii) Sampler identification.

5.1.1 FIELD PROCEDURES

The data quality can be affected by sample collection activities. If the integrity of collected samples is questionable, the data, regardless of its analytical quality, will also be questionable.

The following procedure describes the process to maintain the integrity of the samples:

- i) Upon collection samples are placed in the proper containers. In general, samples collected for organic analysis will be placed in pre-cleaned glass containers, and samples collected for inorganic analysis will be placed in pre-cleaned plastic (polyethylene) bottles. The sample container, preservation methods, shipping, and packaging requirements are presented in Table 4.1.
- ii) Samples will be assigned a unique sample number and will be affixed to a sample label. The information to be placed on the sample label will include the sample ID number, the sample type, the sampler's name, date collected, preservation technique, and analytical parameter and method to be performed. Information on the labels will be completed with a ballpoint pen or indelible marker.

- iii) Samples will be collected in appropriately laboratory preserved sample containers by field personnel in order to minimize loss of the constituent(s) of interest due to physical, chemical or biological mechanisms.
- iv) Appropriate volumes will be collected to ensure that the EQLs can be successfully achieved and that the required QC Sample Analyses can be completed.

5.1.2 TRANSFER OF CUSTODY AND SHIPMENT PROCEDURES

- i) A chain-of-custody (COC) record will be completed during sample collection and will accompany each shipment identifying the contents of the shipment. The COC record will accompany the samples to the laboratory. The field personnel collecting the samples will be responsible for the custody of the samples until the samples are relinquished to the laboratory. Sample transfer will require the individuals relinquishing and receiving the samples to sign, date and note the time of sample transfer on the COC record. As few people as possible should handle the samples.
- ii) Samples will be shipped or delivered in a timely fashion to the laboratory so that holding-times and/or analysis times as prescribed by the methodology can be met.
- iii) Samples will also be transported in containers (coolers) packed with ice to maintain the temperatures prescribed in Table 4.1. Samples will be packaged for shipment and shipped to the appropriate laboratory for analysis with a separate signed chain-of-custody record enclosed in each sample cooler. VOC samples will be placed in bubble wrap bags or foam sleeves. The remaining samples in glass containers will be wrapped in bubble wrap and placed in the sample cooler. Samples in polyethylene containers will be placed upright directly in the sample cooler. All samples will be placed in an upright position and limited to one layer of samples per each cooler. Additional bubble wrap or packaging material will be added to fill the cooler. Shipping containers will be secured with strapping tape and custody tape for shipment to the laboratory.
- iv) When samples are split with the Agency and Site representatives, a separate chain-of-custody will be prepared for the samples and marked to indicate to whom the

- samples are being split. The person relinquishing the samples to the Agency or the Site will require the representatives signature acknowledging sample receipt.
- v) If samples are sent by a commercial carrier, a bill of lading will be used. A copy of the bill of lading will be retained as part of permanent documentation. Commercial carriers are not required to sign the custody record as long as the custody record is sealed inside the sample cooler and the custody tape remains intact.
 - vi) Samples will be picked up by a laboratory courier or transported overnight by a courier to the laboratory the same day they are collected unless collected on a weekend or holiday. In these cases, the samples will be stored in a secure location until delivery to the lab. Additional ice will be added to the cooler as needed to maintain proper preservation temperatures.

5.2 LABORATORY CHAIN-OF-CUSTODY PROCEDURES

A full-time sample receiving group leader supervises the sample receiving group who are assigned the responsibility of sample control. It will be the responsibility of the sample receiving group leader to receive all incoming samples. Once received, the receiving group leader will document that the custody tape on the coolers is unbroken, that each sample is received in good condition (i.e., unbroken, cooled, etc.), that the associated paperwork, such as chain-of-custody forms have been completed and will sign the chain-of-custody forms. In special cases, the receiving group leader will document from appropriate sub-samples that chain-of-custody with proper preservation has been accomplished. The receiving group leader will also document that sufficient sample volume has been received to complete the analytical program. The sample receiving group leader will then place the samples into secure, limited access storage (refrigerated storage, if required). The sample receiving group leader will assign a unique number to each incoming sample for use in the laboratory. The unique number will then be entered into the sample-receiving log. The laboratory date of receipt will also be noted.

Consistent with the analyses requested on the chain-of-custody form, analyses by the laboratory's analysts will begin in accordance with the appropriate methodologies. Samples will be removed from secure storage only after internal chain-of-custody sign-out procedures have been followed.

5.3 STORAGE OF SAMPLES

Sample containers with volume remaining will be returned to secure and limited access storage. Upon completion of all laboratory analyses for each sample submittal and generation of the laboratory report, samples will be stored by the sample receiving group leader. The length of time that samples are held will be at least thirty (30) days after reports have been submitted. Disposal of remaining samples will be completed in compliance with all Federal, State, and local requirements.

Laboratory custody procedures and document control for those samples analyzed by the project laboratory will be carried out using the laboratory's standard operating procedures.

5.4 FINAL PROJECT FILES CUSTODY PROCEDURES

The final project file will be the central repository for all documents with information relevant to sampling and analysis activities as described in this QAPP. The Project Manager will be the receiving group leader of the project file. The project files for the RI, including all relevant records, reports, logs, field notebooks, pictures, subcontractor reports, and data reviews will be maintained in a secured, limited access area and under custody of the CRA Project Manager or his designee.

The final project file will include:

- i) Project plans and drawings;
- ii) Field data records;
- iii) Sample identification documents and soil boring/ monitoring well logs;
- iv) All chain-of-custody documentation;
- v) Correspondence;
- vi) References, literature;
- vii) Laboratory data deliverables;
- viii) Data validation and assessment reports;
- ix) Progress reports, QA reports; and
- x) Final report.

The laboratory will be responsible for maintaining analytical logbooks, laboratory data and sample chain of custody documents. Raw laboratory data files and copies of hard copy

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reports will be inventoried and maintained by the laboratory for a period of five (5) years at which time the laboratory will contact CRA regarding the disposition of the project related files

6.0 CALIBRATION PROCEDURES AND FREQUENCY

This section describes procedures for maintaining the accuracy for all the instruments and measurement equipment, which will be used for conducting field tests and laboratory analyses. These instruments and equipment will be calibrated prior to each use or according to a periodic schedule.

6.1 FIELD INSTRUMENT CALIBRATION PROCEDURES

Instruments and equipment used to gather, generate, or measure environmental data will be calibrated as specified in the ENCORE FMG.

The field instruments are likely to include water quality multi-meters capable of measuring pH, temperature, specific conductivity, turbidity, DO, and ORP or individual meters capable of measuring these parameters separately measuring and PIDs. Field instruments will be used for real-time sample measurement during monitoring well sampling and organics screening for both on-site screening of soil samples and for health and safety air monitoring, as described in the HASP. On-site air monitoring for health and safety purposes and the screening of soil samples may be accomplished using PIDs.

Field instruments will be calibrated prior to use and the calibration will be verified on a daily basis. Specific information concerning calibration frequency, acceptance criteria, and the conditions that require more frequent calibration is contained in the ENCORE FMG in Attachment 1.

Satisfactory completion of the pre-operation inspection will be noted on the Field Sampling Record, along with the results of each field measurement.

6.2 LABORATORY INSTRUMENT CALIBRATION PROCEDURES

Calibration procedures for a specific laboratory instrument will consist of initial calibration, initial calibration verification and continuing calibration verification. The SOPs in Attachment 2 present the specific calibration procedures for each method of analysis. The SOP for each analysis performed in the laboratory describes the calibration procedures, their frequency, acceptance criteria and the conditions that will require calibration. In all

cases, the initial calibration will be verified using an independently prepared calibration verification solution.

The use of materials of known purity and quality will be utilized for the analysis of environmental samples. The laboratory will carefully monitor the use of all laboratory materials including solutions, standards and reagents through well-documented procedures.

All solid chemicals and acids/bases used by the laboratory will be reagent grade or better. All gases will be high purity or better. All Standard Reference Materials (SRMs) or Performance Testing (PT) Materials will be obtained from approved vendors of the National Institute of Standards and Technology (NIST), or the National Environmental Laboratory Accreditation Program (NELAP) accredited supplier.

All materials including standards or standard solutions will be dated upon receipt, and will be identified by material name, lot number, purity or concentration, supplier, receipt/preparation date, recipient/preparer's name, expiration date and all other pertinent information.

7.0 ANALYTICAL PROCEDURES

Analytical procedures to be utilized for off-Site analysis of environmental samples will be based on referenced U.S. EPA analytical protocols and the laboratory SOPs that implement these methods. These project specific SOPs are provided in Attachment 2 to this QAPP.

7.1 FIELD ANALYTICAL PROCEDURES

Field analytical procedures include the measurement of pH/temperature, specific conductivity, turbidity, DO, and ORP during sampling of groundwater, and the qualitative measurement of VOC with PIDs during the collection of soil samples at the Site. Specific guidance in the measurement of these parameters is presented in the ENCORE FMG provided in Attachment 1 of this QAPP.

7.2 LABORATORY ANALYTICAL PROCEDURES

Laboratory preparation and analytical SOPs and the methods upon which they are based are presented in Table 7.1. The referenced SOPs provided in Attachment 2 of this document are based on the U.S. EPA methodology requirements published in:

- i) "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods", SW-846 EPA, U.S. EPA office of Solid Waste, 3rd Edition and promulgated updates, 1986;
- ii) "Methods for Chemical Analysis of Water and Wastes", EPA-600/4-79-020, March 1983,
- iii) "Standard Methods for Examination of Water and Wastewater", APHA, AWWA & WEF, 19th Edition, 1995, and;
- iv) "Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air", EPA-625/R-96/10b, January 1999.

The EQLs for the target analytes and compounds for the environmental media to be analyzed as part of the investigation are presented in Table 1.2, Table 1.3, Table 1.4, and Table 1.5.

7.2.1 LIST OF PROJECT TARGET COMPOUNDS AND LABORATORY DETECTION LIMITS

A complete listing of project target compounds and project EQLs for each analyte group are listed in Table 1.2, Table 1.3, Table 1.4, and Table 1.5. MDLs have been experimentally determined by the project laboratory using the procedure identified in 40 CFR, Part 136 Appendix B. The laboratory's MDLs are provided in Attachment 3.

7.2.2 LIST OF METHOD SPECIFIC QUALITY CONTROL (QC) CRITERIA

The laboratory SOPs include a section that presents the minimum QC requirements for the project analyses. Section 8.0 references the frequency of the associated QC samples for each sampling effort and matrix.

8.0 INTERNAL QUALITY CONTROL CHECKS

This section presents the internal quality control checks that will be employed for field and laboratory measurements.

8.1 FIELD QUALITY CONTROL

QC procedures for pH/temperature, specific conductivity, turbidity, DO, and ORP of water samples and PID screening soil samples will include calibrating the instruments as described in Section 6.1 of this QAPP, measuring duplicate samples and checking the reproducibility of the measurements by taking multiple readings on a single sample or the measurement reference standards. The QC information for field equipment is stated in Section 3.0 of this QAPP. Assessment of field sampling precision and bias will be made by collecting field duplicates and equipment rinsate blanks for laboratory analysis. Collection of the samples will be in accordance with the applicable procedures in Section 4.3 of this QAPP.

8.1.1 EQUIPMENT RINSATE BLANKS

Internal quality control checks will include analysis of equipment rinsate blanks to validate successful equipment cleaning activities. Whenever possible, dedicated equipment will be employed to reduce the possibility of cross-contamination of samples.

The frequency of equipment rinsate blank sample preparation will be one for every 20 investigative samples. However, at a minimum, one will be collected each day for each type of sampling equipment on which decontamination procedures have been performed.

8.1.2 TRIP BLANKS

Trip blanks samples will be supplied by the project laboratory using laboratory purchased purified water for water samples and purge and trap grade methanol for soil samples placed within pre-cleaned 40 milliliter (ml) VOC vials equipped with teflon septa. Trip blanks will accompany each sample delivery group (SDG) of environmental samples collected for analysis of VOCs.

Appropriate trip blank samples will be placed in each cooler which stores and transports project samples to be analyzed for VOCs along with the project samples by matrix.

8.1.3 FIELD DUPLICATE SAMPLES

Field duplicate samples are collected in a similar fashion to investigative samples at a minimum frequency of one duplicate per at least one in every 20 or fewer investigative samples by matrix at a minimum, one per sampling event. Field duplicate samples are analyzed by the laboratory to evaluate matrix, sample and analytical reproducibility.

8.2 LABORATORY PROCEDURES

The laboratories identified in Section 7.0 of this QAPP have QC programs to ensure the reliability and validity of the analysis performed at the laboratory. All analytical procedures are documented in writing as SOPs and each SOP includes a QC section, which addresses the minimum QC requirements for the procedure. The internal quality control checks may vary slightly for each individual procedure but in general will include the following QC requirements:

- i) Calibration Standards;
- ii) Instrument Performance Checks – Organics;
- iii) Initial and Continuing Calibration Checks;
- iv) Internal Standard Performance;
- v) Method Blank Samples;
- vi) Laboratory Control Samples and QC Check Samples;
- vii) Matrix Spike/Matrix Spike Duplicates;
- viii) Surrogates;
- ix) ICP Interference Check Samples (ICS);
- x) ICP Serial Dilution;
- xi) ICP and ICP/MS QC Analyses;
- xii) Reagent Checks; and
- xiii) Blind Check Samples.

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All data will be properly recorded. The data package will include a summary of QC data as presented in Section 9.3.2. Any samples analyzed in nonconformance with QC criteria will be re-analyzed as defined in the SOPs by the laboratory, if sufficient volume is available.

9.0 DATA REDUCTION, VALIDATION AND REPORTING

All data generated through in field activities or by the laboratory operation shall be reduced and validated prior to reporting in accordance with the following procedures:

9.1 DATA REDUCTION

9.1.1 FIELD DATA REDUCTION PROCEDURES

Field data reduction procedures will be minimal in scope compared to those implemented in the laboratory setting. Only direct read instrumentation will be employed in the field. The pH, conductivity, temperature, turbidity, DO, ORP and PID readings collected in the field will be generated from direct read instruments following calibration per manufacturer's recommendations. Such data will be written into field logbooks immediately after measurements are taken. If errors are made, results will be legibly crossed out, initialed and dated by the field member, and corrected in a space adjacent to the original entry. Later, when the results forms required for this study are being filled out, the Project Coordinator or designee will proof the forms to determine whether any transcription errors have been made by the field crew.

9.1.2 LABORATORY DATA REDUCTION PROCEDURES

For this project, the equations that will be employed in reducing data are found in the appropriate chapter of SW-846, Third Edition. Two of these equations, expressing analytical accuracy and precision, are presented in Section 3 of this QAPP. Such formulae make pertinent allowances for matrix type. All calculations are checked at the conclusion of each operating day. Errors are noted; corrections are made, but the original notations are crossed out legibly. Analytical results for soil samples shall be calculated and reported on a dry weight basis.

Quality control data (e.g., laboratory duplicates, surrogates, matrix spikes, and matrix spike duplicates) will be compared to the method acceptance criteria. Data considered to be acceptable will be entered into the laboratory computer system. Data summaries will be sent to the Laboratory QA Officer for review. If approved, data are logged into the project database format. Unacceptable data shall be appropriately qualified in the project report.

Case narratives will be prepared which will include information concerning data that fell outside acceptance limits and any other anomalous conditions encountered during sample analysis.

9.2 DATA VALIDATION

Data validation procedures shall be performed for both field and laboratory operations as described below:

9.2.1 PROCEDURES USED TO EVALUATE FIELD DATA

Procedures to evaluate field data for this project will include review of field logbooks and checking for transcription errors to project specific documents. This task will be the responsibility of the Field QA Officer or designee.

9.2.2 PROCEDURES TO VALIDATE LABORATORY DATA

The CRA QA Officer or designee will perform analytical data validation using the following documents as guidance for the review process.

"U.S. EPA Contract Laboratory Program National Functional Guidelines for Organic Data Review", EPA-540/R-99/008, October 1999 and the "U.S. EPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review ", EPA-540/R-94-013, February 1994.

The specific data qualifiers used will be as presented and defined in the CLP National Functional Guidelines. A reduced data review and validation will be performed on all investigative samples (waste characterization samples will not be validated) that will consist of the following components:

- i) Technical holding times;
- ii) method, trip and field blanks;
- iii) system monitoring compounds (surrogate spikes organics);
- iv) MS/MSD/MD results; and

- v) LCS/LCD results.

The data validator will evaluate the completeness of each data package. Completeness checks will be administered on all data to determine whether deliverables specified in the QAPP are present. At a minimum, deliverables will include sample chain-of-custody forms, analytical results, QC summaries and supporting raw data from instrument printouts. The review will determine whether all required items are present and request copies of missing deliverables.

9.3 DATA REPORTING

Data reporting procedures shall be carried out for field and laboratory operations as indicated below:

9.3.1 FIELD DATA REPORTING

Field data reporting shall be conducted principally through the transmission of report sheets containing tabulated results of all measurements made in the field and documentation of all field calibration activities.

9.3.2 LABORATORY DATA REPORTING

The laboratory data reporting package will be sufficient to perform a data validation in accordance with protocols described in Section 9.2.2. The task of reporting laboratory data by GM will be initiated after the completion of data validation.

The laboratory Project Manager will perform a final review of the QC data summary packages and case narratives to determine whether the report meets the project requirements. In addition to the record of the chain-of-custody, the final laboratory data report format shall consist of the following.

- i) Title Page
- project name and number;
 - laboratory project or lot number;

- signature of the Laboratory QA Officer or his designee; and
 - date issued.
- ii) Table of Contents - laboratory report contents
- iii) Case Narrative
- number of samples and respective matrices;
 - laboratory analysis performed;
 - any deviations from intended analytical strategy;
 - definition of data qualifiers used;
 - QC procedures utilized and references to the acceptance criteria;
 - condition of samples "as received";
 - discussion of whether or not sample holding times were met;
 - discussion of technical problems or other observations which may have created analytical difficulties; and
 - discussion of laboratory QC checks which failed to meet project criteria.
- iv) Analytical Methods Summary - methods of sample preparation and analyses for samples.
- v) Analytical Sample Summary - cross-reference table of laboratory sample to project sample identification numbers.
- vi) Shipping and Receiving Documents
- sample container documentation; and
 - sample reception information and original chain of custody record.
- vii) Chemistry Data Package by Analysis
- Sample Results
 - sample quantitation (report) limits (RL), reporting MDL and estimated values between the RL and MDL,
 - methods of sample preparation and analyses for samples;
 - QC Summary Data with Current Control Limits
 - matrix spike and matrix spike duplicate recoveries, laboratory control samples, method blank results, surrogate recoveries (inorganics),

Note: Only the TCL parameter list identified in Table 1.2 shall be included in the laboratory chromatographic quantitation reports.

The project laboratory will provide electronic data deliverables (EDDs) in an EQUiS® 4-file format. The laboratory data will be downloaded into the EDDs directly from the laboratory information management system (LIMS). The EDDs are imported into EQUiS and the data are maintained in the database for manipulation and presentation in accordance with the project Data Management Plan (DMP).

The CRA QA Officer will verify the correctness of the analytical database by comparing the data from the database to the hardcopy analytical reports for a minimum of 10 percent of the sample results. If discrepancies between the database and hardcopy analytical reports are detected, a complete verification of the database will be performed.

10.0 PERFORMANCE AND SYSTEM AUDITS

A performance audit is an independently obtained quantitative comparison with data routinely obtained in the field or the laboratory. Performance audits include two separate, independent parts: internal and external audits.

10.1 FIELD PERFORMANCE AND SYSTEM AUDITS

10.1.1 INTERNAL FIELD AUDIT RESPONSIBILITIES

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

- i) Field sampling records, screening results, instrument operating records;
- ii) Sample collection;
- iii) Handling and packaging in compliance with procedures;
- iv) Maintenance of QA procedures; and
- v) Chain-of-custody reports.

Follow up audits will be conducted to correct deficiencies and to verify that procedures are maintained throughout the investigation. The field audit checklist is included in Appendix 4.

10.1.2 EXTERNAL FIELD AUDIT RESPONSIBILITIES

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

- i) Sampling equipment decontamination procedures;
- ii) Sample bottle preparation procedures;

- iii) Sampling procedures;
- iv) Examination of health and safety plans;
- v) Procedures for verification of field duplicates; and
- vi) Field screening practices.

10.2 LABORATORY PERFORMANCE AND SYSTEM AUDITS

10.2.1 INTERNAL LABORATORY AUDIT RESPONSIBILITIES

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

The system audit will include an examination of laboratory documentation including: sample receiving logs, sample storage, chain-of-custody procedures, sample preparation and analysis, and instrument operating records.

The performance audits will include submittal of blind performance evaluation samples along with project samples. The Laboratory QA Officer will evaluate the analytical results to ensure the lab is maintaining acceptable QC performance. The laboratory audit checklist is provided in Attachment 5.

System audits, as opposed to performance audits, are strictly qualitative and consist of an on-site review of a laboratory's quality assurance system and physical facilities for calibration and measurement.

At the conclusion of internal or external system audits, reports are provided to the laboratory's operating divisions for appropriate comment and remedial/corrective action where necessary. Written response to internal as well as external audits will be required. Records of audits and corrective actions are maintained by the Laboratory QA Officer.

10.2.2 EXTERNAL LABORATORY AUDIT RESPONSIBILITIES

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

External audits may include any of the following:

- i) Review of laboratory analytical procedures;
- ii) Laboratory on-site visits; and
- iii) Submission of performance evaluation samples for analysis.

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

- i) Sample receipt procedures;
- ii) Custody, sample security, and log-in procedures;
- iii) Review of instrument calibration logs;
- iv) Review of QA procedures;
- v) Review of log books;
- vi) Review of analytical SOPs; and
- vii) Personnel interviews.

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

- i) Comparison of resulting data to the SOP or method;
- ii) Verification of initial and continuing calibrations within control limits;
- iii) Verification of surrogate recoveries and instrument timing results;
- iv) Review of extended quantitation reports for comparisons of library spectra to instrument spectra, where applicable; and
- v) Assurance that samples are run within holding times.

11.0 PREVENTATIVE MAINTENANCE

11.1 FIELD INSTRUMENT PREVENTATIVE MAINTENANCE

The field equipment preventative maintenance program ensures the effective completion of the sampling effort and is designed to minimize equipment down time. Program implementation is concentrated in three areas:

- Maintenance responsibilities.
- Maintenance schedules.
- Inventory of critical spare parts and equipment.

The maintenance responsibilities for field equipment will be assigned to the task leaders in charge of specific field operations. Field personnel will be responsible for daily field checks and calibrations and for reporting any problems with the equipment. The maintenance schedule will follow the manufacturer's recommendations. In addition, the field personnel will be responsible for determining that critical spare parts are included with the field equipment. An adequate inventory of spare parts will be maintained. The inventory will primarily contain parts that are subject to frequent failure, have limited useful lifetimes and/or cannot be obtained in a timely manner.

11.2 LABORATORY INSTRUMENT PREVENTATIVE MAINTENANCE

Analytical instruments at the laboratory will undergo routine and/or preventative maintenance. The extent of the preventative maintenance will be a function of the complexity of the equipment.

Generally, annual preventative maintenance service will involve cleaning, adjusting, inspecting and testing procedures designed to deduce instrument failure and/or extend useful instrument life. Between visits, routine operator maintenance and cleaning will be performed according to manufacturer's specifications by laboratory personnel.

Maintenance records will be placed on file at the laboratory and can be made available upon request.

12.0 SPECIFIC ROUTINE PROCEDURES USED TO ASSESS DATA PRECISION, ACCURACY, AND COMPLETENESS

The following sections include the procedures and formulae utilized to assess the levels of precision, accuracy and completeness achieved during the associated sample analyses.

12.1 FIELD MEASUREMENTS

Field generated information such as pH and specific conductance data will be reviewed for validity. The review will be performed by the Field QA Officer or designee and typically include bound logbooks/forms, data entry and calculation checks. Field data will be assessed by the Project Field QA Officer or designee who will review the field results for compliance with the established QC criteria that are specified in Section 3.0 of this QAPP. The accuracy of the field measurements will be assessed using daily instrument calibration, calibration check, and blank data. Accuracy will be measured by determining the percent recovery of calibration check standards as defined in Section 12.2.2. Precision of the field measurements will be assessed on the basis of the reproducibility of duplicate readings of a single sample and will be measured by determining the relative percent difference of the readings as defined in Section 12.2.1. Accuracy and precision of the soil VOC screening will be determined using duplicate readings of calibration checks. Field data completeness will be calculated using the following equation:

$$\text{Completeness} = \frac{\text{Valid (usable) Data Obtained}}{\text{Total Data Planned}} \times 100$$

12.2 LABORATORY DATA

Laboratory results will be assessed for compliance with required precision, accuracy and completeness detailed in the following subsections:

12.2.1 PRECISION

The precision of laboratory analysis will be assessed by comparing the analytical results between MS/MSD analyses. The relative percent difference (RPD) will be calculated for each pair of duplicate analyses (laboratory MS/MSDs and field duplicates).

12.2.2 ACCURACY

The accuracy of laboratory results will be assessed for compliance with the established QC criteria that are described in Sections 3.0 and 8.0 of the QAPP using the analytical results of method blanks, reagent/preparation blank, SRMs or QC check samples and MS/MSD samples. The percent recovery (%R) of matrix spike samples and SRMs will be calculated.

12.2.3 COMPLETENESS

Completeness will be assessed by comparing the number of valid (usable) results (as determined by the QA Officer) to the total possible number of results using the formula presented in Section 12.1.

12.3 STATISTICAL EVALUATIONS

In the examination of data and determination of their precision and accuracy, standard statistical formulae will be used. Further details are provided in the following subsections.

12.3.1 PERCENT RECOVERY

The percent recovery of a parameter is calculated by dividing the amount recovered by the true amount added and multiplying by 100. The percent recoveries of spiked samples are evaluated to establish the analytical accuracy of a measurement. Percent recovery is calculated using the following formula:

$$\%R = \frac{SSR - SR}{SA} \times 100$$

where:

SSR = Spiked Sample Result
SR = Sample Result or Background
SA = Spike Added

12.3.2 RELATIVE PERCENT DIFFERENCE

The relative percent difference (RPD) is calculated by dividing the absolute value of the difference between two numbers by their arithmetic mean and multiplying by 100. The RPD is used to evaluate the analytical precision of two replicate measurements (e.g., matrix spike/ matrix spike duplicate). RPD is calculated using the following formula:

$$\text{RPD} = \frac{(R_1 - R_2)}{R_1 + R_2} \times 200$$

where:

R₁ = value of first result
R₂ = value of second result

13.0 CORRECTIVE ACTION

13.1 FIELD CORRECTIVE ACTION

Corrective action is intended to address problems that arise by identification, recommendation, approval, and implementation of measures that counter unacceptable procedures or deficient quality control performance. The Field QA Officer and CRA QA Officer will be responsible for ensuring the quality of the sampling procedures and environmental data and as such, will be responsible for initiating corrective action when appropriate.

The corrective action procedures will be as follows:

- i) Identify/define the problem.
- ii) Assign responsibility for investigating the problem.
- iii) Investigate/determine the cause of the problem.
- iv) Determine an appropriate corrective action to eliminate the problem.
- v) Implement the corrective action.
- vi) Evaluate the effectiveness of the corrective action.
- vii) Verify that the corrective action has eliminated the problem.
- viii) Prepare a written record detailing the problem, corrective action utilized, and solution of the problem.
- ix) Submit the Corrective Action Record (CAR) to the Task Coordinator who initiated the corrective action and the Project QA Officer, and Project Manager.

The above procedures may be implemented through the use of the Systems Audit as described previously. Any Field Team member of the project may initiate corrective action procedures by reporting in writing the nature of the suspected problem to the CRA Project Manager or CRA QA Officer. The CRA Project Manager will begin corrective action by relating the problem to appropriate personnel.

13.2 LABORATORY CORRECTIVE ACTION

The following paragraphs define the corrective action decision process relative to possible non-compliant events encountered during laboratory analysis of the project samples. Corrective actions will be initiated by the laboratory QA personnel and will be implemented

by laboratory staff chemists under the oversight of the laboratory QA personnel. As with field corrective actions, the laboratory QA personnel will document the problem, the corrective action undertaken and the resolution of the problem. The corrective actions will be performed prior to release of the data from the laboratory.

Documentation will be provided to the laboratory QA Officer, CRA QA Officer, CRA Project Manager and GM Project Manager.

13.3 CORRECTIVE ACTION DURING DATA VALIDATION AND DATA ASSESSMENT

The CRA QA Officer may identify the need for corrective action during either the data validation or data assessment processes. Potential types of corrective action may include re-sampling by the field team or re-injection/reanalysis of samples by the laboratory (if possible).

These actions are dependent upon the ability to mobilize the field team, whether the data to be collected is necessary to meet the required quality assurance objectives (e.g., the holding time for samples is not exceeded). When the CRA QA Officer identifies a corrective action situation, GM Project Manager will be responsible for approving the implementation of corrective action, including re-sampling, during data assessment. All corrective actions will be documented by the CRA Project Manager.

14.0 QUALITY ASSURANCE (QA) REPORTS

Critically important to the successful implementation of the QA Plan is a reporting system that provides the means by which the program can be reviewed, problems identified and programmatic changes made to improve the plan.

QA reports to management include:

- Audit reports, internal and external audits with responses
- Performance evaluation sample results; internal and external sources
- Daily QA/QC exception reports/corrective actions

QA/QC corrective action reports will be prepared by the CRA QA Officer when appropriate and presented to the project and/or laboratory management personnel so that performance criteria can be monitored for all analyses from each analytical department. The updated trend/QA charts prepared by the laboratory QA personnel will be distributed and reviewed by various levels of the laboratory management.

15.0 REFERENCES

1. United States Environmental Protection Agency, (1999). EPA Requirements for Quality Assurance Project Plans for Environmental Data Operations. EPA QA/R-5 Interim Final, November 1999.
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3. United States Environmental Protection Agency (1991). Preparation Aids for the Development of Category I Quality Assurance Project Plans. U.S. EPA/600/8-91/003, Risk Reduction Engineering Laboratory, Office of Research and Development, Cincinnati, Ohio, February 1991.
4. United States Environmental Protection Agency, (1993). Data Quality Objectives Process for Superfund Interim Final Guidance. U.S. EPA/540/R-93-071, Office of Solid Waste and Emergency Response (OSWER), September 1993.
5. United States Environmental Protection Agency, (1992). Specifications and Guidance for Contaminant-Free Sample Containers. OSWER Directive 9240.0-05A, April 1992.
6. United States Environmental Protection Agency. U.S. EPA Contract Laboratory Program National Functional Guidelines for Organic Data Review. U.S. EPA 540/R-99-012.
7. United States Environmental Protection Agency. U.S. EPA Contract Laboratory Program National Functional Guidelines for Organic Data Review. U.S. EPA 540/R-94-013.
8. United States Environmental Protection Agency. Test Methods for Evaluating Solid Waste, Office of Solid Waste, U.S. EPA, SW-846, November 1986, with updates.

TABLE 1.1

SUMMARY OF SAMPLING AND ANALYSIS PROGRAM
REMEDIAL INVESTIGATION ACTIVITIES
FORMER WILLOW RUN ASSEMBLY PLANT
YPSILANTI, MICHIGAN

Activity/Description	Sample Matrix	Field Parameters	Potential Laboratory Parameters	Investigative Samples	Quality Control Samples (1)		
					Field Blanks (2)	Field Duplicates	MS/MSD LCS/LCD (3) Total
Soil Investigation	Soil	PID VOC Screen	TCL VOC, TCL SVOC, TCL PCB, Site TAL Metals (4), Total Cyanide, Fractionated Lead, Hexavalent/Trivalent Chromium	TBD	1/20	1/20	1/20 (5)
Groundwater Monitoring	Groundwater	pH/Temperature, DO, Specific Conductivity, Turbidity, ORP	TCL VOC, TCL SVOC, TCL PCB, Site TAL Metals (4), Amenable Cyanide, Hexavalent/Trivalent Chromium	TBD	1/20	1/20	1/20 (5)
Natural Attenuation Monitoring	Groundwater	pH/Temperature, DO, Specific Conductivity, Turbidity, ORP	TCL VOC, Total and Dissolved Metals (6), Alkalinity, BOD, COD, Dissolved Gases, Nitrate, Nitrite, Sulfate, Sulfide, TOC, Select Metals (7), Hexavalent/Trivalent Chromium	TBD	1/20	1/20	1/20 (5)
Waste Characterization	Soil	n/a	TCLP VOC, TCLP SVOC, TCLP Metals, TCL PCB, Corrosivity, Ignitability	TBD	--	--	-- (5)
	Water	n/a	TCLP VOC, TCLP SVOC, TCLP Metals, TCL PCB, Corrosivity, Ignitability	TBD	--	--	-- (5)
	NAPL	n/a	TCLP VOC, TCLP SVOC, TCLP Metals, TCL PCB, Corrosivity, Ignitability	TBD	--	--	-- (5)
NAPL Characterization	NAPL	n/a	TCL VOC, TCL SVOC, TCL PCB, Site TAL Metals (4) Specific gravity, viscosity, Flashpoint, Fingerprinting	TBD	--	--	-- (5)

TABLE 1.1

**SUMMARY OF SAMPLING AND ANALYSIS PROGRAM
REMEDIAL INVESTIGATION ACTIVITIES
FORMER WILLOW RUN ASSEMBLY PLANT
YPSILANTI, MICHIGAN**

Activity/Description	Sample Matrix	Field Parameters	Potential Laboratory Parameters	Investigative Samples	Quality Control Samples (1)		
					Field Blanks (2)	Field Duplicates	MS/MSD LCS/LCD (3)
Surface Water Investigation	Surface Water	pH/Temperature, Specific Conductivity	Hardness, pH	TBD	1/20	1/20	1/20
Sewer Investigation	Waste Water	pH/Temperature, Specific Conductivity	TCL VOC, TCL SVOC, TCL PCB, Site TAL Metals (4), Hexavalent/Trivalent Chromium, Amenable Cyanide	TBD	1/20	1/20	1/20
Sediment Investigation	Sediment	PID VOC Screen	TCL VOC, TCL SVOC, TCL PCB, Site TAL Metals (4)	TBD	1/20	1/20	1/20
Soil Gas Sampling and Ambient Air Sampling	Air	None	TCL VOC	TBD	0	1/20	1/20

Notes:

- (1) - A laboratory trip blank will be submitted with each shipment of samples for TCL VOC analysis.
 (2) - Field blank samples will not be required if dedicated or disposable sampling equipment is used.
 (3) - Matrix Spike/Matrix Spike duplicate (MS/MSD) analyses are required for samples submitted for organic and inorganic analyses, Laboratory Control Samples/Laboratory Control Duplicates analyses are required for air samples and water samples without adequate volume for MS/MSDs. These are to be analyzed at a frequency of one per group of twenty (20) or fewer investigative samples.
 (4) - Site TAL Metals includes the TAL Metals excluding Aluminum, Calcium, Iron, Magnesium, Potassium and Sodium.
 (5) - The frequency of Field Blanks and Field Duplicates will be one per 20 investigative samples and will be combined from multiple PAOC.
 The total sample quantity will vary depending on which PAOC the QC samples are collected from.
 (6) - Total and Dissolved Metals within the natural attenuation monitoring include Manganese and Iron.
 (7) - Select Metals include Arsenic, Chromium, and Sodium.

PID = Photo-Ionization Detector
 VOC = Volatile Organic Compounds
 TCL = Target Compound List
 PCB = Polychlorinated Biphenyls

SVOC = Semi-volatile Organic Compounds
 TAL = Target Analyte List
 BOD = Biochemical Oxygen Demand
 COD = Chemical Oxygen Demand

DO = Dissolved Oxygen
 ORP = Oxidation-Reduction Potential
 TCLP = Toxicity Characteristic Leaching Procedure
 TBD = To be determined

RI TARGET COMPOUND AND TARGET ANALYTE PARAMETER LIST
 REMEDIAL INVESTIGATION ACTIVITIES
 FORMER WILLOW RUN ASSEMBLY PLANT
 YPSILANTI, MICHIGAN

Compound	<i>Estimated</i> <i>Quantitation Limits (EQL) ¹</i>			<i>Method</i> <i>Detection Limits (MDL) ²</i>		
	<i>Water</i>	<i>Soil</i>	<i>NAPL</i>	<i>Water</i>	<i>Soil</i>	<i>NAPL</i>
	(µg/L)	(µg/kg)	(µg/kg)	(µg/L)	(µg/kg)	(µg/kg)
<i>Target Compound List (TCL) Volatile Organic Compounds (VOC) ³</i>						
Acetone	25	600	2500	0.74	99	99
Benzene	1	40	620	0.22	6.4	6.4
Bromodichloromethane	1	80	620	0.14	12	12
Bromoform	1	80	620	0.17	13	13
Bromomethane	1	160	1200	0.36	25	25
2-Butanone	25	600	2500	0.39	49	49
Carbon disulfide	5	200	620	0.28	20	20
Carbon tetrachloride	1	40	620	0.19	12	12
Chlorobenzene	1	40	620	0.20	6.3	6.3
Chloroethane	1	200	1200	0.24	65	65
Chloroform	1	40	620	0.16	12	12
Chloromethane	1	200	1200	0.14	5.2	5.2
Cyclohexane	1	960	2500	0.12	7.7	7.7
Dibromochloromethane	1	40	620	0.19	6.9	6.9
1,2-Dibromo-3-chloropropane	1	200	1200	0.28	60	60
1,2-Dibromoethane	1	200	620	0.24	9.9	9.9
1,2-Dichlorobenzene	1	80	1200	0.20	17	17
1,3-Dichlorobenzene	1	80	1200	0.18	7.2	7.2
1,4-Dichlorobenzene	1	80	1200	0.22	7.9	7.9
Dichlorodifluoromethane	1	200	1200	0.25	5.4	5.4
1,1-Dichloroethane	1	40	620	0.21	7.3	7.3
1,2-Dichloroethane	1	40	620	0.16	9.3	9.3
1,1-Dichloroethene	1	40	620	0.18	8.3	8.3
cis-1,2-Dichloroethene	1	40	620	0.21	14	14
trans-1,2-Dichloroethene	1	40	620	0.16	11	11
1,2-Dichloropropane	1	40	620	0.15	7.4	7.4
cis-1,3-Dichloropropene	1	40	620	0.12	5.5	5.5
trans-1,3-Dichloropropene	1	40	620	0.17	5.4	5.4
Ethylbenzene	1	40	620	0.19	6.8	6.8
2-Hexanone	50	2,000	2500	0.35	24	24
Isopropylbenzene	5	200	1200	0.15	5.1	5.1
Methyl acetate	10	960	1200	0.52	52	52
Methylene chloride	5	200	3100	0.19	99	99
Methylcyclohexane	1	960	620	0.50	5.7	8.9
4-Methyl-2-pentanone	50	2,000	2500	0.32	11	11
Methyl tert-butyl ether	5	200	2500	0.18	10	10
Styrene	1	40	620	0.13	28	28
1,1,2,2-Tetrachloroethane	1	40	620	0.22	8.2	8.2
Tetrachloroethene	1	40	620	0.19	9.0	9.0
Toluene	1	80	620	0.17	9.1	9.1
1,2,4-Trichlorobenzene	5	200	1200	0.19	12	12

RI TARGET COMPOUND AND TARGET ANALYTE PARAMETER LIST
 REMEDIAL INVESTIGATION ACTIVITIES
 FORMER WILLOW RUN ASSEMBLY PLANT
 YPSILANTI, MICHIGAN

Compound	Estimated Quantitation Limits (EQL) ¹			Method Detection Limits (MDL) ²		
	Water	Soil	NAPL	Water	Soil	NAPL
	(µg/L)	(µg/kg)	(µg/kg)	(µg/L)	(µg/kg)	(µg/kg)
<i>TCL VOC (continued)</i>						
1,1,1-Trichloroethane	1	40	620	0.21	9.5	9.5
1,1,2-Trichloroethane	1	40	620	0.22	9.9	9.9
Trichloroethene	1	40	620	0.28	12	12
Trichlorofluoromethane	1	80	1200	0.16	8.3	8.3
1,1,2-Trichloro-1,2,2-trifluoroethane	1	200	2500	0.26	10	10
Vinyl chloride	1	32	1200	0.21	16	16
Xylenes (total)	2	120	620	0.44	15	15
<i>TCL Semi-Volatile Organic Compounds (SVOC)</i>						
Acenaphthene	5	264	20,000	0.054	1.3	55
Acenaphthylene	5	264	20,000	0.054	1.2	84
Acetophenone	5	264	20,000	0.550	26.0	330
Anthracene	5	264	20,000	0.054	1.3	138
Atrazine	3	40	20,000	0.650	21.0	660
Benzaldehyde	10	264	20,000	0.750	21.0	414
Benzo(a)anthracene	1	264	20,000	0.052	0.95	84
Benzo(a)pyrene	1	264	20,000	0.048	1.3	138
Benzo(b)fluoranthene	1	264	20,000	0.049	1.2	138
Benzo(g,h,i)perylene	1	264	20,000	0.053	1.3	108
Benzo(k)fluoranthene	1	264	20,000	0.049	1.7	138
1,1'-Biphenyl	10	264	20,000	0.550	23.0	432
4-Bromophenylphenyl ether	5	264	20,000	0.520	21.0	282
Butylbenzylphthalate	5	264	20,000	0.510	19.0	222
di-n-Butylphthalate	5	264	20,000	0.610	19.0	300
Caprolactam	10	264	20,000	0.610	37.0	468
Carbazole	10	264	20,000	0.540	19.0	558
4-Chloroaniline	10	150	20,000	0.560	17.0	312
bis(2-Chloroethoxy)methane	5	264	20,000	0.490	22.0	960
bis(2-Chloroethyl)ether	1	80	20,000	0.088	2.0	246
2,2'-oxibis(1-Chloropropane)	5	264	20,000	0.520	26.0	312
4-Chloro-3-methylphenol	5	264	20,000	0.410	21.0	3,060
2-Chloronaphthalene	5	264	20,000	0.620	22.0	378
2-Chlorophenol	5	264	20,000	1.100	26.0	216
4-Chlorophenyl phenyl ether	5	264	20,000	0.550	24.0	216
Chrysene	1	264	20,000	0.048	0.9	59
Dibenz(a,h)anthracene	2	264	20,000	0.039	1.3	90
Dibenzofuran	4	264	20,000	0.540	20.0	50
3,3'-Dichlorobenzidine	4	1,600	96,000	0.480	18.0	294
2,4-Dichlorophenol	10	264	20,000	1.100	20.0	318
Diethylphthalate	5	264	20,000	0.630	19.0	372
2,4-Dimethylphenol	5	264	20,000	0.560	20.0	408

RI TARGET COMPOUND AND TARGET ANALYTE PARAMETER LIST
 REMEDIAL INVESTIGATION ACTIVITIES
 FORMER WILLOW RUN ASSEMBLY PLANT
 YPSILANTI, MICHIGAN

Compound	<i>Estimated</i> <i>Quantitation Limits (EQL) ¹</i>			<i>Method</i> <i>Detection Limits (MDL) ²</i>		
	<i>Water</i>	<i>Soil</i>	<i>NAPL</i>	<i>Water</i>	<i>Soil</i>	<i>NAPL</i>
	(µg/L)	(µg/kg)	(µg/kg)	(µg/L)	(µg/kg)	(µg/kg)
<i>TCL Semi-Volatile Organic Compounds (cont'd)</i>						
Dimethylphthalate	5	264	20,000	0.440	21.0	384
4,6-Dinitro-2-methylphenol	20	150	96,000	0.270	13.0	2,820
2,4-Dinitrophenol	20	150	96,000	3.500	83.0	2,460
2,4-Dinitrotoluene	5	264	20,000	0.400	18.0	342
2,6-Dinitrotoluene	5	264	20,000	0.470	21.0	348
bis(2-Ethylhexyl)phthalate	5	264	20,000	0.880	18.0	960
Fluoranthene	1	264	20,000	0.036	1.2	56
Fluorene	5	264	20,000	0.043	1.2	78
Hexachlorobenzene	0.2	264	20,000	0.065	2.1	84
Hexachlorobutadiene	1	40	20,000	0.510	26.0	150
Hexachlorocyclopentadiene	5	264	96,000	0.740	16.0	174
Hexachloroethane	5	264	20,000	0.580	28.0	294
Indeno(1,2,3-cd)pyrene	2	264	20,000	0.065	1.5	120
Isophorone	5	264	20,000	0.500	21.0	210
2-Methylnaphthalene	5	264	20,000	0.061	1.5	59
2-Methylphenol	5	264	20,000	0.560	28.0	402
4-Methylphenol	5	264	20,000	0.640	22.0	348
Naphthalene	5	264	20,000	0.069	1.6	53
2-Nitroaniline	20	200	96,000	0.430	22.0	306
3-Nitroaniline	20	200	96,000	0.670	16.0	192
4-Nitroaniline	20	200	96,000	0.470	26.0	216
Nitrobenzene	3	264	20,000	0.053	2.2	384
2-Nitrophenol	5	264	20,000	1.300	19.0	204
4-Nitrophenol	20	330	96,000	0.630	110.0	4,860
N-Nitroso-di-n-propylamine	5	264	20,000	0.530	23.0	456
N-Nitrosodiphenylamine	5	264	20,000	0.460	21.0	246
di-n-Octylphthalate	5	264	20,000	0.390	18.0	660
Pentachlorophenol	5	150	20,000	0.480	82.0	2,700
Phenanthrene	2	264	20,000	0.087	2.0	66
Phenol	5	264	20,000	0.960	25.0	342
Pyrene	5	264	20,000	0.048	1.1	60
2,4,5-Trichlorophenol	5	264	20,000	0.960	25.0	294
2,4,6-Trichlorophenol	4	264	20,000	1.400	21.0	408

RI TARGET COMPOUND AND TARGET ANALYTE PARAMETER LIST
 REMEDIAL INVESTIGATION ACTIVITIES
 FORMER WILLOW RUN ASSEMBLY PLANT
 YPSILANTI, MICHIGAN

Compound	<i>Estimated</i> <i>Quantitation Limits (EQL)¹</i>			<i>Method</i> <i>Detection Limits (MDL)²</i>		
	<i>Water</i>	<i>Soil</i>	<i>NAPL</i>	<i>Water</i>	<i>Soil</i>	<i>NAPL</i>
	(µg/L)	(µg/kg)	(µg/kg)	(µg/L)	(µg/kg)	(µg/kg)
<i>TCL Polychlorinated Biphenyls (PCB)</i>						
Aroclor 1016	0.1	264	1,000	0.044	6.7	190.0
Aroclor 1221	0.1	264	1,000	0.05	10	220
Aroclor 1232	0.1	264	1,000	0.1	5	170
Aroclor 1242	0.1	264	1,000	0.060	10	290
Aroclor 1248	0.1	264	1,000	0.061	4.8	200.0
Aroclor 1254	0.1	264	1,000	0.032	4	120
Aroclor 1260	0.1	264	1,000	0.038	8.0	130.0

Compound	<i>Estimated</i> <i>Quantitation Limits (EQL)¹</i>			<i>Method</i> <i>Detection Limits (MDL)²</i>		
	<i>Water</i>	<i>Soil</i>	<i>NAPL</i>	<i>Water</i>	<i>Soil</i>	<i>NAPL</i>
	(µg/L)	(mg/kg)	(mg/kg)	(µg/L)	(mg/kg)	(mg/kg)
<i>Site TAL Inorganics</i>						
Antimony	2	0.16	6	0.06500	0.013	0.33
Arsenic	5	0.08	30	4.30	0.030	0.34
Barium	100	0.8	20	3.2	0.2	0.20
Beryllium	1	0.16	0.5	0.3	0.029	0.029
Cadmium	1	0.08	0.5	0.42	0.027	0.027
Chromium	5	0.4	1	1.6	0.13	0.13
Cobalt	7	0.4	5	1.2	0.34	0.34
Copper	2	0.8	2.5	0.51	0.33	0.33
Lead	3	0.24	10	1.7	0.24	0.24
Manganese	15	0.8	1.5	0.23	0.042	0.042
Mercury	0.2	0.04	0.1	0.09	0.013	0.013
Nickel	20	0.8	4	1.4	0.28	0.28
Selenium	5	0.16	25	2.4	0.076	0.30
Silver	0.2	0.08	1	0.047	0.023	0.29
Thallium	1	0.08	200	0.022	0.0022	0.53
Vanadium	4	0.8	5	1.9	0.097	0.097
Zinc	20	0.8	2	6.6	0.39	0.56
Cyanide (amenable)	5	NA	NA	1.3	NA	NA
Cyanide (total)	NA	0.1	0.1	NA	0.057	0.057

RI TARGET COMPOUND AND TARGET ANALYTE PARAMETER LIST
 REMEDIAL INVESTIGATION ACTIVITIES
 FORMER WILLOW RUN ASSEMBLY PLANT
 YPSILANTI, MICHIGAN

Compound	<i>Estimated</i>			<i>Method</i>		
	<i>Quantitation Limits (EQL) ¹</i>			<i>Detection Limits (MDL) ²</i>		
	<i>Water</i> ($\mu\text{g/L}$)	<i>Soil</i> (mg/kg)	<i>NAPL</i> (mg/kg)	<i>Water</i> ($\mu\text{g/L}$)	<i>Soil</i> (mg/kg)	<i>NAPL</i> (mg/kg)
<i>Additional Parameters</i>						
Hexavalent chromium	20	0.8	NA	5	0.2	0.2
Low Level Mercury	0.0005	NA	NA	0.00016	NA	NA
pH	NA	NA	NA	NA	NA	NA
Hardness	5000	NA	NA	2800	NA	NA
Specific Gravity	NA	NA	---	NA	NA	---
Viscosity	NA	NA	---	NA	NA	---
Heating Value	NA	NA	---	NA	NA	---
Petroleum Fingerprinting	NA	NA	---	NA	NA	---

Notes:

- ¹ - Please note that these are estimated quantitation limits and are presented for guidance only. Actual quantitation limits are highly matrix dependent and may be elevated due to matrix effects, QA/QC problems and high concentrations of target and non-target analytes.
- ² - Method Detection Limits (MDL) are also presented for guidance only. Actual MDLs will vary depending on sample specific preparation factors. The MDLs are also highly matrix dependant and may be elevated due to matrix effects, QA/QC problems and high concentrations of target and non-target analytes. Laboratory MDLs are updated on a periodic basis and the MDLs in effect when the samples are analyzed will be used for reporting purposes.
- ³ - U.S. EPA Contract Laboratory Program, "Statement of Work for Organic Analysis, Multi-Media, Multi-Concentration", OLM4.2, May 1999 Target Compound List.

TABLE 1.3

WASTE CHARACTERIZATION PARAMETER LIST
 REMEDIAL INVESTIGATION ACTIVITIES
 FORMER WILLOW RUN ASSEMBLY PLANT
 YPSILANTI, MICHIGAN

<i>Compound</i>	<i>Estimated</i>	<i>Method</i>
	<i>Quantitation Limits (EQL) ¹</i>	<i>Detection Limits (MDL) ²</i>
	<i>Waste Leachate</i>	<i>Waste Leachate</i>
	<i>(mg/L)</i>	<i>(mg/L)</i>
<i>Toxic Characteristic Leachate Procedure (TCLP) VOC</i>		
Benzene	0.025	0.00022
2-Butanone	0.050	0.00039
Carbon tetrachloride	0.025	0.00019
Chlorobenzene	0.025	0.0002
Chloroform	0.025	0.00016
1,2-Dichloroethane	0.025	0.00016
1,1-Dichloroethene	0.07	0.00018
Tetrachloroethene	0.07	0.00019
Trichloroethene	0.05	0.00028
Vinyl chloride	0.025	0.00021
<i>TCLP SVOC</i>		
m-Cresols & p-Cresol	0.04	0.00064
o-Cresol	0.004	0.00056
1,4-Dichlorobenzene	0.004	0.00052
2,4-Dinitrotoluene	0.02	0.0004
Hexachlorobenzene	0.02	0.000065
Hexachlorobutadiene	0.02	0.00051
Hexachloroethane	0.02	0.00058
Nitrobenzene	0.004	0.000053
Pentachlorophenol	0.04	0.00048
Pyridine	0.02	0.00078
2,4,5-Trichlorophenol	0.02	0.00096
2,4,6-Trichlorophenol	0.02	0.0014
<i>TCLP Metals</i>		
Arsenic	0.02	0.0043
Barium	10	0.0032
Cadmium	0.005	0.00042
Chromium	0.5	0.0016
Lead	0.1	0.0017
Mercury	0.002	0.00009
Selenium	0.05	0.0024
Silver	0.1	0.0021

TABLE 1.3

WASTE CHARACTERIZATION PARAMETER LIST
 REMEDIAL INVESTIGATION ACTIVITIES
 FORMER WILLOW RUN ASSEMBLY PLANT
 YPSILANTI, MICHIGAN

	<i>Estimated</i> <i>Quantitation Limits (EQL) ¹</i>	<i>Method</i> <i>Detection Limits (MDL) ²</i>
	<i>Waste</i> <i>(mg/kg)</i>	<i>Waste</i> <i>(mg/kg)</i>
<i>Waste Characteristics</i>		
Ignitability (flashpoint)	---	NA
Corrosivity (pH)	---	NA

Notes:

- ¹ - Please note that these are estimated quantitation limits and are presented for guidance only. Actual quantitation limits are highly matrix dependent and may be elevated due to matrix effects, QA/QC problems and high concentrations of target and non-target analytes.
- ² - Method Detection Limits (MDL) are also presented for guidance only. Actual MDLs will vary depending on sample specific preparation factors. The MDLs are also highly matrix dependant and may be elevated due to matrix effects, QA/QC problems and high concentrations of target and non-target analytes. Laboratory MDLs are updated on a periodic basis and the MDLs in effect when the samples are analyzed will be used for reporting purposes.

TABLE 1.4

AIR MONITORING PARAMETER LIST
 REMEDIAL INVESTIGATION ACTIVITIES
 FORMER WILLOW RUN ASSEMBLY PLANT
 YPSILANTI, MICHIGAN

<i>Compound</i>	<i>Estimated</i>	<i>Method</i>
	<i>Quantitation Limits (EQL)¹</i>	<i>Detection Limits (MDL)²</i>
	<i>Air</i>	<i>Air</i>
	<i>($\mu\text{g}/\text{M}^3$)</i>	<i>($\mu\text{g}/\text{M}^3$)</i>
<i>Site-Specific Volatile Organic Compounds (VOC)</i>		
Acetone	2	0.47
Benzene	0.64	0.26
Bromodichloromethane	1.3	0.40
Bromoform	2.1	0.72
Bromomethane	0.78	0.46
2-Butanone	2.9	0.59
Carbon disulfide	3.1	0.44
Carbon tetrachloride	1.3	0.44
Chlorobenzene	0.92	0.41
Chloroethane	1.1	0.37
Chloroform	0.97	0.29
Chloromethane	0.82	0.37
Dibromochloromethane	1.7	0.68
1,2-Dibromoethane	1.5	0.46
1,2-Dichlorobenzene	1.2	0.42
1,3-Dichlorobenzene	1.2	0.48
1,4-Dichlorobenzene	1.2	0.36
Dichlorodifluoromethane	0.99	0.30
1,1-Dichloroethane	0.81	0.20
1,2-Dichloroethane	0.81	0.24
1,1-Dichloroethene	0.79	0.24
cis-1,2-Dichloroethene	0.79	0.20
trans-1,2-Dichloroethene	0.79	0.20
1,2-Dichloropropane	0.92	0.37
cis-1,3-Dichloropropene	0.91	0.36
trans-1,3-Dichloropropene	0.91	0.36
Ethylbenzene	0.87	0.30
2-Hexanone	1.6	0.82
Methylene chloride	0.69	0.24
4-Methyl-2-pentanone	1.6	0.37
Styrene	0.85	0.26
Tetrachloroethene	1.4	0.61
Toluene	1.1	0.34
1,2,4-Trichlorobenzene	5.9	2.5
1,1,1-Trichloroethane	1.1	0.44
1,1,2-Trichloroethane	1.1	0.44
Trichloroethene	1.1	0.43
Trichlorofluoromethane	2.2	1.1
1,1,2-Trichloro-1,2,2-trifluoroethane	3.1	0.54
Vinyl chloride	0.51	0.15
Xylenes (total)	2.2	0.87

AIR MONITORING PARAMETER LIST
 REMEDIAL INVESTIGATION ACTIVITIES
 FORMER WILLOW RUN ASSEMBLY PLANT
 YPSILANTI, MICHIGAN

<i>Compound</i>	<i>Estimated</i>	<i>Method</i>
	<i>Quantitation Limits (EQL)¹</i>	<i>Detection Limits (MDL)²</i>
	<i>Air</i> <i>($\mu\text{g}/\text{M}^3$)</i>	<i>Air</i> <i>($\mu\text{g}/\text{M}^3$)</i>

Notes:

- ¹ - Please note that these are estimated quantitation limits and are presented for guidance only. Actual quantitation limits are highly matrix dependent and may be elevated due to matrix effects, QA/QC problems and high concentrations of target and non-target analytes.
- ² - Method Detection Limits (MDL) are also presented for guidance only. Actual MDLs will vary depending on sample specific preparation factors. The MDLs are also highly matrix dependant and may be elevated due to matrix effects, QA/QC problems and high concentrations of target and non-target analytes. Laboratory MDLs are updated on a periodic basis and the MDLs in effect when the samples are analyzed will be used for reporting purposes.

TABLE 1.5

NATURAL ATTENUATION MONITORING PARAMETER LIST
 REMEDIAL INVESTIGATION ACTIVITIES
 FORMER WILLOW RUN ASSEMBLY PLANT
 YPSILANTI, MICHIGAN

<i>Compound</i>	<i>Estimated</i>	<i>Method</i>
	<i>Quantitation Limits (EQL)¹</i>	<i>Detection Limits (MDL)²</i>
	<i>Water</i>	<i>Water</i>
	<i>(mg/L)</i>	<i>(mg/L)</i>
<i>Metals (Total and Dissolved)</i>		
Manganese	0.015	0.00023
Iron	0.1	0.032
<i>Inorganic - General Chemistry Parameters</i>		
Alkalinity	5	0.71
Biological Oxygen Demand	2	2
Chemical Oxygen Demand	20	4.2
Sulfate	1	0.12
Sulfide	1	0.7
Nitrate, Nitrogen	0.1	0.031
Nitrite, Nitrogen	0.1	0.022
Total Organic Carbon	1	0.29
<i>Compound</i>	<i>Estimated</i>	<i>Method</i>
	<i>Quantitation Limits (EQL)¹</i>	<i>Detection Limits (MDL)²</i>
	<i>Water</i>	<i>Water</i>
	<i>(µg/L)</i>	<i>(µg/L)</i>
<i>Dissolved Gases</i>		
Methane	0.5	0.11
Ethane	0.5	0.16
Ethene	0.5	0.16

Notes:

- ¹ - Please note that these are estimated quantitation limits and are presented for guidance only. Actual quantitation limits are highly matrix dependent and may be elevated due to matrix effects, QA/QC problems and high concentrations of target and non-target analytes.
- ² - Method Detection Limits (MDL) are also presented for guidance only. Actual MDLs will vary depending on sample specific preparation factors. The MDLs are also highly matrix dependant and may be elevated due to matrix effects, QA/QC problems and high concentrations of target and non-target analytes. Laboratory MDLs are updated on a periodic basis and the MDLs in effect when the samples are analyzed will be used for reporting purposes.



TABLE 4.1

**CONTAINER, PRESERVATION, SHIPPING AND PACKAGING REQUIREMENTS
REMEDIAL INVESTIGATION ACTIVITIES
FORMER WILLOW RUN ASSEMBLY PLANT
YPSILANTI, MICHIGAN**

<i>Analyses</i>	<i>Sample Containers¹</i>	<i>Preservation</i>	<i>Maximum Holding Time from Sample Collection²</i>	<i>Volume of Sample</i>	<i>Shipping</i>	<i>Normal Packaging</i>
WATER (Groundwater, Surface Water and Wastewater)						
VOC	Three 40 ml Teflon-lined septum vials per analysis	HCl to pH < 2 Iced, 4 ± 2° C	14 days for analysis	Fill completely, no air bubbles	Overnight or Hand Deliver	Foam Liner or Bubble-wrap
SVOC, PCB	Two 1 liter amber glass bottles per analysis	Iced, 4 ± 2° C	7 days for extraction 40 days after extraction for analysis	Fill to neck of bottle	Overnight or Hand Deliver	Foam Liner or Bubble-wrap
Metals	One 1 liter plastic bottle	HNO ₃ to pH < 2 Iced, 4 ± 2° C	180 days (mercury-28 days) for analysis	Fill to neck of bottle	Overnight or Hand Deliver	Foam Liner or Bubble-wrap
Cyanide (amenable)	One 250 ml plastic bottle	NaOH to pH>12 Iced, 4 ± 2° C	14 days for analysis	Fill to neck of bottle	Overnight or Hand Deliver	Foam Liner or Bubble-wrap
Hexavalent Chromium, pH	One 250 ml plastic bottle	Iced, 4 ± 2° C	24 hours for analysis	Fill to neck of bottle	Overnight or Hand Deliver	Foam Liner or Bubble-wrap
Hardness (calculated)	One 250 ml plastic bottle	HNO ₃ to pH < 2 Iced, 4 ± 2° C	180 days (mercury-28 days) for analysis	Fill to neck of bottle	Overnight or Hand Deliver	Foam Liner or Bubble-wrap
Alkalinity	One 500-ml plastic bottle	Iced, 4 ± 2° C	14 days for analysis	Fill to neck of bottle	Overnight or Hand Deliver	Bubble Pack or Foam Chips
BOD	One 1-liter plastic bottle	Iced, 4 ± 2° C	48 hours to start analysis	Fill to neck of bottle	Overnight or Hand Deliver	Bubble Pack or Foam Chips

TABLE 4.1

CONTAINER, PRESERVATION, SHIPPING AND PACKAGING REQUIREMENTS
 REMEDIAL INVESTIGATION ACTIVITIES
 FORMER WILLOW RUN ASSEMBLY PLANT
 YPSILANTI, MICHIGAN

<i>Analyses</i>	<i>Sample Containers¹</i>	<i>Preservation</i>	<i>Maximum Holding Time from Sample Collection²</i>	<i>Volume of Sample</i>	<i>Shipping</i>	<i>Normal Packaging</i>
<i>WATER (Groundwater, Surface Water and Wastewater) (Cont'd)</i>						
COD	One 250-ml plastic bottle	H ₂ SO ₄ to pH < 2 Iced, 4 ± 2° C	28 days for analysis	Fill to neck of bottle	Overnight or Hand Deliver	Bubble Pack or Foam Chips
Nitrate	One 250-ml plastic bottle	Iced, 4 ± 2° C	48 hours to start analysis	Fill to neck of bottle	Overnight or Hand Deliver	Bubble Pack or Foam Chips
Nitrite	One 250-ml plastic bottle	Iced, 4 ± 2° C	48 hours to start analysis	Fill to neck of bottle	Overnight or Hand Deliver	Bubble Pack or Foam Chips
Sulfate	One 250-ml plastic bottle	Iced, 4 ± 2° C	28 days for analysis	Fill to neck of bottle	Overnight or Hand Deliver	Bubble Pack or Foam Chips
Sulfide	One 250-ml plastic bottle	Zinc Acetate/ NaOH to pH > 9 Iced, 4 ± 2° C	7 days for analysis	Fill to neck of bottle	Overnight or Hand Deliver	Bubble Pack or Foam Chips
TOC	Two 40 ml Teflon-lined septum vials per analysis	H ₂ SO ₄ to pH < 2 Iced, 4 ± 2° C	28 days for analysis	Fill completely, no air bubbles	Overnight or Hand Deliver	Foam Liner or Bubble-wrap
TCLP VOC	One 250 ml glass bottle	Iced, 4 ± 2° C	14 days for TCLP and 14 days for analysis	Fill to shoulder of jar	Overnight or Hand Deliver	Bubble Pack or Foam Chips
TCLP SVOC	Two 1 liter amber glass bottles	Iced, 4 ± 2° C	7 days for TCLP, 7 days for preparation and 40 days for analysis	Fill to shoulder of jar	Overnight or Hand Deliver	Bubble Pack or Foam Chips

TABLE 4.1

**CONTAINER, PRESERVATION, SHIPPING AND PACKAGING REQUIREMENTS
REMEDIAL INVESTIGATION ACTIVITIES
FORMER WILLOW RUN ASSEMBLY PLANT
YPSILANTI, MICHIGAN**

<i>Analyses</i>	<i>Sample Containers¹</i>	<i>Preservation</i>	<i>Maximum Holding Time from Sample Collection²</i>	<i>Volume of Sample</i>	<i>Shipping</i>	<i>Normal Packaging</i>
<i>WATER (Groundwater, Surface Water and Wastewater) (Cont'd)</i>						
TCLP Metals	Two 1 liter amber glass bottles	Iced, 4 ± 2° C	180 days (mercury 28 days) for TCLP and analysis	Fill to shoulder of jar	Overnight or Hand Deliver	Bubble Pack or Foam Chips
Corrosivity, Ignitibility	One 1 liter plastic bottle	Iced, 4 ± 2° C	14 days for analysis	Fill to shoulder of jar	Overnight or Hand Deliver	Bubble Pack or Foam Chips
<i>SOLID (Soil/Sediment)</i>						
VOC	One 40 ml Teflon-lined septum vial	10 ml methanol (1), Iced, 4 ± 2° C	14 days for analysis	10 g soil	Overnight or Hand Deliver	Foam Liner or Bubble-wrap
SVOC, PCB	One 4-ounce glass jar per analysis	Iced, 4 ± 2° C	14 days for extraction 40 days after extraction for analysis	Fill to shoulder of jar	Overnight or Hand Deliver	Foam Liner or Bubble-wrap
Metals	One 4-ounce glass jar	Iced, 4 ± 2° C	180 days (mercury 28 days) for analysis	Fill to shoulder of jar	Overnight or Hand Deliver	Foam Liner or Bubble-wrap
Hexavalent Chromium	One 4-ounce glass jar	Iced, 4 ± 2° C	30 days for extraction 24 hours for analysis	Fill to shoulder of jar	Overnight or Hand Deliver	Foam Liner or Bubble-wrap
Cyanide (total)	One 4-ounce glass jar	Iced, 4 ± 2° C	14 days for analysis	Fill to shoulder of jar	Overnight or Hand Deliver	Foam Liner or Bubble-wrap
TCLP VOC	One 4-ounce glass jar	Iced, 4 ± 2° C	14 days for TCLP and 14 days for analysis	Fill to shoulder of jar	Overnight or Hand Deliver	Bubble Pack or Foam Chips

TABLE 4.1

**CONTAINER, PRESERVATION, SHIPPING AND PACKAGING REQUIREMENTS
REMEDIAL INVESTIGATION ACTIVITIES
FORMER WILLOW RUN ASSEMBLY PLANT
YPSILANTI, MICHIGAN**

<i>Analyses</i>	<i>Sample Containers¹</i>	<i>Preservation</i>	<i>Maximum Holding Time from Sample Collection²</i>	<i>Volume of Sample</i>	<i>Shipping</i>	<i>Normal Packaging</i>
SOLID (Soil/Sediment) (Cont'd)						
TCLP SVOC	One 4-ounce glass jar	Iced, 4 ± 2° C	14 days for TCLP, 7 days for preparation and 40 days for analysis	Fill to shoulder of jar	Overnight or Hand Deliver	Bubble Pack or Foam Chips
TCLP Metals	One 4-ounce glass jar	Iced, 4 ± 2° C	180 days (mercury 28 days) for TCLP and analysis	Fill to shoulder of jar	Overnight or Hand Deliver	Bubble Pack or Foam Chips
Corrosivity	One 4-ounce glass jar	Iced, 4 ± 2° C	14 days for analysis	Fill to shoulder of jar	Overnight or Hand Deliver	Bubble Pack or Foam Chips
Ignitibility	One 4-ounce glass jar	Iced, 4 ± 2° C	14 days for analysis	Fill to shoulder of jar	Overnight or Hand Deliver	Bubble Pack or Foam Chips
LIQUID (LNAPL/DNAPL)						
VOC	One 4-ounce glass jar	Iced, 4 ± 2° C	14 days for analysis	10 g soil 5 g soil each	Overnight or Hand Deliver	Foam Liner or Bubble-wrap
SVOC, PCB	One 4-ounce glass jar	Iced, 4 ± 2° C	14 days for extraction 40 days after extraction for analysis	Fill to shoulder of jar	Overnight or Hand Deliver	Foam Liner or Bubble-wrap
Metals	One 4-ounce glass jar	Iced, 4 ± 2° C	180 days (mercury 28 days) for analysis	Fill to shoulder of jar	Overnight or Hand Deliver	Foam Liner or Bubble-wrap

TABLE 4.1

**CONTAINER, PRESERVATION, SHIPPING AND PACKAGING REQUIREMENTS
REMEDIAL INVESTIGATION ACTIVITIES
FORMER WILLOW RUN ASSEMBLY PLANT
YPSILANTI, MICHIGAN**

<i>Analyses</i>	<i>Sample Containers¹</i>	<i>Preservation</i>	<i>Maximum Holding Time from Sample Collection²</i>	<i>Volume of Sample</i>	<i>Shipping</i>	<i>Normal Packaging</i>
LIQUID (LNAPL/DNAPL) (Cont'd)						
Hydrocarbon Fuel Scan	One 4-ounce glass jar	Iced, 4 ± 2° C	14 days for extraction 40 days after extraction for analysis	Fill to shoulder of jar	Overnight or Hand Deliver	Foam Liner or Bubble-wrap
Specific gravity	One 4-ounce glass jar	Iced, 4 ± 2° C	28 days for analysis	Fill to shoulder of jar	Overnight or Hand Deliver	Foam Liner or Bubble-wrap
Viscosity	One 4-ounce glass jar	Iced, 4 ± 2° C	28 days for analysis	Fill to shoulder of jar	Overnight or Hand Deliver	Foam Liner or Bubble-wrap
Heating Value, BTU	One 4-ounce glass jar	Iced, 4 ± 2° C	28 days for analysis	Fill to shoulder of jar	Overnight or Hand Deliver	Foam Liner or Bubble-wrap
TCLP VOC	One 4-ounce glass jar	Iced, 4 ± 2° C	14 days for TCLP and 14 days for analysis	Fill to shoulder of jar	Overnight or Hand Deliver	Bubble Pack or Foam Chips
TCLP SVOC	One 4-ounce glass jar	Iced, 4 ± 2° C	14 days for TCLP, 7 days for preparation and 40 days for analysis	Fill to shoulder of jar	Overnight or Hand Deliver	Bubble Pack or Foam Chips
TCLP Metals	One 4-ounce glass jar	Iced, 4 ± 2° C	180 days (mercury 28 days) for TCLP and analysis	Fill to shoulder of jar	Overnight or Hand Deliver	Bubble Pack or Foam Chips
Corrosivity, Ignitibility	One 4-ounce glass jar	Iced, 4 ± 2° C	14 days for analysis	Fill to shoulder of jar	Overnight or Hand Deliver	Bubble Pack or Foam Chips

TABLE 4.1

CONTAINER, PRESERVATION, SHIPPING AND PACKAGING REQUIREMENTS
 REMEDIAL INVESTIGATION ACTIVITIES
 FORMER WILLOW RUN ASSEMBLY PLANT
 YPSILANTI, MICHIGAN

<i>Analyses</i>	<i>Sample Containers¹</i>	<i>Preservation</i>	<i>Maximum Holding Time from Sample Collection²</i>	<i>Volume of Sample</i>	<i>Shipping</i>	<i>Normal Packaging</i>
AIR (Soil Gas, Ambient Air)						
VOC	One 6-L Summa Canister	None	14 days for analysis	Fill canister maintaining slight negative pressure	Overnight or Hand Deliver	Cardboard Shipper

Notes:

- ¹ - Multiple parameters on a single sample may be combined into a single sample container with similar preservation requirements.
- ² - These are technical holding times, i.e., are based on time elapsed from time of sample collection.
- ³ - Soil VOC samples will require an additional container of sample for dry weight determination if no other analyses are required. Sediment samples if non-cohesive, may require standard bulk sampling techniques using a 4 ounce glass jar with no head space.

TABLE 7.1

**SUMMARY OF ANALYTICAL METHODS
REMEDIAL INVESTIGATION ACTIVITIES
FORMER WILLOW RUN ASSEMBLY PLANT
YPSILANTI, MICHIGAN**

<i>Parameter¹</i>	<i>Preparation Method²</i>	<i>Laboratory Preparation SOP</i>	<i>Analytical Method²</i>	<i>Laboratory Analytical SOP</i>
<u>Groundwater and Surface Water Samples</u>				
VOC	SW-846 5030B	CORP-MS-0002NC	SW-846 8260B	CORP-MS-0002NC
SVOC	SW-846 3520C	CORP-OP-0001NC	SW-846 8270C	CORP-MS-0001NC
PCB	SW-846 3500C	CORP-OP-0001NC	SW-846 8082	CORP-GC-0001NC
Metals ³				
ICP Metals	SW-846 3010A/3020A	CORP-IP-0003NC	SW-846 6010B	CORP-MT-0001NC
ICP/MS Metals	SW-846 3010A/3020A	CORP-IP-0003NC	SW-846 6020	NC-MT-0002
Mercury	SW-846 7470A	CORP-MT-0005NC	SW-846 7470A	CORP-MT-0005NC
Cyanide (Amenable)	SW-846 9012A	NC-WC-0032	SW-846 9012A	NC-WC-0031
Hexavalent Chromium	SW-846 7196A	NC-WC-0024	SW-846 7196A	NC-WC-0024
pH	NA	NA	EPA-WW 150.1	NC-WC-0010
Hardness (calculation)	NA	NA	SM 2340 B	NC-WC-0036
<u>Natural Attenuation Monitoring Parameters</u>				
Metals (Total and Dissolved)				
Manganese	SW-846 3010A/3020A	CORP-IP-0003NC	SW-846 6010B	CORP-MT-0001NC
Iron	SW-846 3010A/3020A	CORP-IP-0003NC	SW-846 6010B	CORP-MT-0001NC
Alkalinity, total	EPA-WW 310	NC-WC-0006	EPA-WW 310	NC-WC-0006
Biological Oxygen Demand	EPA-WW 405.1	NC-WC-0008	EPA-WW 405.1	NC-WC-0008
Chemical Oxygen Demand	EPA-WW 410	NC-WC-0019	EPA-WW 410	NC-WC-0019
Nitrate, Nitrogen	SW-846 9056	NC-WC-0084	SW-846 9056	NC-WC-0084
Nitrite, Nitrogen	SW-846 9056	NC-WC-0084	SW-846 9056	NC-WC-0084
Sulfate	SW-846 9056	NC-WC-0084	SW-846 9056	NC-WC-0084
Sulfide	SW-846 9030	NC-WC-0060	SW-846 9030	NC-WC-0060
Total Organic Carbon	SW-846 9060	NC-WC-0017	SW-846 9060	NC-WC-0017
Dissolved Gases	EPA SOP RSK 175	NC-GC-0032	EPA SOP RSK 175	NC-GC-0032
<u>Soil, Sediment and Sludge Samples</u>				
VOC	SW-846 5035 ⁴	CORP-MS-0002NC	SW-846 8260B	CORP-MS-0002NC
SVOC	SW-846 3550B	CORP-OP-0001NC	SW-846 8270C	CORP-MS-0001NC
PCB	SW-846 3550B	CORP-OP-0001NC	SW-846 8082	CORP-GC-0001NC
Metals ³				
ICP Metals	SW-846 3050B	CORP-IP-0002NC	SW-846 6010B	CORP-MT-0001NC
ICP/MS Metals	SW-846 3050B	CORP-IP-0002NC	SW-846 6020	NC-MT-0002
Mercury	SW-846 7471A	CORP-MT-0007NC	SW-846 7471A	CORP-MT-0007NC
Coarse/Fine Lead	MDEQ SOP	MDEQ SOP	SW-846 6010B	CORP-MT-0001NC
Cyanide (Total)	SW-846 9012A	NC-WC-0032	SW-846 9012A	NC-WC-0031
Hexavalent Chromium	SW-846 3060	NC-WC-0086	SW-846 7196A	NC-WC-0024
<u>Air Samples</u>				
VOC	EPA-AA TO-15	COI-MS-0007	EPA-AA TO-15	COI-MS-0007

TABLE 7.1

SUMMARY OF ANALYTICAL METHODS
REMEDIAL INVESTIGATION ACTIVITIES
FORMER WILLOW RUN ASSEMBLY PLANT
YPSILANTI, MICHIGAN

Waste Characterization

TCLP	SW-846 1311	CORP-IP-0004NC	NA	NA
VOC	SW-846 5030B	CORP-MS-0002NC	SW-846 8260B	CORP-MS-0002NC
SVOC	SW-846 3520C	CORP-OP-0001NC	SW-846 8270C	CORP-MS-0001NC
Metals				
ICP Metals	SW-846 3010A	CORP-IP-0003NC	SW-846 6010B	CORP-MT-0001NC
mercury	SW-846 7470A	CORP-MT-0005NC	SW-846 7470A	CORP-MT-0005NC
PCB (solids)	SW-846 3550B	CORP-OP-0001NC	SW-846 8082	CORP-GC-0001NC
PCB (waters)	SW-846 3500C	CORP-OP-0001NC	SW-846 8082	CORP-GC-0001NC
Corrosivity	NA	NA	SW-846 9045	NC-WC-0010
Ignitibility (flashpoint)	NA	NA	SW-846 1010	NC-WC-0034

Additional LNAPL/DNAPL Characterization

Petroleum Fingerprinting	CORP-OP-0001NC	SW-846 8015	CORP-GC-0001NC
Specific gravity (STL Buffalo)	NA	ASTM D1429-87	AWC-DENSITY-115
Viscosity (STL Buffalo)	NA	ASTM D2983-87	AWC-VISCOSITY-125
Heating Value (BTU), (STL Buffalo)	NA	ASTM D240-87	AWC-BTU-21

Notes:

- ¹ Refer to Tables 1.2 for the compounds/elements of each parameter group.
- ² Preparation and Analytical Method References:
 - SW-846 - "Test Methods for Evaluating Solid Wastes, Physical/Chemical Methods ", SW-846, 3rd Edition, and Promulgated Updates, November 1986.
 - EPA-WW - "Methods for Chemical Analysis of Water and Wastes", EPA-600/4-79-020, March 1983.
 - SM - "Standard Methods for the Examination of Water and Wastewater", APHA, AWWA, & WEF, 19th Edition, 1995.
 - EPA-AA - "
 - EPA SOP RSK 175 -
- ³ Metals by Method

Water ICP:	Arsenic, Barium, Beryllium, Cadmium, Chromium, Cobalt, Lead, Manganese, Nickel, Selenium, Vanadium, Iron, and Zinc.
Water ICP/MS:	Antimony, Copper, Silver, and Thallium.
Soil ICP:	Barium, Beryllium, Cadmium, Chromium, Cobalt, Lead, Manganese, Nickel, Selenium, Vanadium.
Soil ICP/MS:	Arsenic, Antimony, Selenium, Silver, Thallium, and Zinc.
Waste/NAPL:	All by ICP
- ⁴ Sediment and sludge samples may be collected as bulk samples which will be prepared in accordance with SW-846 Method 5030B.

TCLP = Toxicity Characteristic Leaching Procedure
 VOC = Volatile Organic Compounds
 SVOC = Semi-Volatile Organic Compounds
 PCB = Polychlorinated Biphenyls

ATTACHMENT 1

FIELD STANDARD OPERATING PROCEDURES

SOIL VOC SCREENING

Scope and Application: This method is applicable to screening VOCs in the headspace of soil samples.

Method: Photoionization

Sensitivity: Approximately 0.5 ppm depending on background

Optimum Range: Background to 2,000 ppm

Sample Handling: Determined on site

Reagents and Apparatus:

1. HNu Photoionizer or Photovac Microtip Photoionization Detector;
2. Calibration gas Isobutylene 100ppm;
3. Calibration apparatus and tubing;
4. Battery charger.

Calibration:

A) Calibration of the HNu

1. Connect the analyzer to the regulator and calibration gas cylinder with a short segment (butt connection) of tubing. The calibration gas consists of a mixture of isobutylene and zero air. Isobutylene is non toxic and safe to use in confined areas. There are no listed exposure levels at any concentration.

It is important that the tubing be clean since contaminated tubing will affect the calibration reading. A cylinder containing less than 30 psig pressure will not be used as readings below that level can deviate up to ten percent from the rated value.

Turn the function switch to the STANDBY position.

2. With the SPAN setting and the function switch at the same positions as listed in the Application Data Sheet or Calibration Report, open the valve on the cylinder until a steady reading is obtained.
3. If the reading is the same as the recorded data, the analyzer calibration for the original species of interest is still correct.
4. If the reading has changed, adjust the SPAN setting until the reading is the same.
5. Shut off the cylinder as soon as the reading is established.
6. Record and maintain this new SPAN setting.
7. Background organic vapor readings should be measured prior to any soil screening.

B) Calibration of MicroTip

1. Connect the supplied regulator to the span gas cylinder. Hand tighten the fittings. Observe proper handling techniques for all gases.
2. Open the valve on the gas bag by turning the valve stem fully counterclockwise.
3. Attach the nut to the regulator. Hand tighten the fittings.
4. Turn the regulator knob counterclockwise about half a turn to start the flow of gas.
5. Fill the gas bag about half full and then close the regulator fully clockwise to turn off the flow of gas.
6. Disconnect the bag from the adapter and empty it. Flush the bag a few times with the span gas and then fill it.
7. Close the gas bag by turning the valve clockwise.
8. Press SETUP and select the desired Cal Memory with the arrow keys and press ENTER. Press EXIT to leave Setup.
9. Press CAL and enter the desired response factor. Use Table 2 from the manual to find the correct response factor. If the compound is not in

Table 2 or you are not looking specifically for one compound then enter 1.00.

The concentration detected by MicroTIP will be multiplied by the response factor before it is displayed and logged.

10. Expose MicroTIP to zero air. Press ENTER and MicroTIP sets its zero point.
11. MicroTIP then asks for the span gas concentration. Enter the known span gas concentration and then connect the span gas bag adapter to the inlet.
12. Press ENTER and MicroTIP sets its sensitivity.
13. When MicroTIP's display reverts to normal, MicroTIP is calibrated and ready for use. Remove the span gas bag from the inlet.

Procedure:

1. Calibrate meter using the correct calibration procedure for the meter used.
2. The samples for VOC headspace screening will be prepared in the field by filling a 4-ounce soil jar to one-half its volume and sealing with a teflon-lined closure. The remaining sample will be placed in the appropriate jars for the analyses required.
3. Allow the sample for VOC headspace screening to remain at ambient temperature for a minimum of 10 minutes. This will allow for VOCs in the soil to reach equilibrium in the headspace of the jar.
4. Remove the lid of the soil jar slightly and insert the probe of the meter into the headspace.
5. Take the highest reading from the meter or readout of the instrument.
6. Record the reading in the field logbook.
7. Recheck calibration with calibration gas after a minimum of every 10 samples and after the last sample.

Quality Control:

1. Calibration check results must be ± 10 percent of the true value. If the result is outside of ± 10 percent, recalibrate the meter as specified above.

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Interferences and Limitations:

Humid conditions will cause a negative bias to the reading. The photoionization detection principle used by the instruments will not detect all VOCs. The instrument is most sensitive to aromatic, alkene and alkyne VOCs.

pH

Scope and Application: This method is applicable to surface water, wastewater and groundwater.

Method: Potentiometric

Reference: "Methods for Chemical Analysis of Water and Wastes",
EPA-600/4-79-020, revised March 1983, Method 150.1

Sensitivity: 0.01 pH unit; 0.1 °C

Optimum Range: pH 1.00 to 12.00

Sample Handling: Determined on site

Reagents and Apparatus:

1. Temperature compensated pH meter, Water Quality Monitoring System;
2. Combination pH electrode;
3. Thermilinear thermister temperature probe;
4. pH buffer solutions, pH 4.00, 7.00, and 10.00 (certified buffer solutions);
5. Distilled or deionized water in wash bottle.

Procedure:

1. Calibrate meter using calibration procedure as per manufacturer calibration directions.
2. Set up meter as outlined in the operating manual.
3. Pour the sample into clean sample jar or plastic cup.
4. Record and pH of the sample in the logbook.
5. Rinse with water followed by a rinse of the next buffer (typically pH 4.00 or 10.00).
6. Store pH electrode in soaker bottle when not in use.

Quality Control:

1. Calibration check results must be ± 0.10 pH unit of the true value. If the result is outside of ± 0.10 pH unit, rinse electrodes and check solution again. If still outside the control limit, recalibrate the meter.
2. All glassware is to be soap and water washed, tap water rinsed and distilled or deionized water rinsed prior to analyses.

Interferences:

Interferences in pH measurements occur with presence of weak organic and inorganic salts and oil and grease. If oil and grease are visible, note in logbook. Clean electrode with soap and water, followed by 10% HCl and deionized water rinse. Recalibrate meter before analysis of next sample.

TURBIDITY

Scope and Application: This method is applicable to surface water, wastewater and groundwater.

Method: Nephelometric

Reference: "Methods for Chemical Analysis of Water and Wastes",
EPA-600/4-79-020, revised March 1983, Method 180.1

Sensitivity: 0.01 Nephelometric Turbidity Unit (NTU)

Optimum Range: 0 - 10; 0 - 100; 0-1,000 NTU

Sample Handling: Determined on site

Reagents and Apparatus:

1. Direct reading turbidity meter, HF Scientific Model DRT-15CE, HACH 2100P, and LaMotte;
2. Cuvettes with screw tops;
3. Battery charger;
4. 0.02 NTU (nominal) reference standard;
5. Distilled or deionized water in wash bottle.

Calibration Check and Operation

The turbidimeter has been calibrated by the manufacturer and the electronic calibration using freshly prepared formazin standards should only be performed if the electronic printed circuit board, the photodetectors or the light source has been replaced.

The procedures for calibration checks and the operation of the meter follows:

1. For accurate measurements in the low range rotate the cuvettes in the well to obtain the minimum reading. Mark the cuvette with one of the adhesive dots provided with the instrument so that orientation of the cuvette will be identical each time it is placed in the instrument.
2. To operate the turbidimeter, switch to the "10" range and place the Reference Standard (0.02 NTU) in the optical well.

3. With the light shield in place over the well, adjust the Reference Adjust knob to cause the meter to read the reference standard value on the scale. The unit is now ready for use in either range.
4. To make a measurement of a sample, clean one of the cuvettes and fill to within approximately 3/4" from the top with sample. Place the top on the cuvette and carefully clean the outside surface of the cuvette with a lint free wiper such as KimWipes. Place the sample in the well and place the light shield over the well. Select the appropriate range for best readability. Record results in field logbook.
5. Repeat steps 3 and 4 for each sample.

Quality Control:

1. Calibration check results must be $\pm 10\%$ of the true value. If the result is outside of $\pm 10\%$, clean cuvettes and check solution again. If still outside the control limit, recalibrate the meter.
2. All glassware is to be soap and water washed, tap rinsed and distilled or deionized water rinsed prior to analyses.

Interferences:

Interferences in turbidity measurements are generally due to dirty or scratched cuvettes. Handle only the top one-third of the cuvettes and wipe clean using a lint-free wiper (KimWipes or equivalent).

SPECIFIC CONDUCTANCE

Scope and Application: This method is applicable to surface water, wastewater and groundwater.

Method: Specific Conductance

Reference: "Methods for Chemical Analysis of Water and Wastes"
EPA-600/4-79-020, revised March 1983, Method 120.1

Sensitivity: 0.1 mmhos/cm

Optimum Range: 0 - 100.0 mmhos/cm

Sample Handling: Determine on site

Reagents and Apparatus:

1. Conductivity meter - YSI Model Water Quality Monitoring System;
2. Conductivity Cell - YSI Model Flow-Through Conductivity Cell (K=5/cm);
3. Thermilinear Thermister - YSI Model Temperature Probe;
4. Deionized water;
5. Conductivity standard, 1.0mmho/cm @25°C.

Notes:

The conductivity meter is factory calibrated. The calibration is checked using a solution of known conductance.

Calibration Check

Connect the cell and the Temperature Probe, and remove them from the sample chamber. Set the conductivity function switch to 2 ATC. Rinse the inside and outside of the cell and the probe with about 1/3 the calibration solution. Place both of the sensors into the remainder of the solution in the bottle and allow them to come to temperature equilibrium. Make sure that the body is immersed so that the liquid level is half way up the knurled portion of the cell. Read the displayed value and determine if the cell/instrument is within specified accuracy. The displayed value is corrected to 25°C automatically and should be 1.000 ±0.070 mmho/cm. If the value is not within specification replace cell.

Procedure:

1. Check calibration of meter.
2. Set up meter as outlined in the operating manual.

3. Before any conductivity cell is used, it should be soaked in distilled or deionized water for 10 minutes. To make conductivity measurements, connect a YSI Flow-Through Conductivity Cell to the monitoring system. Set the conductivity function switch to 2 and observe the displayed value after the reading is stable. The display reads out in mmho/cm.
4. If the overrange signal (1._____) is displayed, the conductivity of the water being measured is greater than 1.999 mmho/cm. Reset the function switch to 20. If the overrange signal is still displayed, reset to 100. If the overrange signal is still displayed, either the conductivity is greater than 100.0 mmho/cm and the YSI Water Quality Monitor can not be used for conductivity determinations.
5. Record conductance readings in field logbook.
6. Repeat steps 3 through 5 for remaining samples.

Quality Control:

1. The quality control calibration check standard must be verified on a daily basis. The standard must be within ± 10 percent of the true value. Record the calibration standard in the field logbook.

DISSOLVED OXYGEN

Scope and Application: This method is applicable to surface water, wastewater and groundwater.

Method: Potentiometric

Reference: "Methods for Chemical Analysis of Water and Wastes",
EPA-600/4-79-020, revised March 1983, Method 360.1

Sensitivity: 0.1 mg/L as O₂

Optimum Range: 0.1 mg/L to 20 mg/L O₂

Sample Handling: Determined on site

Reagents and Apparatus:

1. Temperature compensated dissolved oxygen (DO) meter, Corning Check Mate System;
2. Zero oxygen standard;
3. DO sensor-filling solution;
4. DO membrane replacement kit;
5. Distilled or deionized water in wash bottle.

Setting Up DO Sensor:

The sensor is shipped dry and must be filled before use.

1. Unscrew the membrane cap from sensor and fill using DO electrolyte.
2. Tap membrane cap gently to remove air bubbles. Gently screw cap onto probe body allowing surplus electrolyte to run out. (Caution: Do not overtighten)
3. Fit sensor to meter module.
4. Allow 30 minutes for polarization of electrode.

Calibration:

1. Remove wetting cap from tip of sensor. Switch on meter.
2. For first calibration point, place sensor in zero oxygen solution. Allow sufficient time for sensor to stabilize.
3. Move the sensor in a gentle circular motion.
4. Make sure sensor is immersed to a depth of 40 mm to cover the temperature-sensing element.
5. Press "CAL" key. CAL 1 is displayed on meter and after endpointing, the display automatically updates to zero.
6. For second calibration point, hold sensor in air. Press "CAL" key. CAL 2 is displayed. After endpointing, the display automatically updates to 100% O₂.
7. To adjust oxygen calibration for salinity and barometric pressure, press "Mode" key. In mg/L O₂ mode, press "CAL" key and 100 is displayed. Use down arrow and up arrow on the keypad to adjust the display according to the salinity and barometric pressure tables contained on the operating instruction leaflet.

Procedure:

1. Calibrate meter using calibration procedure.
2. Pour the sample into clean sample jar or plastic cup.
3. Place sensor in sample. After following the immersion, stirring and stabilization steps referred to during calibration, press "READ" key to obtain sample result.
4. Record result in the field logbook.
5. Repeat steps 2 through 4 for each sample.

Quality Control:

1. Duplicate 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate is still required. Duplicates must be within 15%.

If the results are outside of the control limits, rinse electrode and repeat analysis. If results are still outside of the control limits, recollect samples and repeat analysis.

If the results are still outside of the control limits, check calibration and recalibrate if necessary (see item 2, below). If unable to recalibrate, replace sensor membrane.

2. Calibration check results must be within 10% of the true value. If the result is outside of 10%, rinse electrodes and check solution again. If still outside the control limit, recalibrate the meter and reanalyze all samples analyzed since the last in control calibration.
3. All glassware is to be soap and water washed, tap rinsed and distilled or deionized water rinsed prior to analyses unless pre-cleaned sample jars are used.

Interferences:

Interferences in DO measurements generally occur due to membrane coating. Clean probe as specified in the sensor manual.

The presence of other gases such as chlorine, nitrous and nitric oxide, hydrogen sulfide and sulfur dioxide interfere with DO measurements. The sulfur-based compounds will tarnish the electrodes resulting in sluggish or erratic measurements. Polishing the electrodes as specified in the operating manual will restore the performance of the meter. Recalibrate meter before analysis of next sample.

OXIDATION-REDUCTION POTENTIAL (ORP)

Scope and Application: This method is applicable to surface water, wastewater and groundwater.

Method: Potentiometric

Reference: "Standard Methods for the Examination of Water and Wastewater", APHA, 18th edition, 1992, Method 2580B.

Sensitivity: 1 mV

Optimum Range: -1,500 to 1,500 mV

Sample Handling: Determined on site

Reagents and Apparatus:

1. ORP meter;
2. ORP electrode assembly;
3. Thermilinear thermistor temperature probe;
4. ZoBell Solution;
5. Distilled or deionized water in wash bottle.

Calibration:

1. Turn on the Water Quality Monitor and set the pH function switch to mV.
2. Connect the shorting cap attached to the to the mV input jack. The display should read 000-±2 mV. This indicates that the electronics are zeroed.
3. Detach the shorting cap and connect the to the mV input jack. If a pH electrode is not attached to the pH input jack, connect the shorting cap to it.
4. Attach the to the TEMP input jack.
5. Rinse with distilled or deionized water, followed by a rinse with a small amount of reconstituted ZoBell Solution.
6. Half fill a disposable 50 ml sample cup with ZoBell Solution and fully immerse the bulb and the end of the sheath. Allow the sensors to equilibrate, and note the reading.

7. The displayed mV values are not temperature compensated and should be corrected to 25°C at 1.3 mV/°C. The temperature coefficient is in reverse proportion to the temperature.
8. Correct the value to 25°C using the following equation:

$$\text{Actual Value mV} = \text{Display Value} + [(\text{Display Temp.} - 25^{\circ}\text{C}) \times (1.3 \text{ mV})]$$

Procedure:

1. Calibrate meter using calibration procedure.
2. Set up meter as outlined in the instruction manual.
3. Record temperature and ORP of the sample in the field logbook.
4. Correct ORP to 25°C using the formula presented above.
5. Record corrected ORP in the field logbook.
6. Repeat steps 3 through 6 for each sample.
7. Store electrode in soaker bottle when not in use.

Quality Control:

1. Calibration check results must be 231±10 mV. If the result is outside of this range, rinse electrodes and check solution again. If still outside this range, recalibrate the meter and reanalyze all samples analyzed since the last in-control calibration.

Interferences:

Interferences in ORP measurements occur when the platinum electrode surface becomes coated. Clean the ORP electrode as follows:

1. Soft coatings should be removed by use of a wash bottle of water or by gently wiping with a soft cloth. Remove the bulb guard if necessary. Be careful not to scratch the platinum.
2. Hard coatings or organic chemicals should be removed by an appropriate chemical solvent, by gently scrubbing with a very fine cleansing powder such as "Softscrub", or by gently polishing with 600 grade wet silicon carbide paper. Wet a piece of the paper with water and gently polish the electrode with a circular twisting motion.

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Note:

After cleaning the platinum surface, soak the electrode for an 8 to 24 hours in 4.0 pH buffer, and then recheck it with ZoBell Solution before further use.

ATTACHMENT 2

LABORATORY ANALYTICAL STANDARD OPERATING PROCEDURES

Controlled Copy

Copy No: _____

Implementation Date: 10/20/04

SOP No. CORP-MS-0002NC

Revision No. 2.4

Revision Date: 09/27/04

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STL STANDARD OPERATING PROCEDURE

**TITLE: DETERMINATION OF VOLATILE ORGANICS BY GC/MS BASED ON METHOD
8260B AND 8260A**

(SUPERSEDES: REVISION 2.3, DATED 05/23/01)

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1.0 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. It may also be used for analysis following method 8260A. The associated LIMS method codes are QK (8260B) and MZ (8260A). Ohio VAP projects are distinguished by Program Code 2J. The following Prep Codes are used: 15 (5 mL purge), 25 (low level 5mL purge), 4B (Methanol preservation, EnCore™), 4D (Sodium Bisulfate preservation, EnCore™), 4P (Frozen, EnCore™), and 73 (5030A Methanol Prep).
- 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 40 µg/L for 25 mL purge waters, 5 to 200 µg/kg for low-level soils, and 250 to 10,000 µg/kg for medium-level soils. Reporting limits are listed in Tables 1 and 3.
- 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. Soils are preserved by extracting the volatile analytes into methanol. Soil samples may be preserved with sodium bisulfate or by freezing 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. Refer to the STL QC Program document (QA-003) for further details of the batch definition.

3.2. Method Blank

- 3.2.1. 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)

- 3.3.1. 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, 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

- 3.4.1. 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)

- 3.5.1. 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)

- 3.6.1. 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)

- 3.7.1. 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, the sample is diluted.

5. SAFETY

- 5.1 Employees must abide by the policies and procedures in the Corporate Safety Manual and this document.
- 5.2. Eye protection that protects against splash, 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. Cut resistant gloves **MUST** be worn when opening VOA vials and when doing any other task that presents a strong possibility of getting cut.
- 5.3. Primary Materials Used
 - 5.3.1. The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.
 - 5.3.2. 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.
 - 5.3.3.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Sodium bisulfate	Irritant	None	Causes mild to severe irritation to the eyes. Prolonged exposure may cause burn if not flushed with water. May cause mild irritation to skin. Prolonged exposure may cause burn if not flushed with water.
Acetic Acid	Corrosive Poison Flammable	10 ppm-TWA	Contact with concentrated solution may cause serious damage to the skin and eyes. Inhalation of concentrated vapors may cause serious damage to the lining of the nose, throat, and lungs. Breathing difficulties may occur.
Sodium Hydroxide	Corrosive	2 Mg/M3-Ceiling	Severe irritant. Effects from inhalation of dust or mist vary from mild irritation to serious damage of the upper respiratory tract, depending on severity of exposure. Symptoms may include sneezing, sore throat or runny nose. Contact with skin can cause irritation or severe burns and scarring with greater exposures. Causes irritation of eyes, and with greater exposures it can cause burns that may result in permanent impairment of vision, even blindness.
Methanol	Flammable Poison Irritant	200 ppm-TWA	A slight irritant to the mucous membranes. Toxic effects exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure may include headache, drowsiness and dizziness. Methyl alcohol is a defatting agent and may cause skin to become dry and cracked. Skin absorption can occur; symptoms may parallel inhalation exposure. Irritant to the eyes.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

- 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 where possible. All samples with a pink stickers that read "Caution/Use Hood!" **must** be opened in the hood. Contact the EH&S co-ordinator if this is not possible. 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 the EH&S coordinator and the laboratory group leader.
- 5.7. 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.
- 5.8. Specific Safety Concerns or Requirements
 - 5.8.1. The gas chromatograph and mass spectrometer contain zones that have elevated temperatures. The analyst needs to be aware of the locations of those zones, and must cool them to room temperature prior to working on them.
 - 5.8.2. The mass spectrometer is under deep vacuum. The mass spectrometer must be brought to atmospheric pressure prior to working on the source.
 - 5.8.3. There are areas of high voltage in both the gas chromatograph and the mass spectrometer. Depending on the type of work involved, either turn the power to the instrument off, or disconnect it from its source of power.
 - 5.8.4. Sodium bisulfate creates Sulfuric Acid when mixed with water.

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 or gas generators, may be used as an alternative to helium for purge gas.
 - 6.8.3. Compressed air: Used for instrument pneumatics.
- 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. One of the traps used is the Vocarb 3000 trap. Other traps such as the OI 10 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:

6.10.1. 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. 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.

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 50 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 $\text{pH} \leq 2$ with 1:1 hydrochloric acid.
- 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 ($< 50 \mu\text{g/kg}$ 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 25 μL of 2500 μg/mL solution for a nominal 25 g sample, 5 μL for a nominal 5 g sample.) Refer to Section 17.5 for Michigan project criteria.
- 8.5.5. Add the correct amount of matrix spiking solution to the matrix spike and matrix spike duplicate samples. (Add 500 μL of 50 μg/mL solution for a nominal 25 g sample, 100 μL for a nominal 5 g sample.) Reduce the volume of methanol added to ensure the final volume is 25 mL for nominal 25 g sample or 5 mL methanol for a nominal 5 g sample. Refer to Section 17.5 for Michigan project criteria.

- 8.5.6. Prepare an LCS for each batch by adding the correct amount of matrix spiking solution to clean methanol. (500 μ L of spike to 25 mL methanol or 100 μ L spike to 5 mL methanol). Refer to Section 17.5 for Michigan project criteria.
- 8.5.7. Shake the samples for two minutes to distribute the methanol throughout the soil.
- 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 25 μ L of 2500 μ g/mL solution for a nominal 25 g sample, 5 μ L for a nominal 5 g sample.) Refer to Section 17.5 for Michigan project criteria.
 - 8.6.9. Add the correct amount of matrix spiking solution to the matrix spike and matrix spike duplicate samples. (Add 500 μ L of 50 μ g/mL solution for a nominal 25 g sample, 100 μ L for a nominal 5 g sample.) Reduce the volume of methanol added to ensure the final volume is 25 mL for nominal 25 g sample or 5 mL methanol for a nominal 5 g sample. Refer to Section 17.5 for Michigan project criteria.
 - 8.6.10. Prepare an LCS for each batch by adding the correct amount of matrix spiking solution to clean methanol. (500 μ L of spike to 25 mL methanol or 100 μ L spike to 5 mL methanol). Refer to Section 17.5 for Michigan project criteria.
 - 8.6.11. Shake the samples for two minutes to distribute the methanol throughout the soil.

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.

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 within 48 hours. The sample must be analyzed within 14 days after sampling and stored at a 45 degree angle in the freezer.

Note: Freezing is not allowed for Ohio VAP soil samples.

- 8.7.8. 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*

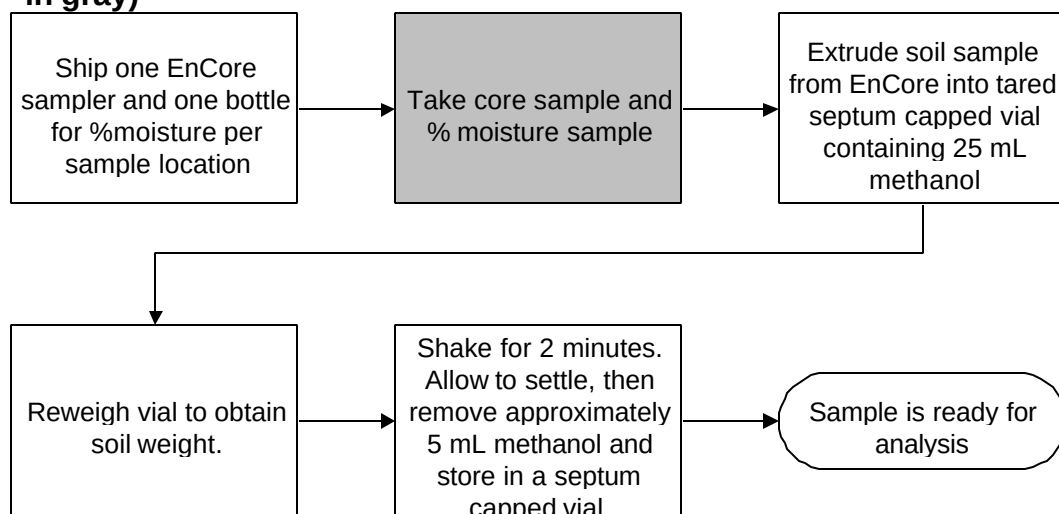
8.8.1. *At specific client request unpreserved soils packed into glass jars or brass tubes may be accepted and subsampled in the lab. This is the old procedure based on method 5030A and method 8260A. It is no longer included in SW846 and is likely to generate results that are biased low, possibly by 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.

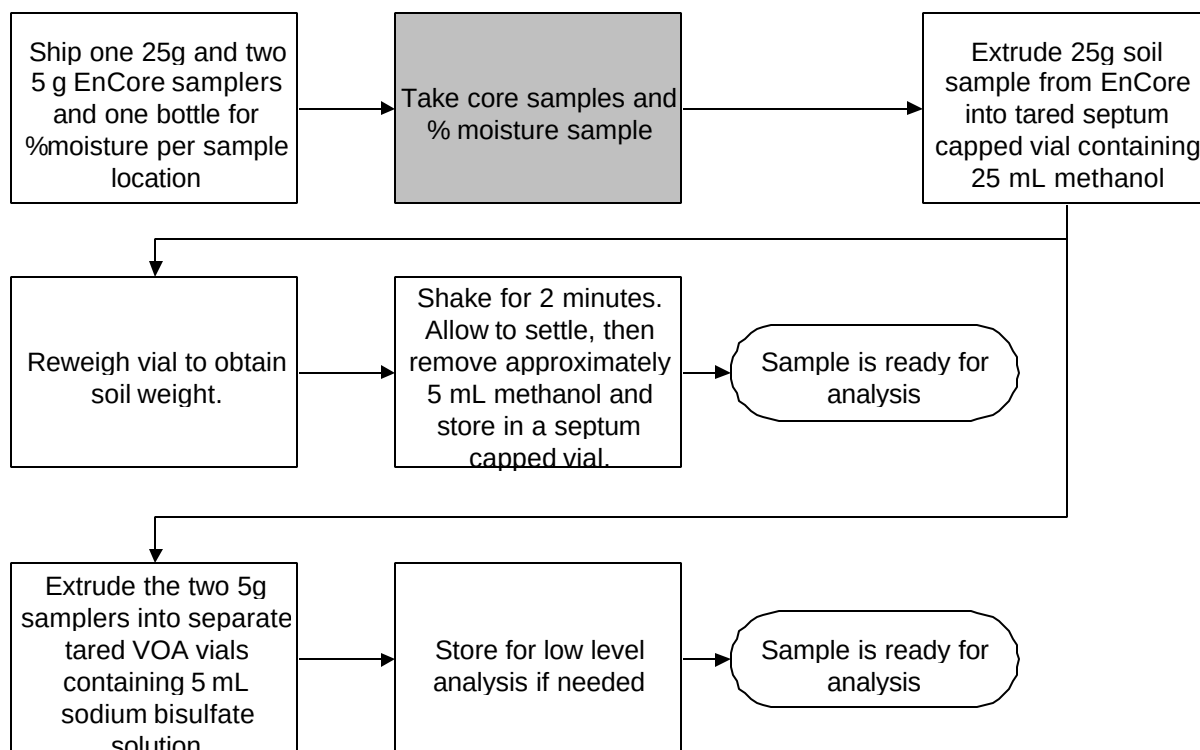
8.10. The maximum holding time is 14 days from sampling until the sample is analyzed. (Samples that are found to be unpreserved still have a 14 day holding time. However they should be analyzed as soon as possible. The lack of preservation should be addressed in the case narrative). Maximum holding time 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 weekly. It is replaced every 7 days.

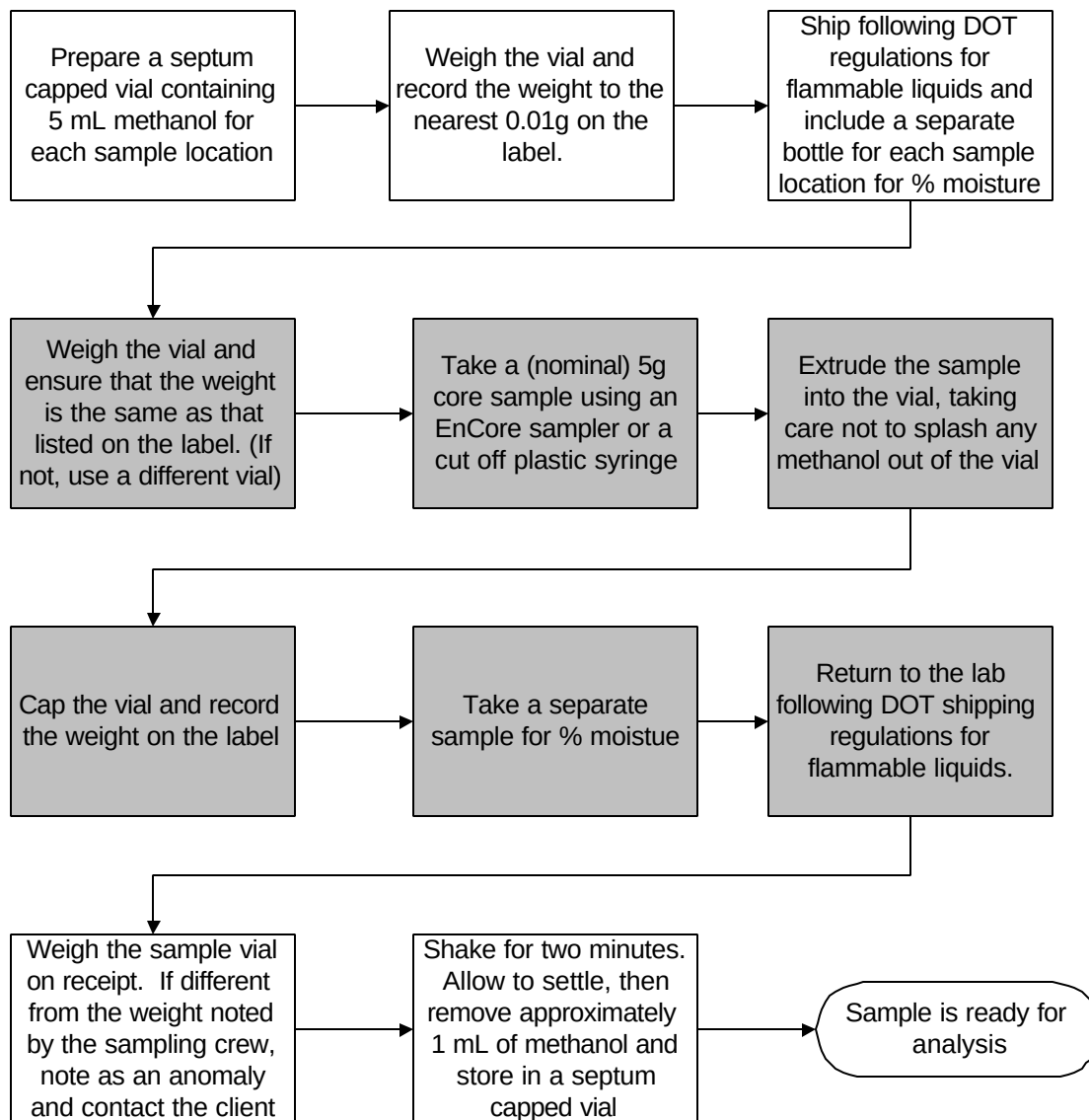
EnCore procedure when low level is not required (field steps in gray)



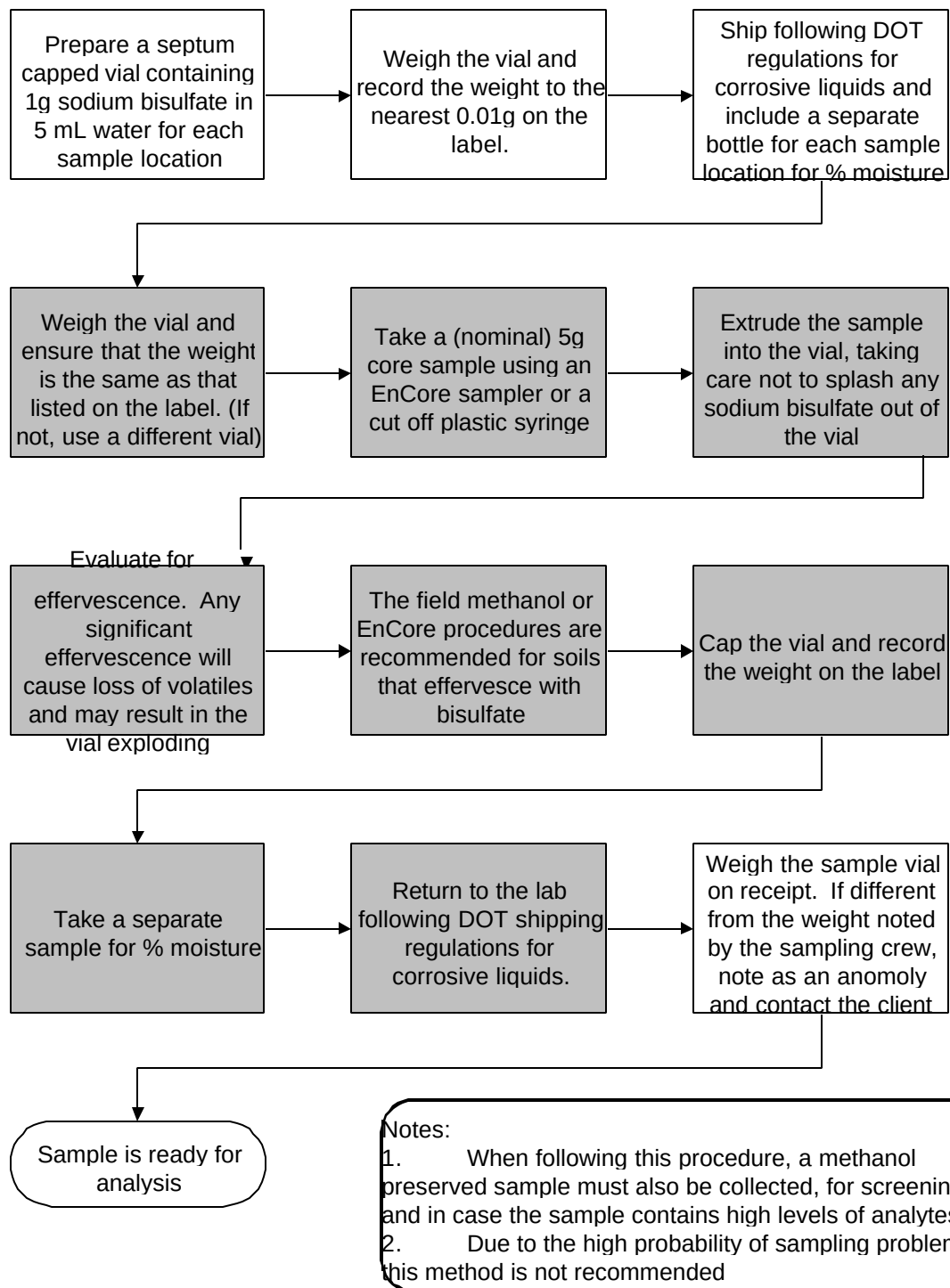
EnCore procedure when low level is required



Field methanol extraction procedure (field steps in gray)



Field bisulfate preservation procedure (field steps in gray)



9. QUALITY CONTROL

9.1. Control Limits

- 9.1.1. 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 $\pm$ 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.
- 9.1.2. 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.
- 9.1.3. Refer to the QC Program document (QA-003) for further details of control limits.

9.2. Surrogates

- 9.2.1. 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 Table 8. 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 if there is sufficient volume. If there is insufficient volume, the surrogate is narrated.

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.

- 9.2.2. 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 reparation 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.

9.2.3. Refer to the STL QC Program document (QA-003) for further details of the corrective actions.

9.3. Method Blanks

9.3.1. For each batch of samples, analyze a method blank. The method blank is analyzed after the calibration standards, normally before any samples. For low-level volatiles, the method blank consists of reagent water. For medium-level volatiles, the method blank consists of the same volume of methanol that was used to prepare the samples. 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.

9.3.2. 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.

9.3.3. 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.

9.3.4. Refer to the STL QC Program document (QA-003) for further details of the corrective actions.

9.4. Laboratory Control Samples (LCS)

- 9.4.1. 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.
- 9.4.2. Refer to the STL QC Program document (QA-003) for further details of the corrective action.
- 9.4.3. 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. Refer to Section 17.2 for Ohio VAP specific analytes.

9.5. Matrix Spikes

- 9.5.1. 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. See Section 17.2 for Ohio VAP specific analytes.
- 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.

9.6. Nonconformance and Corrective Action

- 9.6.1. Any deviations from QC procedures must be documented as a nonconformance, with applicable cause and corrective action approved by the facility QA Manager.

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-Bromofluorobenzene (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.

10.1.2. 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

10.3.1. 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 at least five initial calibration standards is prepared and analyzed for the target compounds and each surrogate compound. Six standards must be used for a quadratic least squares calibration. Suggested 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. Suggested calibration levels for a low level 5mL purge are 1, 5, 10, 20, and 40 µg/L. Again, some analytes are prepared at higher levels. Tables 2 and 4 list the calibration levels for each analyte. Other calibration levels and purge volumes may be used depending on the capabilities of the specific instrument. (For example, adequate sensitivity can be obtained on the Agilent 5973 instruments to use a 5 mL purge volume to reach the same reporting limits that once required a 25 mL purge. The calibration levels will still be the same 1, 5, 10, 20, 40µg/L.) 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. For any analyte with %RSD >15%, linear or quadratic curve fits may be used. The analyst should consider instrument maintenance to improve the linearity of response. If the % RSD is > 15%, the analyst may drop the low or high in the ICAL, as long as a minimum of 5 points are maintained (6 points for quadratic) and the quantitation range is adjusted accordingly. Otherwise the correlation coefficient, (coefficient of determination, r^2 for non-linear curves) must be ≥ 0.990 . If the correlation coefficient is < 0.990 , then any hit for these compounds must be flagged as estimated.
- 10.4.6.1. Refer to Section 17.2 for specific Ohio VAP criteria.
- 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. The calibration standards for the initial 5-point calibration for low level soils that are not preserved in sodium bisulfate (i.e. are preserved by freezing, or not preserved) must be

heated to 40°C for purging. Using this calibration curve for water samples is acceptable as long as all calibration, QC, and samples are also heated to 40°C. A separate five point calibration must be prepared for analysis of low level soils that are preserved with sodium bisulfate. 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 for analysis of sodium bisulfate preserved samples 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.

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.

Note: This procedure may not be used for Ohio VAP samples.

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. A midpoint 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. Refer to Table 12 for specific Ohio VAP analytes.

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 μ L 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 $\geq 5 \mu\text{L}$. Check and document the pH of the remaining sample.

11.4.3. Add 250 ng of each internal and surrogate standard (5 μL of a 50 $\mu\text{g/mL}$ solution, refer to Tables 7 and 8). The internal standards and the surrogate standards may be mixed and added as one spiking solution (this results in a 50 $\mu\text{g/L}$ solution for a 5 mL sample, and a 10 $\mu\text{g/L}$ solution for a 25 mL sample). Inject the sample into the purging chamber.

11.4.3.1. For TCLP samples use 1 mL of TCLP leachate with 4 mL reagent water. (Note that TCLP reporting limits will be 5 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 approximately 3-10 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 μ L 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 1 μ L of methanolic extract is to be added to the water, dilute the methanolic extract such that a volume greater than 1 μ L will be added to the water in the syringe. Refer to Section 17.5 for Michigan project requirements.

11.6. Liquid wastes that are soluble in methanol and insoluble in water.

11.6.1. Pipet 1 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 4 mL of methanol, then add 5 μ L of a 2500 μ g/mL surrogate spiking solution to bring the final volume to 5 mL. Cap the vial and shake for 2 minutes to mix thoroughly. For a MS/MSD or LCS, 4.9 mL of methanol, 5 μ L of a 2500 μ g/mL surrogate spiking solution, and 0.1 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 μ L 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 5 μ L of methanolic extract is to be added to the water, dilute the methanolic extract such that a volume greater than 5 μ L 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 be analyzed as soils.

11.7.3. Soil samples which are preserved with sodium bisulfate 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.

11.8. *Low-Level Solids Analysis using discrete autosamplers, Method 8260A, 5030A.*

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 soil/sediment sample mixed with reagent water containing the surrogates and internal 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 0.5 g. If the sample is contaminated with analytes such that a purge amount less than 0.5 g is appropriate, use the medium level method. For the medium level method, add 5g soil to 5 mL methanol containing the surrogates, mix for two minutes, allow to settle then remove a portion of the methanol and store in a clean Teflon capped vial at 4°C until analysis. Analyze as described in section 11.5.*

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 11.5.1.*

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. Medium-Level Soil/Sediment and Waste Samples

11.9.1. Sediments/soils and waste that are insoluble in methanol.

11.9.1.1. Sediments/soils and waste that are insoluble in methanol.

11.9.1.1.1. Gently mix the contents of the sample container with a narrow metal or wood spatula. Weigh 5 g (wet weight) into a tared vial. Use a top-loading balance. Record the weight to 0.1 gram. Do not discard any supernatant liquids.

11.9.1.1.2. Quickly add 5 mL of methanol, and 5 μ L of 2500 μ g/mL surrogate spiking solution to bring the final volume of methanol to 5 mL. For an LCS or MS/MSD sample add 4.9 mL of methanol, 5 μ L of surrogate spike solution, and 0.1 mL of matrix spike solution. Cap the vial and shake or vortex to mix thoroughly.

NOTE: Sections 11.9.1.1.1 and 11.9.1.1.2 must be performed rapidly and without interruption to avoid the loss of volatile organics.

11.10. Initial review and corrective actions

11.10.1. 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.

11.10.2. 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.

11.10.2.1. 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, the sample is reanalyzed to confirm. If the change in sensitivity is due to instrumental problems all affected samples must be reanalyzed after the problem is corrected.

11.10.3. 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, at the same dilution as the original run, to demonstrate matrix effect, but reanalysis at a dilution could be considered for severe matrix effect.

11.11. 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.
- The relative intensities of ions should agree to within $\pm 30\%$ 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

$$SD = \sqrt{\sum_{i=1}^N \frac{(X_i - X)^2}{N - 1}}$$

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

$$\%RSD = \frac{\text{Standard Deviation}}{RF_i} \cdot 100$$

 RF_i = Mean of RF values in the curve

12.3.4. Percent drift between the initial calibration and the continuing calibration:

Equation 4

$$\% \text{ Drift} = \frac{C_{\text{expected}} - C_{\text{found}}}{C_{\text{expected}}} \times 100$$

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

$$\text{Concentration mg / L} = \frac{x}{RF}$$

12.3.5.2. Calculation of concentration using Linear fit

Equation 6

$$\text{Concentration mg / L} = A + Bx$$

12.3.5.3. Calculation of concentration using Quadratic fit

Equation 7

$$\text{Concentration mg / L} = A + Bx + Cx^2$$

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:

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)

A_{is} = Area of the characteristic ion for the internal standard

I_s = Amount of internal standard added in ng

$$\text{Dilution Factor} = D_f = \frac{\text{Total volume purged (mL)}}{\text{Volume of original sample used (mL)}}$$

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:

A_x , I_s , D_f , A_{is} , same as for water.

V_t = Volume of total extract, mL (Typically 25 mL)

V_a = Volume of extract added for purging, μL

W_s = Weight of sample extracted, g

$$D = \frac{100 - \% \text{moisture}}{100}$$

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:

A_x , I_s , A_{is} , same as for water.

D is as for medium level soils

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:

A_x = Area in the total ion chromatogram for the compound being measured

A_{is} = Area of the total ion chromatogram for the nearest internal standard without interference

$RF = 1$

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

$$\text{Matrix Spike Recovery, \%} = \frac{SSR - SR}{SA} \times 100$$

SSR = Spike sample result

SR = Sample result

SA = Spike added

12.3.7. Relative % Difference calculation for the MS/MSD

Equation 12

$$RPD = \frac{|\text{MSR} - \text{MSDR}|}{\frac{1}{2}(\text{MSR} + \text{MSDR})} \times 100$$

Where:

RPD = Relative percent difference

MSR = Matrix spike result

MSDR = Matrix spike duplicate result

13. METHOD PERFORMANCE

13.1. Method Detection Limit

13.1.1. 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 #: S-Q-003 and NC-QA-0021. 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.

13.1.2. 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.

13.2. Initial Demonstration

13.3. 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.)

13.3.1. Four aliquots of the QC check sample are analyzed using the same procedures used to analyze samples, including sample preparation.

13.3.2. 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%.

13.3.3. If any analyte does not meet the acceptance criteria, check the acceptance limits in the reference methods. 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.

13.3.4. Training Qualification

- 13.3.4.1. 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.

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. 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.
- 15.2. All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."
- 15.3. The following waste streams are produced when this method is carried out.
- 15.3.1. **Acidic material from the auto-sampler:** Waste stream must be collected and neutralized before discharge to a sewer system if the pH is less than 4.
- 15.3.2. **Methanol waste from rinses and standards:** Methanol waste is discarded as a flammable liquid in a solvent waste container located in the lab.
- 15.3.3. **All samples including purged and extracted soils and waters:** Samples are collected in boxes and removed from the lab to storage. The waste coordinator handles crushing the vials and proper disposal.
- 15.3.4. **Solid samples** - Stirbars are removed from the sample. The contents of the vial are poured into a beaker and the soil allowed to settle out. The soil is disposed of in the solid waste container.

16. REFERENCES

- 16.1. References

16.1.1. SW846, *Test Methods for Evaluating Solid Waste*, Third Edition, Gas Chromatography/Mass Spectrometry for Volatile Organics, Method 8260B, Update III, December 1996

16.1.2. SW846, *Test Methods for Evaluating Solid Waste*, Third Edition, Gas Chromatography/Mass Spectrometry for Volatile Organics, Method 8260A, Update II, September 1994.

16.1.3. Corporate Quality Management Plan (QMP), current version.

16.1.4. STL Laboratory Quality Manual (LQM), current version.

16.1.5. STL Corporate Safety Manual, M-E-0001 and STL North Canton Facility Addendum and Contingency Plan, current version.

16.2. Associated SOPs and Policies, latest version

16.2.1. QA Policy, QA-003

16.2.2. Glassware Washing, NC-QA-0014

16.2.3. Statistical Evaluation of Data and Development of Control Charts, NC-QA-0018

16.2.4. Method Detection Limits and Instrument Detection Limits, S-Q-003 and NC-QA-0021

16.2.5. Navy/Army SOP, NC-QA-0016

17. MISCELLANEOUS

17.1. Modifications from the 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. The following are protocols that must be followed when analyzing OhioVAP samples:

- Sections 9.4 and 9.5: n-Hexane must be spiked and reported for both the LCS and MS/MSD.
 - Sections 10.4.6: All analytes must have a %RSDs $\leq$ 15%. Corrective action must be completed for any compounds failing the <15% requirement.
 - Section 11.1 and 17.1.5 (Method deviations) are not to be performed.
 - Section 11.10.2: For OhioVAP projects, the laboratory will reanalyze any sample where the internal standard fails and there is no evidence of matrix interference.
- 17.3. The following are protocols that must be followed when analyzing BP Oil – Lima Refinery RFI work plan.
- Section 8.1 STL will continue to follow the 14 day holding time specified in the Corporate SOP.
 - Delete for this project Section 8.3 At specific client request, unpreserved soil samples may be accepted.
 - Delete for this project Section 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.
 - Modify Section 8.5 For the purpose of this project, the soil/methanol mixture may be stored for two days prior to analysis.
 - Modify Section 8. For the purpose of this project, the soil/methanol mixture may be stored for two days prior to analysis.
 - Modify (per discussion with Region V representative) to Section 10.4.6 Compounds with %RSD >15% are to be calibrated using an alternate calibration technique (e.g. linear or quadratic calibration curve). For poor responders, the alternate calibration technique requirements may not be met either. This sentence is added for those cases. If the correlation coefficient is < 0.990, then any hit for these compounds must be flagged as estimated.
 - Modify Section 10.4.2 It is necessary to analyze the Appendix IX standard separately from the primary standard due to the presence of xylene solvent in the Appendix IX standard. Alternatively, STL will purchase the Appendix IX standard in a solvent other than xylene.
 - Modify Section 10.4.9 For this project, this section will be modified to comply with the requirement of adding methanol to the calibration standards so that those standards contain the same amount of methanol as the diluted soil extracts.

- Modify Table 6
- For the project specific SOP, acetonitrile will be removed from table 6, page 49 and appended onto table 5, page 48. Acetonitrile will be calibrated as part of the STL primary standard, using a separate acetonitrile standard. This will ensure that the calibration curve for acetonitrile will be done free from any interference from allyl chloride.

17.4. The following are protocols that must be followed when analyzing South Carolina Projects only.

- **Delete** from Section 10.4.6 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.
- **Delete** from Section 12.3.5 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.
- **Delete** from Section 12.3.5.3
 - Calculation of concentration using Quadratic fit

Equation 7

$$\text{Concentration mg / L} = A + Bx + Cx^2$$

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

- **Change** Section 9.2 The compounds included in the surrogate spiking solutions are listed in Tables 8 *and* 9.

17.5. The following are protocols that must be followed to achieve the lower reporting limits required when analyzing Michigan projects.

17.5.1. Modify Section 8.5.4 and 8.6.8 (add 5 uL of 2500 ug/mL surrogate solution for a nominal 25 g sample).

17.5.2. Modify Section 8.5.5 and 8.6.9 (add 100 uL of 50 ug/mL spike solution for a nominal 25 g sample).

- 17.5.3. Modify Section 8.5.6 and 8.6.10 (add 100 uL of 50 ug/mL spike solution for a nominal 25g sample).
- 17.5.4. Michigan reporting limits for methanol preserved soils are achieved by injecting 100 uL of the methanol extract in a 5 mL purge. The instrument is calibrated using the recommended calibration levels in water of 0.5 ug/L, 1 ug/L, 5 ug/L, 10 ug/L, 20 ug/L, and 50 ug/L. Some analytes are prepared at higher concentrations.
- 17.5.5. Samples for Michigan projects frequently require calibration for 2-Methylnaphthalene. Recommended calibration levels for this compounds are 2 ug/L, 10 ug/L, 20 ug/L, 40 ug/L and 80 ug/L.

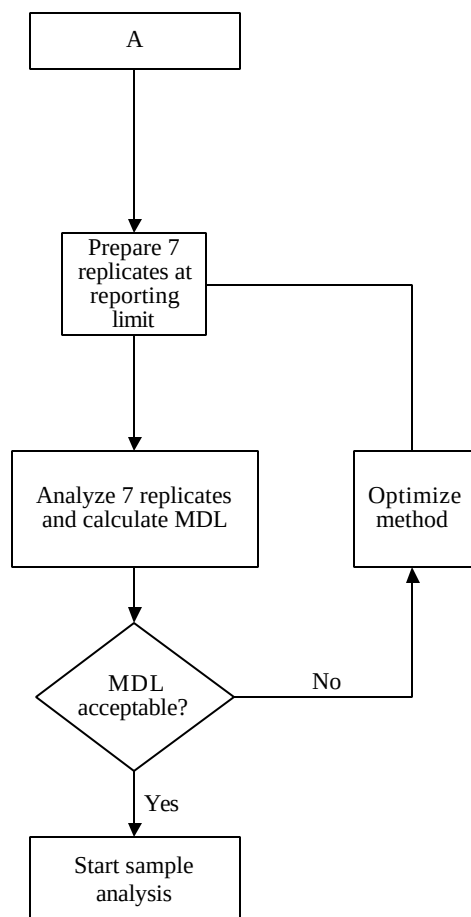
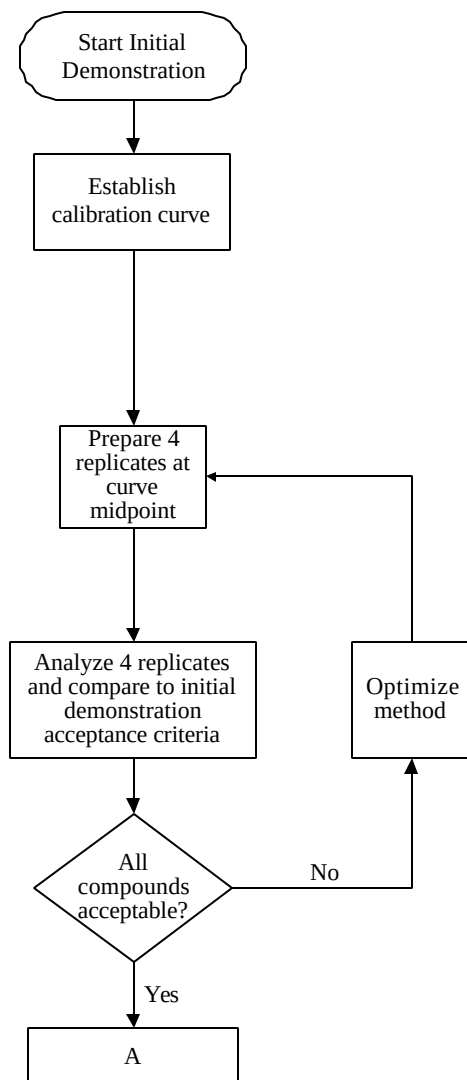


Table 1
STL Primary Standard and Reporting Limits

Compound	CAS Number	Reporting Limits ¹				
		5 mL Water µg/L	Low Level 5 mL water µg/L	Low soil µg/kg	8260B/ 5035 Soil ug/kg	8260A 5030A Med Level Soil µg/kg
Dichlorodifluoromethane	75-71-8	5	1	5	250	1200
Chloromethane	74-87-3	5	1	5	250	1200
Bromomethane	74-83-9	5	1	5	250	1200
Vinyl chloride	75-01-4	5	1	5	250	1200
Chloroethane	75-00-3	5	1	5	250	1200
Trichlorofluoromethane	75-69-4	5	1	5	250	1200
Acrolein	107-02-8	100	20	100	5000	12000
Acetone	67-64-1	20	10	20	1000	2500
Trichlorotrifluoroethane	76-13-1	5	1	5	250	620
Iodomethane	74-88-4	5	1	5	250	620
Carbon disulfide	75-15-0	5	1	5	250	620
Methylene chloride	75-09-2	5	1	5	250	620
tert-Butyl alcohol	75-65-0	200	50	200	10,000	25000
1,1-Dichloroethene	75-35-4	5	1	5	250	620
1,1-Dichloroethane	75-34-3	5	1	5	250	620
trans-1,2-Dichloroethene	156-60-5	5.0	1.0	5.0	250	310
Acrylonitrile	107-13-1	100	20	100	5000	12000
Methyl tert-butyl ether (MTBE)	1634-04-4	20	5	20	1000	2500
Hexane	110-54-3	5	1	5	250	620
cis-1,2-Dichloroethene	156-59-2	5	1	5	250	620
1,2-Dichloroethene (Total)	540-59-0	10	2	10	500	620
Tetrahydrofuran	109-99-9	20	5	20	1000	2500
Chloroform	67-66-3	5	1	5	250	620
1,2-Dichloroethane	107-06-2	5	1	5	250	620
Dibromomethane	74-95-3	5	1	5	250	620
2-Butanone	78-93-3	20	5	20	1000	2500
1,4-Dioxane	123-91-1	500	200	500	25000	62000
1,1,1-Trichloroethane	71-55-6	5	1	5	250	620
Carbon tetrachloride	56-23-5	5	1	5	250	620
Bromodichloromethane	75-27-4	5	1	5	250	620
1,2-Dichloropropane	78-87-5	5	1	5	250	620
cis-1,3-Dichloropropene	10061-01-5	5	1	5	250	620

Table 1

STL Primary Standard and Reporting Limits

Compound	CAS Number	Reporting Limits ¹				
		5 mL Water µg/L	Low Level 5 mL water µg/L	Low soil µg/kg	8260B/ 5035 Soil ug/kg	8260A 5030A Med Level Soil µg/kg
Trichloroethene	79-01-6	5	1	5	250	620
Dibromochloromethane	124-48-1	5	1	5	250	620
1,2-Dibromoethane	106-93-4	5	1	5	250	620
1,2,3-Trichloropropane	96-18-4	5	1	5	250	620
1,1,2-Trichloroethane	79-00-5	5	1	5	250	620
Benzene	71-43-2	5	1	5	250	620
Ethylmethacrylate	97-63-2	5	1	5	250	620
trans-1,3-Dichloropropene	10061-02-6	5	1	5	250	620
Bromoform	75-25-2	5	1	5	250	620
4-Methyl-2-pentanone	108-10-1	20	5	20	1000	2500
2-Hexanone	591-78-6	20	5	20	1000	2500
Tetrachloroethene	127-18-4	5	1	5	250	620
Toluene	108-88-3	5	1	5	250	620
1,1,2,2-Tetrachloroethane	79-34-5	5	1	5	250	620
2-Chloroethyl vinyl ether	110-75-8	N/A ²	N/A	50	1000	6200
Vinyl acetate	108-05-4	10	2	10	500	1200
Chlorobenzene	108-90-7	5	1	5	250	620
Ethylbenzene	100-41-4	5	1	5	250	620
Styrene	100-42-5	5	1	5	250	620
t-1,4-Dichloro-2-butene	110-57-6	5	1	5	250	620
m and p Xylenes		10	2	10	500	1200
o-xylene	95-47-6	5.0	1	5	250	620
Total xylenes	1330-20-7	10	2	10	500	1200
1,3-Dichlorobenzene	541-73-1	5	1	5	250	620
1,4-Dichlorobenzene	106-46-7	5	1	5	250	620
1,2-Dichlorobenzene	95-50-1	5	1	5	250	620
2,2-Dichloropropane	590-20-7	5	1	5	250	
Bromochloromethane	74-97-5	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	

Table 1

STL Primary Standard and Reporting Limits

Compound	CAS Number	Reporting Limits ¹				
		5 mL Water µg/L	Low Level 5 mL water µg/L	Low soil µg/kg	8260B/ 5035 Soil ug/kg	8260A 5030A Med Level Soil µg/kg
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	
4-Isopropyltoluene	99-87-6	5	1	5	250	
n-Butylbenzene	104-51-8	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	
Acetonitrile	75-05-8	100	20	100	5000	
Cyclohexane	110-82-7	10	1	10	500	
Methyl Acetate	79-20-9	10	10	10	500	
Methyl cyclohexane	108-87-2	10	1	10	500	

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 purge¹

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	50	200	500	1000	2000
Acetone	5	20	50	100	200
Trichlorotrifluoroethane	5	20	50	100	200
Iodomethane	5	20	50	100	200
Carbon disulfide	5	20	50	100	200
Methylene chloride	5	20	50	100	200
tert-Butyl alcohol	100	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	50	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	250	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
Dibromochloromethane	5	20	50	100	200

Table 2

STL Primary Standard Calibration Levels, 5 mL purge¹

Compound	Calibration Level ug/L				
	Level 1	Level 2	Level 3	Level 4	Level 5
1,2-Dibromoethane	5	20	50	100	200
1,2,3-Trichloropropane	5	20	50	100	200
Acetonitrile	50	200	500	1000	2000
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
2,2-Dichloropropane	5	20	50	100	200
Bromochloromethane	5	20	50	100	200
1,1-Dichloropropene	5	20	50	100	200
Bromodichloromethane	5	20	50	100	200
1,2-Dichloropropane	5	20	50	100	200
1,3-Dichloropropane	5	20	50	100	200
Isopropylbenzene	5	20	50	100	200
Bromobenzene	5	20	50	100	200
n-Propylbenzene	5	20	50	100	200
2-Chlorotoluene	5	20	50	100	200
4-Chlorotoluene	5	20	50	100	200
1,3,5-Trimethylbenzene	5	20	50	100	200
tert-Butylbenzene	5	20	50	100	200

Table 2

STL Primary Standard Calibration Levels, 5 mL purge¹

Compound	Calibration Level ug/L				
	Level 1	Level 2	Level 3	Level 4	Level 5
1,2,4-Trimethylbenzene	5	20	50	100	200
sec-butylbenzene	5	20	50	100	200
4-Isopropyltoluene	5	20	50	100	200
n-Butylbenzene	5	20	50	100	200
1,2,4-Trichlorobenzene	5	20	50	100	200
Napthalene	5	20	50	100	200
Hexachlorobutadiene	5	20	50	100	200
1,2,3-Trichlorobenzene	5	20	50	100	200

¹ Levels for 25 mL purge are 5 times lower in all cases

Table 2A

STL Primary Standard Calibration Levels, Low Level¹

Compound	Calibration Level ug/L				
	Level 1	Level 2	Level 3	Level 4	Level 5
Dibromofluoromethane (Surrogate)	1	5	10	20	40
1,2-Dichloroethane-d4 (Surrogate)	1	5	10	20	40
Toluene-d8 (Surrogate)	1	5	10	20	40
Bromofluorobenzene (Surrogate)	1	5	10	20	40
Dichlorodifluoromethane	1	5	10	20	40
Chloromethane	1	5	10	20	40
Vinyl Chloride	1	5	10	20	40
Bromomethane	1	5	10	20	40
Chloroethane	1	5	10	20	40
Trichlorofluoromethane	1	5	10	20	40
Acrolein	10	50	100	200	400
Acetone	2	10	20	40	80
1,1-Dichloroethene	1	5	10	20	40
Trichlorotrifluoroethane	1	5	10	20	40
Iodomethane	1	5	10	20	40
Carbon Disulfide	1	5	10	20	40
Methylene Chloride	1	5	10	20	40
Acetonitrile	10	50	100	200	400
Acrylonitrile	10	50	100	200	400
Methyl tert-butyl ether	1	5	10	20	40

Table 2A

STL Primary Standard Calibration Levels, Low Level ¹

Compound	Calibration Level ug/L				
	Level 1	Level 2	Level 3	Level 4	Level 5
trans-1,2-Dichloroethene	1	5	10	20	40
Hexane	1	5	10	20	40
Vinyl acetate	1	5	10	20	40
1,1-Dichloroethane	1	5	10	20	40
tert-Butyl Alcohol	20	100	200	400	800
2-Butanone	2	10	20	40	80
cis-1,2-dichloroethene	1	5	10	20	40
2,2-Dichloropropane	1	5	10	20	40
Bromochloromethane	1	5	10	20	40
Chloroform	1	5	10	20	40
Tetrahydrofuran	1	5	10	20	40
1,1,1-Trichloroethane	1	5	10	20	40
1,1-Dichloropropene	1	5	10	20	40
Carbon Tetrachloride	1	5	10	20	40
1,2-Dichloroethane	1	5	10	20	40
Benzene	1	5	10	20	40
Trichloroethene	1	5	10	20	40
1,2-Dichloropropane	1	5	10	20	40
1,4-Dioxane	50	250	500	1000	2000
Dibromomethane	1	5	10	20	40
Bromodichloromethane	1	5	10	20	40
2-Chloroethyl vinyl ether	2	10	20	40	80
cis-1,3-Dichloropropene	1	5	10	20	40
4-Methyl-2-pentanone	2	10	20	40	80
Toluene	1	5	10	20	40
trans-1,3-Dichloropropene	1	5	10	20	40
Ethyl Methacrylate	1	5	10	20	40
1,1,2-Trichloroethane	1	5	10	20	40
1,3-Dichloropropane	1	5	10	20	40
Tetrachloroethene	1	5	10	20	40
2-Hexanone	2	10	20	40	80
Dibromochloromethane	1	5	10	20	40
1,2-Dibromoethane	1	5	10	20	40
Chlorobenzene	1	5	10	20	40
1,1,1,2-Tetrachloroethane	1	5	10	20	40
Ethylbenzene	1	5	10	20	40
m + p-Xylene	2	10	20	40	80
Xylene-o	1	5	10	20	40

Table 2A

STL Primary Standard Calibration Levels, Low Level ¹

Compound	Calibration Level ug/L				
	Level 1	Level 2	Level 3	Level 4	Level 5
Styrene	1	5	10	20	40
Bromoform	1	5	10	20	40
Isopropylbenzene	1	5	10	20	40
1,1,2,2-Tetrachloroethane	1	5	10	20	40
1,4-Dichloro-2-butene	1	5	10	20	40
1,2,3-Trichloropropane	1	5	10	20	40
Bromobenzene	1	5	10	20	40
n-Propylbenzene	1	5	10	20	40
2-Chlorotoluene	1	5	10	20	40
1,3,5-Trimethylbenzene	1	5	10	20	40
4-Chlorotoluene	1	5	10	20	40
tert-Butylbenzene	1	5	10	20	40
1,2,4-Trimethylbenzene	1	5	10	20	40
sec-Butylbenzene	1	5	10	20	40
4-Isopropyltoluene	1	5	10	20	40
1,3-Dichlorobenzene	1	5	10	20	40
1,4-Dichlorobenzene	1	5	10	20	40
n-Butylbenzene	1	5	10	20	40
1,2-Dichlorobenzene	1	5	10	20	40
1,2-Dibromo-3-chloropropane	1	5	10	20	40
1,2,4-Trichlorobenzene	1	5	10	20	40
Hexachlorobutadiene	1	5	10	20	40
Naphthalene	1	5	10	20	40
1,2,3-Trichlorobenzene	1	5	10	20	40
Cyclohexane	1	5	10	20	40
Methyl Acetate	2	10	20	40	80
Methylcyclohexane	1	5	10	20	40
1,3,5-Trichlorobenzene	1	5	10	20	40

¹ 25 mL purge samples analyzed at 5 mL purge on more sensitive equipment.

Table 3

STL Appendix IX Standard and Reporting Limits, 5 mL purge

Compound	CAS Number	Reporting Limits			
		5 mL Water µg/L	Low Level 5mL purge 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	2	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	2	5	250
Isobutanol	78-83-1	200	50	200	10,000
Methyl methacrylate	80-62-6	5	2	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	4	10	500
Cyclohexanone	108-94-1	50	20	50	2500
Isopropylbenzene	98-82-8	5	1	5	250
2-Methylnaphthalene (Michigan only)	91-57-6	NA	5	NA	330

Table 4

Recommended/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	50	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	100	400	1,000	2,000	4,000
Propionitrile	10	40	100	200	400
Methacrylonitrile	5	20	50	100	200
Isobutanol	100	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	50	200	500	1,000	2,000
2-Methylnaphthalene (Michigan only)	2	10	20	40	80

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	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	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-Butyl 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			X		
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
Trichloroethene	79-01-6	X	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
Dibromochloromethane	124-48-1	X		X	X	X
1,2-Dibromoethane	106-93-4			X	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	X		X		
1,4-Dichlorobenzene	106-46-7	X		X		
1,2-Dichlorobenzene	95-50-1	X		X		
Cyclohexane	110-82-7	X		X		
Methyl Acetate	79-20-9	X		X		
Methyl cyclohexane	108-87-2	X		X		
Isopropylbenzene	98-82-8			X		
1,2-Dibromo-3-chloropropane	96-12-8			X	X	X
1,2,4-Trichlorobenzene	120-82-1			X		

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
Ethyl ether	60-29-7					X
Ethyl Acetate	141-78-6					X
2-Nitropropane	79-46-9					
Cyclohexanone	108-94-1					X

Table 7
Internal Standards

	Standard Concentration µg/mL	Quantitation ion (5 mL purge)
Fluorobenzene	50	96
Chlorobenzene-d5	50	117
1,4-Dichlorobenzene-d4	50	152

Notes:

- 1) 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	50
Dibromofluoromethane	50
Toluene-d ₈	50
4-Bromofluorobenzene	50

Notes:

- 1) Except for medium level soils, the surrogate and internal standards may be combined in one solution.
- 2) Recovery limits for surrogates are generated from historical data and are maintained by the QA department.

Table 9

Matrix Spike / LCS Control Compounds

Compound	Standard Concentration µg /mL
1,1-Dichloroethene	50
Trichloroethene	50
Toluene	50
Benzene	50
Chlorobenzene	50
n-Hexane (Ohio VAP only)	50

Notes:

- 1) 5 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 department.
- 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, 8260A 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
n-Hexane (Ohio VAP only)	<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

Table 13
Characteristic ions

Compound	Primary*	Secondary	Tertiary
1,1-Dichloroethene	96	61	98
Acrolein	56	55	58
Iodomethane	142	127	141
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

Table 13
Characteristic ions

Compound	Primary*	Secondary	Tertiary
Tetrachloroethene	164	166	131
Ethyl methacrylate	69	41	99, 86, 114
2-Hexanone	43	58	57, 100
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	
Cyclohexane	56	69	84
Methyl Acetate	43	74	
Methyl cyclohexane	83	55	98

* 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.

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STL NORTH CANTON STANDARD OPERATING PROCEDURE

**TITLE: GAS CHROMATOGRAPHIC ANALYSIS BASED ON METHOD 8000B,
8021B, 8081A, 8082, 8151A, 8310, 8141A, 8015B, and 615**

(SUPERSEDES: Revision 5.7, Dated 10/01/03)

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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. Appendix F describes procedures for the analysis of petroleum hydrocarbons by SW-846 8015B methodology. Appendix G includes criteria for the analysis of non-halogenated organic compounds by Method 8015B, Direct Injection.

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-0001NC). Solid samples are prepared using sonication, Soxhlet or automated Soxhlet (PCB only) (SOP # CORP-OP-0001NC). 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 STL North Canton Laboratory Quality Manual (LQM), current version.

4. INTERFERENCES

Contamination by carryover can occur when a low concentration sample is analyzed after a high concentration sample. 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. Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual and this document.

5.2. Eye protection that prevents splash, 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 North Canton Chemical Hygiene plan for a complete description of personal protection equipment. Latex, Nitrile and vinyl gloves all provide adequate protection against the methanol used in this method.

5.3. The following is a list of the materials used in this method, which have a serious or significant hazard rating.
NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table. A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Methanol	Flammable Poison Irritant	200 ppm-TWA	A slight irritant to the mucous membranes. Toxic effects exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure may include headache, drowsiness and dizziness. Methyl alcohol is a defatting agent and may cause skin to become dry and cracked. Skin absorption can occur; symptoms may parallel inhalation exposure. Irritant to the eyes.
Acetone	Flammable	1000 ppm-TWA	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.
Hexane	Flammable Irritant	500 ppm-TWA	Inhalation of vapors irritates the respiratory tract. Overexposure may cause lightheadedness, nausea, headache, and blurred vision. Vapors may cause irritation to the skin and eyes.
Methylene Chloride	Carcinogen Irritant	25 ppm-TWA 125 ppm-STEL	Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting and headache. Causes irritation, redness and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degrades the skin. May be absorbed through skin.
Sulfuric Acid	Corrosive Oxidizer Dehydrator Poison Carcinogen	1 Mg/M3-TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.
Hydrochloric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Sodium Bisulfate	Corrosive	None Listed	Contact may cause skin/eye burns. Inhalation can cause irritation of the respiratory tract with burning pain in the nose and throat, coughing, wheezing and shortness of breath. Causes chemical burns to the respiratory tract. May cause fatal spasms, inflammation or pulmonary/respiratory edema.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

5.4. Opened containers of neat standards will be handled in a fume hood.

5.5. Sample extracts and standards, which are in a flammable solvent, shall be stored in an explosion-proof refrigerator.

5.6. When using hydrogen gas as a carrier, all precautions listed in the CSM shall be observed.

5.7. Standard preparation and dilution shall be performed inside an operating fume hood.

5.8. The gas chromatograph contains zones that have elevated temperatures. The analyst needs to be aware of the locations of those zones, and must cool them to room temperature prior to working on them.

5.9. There are areas of high voltage in both the gas chromatograph and the mass spectrometer. Depending on the type of work involved, either turn the power to the instrument off, or disconnect it from its source of power.

6. EQUIPMENT AND SUPPLIES

6.1. 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 as recommended by the manufacturer. 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 demonstration). 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 $\leq 6^{\circ}\text{C}$ 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, Zero Air.

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 $\leq 6^{\circ}\text{C}$ 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 North Canton 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 may 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. Project or program specific control limits may be used in place of in-house limits. 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.
 - 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 reparation is not necessary. If the sample is out of control and the MS and/or MSD is in control, then reparation or flagging of the data is required. Re-preparation includes the parent sample and MS/MSD.
- 9.4.3. Refer to the STL North Canton QC Program document (QA-003) for further details of the corrective actions.

Note: For Ohio VAP Projects, all surrogates must meet criteria.

9.5. Method Blanks

For each batch of samples, analyze a method blank. The method blank consists of reagent water for aqueous semivolatile samples, and sodium sulfate for semivolatile soils tests (Refer to SOP No. CORP-OP-0001NCNC 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 North Canton QC Program document (QA-003) for further details of the corrective actions.

9.6. 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 with a subset of control analytes. If any control analyte or surrogate is outside established control limits, the system is out of control and corrective action must occur. Corrective action will

normally be reparation and reanalysis of the batch; however, if the matrix spike and matrix spike duplicate are within limits; the batch may be acceptable.

- 9.6.1. Refer to the STL North Canton QC Program document (QA-003) for further details of the corrective action.
- 9.6.2. 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.
- 9.6.3. LCS compound lists are included in the appendices.

9.7. 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 reparation 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.

- 9.7.1. 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.

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.

$$\text{Calibration Factor (CF)} = \frac{\text{Area or Height of Peak}}{\text{Mass Injected (ng)}}$$

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:

$$\text{Average response factor} = \overline{RF} = \frac{\sum_{i=1}^n RF_i}{n}$$

Where: n = Number of calibration levels

$$\sum_{i=1}^n RF_i = \text{Sum of response factors for each calibration level}$$

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 $\pm$ 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 $\leq 20\%$.
- 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

10.11.1.1. 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 or calibration verification.

10.11.2. Calibration Verification

10.11.2.1. 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 < 15% meet the calibration criteria. The calibration verification is also acceptable if the average of the %D for all the analytes is < 15%. This average is calculated by summing the entire absolute %D results in the calibration (including surrogates) and dividing by the number of analytes. Any analyte that is reportable as found must have a % difference of < 15% in the calibration verification or 12 hour calibration, on the column used for quantitation. Refer to section 12.1.2 for which result to report.

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. The bracketing standards on the column used for calibration must meet the same criteria as the opening standards. 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 proceeding 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

10.11.9.1. % Difference for internal and external methods is calculated as follows

Internal Standard:

External standard:

$$\%D = \frac{RF_c - \overline{RF}}{\overline{RF}} \times 100$$

$$\%D = \frac{CF_c - \overline{CF}}{\overline{CF}} \times 100$$

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

- 10.11.10.1. % Drift is used for comparing the continuing calibration to a linear or quadratic curve. The criteria for % drift are the same as for % difference

$$\% \text{ Drift} = \frac{\text{Calculated Conc.} - \text{Theoretical Conc.}}{\text{Theoretical Conc.}} \times 100\%$$

10.11.11. Corrective Actions for Continuing Calibration

- 10.11.11.1. If the overall average %D of all analytes is greater than $\pm 15\%$ 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 $\pm 15\%$, a new calibration curve must be prepared.

10.11.12. Corrective Action for Samples

- 10.11.12.1. For internal standard methods, any samples injected after a standard not meeting the calibration criteria must be re-injected.
- 10.11.12.2. For external standard methods, any samples injected after the last good continuing calibration standard must be re-injected.
- 10.11.12.3. 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 $\%D \leq 15\%$, then the analysis is acceptable for that sample.

11. PROCEDURE

11.1. Extraction

- 11.1.1. Extraction procedures are referenced in the SOP CORP-OP-0001NC, latest revision.

11.2. Cleanup

- 11.2.1. Cleanup procedures are referenced in the SOP NC-OP-0025, latest revision.

11.3. Gas Chromatography

- 11.3.1. Chromatographic conditions for individual methods are presented in the appendices.

11.4. Sample Introduction

- 11.4.1. In general, volatile analytes are introduced using purge and trap as described in Appendix A.
- 11.4.2. 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

- 11.5.1. 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.
- 11.5.2. The daily calibration includes analysis of standards containing all single response analytes and updating the retention time windows.
- 11.5.3. 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 determined for all analytes. 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 multi-response 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. If the retention time window as calculated above is less than ± 0.05 minutes, use a retention time window appropriate for the analysis and run time. This allows for slight variations in retention times caused by sample matrix.
- 11.6.4. The 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

- 11.6.5.1. The retention times of all compounds in the 12 hour calibration or calibration verification standard must be within the retention time window. 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:
- 11.6.5.2. The retention time of that compound in the standard must be within a retention time range equal to twice the original window.
- 11.6.5.3. 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

- 11.7.1. 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 or continuing calibration verification 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 or continuing calibration verification.

11.8. Procedural Variations

- 11.8.1. 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:

- 12.1.2.2. 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.)

12.1.2.3. Better result approach

The higher of the two results is normally reported. The higher result is considered better because the higher result is generally higher because of chromatographic interference. The lower result is reported if any of the following two bulleted possibilities are true.

- There is obvious chromatographic interference on the column with the higher result
- The continuing or bracketing calibration on the column with the higher 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:

$$RPD = \frac{R_1 - R_2}{\frac{1}{2}(R_1 + R_2)}$$

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

- 12.2.1. 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

- 12.3.1. 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.

12.3.1.1. Guidance for Dilutions Due to Matrix

If the sample is initially run at a dilution and only minor matrix peaks are detected, 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 may be reported at client request, if the lower dilutions will not cause detector saturation, column overload, or carryover. Analyst judgement and client site history will factors in the reporting of dual dilutions.

12.4. Interferences

- 12.4.1. 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

- 12.5.1. 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

- 12.6.1.1. 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.

12.6.2. External Standard Calculations

12.6.2.1. Aqueous samples

$$\text{Concentration (mg / L)} = \frac{(A_x \times V_t \times D_f)}{(CF \times V_i \times V_s)}$$

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

12.6.2.2. Non-aqueous Samples

$$\text{Concentration (mg / kg)} = \frac{(A_x \times V_t \times D_f)}{(CF \times V_i \times W \times D)}$$

Where:

W = Weight of sample extracted or purged, g

$$D = \frac{100 - \% \text{Moisture}}{100} \quad (\text{D} = 1 \text{ if wet weight is required})$$

12.6.3. Internal Standard Calculations

12.6.3.1. Aqueous Samples

$$\text{Concentration (mg / L)} = \frac{(A_x \times C_{is} \times D_f)}{(A_{is} \times RF \times V_s)}$$

Where:

C_{is} = Amount of internal standard added, ng

A_{is} = Response of the internal standard

RF = Response factor for analyte

12.6.3.2. Non-aqueous Samples

$$\text{Concentration (mg / kg)} = \frac{(A_s \times C_{is} \times D_f)}{(A_{is} \times RF \times W \times D)}$$

12.6.4. Surrogate Recovery

12.6.4.1. 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:

$$\% \text{ Recovery} = \frac{\text{Concentration (or amount) found}}{\text{Concentration (or amount) spiked}} \times 100$$

13. METHOD PERFORMANCE

13.1. Method Detection Limit

13.1.1. 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 SOP NC-QA-0021 and S-Q-003.

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

- 13.3.1. The group/team leader has the responsibility to ensure that an analyst 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. All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

15.2. Waste Streams Produced by the Method.

- 15.2.1. The following waste streams are produced when this method is carried out.

15.2.1.1. **Vials containing sample extracts:** These vials are placed in the vial waste located in the GC/MS laboratory.

15.2.1.2. **Tubes containing sample extracts for TPH, Pesticides, PCBs and Herbicides:** These capped tubes are placed in the PCB/flammable waste located in the GC prep laboratory.

15.2.1.3. **Samples, standards, and all extraction materials contaminated with high levels (>50ppm) of PCB's must be segregated into their own waste stream.** PCB wastes are collected in one of three waste streams, solid PCB, liquid PCB and PCB vial waste. PCB containing samples are located through a LIMS query and disposed of as PCB containing.

15.2.1.4. **Extracted solid samples contaminated with methylene chloride/acetone or acetone/hexane.** These materials are disposed of in the solid waste and debris in a red container located in the extractions lab.

15.2.1.5. **Discarded samples.** These samples are collected in the solid debris drum.

16. REFERENCES

- 16.1. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW846, 3rd Edition, Final Update III, December 1996, and Section 8000B

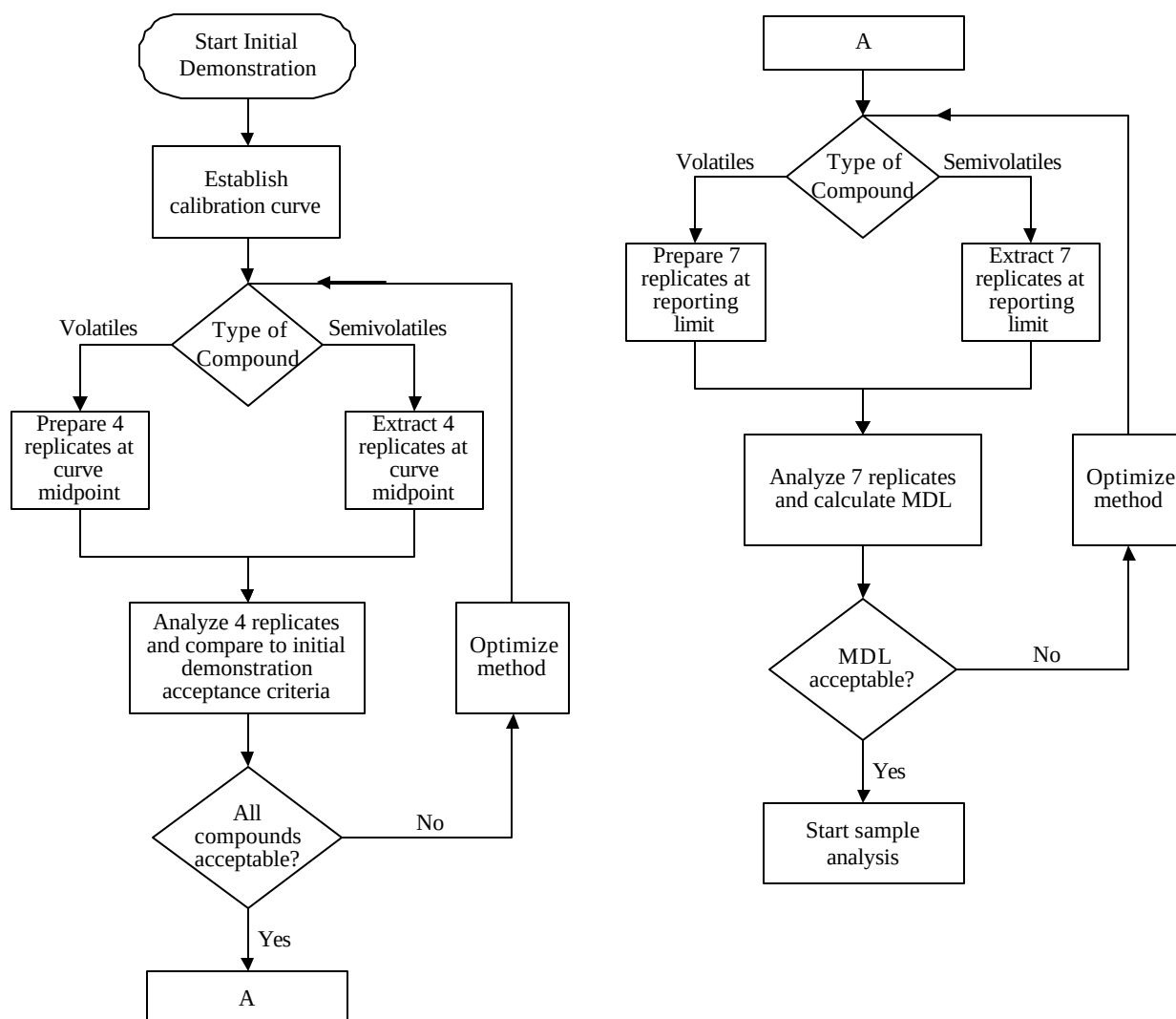
17. MISCELLANEOUS

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.

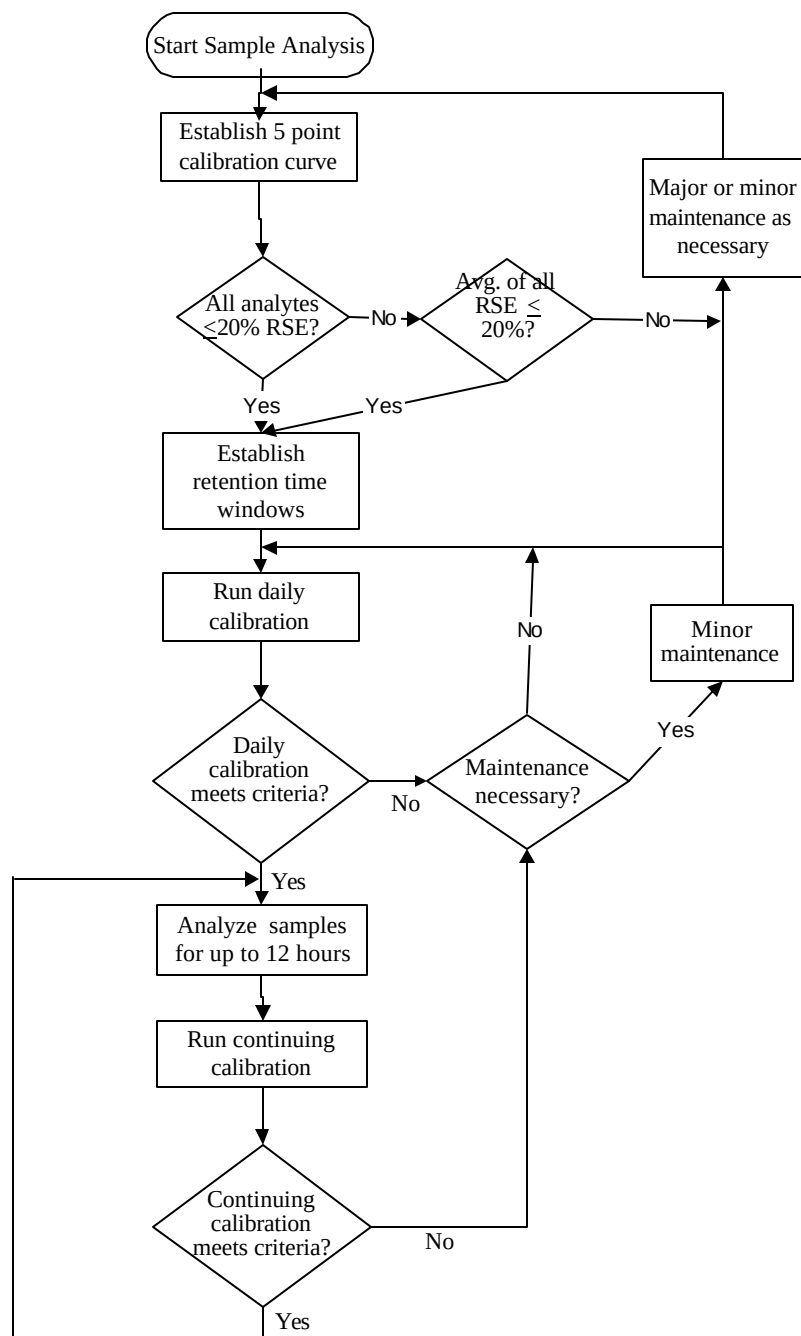
17.2. Flow Diagrams

17.2.1. Initial demonstration and MDL¹



¹ This flow diagram is for guidance and cannot cover all eventualities. Consult the SOP text and a supervisor if in doubt.

17.2.2. Sample Analysis¹



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. 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 insoluble 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.
- 1.5. The associated LIMS method code is QR.

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 back-flushed 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

- 3.1. Refer to the STL North Canton Laboratory Quality Manual (LQM), current version, 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. A holding blank is kept in the sample refrigerator. This is analyzed and replaced every 7 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 7-day period prior to the analysis of the contaminated holding blank is required.

4.6. 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. The following method analytes have been tentatively classified as known or suspected human or mammalian carcinogens: Benzene, Carbon Tetrachloride, 1,4-Dichlorobenzene, 1,2-Dichloroethane, Hexachlorobutadiene, 1,1,2,2-Tetrachloroethane, 1,1,2-Trichloroethane, Chloroform, 1,2-Dibromoethane, Tetrachloroethene, Trichloroethene, Vinyl Chloride. Pure standard materials and stock standard solutions of these compounds should be handled in a hood.

5.3. GC VOA instruments use an ultraviolet (UV) light source, which must be shielded from view.

5.4. Sodium bisulfate creates Sulfuric Acid when mixed with water.

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

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- 6.10. Balance capable of weighing to 0.01g for samples.
- 6.11. Chlorine Test Strips
- 6.12. Hach Chlorine Test Pillows

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
 - 7.2.1. Organic free water is defined as water in which an interferent is not observed at the reporting limit of the compounds of interest. The suggested method for generating organic free water is continuously sparging water with helium or nitrogen.
 - 7.2.2. Other methods may be used, so long as the requirement that the water show no interference is met. The procedure used should be documented in a lab specific attachment.
- 7.3. Methanol -- Purge and Trap Grade
- 7.4. Standards
 - 7.4.1. 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.
 - 7.4.2. 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.
- 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.

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- 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°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 $\geq -10^{\circ}\text{C}$ 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.

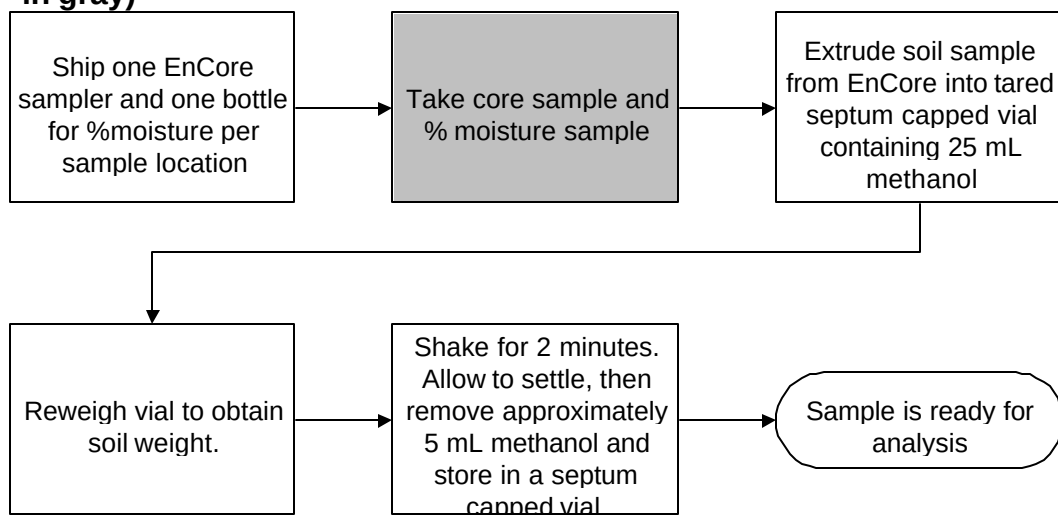
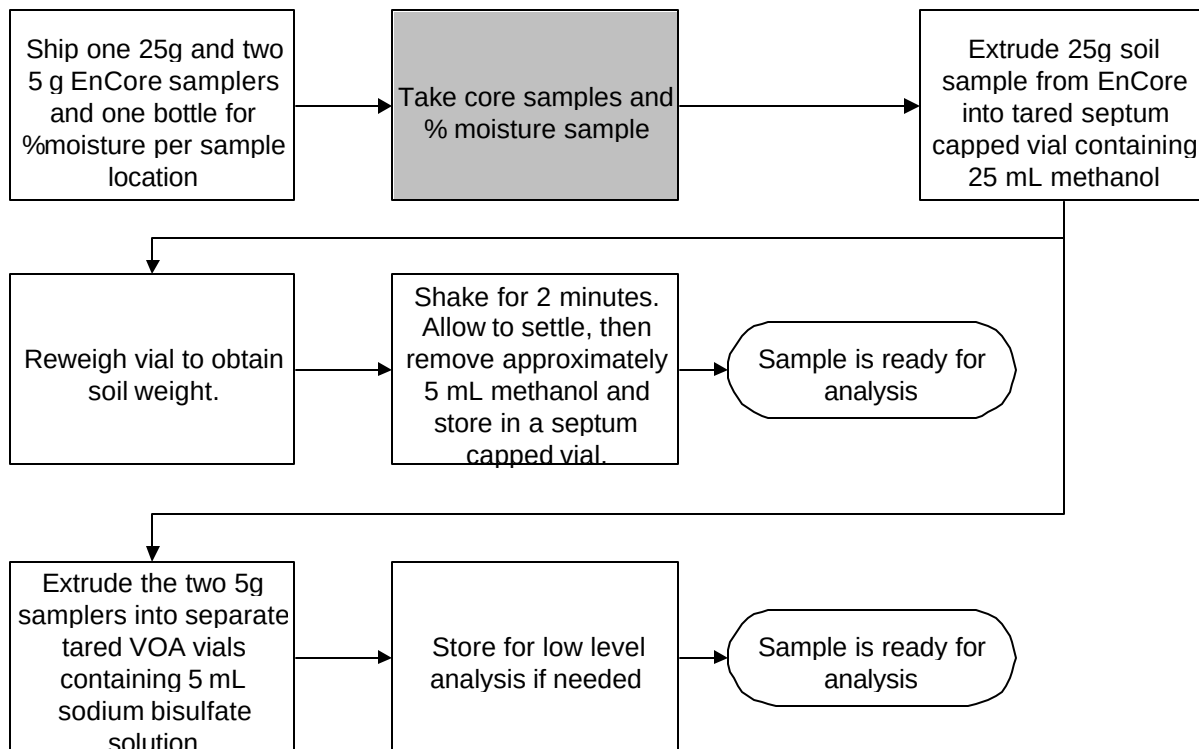
8.8. Aqueous samples are stored in glass containers with Teflon lined septa at $4^{\circ}\text{C} \pm 2^{\circ}\text{C}$, with minimum headspace.

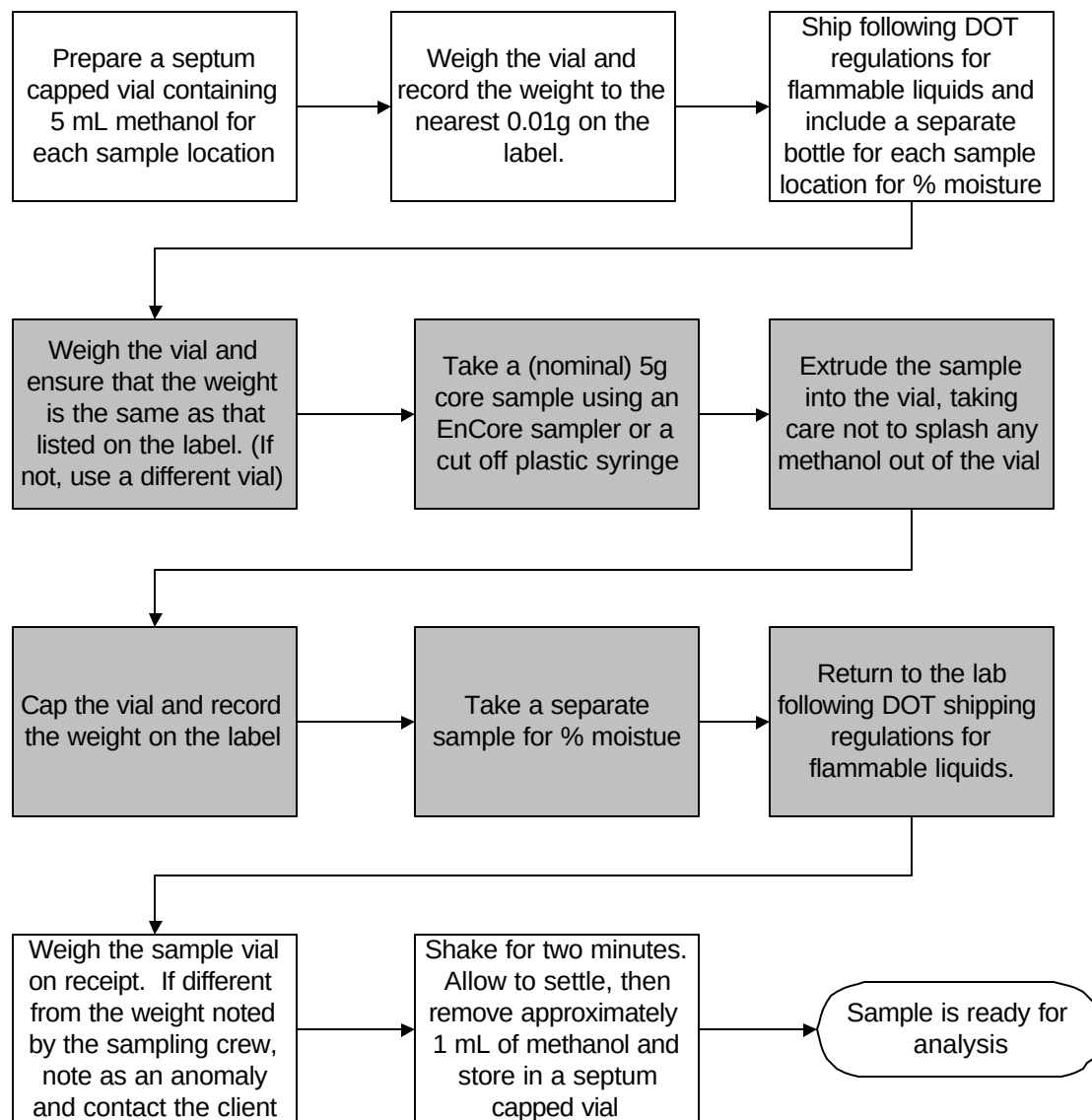
8.9. Medium level solid extracts are aliquoted into 2 - 5 mL glass vials with Teflon lined caps and stored at $4^{\circ}\text{C} \pm 2^{\circ}\text{C}$. The extracts are stored with minimum headspace.

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.

Note: Freezing is not allowed for Ohio VAP solids.

**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.

- 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

- 11.2.1. The analytical sequence starts with an initial calibration of at least five points.

11.3. Confirmation

- 11.3.1. 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.

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.

11.4. Aqueous and Soil Sample Analysis (Purge and Trap units that sample directly from the VOA vial)

- 11.4.1. Check the pH of the sample remaining in the VOA vial prior to analysis. Samples are also checked for residual chlorine at this time.
- 11.4.2. Units, which sample from the VOA vial, should be equipped with a module, which automatically adds surrogate and internal standard solution, as needed, to the sample prior to purging the sample.
- 11.4.3. 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 be analyzed as soils.
- 11.4.4. 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.
- 11.4.5. Check the pH of the sample remaining in the VOA vial after analysis is completed.

11.5. Low-Level Solids Analysis using discrete autosamplers Bulk Solids

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.

- 11.5.1. Do not discard any supernatant liquids. Mix the contents of the container with a narrow metal spatula.
- 11.5.2. Weigh out 5 g (or other appropriate aliquot) of sample into a disposable culture tube or 40 mL vial. 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 0.5 g. If the sample is contaminated with analytes such that a purge amount less than 0.5 g is appropriate, use the medium level method described in section 11.7.
- 11.5.3. Place in Autosampler.
- 11.5.4. Add 5 mL of organic free water to each vial. 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.

11.5.5. *The above steps should be performed rapidly and without interruption to avoid loss of volatile organics.*

11.5.6. *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.*

11.6. Methanol Extract Soils

11.6.1. 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.

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. All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

15.2. Waste streams produced by the method.

15.2.1. The following waste streams are produced when this method is carried out.

15.2.1.1. **Acidic material from the auto-sampler.** Waste stream must be collected and neutralized before discharge to a sewer system if the pH is less than 4.

15.2.1.2. **Methanol waste from rinses and standards.** Methanol waste is discarded as a flammable liquid .

15.2.1.3. **All samples including purged and extracted soils and waters:** Samples are collected in boxes and removed from the lab to storage. The waste coordinator handles crushing the

vials and proper disposal.

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. TABLES

Table A-1				
Standard Analyte List for Method 8021B				
Compound	CAS No.	Reporting Limit, µg/L or µg/kg		
		Aqueous	Low Soil	Medium Soil
1,1,1,2-Tetrachloroethane	630-20-6	1.0		
1,1,1-Trichloroethane	71-55-6	1.0		
1,1,2,2-Tetrachloroethane	79-34-5	1.0		
1,1,2-Trichloroethane	79-00-5	1.0		
1,1-Dichloroethane	75-34-3	1.0		
1,1-Dichloroethene	75-45-4	1.0		
1,1-Dichloropropene	563-58-6	1.0		
1,2,3-Trichlorobenzene	87-61-6	1.0		
1,2,3-Trichloropropane	96-18-4	1.0		
1,2,4-Trichlorobenzene	120-82-1	1.0		
1,2,4-Trimethylbenzene	95-63-6	1.0	1.0	50
1,2-Dibromo -3-Chloropropane(DBCP)	96-12-8	1.0		
1,2-Dibromoethane(EDB)	106-93-4	1.0		
1,2-Dichlorobenzene	95-50-1	1.0		
1,2-Dichloroethane	107-06-2	1.0		
1,2-Dichloropropane	78-87-5	1.0		
1,3,5-Trimethylbenzene	108-67-8	1.0	1.0	50
1,3-Dichlorobenzene	541-73-1	1.0		
1,3-Dichloropropane	142-28-9	1.0	1.0	50
1,4-Dichlorobenzene	106-46-7	1.0		
2,2-Dichloropropane	590-20-7	1.0	1.0	50
2-Chloroethyl vinyl ether	110-75-8	5.0		
2-Chlorotoluene	95-49-8	1.0		
4-Chlorotoluene	106-43-4	1.0		
Acetone	67-64-1	10		
Benzene	71-43-2	1.0	1.0	50
Benzyl Chloride	100-44-7	5.0		
Bromobenzene	108-86-1	1.0		
Bromochloromethane	74-97-5	1.0		
Bromodichloromethane	75-27-4	1.0		
Bromoform	75-25-2	1.0		
Bromomethane	74-83-9	1.0		
Carbon Tetrachloride	56-23-5	1.0		
Chlorobenzene	108-90-7	1.0		
Chlorodibromomethane	124-48-1	1.0		

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Table A-1				
Standard Analyte List for Method 8021B				
Compound	CAS No.	Reporting Limit, µg/L or µg/kg		
		Aqueous	Low Soil	Medium Soil
Chloroethane	70-00-3	1.0		
Chloroform	67-66-3	1.0		
Chloromethane	74-87-3	1.0		
cis -1,2 Dichloroethene	156-59-4	1.0		
cis -1,3-Dichloropropene	10061-01-5	1.0		
Dibromomethane	74-95-3	1.0		
Dichlorodifluoromethane	75-71-8	1.0		
Ethyl Benzene	100-41-4	1.0	1.0	50
Freon 113	76-13-1	1.0		
Hexachlorobutadiene	87-68-3	1.0		
Isopropylbenzene	98-82-8	1.0		
MEK (2-butanone)	78-93-3	5.0		
Methyl tert-butyl ether (MTBE)	1634-04-4	1.0		
Methylene Chloride	75-09-2	5.0		
MIBK (4-methyl-2-pentanone)	108-10-1	5.0		
Naphthalene	91-20-3	2.0	2.0	250
n-butylbenzene	104-51-8	1.0		
n-Propylbenzene	10306501	1.0		
p-Isopropyltoluene	99-87-6	1.0		
sec-Butylbenzene	135-98-8	1.0		
Styrene	100-42-5	1.0		
tert-Butylbenzene	98-06-6	1.0		
Tetrachloroethene	127-18-4	1.0		
Toluene	108-88-3	1.0	1.0	50
trans-1,2-Dichloroethene	156-60-5	1.0		
trans-1,3-Dichloropropene	10061-02-6	1.0		
Trichloroethene	79-01-6	1.0		
Trichlorofluoromethane	75-69-4	1.0		
Vinyl Chloride	75-01-4	1.0		
Xylenes (total)	1330-20-7	1.0	1.0	50

Table A-2 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-3 Surrogate and Internal Standard Concentrations				
Standard	Components	Working Solution µg/mL	Spike amount µL (for 5 mL purge)	Final concentration µg/L (µg/kg)
Combined aromatic and halogenated volatiles IS/SS	Fluorobenzene (SS)	50	1	10
	1,4-Dichlorobutane (SS)	50	1	10
	a,a,a-Trifluorotoluene	50	1	10

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

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-4				
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

- 1.1. 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 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 North Canton sample extraction SOPs. (CORP-OP-0001NC)
- 1.2. 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.
- 1.3. At client request, this method may also be used for the analysis of PCBs (Aroclors) 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.
- 1.4. The associated LIMS method code is QJ (8081A).

2. SUMMARY OF METHOD

- 2.1. 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

- 3.1. Refer to the STL North Canton Laboratory Quality Manual (LQM), current version, 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. Avoiding contact with any plastic materials minimizes interferences from phthalates.
- 4.3. Sulfur will interfere and can be removed using procedures described in SOP NC-OP-0025, Cleanup SOP.
- 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) and Sulfur cleanup (Method 3660). These cleanup procedures are included in SOP # CORP-OP-0001NC. Using 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.

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- 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. The following parameters covered by this method have been tentatively classified as known or suspected, human or mammalian carcinogens: 4,4'-DDT, 4,4'-DDD, and the BHCs. Primary standards of these toxic compounds should be prepared in a hood.
- 5.4. All ^{63}Ni sources shall be leak tested every six months, or in accordance with the manufacturer's general radioactive material license.
- 5.5. 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
- 7.3.1. 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
- 7.4.1. 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

- 8.1. 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.

10. CALIBRATION AND STANDARDIZATION

- 10.1. Refer to Section 10 of the 8000B section of this SOP for general calibration requirements.

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- 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
- 10.3.1. 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.
- 10.3.2. If the breakdown of DDT and/or endrin exceeds the limits given above, corrective action must be taken. This action may include:
- 10.4. Replacement of the injection port liner or the glass wool.
- 10.5. Cutting off a portion of the injection end of a capillary column.
- 10.6. Replacing the GC column.
- 10.7. Initial Calibration
- 10.7.1.1. Refer to Section 10 of the 8000B section of this SOP for details of calibration procedures.
- 10.7.2. Refer to Table B-7 for the initial calibration analytical sequence.
- 10.7.3. The response for each single-peak analyte will be calculated by the procedures described in the general method for GC analysis.
- 10.7.4. 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.
- 10.7.5. For multi-component pesticides:
- 10.7.5.1. A 5 point calibration is used for multi-component 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.
- 10.7.6. The analyst may include a full 5 point calibration for any of the multi-component analytes with the initial calibration.
- 10.8. 12 hour Calibration Verification
- 10.8.1. 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.
- 10.8.2. At a minimum, the 12 hour calibration includes analysis of the breakdown mix followed by mid level standards of any single and multi-component analytes.
- 10.8.3. The retention time windows for any analytes included in the 12 hour calibration are updated.
- 10.9. Continuing Calibration
- 10.9.1. 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 multi-component 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.

10.9.2. 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

11.2.1. The extraction procedure is described in SOP No. CORP-OP-0001NC.

11.3. Cleanup

11.3.1. Cleanup procedures are described in SOP No. NC-OP-0025.

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-7.

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 Multi-component Analytes

12.2.1. 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 Multi-component Analytes

12.3.1. Use 3-10 major peaks (or total area for quantitation) as described in section 10.4.4, initial calibration of multi-component analytes.

12.3.2. If there are no interfering peaks within the envelope of the multi-component 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.

12.3.2.1. Multiple peak option

12.3.3. 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.)

- 12.3.4. 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.

12.4. Total area option

- 12.4.1. The total area of the standards and samples may be used for quantitation of multi-component 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 multi-component pattern in the samples. The retention time window for total area measurement must contain at least 90% of the area of the analyte.

- 12.5. 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.

- 12.6. Surrogate recovery results are calculated and reported for decachlorobiphenyl (DCB) and tetrachloro-m-xylene (TCMX). Corrective action is only necessary if DCB and TCMX are both outside of acceptance limits.

12.7. Calculation of Column Degradation/% Breakdown (%B)

Equation 9

$$12.7.1. \text{ DDT \%B} = \frac{A_{DDD} + A_{DDE}}{A_{DDD} + A_{DDE} + A_{DDT}} \times 100$$

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.

Equation 10

$$\text{Endrin \%B} = \frac{A_{EK} + A_{EA}}{A_{EK} + A_{EA} + A_E} \times 100$$

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. The spiking level should be equivalent to a mid level calibration.

14. POLLUTION PREVENTION

- 14.1.1. Refer to section 14 of the 8000B section of this SOP.

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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. SW846, Update III, December 1996, Method 8081A

17. MISCELLANEOUS

- 17.1. Modifications from Reference Method
17.1.1. None

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17.2. TABLES

Table B-1 Standard Analyte List and Reporting Limits for Method 8081A			
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
Chlorobenzilate	0.1	3.3	100
<i>Kepone</i> 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:

	<u>Extraction Vol.</u>	<u>Final Vol.</u>
Ground water	1000 mL	10 mL
Low-level Soil	30 g	10 mL
High-level soil / waste	1 g	10 mL

Table B-2 Recommended Conditions for Method 8081A	
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

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Table B-3						
Calibration Levels ng/mL for Method 8081A						
	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6²
Individual Mix AB¹						
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
Multi-component 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 for Method 8081A	
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 mg/L or mg/kg for Method 8081A			
	Aqueous	Soil	Waste
gamma BHC (Lindane)	0.20	33.3	200
Aldrin	0.20	33.3	200
Heptachlor	0.20	33.3	200
Dieldrin	0.50	33.3	500
Endrin	0.50	33.3	500
4,4'-DDT	0.50	33.3	500
Tetrachloro-m-xylene (Surrogate)	0.20	33.3	200
Decachlorobiphenyl (Surrogate)	0.20	33.3	200

Table B-6		
LCS/Matrix Spike and Surrogate Spike levels for TCLP mg/L or mg/kg for Method 8081A		
	Aqueous	Waste
Heptachlor	5	500
Heptachlor epoxide	5	500
Lindane	5	500
Endrin	5	500
Methoxychlor	10	1000

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Table B-7**Suggested Analytical Sequence for Method 8081A****Initial Calibration**

Solvent blank (optional)	
Breakdown Mix	
Individual mix AB	All levels
Technical Chlordane	Level 3 ¹
Toxaphene	Level 3 ¹
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 multi-component analytes

¹ A five point curve for any of the multi-component analytes may be included
If Aroclors are included, a 5 point calibration for Aroclor 1016/1260 should be included with the initial calibration and a single point for the other Aroclors. The mid point 1016/1260 mix is included with the daily calibration (every 12 hours).

Note: A solvent blank or primer may be analyzed at any time during the sequence when highly contaminated samples are expected. A solvent blank or primer may not be analyzed as routine immediately prior to standards.

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.

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-0001NC). The PCBs are determined and quantitated as Aroclor mixes.

1.2. 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.

1.2.1.1. Note: SW-846 method 8082 provides incomplete guidance for determination of individual PCB congeners. This SOP does not include directions for congener specific analysis.

1.3. The associated LIMS method code is QH (8082).

2. SUMMARY OF METHOD

2.1. 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

3.1. Refer to the STL North Canton Laboratory Quality Manual (LQM), current version, 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. Avoiding contact with any plastic materials minimizes interferences from phthalates.

4.3. Sulfur will interfere and can be removed using procedures described in SOP NC-OP-0025.

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, but not limited to Mercury, Tetrabutylammonium sulfite (TBA), Sulfuric Acid Cleanup, Silica Gel Cleanup, and Florisil® Cleanup of semivolatile organic compound extracts based on SW846 Methods 3660B, 3665A, 3630C, and 3620B. These cleanup procedures are included in SOP # NC-OP-0025.

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. The standards must be replaced at least every six months or sooner if comparison with check standards indicates a problem.

7.2. Refer to Table C-3 for details of calibration standards.

7.3. Surrogate Standards

7.3.1. Tetrachloro-m-xylene and decachlorobiphenyl are the surrogate standards. Refer to Table C-4 for details of surrogate standards.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1.1. Refer to Section 8 of the 8000B section of this SOP.

9. QUALITY CONTROL

9.1.1. 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-6 for the initial calibration analytical sequence.

10.2.2. The response for each Aroclor will be calculated by the procedures described in the general method for GC analysis, with the following modifications.

10.2.3. A minimum five-point calibration of all Aroclors is generated. The average response factor is used to quantitate Aroclors.

10.2.4. The high and low standards for the initial five-point calibration of 1016 / 1260 define the acceptable quantitation range for the other Aroclors. If any Aroclor is determined above this concentration the extract must be diluted and reanalyzed.

10.2.4.1. NOTE: For Ohio VAP, Arclor 1268 and Arclor1262 may be analyzed. In order to meet project specific reporting limits, a lower concentration standard may be added to the calibration curve.

- 10.2.5. If the analyst knows that a specific Aroclor is of interest for a particular project, that Aroclor may be used for the five point calibration rather than the 1016 / 1260 mix.
- 10.2.6. 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.
- 10.2.7. The following is used for the quantitation of all Aroclors. The same quantitation option must be used for standards and samples.
 - 10.2.7.1. Multiple peak option.
 - 10.2.7.2. Select 3-10 major peaks in the analyte pattern. Calculate the response using the total area or total height of these peaks.
- 10.3. 12 hour Calibration
 - 10.3.1. 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.
 - 10.3.2. At a minimum, the 12 hour calibration includes analysis of the Aroclor 1260 / 1016 mix.
 - 10.3.3. Other Aroclors are included in the daily calibration check.
 - 10.3.4. The retention time windows for any analytes included in the daily calibration and CCVs are updated.
 - 10.3.5. For this method samples must be bracketed with successful calibration verification runs.
- 10.4. Calibration verification standards
 - 10.4.1. The Aroclor 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.).
 - 10.4.2. 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
 - 11.2.1. The extraction procedure is described in SOP No. CORP-OP-0001NC.
- 11.3. Cleanup
 - 11.3.1. Cleanup procedures are described in SOP No. NC-OP-0025.
- 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-6.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Identification of Aroclors

- 12.1.1. Retention time windows are used for identification of Aroclors, 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.

- 12.1.2. A clearly identifiable Aroclor pattern serves as confirmation of single column GC analysis. Dual column confirmation may be used for specific program requirements or by client request.

12.2. Quantitation of Aroclors

- 12.2.1. Use 3-10 major peaks or total area for quantitation

- 12.2.2. 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 Aroclor is quantitated and reported, but the suspicion of multiple Aroclors is discussed in the narrative. If well separated Aroclor patterns are present, and then multiple Aroclors may be quantitated and reported.

- 12.3. Second column confirmation of Aroclors will only be performed when requested by the client. The appearance of the multiple peaks in the sample usually serves as a confirmation of Aroclor presence.

- 12.4. Surrogate recovery results are calculated and reported for decachlorobiphenyl (DCB) and tetrachloro-*m*-xylene (TCMX). Corrective action is only necessary if DCB and TCMX are both outside of acceptance limits, or if one is <10%.

- 12.4.1. NOTE: For Ohio VAP samples, all surrogates must meet acceptance limits.

13. METHOD PERFORMANCE

- 13.1. Performance limits for the four replicate initial demonstration of capability are required as referenced under Section 13.1 of the main body of this SOP.

- 13.2. Method detection limits (MDL) are determined for all Aroclors.

14. POLLUTION PREVENTION

- 14.1. Refer to Section 14 of the 8000B section of this SOP.

15. WASTE MANAGEMENT

- 15.1. Refer to Section 15 of the 8000 section of this SOP

- 15.2. 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. 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. TABLES

Table C-1			
Standard Analyte list and Reporting Limits for Method 8082			
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:

	<u>Extraction Vol.</u>	<u>Final Vol.</u>
Ground water	1000 mL	10 mL
Low-level Soil	30 g	10 mL
High-level soil / waste	1 g	10 mL

Table C-2	
Instrumental Conditions for Method 8082	
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 for Method 8082						
	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6 ¹
Aroclor 1016/1260	0.05	0.1	0.2	0.5	1.0	2.0
Aroclor 1242 ²	0.05	0.1	0.2	0.5	1.0	2.0
Aroclor 1221 +1254 ²	0.05	0.1	0.2	0.5	1.0	2.0
Aroclor 1232 ²	0.05	0.1	0.2	0.5	1.0	2.0
Aroclor 1248 ²	0.05	0.1	0.2	0.5	1.0	2.0
Aroclor 1262	0.05	0.1	0.2	0.5	1.0	2.0
Aroclor 1268	0.05	0.1	0.2	0.5	1.0	2.0
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 mg/L or mg/kg for Method 8082			
	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			
Michigan Analyte List and Reporting Limits¹ for Method 8082			
Compound	Reporting Limit		
	water (µg/L)	soil (µg/Kg)	
Aroclor-1016	0.2	330	
Aroclor-1221	0.2	330	
Aroclor-1232	0.4	330	
Aroclor 1242	0.2	330	
Aroclor-1248	0.2	330	
Aroclor-1254	0.2	330	
Aroclor-1260	0.2	330	

¹ Reporting Limits are only for samples performed under the Michigan program

Table C-6**Suggested Analytical Sequence for Method 8082****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	An Initial Calibration includes Levels 1-5. A midpoint is used as CCV.
8	Aroclor 1242	An Initial Calibration includes Levels 1-5. A midpoint is used as CCV.
9	Aroclor 1248	An Initial Calibration includes Levels 1-5. A midpoint is used as CCV.
10	Aroclor 1221/1254	An Initial Calibration includes Levels 1-5. A midpoint is used as CCV.
11	Aroclor 1268 or 1262	An Initial Calibration includes Levels 1-5. A midpoint is used as CCV.
12	ICV	
13-32	Sample 1-20 (or as many samples as can be analyzed in 12 hours)	
33	Aroclor 1016/1260	Level 3

etc

Note: A solvent blank or primer may be analyzed at any time during the sequence when highly contaminated samples are expected. A solvent blank or primer may not be analyzed as routine immediately prior to standards.

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

- 1.1. This method is applicable to the gas chromatographic determination of Chlorinated phenoxy acid herbicides in extracts prepared by SOP CORP-OP-0001NC. 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.
- 1.2. The associated LIMS method code is QS.

2. SUMMARY OF METHOD

- 2.1. 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

- 3.1.1. Refer to the STL North Canton Laboratory Quality Manual (LQM), current version, 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# NC-OP-0025.

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 Ni₆₃ 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.

8. SAMPLE PREPARATION, PRESERVATION AND STORAGE

- 8.1.1. 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-3 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 prepared from purchased standards in the methyl ester form.
- 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
 - 11.2.1. The extraction procedure is described in SOP #CORP-OP-0001NC.
- 11.3. Cleanup
 - 11.3.1. The alkaline hydrolysis and subsequent extraction of the basic solution described in the extraction procedure provides an effective cleanup.
- 11.4. Analytical Sequence
 - 11.4.1. 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.
 - 11.4.2. 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.
 - 11.4.3. The daily calibration consists of mid level standards of all analytes of interest. Retention time windows must be updated with the daily calibration.
 - 11.4.4. 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
 - 11.5.1. 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

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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.

- 12.3. A routine 10X dilution occurs on final extracts for all samples. Due to a QuantIMS limitation, the dilution factor field in QuantIMS cannot be used when a dilution is routine, because the dilution factor is automatically applied to all reference values creating reporting problems. For the herbicide analysis, the extract volume will be 10mL and an aliquot at 10X dilution will be analyzed. The final extract volume recorded on the laboratory bench sheet will be recorded as 100mL to avoid using the dilution factor field in QuantIMS.

13. METHOD PERFORMANCE

- 13.1. The EPA for this method has not published multiple laboratory performance data. Performance limits for the four replicate initial demonstration of capability are required as referenced under Section 13.1 of the main body of this SOP.

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 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. Method 8151A, SW-846, Update III, December 1996

17. MISCELLANEOUS

- 17.1. Modifications from Reference Method
- 17.1.1. Refer to the method 8000B section of this SOP for modifications from the reference method.
- 17.2. Modifications from Previous Revision
- 17.2.1. The calibration procedure has been changed to require esterification of the calibration standards

17.3. TABLES

Table D-1				
Standard Analyte List for Method 8151A				
Compound	CAS Number	Reporting Limit, µg/L or µg/kg		
		Aqueous	Soil	Waste
2,4-D	94-75-7	4	80	4000
2,4-DB	94-82-6	4	80	4000
2,4,5-TP (Silvex)	93-72-1	1	20	1000
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
MCPB	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 for Method 8151A	
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, 0.5µm
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 mg/L or mg/kg ¹ for Method 8151A			
	Aqueous	Soil	Waste
2,4-D	16	800	16000
Silvex	4	200	4000
2,4,5-T	4	200	4000
2,4-DB	16	800	16000
Dalapon	8	400	8000
DCAA (surrogate)	16	800	16000

¹ LCS, MS and SS spikes are as the free acid.

1. SCOPE AND APPLICATION

- 1.1. This method is applicable to the determination of the concentration of certain Organophosphorus Pesticides in waters, wastewaters, oils, soils, and sludges. It is based on SW846 Method 8141A. Table E1 shows reporting limits for compounds routinely analyzed by this method. The compounds include, but are not limited to, those shown in Table E1.
- 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 by the laboratory QA department.
- 1.3. The associated LIMS method code is P2.

2. SUMMARY OF METHOD

- 2.1. An aliquot of prepared sample is injected in a gas chromatograph (GC) and compounds in the effluent are detected by a flame photometric detector. Appropriate preparation techniques are described in SOP CORP-OP-0001NC. Ultrasonic Extraction (Method 3550) is **NOT** an appropriate sample preparation for Method 8141 and should not be used because of the potential for destruction of target analytes during the ultrasonic extraction process.

3. DEFINITIONS

- 3.1. Refer to the STL North Canton Laboratory Quality Manual (LQM), current version, 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. Analytical difficulties encountered for target analysis include:
 - 4.2.1. The water solubility of Dichlorvos (DDVP) is 10 g/L at 20°C, and recovery is poor from aqueous solution.
 - 4.2.2. Naled is converted to Dichlorvos (DDVP) on column by debromination. This reaction may also occur during sample workup.
 - 4.2.3. Trichlorfons rearranges and is dehydrochlorinated in acidic, neutral, or basic media to form Dichlorvos (DDVP) and hydrochloric acid. If this method is to be used for the determination of organophosphates in the presence of Trichlorfons, the analyst should be aware of the possibility of rearrangement to Dichlorvos to prevent misidentification.
 - 4.2.4. Merphos is a single component pesticide that is readily oxidized to Merphos oxone. Chromatographic analysis of Merphos almost always results in two peaks.

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.

6.2. Refer to Table E2 for Instrument settings.

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 E-3 for details of calibration and other standards.

7.3. Surrogate Standards

7.3.1. Triphenyl phosphate is the surrogate standard. Refer to Table E-4 for details of the surrogate standard.

8. SAMPLE PREPARATION, PRESERVATION AND STORAGE

8.1. 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 E-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 purchased solutions. Table E-3 lists the calibration levels.

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.

11. PROCEDURE

11.1. Refer to the method 8000B section of this SOP for procedural requirements.

11.2. Extraction

11.2.1. The extraction procedure is described in SOP #CORP-OP-0001NC.

11.3. Analytical Sequence

11.3.1. 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.

11.3.2. 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.

11.3.3. The daily calibration consists of mid level standards of all analytes of interest. Retention time windows must be updated with the daily calibration.

11.3.4. 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.

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. Surrogate recovery results are calculated and reported for Triphenylphosphate unless it is determined that sample interference has adversely affected the quantitation of one of the surrogates. The surrogate must be within QC criteria. Corrective action is only necessary if Triphenylphosphate is outside of acceptance limits.

13. METHOD PERFORMANCE

13.1. Performance limits for the four replicate initial demonstration of capability are required as referenced under Section 13.1 of the main body of this SOP.

14. POLLUTION PREVENTION

14.1. 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

16.1. SW846, Update III, December 1996, Method 8141A.

18. MISCELLANEOUS

18.1. Reporting limits

18.1.1. The lower standard reporting limits are listed in Table E-1

18.1.2. If samples require dilution or smaller volumes than specified in this method, the RL will be elevated.

18.1.3. The nature of the FPD detector contributes to high dilutions for Method 8141A. There is a phenomenon known as quenching that occurs. This happens when light absorption occurs in the flame of the FPD due to hydrocarbons, sulfur, and certain light absorbing compounds. When this happens the analytes of interest do not reach the photomultiplier tube and are not detected even though they may be present. Due to this phenomenon, highly viscous or dark or highly colored samples are analyzed at a dilution.

18.2. Elution time

18.2.1. For any positive detection in a sample, the chromatogram is overlaid on screen with the nearest standard for elution time matching and pattern recognition using the Target system.

18.3. Troubleshooting guide

18.3.1. Consult the instrument manufacturer's operating manual for guidance.

Table E-1
Analyte and Reporting Limits for Method 8141A

Compound	CAS Number	Reporting	Limits
		Water, µg/L	Solid, µg/kg
Azinphos methyl	86-50-0	1.0	33
Bolstar (Suprofos)	35400-43-2	1.0	33
Chlorpyrifos	2921-88-2	1.0	33
Coumaphos	56-72-4	1.0	33
Demeton, O and S	8065-48-3	1.0	33
Diazinon	333-41-5	1.0	33
Dichlorvos	62-73-7	1.0	33
Disulfoton	298-04-4	1.0	33
Ethoprop	13194-48-4	1.0	33
Fensulfothion	115-90-2	1.0	33
Fenthion	55-38-9	1.0	33
Malathion	121-75-5	1.0	33
Merphos	150-50-5	1.0	33
Methyl Parathion	298-00-0	1.0	33
Mevinphos	7786-34-7	1.0	33
Naled	300-76-5	1.0	33
Phorate	298-02-2	1.0	33
Ronnel	299-84-3	1.0	33
Stirophos	22248-79-9	1.0	33
Tokuthion	34643-46-4	1.0	33
Trichloronate	327-98-0	1.0	33
O,O,O-Trientyl phosphorothioate	126-68-1	1.0	33
Thionazin	297-97-2	1.0	33
Sulfotepp	3689-24-5	1.0	33
Dimethoate	60-51-5	1.0	33
Parathion	56-38-2	1.0	33
Famphur	52-85-7	1.0	33

Table E-2	
Instrumental Conditions for Method 8141A	
PARAMETER	Recommended conditions
Injection port temp	175°C
Detector temp	230°C
Initial temp	135°C
Temperature program	(A) 5°C/minute (B) 20°C/minute
Final Temp	(A) 245°C (B) 295°C
Final Hold Time	(A) 0 minutes (B) 7 minutes
Column 1	RTX-OPP, 30 meter, 0.32 mm, 0.5 µm film
Column 2	RTX-1, 30 meter, 0.32 mm, 0.5 µm film
Injection	1-2µL
Carrier gas	Helium / Hydrogen
Make up gas	Nitrogen

Table E-3
Initial Calibration Concentrations (ng/uL) for method 8141A

COMPOUND	LEVEL 1	LEVEL 2	LEVEL 3	LEVEL 4	LEVEL 5	LEVEL 6	LEVEL 7
o,o,o-Triethylp-hosphate	0.2	0.5	1	2	5	10	20
Dichlorvos	0.2	0.5	1	2	5	10	20
Mevinphos	0.2	0.5	1	2	5	10	20
Thionazin	0.2	0.5	1	2	5	10	20
Ethoprop	0.2	0.5	1	2	5	10	20
Naled	0.2	0.5	1	2	5	10	20
Sulfotepp	0.2	0.5	1	2	5	10	20
Phorate	0.2	0.5	1	2	5	10	20
Demeton	0.2	0.5	1	2	5	10	20
Dimethoate	0.2	0.5	1	2	5	10	20
Diazinon	0.2	0.5	1	2	5	10	20
Disulfoton	0.2	0.5	1	2	5	10	20
Methyl Parathion	0.2	0.5	1	2	5	10	20
Ronnel	0.2	0.5	1	2	5	10	20
Fenthion	0.2	0.5	1	2	5	10	20
Chlorpyrofos	0.2	0.5	1	2	5	10	20
Parathion	0.2	0.5	1	2	5	10	20
Malathion	0.2	0.5	1	2	5	10	20
Trichloronate	0.2	0.5	1	2	5	10	20
Merphos	0.2	0.5	1	2	5	10	20
Stirophos	0.2	0.5	1	2	5	10	20
Tokuthion	0.2	0.5	1	2	5	10	20
Fensulfothion	0.2	0.5	1	2	5	10	20
Bolstar	0.2	0.5	1	2	5	10	20
Famphur	0.2	0.5	1	2	5	10	20
Azinphos methyl	0.2	0.5	1	2	5	10	20
Coumaphos	0.2	0.5	1	2	5	10	20

Table E-4 LCS/Matrix Spike and Surrogate Spike Compounds – 20 ug/mL for Method 8141A	
Compound	Compound
Thinazin	Sulfotepp
Phorate	Disulfoton
Methyl Parathion	Parathion
Famphur	O,O,O-Triethylphosphate
Dimethoate	Triphenyl Phosphate - Surrogate

1. SCOPE AND APPLICATION

- 1.1. This method is applicable to the determination of the concentration and **tentative** identification of petroleum hydrocarbon mixes in waters, wastewaters, soils, and sludges.
- 1.2. This SOP is based on SW-846 Method 8015B, Modified, Revision 3, December 1996.
- 1.3. The associated LIMS method codes are HS (8015 MOD) and KI (8015B).

2. SUMMARY OF METHOD

- 2.1. This method provides gas chromatographic conditions for detection and identification of total petroleum hydrocarbons. Prior to the use of this method, appropriate sample preparation techniques are used.
- 2.2. An aliquot of the prepared sample is injected into a gas chromatograph (GC) and compounds in the effluent are detected by a flame ionization detector (FID).
- 2.3. The carbon range for Ohio VAP projects is C10-C20 and C20-C32. The carbon range for BUSTR Projects is C10-C20 and C20-C34.

3. DEFINITIONS

- 3.1. Refer to the glossary in the STL North Canton Laboratory Quality Manual (LQM), current version.

4. INTERFERENCES

- 4.1. Refer to the method 8000B section of this SOP for general information regarding chromatographic interferences.

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.
- 6.2. 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.
- 7.2. The petroleum hydrocarbons are purchased from a chemical supplier when available. When no chemical supplier is available, the fuels are purchased from public sources.
- 7.3. The OVAP and BUSTR standard is a commercially prepared standard containing alkanes from C10-C34.

8. SAMPLE PREPARATION, PRESERVATION AND STORAGE

- 8.1. 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. MS/MSD recoveries are calculated from a Diesel calibration.
- 9.3. Surrogates
 - 9.3.1. Because of the nature of the TPH analysis, whereas certain petroleum mixtures can override the C9 surrogate, the C9 surrogate recoveries are advisory. Re-extraction due to surrogate recoveries is determined by analyst judgement.
 - 9.3.1.1. NOTE: Ohio VAP rules require reanalysis when surrogate recoveries are outside of control limits.

10. CALIBRATION AND STANDARDIZATION

- 10.1. Recommended Instrument Conditions
 - 10.1.1. Hydrogen carrier gas - flow rate 5 - 6 mL/min
 - 10.1.2. Detector gas mixture - air hydrogen mixture in a 10:1 ratio, air 80 - 120 mL/min, hydrogen 8 -12 mL/min
 - 10.1.3. Temperature Program - refer to Table F1 Appendix
 - 10.1.4. Injection volume - 1 µL
- 10.2. Initial Calibration
 - 10.2.1. Analyze a five point Diesel calibration standard referring to the recommended instrument conditions. The calibration concentrations are 100, 200, 500, 1000, and 2000 ng/uL. A 5000ng/uL standard may be analyzed if needed. The retention time window of C10-C32 shall be used for the Diesel calibration.
 - 10.2.2. For Ohio VAP and BUSTR calibrations, analyze a five point calibration for the carbon range C10-C20. The concentrations are 60, 120, 240, 600 and 1200 ug/mL. Analyze a five point of the carbon range C20-C34. The concentration ranges are 80, 160, 320, 800, and 1600 ug/mL.
- 10.3. Continuing Calibration
 - 10.3.1. Refer to Section 10 of the 8000B section of this SOP for general calibration requirements.

11. PROCEDURE

- 11.1. Refer to the method 8000B section of this SOP for procedural requirements.
- 11.2. Extraction
 - 11.2.1. The extraction procedure is described in SOP #CORP-OP-0001NC.

11.3. Analytical Sequence – Refer to Section 11 in the 8000B Section of this SOP.

11.4. Petroleum Hydrocarbon Identification and/or Fingerprinting

11.4.1. To identify the type of petroleum hydrocarbon, compare the chromatographic peak pattern to the patterns of known petroleum hydrocarbons analyzed under identical chromatographic conditions. Samples are quantified against diesel, but fingerprinting may be done when client requested.

11.4.2. Positive matching may not be possible, even using site-specific hydrocarbons. Degradation of the pattern can occur during environmental exposure of the fuel. See Table 2 for possible fingerprints.

11.4.3. Sample Quantification

11.4.4. Samples are quantified against the initial calibration of diesel or DRO on a single column.

11.4.5. The total height or area of the hydrocarbon is determined in the same manner used for the hydrocarbon standard.

11.4.6. If the amount of sample injected into the GC exceeds the working range of the calibration curve, an appropriate dilution is performed before reanalysis.

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. Surrogate recovery results are calculated and reported for Nonane (C-9). The surrogate must be within QC criteria. Corrective action is only necessary if Nonane (C-9) is outside of acceptance limits.

13. METHOD PERFORMANCE

13.1. Performance limits for the four replicate initial demonstration of capability are required as referenced under Section 13.1 of the main body of this SOP.

14. POLLUTION PREVENTION

14.1. 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

16.1. SW846, Method 8015B, Nonhalogenated Organics Using GC/FID, Test Methods for Evaluating Solid Waste, Third Edition, USEPA

16.2. Related SOP

16.2.1. CORP-OP-0001NC, Extraction and Cleanup of Organic Compounds from Waters and Soils, Based on SW846 3500 Series, 3600 Series, 8150, 8151, and 600 Series Methods

Table F-1
Suggested GC Temperature Program for TPH Analysis

Initial Temperature	40°C
Initial Hold Time	4 minutes
Temperature Program	10°C/minute
Final Temperature	280°C
Final Hold Time	10 minutes

Table F-2
Reporting Limits for TPH Analysis

Analyte	Reporting Limits		
	Water (mg/L)	Solids (mg/kg)	Waste Dilution (mg/kg)
TPH (as Diesel) or DRO	100	3.3	200
C10-C20 (OVAP & BUSTR)	60	2.0	
C20-C32 (OVAP)	80	2.3	
C20-C34 (BUSTR)	80	2.3	
Fingerprint Compounds ¹			
Mineral Spirits	Kerosene	Motor Oil	
Hydraulic Oil	Jet Fuel	Stoddard Solvent	
DRO Spiking Solution			
Decane	Dodecane	Tetradecane	
Hexadecane	Octobecane	Eicosane	
Docosane	Tetracosane	Hexacosane	
Octacosane			

¹ This list represents most of the common petroleum hydrocarbons. The list may be expanded to include other petroleum hydrocarbons.

**ANALYSIS OF NON-HALOGENATED ORGANIC COMPOUNDS
BY METHOD 8015B, DIRECT INJECTION**

Revision No: 5.8

Revision Date: 02/06/06

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1. SCOPE AND APPLICATION

- 1.1. This method is applicable to the determination of the concentration of various Non-halogenated Organic Compounds in waters, wastes, sludges, and solids. It is based on SW-846 Method 8015B.
- 1.2. The applicable LIMs method codes are J7 (GC/FID 8015) and QU (Semivolatile Organics, 8015B). The preparation code is 88.

2. SUMMARY OF METHOD

- 2.1. This method provides gas chromatographic conditions for the detection of various nonhalogenated organic compounds. Samples are introduced to the GC by direct injection. Detection is achieved by a flame ionization detector (FID).

3. DEFINITIONS

- 3.1. Refer to the glossary in the STL North Canton Laboratory Quality Manual (LQM).

4. INTERFERENCES

- 4.1. Refer to the method 8000B section of this SOP for general information regarding chromatographic interferences.

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.
- 6.2. Recommended Columns:
- 6.2.1. RTX 200 Stabilwax, fused silica, 60 m x 0.53, 0.5 µm film thickness, or equivalent column.
- 6.2.2. Stabilwax, fused silica, 60 m x 0.53, 0.5 µm film thickness, or equivalent column.
- 6.3. Detectors: Flame ionization (FID)
- 6.4. 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.
- 7.1.1. Reagent water
- 7.2. Standards
- 7.2.1. Refer to Table G2.

**ANALYSIS OF NON-HALOGENATED ORGANIC COMPOUNDS
BY METHOD 8015B, DIRECT INJECTION**

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8. SAMPLE PREPARATION, PRESERVATION AND STORAGE

8.1. 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).

10. CALIBRATION AND STANDARDIZATION

10.1. Recommended Instrument Conditions

10.1.1. The following conditions are recommended. The following table lists specific information for various compounds.

10.1.2. RTX- 200 Stabilwax and Stabilwax-DA Columns:

Carrier Gas:	Hydrogen
Initial Temp:	45 °C
Initial Hold:	3 mins
Ramp Rate A:	5 °C/min
Ramp Rate B:	30 °C/min
Final Hold A:	0 min
Final Hold B:	3 mins
Analysis Time:	17.83 mins
Injector Temp:	275 °C
FID Temp:	300 °C
Injection Vol:	1 µL

10.2. Initial Calibration

10.2.1. For each non-halogenated organic compound and surrogate standard, analyze five or more calibration standards referring to the recommended GC conditions in Section 10.1. One of the standards analyzed should be at or near the concentration which corresponds to the calibration range.

10.2.2. Refer to Section 10 of the 8000B section of this SOP for general calibration requirements.

11. PROCEDURE

11.1. Refer to the method 8000B section of this SOP for procedural requirements.

11.2. Sample Preparation Summary

11.2.1. Samples received fall into three general categories: waters, soils, or wastes.

11.3. Sample Preparation Procedure

11.3.1. Waters

11.3.1.1. Add surrogate solution to the sample to achieve a concentration of 100 mg/L.

**ANALYSIS OF NON-HALOGENATED ORGANIC COMPOUNDS
BY METHOD 8015B, DIRECT INJECTION**

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11.3.2. Sediments/soils and waste

11.3.2.1. Mix the contents of the sample container with a narrow metal or wood spatula. Weigh 5 g (wet weight) into a tarred culture tube. Use a top-loading balance. Record the weight to 0.01 gram.

11.3.2.2. Quickly add 5 mL of reagent water. Add surrogate standard. Cap the vial and vortex to mix for two minutes.

11.3.2.3. If extract is cloudy or has suspended sediment particles, refrigerate and allow sample to sit for a maximum of 24 hours. Filter sample if necessary.

11.4. Sample Analysis

11.4.1. Preliminary Evaluation

11.4.1.1. The sample or sample extract is introduced to the GC column by direct inject techniques. The concentration of the sample components is then calculated from the resulting chromatograms.

11.4.2. Analytical Sequence – Refer to Section 11 in the 8000B Section of this SOP.

11.4.3. Inject 1 µL of the sample extract or diluted sample into the GC using the same operating conditions and techniques as those used in the calibration of the instrument.

11.5. Analytical Documentation

11.5.1. 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.

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.

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. Surrogate recovery results are calculated and reported unless it is determined that sample interference has adversely affected the quantitation of the surrogate. The surrogate must be within QC criteria. Corrective action is only necessary if the surrogate is outside of acceptance limits.

13. METHOD PERFORMANCE

13.1. Performance limits for the four replicate initial demonstration of capability are required as referenced under Section 13.1 of the main body of this SOP.

**ANALYSIS OF NON-HALOGENATED ORGANIC COMPOUNDS
BY METHOD 8015B, DIRECT INJECTION**

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14. POLLUTION PREVENTION

- 14.1. 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

- 16.1. SW846, Method 8015B, Nonhalogenated Organics Using GC/FID, Test Methods for Evaluating Solid Waste, Third Edition, USEPA

17. Miscellaneous (Tables, Appendices, Etc...)

Table G-1
Non-Halogenated Organic Compounds, Reporting Limits¹

Compound	CAS Number	Reporting Limits	
		Water, mg/L	Solid, mg/kg
2-Methoxyethanol	109-86-4	1.0	1.0
Methanol	67-56-1	1.0	0.5
Isopropyl alcohol	67-63-0	1.0	0.5
n-Propyl alcohol	71-23-8	1.0	0.5
Ethanol	64-17-5	1.0	0.5
n-Butanol	71-36-3	1.0	0.5
1,4-Dioxane	123-91-1	1.0	0.5
Ethylene oxide	75-21-8	1.0	0.5
iso-Butanol	78-83-1	1.0	0.5

¹ If samples require dilution or smaller volumes than specified in this method, the RL will be elevated.

**ANALYSIS OF NON-HALOGENATED ORGANIC COMPOUNDS
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Table G-2
Non-Halogenated Organic Compounds Working Standards

COMPOUND	LEVEL 1	LEVEL 2	LEVEL 3	LEVEL 4	LEVEL 5	LEVEL 6
2-Methoxyethanol	1.0	2.0	5.0	10.0	20.0	50.0
Methanol	1.0	2.0	5.0	10.0	20.0	50.0
Isopropyl alcohol	1.0	2.0	5.0	10.0	20.0	50.0
n-Propyl alcohol	1.0	2.0	5.0	10.0	20.0	50.0
Ethanol	1.0	2.0	5.0	10.0	20.0	50.0
n-Butanol	1.0	2.0	5.0	10.0	20.0	50.0
1,4-Dioxane	1.0	2.0	5.0	10.0	20.0	50.0
Ethylene oxide	1.0	2.0	5.0	10.0	20.0	50.0
iso-Butanol	1.0	2.0	5.0	10.0	20.0	50.0

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SOP No. NC-GC-0032

Revision No. 1

Revision Date: 11/16/04

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Implementation Date 12/29/04

**STL North Canton
STANDARD OPERATING PROCEDURE**

**TITLE: Analysis of Dissolved Gases In Groundwater by
Modified Method RSK-175**

(SUPERSEDES: REVISION 0, REVISION DATE 05/13/02)

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Approved by: *Beth Ann* 12/27/04
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1. SCOPE AND APPLICATION

- 1.1 This document describes a procedure for the determination of dissolved gases in groundwater. The method is applicable to the preparation of water samples for the analysis of the headspace to quantify part-per-billion levels of dissolved gases in water samples.
- 1.2 The associated QuantIMs method code is MM.
- 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. A water sample is collected in the field in a 43-mL VOA vial with no headspace. Prior to analysis the sample is transferred into a 22-mL serum vial with a crimp cap. Headspace is generated using UHP helium. The sample is loaded onto the headspace autosampler and analyzed by a Gas Chromatograph (GC) equipped with an FID detector.

3. DEFINITIONS

- 3.1. Refer to the glossary in the Laboratory Quality Manual (LQM), latest version.

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. Specific selection of reagents may be required to avoid introduction of contaminants.

5. SAFETY

- 5.1. Employees must abide by the policies and procedures in the Corporate Safety Manual and this document.
- 5.2. There are no materials used in this method that have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.
- 5.3. Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Cut resistant gloves must be worn doing any other task that presents a strong possibility of getting cut.

Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

- 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, where possible. All samples with a pink stickers that read "Caution/Use Hood!" **must** be opened in the hood. Contact the EH&S co-ordinator if this is not possible. 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. It is recommended that neat standards be purchased only as a last resort. The preparation of standards from neat materials and reagents should be conducted in a fume hood with the sash closed as far as the operations will permit.
- 5.7. Standards in solution may be diluted in the open laboratory when syringes and the like are utilized.
- 5.8. 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 the EH&S coordinator and to a laboratory supervisor.

6. EQUIPMENT AND SUPPLIES

- 6.1 Sample Containers: 44mL VOA vials, 22mL crimp cap vials.
- 6.2 Instrumentation
 - 6.2.1 Column(FID) - Restek Rt-UPLLOT; 30m, 0.53mm ID
 - 6.2.2 Autosampler - Tekmar 7000 Headspace Autosampler
- 6.3 Syringes - 10µL - 5.0-mL gas tight syringes.
- 6.3 Data System – Chemstation for acquisition and Target™ for data processing.

7. REAGENTS AND STANDARDS

- 7.1. Gas cylinders of ultrahigh purity helium, hydrogen, and nitrogen.
- 7.2. Calibration Standards: The primary standard is purchased through Scott Specialty Gases. The FID calibration standard is composed of nominally 1% (mole basis) methane, ethane, ethene, acetylene, and propane.
- 7.3. The calibration levels are achieved by injecting different amounts of the standard into a 22-mL vial that contains 18 mL of deionized water and 4 mL of headspace.
- 7.4. Laboratory Control and Initial Calibration Verification Samples: The LCS and ICV are fortified to the concentration of the middle calibration standard.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

- 8.1. Samples are collected in the field in a 43-mL VOA vial. The samples are preserved with 1:1 HCl to a pH of less than 2. Acid converts inorganic carbon to carbon dioxide. Care should be taken that no headspace is present when capping the vials. Samples are maintained at a temperature of 4°C and should be analyzed within 14 days of collection.

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, MS, MSD) 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. Method Blank

- 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, with the exception of common laboratory contaminants.

9.2.1.1. The common laboratory contaminant for this method is Methane.
Methane can be present up to 5 times the reporting limit.

9.2.2. Corrective Action for Blanks

9.2.2.1. 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 addressed in the project narrative.**

9.2.2.2. 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 (LCS)

- 9.3.1. One LCS from an independent source must be processed with each preparation batch. The hydrocarbon LCS is fortified to the concentration of the middle calibration level. The LCS must be carried through the entire analytical procedure. 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.

9.3.2. Corrective Action for LCS

9.3.2.1.If any analyte is outside established control limits the system is out of control and corrective action must occur.

9.3.2.2.The only exception is that if the LCS recoveries are biased high and the associated sample is ND for the parameter(s) of interest, the batch is acceptable. **This must be addressed in the project narrative.**

9.3.2.3.Corrective action will be reparation and reanalysis of the batch unless the client agrees that other corrective action is acceptable.

9.4. Control Limits

9.4.1. Control limits are established by the laboratory as described in SOP, NC-QA-0018.

9.4.2. Laboratory control limits are internally generated and updated periodically unless method specified. Control limits are listed in the Laboratory Quality Manual (LQM) and the latest version is easily accessible via the LIMs (QC Browser program).

9.5. Method Detection Limits (MDLs) and MDL Checks

9.5.1. MDLs and MDL Checks are established by the laboratory as described in SOP, NC-QA-0021.

9.5.2. MDLs are listed in the Laboratory Quality Manual (LQM) and the latest version is easily accessible via the LIMs (QC Browser program).

9.6. Nonconformance and Corrective Action

9.6.1. Any deviations from QC procedures must be documented as a nonconformance, with applicable cause and corrective action approved by the facility QA Manager.

10. CALIBRATION AND STANDARDIZATION

10.1 Initial Calibration –Establish an initial calibration curve using the concentrations noted in the table below.

Compound	Cal Level 1	Cal Level 2	Cal Level 3	Cal Level 4	Cal Level 5	Cal Level 6
Volume Injected (uL)		1.3	50	200	600	1000
Methane		0.47	18	73	219	364
Ethane	0.45	0.89	34	137	410	683
Ethene	0.42	0.83	32	127	383	638
Acetylene		0.77	30	118	355	592

Concentrations are in µg/L unless noted otherwise.

10.1.1. For each analyte, calculate the mean calibration factor from analyses of the calibration solutions.

10.1.2. Calculate the standard deviation (SD) and relative standard deviation (RSD) from each mean.

10.1.3. The %RSD average of all analytes must be $\leq 30\%$.

10.1.4. Removal or replacement of levels from the middle of a calibration (i.e., levels other than the highest or lowest) is not permitted unless an injection or instrument problem confined to that point can be clearly documented as described below. Removal of points for individual analytes from levels other than the highest and lowest is not permitted in any event.

10.1.5. If the analyst can document that a level is not valid because of an injection or instrument problem confined to that run, the level may be excluded if the curve still has sufficient levels, or the run may be repeated once only. The whole level (all compounds) must be removed or replaced. The curve is evaluated with the level removed or replaced. If the curve still fails to meet criteria, then corrective action must be taken and the whole curve reanalyzed. Corrective action may include, but is not limited to, instrument maintenance and/or re-preparation of standards.

10.1.6. One of the following conditions must be satisfied to allow removal or replacement of a level.

- The data file is corrupted and unusable or the run is interrupted before completion.
- The analyst observes and documents a problem such as leaking of a purge vessel.
- For internal standard methods, the recovery of the internal standards is less than 70% or greater than 130% of the recovery in the other standards, or the amount of analyte recovered is less than 70% or greater than 130% of the expected values (indicating an improperly made up standard).
- For external standard methods the average amount of analyte recovered is less than 70% or greater than 130% of the expected value.

10.1.7. The reason for replacing the level **must** be documented in the run log. The fact that the curve passes criteria with the level removed is **not** alone sufficient evidence to document an injection or instrument problem confined to the level.

10.1.8. Removal of the highest or lowest levels is permitted, but the calibration range must be adjusted accordingly. If the lowest level is removed then the reporting limit is raised to be equivalent to the lowest level used in the calibration curve. In any event the number of levels remaining in the calibration must be at least that required by the method.

10.1.9. Removal of the highest or lowest point is permitted on a compound specific basis. This may be necessary when strongly responding and poorly responding analytes are included in the same standard mix at the same level. Each compound must have at least the minimum number of calibration levels required by the method

10.2 Continuing Calibration Verification – Analyze a continuing calibration verification at the beginning of each 24-hr analytical window. The CCV is fortified to the concentration of the middle calibration level. The %D between the CCV CF and the calibration average CF for each analyte must be less than or equal to 30%.

10.3 Initial Calibration Verification - An ICV must be analyzed run following the acquisition of the five-point initial calibration. The ICV is fortified to the concentration of the middle calibration standard. The calibration factor (CF) for the ICV must be within 30%D of that from the initial calibration.

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 Analysis

11.3.1. Sample Analysis (GC-FID) - Remove the samples from the refrigerator and allow to come to room temperature. Transfer the sample into a 22-mL vial with a crimp cap. Place the vial upside down in a three-finger clamp attached to a ring stand. Insert a 22-gauge needle into the septum. Using a 5-mL gastight syringe, inject 4 mL of UHP helium into the sample. The helium forces out an equal amount of sample through the 22-gauge needle to create a headspace volume of 4 mL. Withdraw the needle and syringe from the vial and load the sample onto the Tekmar headspace autosampler. The autosampler allows the sample's water and headspace phases to equilibrate at 40°C. 100 µL of the sample headspace are injected directly onto the GC column where the target compounds, if present, are

detected by FID. Acquire the data and process on Target. The instrument operating conditions are outlined below.

GC Conditions

Gas Flows:

Carrier (Helium): 20 mL/min

Oven Program: 50°C for 2.1 minutes

FID Conditions

FID Temp.: 200°C

Hydrogen Flow: 40 mL/min

Air Flow: 450 mL/min

11.4. Analytical Documentation

11.4.1. Record all analytical information in the analytical logbook/logsheet which may be in an electronic format, including the analytical data from standards, blanks, LCSs, MS/MSDs, and any corrective actions or modifications to the method.

11.4.2. All standards are logged into a department standard logbook. All standards are assigned an unique number for identification. Logbooks are reviewed by the supervisor or designee.

11.4.3. 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.

11.4.4. Sample results and associated QC are entered into the LIMs after final technical review.

12. DATA ANALYSIS AND CALCULATIONS

12.1 Calibration Factor for GC-FID

$$CF_c = A_c/C_c$$

where:

CF_χ = Calibration factor of compound χ

A_x = Peak height or area

12.2 Percent Difference for Calibration Factors

$$\% D = (CF_{ave} - CF_c / CF_{ave}) \times 100$$

where:

CF_{ave} = Average CF for an analyte from the initial calibration

CF_c = CF for an analyte from current check standard

12.3 Relative Standard Deviation

$$\%RSD = (SD / CF_{ave}) \times 100$$

where:

CF_{ave} = Average CF for an analyte from the initial calibration

SD = Standard Deviation of average CFs for a compound

12.4 Sample Concentration in water

$$C_c = (A_c / CF_{ave}) \times DF$$

where:

C_χ = Concentration of target analyte χ in sample (ug/L)

A_χ = Peak area of analyte χ

CF_{ave} = Average calibration factor for an analyte from the calibration

DF = Dilution factor

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.

13.2.2. Method validation information (where applicable) in the form of laboratory demonstrations of capabilities is maintained for this method in the laboratory QA files.

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. All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

15.2. Waste Streams Produced by the Method

15.2.1. There are no waste streams produced when this method is carried out

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. RSKSOP-175, Revision 0, August 11, 1994.

16.1.2. Corporate Quality Management Plan (QMP), current version.

16.1.3. STL Laboratory Quality Manual (LQM), current version.

16.1.4. STL Corporate Safety Manual, M-E-0001 and STL North Canton Facility Addendum and Contingency Plan, current version.

16.2. Associated SOPs and Policies, latest version

16.2.1. QA Policy, QA-003

16.2.2. Glassware Washing, NC-QA-0014

16.2.3. Statistical Evaluation of Data and Development of Control Charts, NC-QA-0018

16.2.4. Method Detection Limits and Instrument Detection Limits, NC-QA-0021

16.2.5. Navy/Army SOP, NC-QA-0016

17. MISCELLANEOUS (TABLES, APPENDICES, ETC...)

17.1. Reporting limits

17.1.1. The reporting limit for all analytes is 1 ug/L.

17.1.2. If samples require dilution or smaller volumes than specified in this method, the RL will be elevated.

17.1.3. Compound Constants

Table 1: Compound Constants

Compound	Molecular Weight (g)
Methane	16
Ethane	30
Ethene	28
Acetylene	26

APPENDIX I – EXAMPLE CALCULATION**(Calculations Based on 22°C at 754 mmHg – Molar Equivalent .04099)****(Level 5) 1000 ul of 10,000 ppmv – 18 mL H₂O**

$$\frac{10,000 \text{ ulCH}_4}{\text{LN}_2} \times \frac{1 \text{ LCH}_4}{1,000,000 \text{ ulCH}_4} \times \frac{.04099 \text{ molesCH}_4}{1 \text{ LCH}_4} \times \frac{16 \text{ gCH}_4}{1 \text{ moleCH}_4} \times \frac{.001 \text{ LN}_2}{.018 \text{ LH}_2\text{O}} \times$$

$$\frac{1,000,000 \text{ ugCH}_4}{1 \text{ gCH}_4} = \frac{6.5584}{.018} = \frac{364 \text{ ugCH}_4}{\text{LH}_2\text{O}}$$

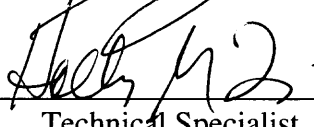
STL KNOXVILLE

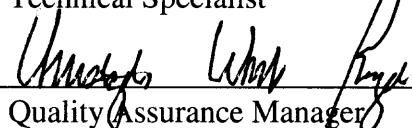
STANDARD OPERATING PROCEDURE

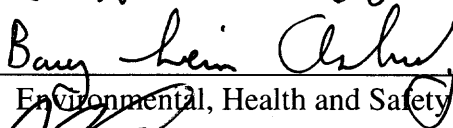
TITLE: VOA CANISTER ANALYSIS

(SUPERSEDES: KNOX-MS-0001, Revision 7)

Prepared By: 

Reviewed By:  4/11/06
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1. Scope and Application

- 1.1. The purpose of this standard operating procedure is to define the procedures and quality control necessary to analyze samples collected in "SUMMATM passivated" stainless steel canisters.
- 1.2. This procedure is applicable to the analysis of ambient air, indoor air, landfill gases, soil gases, vapor intrusion, and other gaseous samples. It is based on EPA Methods TO-14, TO14A and TO-15.
- 1.3. Responsibilities to perform this procedure in the lab are as follows:

Position	Responsibilities
Analyst	- Prepares and analyzes samples - Summarizes/assembles data package - Reviews the data package
Team/Group Leader	- Schedules/assigns analyses - Reviews data package

2. Summary of Method

- 2.1. Microscale Purge and Trap (MSPT): A precisely measured aliquot is removed from the canister or Tedlar bag and concentrated on a cryogenic trap. The cryogenic trap is desorbed. Polar and nonpolar compounds are quantitatively transferred to a subambient TenaxTM trap. Most of the water remains on the Cryotrap and CO₂ passes through the Tenax trap and is vented. The TenaxTM trap is thermally desorbed to the on-column cryofocuser. Sample components are separated by temperature programmed gas chromatography and detected with a quadrupole mass spectrometer.
- 2.2. The compounds analyzed by this method are listed in Tables 1, 2 and 3.

3. Definitions

- 3.1. Canister - a stainless steel container, typically 6-liter volume, equipped with a stainless steel shut-off valve, suitable for use from vacuum to 40 psig. 1-L cans are available for reduced volume analysis.
- 3.2. SUMMATM Passivation - a proprietary treatment process used to deactivate stainless steel surfaces. It produces a pure chrome/nickel oxide surface that features a high level of inertness.

- 3.3. Absolute pressure - pressure measured with reference to absolute zero pressure, expressed as kpa, mmHg, or psia.
- 3.4. Gauge pressure - pressure above atmospheric pressure as measured by a standard gauge. Zero gauge pressure is equal to ambient atmospheric pressure, expressed as mmHg, inches Hg, or psig.
- 3.5. Polar compound - Oxygen-containing compound capable of forming hydrogen bonds in water; compound having significant solubility in water.
- 3.6. Batch – A batch is a set of up to 20 samples of the same matrix processed using the same procedures and reagents within the same 24 hour time period. The Quality Control batch must contain a blank and a Laboratory Control Sample (LCS). Refer to the QC Program document (QA-003, current revision) for further details of the batch definition.
- 3.7. Additional definitions can be found in the STL Knoxville LQM glossary and in the STL Quality Management Plan.
- 3.8. Tedlar bag - Tedlar bags are manufactured from PVF (Tedlar) film with a polypropylene valve and septum. Various volume capacities available.

4. Interferences

- 4.1. Only compounds having both a similar mass spectrum and GC retention time would be expected to interfere in the method. The most common occurrence of this would be with structural isomers.
- 4.2. Large concentrations of water, methane, or carbon dioxide may limit the size of the aliquot that can be effectively cryotrapped. This may elevate the quantitation limits obtainable for samples of this type.
- 4.3. Matrix interferences may be caused by non-target contaminants that are present in 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, or evaluate the next sample for blank acceptance criteria. The autosampler and concentrator may require extensive bake-out and cleaning after a high-level sample.

5. Safety

- 5.1. Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual and this document.
- 5.2. Procedures shall be carried out in a manner that protects the health and safety of all associates. Exposure to chemicals and samples will 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. The preparation of all standards, reagents and glassware cleaning procedures that involve solvents will be conducted in a fume hood with the sash closed as far as the operations will permit.
- 5.3. All work must be stopped in the event of a known or potential compromise to the health and safety of any associate. The situation must be reported **immediately** to a laboratory supervisor.
- 5.4. Specific Safety Concerns or Requirements
 - 5.4.1. The effluents of sample splitters for the gas chromatograph and roughing pumps on the mass spectrometer must be vented to the laboratory hood exhaust system or must pass through an activated charcoal filter.
 - 5.4.2. The gas chromatograph and mass spectrometer contain zones that have elevated temperatures. The analyst needs to be aware of the locations of those zones, and must cool them to room temperature prior to working on them.
 - 5.4.3. The mass spectrometer is under deep vacuum. The mass spectrometer must be brought to atmospheric pressure prior to working on the source.
 - 5.4.4. There are areas of high voltage in both the gas chromatograph and the mass spectrometer. Depending on the type of work involved, either turn the power to the instrument off, or disconnect it from its source of power
- 5.5. Primary Materials Used: The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material	Hazards	Exposure Limit (1)	Signs and symptoms of exposure
Methanol	Flammable Poison Irritant	200 ppm-TWA	A slight irritant to the mucous membranes. Toxic effects exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure may include headache, drowsiness and dizziness. Methyl alcohol is a defatting agent and may cause skin to become dry and cracked. Skin absorption can occur; symptoms may parallel inhalation exposure. Irritant to the eyes.
Methylene Chloride	Carcinogen Irritant	25 ppm-TWA 125 ppm-STEL	Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting and headache. Causes irritation, redness and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degreases the skin. May be absorbed through skin.
Acetonitrile	Flammable Poison	40 ppm-TWA	Early symptoms may include nose and throat irritation, flushing of the face, and chest tightness. Prolonged exposure to high levels of vapors may cause formation of cyanide anions in the body.
Hexane	Flammable Irritant	500 ppm-TWA	Inhalation of vapors irritates the respiratory tract. Overexposure may cause lightheadedness, nausea, headache, and blurred vision. Vapors may cause irritation to the skin and eyes.
Acetone	Flammable	1000 ppm (TWA)	Inhalation may cause coughing, dizziness, dullness, and headache. Contact causes redness, pain, drying and cracking of the skin. Vapors cause eye irritation. Eye splashes may cause severe irritation, with stinging, tearing, redness and pain.
Benzene	Carcinogen Flammable Poison	1 ppm-TWA 5 ppm-STEL	Toxic by ingestion, inhalation and absorption. Causes headache, nausea, dizziness, weakness and breathing difficulties. This material is irritating on contact with the skin and eyes and may cause permanent eye damage.
Carbon Tetrachloride	Carcinogen Poison	10 ppm-TWA 200 ppm-STEL	Toxic by ingestion, inhalation and absorption. Causes headache, nausea, dizziness and narcosis. Contact with skin or eyes may cause irritation. Consumption of alcohol may increase toxic effects
Chloroform	Carcinogen Irritant	50 ppm Ceiling	Acts as a relatively potent anesthetic. Irritates respiratory tract and causes central nervous system effects, including headache, drowsiness, dizziness. Causes skin irritation resulting in redness and pain. Removes natural oils. May be absorbed through skin. Vapors cause pain and irritation to eyes. Splashes may cause severe irritation and possible eye damage.
1,4-Dichlorobenzene	Irritant	75 ppm-TWA	Can cause irritation by ingestion and inhalation. Causes nausea, vomiting and diarrhea. Contact with material or vapors can cause irritation to skin and eyes.
Vinyl Chloride	Carcinogen Flammable Poison	1 ppm TWA	Toxic by inhalation, ingestion and absorption. Can cause respiratory irritation, dizziness, weakness, fatigue, nausea and headache. Contact with the material can cause eye and skin irritation.
1 – Exposure limit refers to the OSHA regulatory exposure limit.			

6. Equipment and Supplies

- 6.1. Canisters, 1, 6-, 15-, and 30-liter sizes, preferably equipped with two valves and integral vacuum/pressure gauge, Scientific Instrumentation Specialists or equivalent.
- 6.2. Static gas dilution bottles (SGDB), nominally 2000 ml, with mininert valves, Tekmar Co., or equivalent.
- 6.3. Syringes, gas-tight, 10 uL, 50 uL, 500 uL, 1000 uL, 2.5 mL, 50 mL, 500 mL, all side port needle, Hamilton, Inc., or equivalent.

- 6.4. Gas Chromatograph/Mass Spectrometer System, Agilent HP 6890 GC and 5973 MSD or equivalent.
- 6.5. Fused silica capillary column, 60 m x 0.32 x 1um film DB-5, J&W Scientific, or equivalent.
- 6.6. Vacuum pump, Model 726.3 TTP, KNF Newberger, or equivalent.
- 6.7. Canister concentrator system, Model 7100 or 7100A, Entech Co., with a Model 7016CA, 16-position auto sampler.
- 6.8. Gauges: The following gauges are certified annually
 - 6.8.1. Test gauge, 0 to 30 in. Hg vacuum, Ashcroft Co., or equivalent
 - 6.8.2. Test gauge, 0-60 psi, Ashcroft Co., or equivalent
 - 6.8.3. Test gauge, 0 to 100 in. Hg pressure, Ashcroft Co., or equivalent
 - 6.8.4. Digital gauge 0 to 30" Hg vacuum, Dwyer or equivalent
 - 6.8.5. Digital gauge 0 to -29.9" Hg vacuum, 0 to 99.9 psi, Dwyer or equivalent
- 6.9. Tedlar Bags: Variety of sizes. SKC or equivalent.

7. Reagents and Standards

- 7.1. Helium, ultra high purity, 99.999+%, Air Products, or equivalent.
- 7.2. Liquid nitrogen, Air Products, or equivalent.
- 7.3. Nitrogen, ultra high purity, Air Products or equivalent
- 7.4. Internal/Surrogate Standard (all at 100 ppb) in nitrogen, 2000 psig, Scott Specialty Gases, or equivalent:

CAS NUMBER	Internal Standards	MOLECULAR WEIGHT (ng/n mole)
74-97-5	bromochloromethane	129.4
540-36-3	1,4-difluorobenzene	114.1
3114-55-4	chlorobenzene-d5	117.6
	Surrogates	
17060-07-0	1,2-dichloroethane-d4	103.0
2037-26-5	toluene-d8	100.2
460-00-4	4-bromofluorobenzene	175.0

- 7.4.1. A sufficient volume from the internal/surrogate standard cylinder is transferred to the 15-liter summa canister to produce a positive pressure.
- 7.4.2. The working internal/surrogate standard may be used as long as the pressure in the canister remains above ambient pressure and is not past its expiration date.
- 7.4.3. The Entech is programmed to add 20 mL of the internal standard/surrogate can. This results in a concentration of 4 ppb/v of internal standard/surrogate (based on 500 mL volume).
- 7.5. Primary Target and Laboratory Control Sample Gaseous Standards: target compounds, 300 ppb v/v, vendor-certified high-pressure aluminum cylinders.
 - 7.5.1. The expiration date for the gaseous standards contained in the certified high-pressure aluminum cylinders has not been specified by the vendor. No significant degradation in response been observed for over 9 years. Due to this stability, a nominal expiration date of 20 years has been assigned to these standards and it is subject to ongoing monitoring of target analytes through second source standards.
 - 7.5.2. If the vendor supplies an expiration date, that expiration date would be used.
- 7.6. Initial Calibration Verification Standard (2nd source) stock cylinder (ICV): TO-14 list compounds, 100 ppb v/v, vendor-certified high-pressure aluminum cylinder (see table 1). Spectra Gases or equivalent.
 - 7.6.1. The calibration verification standard stock cylinder may be used for 20 years from date of certification or until the vendor assigned expiration date, whichever is earlier.
- 7.7. Standard grade neat compounds of hexachlorobutadiene (HCBD) and naphthalene, 99+% or of known purity, Chem Service, or equivalent.
 - 7.7.1. Naphthalene/Hexachlorobutadiene (HCBD) Stock Standard:
Approximately 3.6 mg of naphthalene is weighed into a glass container small enough to be dropped into a SGDB. The glass container is introduced into the SGDB and the bottle is capped with a mininert valve. Approximately 4.4 uL of HCBD is added to the SGDB using a 10 uL syringe. The SGDB is placed in an oven at approximately 60°C. The exact weight/volume to be added is calculated from the volume of the

SGDB such that adding 2.5 milliliters from the SGDB to a 15-L can (or 1 mL in a 6-L can) pressurized to 30 psig yields a concentration of 25 ppb (v/v) of HCBD and Naphthalene in the working standard. See section 12.7 and 12.8 for calculations.

- 7.8. Prepared Standard, polar compounds, vendor certified mix containing methanol, ethyl ether, acetone, acrylonitrile, vinyl acetate, 2-butanone, 1-butanol, 4-methyl-2-pentanone, 2-hexanone, methyl-tert-butyl ether, acrolein, acetonitrile, 99+% or of known purity, Ultra Scientific or equivalent.
- 7.9. Polar stock standard and 1,2,3-trichloropropane, 99+% or of known purity, Chem Service or equivalent.
 - 7.9.1. SGDB stock method: Approximately 27 μ L of the polar standard mix (section 7.8) and approximately 1.3 μ L of 1,2,3-trichloropropane is injected into a SGDB. The exact volume to be added is calculated from the volume of the SGDB such that adding 5 mL from the SGDB to the working standard yields a concentration of 100 ppb (v/v) for methanol and 50 ppb (v/v) for the other polar compounds and 25 ppb (v/v) of 1,2,3-trichloropropane in the working standard.
 - 7.9.2. Water stock method: 67.5 μ L of the polar standard mix and 3.25 μ L of 1,2,3-trichloropropane are dissolved in water to a final volume of 10 mL.
- 7.10. Additional Standards: Neat materials, not contained in the certified cylinders, can be added to a SGDB either individually or as a mix.
 - 7.10.1. If the desired compound is a gas at room temperature, a measured volume is injected into an evacuated summa canister and pressurized. See section 12.9 and 12.10 for calculation. If the desired compound is a liquid or solid at room temperature, the volume of each compound to be added to the SGDB should be back calculated to the desired final concentration in the canister. See section 12.7 and 12.8 for calculation.
- 7.11. 25 ppb v/v Canister Working Standard (for a 15-L can. For a 6-L can, reduce the volume of the standards appropriately).
 - 7.11.1. 90 μ L of reagent water is injected through a septum (inserted into a 1/4-in. nut) into a clean evacuated 15-liter canister. The canister is allowed to stand for at least 20 minutes to allow all the water to evaporate from the valve area.
 - 7.11.2. 10 μ L from the water standard in 7.9.2 (or 5 mL of the polar stock from the SGDB in 7.9.1) and 2.5 mL of the naphthalene/HCBD stock in 7.7.1

are injected through the septum. This step should be done quickly and the syringe for the naphthalene/HCBD stock should be heated in the oven along with the SGDB. The canister is then brought up to exactly zero inches gauge pressure with UHP nitrogen.

7.11.3. 5 in. (Hg) of each 300 ppb v/v high-pressure gas standard from section 7.5 is added to the 15-liter canister. The can is pressurized to 30" Hg with UHP nitrogen for a final volume of 30L and final concentration of 25 ppb v/v.

7.11.4. Alternate concentrations of the working standards may be made as long as the calculations, concentrations and volumes are adjusted appropriately and preparation is clearly documented in the standard preparation logbook.

7.12. Low Standard Preparation: Typically 1 ppb v/v or 2 ppb v/v calibration point

7.12.1. 40 μ L of reagent water is injected through a septum (inserted into a 1/4 inch nut) into a clean evacuated 6-liter canister. The canister is allowed to stand for at least 20 minutes to allow all the water to evaporate from the valve area.

7.12.2. 480 mL (2.4" Hg) (for the 1 ppb v/v standard) or 960 mL (4.8" Hg) (for the 2 ppb v/v standard) of the 25 ppb (v/v) standard is transferred to the 6-liter canister.

7.12.3. The canister is pressurized to 30 in. Hg with UHP nitrogen.

7.13. 50 ppb v/v Initial Calibration Verification Standard (ICV)

7.13.1. 8 μ L of polar stock water standard in 7.9.2 and 2 mL of the naphthalene/HCBD stock in 7.7.1, each independently prepared from the primary calibration stock, is added through a septum (inserted into a 1/4-in. nut) into a clean evacuated 6 liter canister. This step should be done quickly and the syringe for the naphthalene/HCBD stock should be heated in the oven along with the SGDB.

7.13.2. 32 μ L of reagent water is injected through the septum. The canister is allowed to equilibrate for at least 20 minutes to allow all the water to evaporate from the valve area.

7.13.3. The canister is brought up to exactly zero inches gauge pressure with UHP nitrogen.

- 7.13.4. 30 in. (Hg) of the 100 ppb v/v (from 7.6) laboratory control standard stock cylinder is added to the 6 liter canister (for a final volume of 12 L and final concentration of 50 ppb v/v).
- 7.13.5. Alternate sources and concentration of the ICV may be prepared as long as it is not the same source as the primary calibration standard, and the calculations, concentrations and volumes are adjusted appropriately.
- 7.14. Approved SGDB and canister stock standards (section 7.7, 7.8, 7.9 and 7.10) may be used for 6 months from the date of preparation or the earliest expiration of parent standard, whichever comes first. Working canister standards (7.11 and 7.12 and 7.13) may be used for two months from the date of preparation or the earliest expiration of parent standard, whichever comes first.
- 7.15. The HCBd/naphthalene SGDB is stored at approximately 60°C. Other SGDB and canister standards are stored at room temperature. If the analytes prove to be plating/condensing in the SGDB at room temperature, then the SGDB should be stored at approximately 60°C. Mixes and neat compounds (that are not in SGDB, cans, or cylinders) are stored at the manufacturer's recommended storage conditions.
- 7.16. Approval of Stock and Working Standards
- 7.16.1. When a new stock is prepared, it can either be verified at the SGDB stage or at the working level stage.
- 7.16.1.1. To compare the SGDB standards, humidify two 6 liter canisters with 40 µL of water each, and spike with equal known volumes (typically 5 - 10 mL) from the SGDB, and bring to an equal final pressure of nominally 15 psig.
- 7.16.1.2. The two standards must agree to within 20 percent difference after taking into account nominal volume differences between the two bottles.
- 7.16.2. Working canister standards are approved for use by passing the daily standard acceptance criteria given in Section 10.5 or the initial calibration verification in section 10.4. The working LCS canister is approved for use by passing the LCS acceptance criteria in section 9.3.

8. Sample Collection, Preservation and Storage

- 8.1. Sampling is not performed for this method by STL Knoxville. For information regarding sample shipping, refer to SOP KNOX-SC-0003, Receipt and Log In of Commercial Samples, current revision.

Container Type	Preservative	Holding Time
SUMMA canister	None	30 days
Tedlar bag	None	72 hours from collection to analysis or transfer to a can. After transfer to a can, the holding time is 30 day from sample collection.

9. Quality Control

9.1. Internal/Surrogate Standards

- 9.1.1. Internal standards and surrogates are added to each analytical standard, blank and sample. The acceptance criteria for each internal standard's area for every analysis must be $\pm 40\%$ recovery of the internal standard area from the continuing calibration standard. The acceptance criteria for each internal standard's retention time in every analysis must be within ± 20 seconds (0.33 minutes) of the internal standard retention time from the continuing calibration standard.
- 9.1.2. Surrogate recoveries must fall within 70% to 130%, or within laboratory historical control limits if available.
- 9.1.3. If the internal standard areas or surrogate recoveries for a sample are outside their limits, the cause is determined. If it is a result of a system problem, then the problem must be corrected and the sample reanalyzed with acceptable results. If it is the result of a matrix effect, the sample must be reanalyzed to confirm this, unless the effect is caused by high levels of target or non-target compounds co-eluting with or interfering with the surrogates or internal standards.

9.2. System Blanks

- 9.2.1. For each 24-hour tune in which samples are analyzed or every 20 samples, whichever is more frequent, an acceptable system blank must be analyzed before samples analysis may begin.
- 9.2.1.1. A system blank is defined as a cleaned canister, humidified with reagent water and filled with UHP nitrogen.
- 9.2.1.2. Typically, a 30L canister, humidified with 200 uL of reagent water and pressurized to 25-30 psi with nitrogen is used for the

blank. A lot check from the can cleaning system can be used as a system blank (See section 9.5).

9.2.1.3. An acceptable system blank is one with all target analytes less than 0.2 ppbv. The data may still be reported if the concentration of the analyte is less than the laboratory reporting limit (see Tables 1, 2 and 3), and meets internal standard and surrogate requirements in section 9.1. Any samples associated with a method blank with results above 0.2 ppbv are flagged in the data report. If a blank has a reportable result between the RL and the MDL, the associated samples are also flagged.

9.2.2. If a system blank does not meet the above criteria, then the blank must be reanalyzed or a new blank prepared and analyzed with acceptable results.

9.3. Laboratory Control Standard (LCS)

9.3.1. The LCS is defined as a working standard made by the same method as analytical standards, using the same source materials. It is used to assess analytical control of this procedure. The LCS is analyzed every 24 hour tune or every 20 samples, whichever is more frequent.

9.3.1.1. The daily calibration verification may also serve as the LCS as long as it meets the criteria of both the LCS and the daily calibration verification.

9.3.2. All non-polar analytes in the LCS must be within 70-130% recovery with the allowance of up to two non-polar analytes having 60-140% recovery. All polar analytes in the LCS must be within 60-140% recovery with the allowance of up to two polar analytes having 45-155% recovery.

9.3.3. The internal standards and surrogates must pass criteria specified in section 9.1.

9.3.4. If the above criteria cannot be met, corrective action must take place.

9.4. Duplicate Analysis

9.4.1. A duplicate is analyzed with every 20 samples. It is not reported unless specifically requested.

- 9.4.2. The acceptance criteria for the duplicate analysis are $\leq 25\%$ RPD for target compounds that are greater than 5 times the RL. No criteria for methanol and n-butanol. The calculations are given in section 12.16.

9.5. Canister Blank Checking

- 9.5.1. From each cleaned lot of canisters, a canister is selected, humidified with 40 μ L reagent water, and pressurized with UHP nitrogen. (See SOP KNOX-SC-0001, current revision, "Canister Cleaning and Preparation").
- 9.5.2. A blank check is analyzed within 24 hours of a valid tune check and calibration.
- 9.5.3. A blank check passes if there are no target analytes above the reporting limit, and the internal standards and surrogates pass criteria in section 9.1. Cans are considered certified "clean" if the result for all analytes are below 0.2 ppbv. However the can may still be used to collect samples if the concentration of the target analyte is less than the reporting limit. If analytes are detected in the can being certified as clean above 0.2 ppbv and below the reporting limit, this will be noted on the blank check quantitation report.
- 9.5.4. If a blank check canister does not pass, the can may be re-analyzed. If the acceptance criteria are still not met, the entire lot of canisters must be re-cleaned, and a blank check from the re-cleaned lot must pass.

9.6. Nitrogen check

- 9.6.1. Before a new nitrogen cylinder is used for pressurization of samples or standards, it must be analyzed as a blank and pass all the criteria in section 9.2.1.3.

- 9.7. Annual gauge calibration: The gauges that are used in calculations to measure cylinder and canister pressure or vacuum must be certified annually.

10. Calibration and Standardization

- 10.1. Instrument Conditions: The following steps are part of the software's automatic tuning procedure and are performed as needed.
- 10.1.1. Mass assignments of the mass spectrometer are checked and adjusted using perfluorotributylamine (PFTBA FC43).

- 10.1.2. The mass spectrometer is tuned to meet the criteria for BFB (see Figure 1).
- 10.1.3. The mass spectrometer is adjusted to minimize noise (see instrument manufacturer instruction manuals).
- 10.1.4. See Appendix III for examples of GC/MS and GC instrument parameters.

10.2. Daily Tune Check

- 10.2.1. 50 ng or less of BFB is analyzed for each 24-hour time tune period; the 24-hour time period begins at the moment of injection of BFB. All abundance criteria for BFB in Figure 1 must be met before the analysis of standards, QC samples or client samples.
- 10.2.2. The BFB must be acquired in the following manner: Three scans (the apex scan, and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction is conducted using a single scan prior to the elution of BFB.
- 10.2.3. Once the BFB passes criteria, the same mass spectral conditions used for the BFB must be used to acquire the data in that 24-hour tune period, until the next BFB event.

10.3. Initial Calibration

- 10.3.1. The GC/MS system must be calibrated with at least 5 concentrations that span the monitoring range of interest. The dynamic range of the curve is generally 0.2 ppb v/v to 30 ppb v/v based on 200 mL sample analysis for normal level reporting limits for most analytes, and 0.01 ppb v/v to 1 ppb v/v based on 500 mL sample analysis for low level reporting limits, for a limited set of analytes. The concentration of the low standard of the calibration must be at or below the reporting limit. If quadratic fit is required, there must be at least 6 points. See Appendix IV for the recommended calibration amounts.
- 10.3.2. See chart below to obtain the typical desired levels of quantitation. This is a typical schematic of the calibration; however the standard can concentration, calibration levels and calculated concentrations may be different, as long as the calibration rules in 10.3.1 and 10.3.11 are followed. See Appendix IV and V for the table of analytes. If the actual standard amount trapped is greater than 5% from the programmed volume, the actual volume trapped is documented and used in calculations.

Normal level RL (calculation based on 200 mL sample analysis)

25 ppb v/v can	240	120	80	40	20	-	-	-	-
1 ppb v/v can	-	-	-	-	-	160	80	40	20
Calculated concentration ppb v/v	30	15	10	5	2.5	0.8	0.4	0.2	0.1

Low level RL (calculation based on 500 mL sample analysis)

2 ppb v/v can	250	125	50	-	-	-	-
0.1 ppb v/v can	-	-	-	500	200	100	50
Calculated concentration ppb v/v	1.0	0.5	0.2	0.1	0.04	0.02	0.01

10.3.3. See Tables 1, 2 and 3 for suggested quantitation ions.

10.3.4. A calibration curve is valid for all target analytes if the relative standard deviation (RSD) of the relative response factors is $\leq 30\%$ for each target analyte, with the following allowance: up to two target analytes may have an RSD $\leq 40\%$.

10.3.5. The internal standard area response at each calibration level must be within 40% of the mean area response over the initial calibration range for each internal standard.

10.3.6. The retention time (RT) shift for each of the internal standards at each calibration level must be within 20 seconds of the retention time of the mean calibration for each internal standard.

10.3.7. Each analyte at each level must be within 0.06 RRT units of the mean RRT.

10.3.8. If the curve is acceptable and there is time remaining in the 24-hour tune, blanks, LCSs and samples may be analyzed.

10.3.9. The concentrations in the samples, LCSs and blanks are calculated using the response factors from the initial calibration curve.

10.3.10. Linear or quadratic curve fits may be used. Use of $1/\text{Concentration}^2$ weighting may be used 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. The correlation coefficient (coefficient of determination for non-linear curves, r^2) must be ≥ 0.990 .

10.3.11. Analyst may elect to drop points from the calibration to improve subsequent quantitation. The rules for dropping points are:

- May drop points below the RL as long as there is a point remaining at or below the RL.
- May drop high points, decreasing linear range.
- May NOT drop a point between points.

For more guidance see “Selection of Calibration Points” Policy P-T-001, current revision.

Rules for curve use/acceptability:

- The Y intercept must be below the RL.
- The r^2 value obtained from Target must be ≥ 0.990 .
- At least 5 points must be used for average or linear curve.
- At least 6 points must be used for a quadratic curve.
- Do not include the origin or force the curve through the origin.
- For quadratic curves, the tangent line to the slope of the curve must be continuous and positive (i.e. no parabola's or breaks in the curve).

10.4. Initial Calibration Verification (ICV)

10.4.1. The ICV is a second source standard containing the TO-14 list compounds at 10 ppb (Table 1) and is analyzed after the initial calibration and before any samples are analyzed. For each analyte, a percent recovery (%R) is calculated using the response factor from the initial calibration.

10.4.2. A working standard from an independently prepared stock containing all analytes is also analyzed as the ICV for analytes not included in the TO-14 list.

10.4.3. The ICV is valid for all analytes if the %R is between 65% and 135% for each TO-14 list analyte in the ICV. Benzyl chloride ICV acceptance criteria is 20-180%.

10.5. Daily Calibration Verification

10.5.1. A mid-level standard is analyzed following the daily tune check (section 10.2) as the calibration verification standard. Typically, this is 80 mL of the 25-ppb (v/v) can. For all target analytes, a percent difference (%D) or percent drift is calculated using the response from the calibration verification standard and compared to the current initial calibration curve.

10.5.2. A calibration verification standard is acceptable if the %D or % drift is $\leq 30\%$ for all target analytes. However, data may be reported from a calibration verification standard with up to four target analytes with % drift up to $\leq 40\%$. These analytes must be clearly noted in the data report.

10.5.2.1. For samples from New Jersey, the target analytes with drift >30% must be noted in the narrative.

10.5.3. The daily calibration verification may also serve as the LCS as long as it meets the criteria of both the LCS and the daily calibration verification (section 9).

10.5.4. If the calibration verification standard does not meet the above criteria, corrective action must be taken and/or a new initial calibration performed unless project specific analytes or client specified QC criteria are met.

11. Procedure

11.1. Canister Preparation

11.1.1. Use the following guidelines when checking a sample upon receipt:

- Tedlar bags are inspected to ensure that the valve is closed and the bags are not leaking. Bags must be analyzed or transferred to a can within 72 hours of collection.
- 1-L cans received between -10" Hg vacuum and a positive pressure are ready for a 20 mL analysis. If more volume is expected to be analyzed, the can will have to be pressurized in order to obtain more volume from the can.
- 6-liter cans received between -10" Hg vacuum and a positive pressure are ready for 200 mL analysis
- If any can is near zero psi (approximately -1" Hg to 1 psi), non-conformance the can as "suspect improper sampling event" and proceed with analysis. The project manager will discuss this with the client.
- Cans received -10" Hg or more vacuum should be pressurized to no more than approximately 5 psi.
- Cans below -20" Hg: non-conformance the can as "suspect improper volume sampled" and proceed with pressurizing the can to no more than approximately 5 psi for analysis. The project manager will discuss with the client that there may have not been enough sample collected for analysis and inform the analyst if sample analysis is to proceed or if the test is to be cancelled.
- Cans received at high vacuum (near -28" Hg or lower) should be inspected to determine if it is a trip blank. If the can is a trip blank, pressurize the can and use a dilution factor of one in analysis. If the sample cannot be determined to be a trip blank, non-conformance the can as "suspect improper sampling event" and proceed with pressurizing

the can for analysis. The project manager will discuss with the client that there was not enough sample collected for analysis, and inform the analyst if sample analysis is to proceed or if the test is to be cancelled.

- 11.1.2. Measure the initial and final pressure/vacuum of the canister using an NIST traceable, certified vacuum or pressure gauge.
- 11.1.3. The barometric pressure, initial pressure/vacuum and final pressure/vacuum are recorded in a laboratory notebook, and used to calculate the dilution factor caused by pressurizing the can to working conditions
- 11.1.4. The canister is allowed to equilibrate for approximately one hour. If the canister was pressurized to greater than 15 psig, pressure should be released from the canister to bring the pressure below 15 psig. For autosampler volumes scheduled to be below 50 mL, the can pressure must be reduced to below 7 psig to more accurately measure the volume injected.
- 11.1.5. This canister may be further diluted, if necessary, by the dilution methods discussed in sections 11.3, 11.5 and 11.6.
- 11.2. Following a successful initial or calibration verification and prior to analysis of actual samples, an acceptable system blank and LCS must be analyzed (see sections 9.2 and 9.3). Following successful system blank and LCS analysis, actual sample analysis may begin. The LCS and blank are analyzed every 24 hour tune or every 20 samples, whichever is more frequent.
 - 11.2.1. The desired sample size of each sample to be analyzed is determined by screening the cans according to SOP KNOX-MS-0010, current revision, Volatile Analyte Screening By Purge and Trap. The standard aliquot size is 200 mL for standard reporting limit work or 500 mL for low-level work. Sample volume injected can range from 10 mL to 1000 mL. For sample volumes below 50 mL, the can pressure must be reduced to below 7 psig to more accurately measure the volume injected. Volumes larger than 1000 mL can cause trap freeze-up when high humidity samples are trapped. If samples have been adequately pressurized with nitrogen, have been diluted, or only a small amount of sample collected in the can, then volumes larger than 1000 mL may be trapped, and the internal standards and surrogates monitored closely for breakthrough or freeze-up problems.
 - 11.2.2. The pressure of each sample canister is checked. If the pressure is above 15 psig, the excess pressure is vented.

- 11.2.3. Each sample name, volume (aliquot), method, and autosampler position are typed into the Entech sequence table.
- 11.2.4. If necessary, the automated flush function is used to sweep each autosampler line in the name list with helium.
- 11.2.5. The cans are then securely tightened onto the autosampler with the canister valves closed.
- 11.2.6. An automated leak check is run on each position. A hard copy of the leak check results is included with the daily calibration package. This is only a check to ensure that the valves are in proper working order and that the cans are attached securely to the autosampler.
- 11.2.7. If all positions pass the leak check, the canister valves are opened.
- 11.2.8. A name list similar to the Entech name list (section 11.2.3) is typed into the GC/MS sequence table. The sample volume programmed, the can number and a notation for in-can or serial dilution are noted in the analytical run log.
 - 11.2.8.1. If the actual sample amount trapped is greater than 5% from the programmed volume, the actual volume trapped is documented and used in calculating the results.
- 11.2.9. The Entech autosampler is started and the GC/MS acquisition program is started. (Note: The scan and GC parameters are controlled by the GC/MS method.)
- 11.2.10. 20 ml of the surrogate/internal standard is trapped on the Entech concentrator prior to sample introduction.
- 11.2.11. The analysis proceeds automatically for each name in the Entech autosampler program.
- 11.2.12. The internal standards and surrogates must pass all the criteria specified in section 9.1.

11.3. Autosampler Dilutions

- 11.3.1. Volumes of 10 to 1000 mL may be analyzed by the autosampler (see section 11.2.1). The standard aliquot is 200 mL for standard reporting limit work and 500 mL for low-level work.

- 11.3.2. If an analyte found in the sample is over the curve by less than a factor of twenty (based on 200 ml nominal volume) or fifty (based on 500 ml nominal volume), then the aliquot size of the sample may be reduced to a volume as low as 10 mL. This dilution factor is multiplied with all other dilution factors for this sample to obtain the final dilution factor.
- 11.3.3. If a dilution is performed to bring one or more analytes within the calibration range, the analyte having the highest concentration should not be diluted to less than 20% of the calibration range unless there are significant amounts of non-target compounds present.
- 11.3.4. 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 five times the height of the internal standards, then the sample should be reanalyzed at a more concentrated dilution (up to the nominal volume). This requirement is approximate and subject to analyst judgment.
- 11.3.5. Only the most concentrated dilution with no target compounds above the calibration range will be reported. Other dilutions will only be reported at client request.
- 11.3.6. The internal standards and surrogates must pass all the criteria specified in section 9.1.

11.4. Water addition

- 11.4.1. The analyst should be aware that humidity plays an important role in the recovery of certain target compounds, particularly polar compounds, and should be prepared to add humidity to canisters where appropriate. The addition of water helps to stabilize the behavior of these compounds, which might otherwise interact with the interior surface of the summa canister or with the stainless-steel lines of the sample manifold.
- 11.4.2. Since it is not practical to know the relative humidity of all canisters received at the laboratory, the analyst should assume that canisters are received at approximately 80 percent relative humidity. When making canister dilutions (see Sections 11.5, and 11.6), the analyst should attempt to preserve the relative humidity of canisters at a level that will minimize recovery loss due to low canister relative humidity.
- 11.4.3. Under normal laboratory conditions, a 6 liter summa canister at ambient pressure will have a relative humidity of 100 percent if approximately 100 uL of water is in the canister.

11.4.3.1. The minimum relative humidity at which canisters containing polar analytes can be analyzed before polar target recovery is negatively affected is approximately 20 - 30 percent.

11.4.3.2. The minimum relative humidity at which canisters containing nonpolar analytes can be analyzed before nonpolar target recovery is negatively affected is approximately 10 percent.

11.5. Serial Dilution

11.5.1. High-level samples, for example, are those containing ppm levels of volatile organic compounds.

11.5.2. The original sample canister must have a positive pressure. If the pressure is less than 0 psig, then proceed to Section 11.1.

11.5.3. A septum cap is attached to the sample canister and a gas-tight syringe is purged with UHP nitrogen. A septum cap is attached to a clean evacuated 6-liter canister (the dilution canister).

11.5.4. 40 uL of deionized water is added to the canister through the septum of the evacuated can (See Section 11.4 for guidance on addition of water).

11.5.5. The syringe is inserted into the septum cap of the canister containing the sample and the canister valve is opened. The syringe is purged twice with sample and vented. The desired volume is then withdrawn and transferred into the dilution canister. The dilution canister is then pressurized using UHP nitrogen.

11.5.6. The final pressure is measured in the serial dilution canister using a NIST traceable, certified gauge.

11.5.7. If the canister was pressurized to greater than 15 psig, pressure should be released from the canister to bring the pressure below 15 psig.

11.5.8. The barometric pressure, the aliquot volume, final canister pressure and canister serial number are recorded in a laboratory notebook. The serial dilution factor is calculated.

11.5.9. If a high level dilution is performed to bring one or more analytes within the curve, the analyte having the highest concentration should not be diluted to less than 20% of the upper calibration range, unless there are significant amounts of non-target compounds present. It is imperative that

high levels of target and non-target analytes not contaminate the analytical system.

11.5.10. This serial dilution canister may be further diluted, if necessary, by another serial dilution or in-can dilution (see section 11.6) or on the autosampler (see section 11.3). The final dilution factor is the product of all the dilution factors for the sample.

11.6. In-canister Dilutions

11.6.1. If an analyte found or suspected to be in the sample is over the calibration range, to a level that an autosampler dilution would be insufficient, an in-canister dilution may be performed.

11.6.2. The canister vacuum/pressure is checked. If the can is under vacuum, then record the vacuum reading and proceed to section 11.6.3. If the canister is under pressure, then the can is bled to ambient pressure, then proceed to section 11.6.3.

11.6.3. The canister is pressurized to the desired pressure. The pressure should be no more than 40 psig.

11.6.4. The final pressure is measured using an NIST traceable, certified gauge.

11.6.5. If the canister was pressurized to greater than 15 psig, pressure should be released from the canister to bring the pressure below 15 psig.

11.6.6. The barometric pressure and the final pressures are recorded in a laboratory notebook and the in-can dilution factor is calculated.

11.6.7. If an in-canister dilution is performed to bring one or more analytes within the curve, the analyte having the highest concentration should not be diluted to less than 20% of the upper calibration range, unless there are significant amounts of non-target compounds present. Care should be taken to avoid over-dilution for in-canister dilutions since the original sample is affected.

11.6.8. This in-can dilution canister may be further diluted, if necessary, by another in-can dilution or a serial dilution (see section 11.6) or on the autosampler (see section 11.3). This dilution factor is multiplied with all other dilution factors for this sample to obtain the final dilution factor.

11.7. Major Maintenance

11.7.1. A new initial calibration is necessary following major maintenance. Major maintenance includes changing the column, cleaning or repairing the source, replacing filaments, changing electronics, replacing the multiplier or changing moisture or Tenax traps.

11.8. Minor Maintenance

11.8.1. Minor maintenance includes cleaning the injector port, replacing filters, changing the pump oil, autotuning, switching filaments (instrument contains two filaments under vacuum), replacing valves or rotors, change/refill the calibration vial, changing seals and o-rings, ballasting pump, replacing fuses, replacing roughing pumps or transfer lines.

11.9. 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, except those specified by project specific instructions, shall be completely documented using a Nonconformance Memo and approved by a Technical Specialist, Project Manager and QA Manager. If contractually required, the client shall be notified.

11.10. 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. Refer to Figure 2 for an example data review checklists used to perform and document the review of the data. Using the data review checklist, the analyst also creates a narrative which includes any qualifications of the sample data.

12.2. Tentatively Identified Compounds (TICs): 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 STL Knoxville SOP KNOX-MS-0014, current revision, "Determination of Tentatively Identified Compounds (TICs)"

12.3. Calculation legend:

A	=	amount of neat compound, uL
CB	=	concentration in SGDB, ug/mL
CC	=	concentration in canister, ppb v/v
CS	=	concentration in mix, ug/uL
Cx	=	the value determined by vendor certification analyses is used in the following calculations, ppb v/v (300 ppb nominal)
d	=	density of neat compound, g/mL

DF	=	dilution factor, unitless
FV	=	final volume in a pressurized canister, liters
GC	=	gas constant at 25°C and standard pressure, 24.45 nL/n mole
MW	=	molecular weight, ng/n mole
PB	=	barometric pressure
PF	=	final pressure, units specified
PI	=	initial pressure, units specified
PT	=	transfer pressure, units specified
Px	=	pressure in X = inches, psia or mmHg
TK	=	temperature in Kelvin
TV	=	transfer volume, liters or uL
V _{bottle}	=	volume of static gas dilution bottle, mL
V _{mix}	=	volume of mix, µL

12.4. Calculations:

12.4.1. Final Canister Volume

$$FV = \frac{\text{Canister size (L)} \times P_F(\text{mm Hg Abs})}{P_B(\text{mm Hg Abs})}$$

$$\text{Pmm Hg} = \text{P inches} \times 25.4$$

$$\text{P inches} = \text{Ppsi} \times 2.036$$

$$\text{Pmm Hg} = \text{P}_{\text{psi}} \times 51.7149$$

12.5. Polar stock:

$$12.5.1. \quad CS \mu\text{g} / \mu\text{L} = \frac{A * d * 1000}{V_{\text{mix}}}$$

$$12.5.2. \quad CB \mu\text{g} / \text{mL} = \frac{CS * TV, \mu\text{L}}{V_{\text{bottle}}}$$

12.6. Polar concentration in target dilution standard

$$CC, \text{ppb v/v} = \frac{TV, \mu\text{L} * CB \times GC}{MW * FV}$$

12.7. Stock standards in SGDB

12.7.1. Liquid formula

$$CB_{LIQUID}, \mu g/mL = \frac{\# \mu L * d * 1000 * 0.8829}{V_{bottle}}$$

where 0.8829 is a temperature correction factor (from 21 °C to 60°C)—only used if the SGDB standard is in the oven at 60 C; = 294 °K / 333 °K.

12.7.2. Solid formula

$$CB_{SOLID}, \mu g/mL = \frac{\# mg * 1000 * 0.8829}{V_{bottle}}$$

where 0.8829 is a temperature correction factor (from 21 °C to 60°C)—only used if the SGDB standard is in the oven at 60 C; = 294 °K / 333 °K.

12.8. Concentration of standards in primary target standard made from SGDB

$$CC, ppb \text{ v/v} = \frac{TV, mL * CB * 1000 * GC}{FV * MW}$$

12.9. Concentration of Cylinder Standards: Concentration of Analytes in Primary Target Standard

$$CC, ppb \text{ v / v} = \frac{(P_T - P_I, psi)(Cx)}{(P_F, psi + PB, psi)}$$

12.10. Target Dilution Standard (CC is the concentration of the Primary Target Standard).

$$CC, ppb \text{ v / v} = \frac{(P_T - P_I)(CC)}{(P_F + PB, psi)}$$

12.11. Dilution Factor of original sample canisters

$$DF = \frac{P_f (mm \text{ Abs})}{P_i (mm \text{ Abs})} \times \frac{\text{Sample volume injected}}{500 \text{ ml}}$$

12.11.1. Serial Dilution Factor

$$DF = FV/TV$$

12.12. Response Factor (RF)

$$RF = \frac{Ax * Cis}{Ais * Cx}$$

where:

x = area of the characteristic ion for the target compound.
Ais = area of the characteristic ion for the internal standard.
Cx = amount of the target compound.
Cis = amount of the internal standard.

12.13. Average Response Factor (ARF)

$$ARF = \frac{RF_1 + RF_2 + \dots + RF_n}{n}$$

where:

n = the number of calibration points

12.14. Standard deviation of the ARF:

$$S = \sqrt{\frac{\sum_i^n (ARF - RF_n)^2}{n - 1}}$$

12.15. Relative standard deviation (RSD) of the ARF:

$$RSD = \frac{S}{ARF} * 100\%$$

12.16. Calibration Verification : Percent deviation (% D) of the daily RF values as compared with the initial ARF values:

$$\% D = \frac{|RF - ARF|}{ARF} * 100\%$$

12.17. Laboratory Control Sample percent recovery (%R):

$$\% R = \frac{\text{FoundAmount, ppb}}{\text{SpikeAmount, ppb}} * 100\%$$

12.18. Duplicate relative percent difference (RPD):

$$RPD = \frac{|A_1 - A_2|}{\overline{A}} \times 100\%$$

where:

A₁ = amount determined in first analysis
 A₂ = amount determined in second analysis
 A = average determination, (A₁ + A₂)/2

12.19. Calibration verification percent drift and difference from the initial calibration:

$$\% \text{ Drift} = \frac{C_{\text{expected}} - C_{\text{found}}}{C_{\text{expected}}} \times 100$$

Where

C_{expected} = Known concentration in standard

C_{found} = Measured concentration using selected quantitation method

$$\% \text{ Difference} = \frac{\overline{RF} - RF}{\overline{RF}} \times 100$$

$\overline{RF}$ = Average Analyte Response Factor from Initial Calibration

RF = Measured Analyte Response Factor from Calibration Verification

12.19.1. Target analyte concentrations in samples are typically calculated using the average response factor from the initial calibration. Quantitation may also be determined using linear or second order curves at the analyst's discretion to improve the quantitation of target analytes.

12.19.1.1. Calculation of concentration using Average Response Factors

$$C_{pv} = \frac{R_x C_{is}}{R_{is} \overline{RF}}$$

12.19.1.2. Calculation of concentration using Linear fit

$$C_{pv} = A + B \frac{(R_x C_{is})}{R_{is}}$$

C_{pv} = Concentration, ppb (v/v)

R_x = Response for analyte (area of quantitation ion)

R_{is} = Response for internal standard (area of quantitation ion)

C_{is} = Concentration of internal standard

A = Intercept

B = Slope

The corresponding Target software calculation is as follows:

$$C_{pv} = C_{is} \left(b + \frac{1}{m1} \times \frac{R_x}{R_{is}} \right)$$

b = Concentration Ratio Intercept

m1 = Inverse of Slope

12.19.1.3. Calculation of concentration using Quadratic fit

$$C_{pv} = A + B \left(\frac{R_x C_{is}}{R_{is}} \right) + C \left(\frac{R_x C_{is}}{R_{is}} \right)^2$$

C = Curvature

The corresponding Target software calculation is as follows:

$$C_{pv} = C_{is} \left(b + m1 \times \frac{R_x}{R_{is}} + m2 \times \left(\frac{R_x}{R_{is}} \right)^2 \right)$$

m1 = First order coefficient

m2 = Curvature (Second order coefficient)

12.20. Sample Quantitation: The amount of target compound detected is determined using the average RF or calibration curve values from the initial calibration (not the continuing calibration):

$$\text{Amount} = C_{pv} * DF$$

12.21. Unit conversions

12.21.1.

$$\text{Amount, } \mu\text{g/m}^3 = \frac{\text{Amount, ppb(v/v)} * \text{MW}}{\text{GC}}$$

12.21.2.

$$\text{Amount, ppm v/v} = \text{amount, } \frac{\text{ppb (v/v)}}{1000}$$

12.22. Quantitation of Unknowns

12.22.1. If required, nontarget peaks are reported with probable identifications as Tentatively Identified Compounds (TICs). These are quantitated using the nearest internal standard and assuming a response factor of 1; correction for dilution factor is also made. Search criteria are those in the STL Knoxville SOP KNOX-MS-0014, current revision, Tentatively Identified Compounds (TICs).

13. Method Performance

- 13.1. Method Detection Limit (MDL) - An MDL must be determined for each analyte in each routine matrix prior to the analysis of any samples. The procedure for determination of the method detection limit is given in the SOP S-Q-003 current revision based on 40 CFR Part 136 Appendix B. The result of the MDL determination must support the reporting limit. MDL summaries are stored on the local area network.
- 13.2. Initial Demonstration of Capability – Each analyst must perform an initial demonstration of capability (IDOC) for each target analyte prior to performing the analysis independently. The IDOC is determined by analyzing four replicate spikes (e.g., LCSs) as detailed in STL Knoxville SOP KNOX-QA-0009. Recovery limits must be 70-130% and RSD must be less than or equal to 25%.
- 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. Refer to SOP KNOX-QA-0009 current revision for further requirements for performing and documenting initial and on-going demonstrations of capability.

14. Pollution Prevention

- 14.1. All attempts will be made by laboratory personnel to minimize the use of solvents when performing this procedure.

15. Waste Management

- 15.1. All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment.

Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for “Waste Management and Pollution Prevention.”

- 15.2. The following waste streams are produced when this method is carried out.
- Expired solid and liquid standards are stored in metal closed-top containers.

16. References

- 16.1. Compendium Method TO-14, “The Determination of Volatile Organic Compounds (VOCs) in Ambient Air Using SUMMATM Passivated Canister Sampler and Gas Chromatographic Analysis,” U.S. EPA 600/4-89/017, June 1988.
- 16.2. Compendium Method TO-14A, “Determination of Volatile Organic Compounds (VOCs) in Ambient Air Using Specially Prepared Canisters With Subsequent Analysis by Gas Chromatography,” U.S. EPA 625/R-96/010b, January 1999.
- 16.3. Compendium Method TO-15, “Determination of Volatile Organic Compounds (VOCs) in Air Collected in Specially-Prepared Canisters and Analyzed by Gas Chromatography/Mass Spectrometry (GCMS),” U.S. EPA 625/R-96/010b, January 1999.
- 16.4. STL Quality Management Plan (QMP), current revision.
- 16.5. STL Knoxville Laboratory Quality Manual (LQM), current revision.
- 16.6. Entech Instruments Inc. 7100 Operators Manual. Version 2.0 for the 7100 Preconcentrator and Accessories.

17. Miscellaneous

- 17.1. Other SOPs cross-referenced in this SOP: KNOX-SC-0001, “Canister Cleaning and Preparation”, latest revision.
- 17.2. Modification from the referenced methods
- 17.2.1. The TO-15 tune criteria were not used in this procedure. The tune criteria listed in TO-14 is tighter and thus was used in this procedure. This SOP also allows for 50 ng or less of BFB to verify tuning of the instrument.
- 17.2.2. The continuing calibration listed in this procedure allows up to 4 target analytes with a %D of $\leq 40\%$, with a narrative note (or data

review checklist note for non-NJ DEP analysis) of those target analytes that are over 30% D, but $\leq$ 40% D.

- 17.2.3. This procedure uses purified nitrogen in place of zero humid air specified in the reference methods.
- 17.2.4. TO-14 requires that the RT shift for the internal standards at each calibration level must be within 20 seconds of the RT of the mid-level calibration for each internal standard. TO-15 specifies that the comparison is made to the mean RT over the initial calibration range for each internal standard. This SOP uses the TO-15 criteria.
- 17.2.5. Section 7.13 Method TO-15 states that the working standard may be stored for 30 days. This laboratory experience has allowed the standard expiration date to be 2 months with no significant degradation of the standards.
- 17.2.6. Surrogates are not required by the methods. This SOP adds surrogates to every sample to help monitor for matrix effects and method performance.
- 17.2.7. The TO-15 method states that the scan time must give 10 scans per peak, not to exceed 1 second per scan. The GC/MS software is set for a sampling rate of 3, which corresponds to approximately 2 to 3 scans per second, depending on the instrument. See the GC/MS operator's manual or "help" on the software for more information about the sampling rate.
- 17.2.8. EPA Method TO-14A specifies that the relative accuracy of the field sampler or sample delivery system must meet 90-110% for a standard at 8 ppb v/v. The laboratory Control Sample (LCS) summary data is evaluated against alternate acceptance criteria based on this laboratory procedure for method TO-14A. When TO-14A work is performed, this must be noted in the case narrative.

17.3. List of Appendices

17.3.1. Appendix I: Target Analyte Tables

17.3.1.1. Table 1: Target Analytes - TO-14 and TO-15 Compounds

17.3.1.2. Table 2: Target Analytes - Other Nonpolar Compounds

17.3.1.3. Table 3: Target Analytes - Other Polar Compounds

17.3.2. Appendix II: Figures

17.3.2.1. Figure 1: BFB Tuning Criteria

17.3.2.2. Figure 2: Example of a Data Review Checklist

17.3.2.3. Figure 3: Flow Chart

17.3.3. Appendix III: Example Instrument Parameters

17.3.4. Appendix IV: Recommended Calibration Levels (normal reporting limits)

17.3.5. Appendix IV: Recommended Calibration Levels (low level reporting limits).

Appendix I: Target Analyte Tables**Table 1: Target Analytes – Method TO-14A Target Compounds**

CAS NUMBER	METHOD TO-14 COMPOUND	REPORTING LIMIT (ppb, v/v) (i)	REPORTING LIMIT (ug/m ³) (i)	Low Level Reporting Limit (ppb, v/v) (j)	MOLECULAR WEIGHT (ng/n mole)	SUGGESTED ION
75-71-8	Dichlorodifluoromethane (b)	0.2	0.99	0.020	120.9	85
76-14-2	1,2-Dichlorotetrafluoroethane (c)	0.2	1.40	0.020	170.9	135
74-87-3	Chloromethane	0.5	1.03	n/a	50.49	52
75-01-4	Vinyl Chloride	0.2	0.51	0.020	62.50	62
74-83-9	Bromomethane	0.2	0.78	0.060	94.94	94
75-00-3	Chloroethane	0.2	0.53	0.030	64.51	64
75-69-4	Trichlorofluoromethane (d)	0.2	1.12	0.030	137.4	101
75-35-4	1,1-Dichloroethene	0.2	0.79	0.090	96.94	96
76-13-1	1,1,2-Trichlorotrifluoroethane (e,f)	0.2	1.53	n/a	187.4	101
75-09-2	Methylene Chloride (f)	0.5	1.74	n/a	84.93	84
75-34-3	1,1-Dichloroethane	0.2	0.81	0.020	98.96	63
156-59-2	cis-1,2-Dichloroethene	0.2	0.79	0.050	96.94	96
67-66-3	Chloroform	0.2	0.98	0.020	119.4	83
71-55-6	1,1,1-Trichloroethane	0.2	1.09	0.020	133.4	97
56-23-5	Carbon Tetrachloride	0.2	1.26	0.020	153.8	117
71-43-2	Benzene	0.2	0.64	0.030	78.11	78
107-06-2	1,2-Dichloroethane	0.2	0.81	0.020	98.96	62
79-01-6	Trichloroethene	0.2	1.07	0.020	131.4	130
78-87-5	1,2-Dichloropropane	0.2	0.92	0.030	113.0	63
10061-01-5	cis-1,3-Dichloropropene	0.2	0.91	0.030	111.0	75
108-88-3	Toluene	0.2	0.75	0.10	92.14	91
10061-02-6	trans-1,3-Dichloropropene	0.2	0.91	0.050	111.0	75
79-00-5	1,1,2-Trichloroethane	0.2	1.09	0.040	133.4	97
127-18-4	Tetrachloroethene	0.2	1.36	0.020	165.8	129
106-93-4	1,2-Dibromoethane (EDB)	0.2	1.54	0.020	187.9	107
108-90-7	Chlorobenzene	0.2	0.92	0.020	112.6	112
100-41-4	Ethylbenzene	0.2	0.87	0.020	106.2	91
IT5-30-5	m/p-Xylene (g, h)	0.2	0.87	0.10	106.2	91
95-47-6	o-Xylene (h)	0.2	0.87	0.030	106.2	91
100-42-5	Styrene	0.2	0.85	0.020	104.2	104
79-34-5	1,1,2,2-Tetrachloroethane	0.2	1.37	0.020	167.8	83
108-67-8	1,3,5-Trimethylbenzene	0.2	0.98	0.020	120.2	120
95-63-6	1,2,4-Trimethylbenzene	0.2	0.98	n/a	120.2	105
541-73-1	1,3-Dichlorobenzene	0.2	1.2	n/a	147.0	146
106-46-7	1,4-Dichlorobenzene	0.2	1.2	n/a	147.0	146
100-44-7	Benzyl Chloride	0.4	2.07	n/a	126.6	91
95-50-1	1,2-Dichlorobenzene	0.2	1.2	n/a	147.0	146
120-82-1	1,2,4-Trichlorobenzene	1.0	7.42	n/a	181.4	180
87-68-3	Hexachlorobutadiene	1.0	10.67	n/a	260.8	225

b) Freon 12

c) Freon 114

d) Freon 11

e) Freon 113

f) This is a common laboratory solvent

g) m-xylene and p-xylene coelute

h) Total xylenes (CAS # 1330-20-7) is the sum of m/p-xylenes and o-xylene.

i) Normal reporting limits (RLs) based on 200 mL sample volume. The ug/m³ values are example RLs using the value listed in the table.

j) Low level reporting limits based on 500 mL sample volume

Table 2: Target Analytes - Other Nonpolar Compounds

CAS NUMBER	OTHER NON-POLAR COMPOUNDS	REPORTING LIMITS (ppb, v/v) (i)	REPORTING LIMIT (ug/m ³) (i)	Low Level Reporting Limit (ppb, v/v) (j)	MOLECULAR WEIGHT (ng/n mole)	SUGGESTED ION
75-45-6	Chlorodifluoromethane (b)	0.2	0.71	n/a	86.47	51
106-97-8	n-Butane	0.4	0.95	n/a	58.12	43
106-99-0	1,3-Butadiene	0.4	0.88	0.030	54.09	54
109-66-0	Pentane	1.0	2.95	n/a	72.15	57
75-15-0	Carbon Disulfide	0.5	1.56	n/a	76.14	76
107-05-1	3-Chloropropene	0.2	0.63	0.060	76.52	39
156-60-5	trans-1,2-Dichloroethene	0.2	0.79	0.10	96.94	96
110-54-3	n-Hexane	0.5	1.76	0.10	86.18	56
110-82-7	Cyclohexane	0.5	1.72	0.040	84.16	69
540-84-1	2,2,4-Trimethylpentane	0.5	2.34	0.020	114.2	57
142-82-5	n-Heptane	0.5	2.05	0.020	100.2	43
74-95-3	Dibromomethane	0.4	2.84	n/a	173.8	93
75-27-4	Bromodichloromethane	0.2	1.34	0.020	163.8	83
111-65-9	n-Octane	0.4	1.87	n/a	114.2	85
124-48-1	Dibromochloromethane	0.2	1.7	0.020	208.3	129
111-84-2	Nonane	0.5	2.62	n/a	128.3	57
75-25-2	Bromoform	0.2	2.07	0.020	252.7	173
98-82-8	Cumene	0.4	1.97	n/a	120.2	105
103-65-1	n-Propylbenzene	0.4	1.97	n/a	120.2	120
95-49-8	2-chlorotoluene	0.4	2.07	n/a	126.6	126
622-96-8	4-ethyltoluene	0.4	1.97	0.020	120.2	105
124-18-5	Decane	1.0	5.82	n/a	142.3	57
98-83-9	alpha-Methylstyrene	0.4	1.93	n/a	118.2	118
135-98-8	sec-butylbenzene	0.4	2.20	n/a	134.2	105
104-51-8	n-Butylbenzene	0.4	2.20	n/a	134.2	91
1120-21-4	n-Undecane	1.0	6.39	n/a	156.3	57
112-40-3	n-Dodecane	1.0	6.97	n/a	170.3	57
91-20-3	Naphthalene	0.5	2.62	n/a	128.2	128

b) Freon 22

i) Normal reporting limits (RLs) based on 200 mL sample volume. The ug/m3 values are example RLs using the value listed in the table.

j) Low level reporting limits based on 500 mL sample volume.

Table 3: Target Analytes – Other Polar Compounds

CAS NUMBER	OTHER POLAR COMPOUNDS	REPORTING LIMITS (ppb, v/v) (i)	REPORTING LIMIT (ug/m ³) (i)	Low Level Reporting Limit (ppb, v/v) (j)	MOLECULAR WEIGHT (ng/n mole)	SUGGESTED ION
67-56-1	Methanol	10	13.1	n/a	32.04	31
593-60-2	Vinyl Bromide	0.2	0.88	0.050	107.0	106
60-29-7	Ethyl Ether	2.0	6.06	n/a	74.12	31
67-64-1	Acetone	5.0	11.88	n/a	58.08	58
75-65-0	Tert-Butanol	2.0	6.06	n/a	74.12	59
107-13-1	Acrylonitrile	2.0	4.34	n/a	53.06	53
108-05-4	Vinyl Acetate	1.0	3.52	n/a	86.09	43
78-93-3	2-Butanone	1.0	2.95	n/a	72.11	72
71-36-3	1-Butanol	2.0	6.06	n/a	74.12	31
108-10-1	4-Methyl-2-Pentanone	0.5	2.05	n/a	100.2	43
591-78-6	2-Hexanone	0.5	2.05	n/a	100.2	58
1634-04-4	Methyl-t-Butyl ether	1.0	3.61	0.050	88.15	73
107-02-8	Acrolein	0.8	1.83	n/a	56.06	56
75-05-8	Acetonitrile	1.0	1.68	n/a	41.05	40
96-18-4	1,2,3-Trichloropropane	0.5	3.01	n/a	147.4	110

i) Normal reporting limits (RLs) based on 200 mL sample volume. The ug/m³ values are example RLs using the value listed in the table.

j) Low level reporting limits based on 500 mL sample volume

Appendix II: Figures

Figure 1: BFB Tuning Criteria

Mass	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	95% to 101% of mass 174
177	5 to 9 % of mass 176

Note: All ion abundances must be normalized to m/z 95, the nominal base peak, even though m/z 174 may be over 100 % of m/z 95.

Figure 2: Example Data Review Checklist

STL Knoxville GC/MS Air Initial Calibration Data Review / Narrative Checklist
Method: TO-14 and TO-15 - KNOX-MS-0001, Rev 8

Analysis Date:		Instrument:		ICAL Batch/Scan Name:		Scanned ☐

Review Items	N/A	Yes	No	If No, why is data reportable?	2nd ••
1. Did BFB meet tune criteria?					
2. Were all standards injected within 24 hr of BFB?					
3. Is the second source analysis of a reference standard within limits? (65-135% R; 20-180% for benzyl chloride)					
4. Was date/time of analysis verified between analysis header and logbook as correct?					
5. Is low level std at or <RL and are the remaining points consecutive?					
6. Were at least 5 levels of each compound analyzed?					
7. Is %RSD for all target analytes $\leq 30\%$? (with up to 2 compounds with RSD $\leq 40\%$)					
8. Have all peaks been auto identified? If not, list:					
9. If curves were used, is correlation coefficient ≥ 0.990 ?					
10. At least 6 consecutive points used for quadratic curves, and at least 5 consecutive points for linear curves?					
11. For linear or quadratic: is a tangent's slope to the curve entirely positive or negative and continuous.					
12. For linear or quadratic: origin NOT included or forced?					
13. Is the "Y" intercept less than the RL for each curve?					
14. RT for each IS ± 20 sec avg. RT?					
15. Area for each IS $\pm 40\%$ avg. area?					
16. Each analyte ± 0.06 RRT of avg. RRT?					
17. If manual integrations were performed, are they clearly identified, initialed, dated and reason given?				Reasons: 1)Corrected split peak; 2)Unresolved peak; 3)tailg; 4)RT shift; 5)wrong peak selected; 6)other	
18. Have alternate hits/manual integrations been verified as correct and are correct RFs listed in ICAL summary?					
19. Was ICAL summary form processed using correct methods and files?					
20. Are the ICAL start and end dates/times correct on ICAL summary?					
21. Elution order checked on isomeric pairs? - dichlorodifluoromethane / 1,2-dichlorotetrafluoroethane - trichlorofluoromethane / 1,1,2-trichlorotrifluoroethane - vinyl acetate / hexane - cis- and trans- isomers - ethyl benzene / m/p-xylene / o-xylene 4-ethyl toluene/1,3,5-trimethylbenzene/1,2,4-trimethylbenzene 1,3- , 1,4- , and 1,2-dichlorobenzene					
22. If criteria were not met, was a NCM generated, approved by supervisor, and copy included in folder?					
23. Does the ICAL folder contain complete data in the following order: Data review checklist, a complete runlog, Entech report, BFB info, ICAL summary, curves, followed by [Quan reports, chromatograms, manual integrations] in increasing amount order.					

Analyst:	Date:	2nd Level Reviewer :	Date:
Comments:		Comments:	

STL Knoxville GC/MS Air Continuing Calibration Review / Narrative Checklist
Method: TO-14 and TO-15 - KNOX-MS-0001, Rev 8

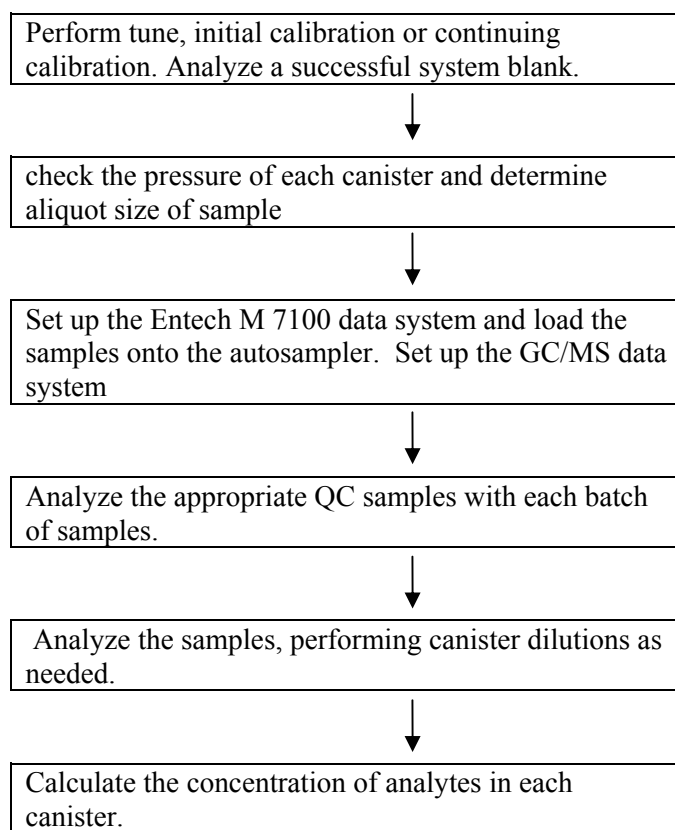
MS017r20.doc, 4/10/06

Figure 2: Example Data Review Checklist (continued)

STL Knoxville GC/MS Air Data Review / Narrative Checklist				LOT/Project # _____	
Method: TO-14 and TO-15 - KNOX-MS-0001, Rev 8				Page 1 of 1	
Instrument:					
Scanned File:					
Review Items					
A. Tune / Continuing Calibration					
	N/A	Yes	No	Why is data reportable?	2nd
1. Were all samples injected within 24 hr of BFB?					
2. Has a Continuing Calibration Checklist been completed for each analytical batch?					
3. Was the correct ICAL used for quantitation?					
B. CLIENT SAMPLE AND QC SAMPLE Results					
	N/A	Yes	No	Why is data reportable?	
1. Were all special project requirements met?					
2. Were dilution factors/can prep information verified?					
3. Have the can number & lab ID been verified between the analysis log & sample prep log?					
4. Were samples received in cans?				☐ [Tedlar1] Samples rec'd on (date) in Tedlar bags & ana by TO-14 (TO-15) within 72 hours from sampling. ☐ [Tedlar2] Samples rec'd on (date) in Tedlar bags & transferred into Summa canisters within 72 hours*.	
5. Sample analyses done within analytical holding time (HT)? If no, list samples: _____				☐ [ht2] Client requested analysis after HT expired. ☐ Other: _____	
6. Are surrogates and internal standards within QC limits? (70-130% R for surr.; 60-140%R from CCAL for IS) If no, list samples/reason (e.g., sur1): Sample Reason Sample Reason _____ _____ _____ _____				☐ [sur1] DUP surr. %R demonstrated same effect. ☐ [sur2] Reanalysis demonstrated same effect. ☐ [sur5] At client's request, data was flagged as estimated & released without further investigation.* ☐ [is1] Per client, reanalysis was not performed * ☐ [is2] Reanalysis confirmed a matrix effect. ☐ Obvious matrix effect	
7. Were positive hits evaluated using qualitative identification criteria and technical judgement?					
8. For dilutions, is highest concentration hit $\geq$ 20% cal range and not above calibration range? List samples and reason (e.g., elev1): Sample Reason Sample Reason _____ _____ _____ _____				☐ [elev1] Elevated RL for (ANALYTE) due to sample matrix interferences. ☐ [elev3] Elevated RLs for all analytes due to difficult sample matrix. ☐ [elev5] Elevated RLs for all analytes due to presence of non-target compounds.	
9. If manual integrations were performed, are they clearly identified, initialed, dated and reason given?				Reasons: 1)Corrected split peak; 2)Unresolved peak; 3)tailing; 4)RT shift; 5)wrong peak selected; 6)other	
10. Have alternate hits/manual integrations been verified as correct?					
11. Final report acceptable? (Results correct, RLs calculated correctly, units correct, surrogate %R correct, appropriate flags used, dilution factor correct, analysis dates correct.)					
12. Was a narrative prepared and all deviations noted?					
13. For NJ samples, analytes $>30\%$ D, $\leq 40\%$ D on CCAL noted in narrative?				☐ [ccal] The calib. verify. exhibited a %D from the ICAL $>30\%$ but $\leq 40\%$ for the following analytes:	
C. Preparation QC					
1. System blank run every 24 hours prior to samples?					
2. System blank surrogate recoveries within QC limits (70-130% R) ?				☐ [mb1] All sample surrogates OK and there is no analyte $>RL$ in samples associated with blank.*	
3. Are all analytes present in the system blank $< RL$? If no, list blank ID: _____				☐ [mb3] No analyte $> RL$ in associated samples.* ☐ [mb4] Sample results $> 20x$ higher than blank.	
4. DUP done per 20 samples and are all RPDs within limits? (for target analytes $>5x$ RL, $\leq 25\%$ RPD; no criteria for methanol and n-butanol) If no, list DUP ID: _____					
D. Other					
1. Are all nonconformances documented appropriately and copy included with deliverable?					
2. Were the standards scanned properly?					
Analyst: _____		Date: _____		2 nd Level Reviewer: _____	
Comments: _____		Date: _____		Comments: _____	

* Such action must be taken in consultation with client.

Figure 3: Flow Chart



Appendix III: Example Instrument parameters

```

                                TOPLEVEL PARAMETERS
                                -----

Method Information For: C:\MSDCHEM\1\METHODS\T014.M

Method Sections To Run:

  ( ) Save Copy of Method With Data
  ( ) Pre-Run Cmd/Macro =
  (X) Data Acquisition
  ( ) Data Analysis
  ( ) Post-Run Cmd/Macro =

Method Comments:
  T014 METHOD USING HP-DB-5 60M X 0.32MM X 1.0 FILM THICKNESS

                                END OF TOPLEVEL PARAMETERS
                                -----


                                INSTRUMENT CONTROL PARAMETERS
                                -----

Sample Inlet:      GC
Injection Source:   Manual
Injection Location: Front
Mass Spectrometer: Enabled

=====
                                HP6890 GC METHOD
=====

OVEN
Initial temp: 35 'C (On)           Maximum temp: 230 'C
Initial time: 5.00 min             Equilibration time: 0.00 min
Ramps:
#   Rate   Final temp   Final time
1   6.00    65          0.00
2  12.00   155          0.00
3  25.00   220          7.00
4   0.0 (Off)
Post temp: 35 'C
Post time: 0.00 min
Run time: 27.10 min

FRONT INLET (UNKNOWN)             BACK INLET ( )
Mode: Split
Initial temp: 200 'C (On)
Pressure: 7.89 psi (On)
Split ratio: 2:1
Split flow: 3.0 mL/min
Total flow: 7.3 mL/min
Gas saver: Off
Gas type: Helium

COLUMN 1                          COLUMN 2
Capillary Column                  (not installed)
Model Number: HP 19091J-216
HP-5 5% Phenyl Methyl Siloxane
Max temperature: 325 'C
Nominal length: 59.0 m
Nominal diameter: 320.00 um
Nominal film thickness: 1.00 um
Mode: constant flow
Initial flow: 1.5 mL/min
Nominal init pressure: 7.90 psi
Average velocity: 31 cm/sec

Method: T014.M                    Wed Apr 30 14:03:13 2003                Page: 1
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```

Inlet: Front Inlet
Outlet: MSD
Outlet pressure: vacuum

FRONT DETECTOR (NO DET)          BACK DETECTOR (NO DET)

SIGNAL 1                         SIGNAL 2
Data rate: 20 Hz                 Data rate: 20 Hz
Type: test plot                  Type: test plot
Save Data: Off                   Save Data: Off
Zero: 0.0 (Off)                  Zero: 0.0 (Off)
Range: 0                          Range: 0
Fast Peaks: Off                  Fast Peaks: Off
Attenuation: 0                   Attenuation: 0

COLUMN COMP 1                    COLUMN COMP 2
(No Detectors Installed)         (No Detectors Installed)

THERMAL AUX 2
Use: MSD Transfer Line Heater
Description:
Initial temp: 150 °C (On)
Initial time: 0.00 min
# Rate Final temp Final time
1 0.0(Off)

POST RUN
Post Time: 0.00 min

TIME TABLE
Time Specifier Parameter & Setpoint

7673 Injector

Front Injector:
Injector not configured, use these parameters if it becomes configured
Sample Washes 2
Sample Pumps 4
Injection Volume 1.0 microliters
Syringe Size 10.0 microliters
PostInj Solvent A Washes 4
PostInj Solvent B Washes 0
Viscosity Delay 0 seconds
Plunger Speed Fast

Back Injector:
No parameters specified

MS ACQUISITION PARAMETERS

General Information
-----
Tune File : bfb.u
Acquisition Mode : Scan

MS Information
-----
Solvent Delay : 3.80 min
EM Absolute : False
EM Offset : 0
Resulting EM Voltage : 1858.8

[Scan Parameters]
Low Mass : 28.5
High Mass : 260.5
Threshold : 200
Sample # : 3 A/D Samples 8
Plot 2 low mass : 28.5
Plot 2 high mass : 260.5

[MSZones]
MS Quad : 105 C maximum 200 C
MS Source : 230 C maximum 250 C

END OF MS ACQUISITION PARAMETERS

PostRun InstCntl macro(s) exist: msacq2.mac

END OF INSTRUMENT CONTROL PARAMETERS

```

Appendix IV: Recommended Calibration levels (normal reporting limit based on 200 mL sample analysis)

Compound	Level, ppb v/v*								
	1	2	3	4	4A	5	6	7	8
Bromochloromethane	10	10	10	10	10	10	10	10	10
1,4-Difluorobenzene	10	10	10	10	10	10	10	10	10
Chlorobenzene-d5	10	10	10	10	10	10	10	10	10
1,2-Dichloroethane-d4	10	10	10	10	10	10	10	10	10
Toluene-d8	10	10	10	10	10	10	10	10	10
4-Bromofluorobenzene	10	10	10	10	10	10	10	10	10
Chlorodifluoromethane	0.1	0.2	0.4	0.8	2.5	5	10	15	30
Dichlorodifluoromethane	0.1	0.2	0.4	0.8	2.5	5	10	15	30
Chloromethane	-	-	0.4	0.8	2.5	5	10	15	30
1,2-Dichlorotetrafluoro-methane	0.1	0.2	0.4	0.8	2.5	5	10	15	30
Vinyl Chloride	0.1	0.2	0.4	0.8	2.5	5	10	15	30
Methanol	-	-	-	3.2	10	20	40	60	120
1,3-Butadiene	0.1	0.2	0.4	0.8	2.5	5	10	15	30
n-Butane	-	0.2	0.4	0.8	2.5	5	10	15	30
Bromomethane	0.1	0.2	0.4	0.8	2.5	5	10	15	30
Chloroethane	0.1	0.2	0.4	0.8	2.5	5	10	15	30
Trichlorofluoromethane	0.1	0.2	0.4	0.8	2.5	5	10	15	30
Acrolein	-	0.4	0.8	1.6	5.0	10	20	30	60
Acetonitrile	-	-	0.8	1.6	5.0	10	20	30	60
Acetone	-	-	-	1.6	5.0	10	20	30	60
Pentane	-	-	0.4	0.8	2.5	5	10	15	30
Ethyl Ether	-	0.4	0.8	1.6	5.0	10	20	30	60
1,1-Dichloroethene	0.1	0.2	0.4	0.8	2.5	5	10	15	30
Acrylonitrile	-	0.4	0.8	1.6	5.0	10	20	30	60
1,1,2-Trichlorotrifluoroethane	0.1	0.2	0.4	0.8	2.5	5	10	15	30
Methylene Chloride	-	-	0.4	0.8	2.5	5	10	15	30
3-chloropropene	0.1	0.2	0.4	0.8	2.5	5	10	15	30
Carbon Disulfide	-	0.2	0.4	0.8	2.5	5	10	15	30
Trans-1,2-Dichloroethene	0.1	0.2	0.4	0.8	2.5	5	10	15	30
Methyl-t-butyl Ether	0.1	0.4	0.8	1.6	5.0	10	20	30	60
1,1-Dichloroethane	0.1	0.2	0.4	0.8	2.5	5	10	15	30
Vinyl Acetate	-	0.4	0.8	1.6	5.0	10	20	30	60
2-Butanone	-	-	0.8	1.6	5.0	10	20	30	60
Hexane	0.1	0.2	0.4	0.8	2.5	5	10	15	30
cis-1,2-Dichloroethene	0.1	0.2	0.4	0.8	2.5	5	10	15	30
Chloroform	0.1	0.2	0.4	0.8	2.5	5	10	15	30
1,1,1-Trichloroethane	0.1	0.2	0.4	0.8	2.5	5	10	15	30
1,2-Dichloroethane	0.1	0.2	0.4	0.8	2.5	5	10	15	30
Benzene	0.1	0.2	0.4	0.8	2.5	5	10	15	30
1-Butanol	-	0.4	0.8	1.6	5.0	10	20	30	60
Cyclohexane	-	0.2	0.4	0.8	2.5	5	10	15	30
Carbon Tetrachloride	0.1	0.2	0.4	0.8	2.5	5	10	15	30
Heptane	0.1	0.2	0.4	0.8	2.5	5	10	15	30
1,2-Dichloropropane	0.1	0.2	0.4	0.8	2.5	5	10	15	30

Appendix IV: Recommended Calibration levels (normal reporting limit based on 200 mL sample analysis), continued

Compound	Level, ppb v/v*								
	1	2	3	4	4A	5	6	7	8
Trichloroethene	0.1	0.2	0.4	0.8	2.5	5	10	15	30
Dibromomethane	0.1	0.2	0.4	0.8	2.5	5	10	15	30
Bromodichloromethane	0.1	0.2	0.4	0.8	2.5	5	10	15	30
4-Methyl-2-Pentanone	-	0.4	0.8	1.6	5.0	10	20	30	60
cis-1,3-Dichloropropene	0.1	0.2	0.4	0.8	2.5	5	10	15	30
trans-1,3-Dichloropropene	0.1	0.2	0.4	0.8	2.5	5	10	15	30
Toluene	0.1	0.2	0.4	0.8	2.5	5	10	15	30
1,1,2-Trichloroethane	0.1	0.2	0.4	0.8	2.5	5	10	15	30
2-Hexanone	-	0.4	0.8	1.6	5.0	10	20	30	60
Octane	-	0.2	0.4	0.8	2.5	5	10	15	30
Dibromochloromethane	0.1	0.2	0.4	0.8	2.5	5	10	15	30
1,2-Dibromoethane	0.1	0.2	0.4	0.8	2.5	5	10	15	30
Tetrachloroethene	0.1	0.2	0.4	0.8	2.5	5	10	15	30
Chlorobenzene	0.1	0.2	0.4	0.8	2.5	5	10	15	30
Ethylbenzene	0.1	0.2	0.4	0.8	2.5	5	10	15	30
m/p-Xylene	0.1	0.2	0.4	0.8	2.5	5	10	15	30
Bromoform	0.1	0.2	0.4	0.8	2.5	5	10	15	30
Nonane	0.1	0.2	0.4	0.8	2.5	5	10	15	30
Styrene	0.1	0.2	0.4	0.8	2.5	5	10	15	30
o-Xylene	0.1	0.2	0.4	0.8	2.5	5	10	15	30
1,1,2,2-Tetrachloroethane	0.1	0.2	0.4	0.8	2.5	5	10	15	30
1,2,3-Trichloropropane	-	-	0.4	0.8	2.5	5	10	15	30
Cumene	0.1	0.2	0.4	0.8	2.5	5	10	15	30
n-Propylbenzene	0.1	0.2	0.4	0.8	2.5	5	10	15	30
4-Ethyltoluene	0.1	0.2	0.4	0.8	2.5	5	10	15	30
1,3,5-Trimethylbenzene	0.1	0.2	0.4	0.8	2.5	5	10	15	30
Alpha-Methylstyrene	-	0.2	0.4	0.8	2.5	5	10	15	30
Decane	-	0.2	0.4	0.8	2.5	5	10	15	30
1,2,4-Trimethylbenzene	-	0.2	0.4	0.8	2.5	5	10	15	30
1,3-Dichlorobenzene	-	0.2	0.4	0.8	2.5	5	10	15	30
Benzyl Chloride	-	0.2	0.4	0.8	2.5	5	10	15	30
1,4-Dichlorobenzene	-	0.2	0.4	0.8	2.5	5	10	15	30
1,2-Dichlorobenzene	-	0.2	0.4	0.8	2.5	5	10	15	30
Undecane	-	0.2	0.4	0.8	2.5	5	10	15	30
Dodecane	-	0.2	0.4	0.8	2.5	5	10	15	30
1,2,4-Trichlorobenzene	-	0.2	0.4	0.8	2.5	5	10	15	30
Naphthalene	-	0.2	0.4	0.8	2.5	5	10	15	30
Hexachlorobutadiene	-	0.2	0.4	0.8	2.5	5	10	15	30
Sec-butylbenzene	-	0.2	0.4	0.8	2.5	5	10	15	30
n-Butylbenzene	-	0.2	0.4	0.8	2.5	5	10	15	30
Vinyl Bromide	-	0.2	0.4	0.8	2.5	5	10	15	30
Tert-Butanol	-	0.4	0.8	1.6	5.0	10	20	30	60
2,2,4-Trimethylpentane	-	0.2	0.4	0.8	2.5	5	10	15	30
2-Chlorotoluene	-	0.2	0.4	0.8	2.5	5	10	15	30

* See section 10.3.11.

Appendix V: Recommended Low Level Calibration levels (normal reporting limit based on 500 mL sample analysis)

Compound	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6	Level 7
For compounds listed in Tables 1, 2, and 3 that are noted for Low Level analysis	0.010	0.020	0.040	0.100	0.200	0.500	1.0

STL KNOXVILLE
ATTACHMENT TO SOP KNOX-MS-0001
TITLE: PROJECT SPECIFIC ANALYTE LIST FOR GIVAUDAN
(SUPERSEDES: NONE)

Prepared By: _____

Reviewed By: _____
Technical Specialist

Approved By: _____
Quality Assurance Manager

Approved By: _____
Environmental, Health and Safety Coordinator

Approved By: _____
Laboratory Director

The following additional analytes will be target analytes for the Givaudan project.

CAS NUMBER	COMPOUNDS	REPORTING LIMITS (ppb, v/v)	MOLECULAR WEIGHT (ng/n mole)	SUGGESTED ION
79-29-8	2,3-Dimethyl butane	0.2	86.18	43
80-56-8	a-Pinene	0.2	136.2	93
79-92-5	Camphene	0.2	136.2	93
127-91-3	b-Pinene	0.2	136.2	93
5989-27-5	d-Limonene	0.2	136.2	68
99-87-6	p-Cymene	0.2	134.2	119
98-51-1	4-tert-Butyltoluene	0.2	148.2	133
464-49-3	Camphor*	5.0	152.2	95

* The initial demonstration of capability indicated poor precision for this analyte by this method as evidenced by the variable recovery of this compound. Any reported values for this analyte should be considered estimated.

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Implementation Date: 12/16/04

SOP No. CORP-IP-0003NC

Revision No. 1.5

Revision Date: 12/07/04

Page 1 of 38

STL STANDARD OPERATING PROCEDURE

TITLE: ACID DIGESTION OF AQUEOUS SAMPLES BY SW846 AND MCAWW 200 SERIES METHODS

(Supersedes: Revision 1.4, Dated 02/19/03)

Prepared by:	<u>Larry R. Williams</u>	<u>12.9.04</u>
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1. SCOPE AND APPLICATION

- 1.1. This procedure describes the preparation of aqueous samples for the analysis of certain metals by Graphite Furnace Atomic Absorption (GFAA), Flame Atomic Absorption (FLAA), Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP), and Inductively Coupled Plasma-Mass Spectrometry (ICP/MS) using the MCAWW 200 series methods (NPDES) and SW846 Methods 3005A, 3010A, 3020A and 7060A/7740 (RCRA).
- 1.2. The applicability of each of these preparation protocols to specific analytes is detailed in Tables I and II (Appendix A) and the applicable determinative methods are illustrated by Figures 6 and 7 (Section 17). Additional elements may be analyzed following digestion by these protocols provided that the method performance criteria specified in Section 13.0 of this SOP are met.
- 1.3. This SOP provides procedures applicable to the preparation of dissolved, suspended, total recoverable and total elements in ground water, aqueous samples, certain aqueous sludges, wastes, and biological tissues, and leachates/extracts.
- 1.4. SW-846 Method 3005A is used to prepare surface and groundwater samples for total recoverable and dissolved metals determination by FLAA, ICP and GFAA (antimony only).
- 1.5. MCAWW Method 200.7 Section 9.4 is used to prepare surface water, domestic and industrial waste samples for total recoverable and dissolved metals determination by ICP.
- 1.6. SW-846 Method 3010A is used to prepare aqueous samples, EP and mobility-procedure extracts, and wastes that contain suspended solids for total metals analysis by FLAA or ICP.
- 1.7. MCAWW Method 200.7 Section 9.3 is used to prepare surface water and wastes that contain suspended solids for total metals analysis by ICP.
- 1.8. MCAWW Methods 206.2 and 270.2, respectively, contain the procedure for the preparation of aqueous samples for arsenic and selenium.
- 1.9. 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 do require digestion of dissolved samples and this must be clarified before project initiation.

2. SUMMARY OF METHOD

2.1. Method 3005A / Method 200.7 Section 9.4 - Preparation for Total Recoverable or Dissolved Metals Analysis by FLAA or ICP Spectroscopy

2.1.1. A representative aliquot of sample is heated with nitric and hydrochloric acids and substantially reduced in volume. The digestate is filtered (if necessary) and diluted to volume.

2.2. Method 3010A / Method 200.7 Section 9.3 - Preparation for Total Metals Analysis by FLAA or ICP Spectroscopy

2.2.1. A representative aliquot of sample is refluxed with nitric acid. After the digestate has been reduced to a low volume, it is refluxed with hydrochloric acid, filtered (if necessary) and brought up to volume.

2.3. Method 200.0 Section 4.1.4 - Total Recoverable GFAA Preparation (NPDES)

A representative aliquot of sample is heated with nitric acid and until the digestate has been reduced to a low volume. The sample is cooled, filtered (if necessary) and brought up to volume.

3. DEFINITIONS

Additional definitions of terms used in this SOP may be found in the glossary of the LQM.

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.

3.4. Total Recoverable Metals: The concentration determined on an unfiltered sample following treatment with hot, dilute mineral acid.

4. INTERFERENCES

- 4.1. There are numerous routes by which samples may become contaminated. Potential sources of trace metals contamination include: metallic or metal-containing labware (e.g., talc gloves which contain high levels of zinc), containers, impure reagents, dirty glassware, improper sample transfers, dirty work areas, atmospheric inputs such as dirt and dust, etc. Be aware of potential sources of contamination and take appropriate measures to minimize or avoid them.
- 4.2. The entire work area, including the bench top and fume hood, should be thoroughly cleaned on a routine schedule in order to minimize the potential for environmental contamination. Refer to Appendix B for additional contamination control guidelines.
- 4.3. Boron and silica from the glassware will migrate into the sample solution during and following sample processing. For critical low level determinations of boron and silica, only quartz and/or plastic labware should be used.
- 4.4. Physical interference effects may contribute to inaccuracies in the determinations of trace elements. Oils, solvents and other matrices may not be digested using these methods if they are not soluble with acids. If physical interferences are present, they should be documented.
- 4.5. Visual interferences or anomalies (such as foaming, emulsions, precipitates, etc.) must be documented.
- 4.6. Allowing samples to boil or go dry during digestion may result in the loss of volatile metals. If this occurs the sample must be reprepared. Antimony is easily lost by volatilization from hydrochloric acid media.
- 4.7. Precipitation of silver chloride (AgCl) may occur when chloride ions and high concentrations of silver (i.e., greater than 1 mg/L) are present in the sample.
- 4.8. Specific analytical interferences are discussed in each of the determinative methods.

5. SAFETY

- 5.1. Employees must abide by the policies and procedures in the Corporate Safety and this document.

- 5.2. Samples that contain high concentrations of carbonates or organic material or samples that are at elevated pH can react violently when acids are added.
- 5.3. The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Hydrochloric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Hydrogen Peroxide	Oxidizer Corrosive	1 ppm-TWA	Vapors are corrosive and irritating to the respiratory tract. Vapors are very corrosive and irritating to the eyes and skin.
Nitric Acid	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.

1 – Always add acid to water to prevent violent reactions.

2 – Exposure limit refers to the OSHA regulatory exposure limit.

- 5.4. Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Cut resistant gloves must be worn doing any other task that presents a strong possibility of getting cut. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.
- 5.5. The acidification of samples containing reactive materials may result in the release of toxic gases, such as cyanides or sulfides. Acidification of samples should be done in a fume hood. The analyst should also be aware of the potential for a vigorous reaction.
- 5.6. 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. All samples with pink stickers that read "Caution/Use Hood!" **must** be opened in the hood. Contact the EH&S Coordinator if this is not possible. Solvent and waste containers will be kept closed unless transfers are being made.
- 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 the EH&S Coordinator and the Laboratory Supervisor.
- 5.8. Always carry bulk concentrated acid bottles in appropriate impact proof containers.
- 5.9. Acid/peroxide spills must be neutralized immediately, flushed with water and cleaned up using appropriate spill kits.
- 5.10. Discard chipped or broken beakers to prevent injury. Chipped glassware may be fire polished as an alternative to disposal.
- 6. **EQUIPMENT AND SUPPLIES**
 - 6.1. Hot plate, digestion block or other adjustable heating source capable of maintaining a temperature of 95°C ($\pm$ 4).
 - 6.2. Calibrated thermometer that covers a temperature range of 0-200°C.

- 6.3. Griffin beakers of assorted sizes or equivalent.
- 6.4. Watch glasses, ribbed or equivalent.
- 6.5. Whatman No. 4 filter paper or equivalent.
- 6.6. Funnels or equivalent filtration apparatus.
- 6.7. Centrifugation equipment (if desired method of removing particulates is centrifugation).
- 6.8. Graduated cylinder or equivalent capable of measuring 50 mL within 3% accuracy.
- 6.9. Analytical balance capable of accurately weighing to the nearest 0.01 grams.
- 6.10. Repipetors or suitable reagent dispensers.
- 6.11. Calibrated automatic pipettes with corresponding pipette tips or Class A glass volumetric pipettes.
- 6.12. Class A volumetric flasks.
- 6.13. pH indicator strips (pH range 0 - 6).
- 6.14. Plastic digestate storage bottles.

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 as defined in the determinative SOPs.
- 7.2. Laboratory Control Sample (LCS) and matrix spike (MS) solutions 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. Working ICP LCS/MS spike solution: Prepare the ICP LCS/MS working spike solution from custom stock standards to the final concentration listed in Table III. The working

spike must be prepared in a matrix of 5% HNO₃. This acid (5 mL of concentrated HNO₃ per 100 mL) must be added to the volumetric flask before the addition of the stock standard aliquot. The working ICP LCS solution must be made fresh every three months.

- 7.4. Working GFAA LCS/MS spike solution: Prepare the GFAA working LCS spike solution by diluting the custom stock solution (7.2) 200x. The working spike solution must be prepared in a matrix of 5% HNO₃. This acid (5 mL of concentrated HNO₃ per 100 mL) must be added to the volumetric flask before the addition of the stock standard aliquot. The working GFAA LCS solution must be made fresh every three months.
- 7.5. The TCLP MS working spike solution is provided directly by the vendor, no further standard preparation is necessary.
- 7.6. The LCS and MS samples must contain all the elements designated for analysis in each batch of samples. If a non-routine element is required that is not contained in the custom STL solution, the individual facility must purchase a solution from the designated vendor that will cover the additional analyte(s) of interest and provide for a final spike concentration that is appropriate to the determinative method.
- 7.7. Aqueous laboratory control samples (LCSW) and matrix spike samples are prepared as described in Sections 9.5 and 9.6. Refer to Tables III and IV(Appendix A) for details regarding the stock, working standard and final digestate spike concentrations for ICP and GFAA LCS and matrix spike preparations.
- 7.8. Nitric acid (HNO₃), concentrated, trace metal grade or better.
- 7.9. Nitric acid, 1:1 - dilute concentrated HNO₃ with an equal volume of reagent water.
- Note:** When preparing diluted acids always add acid to water. If the water is added to the acid a violent reaction may occur.
- 7.10. Hydrochloric acid (HCl), concentrated, trace metal grade or better.
- 7.11. Hydrochloric acid, 1:1 - dilute concentrated HCl with an equal volume of reagent water.
- Note:** When preparing diluted acids always add acid to water. If the water is added to the acid a violent reaction may occur.
- 7.12. 30% Hydrogen peroxide (H₂O₂), reagent grade.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

- 8.1. Sample holding time for metals included under the scope of this SOP is 180 days from the date of collection to the date 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.
- 8.3. For dissolved metals analysis, the samples should be filtered through a 0.45 um filter prior to preservation. Filtration must be done in the field or within 24 hours of collection.

Note: If a sample being analyzed for dissolved metals is found to contain sediment the analyst should contact their supervisor or group leader. The client should be notified of the problem to decide how to treat the sample.

9. QUALITY CONTROL

Table VI (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 any method contained within this SOP 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. MDL's 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 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, which should contain all the analytes of interest. The results of the initial demonstration study must be acceptable before analysis of samples may begin. The results of the initial demonstration study may be used to

extend a method for the analysis of other elements provided all acceptance criteria are met.

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.

9.1.2.2. Calculations and acceptance criteria for QC check samples are given in the determinative SOPs (CORP-MT-0001, CORP-MT-0003).

- 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. Criteria for the acceptance of blanks are contained within the individual analytical method SOP's. If the method blank does not meet the criteria contained within the analytical method SOPs; the blank and all associated samples in the batch must be redigested.
- 9.4.1. Aqueous method blanks are prepared by taking 50 mL or 50 g of reagent water through the appropriate procedure as described in Section 11.
- 9.4.2. TCLP method blanks are prepared by taking 50 mL or 50 g of leachate fluid through the appropriate procedure as described in Section 11.
- 9.5. 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. 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. Criteria for the acceptance of LCS results are contained within the individual analytical method SOP's. Corrective action when LCS results fail to meet control limits will be reparation and reanalysis of the batch. Refer to Section 7.3 and 7.4 for instructions on preparation of the aqueous LCS spike solution.

9.5.1. The aqueous LCS is prepared by spiking a 50 mL aliquot of reagent water with 1.0 mL of the working LCS/MS spike solution (7.3 or 7.4). The LCS is then processed through the appropriate procedure as described in Section 11.

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. Samples identified as field blanks cannot be used for MS/MSD analysis. If any analyte recovery or RPD falls outside the acceptance range, the recovery of that analyte must be in control for the LCS. If the recovery of the LCS is outside limits, corrective action must be taken. Corrective action will include reparation and reanalysis of the batch. Corrective action when MS results fail to meet control limits does not include reparation of samples unless the results indicate that a spiking error may have occurred.

9.6.1. The aqueous matrix spike sample is prepared by spiking a 50 mL aliquot of a sample with 1.0 mL of the working LCS/MS spike solution (7.3 or 7.4). The matrix spike sample is then processed as described in Section 11.

9.6.2. The TCLP matrix spike sample is prepared by spiking a 50 mL aliquot of a leachate with 0.5 mL of the working TCLP spike solution (7.5). The matrix spike sample is then processed as described in Section 11.

NOTE: The TCLP matrix spike must be added prior to preservation of the leachate.

9.6.3. If insufficient sample is available to process a MS/MSD, then a second LCS must be processed. The LCS pair is then evaluated according to the MS/MSD criteria.

- 9.7. Quality Assurance Summaries - Certain clients may require specific project or program QC that may supersede the SOP requirements. Quality Assurance Summaries (QAS) should be developed to address these requirements.

10. **CALIBRATION AND STANDARDIZATION**

- 10.1 Hotplate temperature must be verified daily for each hotplate used and must be recorded on either the metals preparation log or in a hotplate temperature logbook. The hotplate temperature should be verified by measuring the temperature of a beaker of reagent water placed on each hotplate.

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. All digestion procedures must be carried out in a properly functioning hood.
- 11.4. All samples are to be checked out of sample control with the chain of custody documentation filled out completely.
- 11.5. Proper sample identification is extremely important in any preparation procedure. Labeling of beakers and bottles must be done in a manner to ensure connection with the proper sample.
- 11.6. Samples are typically logged in as either waters or soils. Wastes such as organic liquids or sludges and tissues (animal/vegetable) are usually logged in with solid test codes. When initiating prep, examine the sample to see if the sample matches the matrix designation. If the sample is logged in as aqueous but it appears more like a waste (biphasic, sludge like, organic liquid, lots of sediment etc.) contact the lab supervisor or project manager for further instructions. In some cases it may be more appropriate to process these samples as solids.

- 11.7. If possible prepare all the samples of a project at the same time to minimize the QC required and streamline the flow of the project through the lab and reporting group.
- 11.8. In most cases, both AA and ICP digests are required on each sample. It is recommended that both aliquots be measured out and processed at the same time.
- 11.9. Guidelines are provided in the appendices on procedures to minimize contamination of samples and standards.
- 11.10. The following procedure must be followed for all aqueous sample preparations:
 - 11.10.1. Measure sample pH with pH paper on a separate aliquot of sample.

Note: If the sample pH is > 2 pH units, the client must be notified of the anomaly.

Note: If sample pH has already been verified and documented in sample receipt this step may be omitted.
 - 11.10.2. Mix sample by shaking the container.
 - 11.10.3. Measure and transfer 50 mL or 50 g of the sample into a beaker.

Note: This SOP allows for samples to be weighed instead of measured volumetrically.
 - 11.10.4. Measure two extra aliquots of sample selected for the MS/MSD analysis. Spike each aliquot with the appropriate spiking solutions (7.3-7.5,9.6).
 - 11.10.5. Measure and transfer 50 mL of reagent water into a beaker for the method blank.
 - 11.10.6. Measure and transfer 50 mL of reagent water into a beaker for the LCS and add the appropriate spiking solutions (7.3-7.5,9.6).

11.11. Proceed to the appropriate Section for the desired method as follows:

Method 3005A or Method 200.7 Section 9.4	11.12
Method 3010A or Method 200.7 Section 9.3	11.13
Method 3020A or Method 200.0 Section 4.1.3	11.14
Method 7060A/7740 or Method 206.2/270.2	11.15
Method 200.0 Section 4.1.4	11.16

11.12. **Method 3005A / Method 200.7 Section 9.4 - Preparation for Total Recoverable or Dissolved Metals Analysis by FLAA or ICP (See Figures 1, 6 and 7)**

11.12.1. To the sample beaker, add 1 mL of concentrated HNO₃ and 2.5 mL of concentrated HCl.

11.12.2. Cover with ribbed watch glass.

11.12.3. Heat at 95°C (± 4) until volume is reduced to between 15 and 20 mL.

NOTE: DO NOT ALLOW SAMPLE TO BOIL OR GO DRY. Doing so will result in the loss of analyte and the sample must be reprepared.

11.12.4. Cool the beaker in a fume hood.

11.12.5. Wash down beaker walls and watch glass with reagent water.

11.12.6. Filter sample, if insoluble materials are present, through Whatman 4 filter paper that has been pre-rinsed with dilute nitric acid.

Note: If any samples in a preparation batch are filtered, the method blank and LCS associated with that batch must also be filtered.

Note: In place of filtering, the samples, after dilution and mixing, may be centrifuged or allowed to settle by gravity overnight to remove insoluble material.

- 11.12.7. Rinse beaker and filter paper with reagent water to ensure complete sample transfer.
- 11.12.8. Adjust the final volume/mass to 50 mL or 50 g with reagent water. The sample is now ready for analysis

11.13. Method 3010A / Method 200.7 Section 9.3 - Preparation for Total Metals Analysis by FLAA or ICP Spectroscopy (See Figures 2, 6 and 7)

- 11.13.1. To the sample beaker, add 3.0mL of concentrated HNO₃.
- 11.13.2. Cover with ribbed watch glass.
- 11.13.3. Place beaker on hotplate 95°C (± 4) and evaporate for 4-5 hours or to low volume of 15-20 mL while ensuring that no portion of the bottom of the beaker is allowed to go dry.

NOTE: DO NOT ALLOW SAMPLE TO BOIL OR GO DRY. Doing so will result in the loss of analyte and the sample must be reprepared.

- 11.13.4. If necessary, add another 1.5 ml portion of concentrated HNO₃ and re-cover the beaker. Reflux 15 minutes.
- 11.13.5. Add 5 mL of 1:1 HCl.
- 11.13.6. Cover and reflux for an additional 15 minutes to dissolve precipitate or residue. Cool in a fume hood.
- 11.13.7. Wash down beaker walls and watch glass with reagent water.
- 11.13.8. Filter sample, if insoluble materials are present, through Whatman 4 filter paper.

Note: If any samples in the QC batch are filtered the method blank and LCS associated with that batch must also be filtered.

Note: In place of filtering, the samples, after dilution and mixing, may be centrifuged or allowed to settle by gravity overnight to remove insoluble material.

11.13.9. Rinse beaker and filter paper with reagent water to ensure complete sample transfer.

11.13.10. Adjust final volume/mass to 50 mL or 50 g with reagent water. The sample is now ready for analysis.

11.14. Method 3020A / Method 200.0 Section 4.1.3 - Preparation for Total Metals Analysis by GFAA or Total Recoverable Metals by ICPMS (See Figures 3, 6 and 7)

11.14.1. To the sample beaker, add 1.5 mL of concentrated HNO₃.

11.14.2. Cover with ribbed watch glass.

11.14.3. Place beaker on hotplate 95°C (± 4) and evaporate to low volume of 15-20 mL while ensuring that no portion of the bottom of the beaker is allowed to go dry.

NOTE: DO NOT ALLOW SAMPLE TO BOIL OR GO DRY. Doing so will result in the loss of analyte and the sample must be reprepared.

11.14.4. If necessary, add another 1.5 mL portion of concentrated HNO₃. Recover, and reflux 15 minutes. Cool the beaker in a fume hood.

11.14.5. Filter sample, if insoluble materials are present, through Whatman 4 filter paper.

Note: If any samples in the QC batch are filtered the method blank and LCS associated with that batch must also be filtered.

Note: In place of filtering, the samples, after dilution and mixing, may be centrifuged or allowed to settle by gravity overnight to remove insoluble material.

11.14.6. Rinse beaker and filter paper with reagent water to ensure complete sample transfer.

11.14.7. Adjust final volume to 50 mL with reagent water. The sample is now ready for analysis.

11.15. Method 7060A/7740 and Method 206.2/270.2 - Preparation for Arsenic and Selenium Analysis by GFAA (See Figures 4, 6 and 7)

- 11.15.1. To the sample beaker, add 1 mL of 30 % H₂O₂ and 1.0 mL of 1:1 HNO₃.
- 11.15.2. Heat, until the digestion is complete, at 95°C (± 4) or until the volume has been reduced to 15-20 mL.
- 11.15.3. Cool beaker.
- 11.15.4. Filter sample, if insoluble materials are present, through Whatman 4 filter paper that has been pre-rinsed with dilute nitric acid.

Note: If any samples in the QC batch are filtered the method blank and LCS associated with that batch must also be filtered.

Note: In place of filtering, the samples, after dilution and mixing, may be centrifuged or allowed to settle by gravity overnight to remove insoluble material.

- 11.15.5. Rinse beaker and filter paper with reagent water to ensure complete sample transfer.
- 11.15.6. Adjust final volume to 50 mL with reagent water. The sample is now ready for analysis.

**11.16. Method 200.0 Section 4.1.4 - Preparation for Total Recoverable GFAA Analyses.
(See Figures 5 and 7)**

- 11.16.1. To the sample beaker, add 1.0 mL of 1:1 HNO₃.
- 11.16.2. Heat, until the digestion is complete, at 95°C (± 4) or until the volume has been reduced to 15 - 20 mL.
- 11.16.3. Cool beaker.
- 11.16.4. Filter sample, if insoluble materials are present, though Whatman 4 filter paper.

Note: If any samples in the QC batch are filtered the method blank and LCS associated with that batch must also be filtered.

Note: In place of filtering, the samples, after dilution and mixing, may be centrifuged or allowed to settle by gravity overnight to remove insoluble material.

11.16.5. Rinse beaker and filter paper with reagent water to ensure complete sample transfer.

11.16.6. Adjust final volume to 50 mL with reagent water. The sample is now ready for analysis.

12. DATA ANALYSIS AND CALCULATIONS

Not Applicable.

13. METHOD PERFORMANCE

13.1. Method performance is determined by the analysis of matrix spike and matrix spike duplicate samples as well as method blanks and laboratory control samples. In general, the matrix spike recovery should fall within +/- 20 % and the matrix spike duplicates should compare within 20% RPD. Method blanks must meet the criteria specified in determinative SOPs. The laboratory control samples should recover within 20% of the true value until in house control limits are established. Acceptance criteria are given in the determinative SOPs.

13.2. The initial demonstration study as detailed in Section 9.1.2 must be acceptable before the analysis of field samples under this SOP may begin. The results of the initial demonstration study may be used to extend a method for the analysis of other elements provided all acceptance criteria are met.

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. All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the

policies in section 13 of the Corporate Safety Manual for “Waste Management and Pollution Prevention.”

15.2. Waste Streams Produced by the Method

15.2.1. The following waste streams are produced when this method is carried out.

15.2.1.1. Acidic waste containing nitric acid generated by the extraction. This waste is disposed of in the designated container labeled “Acid Waste”.

15.2.1.2. Contaminated disposable materials utilized for the analysis. This waste is disposed of in a designated container identified as “Solid Waste”.

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. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition, Final Update I, Revision 1, July 1992. Methods 3005A, 3010A, 3020A, 7060A and 7740A.

16.1.2. Methods for the Chemical Analysis of Water and Waste (MCAWW), 1983.

16.1.3. CORP-MT-0001, Inductively Coupled Plasma-Atomic Emission Spectroscopy, Spectrometric Method for Trace Element Analysis of Water and Wastes, Method 6010A and Method 200.7.

16.1.4. CORP-MT-0003, Graphite Furnace Atomic Absorption Spectroscopy, SW846 Method 7000A and MCAWW 200 Series Methods.

16.1.5. Corporate Quality Management Plan (QMP), current version.

16.1.6. STL Laboratory Quality Manual (LQM), current version.

16.1.7. STL Corporate Safety Manual, M-E-0001 and STL North Canton Facility Addendum and Contingency Plan, current version.

16.2. Associated SOPs and Policies, latest version

16.2.1. QA-003, STL QC Program.

16.2.2. QA-004, Rounding and Significant Figures.

16.2.3. Glassware Washing, NC-QA-0014

16.2.4. Statistical Evaluation of Data and Development of Control Charts, NC-QA-0018

16.2.5. Method Detection Limits and Instrument Detection Limits, S-Q-003 and NC-QA-0021

16.2.6. Navy/Army SOP, NC-QA-0016

17. MISCELLANEOUS (TABLES, APPENDICES, ETC. . .)

17.1. Modifications/Interpretations from reference methods.

17.1.1. Modifications applicable to SW-846 reference methods.

17.1.1.1. 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.

17.1.1.2. The referenced methods as well as Table 3-1 of SW-846 refer to the use of a 100 mL aliquot for digestion. This SOP requires the use of a 50 mL sample size to reduce waste generation. The use of reduced sample volumes are supported in EPA's document "Response to Public Comments Background Document, Promulgation of the Second Update to SW-846, Third Edition" dated November 3, 1994. This document stated "flexibility to alter digestion volumes is addressed and "allowed" by the table (3-1) and is also inherently allowed by specific digestion methods. Table 3-1 is only to be used as guidance when collecting samples..." EMSL-Ci has also taken the stance that "reduction in

sample size and appropriate corresponding reduction in sample volume is not considered a significant change in the methodology.” Additionally, in written correspondence from the Office of Solid Waste, Olliver Fordham stated “ As a “representative sample” can be assured, scaling causes no loss of precision and accuracy in the analysis.”

17.1.2. Modifications Specific to Method 3010A

17.1.2.1. Section 11.13.7 of this SOP requires the sample be reduced to a volume of 15 - 20 mL. Section 7.2 of Method 3010A states the volume should be reduced to 3 mL but also states that no portion of the bottom of the beaker should go dry. The SOP required volume is a closer approximation of the volume required to provide an adequate covering of the beaker so as to prevent the loss of critical analytes through volatilization.

17.1.2.2. The scope of 3010A has been expanded to include silver based on comparison studies with 7760A. Method 3010A consistently demonstrated improved accuracy and precision over Method 7760A in the matrices tested (reagent water, surface water and TCLP leachate) up to a concentration of 1 ppm silver.

17.1.3. Modifications Specific to Method 3020A

17.1.3.1. Section 11.14.3 of this SOP requires the sample be reduced to a volume of 15 - 20 mL. Section 7.2 of Method 3010A states the volume should be reduced to 3 mL but also states that no portion of the bottom of the beaker should go dry. The SOP required volume is a closer approximation of the volume required to provide an adequate covering of the beaker so as to prevent the loss of critical analytes through volatilization.

17.1.4. Modifications Specific to Method 7060A/7740

17.1.4.1. Methods 7060A and 7740A incorporate the use of a two step dilution to accommodate the addition of a nickel nitrate modifier. This SOP performs the dilution directly in one step and omits the addition of the modifier. The modifier is added automatically at the instrument by direct injection into the furnace.

17.1.5. Modifications Specific to MCAWW Methods

It was determined by technical review that several of the MCAWW methods were equivalent to the SW-846 methods and therefore were combined under the scope of this SOP as described in Section 11.0. The nature of the differences were deemed insignificant in regards to the amount of acid added and the evaporative volume based on the flexibility allowed by the methods (i.e., add additional acid as required) and the subjective wording of the methods (i.e., evaporate to near dryness vs. an exact volume).

17.2. Modifications from previous SOP

17.2.1. Added ICP/MS to the digestion procedures.

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 preparation benchsheet should, at a minimum, include the following information:

- Preparation date, analyst name, matrix, prep type (ICP or GFAA), SOP reference.
- Sample ID; initial weight/volume and final weight/volume.
- Standards Documentation (source, lot, prep date, volume added).
- Analyst Signature.
- Reviewer's Signature and date.

Figure 1. Method 3005A / Method 200.7 Section 9.4 (Section 11.12)

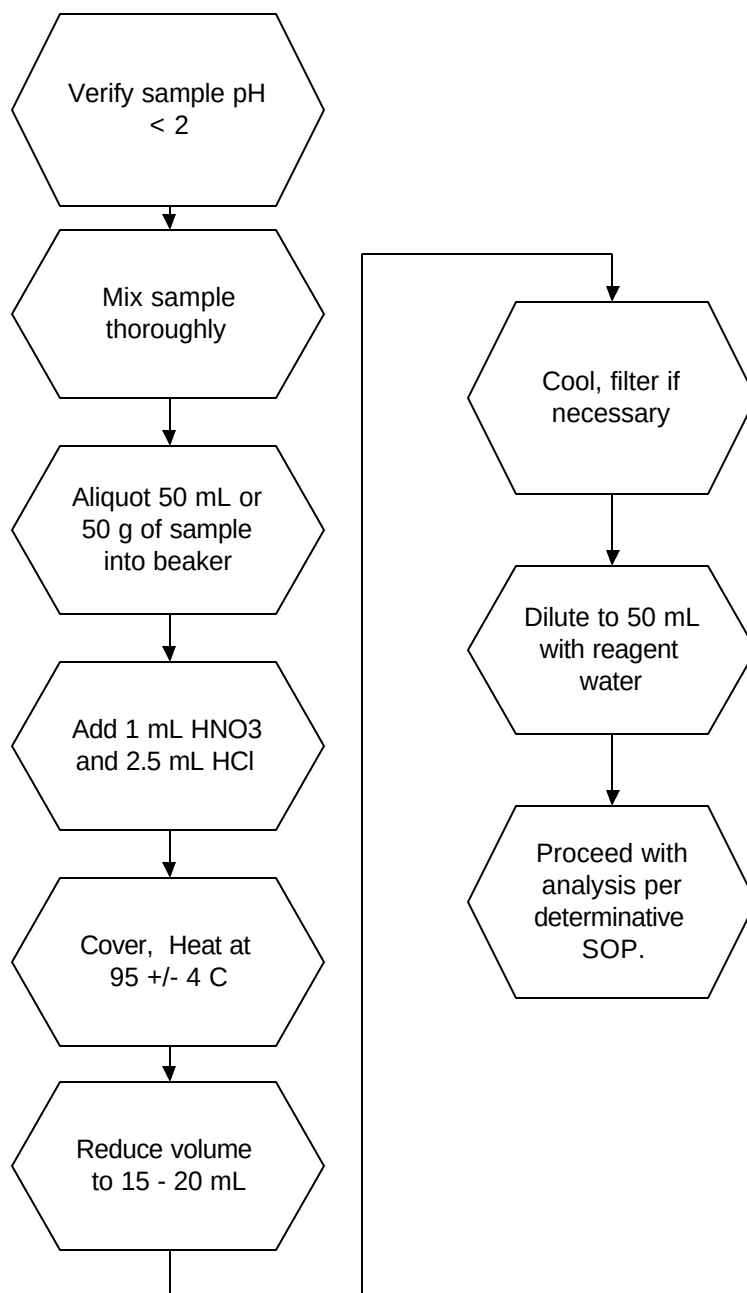


Figure 2. Method 3010A / Method 200.7 Section 9.3 (Section 11.13)

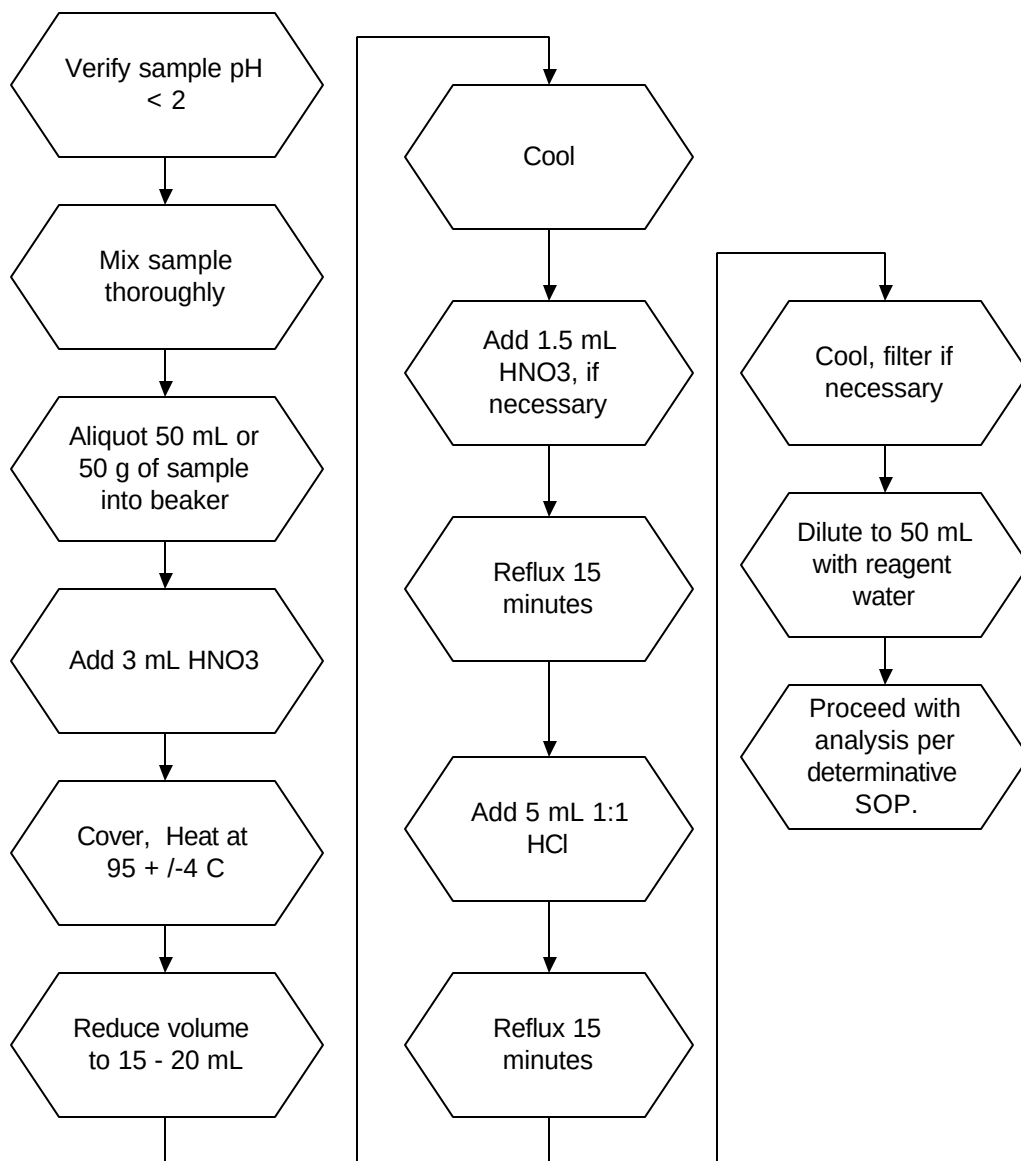


Figure 3. Method 3020A / Method 200.0 Section 4.1.3 (Section 11.14)

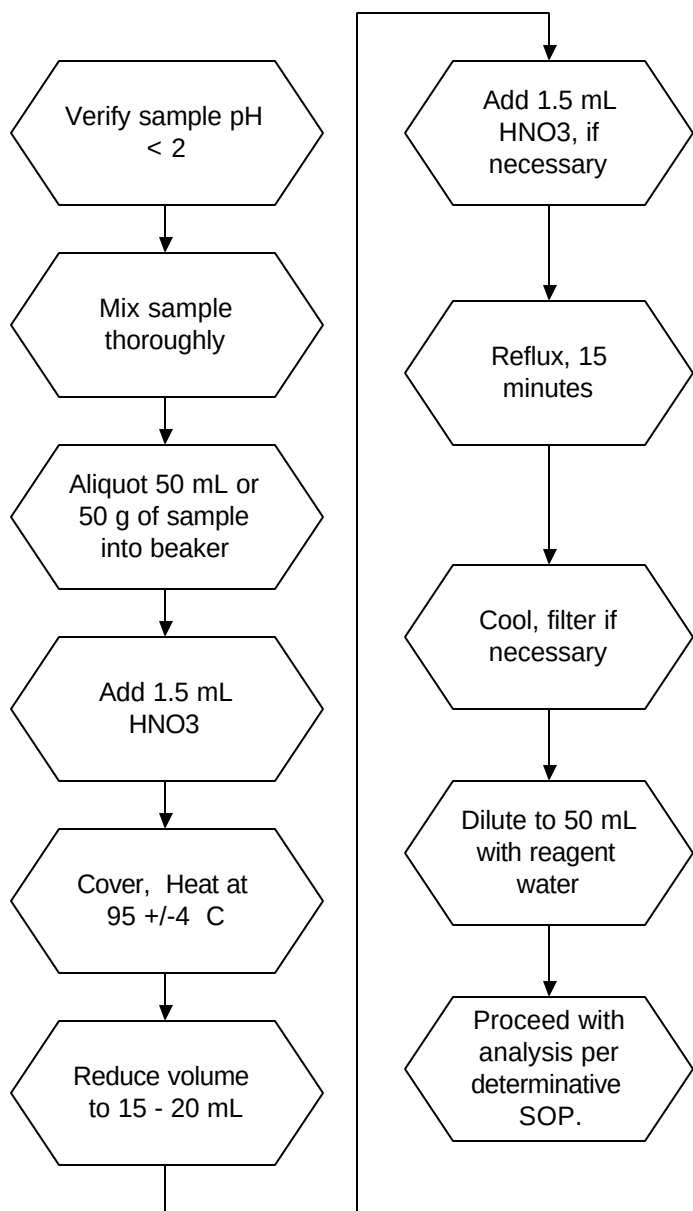


Figure 4. Method 7060A/7740A and Method 206.2/270.2 (Section 11.15)

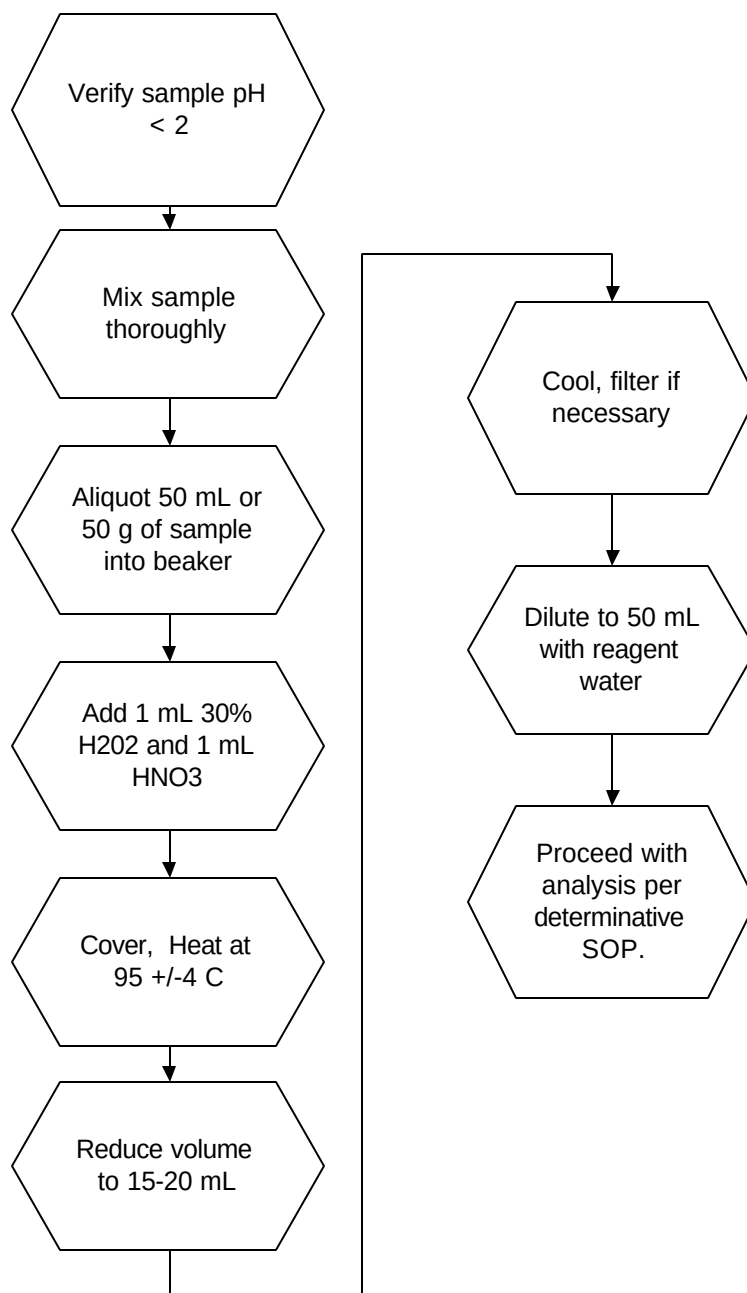


Figure 5. Method 200.0 Section 4.1.4 (Section 11.16)

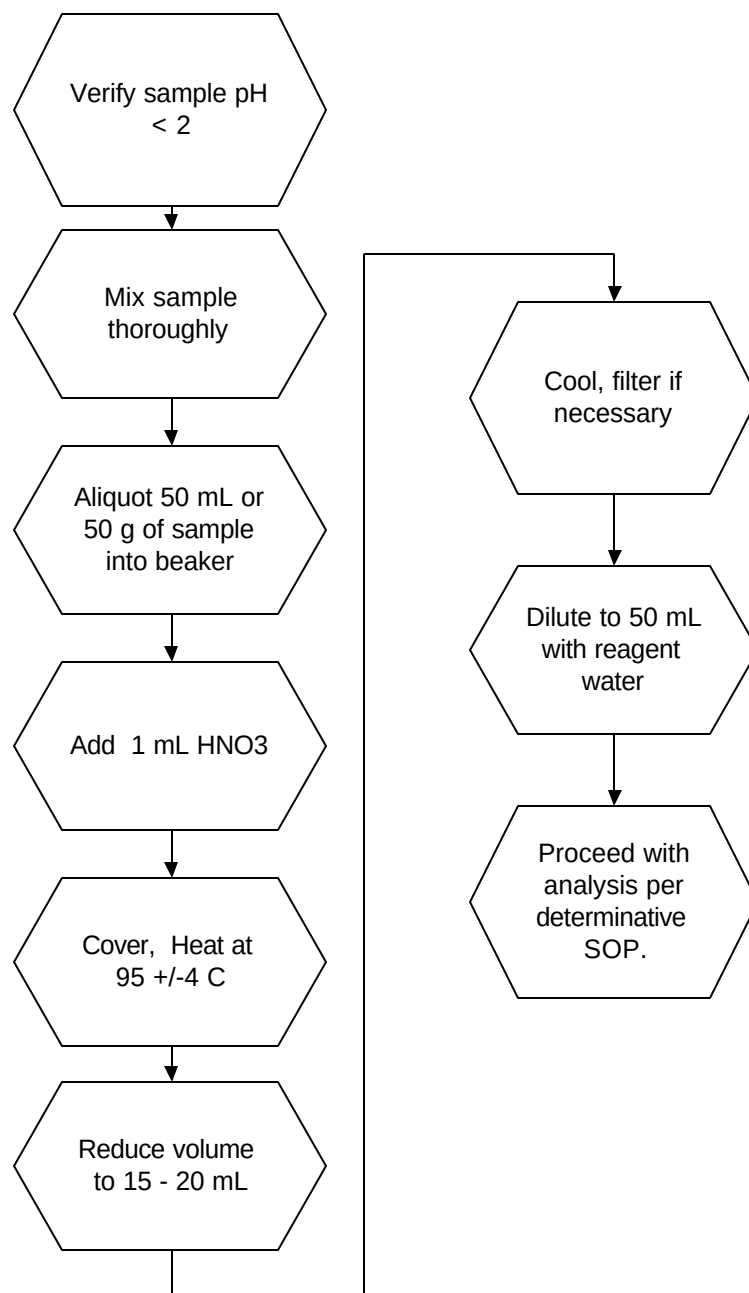
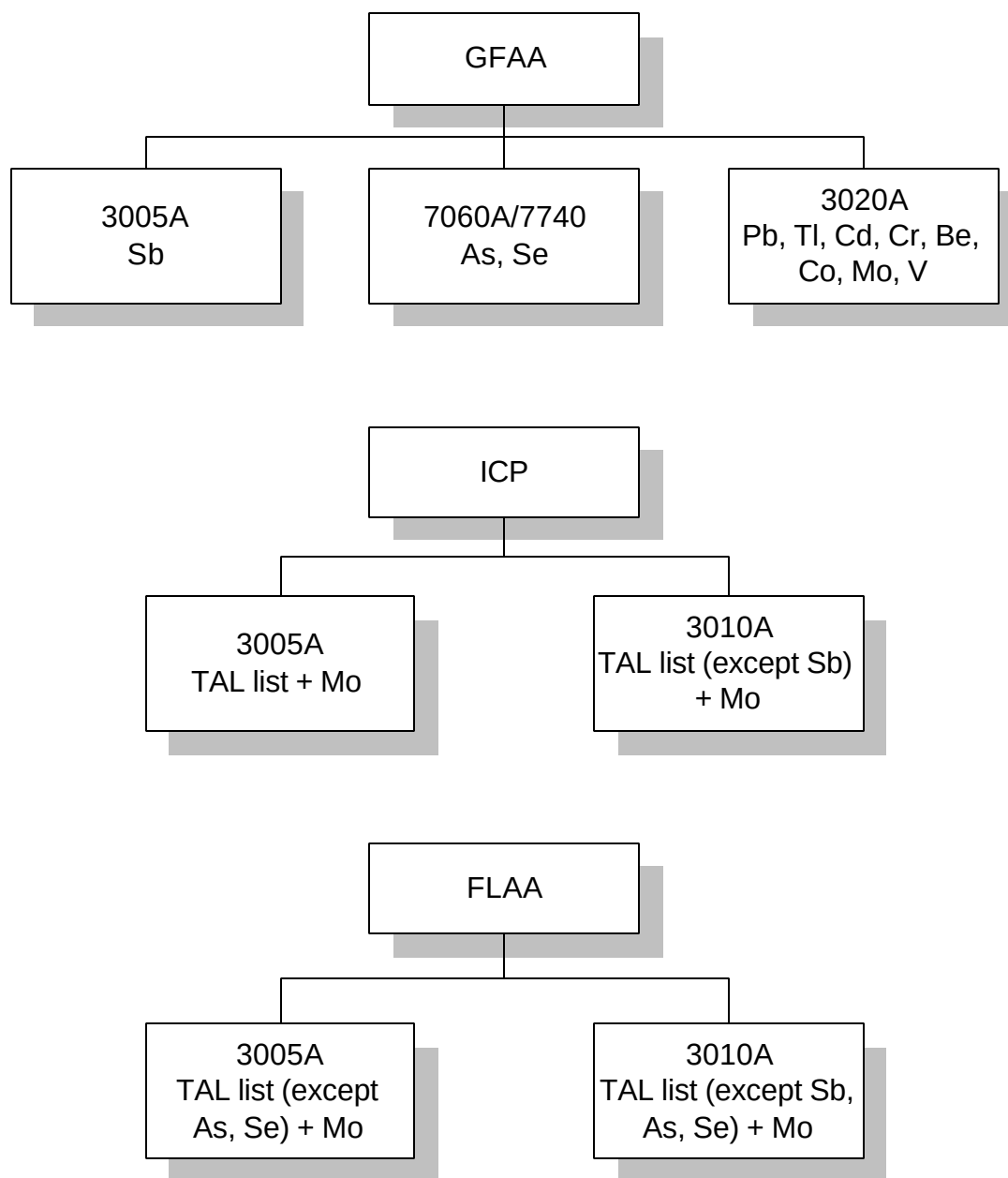
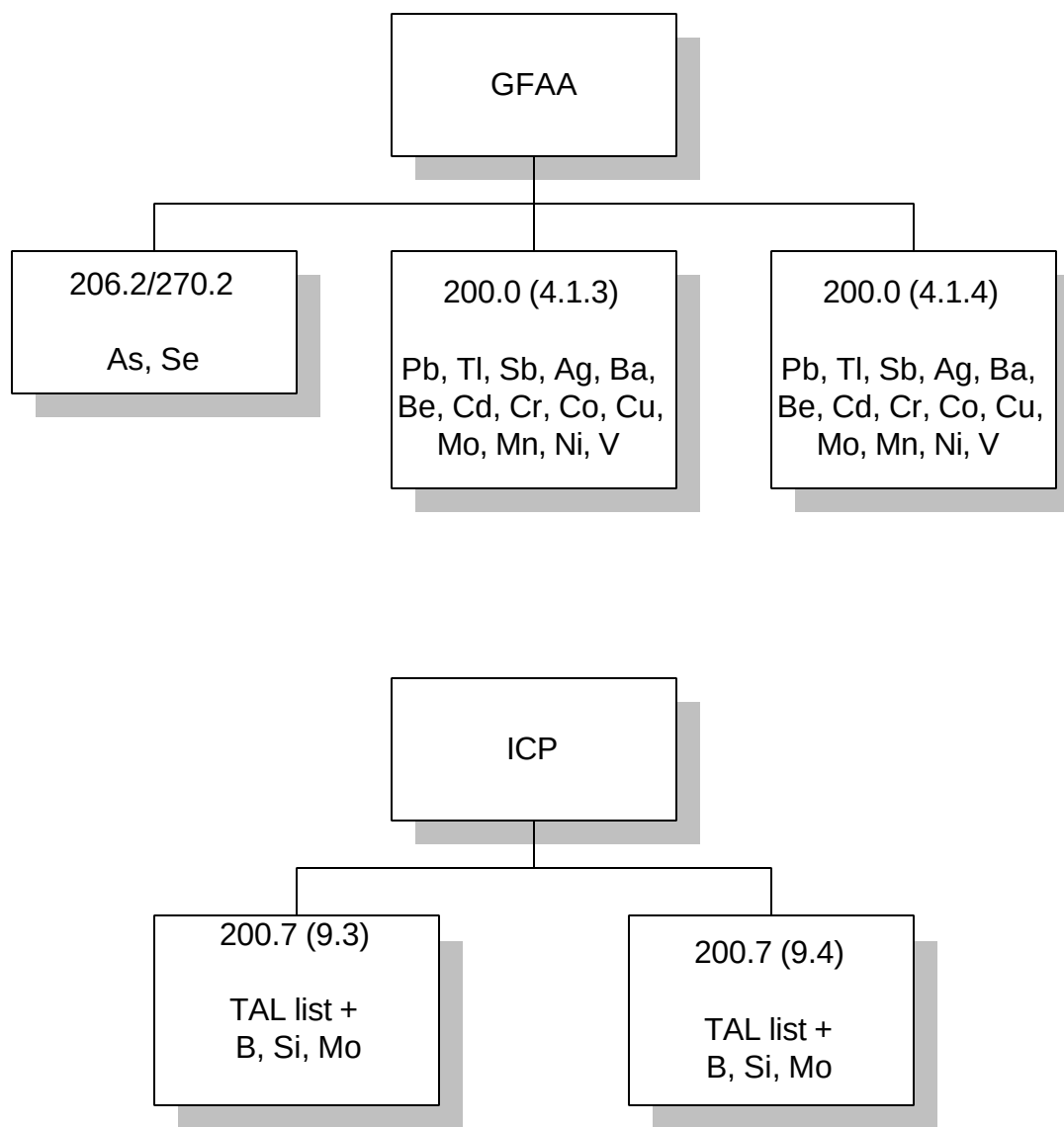


Figure 6. Overview of SW846 Aqueous Preparation Methods by Determinative Method



TAL list: Al, Sb, As, Ba, Be, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Ni, K, Se, Ag, Na, Tl, V, Zn

Figure 7. Overview of MCAWW Aqueous Preparation Methods by Determinative Technique



TAL list: Al, Sb, As, Ba, Be, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Ni, K, Se, Ag, Na, Tl, V, Zn

APPENDIX A

TABLES

TABLE I. Approved Preparation Method Analytes - SW846

ELEMENT	Symbol	CAS Number	3005A	3010A	3020A	7060A 7740
Aluminum	Al	7429-90-5	X	X		
Antimony	Sb	7440-36-0	X			
Arsenic	As	7440-38-2	X	X		X
Barium	Ba	7440-39-3	X	X		
Beryllium	Be	7440-41-7	X	X	X	
Cadmium	Cd	7440-43-9	X	X	X	
Calcium	Ca	7440-70-2	X	X		
Chromium	Cr	7440-47-3	X	X	X	
Cobalt	Co	7440-48-4	X	X	X	
Copper	Cu	7440-50-8	X	X		
Iron	Fe	7439-89-6	X	X		
Lead	Pb	7439-92-1	X	X	X	
Magnesium	Mg	7439-95-4	X	X		
Manganese	Mn	7439-96-5	X	X		
Molybdenum	Mo	7439-98-7	X	X	X	
Nickel	Ni	7440-02-0	X	X		
Potassium	K	7440-09-7	X	X		
Selenium	Se	7782-49-2	X	X		X
Silver	Ag	7440-22-4	X	X		
Sodium	Na	7440-23-5	X	X		
Thallium	Tl	7440-28-0	X	X	X	
Vanadium	V	7440-62-2	X	X	X	
Zinc	Zn	7440-66-6	X	X		

X - Designates that the preparation method is approved for an element

Note: Additional elements may be analyzed following digestion by these protocols provided the method performance criteria specified in Section 13.0 of the SOP are met.

TABLE II. Approved Preparation Method Analytes - NPDES

ELEMENT	Symbol	CAS Number	200.7 (9.4)	200.7 (9.3)	200.0 (4.1.4)	200.0 (4.1.3)	206.2 270.2
Aluminum	Al	7429-90-5	X	X			
Antimony	Sb	7440-36-0	X	X	X	X	
Arsenic	As	7440-38-2	X	X			X
Boron	B	7440-42-8	X	X			
Barium	Ba	7440-39-3	X	X	X	X	
Beryllium	Be	7440-41-7	X	X	X	X	
Cadmium	Cd	7440-43-9	X	X	X	X	
Calcium	Ca	7440-70-2	X	X			
Chromium	Cr	7440-47-3	X	X	X	X	
Cobalt	Co	7440-48-4	X	X	X	X	
Copper	Cu	7440-50-8	X	X	X	X	
Iron	Fe	7439-89-6	X	X	X	X	
Lead	Pb	7439-92-1	X	X	X	X	
Magnesium	Mg	7439-95-4	X	X			
Manganese	Mn	7439-96-5	X	X	X	X	
Molybdenum	Mo	7439-98-7	X	X	X	X	
Nickel	Ni	7440-02-0	X	X	X	X	
Potassium	K	7440-09-7	X	X			
Selenium	Se	7782-49-2	X	X			X
Silicon	Si	7631-86-9	X	X			
Silver	Ag	7440-22-4	X	X	X	X	
Sodium	Na	7440-23-5	X	X			
Thallium	Tl	7440-28-0	X	X	X	X	
Vanadium	V	7440-62-2	X	X	X	X	
Zinc	Zn	7440-66-6	X	X			

X - Designates that the preparation method is approved for an element

Note: Additional elements may be analyzed following digestion by these protocols provided the method performance criteria specified in Section 13.0 of the SOP are met.

TABLE III. ICP and FLAA Matrix Spike and Aqueous Laboratory Control Sample Levels

ELEMENT	Working LCS/MS Standard (mg/L)	Aqueous LCS/ MS Level * (ug/l)
Aluminum	100	2000
Antimony	25	500
Arsenic	100	2000
Barium	100	2000
Beryllium	2.5	50
Cadmium	2.5	50
Calcium	2500	50000
Chromium	10	200
Cobalt	25	500
Copper	12.5	250
Iron	50	1000
Lead	50	500
Magnesium	2500	50000
Manganese	25	500
Molybdenum	50	1000
Nickel	25	500
Phosphorous	500	10000
Potassium	2500	50000
Selenium	100	2000
Silver	2.5	50
Sodium	2500	50000
Thallium	100	2000
Vanadium	25	500
Zinc	25	500
Boron	50	1000
Tin	100	2000
Titanium	50	1000

* Levels shown indicate the spike concentration in the final digestate of the aqueous LCS or matrix spike based on the addition of 1.0 mL working spike (7.3) to 50 mL of sample.

APPENDIX A - TABLES

TABLE IV. GFAA Matrix Spike and Aqueous LCS Spike Levels

ELEMENT	Stock LCS/MS Standard (mg/L)	Working LCS/MS Standard (ug/L)	Aqueous LCS/ MS Level * (ug/l)
Arsenic	400	2000	40
Selenium	400	2000	40
Lead	400	2000	40
Thallium	400	2000	40
Antimony	400	2000	40
Cadmium	40	200	4
Chromium	100	500	10
Silver	50	250	5

* Levels shown indicate the spike concentration in the final digestate of the aqueous LCS or matrix spike based on the addition of 1.0 mL working spike (7.4) to 50 mL of sample.

TABLE V. TCLP Reporting Limits, Regulatory Limits and Matrix Spike Levels

ELEMENT	RL (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

* Levels shown indicate the spike concentration in the final digestate of the aqueous LCS or matrix spike based on the addition of 0.5 mL working spike (7.4) to 50 mL of sample

TABLE VI. Summary of Quality Control Requirements

QC PARAMETER	FREQUENCY	ACCEPTANCE CRITERIA	CORRECTIVE ACTION
Method Blank	One per sample preparation batch of up to 20 samples.	Refer to determinative SOPs: NC-MT-0002 CORP-MT-0001 CORP-MT-0003	Redigest and reanalyze samples associated with the method blank.
Laboratory Control Sample (LCS)	One per sample preparation batch of up to 20 samples.	Refer to determinative SOPs: NC-MT-0002 CORP-MT-0001 CORP-MT-0003	Redigest and reanalyze all samples associated with the LCS.
Matrix Spike	One per sample preparation batch of up to 20 samples.	Refer to determinative SOPs: NC-MT-0002 CORP-MT-0001 CORP-MT-0003	Reprep not required unless preparation error suspected.
Matrix Spike Duplicate	See Matrix Spike	Refer to determinative SOPs: NC-MT-0002 CORP-MT-0001 CORP-MT-0003	See Corrective Action for Matrix Spike.

APPENDIX B
CONTAMINATION CONTROL GUIDELINES

APPENDIX B. 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.

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STL NORTH CANTON STANDARD OPERATING PROCEDURE

TITLE: ACID DIGESTION OF SOILS, SW846 METHOD 3050B

(SUPERSEDES: REVISION 2.4, DATED 02/19/03)

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1. SCOPE AND APPLICATION

- 1.1. This procedure describes the preparation of soil samples for the analysis of certain metals by Graphite Furnace Atomic Absorption (GFAA), Flame Atomic Absorption (FLAA), Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP), and Inductively Coupled Plasma-Mass Spectrometry (ICP/MS) as specified in SW846 Method 3050B.
- 1.2. Samples prepared by the protocols detailed in this SOP may be analyzed by ICP, ICP/MS, FLAA or GFAA for the elements listed in Table I (Appendix A). Other elements and matrices may be analyzed following digestion by these protocols provided that the method performance criteria specified in Section 13.0 of this SOP are met.
- 1.3. This method is not a total digestion, but will dissolve almost all metals that could become “environmentally available”. By design, metals bound in silicate structures are not dissolved by this procedure, as they are not usually mobile in the environment. This SOP can be applied to metals in solids, sludges, wastes and sediments.
- 1.4. 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

A representative 1 gram (wet weight) portion of sample is digested in nitric acid and hydrogen peroxide. The digestate is refluxed with hydrochloric acid for ICP or FLAA analysis. The digestates are then filtered and diluted to 100 mL/100 g.

3. DEFINITIONS

- 3.1. Refer to the glossary in the Laboratory Quality Manual (LQM), latest version.
- 3.2. Total Metals: The concentration determined on an unfiltered sample following digestion. Note that this method is designed to determine the total *environmentally available* metals.

4. INTERFERENCES

- 4.1. There are numerous routes by which samples may become contaminated. Potential sources of trace metals contamination include: metallic or metal-containing labware (e.g., talc gloves which contain high levels of zinc), containers, impure reagents, dirty glassware, improper sample transfers, dirty work areas, atmospheric inputs such as dirt and dust, etc. Be aware of potential sources of contamination and take appropriate measures to minimize or avoid them.

- 4.2. The entire work area, including the bench top and fume hood, should be thoroughly cleaned on a routine schedule in order to minimize the potential for environmental contamination.
- 4.3. Boron and silica from the glassware will grow into the sample solution during and following sample processing. For critical low level determinations of boron and silica, only quartz and/or plastic labware should be used.
- 4.4. Physical interference effects may contribute to inaccuracies in the determinations of trace elements. Oils, solvents and other matrices may not be digested using these methods if they are not soluble with acids. If physical interferences are present, they should be documented.
- 4.5. Visual interferences or anomalies (such as foaming, emulsions, precipitates, etc.) must be documented.
- 4.6. Allowing samples to boil or go dry during digestion may result in the loss of volatile metals. If this occurs the sample must be reprepared. Antimony is easily lost by volatilization from hydrochloric media.
- 4.7. Specific analytical interferences are discussed in each of the determinative methods.

5. SAFETY

- 5.1. Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual and this document.
- 5.2. Samples that contain high concentrations of carbonates or organic material or samples that are at elevated pH can react violently when acids are added.
- 5.3. The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure

Hydrochloric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Hydrogen Peroxide	Oxidizer Corrosive	1 ppm-TWA	Vapors are corrosive and irritating to the respiratory tract. Vapors are very corrosive and irritating to the eyes and skin.
Nitric Acid	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

- 5.4. Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Cut resistant gloves must be worn doing any other task that presents a strong possibility of getting cut. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately
- 5.5. The acidification of samples containing reactive materials may result in the release of toxic gases, such as cyanides or sulfides. Acidification of samples should be done in a fume hood. The analyst should also be aware of the potential for a vigorous reaction.

- 5.6. 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. All samples with pink stickers that read "Caution/Use Hood!" **must** be opened in the hood. Contact the EH&S Coordinator if this is not possible. Solvent and waste containers will be kept closed unless transfers are being made.
- 5.7. The preparation of standards and reagents will be conducted in a fume hood with the sash closed as far as the operation will permit or under other means of mechanical ventilation.
- 5.8. All work must be stopped in the event of a known or potential compromise to the health and safety of a STL North Canton associate. The situation must be reported **immediately** to the EH&S Coordinator and the Laboratory Supervisor.
- 5.9. Always carry bulk concentrated acid bottles in appropriate impact proof containers.
- 5.10. Acid/peroxide spills must be neutralized immediately, flushed with water and cleaned up using appropriate spill kits.
- 5.11. Discard chipped or broken beakers to prevent injury. Chipped glassware may be fire polished as an alternative to disposal.

6. **EQUIPMENT AND SUPPLIES**

- 6.1. Hot plate, digestion block, steam bath or other heating source capable of maintaining a temperature of 90-99°C.
- 6.2. Calibrated thermometer that covers a temperature range of 0-200°C.
- 6.3. Griffin beakers of assorted sizes or equivalent.
- 6.4. Vapor recovery device (Watch glasses, ribbed or other device).
- 6.5. Whatman No. 41 filter paper or equivalent.
- 6.6. Funnels or equivalent filtration apparatus.
- 6.7. Centrifugation equipment (if desired method of removing particulates is centrifugation).
- 6.8. Graduated cylinder or equivalent capable of measuring 100 mL within 3% accuracy.

- 6.9. Analytical balance capable of accurately weighing to the nearest 0.01 grams.
- 6.10. Repipetors or suitable reagent dispensers.
- 6.11. Calibrated automatic pipettes with corresponding pipette tips or Class A glass volumetric pipettes.
- 6.12. Class A volumetric flasks.
- 6.13. pH indicator strips (pH range 0 - 6).
- 6.14. Plastic bottles.

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 as defined in the determinative SOPs.
- 7.2. Laboratory Control Sample (LCS) and matrix spike (MS) solutions are purchased as custom STL North Canton 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. Working ICP LCS/MS spike solution: Prepare the ICP LCS/MS working spike solutions from custom stock standards to the final concentration listed in Table II. The working spike must be prepared in a matrix of 5% HNO₃. This acid (5 mL of concentrated HNO₃ per 100 mL) must be added to the volumetric flask before the addition of the stock standard aliquot. The working ICP LCS solution must be made fresh every three months.
- 7.4. Working GFAA LCS/MS spike solution: Prepare the GFAA working LCS/MS spike solutions by diluting the custom stock solution (7.2) 200x. The working spike solution must be prepared in a matrix of 5% HNO₃. This acid (5 mL of concentrated HNO₃ per 100 mL) must be added to the volumetric flask before the addition of the stock standard aliquot. The working GFAA LCS/MS solution must be made fresh every three months.
- 7.5. The LCS and MS samples must contain all the elements designated for analysis in each batch of samples. If a non-routine element is required that is not contained in the custom STL North Canton solution, the individual facility must purchase a solution from the designated

vendor that will cover the additional analyte(s) of interest and provide for a final spike concentration that is appropriate to the determinative method.

7.6. Aqueous laboratory control samples (LCSW) and matrix spike samples are prepared as described in Sections 9.5 and 9.6. Refer to Tables II through IV (Appendix A) for details regarding the stock, working standard and final digestate spike concentrations for ICP and GFAA LCS and matrix spike preparations.

7.7. Nitric acid (HNO_3), concentrated, trace metal grade or better.

7.8. Nitric acid, 1:1 - dilute concentrated HNO_3 with an equal volume of reagent water.

Note: When preparing diluted acids always add acid to water. If the water is added to the acid a violent reaction may occur.

7.9. Hydrochloric acid (HCl), concentrated, trace metal grade or better.

7.10. Hydrochloric acid, 1:1 - dilute concentrated HCl with an equal volume of reagent water.

Note: When preparing diluted acids always add acid to water. If the water is added to the acid a violent reaction may occur.

7.11. 30% Hydrogen peroxide (H_2O_2), reagent grade.

8. **SAMPLE COLLECTION, PRESERVATION AND STORAGE**

8.1. Sample holding time for metals included under the scope of this SOP is 180 days from the date of collection to the date of analysis.

8.2. Soil samples do not require preservation but must be stored at $4\text{ }^\circ\text{C} \pm 2\text{ }^\circ\text{C}$ until the time of analysis.

9. **QUALITY CONTROL**

Table V (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 Method 3050B 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 or verified as detailed in STL North Canton QA Policy QA-005. 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 North Canton 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, which should contain all the analytes of interest. The results of the initial demonstration study must be acceptable before analysis of samples may begin. The results of the initial demonstration study may be used to extend a method for the analysis of other elements provided all acceptance criteria are met.
 - 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.
 - 9.1.2.2. Calculations and acceptance criteria for QC check samples are given in the determinative SOPs (CORP-MT-0001, CORP-MT-0003).
- 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, MS/MSD) are not counted towards the maximum 20 samples in a batch. Field QC samples are included in the batch count.
- 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. Criteria for the acceptance of blanks are contained within the individual analytical method SOP's. If the method blank does not meet the criteria contained within the analytical method SOPs, the blank and all associated samples in the batch must be redigested.

- 9.5. 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. 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. Criteria for the acceptance of LCS results are contained within the individual analytical method SOP's. Corrective action when LCS results fail to meet control limits will be repreparation and reanalysis of the batch. Tables II and III provide the details regarding the stock, working standards and final spike concentrations for ICP and GFAA. Refer to Section 7.3 or 7.4 for instructions on preparation of the aqueous LCS.

9.5.1. The LCS is prepared by spiking a 1mL or 1 g aliquot of reagent water with 2 mL of the working LCS/MS spike solution (7.3 or 7.4). The LCS is then processed as described in either Section 11.10.

- 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. Samples identified as field blanks cannot be used for MS/MSD analysis. If any analyte recovery or RPD falls outside the acceptance range, the recovery of that analyte must be in control for the LCS. If the recovery of the LCS is outside limits, corrective action must be taken. Corrective action will include repreparation and reanalysis of the batch. Corrective action when MS results fail to meet control limits does not include repreparation of samples unless the results indicate that a spiking error may have occurred. Tables II through IV provide the details regarding the stock, working standards and final matrix spike concentrations for ICP and GFAA. Refer to Sections 7.3 and 7.4 for instructions on preparation of the working matrix spike solutions.

9.6.1. The soil matrix spike sample is prepared by spiking a 1 g aliquot of a sample with 2mL of the working LCS/MS spike solution (7.3 or 7.4). The matrix spike sample is then processed as described in either Section 11.10.

- 9.7. 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. Hotplate or block temperature must be verified daily for each unit used and must be recorded on either the metals preparation log or in a hotplate temperature logbook. The hotplate temperature should be verified by measuring the temperature of a beaker of reagent water placed on each hotplate. For block digestors, use a tube containing water.

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. The heating procedures are carried out in a properly functioning hood.
- 11.4. All samples are to be checked out of sample control with the chain of custody documentation filled out completely.
- 11.5. Proper sample identification is extremely important in any preparation procedure. Labeling of beakers and bottles must be done in a manner to ensure connection with the proper sample. The use of automatic label printing programs is recommended to reduce transcription errors (QuantIMS option).
- 11.6. Samples are typically logged in as either waters or soils. Wastes such as organic liquids or sludges and tissues (animal/vegetable) are usually logged in with solid test codes. When initiating prep, examine the sample to see if the sample matches the matrix designation. If the sample is logged in as aqueous but it appears more like a waste (biphasic, sludge like, organic liquid, lots of sediment etc.) contact the lab supervisor or project administrator for further instructions. In some cases it may be more appropriate to process these samples as solids.

- 11.7. If possible prepare all the samples of a project at the same time to minimize the QC required and streamline the flow of the project through the lab and reporting group.
- 11.8. In some cases, both AA and ICP digests are required on each sample. It is recommended that both aliquots be weighed out and processed at the same time.
- 11.9. Guidelines are provided in the appendices on procedures to minimize contamination of samples and standards.
- 11.10. Preparation of Soils, Sediments and Sludges for Analysis by GFAA, ICP, ICP/MS and FLAA.
 - 11.10.1. Mix sample thoroughly by stirring with a clean plastic or wooden spoon or spatula. Some project plans may require, when possible, transfer of the entire sample from the original container to butcher paper or a clean beaker, mixing thoroughly, then returning the sample to its original container.
 - 11.10.2. For each digestion procedure required (i.e., ICP or GFAA), weigh a 1.0 portion of solid and record the exact weight to the nearest 0.01 g. A 2 g sample size may also be used if needed to meet the reporting limits.
 - 11.10.3. Measure additional aliquots of the designated samples for the MS and MSD analyses.
 - 11.10.4. Spike each of the MS and MSD aliquots with 2 mL of the working LCS/MS spiking solution (7.3 or 7.4).
 - 11.10.5. Prepare a beaker for the method blank.
 - 11.10.6. Prepare a beaker for the LCS. Add 2 mL of the working LCS/MS spiking solution (7.3 or 7.4).
 - 11.10.7. Add 10 mL of 1:1 HNO₃ and mix the sample.
 - 11.10.8. Heat sample to 95° ± 4° C and reflux for 10 minutes without boiling, using a vapor recovery device.

Note: DO NOT ALLOW SAMPLE TO BOIL OR GO DRY during any part of the digestion. Doing so will result in the loss of analyte and the sample must be reprepared.

- 11.10.9. Allow sample to cool, if necessary.
- 11.10.10. Add 5 mL of concentrated HNO_3 and replace vapor recovery device.
- 11.10.11. Reflux at $95^\circ \pm 4^\circ \text{C}$ for 30 minutes. (Add reagent water as needed to ensure that the volume of solution is not reduced to less than 5 mL.)
- 11.10.12. If brown fumes are observed, repeat step 11.10.10 until no more fumes are evolved.
- 11.10.13. Allow the samples to cool, if necessary.
- 11.10.14. Add approximately 2 mL of reagent water and 1 mL of 30 % H_2O_2 . Care must be taken to ensure that losses do not occur due to excessively vigorous effervescence.
- 11.10.15. Replace the vapor recovery device and heat sample until effervescence subsides.
- 11.10.16. Allow the sample to cool, if necessary.
- 11.10.17. Continue adding 30% H_2O_2 in 1 mL aliquots with warming until effervescence is minimal or sample appearance is unchanged.
- Note:** Do not add more than a total of 10 mL of 30 % H_2O_2 .
- 11.10.18. Continue heating at $95^\circ \pm 4^\circ \text{C}$ for 75 minutes until the volume is reduced to approximately 5-10 mL. Alternatively the sample may be heated for 2 hours.
- 11.10.19. If the sample is being prepared for ICP or FLAA analyses add 10 mL of concentrated HCl and reflux for an additional 10 minutes without boiling. This step is omitted for analysis by ICP-MS and GFAA
- Note:** Antimony and silver have poor solubility in dilute nitric acid solution. Therefore it is strongly recommended that these elements are determined by the ICP procedure that includes HCl as the final digestion acid.
- 11.10.20. Allow the sample to cool.
- 11.10.21. Wash down beaker walls and vapor recovery device with reagent water.

- 11.10.22. Filter sample through Whatman 41 filter paper or equivalent into a graduated cylinder or equivalent or a pre-weighed bottle. Other measuring bottles (for example, Corning Snap Seals™) may be used if their accuracy is documented and is better than $\pm 2\%$. Rinse beaker and filter paper with reagent water to ensure complete sample transfer.

Note: In place of filtering, the samples, after dilution and mixing, may be centrifuged or allowed to settle by gravity overnight to remove insoluble material

- 11.10.23. Dilute sample to 100 mL or 100g with reagent water. The sample is now ready for analysis.

Note: This SOP allows for samples to be weighed instead of measured volumetrically. This assumes the density of the diluted sample is close to 1.0 g/mL (See Section 17.1.2).

12. DATA ANALYSIS AND CALCULATIONS

Not Applicable.

13. METHOD PERFORMANCE

- 13.1. Method performance is determined by the analysis of matrix spike and matrix spike duplicate samples as well as method blanks and laboratory control samples. In general, the matrix spike recovery should fall within $\pm 20\%$ and the matrix spike duplicates should compare within 20% RPD. Method blanks must meet the criteria specified in the determinative SOPs. The laboratory control samples should recover within 20% of the true value until in house control limits are established. Acceptance criteria are given in the determinative SOPs.

- 13.2. The initial demonstration study as detailed in Section 9.1.2 must be acceptable before the analysis of field samples under this SOP may begin. The results of the initial demonstration study may be used to extend a method for the analysis of other elements provided all acceptance criteria are met.

- 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. All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for “Waste Management and Pollution Prevention.”
- 15.2. Waste Streams Produced by the Method
- 15.2.1. The following waste streams are produced when this method is carried out.
- 15.2.1.1. Acidic waste containing nitric acid generated by the extraction. This waste is disposed of in a designated container labeled “Acid Waste”.
- 15.2.1.2. Contaminated disposable materials utilized for the analysis. This waste is disposed of in a designated container labeled “Solid Waste”.

16. **REFERENCES**

16.1. References

- 16.1.1. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition, Final Update III, December 1996. Method 3050B.
- 16.1.2. CORP-MT-0001, Inductively Coupled Plasma-Atomic Emission Spectroscopy, Spectrometric Method for Trace Element Analysis of Water and Wastes, Method 6010B and Method 200.7.
- 16.1.3. CORP-MT-0003, Graphite Furnace Atomic Absorption Spectroscopy, SW846 Method 7000A and MCAWW 200 Series Methods.
- 16.1.4. NC-MT-0002, Inductively Coupled Plasma-Mass Spectrometry, EPA Methods 6020 and 200.8.
- 16.1.5. Corporate Quality Management Plan (QMP), current version.

16.1.6. STL Laboratory Quality Manual (LQM), current version.

16.1.7. STL Corporate Safety Manual, M-E-0001 and STL North Canton Facility Addendum and Contingency Plan, current version.

16.2. Associated SOPs and Policies, latest version

16.2.1. QA-003, STL North Canton QC Program.

16.2.2. QA-004, Rounding and Significant Figures.

16.2.3. Glassware Washing, NC-QA-0014

16.2.4. Statistical Evaluation of Data and Development of Control Charts, NC-QA-0018

16.2.5. Method Detection Limits and Instrument Detection Limits, S-Q-003 and NC-QA-0021

16.2.6. Navy/Army SOP, NC-QA-0016

17. **MISCELLANEOUS (TABLES, APPENDICES, ETC. . .)**

17.1. Modifications/Interpretations 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 MDL. This SOP states that the method blank must not contain any analyte of interest at or above the reporting limit. Common lab contaminants, as defined in the determinative SOPs, are allowed up to two times the reporting limit in the blank following consultation with the client.

17.1.2. This SOP allows for aqueous samples to be weighed instead of measured volumetrically. This assumes the density of the sample is close to 1.0 g/mL. Samples with large amounts of sediment or suspended solids, sludges, non-aqueous liquids must be processed volumetrically. Weighing samples directly into the digestion vessel minimizes the potential for cross contamination, offers improved accuracy over the use of graduated cylinders (comparable to volumetric flask accuracy), uses less glassware and is more efficient.

17.2. Modifications from previous SOP

17.2.1. ICP/MS has been added as an appropriate determinative technique.

17.2.2. The approved analyte list may be modified provided that additional elements meet the requirements in section 13.

17.2.3. Directions for digestion for set time periods rather than reduction to set volumes have been added.

17.2.4. The order of two steps in the digestion has been changed. (See section 11.10.20)

17.2.5. Definition of the method as determining total environmentally available metals has 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. Refer to the Appendices for any facility specific information required supporting this SOP.

17.4. Documentation and Record Management

The preparation benchsheet should, at a minimum, include the following information:

- Preparation date, analyst initials, matrix, prep type (ICP or GFAA).
- Sample ID; initial weight/volume and final weight/volume.
- Standards Documentation (source, lot, prep date, volume added).
- Analyst initials.

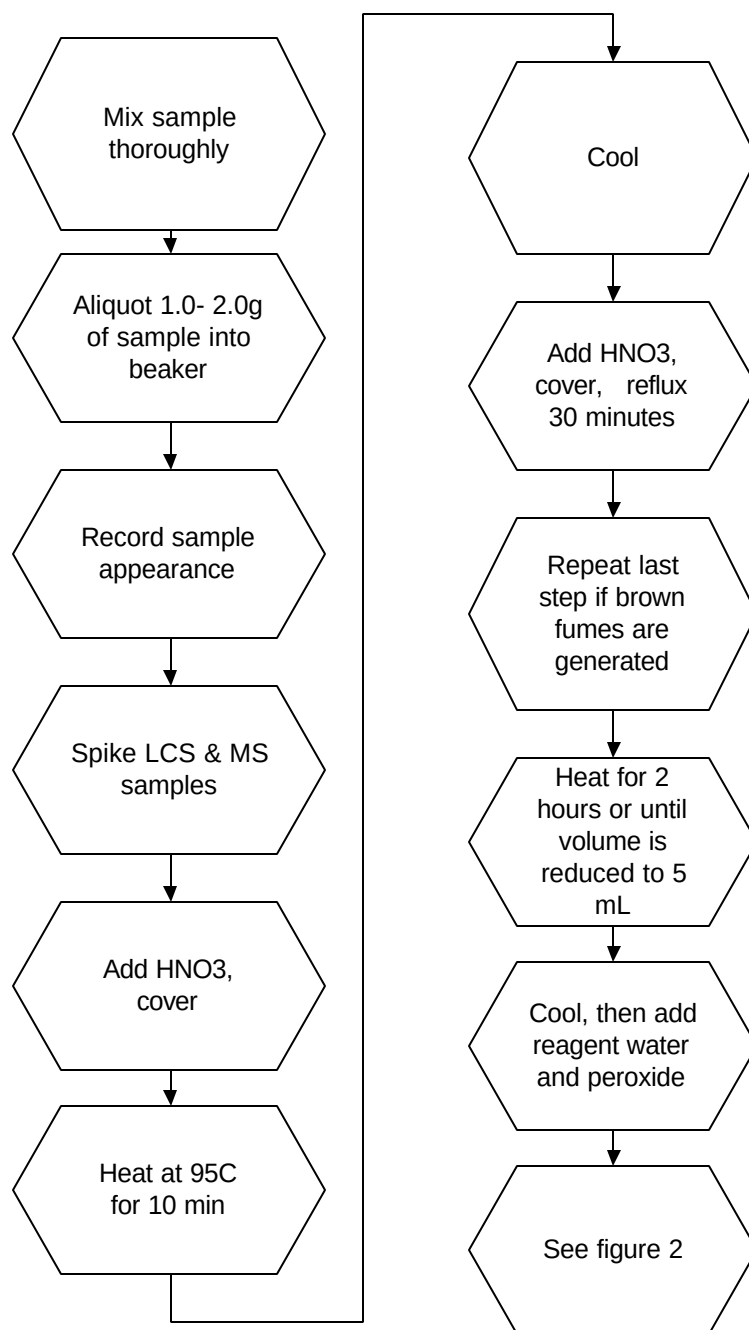
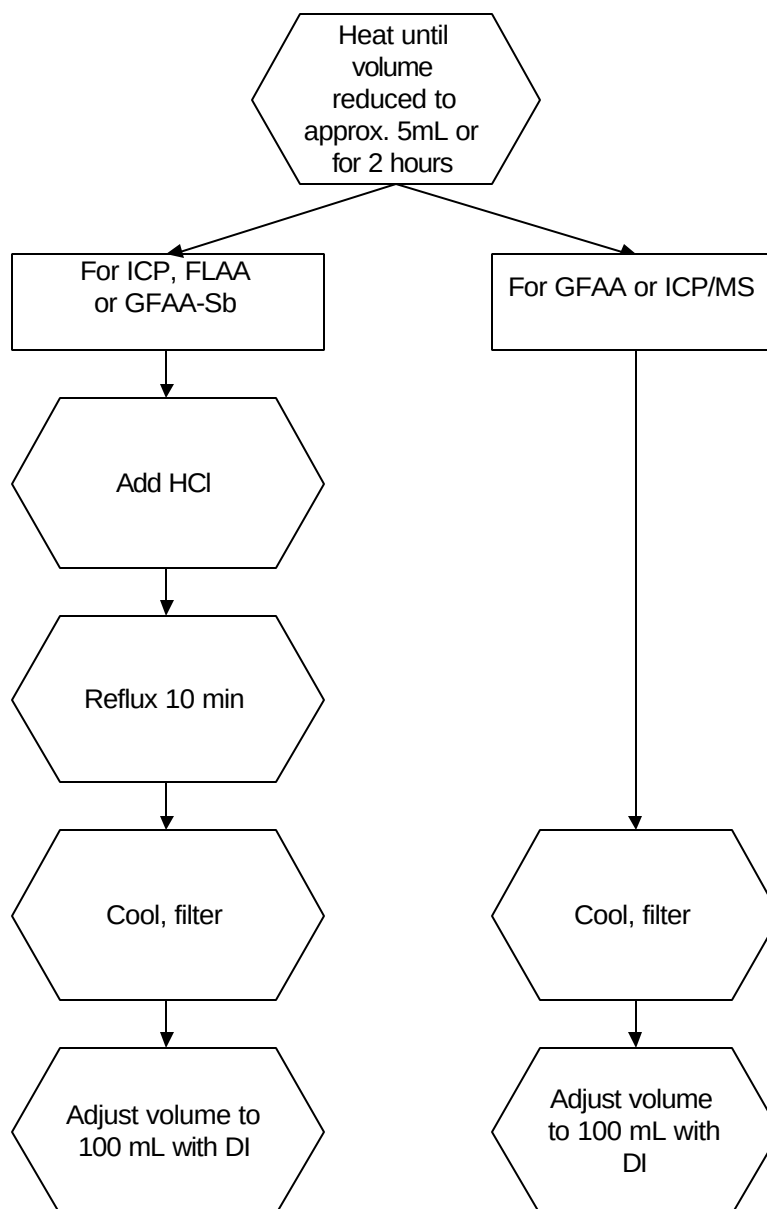
Figure 1. Soil Sample Preparation (Section 11.10)

Figure 2. Soil Sample Preparation (continued)

APPENDIX A

TABLES

TABLE I. Method 3050A Approved Analyte List

ELEMENT	Symbol	CAS Number
Aluminum	Al	7429-90-5
Antimony	Sb	7440-36-0
Arsenic	As	7440-38-2
Barium	Ba	7440-39-3
Beryllium	Be	7440-41-7
Cadmium	Cd	7440-43-9
Calcium	Ca	7440-70-2
Chromium	Cr	7440-47-3
Cobalt	Co	7440-48-4
Copper	Cu	7440-50-8
Iron	Fe	7439-89-6
Lead	Pb	7439-92-1
Magnesium	Mg	7439-95-4
Manganese	Mn	7439-96-5
Molybdenum	Mo	7439-98-7
Nickel	Ni	7440-02-0
Potassium	K	7440-09-7
Selenium	Se	7782-49-2
Silver	Ag	7440-22-4
Sodium	Na	7440-23-5
Thallium	Tl	7440-28-0
Vanadium	V	7440-62-2
Zinc	Zn	7440-66-6

TABLE II. ICP and FLAA Soil Matrix Spike and Aqueous LCS Levels

ELEMENT	Working LCS/MS Standard (mg/L)	Aqueous LCS/MS Level* (ug/L)	Soil MS Level ** (mg/Kg)
Aluminum	100	2000	200
Antimony	25	500	50
Arsenic	100	2000	200
Barium	100	2000	200
Beryllium	2.5	50	5
Cadmium	2.5	50	5
Calcium	2500	50000	5000
Chromium	10	200	20
Cobalt	25	500	50
Copper	12.5	250	25
Iron	50	1000	100
Lead	25	500	50
Lithium	50	1000	100
Magnesium	2500	50000	5000
Manganese	25	500	50
Molybdenum	50	1000	100
Nickel	25	500	50
Potassium	2500	50000	5000
Selenium	100	2000	200
Silver	2.5	50	5
Sodium	2500	50000	5000
Strontium	50	1000	100
Thallium	100	2000	200
Vanadium	25	500	50
Zinc	25	500	50
Boron	50	1000	100
Tin	100	2000	200
Titanium	50	1000	100

* Levels shown indicate the spike concentration in the final digestate of the aqueous LCS or matrix spike based on the addition of 2.0 mL working spike (7.3) to 100 mL of sample.

** Final soil spike concentration based on the addition of 2.0 mL working spike (7.3) to 1.0 g of sample/100 mL final volume (assumes 100% solids).

TABLE III. ICPMS Soil Matrix Spike and Aqueous LCS Levels

ELEMENT	Working LCS/MS Standard (mg/L)	Aqueous LCS/MS Level* (ug/L)	Soil MS Level ** (mg/Kg)
Aluminum	100	1000	100
Antimony	10	100	10
Arsenic	10	100	10
Barium	10	100	10
Beryllium	10	100	10
Cadmium	10	100	10
Calcium	100	1000	100
Chromium	10	100	10
Cobalt	10	100	10
Copper	10	100	10
Iron	100	1000	100
Lead	10	100	10
Magnesium	100	1000	100
Manganese	10	100	10
Molybdenum	10	100	10
Nickel	10	100	10
Potassium	100	1000	100
Selenium	10	100	10
Silver	10	100	10
Sodium	100	1000	100
Strontium	10	100	10
Thallium	10	100	10
Vanadium	10	100	10
Zinc	10	100	10
Boron	10	100	10
Tin	10	100	10
Titanium	10	100	10
Zirconium	10	100	10

* Levels shown indicate the spike concentration in the final digestate of the aqueous LCS or matrix spike based on the addition of 1.0 mL working spike (7.4) to 100 mL of sample.

** Final soil spike concentration based on the addition of 1.0 mL working spike (7.4) to 1.0 g of sample/100 mL final volume (assumes 100% solids).

TABLE IV. GFAA Soil Matrix Spike and Aqueous LCS Spike Levels

ELEMENT	Stock LCS/MS Standard (mg/L)	Working LCS/MS Standard (ug/L)	Aqueous LCS/ MS Level * (ug/L)	Soil MS Level** (mg/Kg)
Arsenic	400	2000	40	4
Selenium	400	2000	40	4
Lead	400	2000	40	4
Thallium	400	2000	40	4
Antimony	400	2000	40	4
Cadmium	40	200	4	0.4
Chromium	100	500	10	1
Silver	50	250	5	0.5

* Levels shown indicate the spike concentration in the final digestate of the aqueous LCS or matrix spike based on the addition of 1.0 mL working spike (7.5) to 50 mL of sample.

** Final soil spike concentration based on the addition of 2.0 mL working spike (7.5) to 1.0 g of sample/100 mL final volume (assumes 100% solids).

TABLE V. Summary of Quality Control Requirements

QC PARAMETER	FREQUENCY	ACCEPTANCE CRITERIA	CORRECTIVE ACTION
Method Blank	One per sample preparation batch of up to 20 samples.	Refer to determinative SOPs: NC-MT-0002 CORP-MT-0001 CORP-MT-0003	Redigest and reanalyze samples.
Laboratory Control Sample (LCS)	One per sample preparation batch of up to 20 samples.	Refer to determinative SOPs: NC-MT-0002 CORP-MT-0001 CORP-MT-0003	Redigest and reanalyze all samples associated with the LCS.
Matrix Spike	One per sample preparation batch of up to 20 samples.	Refer to determinative SOPs: NC-MT-0002 CORP-MT-0001 CORP-MT-0003	Reprep not required unless preparation error suspected.
Matrix Spike Duplicate	See Matrix Spike	Refer to determinative SOPs: NC-MT-0002 CORP-MT-0001 CORP-MT-0003	See Corrective Action for Matrix Spike.

APPENDIX B
CONTAMINATION CONTROL GUIDELINES

APPENDIX B. 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.

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Page: 1 of 48

STL STANDARD OPERATING PROCEDURE

TITLE: TOXICITY CHARACTERISTIC LEACHING PROCEDURE AND SYNTHETIC PRECIPITATION LEACHING PROCEDURE

(SUPERSEDES: REVISION 1.1, REVISION DATE 10/10/00)

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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 that 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 due to potential analyte loss into the headspace during the bottle extraction.

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 or recombination with the leachate. 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 filtrate 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 solutions generated from these procedures (TCLP, SPLP, deionized water leach).
- 3.2. "Wet Solids" is that fraction of a waste sample from which no liquid may be forced out by pressure filtration.

4. INTERFERENCES

- 4.1. Oily wastes may present unusual filtration and drying problems. If requested by the client and as recommended by EPA (see Figure 3), oily wastes can 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. Alternately, the oil may be subjected to pressure filtration. The portion that passes through the filter will be prepared and analyzed separately as an organic waste. The "wet solid" portion that remains behind on the filter will be subjected to leaching, prepared and analyzed. The results will then be mathematically combined.
- 4.2. Wastes containing free organic liquids (e.g., oil, paint thinner, fuel) usually require dilution prior to analysis to address the matrix interferences. In most instances this results in reporting limits elevated above the TCLP regulatory 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 Section 9 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. Employees must abide by the policies and procedures in the Corporate Safety Manual and this document.
- 5.2. 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.
- 5.3. The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Acetic Acid	Corrosive Poison Flammable	10 ppm-TWA	Contact with concentrated solution may cause serious damage to the skin and eyes. Inhalation of concentrated vapors may cause serious damage to the lining of the nose, throat, and lungs. Breathing difficulties may occur.
Glacial Acetic Acid	Corrosive Poison Flammable	10 PPM-TWA	Contact with concentrated solution may cause serious damage to the skin and eyes. Inhalation of concentrated vapors may cause serious damage to the lining of the nose, throat, and lungs. Breathing difficulties may occur.

TCLP and SPLP Leaching Procedure

Methanol	Flammable Poison Irritant	200 ppm-TWA	A slight irritant to the mucous membranes. Toxic effects exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure may include headache, drowsiness and dizziness. Methyl alcohol is a defatting agent and may cause skin to become dry and cracked. Skin absorption can occur; symptoms may parallel inhalation exposure. Irritant to the eyes.
Sulfuric Acid	Corrosive Oxidizer Dehydrator Poison Carcinogen	1 Mg/M3-TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.
Hydrochloric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Nitric Acid	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.

TCLP and SPLP Leaching Procedure

Methylene Chloride	Carcinogen Irritant	25 ppm-TWA 125 ppm-STEL	Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting and headache. Causes irritation, redness and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degreases the skin. May be absorbed through skin.
Sodium Hydroxide	Corrosive	2 Mg/M3-Ceiling	Severe irritant. Effects from inhalation of dust or mist vary from mild irritation to serious damage of the upper respiratory tract, depending on severity of exposure. Symptoms may include sneezing, sore throat or runny nose. Contact with skin can cause irritation or severe burns and scarring with greater exposures. Causes irritation of eyes, and with greater exposures it can cause burns that may result in permanent impairment of vision, even blindness.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

- 5.4. Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Cut resistant gloves must be worn doing any other task that presents a strong possibility of getting cut. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.
- 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. Turning the jar or bottle sideways rather than tumbling end over end may also reduce the chance of breakage. If sideways tumbling is used, note this change in the logbook comment section.
- 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 hazardous 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, where possible. All samples with pink stickers that read "Caution/Use Hood!" **must** be opened in the hood. Contact the EH&S Coordinator if this is not possible. 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 the EH&S Coordinator and laboratory supervisor.
- 5.11. Due to the potential for ignition, flammability or production of noxious fumes, do not attempt to dry non-aqueous liquid samples in an oven. Use extended drying in a ventilation hood.

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 (2.5 L, with Teflon lid inserts) or 2.5 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 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, 9.0 cm, 4.7 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, or purchase pre-washed filters. 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 Device: Gas-tight syringes, 50 or 100 mL capacity, Hamilton 0158330 or equivalent.
- 6.6. Top loading balance, capable of $0 - 4000 \pm 0.01\text{g}$ (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, 40 mL, with caps and septa.
- 6.11. Glass bottles, 1 liter, with Teflon lid-inserts.
- 6.12. Nalgene plastic bottles or equivalent, 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. 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.

- 7.4. Acetic acid, glacial: concentrated, reagent grade liquid (HOAc).
- 7.6. pH calibration solutions: buffered to a pH of 4, 7, and 10. Commercially available.
- 7.5. TCLP Leaching Fluids

7.5.1. General Comments

7.5.1.1. The pH of both solutions listed below should be monitored daily and the pH probes are to be calibrated prior to use.

7.5.1.2. 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.

7.5.1.3. Additional volumes of extraction fluids listed below may be prepared by multiplying the amounts of acetic acid and NaOH by the number of liters of extraction fluid required.

7.5.2. 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. For 8 L of fluid use 45.6 mL glacial acetic acid and 514 mL 1N NaOH, dilute to 8 L with reagent water. When correctly prepared, the pH of this solution is 4.93 ± 0.05 . The density of TCLP fluid #1 is 0.997 g/mL.

7.5.3. 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. For 8 L of fluid use 45.6 mL glacial acetic acid, dilute to 8 L with reagent water. When correctly prepared, the pH of this solution is 2.88 ± 0.05 . The density of TCLP fluid #2 is 0.997 g/mL.

7.6. Nitric acid, 50% solution: Slowly and carefully add 500 mL concentrated HNO_3 to 500 mL reagent water. Cap and shake to mix well.

7.7. Sulfuric acid / nitric acid (60/40 weight percent mixture) $\text{H}_2\text{SO}_4/\text{HNO}_3$. Cautiously mix 60 g of concentrated sulfuric acid with 40 g of concentrated nitric acid.

7.8. SPLP Leaching fluids

7.8.1. 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.

7.8.2. 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.

7.8.3. 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.

7.8.4. 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.

7.9. 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 $4 \pm 2^{\circ}\text{C}$). Samples should be opened only immediately prior to extraction.

8.4. Samples should be refrigerated to $4 \pm 2^{\circ}\text{C}$ 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 ($4 \pm 2^{\circ}\text{C}$) 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 Start of TCLP Leach	End of TCLP Tumble to Preparation	Start of TCLP Leach or Semi-volatile Prep Extraction 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 TCLP extraction started. (This should be the TCLP extraction date in QuanTims.) Semi-volatile method prep holding time is measured from the day tumbling is complete to the start of method extraction. Subsequent analysis holding times are measured from the date extraction (TCLP or method prep) 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. The Total Elapsed Time is to be used as guidance. If preps are initiated at the last possible moment of a holding time, the elapsed times may be exceeded.

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. 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). ZHE Extraction vessels will be uniquely numbered. Consult the STL QC Program and the individual analysis SOPs for blank acceptance criteria.
- 9.3. 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 or reagent water. Consult the individual analysis SOPs for additional LCS guidance (i.e., spike amounts, spike levels, recovery criteria, etc.).
- 9.4. 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.
- 9.4.1. 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.
- 9.4.2. Consult the individual analysis SOPs for additional guidance on spike compounds and levels.
- 9.5. Corrective Actions
- 9.5.1. Consult the STL QC Program and individual analysis SOPs for corrective action for blanks and LCS
- 9.5.2. 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.

11.1.2. All masses should be recorded to the nearest 0.1 g.

11.2. PRELIMINARY SAMPLE EVALUATIONS (Refer to Flow Chart #1, Appendix D)

11.2.1. 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. Recommended TCLP Leachate Volume

Analysis	TCLP Required Volume (mL)	SPLP Required Volume (mL)
Volatiles	3 x 40	3 x 40
Semi-volatiles	500	1000
Pesticides	500	1000
Herbicides	500	1000
Metals	300	300

11.2.1.1. For TCLP and SPLP samples used for matrix spike and matrix spike duplicate analysis, two to three times the listed volumes are required.

11.2.2. Sample Description (determine sample matrix)

11.2.2.1. Solid - If the waste will obviously yield no free liquid when subjected to pressure filtration, then proceed to Section 11.2.5 or 11.4 (Bottle Extraction Procedure or ZHE Procedure).

11.2.2.2. Liquid - If the sample is a monophasic liquid, proceed to Section 11.2.3 (Percent Solid Determination).

11.2.2.3. Multiphasic – The sample has discernible layers (liquid/liquid or liquid/solid). If more than one container of multi-phasic materials is received from the field, each container might show different amounts of each phase. Consult client to determine sample selection alternatives (composite all sample containers, select one, resample, etc.) if this occurs.

11.2.3. Solids Determination

11.2.3.1. Determine Type of Filtration Apparatus and Process

11.2.3.1.1. 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 (ZHE Extraction Procedure, Volatile Constituents). Otherwise, continue with Section 11.2.3.2. The aliquot of sample used here cannot be used again for the ZHE extraction.

11.2.3.1.2. If the sample is mostly a non-viscous liquid (water or non-viscous organic liquid) of low solids content (expected to be < 0.5%), vacuum filtration should be used initially. Proceed to determination of percent dry solids (Section 11.2.3.2)

11.2.3.1.3. If the sample is viscous (sludge, oil, or is expected to have solids content > 0.5%), use pressure filtration. Proceed to determination of wet solids (Section 11.2.3.3).

11.2.3.2. Determination of percent dry solids

11.2.3.2.1. Measure and record the weight of the filter. Load the filter into the filter holder and assemble vacuum filter apparatus.

- 11.2.3.2.2. Homogenize the waste, then transfer 100 g subsample to a glass beaker. Record the sample weight in the percent dry solids section of the logbook.
- 11.2.3.2.3. Turn on vacuum source. Transfer the sample to the vacuum filtration device attempting to spread the waste sample evenly over the surface of the filter. Be sure to transfer all particulates from the beaker to the filter. Use a reagent water rinse if necessary.
- 11.2.3.2.4. Once all liquid has been pulled through the filter, remove the filter with the wet solids from the vacuum filtration apparatus.
- 11.2.3.2.5. Dry the filter and solid phase at $100 \pm 20^\circ \text{C}$ for approximately 15 minutes.
- 11.2.3.2.6. Remove the filter from the oven and allow to cool in a desiccator.
- 11.2.3.2.7. Weigh and record the dry weight of filter + particulates.
- 11.2.3.2.8. Calculate and record the percent dry solids.
- 11.2.3.2.9. If the percent dry solids is $\geq 0.5\%$, repeat the drying step. Weigh and record the second filter + particulates dry weight. If the two weighings do not agree within 1%, perform additional drying and weighing until successive weighings agree within 1%.
- 11.2.3.2.10. If the dry solids result is $\geq 0.5\%$, proceed to Section 11.2.3.3 using a fresh wet portion of the multiphase waste.
- 11.2.3.2.11. If the percent solids result is less than 0.5%, discard the solid phase. No leaching will be necessary. Filter sufficient sample with either the pressure filtration system or ZHE system as described in Sections 11.3 and 11.4. The filtrate is the TCLP leachate.
- 11.2.3.3. Determination of wet solids
- 11.2.3.3.1. Assemble the pressure filtration apparatus (use blunt forceps to handle the 0.6 to 0.8 μm filter membrane).

- 11.2.3.3.2. Homogenize the waste, transfer a minimum of a 100 mL subsample to the glass beaker. Measure and record the gross weight (logbook column A).
- 11.2.3.3.3. Measure and record the tare weight of the filtrate collection bottle (logbook column D).
- 11.2.3.3.4. 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 glass beaker and any residual sample (logbook column B).
- 11.2.3.3.5. Calculate and record the net weight of sample used for testing (logbook column C).
- 11.2.3.3.6. Slowly apply gentle pressure 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.
- 11.2.3.3.7. If necessary, 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 do not pass through the filter are classified by the method as a solid.
- 11.2.3.3.8. Remove the filtrate collection bottle, weigh and record the gross weight (logbook column E).
- 11.2.3.3.9. Calculate and record the net weight of filtrate (logbook column F). This result will be used in the percent solids calculation.
- 11.2.3.3.10. Pour the filtrate into an appropriately sized graduated cylinder. Measure and record the volume of the filtrate in the logbook.

11.2.3.3.11. Retain the filtrate for possible recombination with the leachate in Section 11.3.6. Retain the filter and wet solids for the leaching in Section 11.3.

11.2.3.3.12. For multiphase sample preparations, calculate the total weight of wet solids and record the result in logbook column G.

11.2.4. Particle-size Reduction for Fluid Selection

11.2.4.1. The subsample used for fluid selection must consist of particles less than approximately 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.

11.2.4.2. Surface area exclusion - size reduction is not required if the sample surface area is greater than or equal to 3.1 cm² per gram.

11.2.4.3. If the sample contains particles greater than approximately 1 mm in diameter, crush, cut, or grind the solids to the required size.

11.2.4.4. Consult a supervisor or manager when dealing with unusual sample matrices (e.g., wood, cloth, metal, brick).

11.2.5. Determination of Appropriate Extraction Fluid

11.2.5.1. 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.

11.2.5.2. 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.

11.2.5.3. For SPLP, refer to Section 7.8 for fluid selection. Record the fluid type in the logbook.

11.2.5.4. The TCLP leaching fluid for all volatiles is TCLP Fluid #1.

11.2.5.5. TCLP leach fluid determination for non-volatile analytes

11.2.5.5.1. Calibrate the pH meter with fresh buffer solution in accordance with the pH SOP.

11.2.5.5.2. Weigh out a 5.0 ± 0.1 g subsample (less than 1 mm particle size) of the solid phase into a glass container, and record in the logbook. Note: If sample quantity is limited, consult supervisor or manager.

Note: Many multiphase samples have limited solids quantity . In these instances use a 5 g aliquot of the whole sample. Document this difference in the logbook comment section.

11.2.5.5.3. Add 96.5 ± 1.0 mL of reagent water, cover with a watchglass, and stir for 5 minutes.

11.2.5.5.4. Measure and record the pre-test sample pH in the logbook.

Note: To avoid damaging a glass pH probe when organic liquid is present, use narrow range pH indicator paper or an ISFET pH meter.

11.2.5.5.5. If the pH is less than or equal to 5.0, use TCLP Fluid #1.

11.2.5.5.6. If the fluid pH is greater than 5.0, add 3.5 mL 1 N HCl. Slurry the sample briefly. Clip thermometer to the inside edge of one sample in each pre-test sample group to monitor the temperature. All samples in the group must go on the hot plate at the same time in order for the temperature of the one monitored sample to represent the others. Heat to 50°C and maintain for 10 minutes.

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.

11.2.5.5.7. Cool to room temperature.

11.2.5.5.8. Measure and record the pH immediately after the sample has reached room temperature.

11.2.5.5.8.1. If the pH is less than or equal to 5.0, use TCLP Fluid #1. Record the buffer in the logbook.

11.2.5.5.8.2. If the pH is greater than 5.0, use TCLP Fluid #2.
Record the buffer in the logbook.

11.2.6. For samples requiring analysis for semi-volatile organics, pesticides, herbicides or metals proceed to Section 11.3.

11.2.7. 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. 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 cm² per gram. If particle size reduction was required, record this in comments column in logbook.

11.3.1.1. 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. Determination of particle size reduction tools should take into account the requested analytes (e.g. avoid chromium steel tools when TCLP metals have been requested). Bricks, rocks, or other solids amenable to grinding may 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.

11.3.2. Determine the minimum total volume of solid phase leachate that needs to be generated. Refer to Section 11.2.1.

11.3.3. Use 100 g of solid unless sample quantity is limited. If limited sample, divide the total volume of solid phase leachate required by 20 to determine the minimum mass of solid phase required for leaching. Round this mass UP to the nearest 5g. Client must be notified if less than 100 g of solid material is used.

Note: Solid phase material is often in limited quantity from multiphase samples. Generally all the *solid* phase material and the filter from Section 11.2.3.3.11 are transferred to the leaching bottle

11.3.4. Weigh the required mass of solid phase into an appropriate bottle (plastic for metals only, glass for all others) and **slowly** add 20 times its mass of appropriate leaching fluid (e.g., 100 g of sample would require 2000 mL of leaching fluid). Record the weight of the sample aliquoted for the extraction. Record the volume of extraction fluid added in the logbook if other than 2000 mL.

11.3.5. 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 $23 \pm 2^{\circ}\text{C}$. Record the rotary agitator I.D. and the date and time extraction is started and completed in the logbook.

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

11.3.6. After tumbling in the rotary agitator is completed, remove the bottle and allow the solids to settle. Record the date and time the extraction is completed in the logbook. If sample was multiphase with an initial filtrate, drop a few drops of the filtrate (with a disposable glass pipette) into the extraction bottle and observe whether the filtrate is insoluble or forms a precipitate with the leachate. If so then the filtrate is not compatible with the leachate and must be bottled and analyzed separately. The results are normally mathematically recombined (Section 12.1.2). If the filtrate is compatible with the leachate (ie completely soluble) then pour the entire filtrate into the leachate bottle, recap and mix. Proceed with the leachate filtration step in the next section.

11.3.7. Filter the sample using pressure filtration by filtering through a new glass fiber filter. 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.

11.3.8. Measure the pH of the TCLP leachate and record in the logbook. (Use narrow range pH paper or ISFET pH meter to measure the pH of oily samples as a glass pH probe may be damaged.)

11.3.9. 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.

11.3.10. Immediately preserve the leachate as follows:

Metals pH < 2 w/ HNO₃ for aqueous filtrates and leachates
(do not acidify oils and other non-aqueous liquids)

All others Refrigerate to 4 ± 2 °C

Note: Refer to Section 8.6 if precipitation occurs upon preservation.

11.3.11. Label each sample with the appropriate information and submit to the appropriate analytical groups for prep and analysis. For multiphase samples requiring mathematical recombination provide copies of the TCLP preparation logbook sheets to the sample preparation and analysis groups. Most mathematically recombined samples will require data entry for the filtrate and leachate portions as well as for the mathematically recombined results. Contact the project manager to ensure the proper sample login is completed.

11.4. ZHE EXTRACTION PROCEDURE: VOLATILE CONSTITUENTS (Refer to Flow Chart #3, Appendix D)

11.4.1. 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, herbicides and semi-volatile organics).

11.4.2. 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.

11.4.3. Install new O-rings and adjust the ZHE piston in the ZHE body to the appropriate height (slightly moisten the O-rings with leaching fluid if necessary).

11.4.4. 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 cm² per gram. If particle size reduction was required record this in the comments column of the logbook.

Note: To minimize loss of volatiles, samples for volatiles that require particle size reduction should be kept in sample storage (at 4°C) 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 11.3.1.

11.4.4.1. 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 may be subcontracted out for particle size reduction (Contact PM).

11.4.5. Homogenize and transfer an appropriate size subsample of the waste into the ZHE and record the mass in the logbook.

11.4.5.1. For wastes that are solid, a 25 g sample is used.

11.4.5.2. 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.

11.4.5.3. If the sample has $\geq 0.5\%$ solids and has non-volatile TCLP/SPLP requested, the appropriate sample size should be estimated based on the wet solids content determined in Section 11.2.3.3. If ZHE only, use visual wet solids estimate to sample subaliquot.

Note: For wastes containing greater than 0.5% wet or dry solids, 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 11.2.3.3 may differ from the ZHE filtration solids due to sample variability or differences in the filtration apparatus.

11.4.6. Carefully place the glass fiber filter between the support screens and secure to the ZHE. Tighten all the fittings.

11.4.7. 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.

11.4.8. If the waste is solid, slowly increase the pressure to a maximum of 50 psi to force out as much headspace as possible and proceed to Section 11.4.13.

11.4.9. If this is a mutliphase sample, 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.

11.4.10. Assemble a syringe and place the plunger in all the way. Attach the pre-weighed syringe to the liquid inlet/outlet valve and open the valve. Record the tare weight of the collection syringe in column D of the logbook. .

11.4.11. 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, weigh, record weight in column E and filtrate volume in the logbook. Return to Section 11.4.10.

11.4.12. 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. Close the valve and discontinue gas pressure. Remove the collection device and record the total weight of the collection device with filtrate in column E and filtrate volume in the logbook. Transfer the filtrate to VOA vials and label appropriately. Calculate the weight of filtrate collected and record in column F in the logbook.

Notes: If the original waste contained less than 0.5% solids (Section 11.2.3.2), this filtrate is defined as the TCLP leachate and you may proceed to Section 11.4.22. Otherwise, save the vials by storing at 4°C under minimal headspace conditions, for recombination as in Section 11.4.21.

The material remaining in the ZHE is defined to be the “solid” phase. Calculate the weight of the solid phase and record in column G of the logbook by subtracting the weight of the filtrate from the weight of the sample.

11.4.13. Determine the amount of buffer to use. Solid samples use 500 mL of leach fluid (20 X 25 g). For multiphase samples use the wet solids (column G) amount and multiply by 20. Record the leach fluid volume in column H of the logbook.

Note: The TCLP ZHE prep uses only TCLP fluid #1; the SPLP ZHE prep uses only SPLP fluid #3.

11.4.14. 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.

- 11.4.15. 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.
- 11.4.16. 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.
- 11.4.17. Pressurize the ZHE to 5-10 psi. If the ZHE appears to be leaking, follow the corrective action protocols recommended by the manufacturer and repeat the analysis.
- 11.4.18. 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.
- 11.4.19. 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 is recorded using a continuous temperature monitor.
- 11.4.20. Confirm that the pressure of 5-10 psi was maintained throughout the leaching. If it was NOT maintained, return to Section 11.4 and repeat the leachate with a new aliquot of sample.
- 11.4.21. If there is an initial liquid filtrate (Sec 11.4.12) determine if it is compatible with the leachate if the filtrate has not been previously tested (Sec. 11.3.6).
- 11.4.21.1. Remove the plunger from the syringe and attach the barrel to the ZHE vessel. Open the outlet valve and pressurize as necessary to transfer about 1 mL of leachate into the syringe. Close the outlet valve.
- 11.4.21.2. With a glass pipette transfer a few drops of initial filtrate into the open syringe barrel. Formation of separate layers or a precipitate indicates the filtrate and leachate are not compatible. Bottle the filtrate for separate preparation and analysis. The results are normally mathematically recombined.
- 11.4.21.3. If the filtrate is compatible gently pour the remainder of the filtrate into the syringe barrel. Install the plunger. Bleed any pressure in the ZHE piston. Open the inlet/outlet valve and depress the syringe plunger to inject the filtrate into the ZHE vessel. Do not inject the air bubble (if present) from the syringe.

11.4.21.4. Close the valve and rotate a few times to mix. Proceed with leachate filtration as described in the next section.

11.4.22. Attach an empty syringe to the outlet valve. Open the valve and pressurize the piston to expel the leachate from the ZHE vessel. Following collection, store the TCLP leachate in 2 or 3 40-mL VOA vials with minimal headspace at 4 ± 2 °C and prepare for analysis as soon as possible using the appropriate organic analysis procedure (see Section 16.3).

11.4.23. If the individual phases are analyzed separately, combine the results mathematically by using the recombination calculation in Section 12.1.2. . Provide copies of the TCLP preparation logbook sheets to the sample preparation and analysis groups. Most mathematically recombined samples will require data entry for the filtrate and leachate portions as well as for the mathematically recombined results. Contact the project manager to ensure the proper sample login is completed.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Calculations

12.1.1. Calculation of weight of extraction fluid to use:

Volume of extraction fluid = 20 X weight of wet solids to be extracted

12.1.2. Mathematical recombination of analytical results:

$$\text{Final Analyte Concentration} = \frac{(V_1 \times C_1) + (V_2 \times C_2)}{V_1 + V_2}$$

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 zero for the “ND” phase and the positive value for the other phase to calculate the combined result. This will produce a minimum known concentration. Alternatively, at client request, the maximum possible concentration can be calculated by using the reporting limit for the “ND” phase rather than zero. The combined reporting limit is based on the reporting limit for both phases

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 NCM form. Some examples of such anomalies are:

12.2.4.1. Sample was monolithic - particle size reduction not possible due to nature of matrix.

12.2.4.2. Insufficient sample - less than the required 100 g minimum was available.

12.3. REVIEW REQUIREMENTS

12.3.1. Review all applicable holding times. If a holding time was exceeded, confirm that a holding time violation was properly documented in an NCM.

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 to demonstrate that lead is less than the TCLP limit.

13. 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.

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. All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for “Waste Management and Pollution Prevention.”

15.2. The following waste streams are produced when this method is carried out.

15.2.1. Acidic waste from sample extract. This waste is collected in the laboratory in a designated container identified as "Acid Waste".

15.2.2. Buffer solutions. This waste can be poured down the drain with copious amounts of water.

15.2.3. Solid waste from sample extract, solid sample waste and used filter paper from the sample filtration step. This waste is disposed of in a designated container identified as “Solid Waste.”

15.2.4. Flammable solvent waste and remaining TCLP extracts. This waste is disposed of in a flammable liquid solvent container identified as "Mixed Flammable Solvent Waste".

15.2.5. Glassware contaminated with acidic sample residue. Broken or unusable glassware is disposed of in a designated container identified as "Solid Waste." Glassware used in this test method is washed per the Glassware Washing SOP.

16. REFERENCES

16.1. Method 1311, Toxicity Characteristic Leaching Procedure, Revision 0, July 1992, SW-846 Final Update I.

16.2. Method 1312, Synthetic Precipitation Leaching Procedure, Revision 0, November 1994, SW-846 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, Quality Control Program

16.3.5. CORP-IP-0003NC: Acid Digestion of Aqueous Samples by SW846 and MCAWW 200 Series Methods.

16.3.6. CORP-MT-0001NC: Inductively Coupled Plasma-Atomic Emission Spectroscopy, Spectrometric Method for Trace Element Analysis, Method 6010B and Method 200.7.

16.3.7. CORP-MT-0003NC: Graphite Furnace Atomic Absorption Spectroscopy, (Thallium only)

16.3.8. CORP-MT-0005NC: Preparation and Analysis of Mercury in Aqueous Samples by Cold Vapor Atomic Absorption, SW-846 7470A and MCAWW 245.1.

16.3.9. CORP-MS-0002NC: Determination of Volatile Organics by GC/MS based on Methods 8260B, 624, and 524.2.

16.3.10. CORP-MS-0001NC : GC/MS Analysis Based on Method 8270C and 625.

16.3.11. CORP-GC-0001NC: Gas Chromatographic Analysis Based on Methods 8000B, 8021B, 8081A, 8082, 8151A, 8310, 610, and 8141A.

16.3.12. CORP-OP-0001NC: Extraction and Cleanup of Organic Compounds from Waters and Soils, Based on SW846 3500 Series, 3600 Series, 8151A and 600 Series Methods.

17. MISCELLANEOUS

17.1. Modifications/Interpretations from Reference Methods

17.1.1. Section 11.2: Preliminary Evaluations. Section 7.1 of the source method 1311 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. Sections 11.3.6 and 11.4.21: 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.

17.1.3. 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.

17.1.4. Section 11.2.5.5.8.1: 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.

17.1.5. 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 LQM 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.

17.1.6. 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

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.

APPENDIX B-FIGURES

APPENDIX A

TABLES

APPENDIX B-FIGURES

Table 3 - Toxicity Characteristic Analytes and Regulatory Levels (Final Rule)	mg/L
Contaminant	
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

APPENDIX B

FIGURES

APPENDIX B-FIGURES

Figure 1 & 2 - Rotary Agitation Apparatus and Zero Headspace Extraction Vessel (ZHE)

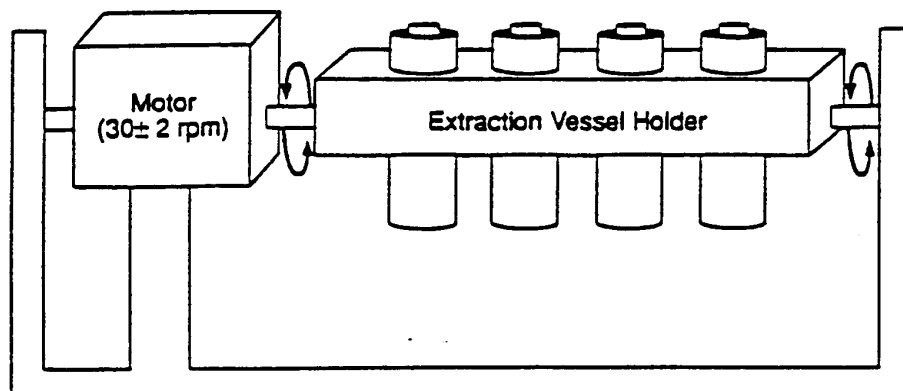
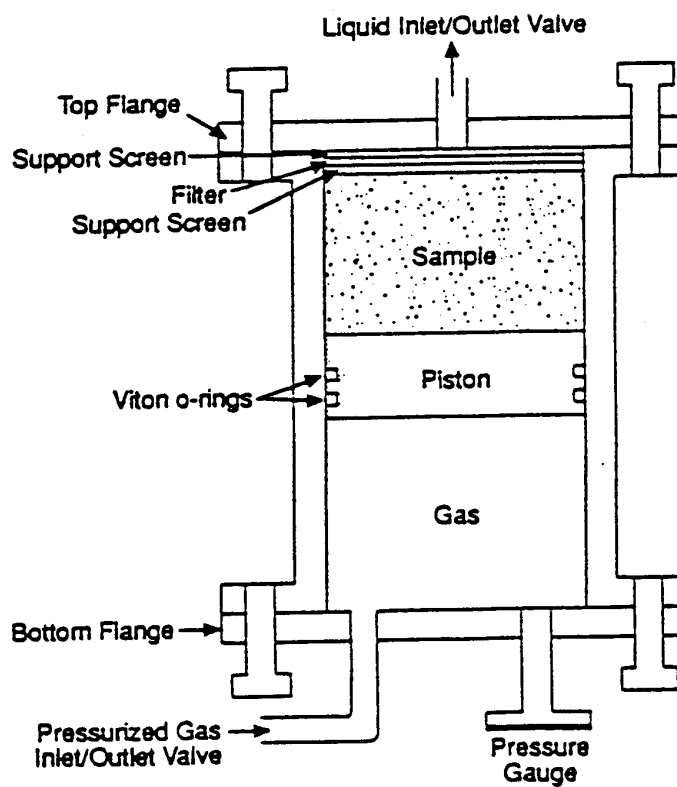


Figure 1. Rotary Agitation Apparatus



APPENDIX B-FIGURES

Figure 3 - US Environmental Protection Agency Memorandum #35, Page 1



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

OFFICE OF
SOLID WASTE AND EMERGENCY RESPONSE

MEMORANDUM # 35

DATE: June 12, 1992
SUBJECT: Notes on RCRA Methods and QA Activities
From: Gail Hansen, Chief *Gail Hansen*
Methods Section (OS-331)

This memo addresses the following topics:

- o 1992 Symposium on Waste Testing and Quality Assurance
- o SW-846 Update
 - Final Rule for January 23, 1989 Proposed Rule
 - Notice, Proposed Rulemaking for the Second Update to the Third Edition
- o Chlorofluorocarbon 113 (CFC-113) Solvent Replacement Update
- o Environmental Monitoring Methods Index (EMMI)
- o Sampling Work Group Formation
- o MICE Update
- o Oily Waste Analysis
- o Electronic SW-846 Availability.

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

Logbook Pages

TCLP/SPLP ZHE Logbook

STL NORTH CANTON ZHE LOGBOOK

Sample Number	Extraction Vessel ID	Matrix	Sample Wt (g)	Extraction Buffer ID	Date On	Time On	Date Off	Time Off	Tumbler ID	Tumbler Speed 30±2 rpm	Extraction Fluid ID	Initial ZHE Pressure	Final ZHE Pressure	Comments

STL NORTH CANTON ZHE LOGBOOK

N:\QAQC\SOPS\Inorgprep\CPIP0004NC TCLP_SPLP.doc 09/28/00

APPENDIX C – Logbook Pages

TCLP/SPLP Bottle Extraction LogbookSOP No.: NC-IP-0005**STL NORTH CANTON TCLP LOGBOOK**

				Pre-Test			% Dry Solids				Leach Start			Leach Finish							
Pre-Prep Batch	Sample Number	Parameters	Matrix	Sample Wt (g)	pH after water	pH after heating	Sample Wt (g)	Filter Wt (g)	Filter + Particulate s Wt (g)	% Dry Solids	Sample Wt (g)	Buffer # / ID	Date On	Time On	pH On	Date Off	Time Off	nH Off	Tumbler ID	Initials	Comments
		M B P H																			
		M B P H																			
		M B P H																			
		M B P H																			
		M B P H																			
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		M B P H																			
		M B P H																			

SOP No.: NC-IP-0005

STL NORTH CANTON TCLP LOGBOOK

	A	B	C	D	E	F		G	H		
Sample Number	Weight of Container + Sample (g)	Weight of Container + Residue (g)	Difference (A – B) Sample Weight (g)	Weight of the Filtrate Bottle (g)	Weight of the Filtrate bottle + Filtrate(g)	Difference (E – D) Filtrate Weight (g)	Volume of Filtrate* (mL)	Difference (C – F) Wet Solids Weight (g)	G x 20 Buffer Amount (mL)	Initial s	Comments

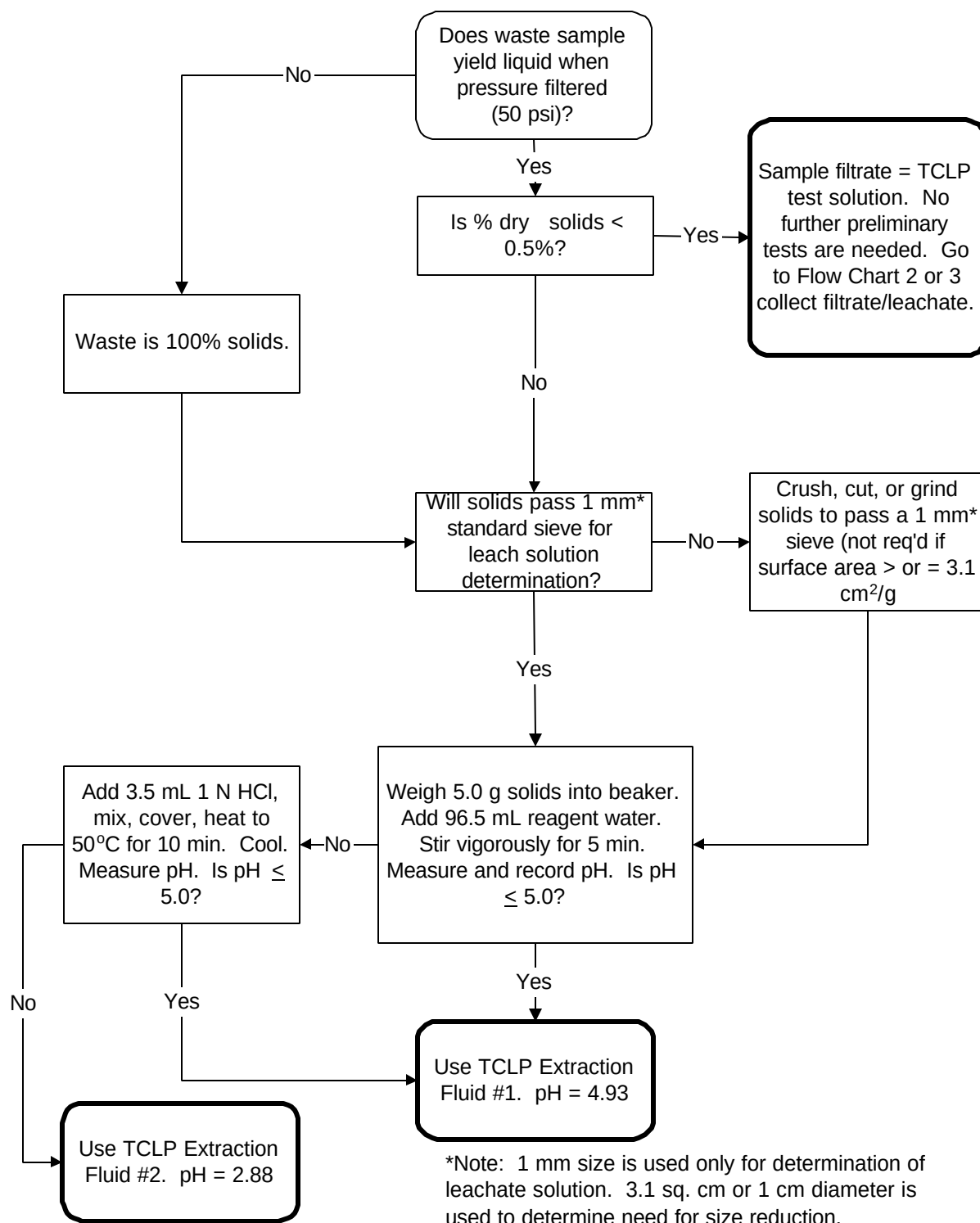
* Filtrate volume only needed when filtrate is incompatible with leachate

APPENDIX D - FLOW CHARTS

APPENDIX D

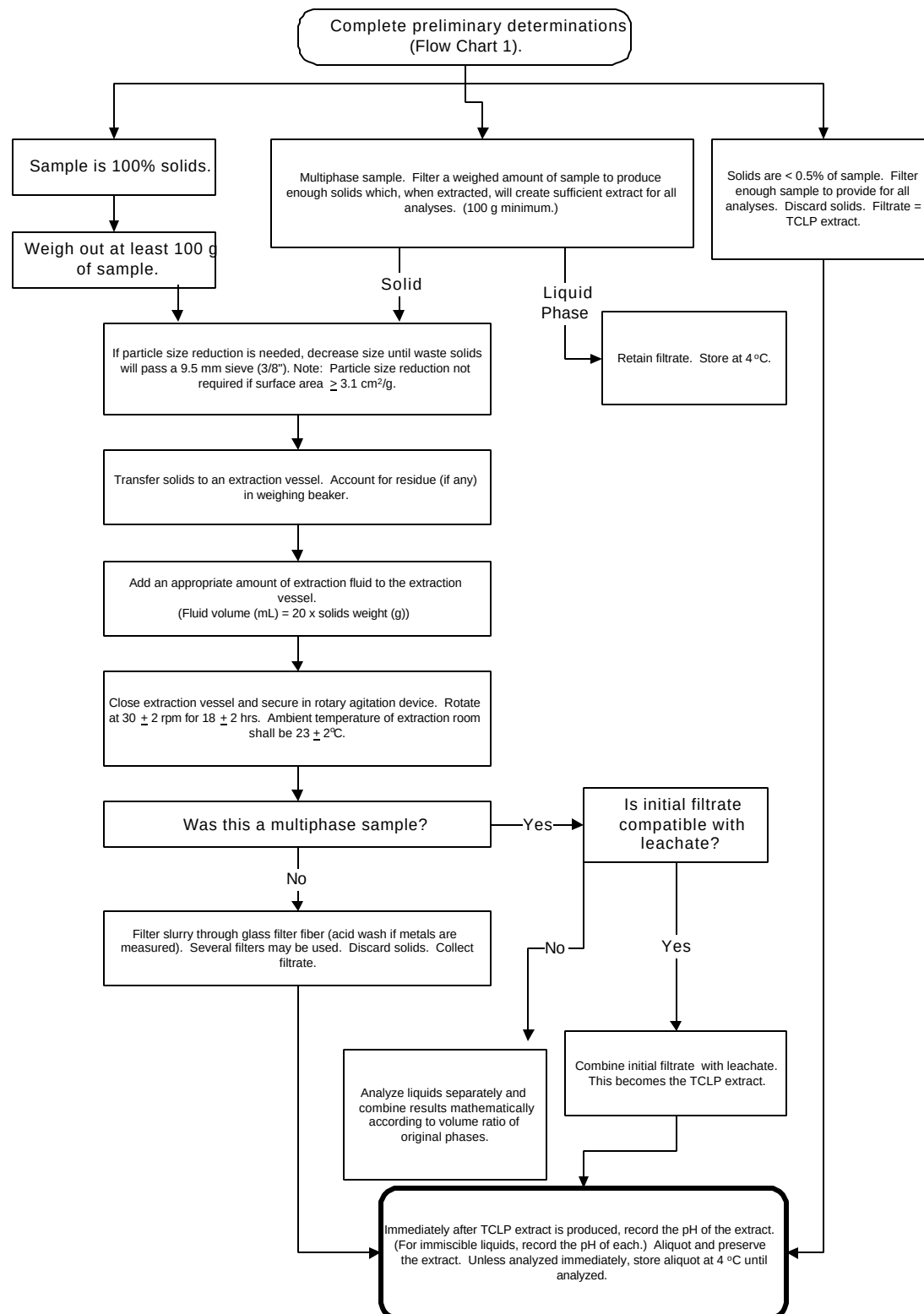
FLOW CHARTS

APPENDIX D - FLOW CHARTS

**Flow Chart 1. Preliminary Sample Evaluation
(Section 11.2)**

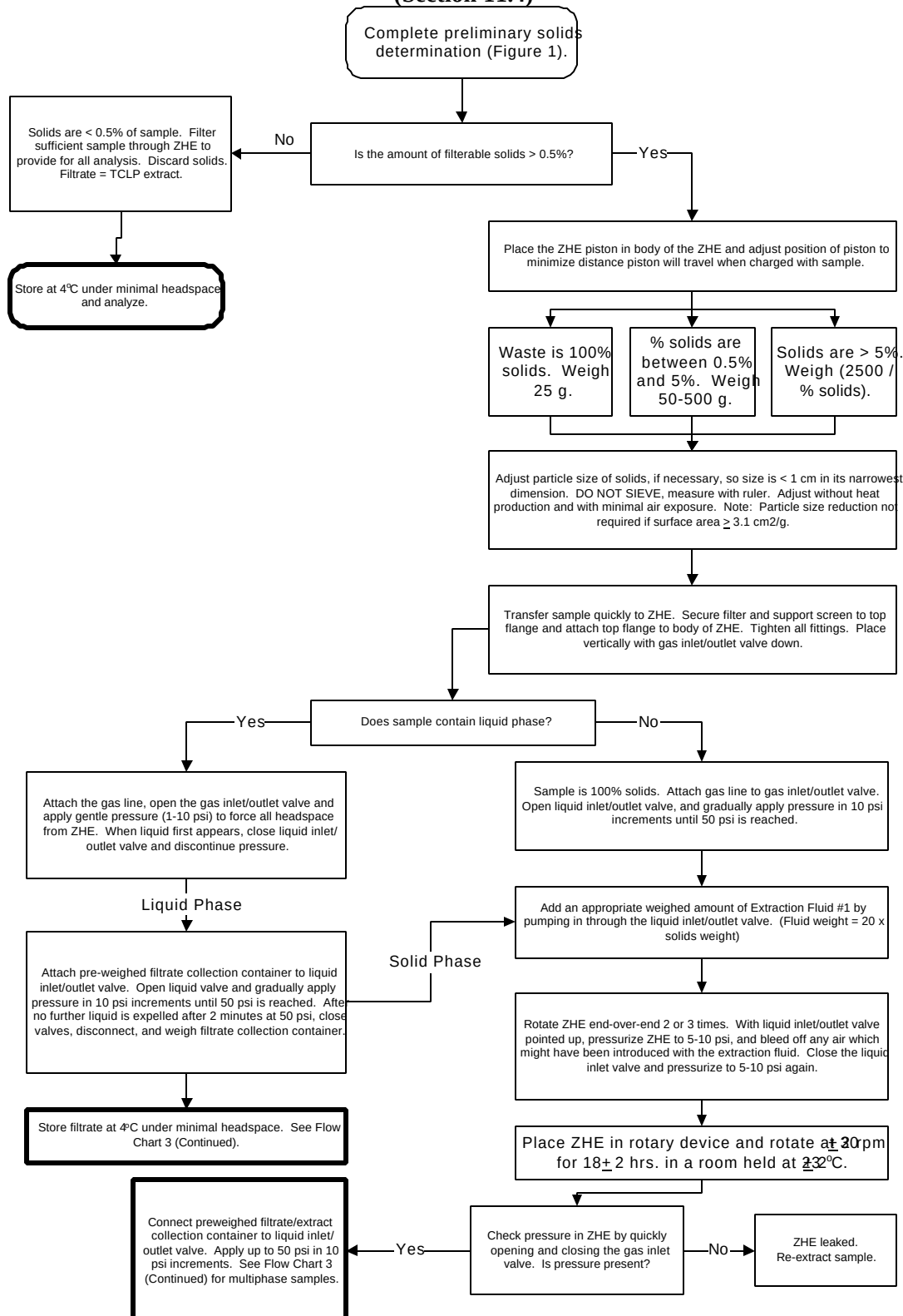
APPENDIX D - FLOW CHARTS

**Flow Chart 2. Bottle Extraction, Non-Volatile Constituents
(Section 11.3)**

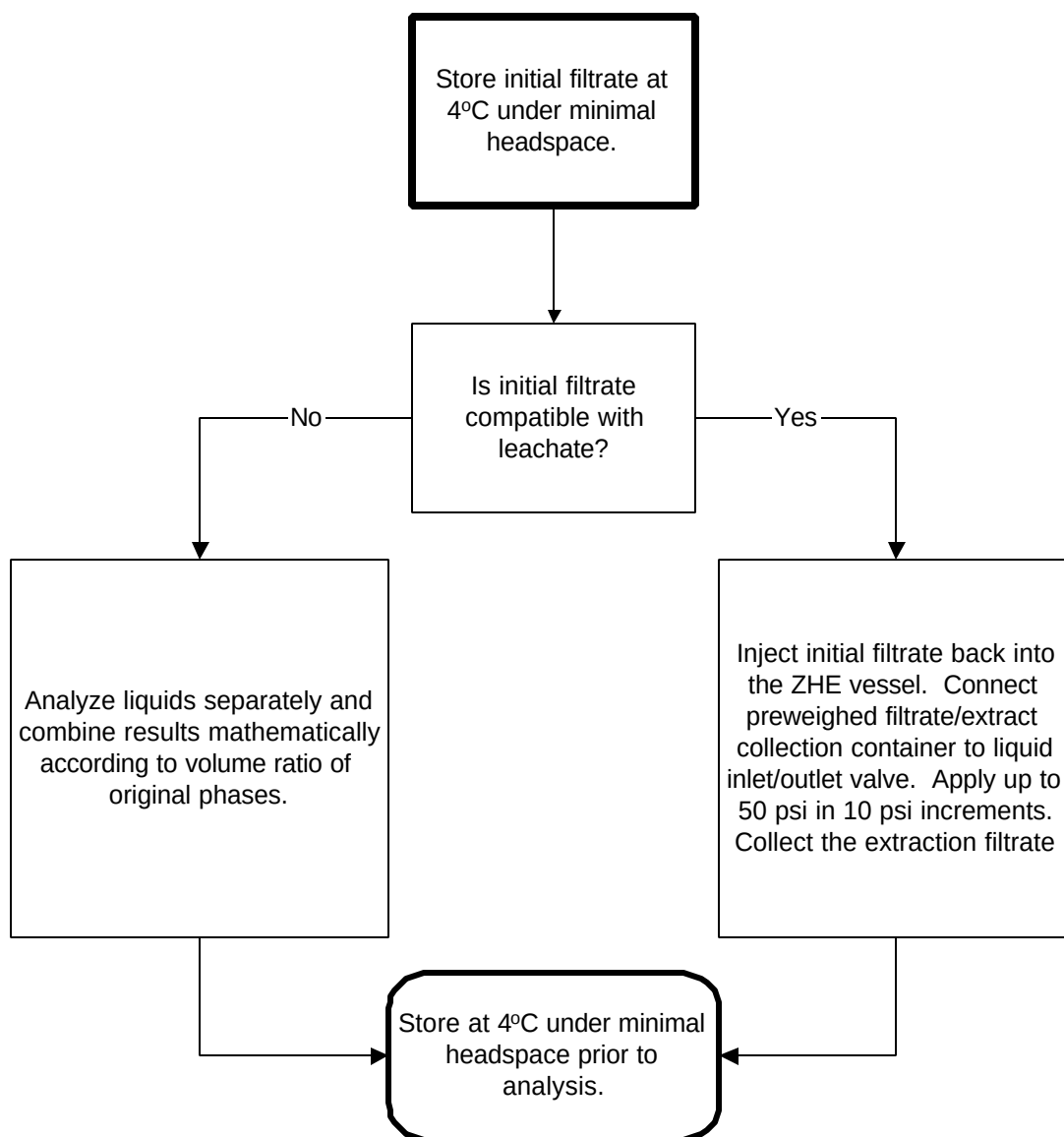


APPENDIX D - FLOW CHARTS

**Flow Chart 3. ZHE Extraction, Volatile Constituents
(Section 11.4)**



APPENDIX D - FLOW CHARTS

**Flow Chart 3. ZHE Extraction
(Continued)**

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Implementation Date: 1/22/04

SOP No. CORP-MT-0001INC

Revision No. 3.4

Revision Date: 01/08/04

Page 1 of 54

STL NORTH CANTON 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 3.3, REVISION DATE (12/05/01))

Approved by:	<u><i>Patrick O'M</i></u>	<u>11/12/04</u>
		Date
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	Laboratory Manager	Date
Approved by:	<u><i>Mark L. Bruce</i></u>	<u>1/22/04</u>
	Technical Director	Date

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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.
- 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, biological, 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.
- 1.5. State-specific requirements may take precedence over this SOP for drinking water sample analyses.
- 1.6. The applicable LIMS method codes are QO (6010B), QM (6010B Trace), AS (200.7), JI (200.7 Trace). The Trivalent Chromium method code is GU.

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 CORP-IP-0002NC, Acid Digestion of Soils, SW846 Method 3050B and CORP-IP-0003NC, Acid Digestion of Aqueous Samples by SW846 and MCAWW 200 Series Methods 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 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 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. Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual and this document.
- 5.2. Eye protection that protects against splash, 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 following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Nitric Acid	Corrosive Oxidizer Poison	2 ppm-TWA 4-ppm STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Hydrochloric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
1 – Always add acid to water to prevent violent reactions			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

- 5.3.1. The plasma emits strong UV light and is harmful to vision. **NOTE: AVOID looking directly at the plasma.**
- 5.3.2. 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. All work must be stopped in the event of a known or potential compromise to the health and safety of a STL North Canton associate. The situation must be reported **immediately** to a laboratory supervisor.

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 North Canton 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. 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.
- 7.3. Concentrated nitric acid (HNO_3), trace metal grade or better.
- 7.4. Concentrated hydrochloric acid (HCl), trace metal grade or better.
- 7.5. 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.
- 8.3. Soil samples do not require preservation but must be stored at $4^\circ\text{C} \pm 2^\circ$ 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
 - 9.1.1. Prior to analysis of any analyte using either Method 200.7 or Method 6010B, the following requirements must be met.
 - 9.1.2. Instrument Detection Limit (IDL) - The IDL for each analyte must be determined for each analyte wavelength used for 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 blank solution, 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 North Canton reporting limit. The CLP IDL procedure can be used for this method.

- 9.1.3. Method Detection Limit (MDL) - An MDL must be determined for each analyte prior to the analysis of any client samples. Refer to STL North Canton SOP NC-QA-0021 for details on MDL analysis and criteria.
- 9.1.4. Linear Range Verification (LR) - The linear range must be verified every 6 months on at least 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 verify the linear range limit must be analyzed during a routine analytical run and must read within 5% of the expected value.

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.

- 9.1.5. 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 ICP instrument manual for specific procedures to be used in setting background correction points.
- 9.1.6. 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 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 $\pm$ the RL as defined in Tables I, IA or II. For elements with a reporting limit 10 ug/L or less, the signal should be $\pm$ 2X the RL. 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 actual 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. Additional spectral interference is present from easily ionizable elements such as potassium and sodium in axial viewing instruments.

9.1.7. Rinse Time Determination - Rinse times must be determined upon initial set-up of an ICP instrument. To determine the appropriate rinse time for a particular ICP system, the linear range verification standard (see 9.1.4) 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 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 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.
- 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. Unless in-house control limits are established, a control limit of 80 - 120% 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% and the sample results are < RL, the data may be reported with qualifiers. Such action 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, MSB (i.e., not calculated). Two other narrative notes for metals analyses: Matrix spike/spike duplicate spike recovery/recoveries was/were outside the acceptance limits of some analytes. The acceptable LCS analysis data indicated that the analytical system was operating within control and this condition is most likely due to matrix interference. See the Matrix Spike Report for the affected analytes which will be flagged with N. Matrix spike/spike duplicate relative percent difference (RPD) exceeded the acceptance limits for some analytes. The imprecision may be attributed to sample heterogeneity. See the Matrix Spike Report for the affected analytes, which will be flagged with *.
- 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 and the data is flagged.
- 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 11.8 or 11.11 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 and at the end of the sample run. The CCV is 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 11.8 or 11.11 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, all affected samples will be re-analyzed with valid CCV/CCB pairs. (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 North Canton 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 interferences 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 11.10 or 11.13 for required run sequence.)
- 9.8.2. The ICSAB results for the interferences must fall within 80 - 120% of the true value. If any ICSAB interference 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 $\mu\text{g/L}$ must fall within the STL North Canton guidelines of $\pm 2x$ RL from zero. ICSA results for the non-interfering elements with RLs > 10 $\mu\text{g/L}$ must fall within the STL North Canton guidelines of $\pm 1x$ RL from zero. If the ICSA results for the non-interfering elements do not fall within $\pm 2x$ RL (RL ≤ 10) or $\pm 1x$ RL (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 $\pm 2x$ 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 $\pm 2x$ 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. CRI - To verify linearity near the RL for ICP analysis, a CRI standard is run at the beginning of each sample analysis run. Additionally, some projects may require CRI analysis at the end of the run. (See Section 11.10 or 11.13 for required run sequence.) Evaluate associated samples based upon advisory limits of +/- 50% of true value.

Note: The custom STL North Canton CRI mix contains most analytes at a level near the standard lab reporting limit.

Note: For certified Ohio drinking water analysis, the CRI concentration must be at or below the reporting limit and must recover at $\pm 30\%$ of true value.

- 9.10. 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 C for specific MSA 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). Refer to the instructions in Appendix G.
- 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 Appendix G for 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 two exposures 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 9.1.5 it can be demonstrated that a shorter rinse time may be used.
- 11.4. 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.
- 11.5. 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.
- 11.6. To facilitate the data review and reporting processes it is strongly recommended that all necessary dilutions be performed before closing out the instrument run.
- 11.7. 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	10	10
SW846 3005	2	5

SW846 3010	6	5

The following procedural guidelines must be followed when using an internal standard:

11.7.1. Typically used internal standards are: yttrium. (Note: Any element can be used that is not typically found in environmental samples at a high rate of occurrence.)

11.7.2. 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.

11.7.3. 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.

11.7.4. The internal standard raw intensity counts must be printed on the raw data.

11.7.5. 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). The instrument automatically adjusts sample results based on comparison of the internal standard intensity in the sample to the internal standard intensity at calibration.

11.7.5.1. If the internal standard counts fall within $\pm 30\%$ of the counts observed in the ICB then the data is acceptable.

11.7.5.2. If the internal standard counts in the field samples are more than $\pm 30\%$ higher than the expected level, the field samples must then be diluted and reanalyzed.

11.8. The following analytical sequence must be used for Methods 6010B and 200.7:

Instrument Calibration

ICV

ICB

CRI

ICSA

ICSAB

7 samples

CCV

CCB

10 samples

CCV

CCB

Repeat sequence of up to 10 samples between CCV/CCB pairs as required to complete run

CRI (The CRI counts as a sample analysis.)

CCV

CCB

Refer to Quality Control Section 9.0 and Table VII (Appendix A) for Method 6010B and 200.7 quality control criteria.

- 11.9. 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-0002NC for details.
- 11.10. Full method required QC must be available for each wavelength used in determining reported analyte results.
- 11.11. The following run sequence provides an illustration of a mid-run CCV or CCB failure and the appropriate corrective action run sequence as described in Section 9.7:

Original Run: Instrument Calibration

ICV

ICB

CRI

ICSA

ICSAB

7 samples

CCV1

CCB1

10 samples

CCV2

CCB2

10 samples **

CCV3 * * Failure occurs at CCV3/CCB3

CCB3 * **Samples requiring rerun for affected analytes

10 samples **

CCV4

CCB4

10 samples

CCV5

CCB5

Reanalysis: Recalibrate

ICV

ICB

CRI

ICSA

ICSAB

CCV2

CCB2

10 samples

CCV3

CCB3

10 samples

CCV4

CCB4

Notes: Samples between CCV4 and CCV5 do not require reanalysis as they were bracketed by compliant QC samples.

See CORP-MT-0002NC for the appropriate reanalysis sequence if CLP requirements must also be met.

- 11.14 The instrument may be reprofiled between CCV/CCB pairs to correct for environment induced drift.
- 11.15 Guidelines are provided in the appendices on procedures to minimize contamination of samples and standards, preventive maintenance and troubleshooting.
- 11.16 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.
- 11.17 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 C provides guidance on performing MSA analyses.

- 11.18 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.

11.19 Nonconformance documentation shall be filed in the project file.

11.20 Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

11.21 Analytical Documentation

11.21.1 Record all analytical information in the analytical logbook/logsheet which may be in an electronic format, including the analytical data from standards, blanks, LCSs, MS/MSDs, and any corrective actions or modifications to the method.

11.21.2 All standards are logged into a department standard logbook. All standards are assigned an unique number for identification. Logbooks are reviewed by the supervisor or designee.

11.21.3 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.

11.21.4 Sample results and associated QC are entered into the LIMs after final technical review.

12 DATA ANALYSIS AND CALCULATIONS

12.1. ICV percent recoveries are calculated according to the equation:

$$\%R = 100 \left(\frac{\text{Found(ICV)}}{\text{True(ICV)}} \right)$$

12.2. CCV percent recoveries are calculated according to the equation:

$$\%R = 100 \left(\frac{\text{Found(CCV)}}{\text{True(CCV)}} \right)$$

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:

$$\%R = 100 \left(\frac{\text{Found}(LCS)}{\text{True}(LCS)} \right)$$

- 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 $\times$ 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 North Canton significant figure policy.

12.11. Trivalent Chromium

12.11.1. Trivalent chromium (Cr^{+3}) is the result obtained by subtracting the hexavalent chromium (Cr^{+6}) results for a sample from the total chromium result from that sample. The total chromium result is determined using the procedures in this SOP. The hexavalent chromium result is determined using the procedures in STL North Canton SOP NC-WC-0024.

12.11.2. Reporting Limits

12.11.2.1. The STL North Canton water reporting limit for trivalent chromium is 0.02 mg/l.

12.11.2.2. The STL North Canton solid reporting limit for trivalent chromium is 2.0 mg/kg, wet weight.

12.11.3. Calculations: $\text{Cr}^{+3} = \text{Cr, total} - \text{Cr}^{+6}$

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% of the true value or within the laboratory's historical acceptance limits.
- 13.4. Training Qualification:
 - 13.4.1. 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

- 14.2. This method does not contain any specific modifications that serve to minimize or prevent pollution.

15. WASTE MANAGEMENT

- 15.1. This method does not contain any specific modifications that serve to minimize or prevent pollution.
- 15.2. All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."
- 15.3. Waste Streams Produced by this Method
 - 15.3.1 The following waste streams are produced when this method is carried out:
 - 15.3.2 Acid waste consisting of sample and rinse solution - Any sample waste generated must be collected and disposed of in the acid waste drum located in the metals lab.

15.3.3 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. References

- 16.1.1. 40 CFR Part 136, Appendix B, 7-5-95, Determination of Method Detection Limits.
- 16.1.2.** Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition, Final Update III, Revision 2, December 1996. Method 6010B.
- 16.1.3.** 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.
- 16.1.4. Inductively Coupled Plasma – Atomic Emission Spectrometric Method for Trace Element Analysis of water and wastes Method 200.7, 40 CFR – Chapter I – Part 136 – Appendix C. Electronic version dated September 30, 2002.
- 16.1.5. CORP-MT-0002NC, Inductively Coupled Plasma-Atomic Emission Spectroscopy, Method 200.7 & CLP-M, SOW ILMO3.0 and ILMO4.0).
- 16.1.6. Corporate Quality Management Plan (QMP), current version
- 16.1.7. STL Laboratory Quality Manual (LQM), current version.

16.2. Associated SOPs and Policies, latest version

- 16.2.1. QA-003, STL North Canton QC Program.
- 16.2.2. Glassware Washing, NC-QA-0014
- 16.2.3. Statistical Evaluation of Data and Development of Control Charts, NC-QA-0018
- 16.2.4. Method Detection Limits and Instrument Detection Limits, NC-QA-0021
- 16.2.5. Navy/Army SOP, NC-QA-0016
- 16.2.6. QA-004, Rounding and Significant Figures.

- 16.2.7. NC-WC-0024, Hexavalent Chromium (Colorimetric)
- 16.2.8. CORP-IP-0002NC, Acid Digestion of Soils, SW846 Method 3050B
- 16.2.9. CORP-IP-0003NC, Acid Digestion of Aqueous Samples by SW846 and MCAWW 200 Series Methods

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 North Canton 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. 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 North Canton has adopted the procedure in EPA CLP ILMO4.0.
- 17.1.1.3. 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 North Canton laboratories receive no prior information from clients regarding when to expect a new or unusual matrix, STL North Canton 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 North Canton, matrix interference is determined by evaluating data for the LCS and MS/MSD. STL North Canton **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 North Canton labs utilize the IDL definition as defined in Section 9.1 of this SOP.
- 17.1.2.2. The calibration blank is prepared in an acid matrix of 5% HNO₃/5% HCl instead of the specified 2% HNO₃/10% 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 $\pm 5\%$ of calibration with a relative standard deviation $<3\%$ from replicate integrations ≥ 4 ." STL North Canton uses a minimum of two exposures.
- 17.1.2.4. The 40 CFR version of Method 200.7 requires the instrument check standard to agree within $\pm 5\%$ of expected values. Also, the 40 CFR version requires the interference check sample to be analyzed at the beginning, end, and at periodic intervals throughout the sample run. At STL North Canton, the instrument check standard equals the CCV, which must agree within $\pm 10\%$ of expected values, and the ICSA standards are analyzed only at the beginning of a sample run. STL's procedures are in line with the Rev. 4.4, May 1994 version of Method 200.7.
- 17.1.2.5. 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.
- 17.1.2.6. 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.

- 17.1.2.7. 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 North Canton 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 IDL. If not, repeat the analysis two or more times and average the results. If the average is not within three standard deviations 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 North Canton 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.

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	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
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
Potassium	K	7440-09-7	X	X	5000	500
Selenium	Se	7782-49-2	X	X	250	25
Silver	Ag	7440-22-4	X	X	10	1
Sodium	Na	7440-23-5	X	X	5000	500
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

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
Magnesium	50000	50000
Manganese	500	500
Molybdenum	1000	1000
Nickel	500	500
Potassium	50000	50000
Selenium	2000	2000
Silver	50	50
Sodium	50000	50000
Thallium	2000	2000
Vanadium	500	500
Zinc	500	500
Boron	1000	1000
Tin	2000	2000
Titanium	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
Magnesium	100000	5000	25000	50000
Manganese	10000	15	1000	5000
Molybdenum	10000	40	1000	5000
Nickel	10000	40	1000	5000
Potassium	100000	5000	25000	50000
Selenium	10000	250	1000	5000
Silver	2000	10	500	1000
Sodium	100000	5000	25000	50000
Thallium	20000	2000	5000	10000
Vanadium	10000	50	1000	5000
Zinc	10000	20	1000	5000
Boron	10000	200	1000	5000
Tin	10000	100	1000	5000
Titanium	10000	50	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
Boron		1000
Titanium		1000

* Custom STL North Canton solutions contain analytes common to all STL North Canton 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		Terminate analysis; Correct the problem; Prepare new standards; Recalibrate following system performance.
ICV	Beginning of every analytical run.	Method 200.7: 95 - 105 % recovery. RSD dupl. exp < 3% Method 6010B: 90 - 110 % recovery. RSD dupl. exp < 5%	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. RSD dupl. exp < 5%	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.
CRI	Beginning of every run	50-150% recovery (advisory)	Evaluate associated samples.
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 11.10 and 11.13 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 (See 9.2). Sample results greater than 20x 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. Samples for which the contaminant is < RL and the LCS results are > 120% 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. 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

CROSS REFERENCE OF TERMS USED IN METHODS 6010B, 200.7, AND BY STL NORTH CANTON

**CROSS REFERENCE OF TERMS COMMONLY USED IN
METHODS EPA 200.7, SW6010B, AND STL NORTH CANTON INC. SOP**

EPA 200.7	SW6010B	STL North Canton 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)

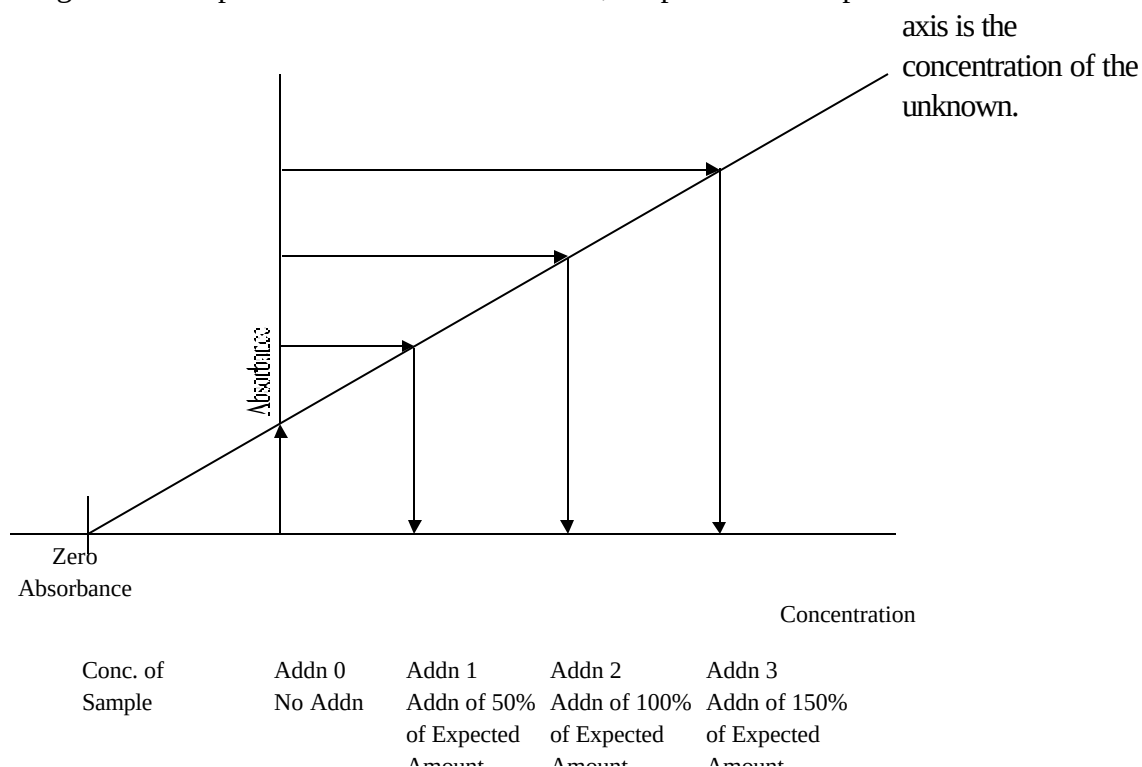
APPENDIX C
MSA GUIDANCE

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 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



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/ 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 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:

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 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.

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)

APPENDIX G

ICP OPERATING INSTRUCTIONS

ICP Analysis (TJA 61E)

(Example)

1. SETUP

- a. Plasma Control Panel (enter)
- b. (F1)-Startup
- c. (F9)-Continue
- d. (F2)-Levels
 1. Change auxiliary gas to low – use space bar to toggle
 2. Change nebulizer gas flow to 0.5 L/min.
 3. Change pump rate to 130
 4. Esc
 5. Allow instrument to warm up approximately 30 minutes.

2. DEVELOPMENT

- a. Methods (enter)
- b. Enter method name
- c. (F3)-Method Info.
- d. Change file name
- e. (F9)-Done
- f. (F9)-Done/Keep

18. OPERATION

a. Analysis (enter)

b. (F5)-Profile

1. (F3)-Automatic

2. (F1)-Run

3. If peak position is greater than +/- .05 units from the center peak position, you must adjust the profile. If it is within +/- .05 units, press (F9)-done.

4. To adjust select (F1)-CalcSS and enter current vernier position. (enter)

5. Adjust to new vernier position(F9)-done

6. Rerun profile until peak position is +/- .05 units.

7. (F9)-Done

c. Autosampler (F9)

1. Enter method name (enter)

2. Enter autosampler table name (enter)

3. (F1)-Run

Controlled Copy
Copy No. _____

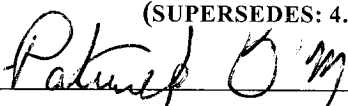
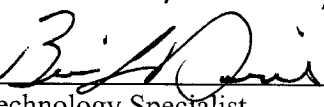
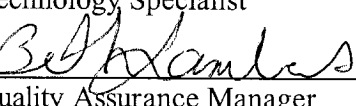
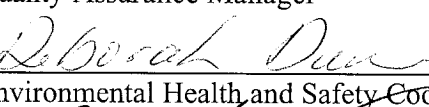
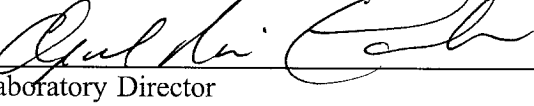
Implementation Date 2/5/04

SOP No. NC-MT-0002
Revision No. 4.2
Revision Date: 01/08/04
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STL North Canton
STANDARD OPERATING PROCEDURE

TITLE: **INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETRY,**
EPA METHODS 6020 AND 200.8

(SUPERSEDES: 4.1 Dated 10/01/03)

Prepared by:	<u></u>	<u>1/21/04</u> Date
Reviewed by:	<u></u> Technology Specialist	<u>1/21/04</u> Date
Approved by:	<u></u> Quality Assurance Manager	<u>1/21/04</u> Date
Approved by:	<u></u> Environmental Health and Safety Coordinator	<u>1/28/04</u> Date
Approved by:	<u></u> Laboratory Director	<u>1/29/04</u> Date

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1. SCOPE AND APPLICATION

- 1.1. This procedure describes multi-elemental analysis by inductively coupled plasma-mass spectrometry (ICP-MS) based on SW-846 protocol as described in EPA Method 6020 and 200.8. The source method lists fifteen elements approved for analysis by ICP/MS (Al, Sb, As, Ba, Be, Cd, Cr, Co, Cu, Pb, Mn, Ni, Ag, Tl, and Zn). Additional elements may be included provided that the method performance criteria presented in Section 9 is met. However, project approval may be required from the controlling agencies for compliance testing beyond the fifteen elements included in the promulgated method.
- 1.2. This procedure also describes the requirements for performing analysis of ground waters, surface waters and drinking water.
- 1.3. The procedure is applicable to the analysis of waters, soils, and wastes. No digestion is required prior to analysis for dissolved elements in water samples, but the samples must be filtered and preserved prior to analysis. Preliminary acid digestion is required for groundwater, aqueous samples, sludges, sediments, and other solid wastes for which total (acid-leachable) elements are requested. See SOP # CORP-IP-0002NC and SOP #CORP-IP-0003NC for preparation details.
- 1.4. The associated QuantIMs method codes are MH (6020) and QV (200.8).
- 1.5. 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. Aqueous samples, digestates, or leachates are nebulized into a spray chamber where a stream of argon carries the sample aerosol through the quartz torch and injects it into an R.F. plasma. There the sample is decomposed and desolvated. The ions produced are entrained in the plasma gas and by means of a water-cooled, differentially pumped interface, introduced into a high-vacuum chamber that houses a quadrupole mass spectrometer capable of providing a resolution better than or equal to 0.9 AMU peak width at 10% of the peak height. For analysis by methods 200.8 the resolution requirement is 1.0 amu at 5% peak height. The ions are sorted according to their mass-to-charge ratio and measured with a channel electron multiplier. Interference must be assessed and valid corrections applied, or the data flagged to indicate problems. Interference correction must include compensation for background ions contributed by the plasma gas, reagents and the constituents of the sample matrix. Recommended elemental equations which correct for many of these interferences are listed in Table I. Use of the internal standard technique is required to compensate for suppressions and enhancements caused by sample matrices.

3. DEFINITIONS

- 3.1. Refer to the glossary in the Laboratory Quality Manual (LQM), latest version.
- 3.2. *Dissolved Metals* - Those elements which pass through a 0.45 μm membrane filter (sample is acidified after filtration).
- 3.3. *Suspended Metals* - Those elements which are retained by a 0.45 μm membrane filter.
- 3.4. *Total Metals* - The concentration determined on an unfiltered sample following vigorous acid digestion.
- 3.5. *Total Recoverable Metals* - The concentration determined on an unfiltered sample following treatment with hot, dilute mineral acids.
- 3.6. *Instrument Detection Limit (IDL)* - See Section 9.1.1.
- 3.7. *Sensitivity* - The slope of the analytical curve (i.e. the functional relationship between raw instrument signal and the concentration).
- 3.8. *Tuning Solution* - This is a multi-element solution containing analytes which are representative of the entire mass range capable of being scanned by the instrument. It is used to optimize the sensitivity of the instrument and to verify the mass resolution meets method criteria.
- 3.9. *Initial Calibration Verification/Quality Control Standard (ICV/QCS)* - A multi-element standard of known concentrations prepared to verify instrument calibration. This solution must be an independent standard prepared near the mid-point of the calibration curve, and at a concentration other than that used for instrument calibration.
- 3.10. *Continuing Calibration Verification (CCV)* - A multi-element standard of known concentrations prepared to monitor and verify the instrument daily continuing performance.
- 3.11. *Interference Check Standard (ICS)* - A solution containing both interfering and analyte elements of known concentration that is used to verify background and interelement correction factors.
- 3.12. *Laboratory Control Sample / Laboratory Fortified Blank (LCS/LFB)* - A multi-element standard of known concentrations which is carried through the entire sample preparation and analysis procedure. This solution is used to verify the accuracy of the sample preparation.

- 3.13. *Reagent Blank* - High purity (> 18 megohm-cm) water carried through the entire digestion process.
- 3.14. *Calibration Blank* - High purity (> 18 megohm- cm) water acidified with the same acid concentrations present in the standards and samples Also referred to as the Initial Calibration Blank (ICB) and Continuing Calibration Blank (CCB).
- 3.15. *Method Detection Limit (MDL)*. See section 9.1.3

4. INTERFERENCES

- 4.1. Isobaric Interferences - Isobaric interferences in the ICPMS are caused by isotopes of different elements forming ions with the same nominal mass-to-charge ratio (m/z). Most interferences of this type are corrected for by the instrument software.
- 4.2. Isobaric Molecular and Doubly Charged Ion Interferences - Isobaric molecular interferences are caused by ions consisting of more than one atom or charge. Table II lists isobaric interferences which might possibly affect required analytes. When these interferences cannot be avoided by the use of another isotope with sufficient natural abundance, corrections must be applied and the data flagged to indicate the presence of interferences.
- 4.3. Physical Interferences - Physical interferences are associated with the transport and nebulization process. Internal standards are used to compensate for these types of interferences.
- 4.3.1. Internal standards should be added at a level to give approximately 100,000 – 1,000,000 counts of raw signal intensity. The mass of the internal standard should ideally be within 20 amu of the mass of the measured analyte.
- 4.3.2. Matrix effects will be monitored by comparing the internal standard intensity in the sample to the internal standard intensity of the calibration blank. When performing method 6020 the internal standard intensities must be between 30% and 120% of the intensities in the calibration blank. If they fall outside this window, a five fold dilution (1:4) is performed on the sample to correct for matrix effects and the sample reanalyzed. When performing method 200.8 the internal standards must be between 60% and 125% of the calibration blank. If they are outside this window the calibration blank is reanalyzed to verify internal standard intensities. If the intensities are within limits the sample is diluted by a factor of 2 (1:1) and reanalyzed.

- 4.3.3. Memory effects are dependent on the relative concentration differences between samples and/or standards which are analyzed sequentially. The rinse period between samples must be long enough to eliminate significant memory interference.
- 4.3.4. 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. Specific selection of reagents may be required to avoid introduction of contaminants.

5. SAFETY

- 5.1. Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual and this document.
- 5.2. Eye protection that protects against splash, 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 following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
<i>Hydrochloric Acid</i>	Corrosive Poison	5 ppm- Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
<i>Nitric Acid</i>	Corrosive Oxidizer Poison	2 ppm- TWA 4 ppm- STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

- 5.4. 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.
- 5.5. 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.
- 5.6. 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 involved solvents such as methylene chloride} should be conducted in a fume hood with the sash closed as far as the operations will permit.
- 5.7. Standards in solution may be diluted in the open laboratory when syringes and the like are utilized.
- 5.8. The ICP plasma emits strong UV light and is harmful to vision. All analysts must avoid looking directly at the plasma.
- 5.9. 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. Argon gas: High purity grade (99.99%).
- 6.2. Inductively Coupled Plasma Mass Spectrometer capable of providing resolution, less than or equal to 0.9 AMU at 10% peak height from 6-253 AMU and 1.0AMU at 5% peak height from 6-253 AMU with a data system that allows corrections for isobaric interferences and the application of the internal standard technique.
- 6.3. A four channel peristaltic pump.
- 6.4. Appropriate water cooling device.
- 6.5. Calibrated automatic pipettes or Class A glass volumetric pipettes.
- 6.6. Autosampler with autosampler tubes.

7. REAGENTS AND STANDARDS

7.1. Calibration standards are purchased as custom STL multielement mixes or as single element solutions. All standards must be stored in FEP fluorocarbon or previously 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. See Table XI.

7.2. Check Calibration Standard (ICV)

A quality control standard similar to the calibration standards and prepared in the same acid matrix. This solution must be made at a concentration near the midpoint of the calibration curve. This standard is composed of analytes from a different source from those used in the calibration of the instrument. See Table XI.

7.3. The tuning solution is purchased as custom STL multielement mixes or as single element solutions. All standards must be stored in FEP fluorocarbon or previously unused polyethylene or polypropylene bottles. The solution 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.

7.4. The use of hydrochloric and sulfuric acids should be minimized due to higher incidence of molecular-ion interferences with the presence of these acids. Excessive amounts of nitric acid can also lead to molecular interferences.

7.5. Reagent water:

ASTM Type I or equivalent for the elements of interest, generated using an ion-exchange water polishing system capable of achieving 18.0 megohm-cm.

7.6. Rinse Solution: Carefully dilute 200 mL of concentrated HNO₃ and 40mL of concentrated HCl to 4.0 L with reagent water.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Aqueous samples are preserved with nitric acid to a pH of 2, and may be stored in plastic or glass. Preservation must be verified prior to analysis.

8.2. Soil samples do not require preservation, but must be stored at 4° ± 2°C until the time of preparation.

8.3. The analytical holding times for metals are six months from the time of collection.

8.4. Solid and aqueous samples must be digested prior to analysis by the appropriate method.

9. QUALITY CONTROL

9.1. Initial Demonstration of Capability

Table X provides a summary of quality control requirements including type, frequency, acceptance criteria and corrective action. Prior to analysis of any analyte the following requirements must be met.

9.1.1. Instrument Detection Limit (IDL) - IDLs can be determined by calculating the average of the standard deviations of the three runs on three non-consecutive days from the analysis of a reagent blank solution with seven consecutive measurements per day. Each measurement must be performed as a separate analytical sample. The IDL should be performed every three months.

9.1.2. Linear Calibration Ranges - Linear calibration ranges are primarily detector limited. The linear range must be determined at instrument setup, and the upper limit must be verified annually or whenever a change in instrument hardware or operating conditions, in the judgement of the analyst, may lower expected ranges. Standards used to determine or verify linear ranges must be analyzed during a routine analytical run. The linear range is the concentration above which sample results cannot be reported.

9.1.2.1. For initial determination of the upper limit of the linear range, determine the signal responses from three different concentration standards across the estimated range. One standard must be at the upper limit of the estimated range. Results must recover within 10% of the expected value for the three standards. The Linear Range is then set at the concentration of the high standard.

9.1.2.2. For verification of the upper limit of the linear range, the high standard must recover within 10% of its expected value.

9.1.3. Method Detection Limit (MDL) - The laboratory shall determine a method detection limit for all analytes of interest initially and annually thereafter. The MDL study is performed and calculated according to STL SOP S-Q-003, which is based on 40CFR Part 136 Appendix B.

9.2. Batch Definition

9.2.1. A batch is a group of no greater than 20 samples excluding QC samples (LCS, Method Blank, MS, MSD) 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.

9.3. Method Blank

9.3.1. 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 (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, calcium, magnesium, potassium, sodium 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. Barium, Chromium and Manganese may also be considered common laboratory contaminants at ICPMS reporting limits. **Such action 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 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.**

9.3.2. 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

9.4. Laboratory Control Sample (LCS)

9.4.1. One LCS from an independent source must be processed with each preparation batch. The LCS must be carried through the entire analytical procedure. 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 historical limits for the LCS for each analyte are in the LIMS system. Initial limits shall be set at 80-120% for method 6020 and 85-115% for method 200.8. If the LCS exceeds these limits for any analyte, that analyte is judged to be out of control and must be corrected before the analysis can be reported

9.4.2. Corrective Action for LCS

9.4.2.1.If any analyte is outside established control limits the system is out of control and corrective action must occur.

9.4.2.2.The only exception is that if the LCS recoveries are biased high and the associated sample is ND for the parameter(s) of interest, the batch is acceptable. **This must be addressed in the project narrative.**

9.4.2.3.Corrective action will be repreparation and reanalysis of the batch unless the client agrees that other corrective action is acceptable.

9.5. Matrix Spike/Matrix Spike Duplicate (MS/MSD)

9.5.1. 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. The historical spike recovery acceptance limits for each analyte are in the LIMS system. Initial limits shall be 70-130% for methods 6020 and 200.8. and the spike concentration must be the same level as the LFB. If they are not in control and all

other quality control criteria have been met then a matrix interference is suspected.

9.5.2. Corrective action for MS/MSDs

9.5.2.1.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 reparation and reanalysis of the batch.

9.5.2.2.If the native analyte concentration in the MS/MSD exceeds 4x the spike level for that analyte, the recovery data is reported as NC (not calculated).

9.5.2.3.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 laboratory limits.

9.5.2.4.If client program requirements specify to confirm matrix interference's, reparation and reanalysis of the MS/MSD may be necessary.

9.6. Sample Duplicate

9.6.1. 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.

9.6.2. Sample duplicates may be performed in lieu of or in addition to MSD's.

9.7. Control Limits

9.7.1. Control limits are established by the laboratory as described in SOP, NC-QA-0018.

9.7.2. Laboratory control limits are internally generated and updated periodically unless method specified. Control limits are listed in the Laboratory Quality Manual

(LQM) and the latest version is easily accessible via the LIMs (QC Browser program).

9.8. Method Detection Limits (MDLs) and MDL Checks

9.8.1. MDLs and MDL Checks are established by the laboratory as described in SOP, NC-QA-0021.

9.8.2. MDLs are listed in the Laboratory Quality Manual (LQM) and the latest version is easily accessible via the LIMs (QC Browser program).

- 9.9. ICV/CCV/QCS - Calibration accuracy is verified at the beginning of each analytical run by analyzing a second-source initial calibration verification (ICV) standard. A continuing calibration verification (CCV) standard is analyzed at a 10% frequency throughout the run. The ICV must be within 10% of the expected value, or the analysis is terminated. The CCV must be within 10% of the expected value for method 6020 or 15% of the expected value for method 200.8. Sample results may only be reported when bracketed by valid CCV's.
- 9.10. RL Verification Standard –An independent standard is analyzed after the ICV to monitor the lab's ability to produce reliable results at RL-level concentrations. There is no set acceptance criteria established for this standard, but generally results should be within 50% of the expected value.
- 9.11. ICB/CCB/CB - The initial calibration blank must be analyzed immediately following the ICV. The continuing calibration blank must be analyzed at a frequency of 10% throughout the remainder of the analytical run. The ICB/CCB must fall within +/- the reporting limit from zero.
- 9.12. Interference Check Solutions (ICSA/ICSAB) **method 6020 only**- The interference check solution is prepared with known concentrations of interfering elements so a determination may be made as to the magnitude of the interference on analytes of interest as well as a test of any software corrections. The required elements and their concentrations are listed in Table V. The interference check solutions must be analyzed at the beginning of every analytical run and every 12 hours thereafter. The results of solution "A" and solution "AB" should be monitored for possible interferences.
- 9.12.1. Control limits of spiked analytes in the ICSA/ICSAB solution are +/- 50% of true value. Some projects may require control limits of +/- 20% of true value. Control limits of non-spiked analytes are +/- 2x the reporting limit or less than 1 ug/L.

Note: It may not be possible to obtain absolutely clean ICSA/ICSAB standards.

If contamination can be confirmed by another method (ICP/GFAA), acceptance criteria will be applied at that level and the data accepted.

9.13. Internal Standards:

The intensities of all internal standards must be monitored throughout the run. The internal standard in the samples must be between 30% and 120% of the intensity of the calibration blank, for Method 6020, and between 60% and 125% for Method 200.8. If the sample falls outside of this criteria, perform the following procedures. First, evaluate nearby CCV's and CCB's. If sample internal standard recoveries appear to be related to instrument drift, then rerun affected samples. If sample internal standard recoveries appear to be primarily sample related, then perform appropriate dilutions until the internal standard recoveries are within the method criteria. In no case, may Method 6020 sample results be reported with internal standard recoveries greater than 40% higher than recoveries in surrounding CCV's/CCB's. Alternately, the run may be reprocessed with an alternative internal standard that is not in the samples and at an appropriate mass for the masses being reported.

- 9.14. Serial Dilution **method 6020 only** - One serial five-fold dilution should be analyzed per batch for each matrix. If the analyte concentration is within linear range of the instrument and sufficiently high (generally, a factor of 100 times above the reporting limit), the serial dilution must agree within 10% of the original analysis. If not, an interference effect must be suspected, the result is flagged and included in the final report narrative. Samples identified as blanks cannot be used for serial dilution.
- 9.15. Post-Digestion Spike Addition (PDS) **method 6020 only** - If the serial dilution fails to meet the acceptance criteria, a PDS must be performed as follows. An analytical spike added to a portion of a prepared sample, or its dilution, should be recovered within 75 - 125% of the known value. If the PDS fails to meet this criterion, matrix interference should be suspected.
- 9.16. General Corrective Action Requirements - The general requirements for evaluation of QC results and corrective action for failures is described in STL Policy # QA-003
- 9.17. Nonconformance and Corrective Action
- 9.17.1. Any deviations from QC procedures must be documented as a nonconformance, with applicable cause and corrective action approved by the facility QA Manager.

10. CALIBRATION AND STANDARDIZATION

10.1. Instrument Start Up

Set up the instrument according to manufacturers operating instructions. Allow the instrument to become thermally stable for at least 30 minutes before tuning.

10.2. Instrument Tuning / Mass Calibration / Daily Performance

10.2.1. Daily Performance – Refer to Appendix A for ICPM/MS Instrument Instructions. Instrument manuals are available as needed. Verify instrument performance daily with a solution containing elements representing all of the mass regions of interest. The relative standard deviations must be less than 5% after running the tuning solution a minimum of 4 times. For method 200.8, the tuning solution must be analyzed 5 times with a relative standard deviation less than 5%.

10.2.2. Check mass calibration and resolution daily.

10.2.2.1. Mass Calibration Check – The mass calibration results must be within 0.1 amu from the true value. If this criterion is not met, the mass calibration must be adjusted before running samples.

10.2.2.2. Mass Resolution Check - The resolution must be verified to be less than 0.9 amu full width at 10% peak height. Due to a limitation of the instrument software, the resolution requirement for method 200.8 of 1.0 amu full width at 5% peak height cannot be verified automatically. If the mass resolution requirement of 0.9AMU at 10% peak height is met the 200.8 requirement is also satisfied.

10.3. Calibrate the instrument for the analytes of interest according to manufacturer's instructions. Routine calibration and calibration verification levels are shown in Table XI. The calibration should include a blank and a three standards. For a linear, multi-point calibration curve, the correlation coefficient must be ≥ 0.995 . Report the average of at least two integrations for both calibration and sample analysis. A calibration must be performed daily and each time the instrument is set up. Instrument run may be continued over periods exceeding 24 hours as long as calibration verification, interference check, and internal standard QC criteria are met.

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. Preliminary acid digestion is required for groundwater, aqueous samples, sludges, sediments, and other solid wastes for which total (acid-leachable) elements are requested. See SOP # CORP-IP-0002NC and SOP #CORP-IP-0003NC for preparation details.

11.4. Sample Analysis

- 11.4.1. Flush the system with the rinse blank for at least 30 seconds between samples and standards during the analytical run.
- 11.4.2. Masses which would affect the data quality must be monitored during the analytical run to determine the potential effects of matrix on a given element.
- 11.4.3. Dilute and reanalyze samples that are more concentrated than the linear range for an analyte or specific isotope of interest. No analyte may be reported from an analysis of a diluted sample in which the analyte concentration is less than 5 times the IDL (the sample should be diluted to the approximate midrange of the analytical curve), unless the dilution is for internal standard recoveries.
- 11.4.4. The analytical run sequence should be performed as follows to meet all quality control criteria:

Warm-up

Verify instrument performance

Calibration blank

Calibration standards

ICV

ICB

RL verification standard

ICSA (6020 Only)

ICSAB (6020 Only)

CCV

CCB

10 Samples

CCV

CCB

11.5. Analytical Documentation

11.5.1. Record all analytical information in the analytical logbook/logsheet which may be in an electronic format, including the analytical data from standards, blanks, LCSs, MS/MSDs, 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 an 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. ICV percent recoveries are calculated according to the equation:

$$\%R = 100 \times \left(\frac{\text{Found (ICV)}}{\text{True (ICV)}} \right)$$

12.2. CCV percent recoveries are calculated according to the equation:

$$\%R = 100 \times \left(\frac{\text{Found (CCV)}}{\text{True (CCV)}} \right)$$

12.3. Matrix Spike Recoveries are calculated according to the following equation:

$$\%R = 100 \times \left(\frac{SSR - SR}{SA} \right)$$

Where:

SSR = Spike Sample Result

SR = Sample Result

SA = Spike Added

Note: When sample concentration is less than the method detection limit, use SR = 0 for purposes of calculating % Recovery.

12.4. The relative percent difference (RPD) of sample duplicates are calculated according to the following equation:

$$RPD = 100 \times \left[\frac{(DU1 - DU2)}{(DU1 + DU2) / 2} \right]$$

Where:

DU1 = Sample result

DU2 = Sample duplicate result

- 12.5. The final concentration for an aqueous sample is calculated as follows:

$$\text{Result (ug/L)} = \frac{(C \times V1 \times D)}{V2}$$

Where:

C = Concentration from instrument readout, ppb

D = Instrument dilution factor

V1 = Final volume in liters after sample preparation

V2 = Initial volume of sample digested in liters

- 12.6. The concentration determined in digested solid samples when reported on a wet weight basis is as follows:

$$\text{Result (ug/kg)} = \frac{(C \times V \times D)}{W}$$

Where:

C = Concentration from instrument readout, ppb

D = Instrument dilution factor

V = Final volume in liters after sample preparation

W = Weight, in g, of wet sample digested

- 12.7. Sample results should be reported according to the following significant figure rules:

12.7.1. All uncorrected values less than the detection limit are reported as "less than" the detection limit.

12.7.2. Positive results for target analytes are reported to three significant figures if the method is used without dilution.

- 12.8. Positive results obtained after dilution and results for non-certified analytes are reported to two significant figures

13. METHOD PERFORMANCE

- 13.1. Each laboratory must have initial demonstration of performance data on file and corresponding method detection limit files.
- 13.2. Refer to Table I for the list of analytes that may be analyzed using this SOP for methods 6020 and 200.8. Additional analytes may be analyzed if all method required QC is acceptable.
- 13.3. Method performance is determined by the analysis of matrix spike and matrix spike duplicate samples as well as method blanks and laboratory control samples. The matrix spike recovery should fall within historical laboratory control limits and the matrix spike duplicates should compare within 20% RPD. Method blanks must meet the criteria specified in Section 9.3. The laboratory control samples should recover within 20% of the true value until in house control limits are established.
- 13.4. Training Qualifications:
- 13.4.1. 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. All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."
- 15.2. Solid materials (gloves, soiled paper products, etc.) are placed in the solid debris container. Do not put liquids in the solid waste container.

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.

15.4. Waste Streams Produced by the Method

15.4.1. Acid waste consisting of sample and rinse solution generated by this method.

15.4.1.1. Aqueous waste can be poured down the drain if the pH is between 4 and 10. Any sample waste generated that is not in this pH range must be collected and disposed of in the acid waste drum located in the metals lab.

16. REFERENCES

16.1. References

16.1.1. Test Methods For Evaluating Solid Waste, EPA SW-846, 3rd Edition, Final Update II, Method 6020: "Inductively Coupled Argon Plasma - Mass Spectrometry", Revision 0, September 1994.

16.1.2. Environmental Monitoring Systems Laboratory, EPA Method 200.8, "Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma - Mass Spectrometry", Revision 5.4, EMMC Version

16.1.3. Corporate Quality Management Plan (QMP), current version.

16.1.4. STL Laboratory Quality Manual (LQM), current version.

16.2. Associated SOPs and Policies, latest version

16.2.1. QA Policy, QA-003

16.2.2. CORP-IP-0002NC, Acid Digestion of Soils, SW846 Method 3050B, latest version.

16.2.3. CORP-IP-0003NC, Acid Digestion of Aqueous Samples by SW846 and MCAWW 200 Series Methods

16.2.4. Glassware Washing, NC-QA-0014

16.2.5. Statistical Evaluation of Data and Development of Control Charts, NC-QA-0018

16.2.6. Method Detection Limits and Instrument Detection Limits, NC-QA-0021

16.2.7. Navy/Army SOP, NC-QA-0016

17. MISCELLANEOUS (TABLES, APPENDICES, ETC...)

17.1. Reporting limits

17.1.1. Refer to Table XII for associated reporting limits

17.1.2. If samples require dilution or smaller volumes than specified in this method, the RL will be elevated.

17.2. Method deviations

17.2.1. Deviations from method 6020

17.2.1.1. Commercially available standards are purchased and verified at the laboratory rather than being prepared from the solid material. These verification records are kept in the laboratory.

17.2.1.2. The results of the calibration blank as well as all other blanks must be less than the reporting limit, not 3 times the instrument IDL.

17.2.1.3. Milli-Q or Nanopure water is substituted when reagent water is called for. This water is tested to be free of contaminants by conductivity (18megOhm) and by the analysis of blanks.

17.2.1.4. Internal standard recoveries may be less than 80% in CCV's and CCB's as long as QC criteria are met. Sample internal standard recoveries may never be greater than 40% higher than recoveries in associated CCV's/CCB's.

17.2.2. Deviations from method 200.8

17.2.2.1. Commercially available standards are purchased and verified at the laboratory rather than being prepared from the solid material. These verification records are kept in the laboratory.

17.2.2.2. The results of the calibration blank as well as all other blanks must be less than the reporting limit, not 3 times the instrument IDL.

- 17.2.2.3. Milli-Q or Nanopure water is substituted when reagent water is called for. This water is tested to be free of contaminants by conductivity (18 megOhm) and by the analysis of blanks.
- 17.2.2.4. Resolution criteria of the mass calibration is met if the resolution criteria for method 6020 is satisfied.
- 17.2.2.5. The concentration of most analytes in the LCS is 100 µg/L. This is made from a commercially available stock solution and has all analytes at the same level. Verification records for this solution are kept in the laboratory.
- 17.2.2.6. Results are reported up to the verified linear range, not up to only 90% of the linear range.

TABLE I: Recommended Elemental Interference Equations

Element	Isobaric Correction	Mathematical Equation
Al	none	$(1.0000)(27M)$
Sb	none	$(1.0000)(121M)$
As	ArCl, Se	$(1.0000)(75M) - (3.1278)(77M) + (1.0177)(78M)$
Ba	none	$(1.0000)(135M)$
Be	none	$(1.0000)(9M)$
Cd	MoO, Sn	$(1.0000)(114M) - (0.0268)(118M) - (1.0000)(135M)$
Ca	none	$(1.0000)(44M)$
Cr	none	$(1.0000)(52M)$
Co	none	$(1.0000)(59M)$
Cu	none	$(1.0000)(65M)$
Fe	none	$(1.0000)(57M)$
Pb	none	$(1.0000)(208M) + (1.0000)(207M) + (1.0000)(206M)$
Mg	none	$(1.0000)(25M)$
Mn	none	$(1.0000)(55M)$
Ni	none	$(1.0000)(60M)$
K	none	$(1.0000)(39M)$
Se	Ar2	$(1.0000)(78M) - (1.1869)(76M)$
Ag	none	$(1.0000)(107M)$
Na	none	$(1.0000)(23M)$
Tl	none	$(1.0000)(205M)$
V	ClO, Cr	$(1.0000)(51M) - (3.1081)(53M) + (0.3524)(52M)$
Zn	none	$(1.0000)(66M)$
6Li	Li (natural)	$(1.0000)(6M) - (0.0813)(7M)$
Sc	none	$(1.0000)(45M)$
Y	none	$(1.0000)(89M)$
Rh	none	$(1.0000)(103M)$
In	Sn	$(1.0000)(115M) - (0.0149)(118M)$
Tb	none	$(1.0000)(159M)$
Ho	none	$(1.0000)(165M)$
Bi	none	$(1.0000)(209M)$

M = Total ion count rate at the specified mass

TABLE II: Isobaric Molecular-Ion Interferences Which Could Affect the Analytes

Analyte	Interferences						
	Oxygen	Hydroxyl	Nitrogen	Chlorine	Sulfur	Carbon	Other
¹²¹ Sb	PdO		AgN			AgC	
¹²³ Sb	AgO		AgN	SrCl	ZrS	CdC	
⁷⁵ As	CoO	NiOH	NiN	ArCl	CaS	CuC	
¹³⁸ Ba	SnO	SbOH					
¹³⁷ Ba	SbO	SnOH		MoCl			
¹³⁶ Ba	SnO	SnOH				SnC	
¹³⁵ Ba	SnO	SnOH		MoCl			
¹³⁴ Ba	SnO	SnOH	SnN	MoCl		SnC	
¹³² Ba	SnO, CdO	InOH	SnN	MoCl	MoS	SnC	
¹³⁰ Ba	CdO	CdOH	SnN, CdN	MoCl	MoS	SnC	
⁹ Be							
¹¹⁴ Cd	MoO	MoOH	MoN	SeCl	SeS		
¹¹² Cd	MoO, ZrO	MoOH	MoN	AsCl, SeCl	SeS	MoC	
¹¹¹ Cd	MoO	MoOH	MoN	GeCl			
¹¹⁰ Cd	MoO, ZrO		MoN, ZrN	GeCl, AsCl	SeS	MoC	
¹¹³ Cd	MoO	MoOH		SeCl, AsCl			
¹¹⁶ Cd	MoO						
¹⁰⁶ Cd	ZrO		MoN, ZrN		GeS	MoC, ZrC	
¹⁰⁸ Cd	MoO, ZrO	ZrOH	MoN, ZrN	GeCl	SeS, GeS	MoC, ZrC	
⁵² Cr	ArO	ClOH				ArC	
⁵³ Cr	ClO	ArOH	KN	NCl, OCl		KC	
⁵⁰ Cr	SO		ArN		SO	ArC	Mo ⁺⁺
⁵⁴ Cr		ClOH	ArN, CaN			CaC	
⁵⁹ Cr	CaO	CaOH	ScN	MgCl	AlS	TiC	Sn ⁺⁺
⁶³ Cu	TiO, PO ₂	TiOH	TiN	SiCl, MgCl	PS	VC	ArNa
⁶⁵ Cu	TiO	TiOH	VN	SiCl	SS, SO ₂ H	CrC	
²⁰⁸ Pb							
²⁰⁶ Pb							
²⁰⁷ Pb							
²⁰⁴ Pb							
⁵⁵ Mn	KO	ArOH	KN		NaS	CaC	Cd ⁺⁺

TABLE II: (cont.) Isobaric Molecular-Ion Interferences Which Could Affect the Analytes

Analyte	Oxygen	Hydroxyl	Nitrogen	Interferences Chlorine	Sulfur	Carbon	Other
²⁰² Hg	WO						
²⁰⁰ Hg	WO	WOH	WN				
¹⁹⁹ Hg	WO	WOH					
²⁰¹ Hg		WOH					
¹⁹⁸ Hg	WO	TaOH	WN			WC	
²⁰⁴ Hg							
¹⁹⁶ Hg			WN				
⁵⁸ Ni	CaO	KOH	CaN	NaCl	MgS	TiC	Cd ⁺⁺ , Sn ⁺⁺
⁶⁰ Ni	CaO	CaOH	TiN	MgCl, NaCl	SiS	TiC	Sn ⁺⁺
⁶² Ni	TiO	ScOH	TiN	AlCl, MgCl	SiS	TiC, CrC	Sn ⁺⁺
⁶¹ Ni	SeO	CaOH	TiN	MgCl	SiS	TiC	
⁶⁴ Ni	TiO	TiOH	TiN, CrN	SiCl, AlCl	SS	CrC	
⁸⁰ Se	ZnO	CuOH	ZnN	ScCl, CaCl	TiS	ZnC	
⁷⁸ Se	NiO	NiOH	ZnN	CaCl, KCl	TiS	ZnC	
⁸² Se	ZnO	CuOH	ZnN	TiCl, ScCl	TiS, CrS		
⁷⁶ Se	NiO	CoOH	NiN	KCl	CaS	ZnC	
⁷⁷ Se	NiO	CuN	CuN	CaCl, ArCl	ScS	CuC	
⁷⁴ Se	NiO	NiN	NiN	ClCl, KCl	CaS	NiC	
¹⁰⁷ Ag	ZrO	ZrOH		GeCl	AsS	MoC	
¹⁰⁹ Ag		MoOH	MoN	GeCl	SeS	MoC	
²⁰⁵ Tl							
²⁰³ Tl		WOH					
⁵¹ V	ClO	SOH	ClN	ClO, ClN	FS	KC	
⁵⁰ V	SO		ArN			ArC	Mo
⁶⁴ Zn	TiO	TiOH	TiN, CrN	SiCl, AlCl	SS	CrC	
⁶⁶ Zn	TiO	TiOH	CrN	PCl, SiCl	SS	FeC	
⁶⁸ Zn	CrO	VOH	FeN	PCl	ArS	FeC	Ba ⁺⁺
⁶⁷ Zn	VO	TiOH, Cr	CrN	SCl	ClS	MnC	Ba ⁺⁺
⁷⁰ Zn	FeO	CrOH	GeN	ClCl	ArS	NiC	

Note: The information provided in this table does not indicate that all of the described interferences need to be tested. However, the table can be consulted for informational purposes if unusual samples are encountered.

Table III: Changes in Isobaric Molecular-Ion Interferences with Changing Plasma Conditions **

	Molecular Interference	Nebulizer Flow Rate		
		High	Average	Low
Oxides:	ScO/Sc	0.00326	0.00055	0.00116
	YO/Y	0.00568	0.00395	0.00353
	TbO/Tb	0.0156	0.00648	0.00614
	ClO, Cl	0.00725	0.00227	0.00233
Hydroxides:	ScOH/Sc	0.00040	0.00011	0.00000
	YOH/Y	0.00078	0.00044	0.00048
	TbOH/Tb	0.00034	0.00008	0.00011
	ClOH/Cl	0.00048	0.00031	0.00029
Chlorine:	ClO/Cl	0.00725	0.00227	0.00233
	ClOH/Cl	0.00048	0.00031	0.00029
	ArCl/Cl	0.00605	0.00091	0.00477

** Information for this table is being determined by the EPA.

Table IV: Recommended Internal Standards

Method 6020	Method 200.8
Li	Sc
Sc	Y
Y	In
Rh	Tb
In	Bi
Tb	
Ho	
Bi	
Ge	

Table V: Interference Check Sample Components and Concentrations

(ICSAB minors are suggested spike levels)

Interference Component	Solution A Concentration (mg/L)	Solution AB Concentration (mg/L)
Al	50	50
Ca	50	50
Fe	50	50
Mg	50	50
Na	50	50
P	50	50
K	50	50
S	50	50
C	100	100
Cl	500	500
Mo	1.0	1.0
Ti	1.0	1.0
As	0.0	0.1
Cd	0.0	0.1
Cr	0.0	0.1
Co	0.0	0.1
Cu	0.0	0.1
Mn	0.0	0.1
Ni	0.0	0.1
Se	0.0	0.1
Ag	0.0	0.1
V	0.0	0.1
Zn	0.0	0.1

Table VI: Sample Preservation and Holding Times

Measurement Parameter	Container (1)	Preservative (2)	Maximum Holding Time (3)
<i>Waters:</i> Metals (4)	P,G	HNO ₃ to pH < 2	6 months
<i>Soils/Sediments/Wastes:</i> The preservation required for soil/sediment/waste samples is maintenance at 4°C (± 2°C) until digestion.			

Footnotes:

- (1) Polyethylene (P) or glass (G).
- (2) Sample preservation is performed by the sampler immediately upon sample collection.
- (3) Samples must be analyzed as soon as possible after collection. The times listed are the maximum times that sample may be held before analysis and still considered valid. Holding times are calculated from the date when the sample was collected.
- (4) Samples are filtered immediately on-site by the sampler before adding preservative for dissolved elements.

Table VII: Suggested Mass Choices

Boldface masses indicate the masses which must have the most impact on data quality and the elemental equations used to collect the data. Suggested masses for method 200.8 are in “quotes”.

Mass	Element of Interest
“27”	Aluminum
121, “123”	Antimony
“75”	Arsenic
138, “137” , 136, 135 , 134, 132, 130	Barium
“9”	Beryllium
114 , 112, “111” , 110, 113, 116, 106	Cadmium
42, 43, 44 , 46, 48	Calcium
“52” , 53 , 50 , 54	Chromium
“59”	Cobalt
“63” , 65	Copper
56 , 54 , 57 , 58	Iron
“208” , “207” , “206” , 204	Lead
24, 25, 26	Magnesium
“55”	Manganese
58, “60” , 62, 61 , 64	Nickel
39	Potassium
80, 78 , “82” , 76 , 77, 74	Selenium
“107” , 109	Silver
23	Sodium
“205” , 203	Thallium
“51” , 50	Vanadium
64, “66” , 68 , 67 , 70	Zinc
72	Germanium
139	Lanthanum
118	Tin
35, 37	Chlorine
“98” , 96, 92, 97 , 94	Molybdenum

Note: It is strongly recommended that elements other than those of interest be monitored to indicate other potential molecular interferences which could affect the data quality.

Table VIII: Tuning Solution

A tuning solution containing elements representing all of the mass regions of interest must be analyzed. Below are two groups of suggested solutions which cover a typical mass calibration range.

Method 6020

<u>Element</u>	<u>Concentration (mg/L)</u>
Solution A	
Mg	10.
Rh	10.
Pb	10.
Solution B	
Li	10.
Co	10.
In	10.
Tl	10.

Method 200.8

<u>Element</u>	<u>Concentration (mg/L)</u>
Be	10.
Mg	10.
Co	10.
In	10.
Pb	10.

Table IX: Suggested Tuning and Response Factor Criteria**Minimum Response from Tuning Solution****With a Peristaltic Pump Speed of 12 RPM:**

Be	>1,000
Mg	>10,000
Rh	>100,000
Pb	>50,000
Li	>2,000
Co	>20,000
In	>1,000
Tl	>1,000

Suggested Mass Calibration:

Be	9.0122
Mg	23.98
Rh	102.91
Pb	207.98
Li	7.016
Co	58.9332
In	114.904
Tl	204.9744

Table X: Summary of Quality Control Requirements

QC Parameter	Frequency*	Acceptance Criteria	Corrective Action
ICV/QCS	Beginning of every analytical run.	90 - 110% recovery.	Terminate analysis; correct the problem; recalibrate.
ICB/CB	Immediately after each ICV	The result must be < RL.	Terminate analysis; correct the problem; recalibrate.
CCV	Beginning and end of run and every 10 samples.	6020- 90 - 110% recovery. 200.8- 85-115% recovery.	If unacceptable, correct the problem recalibrate the instrument, reverify calibration and rerun all samples associated with unacceptable CCV's.
CCB	Immediately following each CCV.	The result must be < RL.	If unacceptable, correct the problem recalibrate the instrument, reverify calibration and rerun all samples associated with unacceptable CCB's.
ICSA (6020 Only)	Beginning and every 12 hours.	Monitor for possible interferences.	See Section 9.12
ICSAB (6020 Only)	Immediately following each ICSA.	Monitor for possible interferences.	See Section 9.12

Table X (cont.) Summary of Quality Control Requirements

QC Parameter	Frequency*	Acceptance Criteria	Corrective Action
Method Blank/Laboratory Reagent Blank	One per lot of 20 field samples or fewer.	The result must be < RL. Sample results greater than 20x the blank concentration or samples for which the contaminant is < RL, do not require redigestion or reanalysis.	Redigest and reanalyze samples. See Section 9.3 for additional requirements.
Laboratory Control Sample/Laboratory Fortified Blank	One per lot of 20 field samples or fewer.	80-120%, or in-house limits (6020), 85-115% (200.8)	Redigest and reanalyze samples. See Section 9.4.
Serial Dilution (6020 Only)	One per lot of 20 field samples or fewer.	90 – 110% recovery	See section 9.14 for additional requirements.
Post-Digestion Spike (6020 Only)	See section 9.15	75-125% recovery	See section 9.15.
Matrix Spike/Matrix Spike Duplicate	One per lot of 20 field samples or fewer.	Must be within laboratory control limits	See section 9.5 for additional requirements.

Table XI: ICP/MS Calibration and Calibration Verification Checklist*Suggested Levels in mg/L*

Element	Calibration			ICV	CCV
	1	2	3		
Aluminum	1000	5000	10000	25	50
Antimony	10	50	100	25	50
Arsenic	10	50	100	25	50
Barium	10	50	100	25	50
Beryllium	10	50	100	25	50
Cadmium	10	50	100	25	50
Chromium	10	50	100	25	50
Cobalt	10	50	100	25	50
Copper	10	50	100	25	50
Iron	1000	5000	10000	25	50
Lead	10	50	100	25	50
Manganese	10	50	100	25	50
Nickel	10	50	100	25	50
Selenium	10	50	100	25	50
Silver	10	50	100	25	50
Thallium	10	50	100	25	50
Vanadium	10	50	100	25	50
Zinc	10	50	100	25	50

This procedure has been developed for additional elements. Additional elements may be included in the calibration solution at the appropriate levels. Levels may be adjusted to meet specific regulatory or client programs.

Table XII: Suggested ICP/MS Reporting Limits*Water 6020 and 200.8 Solid 6020 (only)*

	Compound	RL	Units	RL	Units
	Aluminum	50	ug/L	--	--
	Antimony	2	ug/L	200	ug/kg
	Arsenic	5	ug/L	500	ug/kg
	Barium	5	ug/L	500	ug/kg
	Beryllium	1	ug/L	100	ug/kg
	Cadmium	1	ug/L	100	ug/kg
	Chromium	2	ug/L	200	ug/kg
	Cobalt	1	ug/L	100	ug/kg
	Copper	5	ug/L	500	ug/kg
	Iron	20	ug/L	--	--
	Lead	1	ug/L	100	ug/kg
	Manganese	5	ug/L	500	ug/kg
	Molybdenum	2	ug/L	200	ug/kg
	Nickel	2	ug/L	100	ug/kg
	Selenium	5	ug/L	500	ug/kg
	Silver	1	ug/L	100	ug/kg
	Thallium	1	ug/L	100	ug/kg
	Tin	10	ug/L	1000	ug/kg
	Vanadium	5	ug/L	500	ug/kg
	Zinc	10	ug/L	1000	ug/kg

APPENDIX A – OPERATION INSTRUCTIONS – P.E. 6100**ICP/MS INSTRUCTIONS****A. Light the plasma and start the peristaltic pump.**

1. Allow the instrument to warm up approximately 30 minutes.

B. Daily Performance

1. Open Daily2_asx workplace.
2. Open the sampling tab in the method screen.
3. Select and initialize the autosampler. Click O.K.
4. Click on probe. Click go to rinse. Send probe to tube #8.
5. Allow solution to reach plasma and then click on analyze sample.
6. When analysis is complete, send probe back to rinse.

C. Analysis Setup

1. Open Analysis workspace.
2. Under the method window, open the report tab and type in your report filename. Save the method.
3. Highlight the dataset window. Go to file and select new. Type in the dataset name (normally the same as the filename).
4. Highlight autosampler window. Type in your autosampler locations and samples. Right click under measurement action and select what needs to be analyzed. Right click under method description and select method. Verify that all times and rpms on table are correct. Go to file and click save as. Type autosampler table name (normally the same as the filename).

D. Analyze samples

1. Highlight samples to be analyzed.
2. Left click on analyze batch.

APPENDIX B – OPTIMIZATIONS – P.E. 6100

X-Y ADJUSTMENT – Adjusts torch to achieve best intensities. This should be done whenever anything is done to the torch or the cones.

1. Open X-Y_asx.wrk.
2. Under the method window, go to the sampling tab and send the probe to tube #8.
3. Allow solution to reach plasma and hit analyze sample.
4. Adjust x and y while watching the signal on the realtime window. Adjust only until signal is at its highest.

NEB LENS – This also is done to get best intensities. It effects the shape and the depth of the plasma. This should be done if your oxides or doubly charged are >3%.

1. Open neb lens power oxides.wrk
2. Under the method window, go to the sampling tab and send the probe to tube #8.
3. Click on the Autooptimize tab. Select nebulizer gas flow.
4. Click get analyte list.
5. Make sure solution has reached the plasma and click optimize.
6. When done, save the optimization file.

AUTOLENS – Each element done represents a section of the mass spectrum. Be is on the low end, CO is in the middle and IN is on the higher end. If there is a problem with any particular section of the spectrum, it may be an indication that this needs done. This should probably be performed on a weekly basis.

1. Open Autolens_asx.wrk.
2. Under the method window, go to the sampling tab and send the probe to tube #8.
3. Click on the autolens tab.
4. Click on clear calibration.
5. Click on get analyte list.

6. Make sure the solution has reached the plasma and click on calibrate.
7. Save the optimization file.
8. In the interactive window, the optimization curve can be printed.

DUAL DETECTOR CALIBRATION – This extends the dynamic range of the detector. This should be done on a weekly basis. All analytes of interest must be included in the solution.

1. Open dual detector2.wrk
2. Under the method window, go to the sampling tab and send the probe to tube #8.
3. Click on dual detector cal tab.
4. Click on clear calibration.
5. Click on get analyte list.
6. Make sure the solution has reached the plasma and click on calibrate.
7. When complete, check to make sure that all r values are at least .999.
8. Save the optimization file.
9. In the interactive window, the plots can be displayed.

TUNING – This adjusts the electronics to assure the accuracy of the mass spec. The resolution adjustment assures that the resolution of each mass of interest is within range. This should be done daily.

1. Open tuning_asx.wrk.
2. Under the method window, go to the sampling tab and send the probe to tube #8.
3. Allow sample to reach the plasma and click on tune mass spec.
4. Make sure measured mass and peak width is within range. If its not, resolution will need adjusted. Adding 30 units will decrease the amu by about 0.1. Subtracting 30 units will increase the amu about 0.1.

GENERAL NOTES –

1. All optimizations can be done with the tuning solution, except the dual detector cal needs the cross cal standard with all the elements of interest.
2. All optimizations can be run at 12 rpm, except the dual detector calibration should be done at 24 rpm.

Appendix D – ICPMS Maintenance Schedule

Daily	Change sample and internal standard 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 sample flow for cross flow nebulizer Check pressure for vacuum systems Check daily performance
As Needed	Clean Sampler and skimmer cones Clean plasma torch assembly to remove accumulated deposits Clean nebulizer Replace sample and internal standard capillary tubing and autosampler sipper probe Replace drain tubing Perform necessary optimizations Clean autolens
Monthly	Inspect air filters; clean or replace as needed
Bi-Yearly	Change oil in vacuum pumps Check water in coolflow

PREPARATION AND ANALYSIS OF MERCURY IN AQUEOUS
SAMPLES BY COLD VAPOR ATOMIC ABSORPTION, SW-846
METHOD 7470A AND MCAWW METHOD 245.1

SOP No. CORP-MT-0005NC
Revision No. 2.5
Revision Date: 01/08/04
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Implementation Date: 2/5/04

STL NORTH CANTON STANDARD OPERATING PROCEDURE

**TITLE: PREPARATION AND ANALYSIS OF MERCURY IN AQUEOUS SAMPLES BY
COLD VAPOR ATOMIC ABSORPTION, SW846 7470A AND MCAWW 245.1**

(SUPERSEDES: REVISION 2.4, DATED 10/28/02)

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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. The associated LIMs method codes are BL (Method 245.1) and O8 (Method 7470A).
- 1.3. 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.
- 1.4. Method 7470A is applicable to the preparation and analysis of mercury in ground water, aqueous samples, TCLP, and other leachates/extracts. Certain solid and sludge type wastes may also be analyzed, however Method 7471A (see CORP-MT-0007NC) is usually the method of choice. All matrices require sample preparation prior to analysis.
- 1.5. Method 245.1 is applicable to the determination of mercury in drinking, surface and saline waters and domestic and industrial wastes. All matrices require sample preparation prior to analysis.
- 1.6. The STL North Canton reporting limit for mercury in aqueous matrices is 0.0002 mg/L except for TCLP or SPLP 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. Sea waters, 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. 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.

-
- 4.5. Samples containing high concentrations of oxidizing 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.
- 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. Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual and this document.
- 5.2. Eye protection that protects against splash, 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 following is a list of the materials used in this method, which have a serious or significant hazard rating. NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table. A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Sulfuric Acid	Corrosive Oxidizer Dehydrator Poison	1 Mg/M3-TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.
Nitric Acid	Corrosive Oxidizer	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be

	Poison		fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Hydrochloric Acid	Corrosive Poison	5 PPM-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Potassium Permanganate	Oxidizer	5 Mg/M3 for Mn Compounds	Causes irritation to the respiratory tract. Symptoms may include coughing, shortness of breath. Dry crystals and concentrated solutions are caustic causing redness, pain, severe burns, brown stains in the contact area and possible hardening of outer skin layer. Diluted solutions are only mildly irritating to the skin. Eye contact with crystals (dusts) and concentrated solutions causes severe irritation, redness, and blurred vision and can cause severe damage, possibly permanent.
Mercury (1,000 ppm in Reagent)	Oxidizer Corrosive Poison	0.1 Mg/M3 Ceiling (Mercury Compounds)	Extremely toxic. Causes irritation to the respiratory tract. Causes irritation. Symptoms include redness and pain. May cause burns. May cause sensitization. Can be absorbed through the skin with symptoms to parallel ingestion. May affect the central nervous system. Causes irritation and burns to eyes. Symptoms include redness, pain, and blurred vision; may cause serious and permanent eye damage.
Potassium Persulfate	Oxidizer	None	Causes irritation to the respiratory tract. Symptoms may include coughing, shortness of breath. Causes irritation to skin and eyes. Symptoms include redness, itching, and pain. May cause dermatitis, burns, and moderate skin necrosis.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

- 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. All work must be stopped in the event of a known or potential compromise to the health and safety of a STL North Canton associate. The situation must be reported **immediately** to a laboratory supervisor.
- 5.6. Do not look directly into the beam of the Hg lamp. The UV light that these lamps radiate is harmful to the eyes.
- 5.7. Cylinders of compressed gas must be handled with caution, in accordance with local regulations. It is recommended that, wherever possible, cylinders are located outside the laboratory and the gas led to the instrument through approved lines.
- 5.8. 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.

- 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 coarse 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 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).
- 6.3. 8oz. HDPE Plastic bottles.
- 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 (10 ppm) mercury standards (in 10% HNO₃) are purchased as custom STL North Canton 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. Working mercury standard (0.1 ppm): Take 1 mL of the stock mercury standard (7.2) 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% HNO₃. This acid (150 uL of concentrated HNO₃) must be added to the flask/bottle before the addition of the stock standard aliquot.
- 7.4. The calibration standards listed in Table I must be prepared fresh daily from the working standard (7.3) by transferring 0, 0.2, 0.5, 1.0, 5.0 and 10.0 mL aliquots of the working mercury standard into 100 mL flasks and diluting to volume with reagent water.
- 7.5. The initial calibration verification standard must be made from a different stock solution than that of the calibration standards.
- 7.6. 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.
- 7.7. Nitric acid (HNO₃), concentrated, trace metal grade or better.
- 7.8. Sulfuric acid (H₂SO₄), concentrated, trace metal grade or better.
- 7.9. Stannous chloride solution: Add 50 g of stannous chloride and 25 mL of concentrated hydrochloric acid to a 500mL volumetric flask and bring to volume with deionized water.
- 7.10. Sodium chloride-hydroxylamine hydrochloride solution: Add 240 g of sodium chloride and 240 g of hydroxylamine hydrochloride to every 2000 mL of reagent water.

7.11. Potassium permanganate, 5% solution (w/v): Dissolve 100 g of potassium permanganate for every 2000 mL of reagent water.

7.12. Potassium persulfate, 5% solution (w/v): Dissolve 100 g of potassium persulfate for every 2000 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 North Canton 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 batch is a group of no greater than 20 samples excluding QC Samples (LCS, Method Blank, MS, MSD) 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. 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. 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 10% 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 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.**

9.4. 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. 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 addressed in the project 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 reparation and reanalysis of the batch unless the client agrees that other corrective action is acceptable.

9.5. 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 reparation 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.

- 9.6. Initial Calibration Verification (ICV/ICB) - Calibration accuracy is verified by analyzing a second source standard (ICV). The ICV result must fall within 10% 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 11.2.8 for required run sequence). If the cause of the ICV or ICB failure was not directly instrument related the corrective action will include reparation of the ICV, ICB, CRA, CCV, and CCB with the calibration curve.
- 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 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 11.2.8 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.
- 9.8. Detection Limit Standard (CRA)-To verify linearity at the reporting limit, a CRA standard is run at the beginning of each sample analysis run after the ICV/ICB. The CRA standard mercury concentration is 0.2 ug/L. Recovery must be $\pm 50\%$ of the true value, or the standard is either rerun or the problem corrected and the instrument recalibrated. (See Section 11.2.8 for the required run sequence.)
- 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 11.2.9 for additional information on when full 4 point MSA is required as well as Appendix B 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 and listed in Appendix F. Allow the instrument to become thermally stable before beginning calibration (approximately 30 minutes of warm-up is required).
- 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 North Canton reporting limit. Analyze standards in ascending order beginning with the blank. Refer to Section 7 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. Transfer 0, 0.2, 0.5, 1.0, 5.0 and 10.0 mL aliquots of the working standard (7.3) into a series of 100 ml class A volumetrics, then dilute to volume. For the ICV, use a 2.5 ml aliquot of the working standard. The ICV working standard must be made from a source other than that used for the calibration standards.

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.

Note: Spiking is done before the addition of acids or reagents.

11.1.3. Add 5 mL of concentrated H_2SO_4 and 2.5 mL of concentrated HNO_3 mixing after each addition.

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 other associated samples and standards 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.

11.1.6. Cool samples.

11.2. Sample Analysis:

11.2.1. Refer to the Appendix F of this SOP for detailed setup and operation protocols.

11.2.2. 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.

11.2.3. Automated determination: Follow instructions provided by instrument manufacturer.

11.2.4. 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.

11.2.5. 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.

11.2.6. 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.

11.2.7. The samples must be allowed to cool to room temperature prior to analysis or a decrease in the response signal can occur.

11.2.8. The following run sequence is consistent with 7470A, CLP and 245.1.

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 Quality Control Section 9.0 and Table II (Appendix A) for Quality Control
criteria to apply to Methods 7470A and 245.1.

11.2.9. 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 B 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 are 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. Analytical Documentation

11.5.1. Record all analytical information in the analytical logbook/logsheets which may be in an electronic format, including the analytical data from standards, blanks, LCSs, MS/MSDs, 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 an 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.

11.6. 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.

11.7. 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:

$$\%R = 100 \left(\frac{\text{Found(ICV)}}{\text{True(ICV)}} \right)$$

12.2. CCV percent recoveries are calculated according to the equation:

$$\%R = 100 \left(\frac{\text{Found(CCV)}}{\text{True(CCV)}} \right)$$

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:

$$\%R = 100 \left(\frac{\text{Found}(LCS)}{\text{True}(LCS)} \right)$$

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 North Canton 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. All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

15.2. 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.

15.3. Waste Streams Produced by the Method

15.3.1. **Acid Waste- Aqueous waste generated by the analysis.** Samples are disposed of in the acid waste drum located in the metals lab. The contents of the drum are neutralized and released to the POTW.

16. REFERENCES

16.1. References

16.1.1. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition, Final Update II, Revision I, September 1994, Method 7470A (Mercury).

16.1.2. "Methods for the Chemical Analysis of Water and Wastes", EPA-600/4-79-020, U.S.EPA, August 1983, Method 245.1.

16.1.3. U.S.EPA Statement of Work for Inorganics Analysis, ILMO3.0 and ILMO4.0.

16.1.4. Corporate Quality Management Plan (QMP), current version.

16.1.5. STL Laboratory Quality Manual (LQM), current version.

16.2. Associated SOPs and Policies, latest version

16.2.1. QA Policy, QA-003.

16.2.2. Glassware Washing, NC-QA-0014.

16.2.3. Statistical Evaluation of Data and Development of Control Charts, NC-QA-0018.

16.2.4. Method Detection Limits and Instrument Detection Limits, NC-QA-0021.

16.2.5. Navy/Army SOP, NC-QA-0016.

16.2.6. Preparation and Analysis of Mercury in Aqueous Samples by Cold Vapor Atomic Absorption, Method 245.1 CLP-M, SOW ILM03.0 and SOW ILM04.0 SOP, CORP-MT-0006NC, current version.

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."

17.1.2. 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.

17.1.3. 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 North Canton reports all Hg results under this SOP to two significant figures.

Figure 1. Aqueous Sample Preparation - Mercury

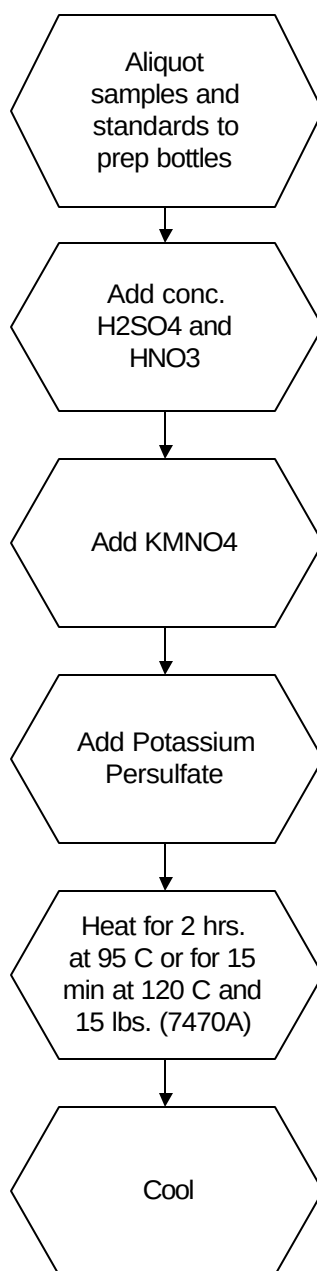
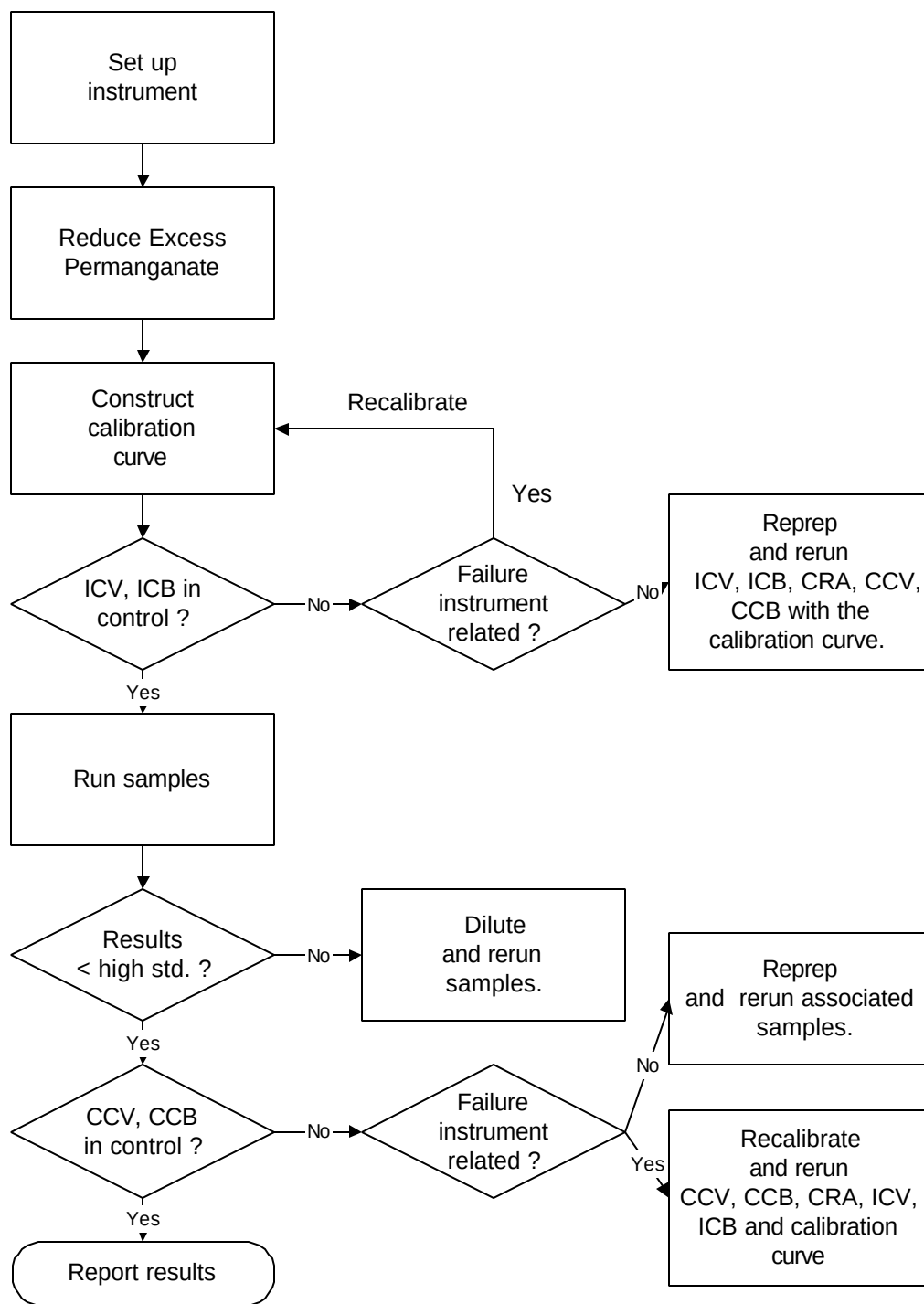


Figure 2. CVAA Mercury Analysis



APPENDIX A

TABLES

TABLE I . MERCURY REPORTING LIMITS, CALIBRATION STANDARD*, QC STANDARD AND SPIKING LEVELS (MG/L)

Standard Aqueous RL	0.0002
TCLP RL	0.002
Std 0	0
Std 1/CRA	0.0002
Std 2	0.0005
Std 3	0.001
Std 4	0.005
Std 5	0.010
ICV	0.0025
LCS/CCV	0.005
Aqueous MS	0.001
TCLP MS	0.005

TABLE II. Summary Of Quality Control Requirements

QC PARAMETER	FREQUENCY	ACCEPTANCE CRITERIA	CORRECTIVE ACTION
ICV	Beginning of every analytical run.	90-110 % recovery.	Terminate analysis; Correct the problem; Recalibrate or reprep with calibration curve. (See Section 9.6).
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 with calibration curve. (See Section 9.6).
CRA	Beginning of every analytical run following the ICB and prior to sample analyses.	50-150% recovery	Rerun to verify; or correct problem and recalibrate or reprep with the calibration curve (See Sec. 9.8)
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 with calibration curve. (See Section 9.7).
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 with calibration curve. (See Section 9.7).

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 9.3).	Redigest and reanalyze samples. Note exceptions under criteria section. See Section 9.3 for additional requirements.

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 9.4).
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 9.5) For TCLP see Section 11.2.9
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
MSA GUIDANCE

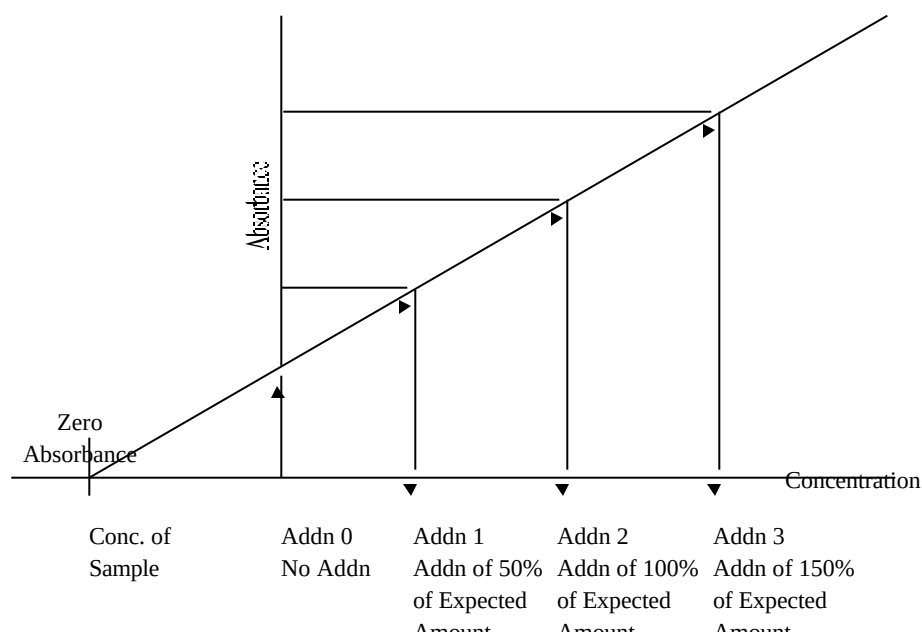
APPENDIX B. MSA GUIDANCE

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 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 gloves must not be used in the metals laboratory since the powder contains silica and zinc, as well as other metallic analytes. Alternatively, 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.

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 200II)

Daily	As Needed
Check nitrogen flow.	Check Hg lamp intensity.
Check tubing.	Clean lens.
Check drain.	Check aperture.
	Replace drying tube.
	Change Hg lamp.
	Check liquid/gas separator.

APPENDIX F
INSTRUMENT SET UP

Hg Analysis (Leeman PS200II)

SYSTEM INITIALIZATION AND WARM UP

1. F1 Menu
2. Instrument
 - a. TASKMASTER
 - b. #4 Wake System Up Enter

The warming up period takes approximately 10 minutes.

TO SET UP INSTRUMENT FOR ANALYSIS

1. F1 Menu
2. Autosampler
 - A. Rack Entry
 - B. Edit (ex. Rack 1), Enter
 - C. Cup ID - Enter (clears sample #'s)
 - D. Extended ID- type in matrix of sample (water or solid), Enter.
 - E. Press Insert Key and move cursor with arrows to cup ID and begin typing labels.
 - F. F3 Print Screen
3. Press F2 Macro key and type in analyst's first name - Enter
 - A. Enter folder name - ex. HG0306, Enter. If folder does not exist, type Y - Enter.
 - B. Type in - "Rack 1", "Rack 2" etc. , Enter.
 - C. Type in : FROM CUP TO CUP

Ex. = 1 30

Do the same for position 2 if needed. If not needed, you must press Enter 3 times to begin analysis.

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Implementation Date: 11/10/05

SOP No. CORP-MT-0007NC

Revision No. 2.5

Revision Date: 11/22/04

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STL NORTH CANTON 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 2.4, DATED 10/28/02)

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PREPARATION AND ANALYSIS OF MERCURY IN SOLID
SAMPLES BY COLD VAPOR ATOMIC ABSORPTION, SW-846

SOP No. CORP-MT-0007NC

Revision No. 2.5

Revision Date: 11/22/04

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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. The associated LIMs method code is O9.
- 1.3. 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.
- 1.4. Methods 7471A and 245.5 are applicable to the preparation and analysis of mercury in soils, sediments, bottom deposits, wastes, wipes and sludge-type materials. All matrices require sample preparation prior to analysis.
- 1.5. The STL North Canton reporting limit for mercury in solid matrices is 0.033 mg/kg based on 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 hydrochloric 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. Employees must abide by the policies and procedures in the Corporate Safety Manual and this document.
- 5.2. Samples that contain high concentrations of carbonates or organic material or samples that are at elevated pH can react violently when acids are added.
- 5.3. The following is a list of the materials used in this method, which have a serious or significant hazard rating. NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table. A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Mercury (1,000 PPM in Reagent)	Oxidizer Corrosive Poison	0.1 Mg/M3 Ceiling (Mercury Compounds)	Extremely toxic. Causes irritation to the respiratory tract. Causes irritation. Symptoms include redness and pain. May cause burns. May cause sensitization. Can be absorbed through the skin with symptoms to parallel ingestion. May affect the central nervous system. Causes irritation and burns to eyes. Symptoms include redness, pain, and blurred vision; may cause serious and permanent eye damage.
Nitric Acid	Corrosive Oxidizer	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia

	Poison		and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Hydrochloric Acid	Corrosive Poison	5 PPM-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Potassium Permanganate	Oxidizer	5 Mg/M3 for Mn Compounds	Causes irritation to the respiratory tract. Symptoms may include coughing, shortness of breath. Dry crystals and concentrated solutions are caustic causing redness, pain, severe burns, brown stains in the contact area and possible hardening of outer skin layer. Diluted solutions are only mildly irritating to the skin. Eye contact with crystals (dusts) and concentrated solutions causes severe irritation, redness, and blurred vision and can cause severe damage, possibly permanent.
Magnesium Perchlorate	Oxidizer	None	Inhalation may cause irritation to the respiratory tract. Symptoms may be coughing or shortness of breath.. May cause irritation of skin and eyes. Symptoms include redness, itching and pain.

Potassium Persulfate	Oxidizer	None	Causes irritation to the respiratory tract. Symptoms may include coughing, shortness of breath. Causes irritation to skin and eyes. Symptoms include redness, itching, and pain. May cause dermatitis, burns, and moderate skin necrosis.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

- 5.4. Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Cut resistant gloves must be worn doing any other task that presents a strong possibility of getting cut. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.
- 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. All samples with pink stickers that read "Caution/Use Hood!" **must** be opened in the hood. Contact the EH&S Coordinator if this is not possible. Solvent and waste containers will be kept closed unless transfers are being made.
- 5.6. All work must be stopped in the event of a known or potential compromise to the health and safety of a STL North Canton associate. The situation must be reported **immediately** to the EH&S Coordinator and the 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).
- 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 coarse 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 (10 ppm) mercury standards (in 10% HNO₃) are purchased as custom STL North Canton 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. Working mercury standard (0.1 ppm): Take 1 mL of the stock mercury standard (7.2) 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% HNO₃. This acid (150 uL of concentrated HNO₃) must be added to the flask/bottle before the addition of the stock standard aliquot.

7.4. The calibration standards must be prepared fresh daily from the working standard (7.3) by transferring 0, 0.2, 0.5, 1.0, 5.0 and 10.0 mL aliquots of the working mercury standard into sample preparation 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.

7.5. The initial calibration verification standard must be made from a different stock solution than that of the calibration standards.

7.6. 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.

7.7. 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.

7.8. Sulfuric acid (H_2SO_4), concentrated, trace metal grade or better.

7.9. Hydrochloric acid (HCl), concentrated, trace metal grade or better.

7.10. Aqua Regia: Prepare immediately before use by carefully adding three volumes of concentrated HCl to one volume of concentrated HNO_3 .

7.11. 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.

7.12. 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.

7.13. Potassium permanganate, 5% solution (w/v): Dissolve 5 g of potassium permanganate 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 $4^\circ \text{C} \pm 2^\circ \text{C}$ 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 North Canton 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, MS/MSD) 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. 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 70-130% recovery must be applied.

- In the instance where the LCS recovery is $> 130\%$ and the sample results are $< \text{RL}$, 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 70 - 130 % 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 reparation 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 10% 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 reparation of the ICV, ICB, CRA, CCV and CCB with the calibration curve.
- 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.
- 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 North Canton 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 (7.3) into a series of sample digestion bottles. For the ICV, transfer a 2.5 mL aliquot of the working standard. The ICV working standard must be made from a source other than that used for the calibration standards.

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 below.

11.1.4. Transfer triplicate 0.2 g portions of a well mixed sample into a clean sample digestion bottle. Add 10 mL of reagent water to each standard bottle. Continue preparation as described under 11.1.5.

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 10 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. Add 40 mL of distilled water.

11.1.5.4. Add 15 mL of potassium permanganate solution.

11.1.5.5. Heat for 30 minutes in the water bath at 90 - 95 °C.

11.1.5.6. Cool.

11.1.5.7. Add 6 mL of sodium chloride-hydroxylamine sulfate solution to reduce the excess permanganate.

11.1.5.8. To each **standard** bottle: Add 50 mL of reagent water.
To each **sample** bottle: Add 50 mL of reagent water.

11.1.5.9. 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% HNO₃ and allow to bubble rinse until the next sample is analyzed.
- 11.2.4. Automated determination: Refer to Appendix G for instrument setup and operation.
- 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 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:

$$\%R = 100 \left(\frac{\text{Found(ICV)}}{\text{True(ICV)}} \right)$$

12.2. CCV percent recoveries are calculated according to the equation:

$$\%R = 100 \left(\frac{\text{Found(CCV)}}{\text{True(CCV)}} \right)$$

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:

$$mg/kg, dry weight = (C \times V \times D)/(W \times S)$$

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:

$$mg/kg, dry weight = (C)/(W \times S)$$

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 North Canton 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 9.1.

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 +/- 30 % and the matrix spike duplicates should compare within 20% RPD. The method blanks must meet the criteria in Section 9.4. 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. All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

15.2. Waste Streams Produced by this Method

15.2.1. The following waste streams are generated by this method.

15.2.1.1. Acid Waste. This waste disposed of in the designated container labeled "Acid Waste".

16. **REFERENCES**

16.1. References

16.1.1. Test Methods for Evaluating Solid Waste , Physical/Chemical Methods, SW-846, 3rd Edition, Final Update II, Revision I, September 1994, Method 7471A (Mercury).

16.1.2. "Methods for the Chemical Analysis of Water and Wastes", EPA-600/4-79-020, U.S.EPA, August 1983, Method 245.5.

16.1.3. U.S.EPA Statement of Work for Inorganics Analysis, ILMO3.0 and IMLO4.0.

16.1.4. Corporate Quality Management Plan (QMP), current version.

16.1.5. STL Laboratory Quality Manual (LQM), current version. Associated SOPs and Policies, latest version

16.1.6. STL Corporate Safety Manual, M-E-0001 and STL North Canton Facility Addendum and Contingency Plan, current version.

16.2. Associated SOPs and Policies, latest version.

16.2.1. QA Policy, QA-003

16.2.2. Glassware Washing, NC-QA-0014

16.2.3. Statistical Evaluation of Data and Development of Control Charts, NC-QA-0018

16.2.4. Method Detection Limits and Instrument Detection Limits, NC-QA-0021

16.2.5. Navy/Army SOP, NC-QA-0016

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.

17.1.3. 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 North Canton 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 0.3 mg/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 - Water Bath Procedure

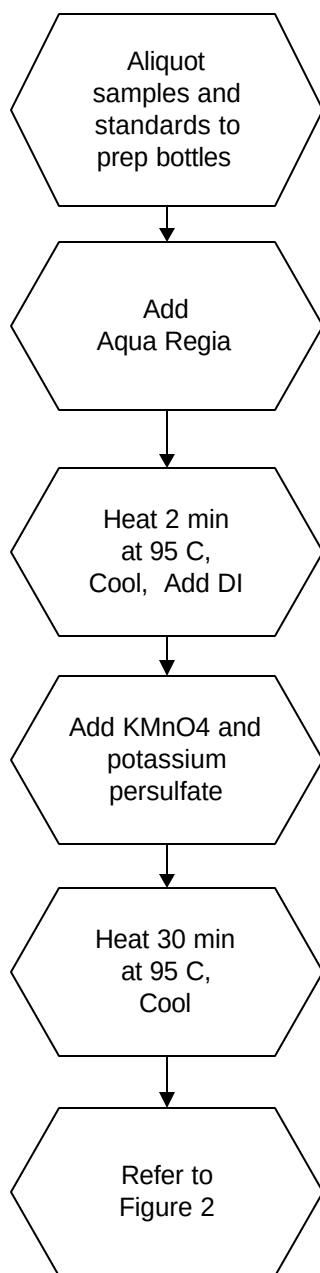
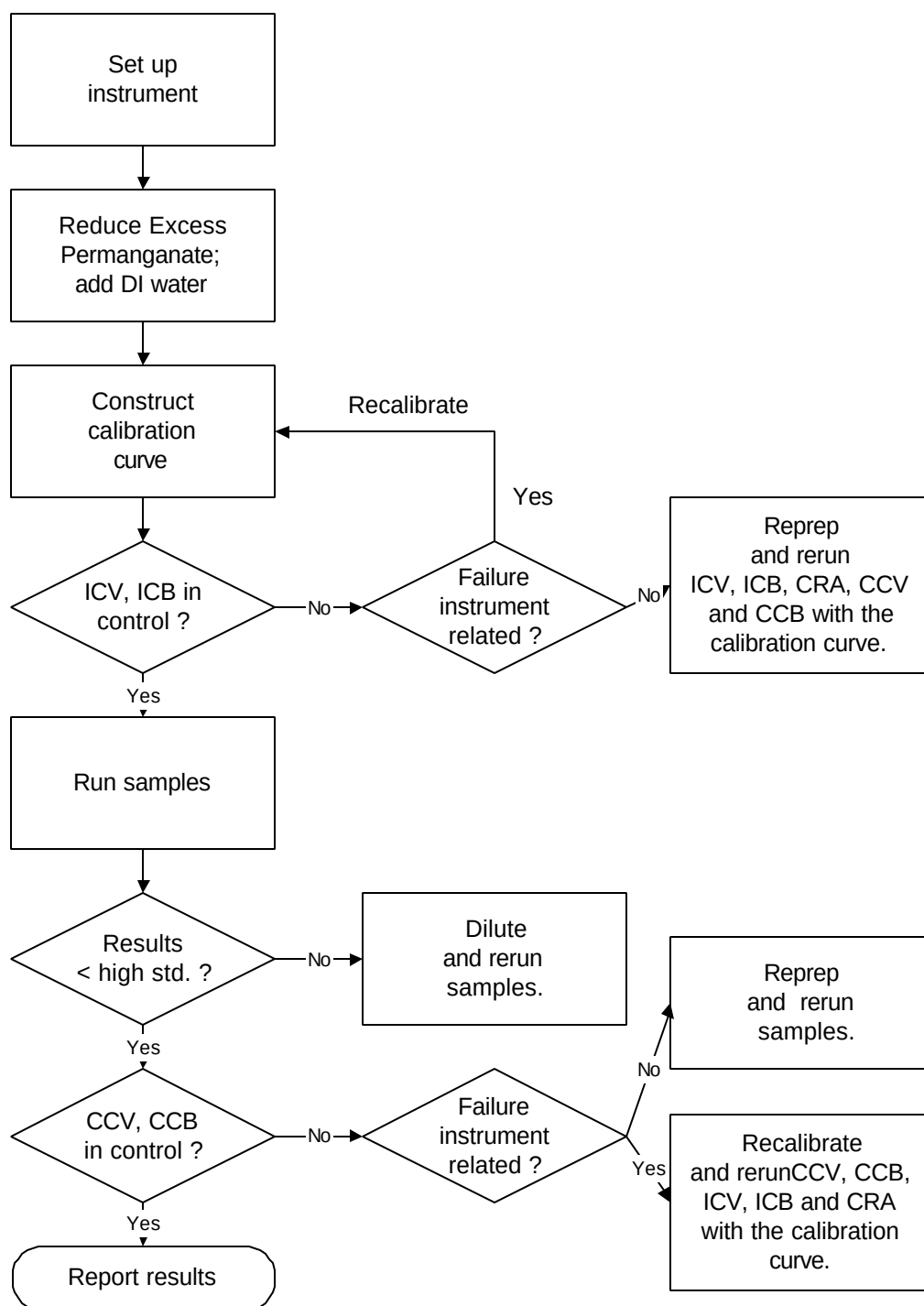


Figure 2. CVAA Mercury Analysis



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)	0.005
Std 5 (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.	90-110 % recovery.	Terminate analysis; Correct the problem; Recalibrate or reprep with calibration curve (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 with calibration curve (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 with calibration curve (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 with calibration curve (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

EXAMPLE

STL NORTH CANTON Hg DATA REVIEW CHECKLIST

Example
STL North Canton 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

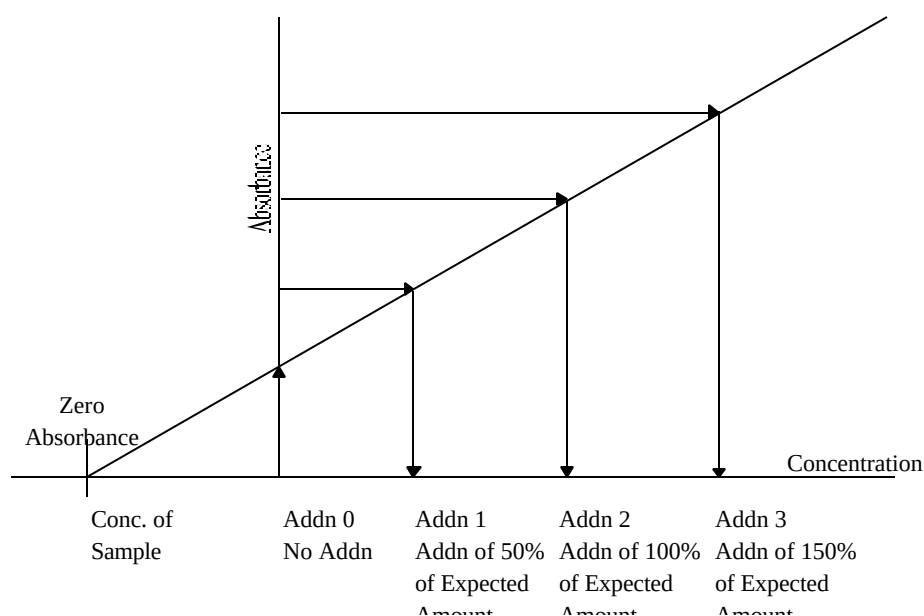
APPENDIX C. MSA GUIDANCE

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.	

APPENDIX G

INSTRUMENT SET UP

Hg Analysis (Leeman PS200II)

SYSTEM INITIALIZATION AND WARM UP

1. F1 Menu
2. Instrument
 - a. Taskmaster
 - b. #4 Wake System Up Enter

The warming up period takes approximately 10 minutes.

TO SET UP INSTRUMENT FOR ANALYSIS

1. F1 Menu
2. Autosampler
 - A. Rack Entry
 - B. Edit (ex. Rack 1), Enter
 - C. Cup ID - Enter (clears sample #'s)
 - D. Extended ID- type in matrix of sample (water or solid), Enter.
 - E. Press Insert Key and move cursor with arrows to cup ID and begin typing labels.
 - F. F3 Print Screen
3. Press F2 Macro key and type in analyst's first name - Enter
 - A. Enter folder name - ex. HG0306, Enter. If folder does not exist, type Y - Enter.
 - B. Type in - "Rack 1", "Rack 2" etc. , Enter.

D. Type in : FROM CUP TO CUP

Ex. = 1 30

Do the same for position 2 if needed. If not needed, you must press Enter 3 times to begin analysis.

Controlled Copy

Copy No. _____

Implementation Date: 1-31-06

SOP No. NC-WC-0006

Revision No. 6

Revision Date: 01/30/06

Page 1 of 15

STL NORTH CANTON STANDARD OPERATING PROCEDURE

TITLE: ALKALINITY (TOTAL)

(SUPERSEDES: REVISION 5, DATED 10/25/04)

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1. SCOPE AND APPLICATION

- 1.1. This method is applicable for the determination of total alkalinity in drinking, surface, saline, domestic, and industrial waters and wastewaters. It is also applicable to the determination of water-soluble alkalinity in solid samples if they have been prepared according to NC-IP-0009. It is based on EPA Method 310.1 and Standard Methods 2320B. The working linear range is 5 to 2500 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 by the laboratory.
- 1.3. QuantIMs reference for total alkalinity is VC (310.1) and LV (2320B).

2. SUMMARY OF METHOD

- 2.1. An unaltered sample is titrated to an electrometrical endpoint of pH 4.5. **The sample must not be filtered, concentrated, or altered in any way.**

3. DEFINITIONS

- 3.1. Refer to the glossary in the STL North Canton Laboratory Quality Manual (LQM), current version.

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. Specific selection of reagents may be required to avoid introduction of contaminants.
- 4.2. Samples with salts of weak organic and inorganic acids and greases or oils will interfere with pH measurements.
- 4.3. The method is suitable for all concentration ranges of alkalinity; however, appropriate aliquots should be used to avoid a titration volume greater than 50 mL.

5. SAFETY

- 5.1. Employees must abide by the policies and procedures in the Corporate Safety Manual and this document.
- 5.2. The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Sulfuric Acid	Corrosive Oxidizer Dehydra-dator	1 mg/m ³	This material will cause burns if comes into contact with the skin or eyes. Inhalation of vapors will cause irritation of the nasal and respiratory system.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

- 5.3. Eye protection, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Cut-resistant gloves must be worn doing any other task that presents a strong possibility of getting cut. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.
- 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 an STL NORTH CANTON associate. The situation must be reported **immediately** to the EH&S Coordinator and the Laboratory Supervisor.

6. EQUIPMENT AND SUPPLIES

- 6.1. Alkalinity – Manual
 - 6.1.1. Stir plate and stir bars
 - 6.1.2. Graduated cylinders: various
 - 6.1.3. Beakers: various
 - 6.1.4. Buret: Class A 25 mL or 50 mL (preferred)
- 6.2. Alkalinity - Automated
 - 6.2.1. Autotitrator
 - 6.2.2. 50 mL centrifuge tubes
- 6.3. Alkalinity – Manual and Automated
 - 6.3.1. pH meter and electrode(s) with temperature compensation

- 6.3.2. Volumetric pipettes: various
- 6.3.3. Autopipettor and disposable tips
- 6.3.4. Top loading balance: Capable of accurately weighing ± 0.01 g
- 6.3.5. Volumetric flasks: various
- 6.3.6. Oven
- 6.3.7. Desiccator

7. REAGENTS AND STANDARDS

7.1. Reagents

- 7.1.1. 0.02 N Sulfuric Acid: reagent grade, purchased, standardized monthly.
- 7.1.2. Sodium Carbonate (Na_2CO_3): standard grade, dry overnight in 180°C oven and cool in a desiccator or purchased primary standard grade.
- 7.1.3. Sodium Carbonate Solution: Add 2.50g of Na_2CO_3 (record exact weight of Na_2CO_3 used) to a 1000mL volumetric flask and dilute to volume with reagent water. Mix well.

7.2. Standards

7.2.1. Target Calibration Standard

- 7.2.1.1. pH Buffers: 4, 7, and 10 (Manufactured)

7.2.2. Laboratory Control Sample

- 7.2.2.1. Alkalinity Standard, 25,000 mg/L CaCO_3 , purchased or other commercially available reference solutions.

7.2.3. Matrix Spike Standard

- 7.2.3.1. Alkalinity Standard, 25,000 mg/L CaCO_3 , purchased

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

- 8.1. Samples are not chemically preserved.
- 8.2. Samples are stored in plastic or glass containers at $4^{\circ}\text{C} \pm 2^{\circ}\text{C}$.
- 8.3. The holding time is fourteen days from sampling to analysis.
- 8.4. The bottle must be filled with no headspace and provided in a separate container.
- 8.5. Do not open sample bottle before analysis. If other tests are to be performed from the same bottle, Alkalinity must be determined first. This is dependent on the client actually sending a separate bottle for alkalinity.

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, MS, MSD) 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. Method Blank

- 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 reagent water blank consisting of 50 mL of reagent water and all other reagents added to samples within the analytical batch is analyzed with each analytical batch of samples.

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 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 (LCS)

9.3.1. One aqueous LCS must be processed with each preparation batch. The LCS must be carried through the entire analytical procedure. The LCS is used to monitor the accuracy of the analytical process. Ongoing monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines.

9.3.2. An LCS consisting of 1mL of the 25,000 mg/L alkalinity standard and 50 mL reagent water or other commercially available reference solution is analyzed with each analytical 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.

9.3.3.2. The only exception is that if the LCS recoveries are biased high and the associated sample is ND for the parameter(s) of interest, the batch is acceptable. **This must be addressed in the project narrative.**

9.3.3.3. 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 1 mL of the 25,000 mg/L alkalinity standard and 50 mL of the sample will be analyzed.

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.
- 9.4.3.4. If client program requirements specify to confirm matrix interferences, repreparation and reanalysis of the MS/MSD may be necessary.

9.5. QC Acceptance Criteria

9.5.1. Control limits are established by the laboratory as described in NC-QA-0018.

9.5.2. Laboratory control limits are internally generated and updated periodically unless method specified. Control limits are listed in the Laboratory Quality Manual (LQM) and the latest version is easily accessible via the LIMs (QC Browser program).

9.6. Method Detection Limits (MDLs) and MDL Checks

9.6.1. MDLs and MDL Checks are established by the laboratory as described in SOPs S-Q-003 and NC-QA-0021.

9.6.2. MDLs are listed in the Laboratory Quality Manual (LQM) and the latest version is easily accessible via the LIMs (QC Browser program).

9.7. Nonconformance and Corrective Action

9.7.1. Any deviations from QC procedures must be documented as a nonconformance, with applicable cause and corrective action approved by the facility QA Manager.

10. CALIBRATION AND STANDARDIZATION

10.1. Instrument Directions

10.1.1. Calibrate the pH meter according to the manufacturer's specifications. See pH Electrode Method SOP # NC-WC-0010.

10.2. Initial Calibration

10.2.1. The pH meter is calibrated everyday with the 4 and the 7 calibration buffers and is verified at the beginning of the run by using the 10 buffer. The pH buffers should bracket the sample concentration.

10.3. Continuing Calibration

10.3.1. The pH meter is checked every ten readings with a midrange (pH 7) buffer to ensure the calibration remain linear. The acceptance range for the calibration check is 7 ± 0.05 pH units or recalibration is necessary.

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. For solids preparation, see SOP NC-IP-0009.

11.3.2. No preparation is necessary for water samples.

11.4. Standardization

11.4.1. To standardize 0.02 N sulfuric acid, titrate 50 mL reagent water and 0.125 g sodium carbonate (weighed accurately and recorded) with 0.02 N H₂SO₄ to a pH of 4.5. This should be performed monthly or on a new lot of acid (whichever is more frequent). Calculate as follows:

$$N = \frac{A \times 1000}{53.00 \times B} \text{ (manual)}$$

$$N = \frac{A \times 1000}{53.00 \times B} \times \frac{20}{50} \text{ (Autotitrator)}$$

A=gNa₂CO₃B=mL .02 N H₂SO₄ titrant

11.5. Repeat standardization two or three more times. Record standardization in the calibration logbook.

11.6. Sample Analysis – Manual

11.6.1. Do not shake sample.

11.6.2. Record the initial pH prior to sample analysis.

11.6.3. Use a sufficiently large volume of titrant (>20 mL in a 50 mL buret) to obtain good precision while keeping the volume low enough to permit a sharp end point

11.6.4. Place 50 mL of sample, or an aliquot diluted to 50 mL with reagent water, in a beaker. Begin mixing; measure and record initial pH of the sample. Titrate the sample to an endpoint of pH 4.5 with 0.02 N H₂SO₄. Record the volume of the titrant on the analytical logsheet. Samples requiring >50 mL titrant (> 75 mL

using autotitrator) should be re-analyzed using less sample volume. Record dilution.

11.6.5. Use a sufficiently large volume of titrant (>20 mL in a 50 mL buret) to obtain good precision while keeping the volume low enough to permit a sharp end point.

11.7. Sample Analysis – Automated – Summary

11.7.1. The samples are analyzed on the autotitrator for Total Alkalinity.

11.7.2. Do not shake sample.

11.7.3. Place 50 mL of sample, or an aliquot diluted to 50 mL with reagent water, in a 50 mL centrifuge tube. See Manufacturer's information for operating instructions.

11.7.4. If a dilution of the sample was done change the volume on the schedule to reflect the dilution.(based on a 20 mL sample inject) For alkalinity the dilution factor will be taken into account in the final calculation. Do not manually multiply the dilution unless it was not typed into the schedule.

11.7.5. After the results have been gathered from the instrument make sure to check the pH of all the samples. If a sample has an initial pH of >4.5 and the Total Alkalinity is zero, the sample must be diluted and reanalyzed.

11.8. Analytical Documentation

11.8.1. 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.

11.8.2. All standards are logged into a department standard logbook. All standards are assigned a unique number for identification. The supervisor or designee reviews logbooks.

11.8.3. 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.

11.8.4. Sample results and associated QC are entered into the LIMs after final technical review.

12. DATA ANALYSIS AND CALCULATIONS

$$12.1. \text{ Alkalinity, mg/L CaCO}_3 \text{ to pH 4.5} = \frac{A \times N \times 50,000}{\text{mL of sample}}$$

$$12.2. \text{ LCS \%} = \frac{\text{mg / L}}{500 \text{ (true)}} \times 100$$

$$\text{MS/MSD \%} = \frac{B - C}{500 \text{ (true)}} \times 100$$

Where:

A = mL of Titrant

N = Normality of Titrant

B = MS/MSD, mg/L

C = Sample, mg/L

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.

13.2.2. Method validation information (where applicable) in the form of laboratory demonstrations of capabilities is maintained for this method in the laboratory QA files.

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. All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in Section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."
- 15.2. Waste Streams Produced by the Method
- 15.2.1. The following waste streams are produced when this method is carried out.
- 15.2.1.1. This waste is drained from the titration cell into the aqueous waste stream since the pH range is between 4 and 10. Any sample waste generated that is not in this pH range is collected in a designated container identified as "Acid Waste".
- 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. EPA-600/4-79-020, Methods for Chemical Analysis of Water and Wastes, Revised March 1983, Alkalinity, Method 310.1.
- 16.1.2. Standard Methods for the Examination of Water and Wastewater, 18th Edition, 1992, Alkalinity Methods, 2320B.
- 16.1.3. EPA 600, Methods for Chemical Analysis of Water and Wastes, pH, Method 150.1.
- 16.1.4. Corporate Quality Management Plant (QMP), current version.
- 16.1.5. STL Laboratory Quality Manual (LQM), current version.
- 16.1.6. STL Corporate Safety Manual, M-E-0001 and STL North Canton Facility Addendum and Contingency Plan, current version.

16.2. Associated SOPs

16.2.1. Solid Extraction for Wet Chemistry Parameters, NC-IP-0009.

16.2.2. pH Electrode Method for Wet Chemistry Parameters, NC-WC-0010.

16.2.3. Statistical Evaluation of Data and Development of Control Charts, NC-QA-0018.

16.2.4. QA Policy, QA-003

16.2.5. Glassware Washing, NC-QA-0014

16.2.6. Method Detection Limits and Instrument Detection Limits, S-Q-003 and NC-QA-0021

16.2.7. Navy/Army SOP, NC-QA-0016

17. MISCELLANEOUS (TABLES, APPENDICES, ETC...)

17.1. Reporting limits

17.1.1. The lower reporting limit (RL) for undiluted samples is 5 mg/L CaCO_3 .

17.1.2. If samples require dilution or smaller volumes than specified in this method, the RL will be elevated.

17.2. Method Deviation

17.2.1. A fixed endpoint of 4.5 is used for all samples since the sample concentration is often unknown.

17.2.2. The Sodium Carbonate (Na_2CO_3) is dried at 180°C overnight instead of at 250° C for 4 hours.

17.2.3. The standard acid solution is not boiled gently for 3-5 minutes under a watch glass cover.

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SOP No. NC-WC-0008
Revision No. 3.4
Revision Date: 10/28/04
Page 1 of 23

Implementation Date: 11-22-04

STL NORTH CANTON STANDARD OPERATING PROCEDURE

TITLE: BIOCHEMICAL OXYGEN DEMAND (BOD) AND CARBONACEOUS BIOCHEMICAL OXYGEN DEMAND (CBOD) BY DISSOLVED OXYGEN PROBE

(SUPERSEDES: REVISION 3.3, DATED 02/07/03)

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1. SCOPE AND APPLICATION

- 1.1. This method measures the consumption of oxygen by microbial processes in waters and wastewater. It is based on EPA Method 405.1 and Standard Methods 5210B for Biochemical Oxygen Demand (BOD). This method also measures Carbonaceous Biochemical Oxygen Demand (CBOD). The approximate working range is 2 to 4000 mg/L.
- 1.2. The associated QuantIMS method codes are JJ and CV.
- 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. Dilutions of the sample are incubated for five days (or another recommended number of days upon request) at $20^{\circ}\text{C} \pm 1.0^{\circ}\text{C}$ in the dark. The reduction of dissolved oxygen concentration during the incubation period yields a measure of the Biochemical Oxygen Demand.

3. DEFINITIONS

- 3.1. Refer to the glossary in the STL North Canton Laboratory Quality Manual (LQM), current version.

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. Specific selection of reagents may be required to avoid introduction of contaminants.
- 4.2. Reactive gases, which pass through the membrane probes, may interfere.
- 4.3. Hydrogen sulfide may interfere by lowering cell sensitivity.
- 4.4. Oil and extremely dirty samples may interfere by coating or plugging the membrane.

5. SAFETY

- 5.1. Employees must abide by the policies and procedures in the Corporate Safety Manual, the facility addendum to the CSM, and this document.
- 5.2. The following is a list of the materials used in this method which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Sulfuric Acid	Corrosive Oxidizer Dehydrator Poison Carcinogen	1 Mg/M3- TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.
Sodium Hydroxide	Corrosive	2 Mg/M3- Ceiling	Severe irritant. Effects from inhalation of dust or mist vary from mild irritation to serious damage of the upper respiratory tract, depending on severity of exposure. Symptoms may include sneezing, sore throat or runny nose. Contact with skin can cause irritation or severe burns and scarring with greater exposures. Causes irritation of eyes, and with greater exposures it can cause burns that may result in permanent impairment of vision, even blindness.
Ammonium Hydroxide	Corrosive Poison	50 ppm- TWA	Vapors and mists cause irritation to the respiratory tract. Causes irritation and burns to the skin and eyes.
Potassium Hydroxide	Corrosive	2 Mg/M3- Ceiling	Severe irritant. Effects from inhalation of dust or mist vary from mild irritation to serious damage of the upper respiratory tract, depending on severity of exposure. Symptoms may include sneezing, sore throat or runny nose. Contact with skin can cause irritation or severe burns and scarring with greater exposures. Causes irritation of eyes, and with greater exposures it can cause burns that may result in permanent impairment of vision, even blindness.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

- 5.3. Eye protection that protects against splash, 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.
- 5.4. 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. It is recommended that neat standards be purchased only as a last resort. The preparation of standards from neat materials and reagents should be conducted in a fume hood with the sash closed as far as the operations will permit.
- 5.7. Standards in solution may be diluted in the open laboratory when syringes and the like are utilized.
- 5.8. 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 the EH&S Coordinator and the Laboratory Supervisor.

6. EQUIPMENT AND SUPPLIES

- 6.1. Incubator: 20°C ($\pm$ 1°C)
- 6.2. Dissolved Oxygen Meter and Probe (BOD Magic)
- 6.3. BOD Incubation Bottles (300 mL), Stoppers, and Caps
- 6.4. Pipettes: Disposable and Pasteur
- 6.5. Volumetric pipettes, various
- 6.6. Auto pipettor and tips

- 6.7. 20 L water bottle
- 6.8. Chlorine test kit (Hach)
- 6.9. pH paper, range 1 - 14
- 6.10. Class A buret: 10 mL or 25 mL
- 6.11. Graduated cylinders, various
- 6.12. Beakers, plastic, various
- 6.13. Top loading balance, capable of accurately weighing ± 0.01 g

7. REAGENTS AND STANDARDS

7.1. Reagents

7.1.1. Nutrient Buffer Pillow, Purchased for 19 liters

7.1.2. Oxygenated Buffer Dilution Water: Add 1 nutrient buffer pillow to 19 liters of water in a 20 L bottle. Mix well to aerate. Prepare daily.

NOTE: The water should sit for 1-2 days to fully aerate prior to adding the pillow, if not, aerate using a pump and bubbling frit for fifteen minutes. In either case the initial dissolved oxygen should be greater than 7.0 mg/L before using the water to set up samples.

7.1.3. Sodium Sulfite: (Na_2SO_3), reagent grade

7.1.4. 0.025N Sodium Sulfite Solution: Dissolve 0.16g Na_2SO_3 into reagent water and dilute to 100 mL. Prepare fresh daily.

7.1.5. Sulfuric Acid: (H_2SO_4), concentrated, reagent grade

7.1.6. 1 N Sulfuric Acid: Slowly add 2.8 mL concentrated H_2SO_4 to 80 mL reagent water, cool and dilute to 100 mL.

7.1.7. Sodium Hydroxide: (NaOH), reagent grade

- 7.1.8. 1 N Sodium Hydroxide: Add 4.0 g NaOH pellets to 80 mL reagent water, cool and dilute to 100 mL.
- 7.1.9. Manganese Sulfate: ($\text{MnSO}_4 \bullet 4\text{H}_2\text{O}$ or $\text{MnSO}_4 \bullet 2\text{H}_2\text{O}$ or $\text{MnSO}_4 \bullet \text{H}_2\text{O}$), reagent grade
- 7.1.10. Manganese Sulfate Solution: Dissolve either 480 g $\text{MnSO}_4 \bullet 4\text{H}_2\text{O}$, 400 g $\text{MnSO}_4 \bullet 2\text{H}_2\text{O}$ or 364 g $\text{MnSO}_4 \bullet \text{H}_2\text{O}$ in reagent water, mix and dilute to 1000 mL. Prepare bi-annually.
- 7.1.11. Potassium Hydroxide: (KOH), reagent grade
- 7.1.12. Potassium Iodide: (KI), reagent grade
- 7.1.13. Azide: (NaN_3), reagent grade
- 7.1.14. Azide Reagent: Dissolve 700 g KOH and 150 g KI in reagent water, mix and dilute to 1000 mL. Add 10g NaN_3 dissolved in 40-mL reagent water. Store in a dark bottle and prepare bi-annually.
- 7.1.15. 0.025 N Sodium Thiosulfate: ($\text{Na}_2\text{S}_2\text{O}_3 \bullet 5 \text{H}_2\text{O}$), reagent grade
- 7.1.16. Starch Solution: Purchased commercially.
- 7.1.17. Nitrification Inhibitor, purchased (HACH)
- 7.1.18. Polyseed Inoculum, purchased (polybac)
- 7.1.19. Seed: Add 1 polyseed pill to either 500-mL fresh buffer water or reagent water. Mix and aerate for one hour, following manufacturer's directions. Prepare fresh daily, good for only six hours.
- 7.1.20. Ammonium Hydroxide : (NH_4OH), reagent grade
- 7.2. Standards
 - 7.2.1. Laboratory Control Sample (Stock standard): 150 mg/L Glucose + 150 mg/L Glutamic Acid- Biochemical Oxygen Demand standard, purchased

- 7.2.2. Laboratory Control Sample (Working standard): 6 mL of 150 mg/L Glucose + 150 mg/L glutamic acid stock standard (true concentration = 198 mg/L), oxygenated buffer dilution water and seed.

8. SAMPLE COLLECTION, PRESENTATION AND STORAGE

- 8.1. Samples are not chemically preserved.
- 8.2. Samples are collected in plastic or glass containers and stored at $4^{\circ}\text{C} \pm 2^{\circ}\text{C}$.
- 8.3. The holding time is 48 hours from sampling to the initiation of sample preparation.

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 Blanks) which are processed similarly, with respect to the procedure. All sample setups must be initiated within a 24-hour period beginning 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. Method Blanks (MB)

- 9.2.1. One buffered dilution blank and three seeded blanks 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. Corrective Action for Blanks

- 9.2.2.1. If the analyte level in the buffered dilution blank exceeds the reporting limit for the analytes of interest in the sample, the probable cause is contamination of glassware. Rinse glassware with 1:1 HCL then rinse six times with DI water. Then 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.**

9.2.2.2.If there is no analyte greater than the RL in the samples associated with an unacceptable 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.**

9.2.2.3.If the buffered dilution blank DO uptake is > 0.2 mg/L, the oxygen uptake will be narrated.

9.2.2.4.Three seeded blanks must be processed with each batch. The average seeded blank DO uptake is reported as the blank for the batch. (Optimum DO uptake is between 0.5-1.0 mg/L) If the seed blank does not meet criteria, the oxygen uptake will be narrated and samples reanalyzed upon client request.

9.2.3. 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. 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.

9.2.3.1.Corrective Action for LCS

9.2.3.1.1.If the LCS recovery is outside established control limits the system is out of control and corrective action must occur.

9.2.3.2. The only exception is that if the LCS recoveries are biased high and the associated sample is ND for the parameter of interest, the batch is acceptable.

This must be addressed in the project narrative.

9.2.3.3. Corrective action will be reparation and reanalysis of the batch unless the client agrees that other corrective action is acceptable.

9.2.4. Duplicates

9.2.4.1. Sample duplicates are performed per analytical batch and must meet laboratory-specific limits for precision.

9.2.4.2. There must be a sample duplicate for regular BOD and for carbonaceous BOD.

9.2.4.3. Sample duplicates may not be possible if there is insufficient sample volume therefore, an LCS Duplicate may be analyzed instead.

9.3. QC Acceptance Criteria

9.3.1. Control Limits are established by the laboratory as described in SOP NC-QA-0018.

9.3.2. Laboratory control limits are internally generated and updated periodically unless method specified. Control limits are listed in the Laboratory Quality Manual (LQM) and the latest version is easily accessible via the LIMS (QC Browser program).

9.4. Nonconformance and Corrective Action

9.4.1. Any deviation from QC procedures must be documented as a nonconformance, with applicable cause and corrective action approved by the facility QA Manager.

10. CALIBRATION AND STANDARDIZATION

10.1. The BOD Magic probe DO meter may be calibrated using several techniques. It is important to determine which technique works best and use the same method when setting up the BOD samples and taking them down after the incubation period.

10.1.1. Oxygen Calibration (Winkler Method)

10.1.1.1. Fill two bottles to the neck with freshly prepared buffer water.

10.1.1.2. Place a stir bar in one of the bottles and carefully insert probe as to not allow excess oxygen in. Begin stirring. Alternatively, place the BOD Magic probe into the bottles with the automatic stirrer on.

10.1.1.3. To the second bottle, remove 5 mL buffer water, add 1.0 mL MnSO_4 solution and mix well. Add 1.0-mL Azide solution and mix well. Add 1.0 mL concentrated H_2SO_4 and mix well. Pour off exactly 100 mL and discard. Add 1 squirt starch solution and titrate with 0.025 N Sodium Thiosulfate solution to a clear end-point. Record mLs of titrant used.

10.1.1.4. Oxygen (mg/L) equals mLs titrant used. With the probe in the first bottle, adjust the oxygen meter to read the concentration of oxygen (mg/L) titrated.

10.1.1.5. Calibrate oxygen meter daily/or with a new batch of buffer water, which ever is more frequent

10.1.2. Instrument Calibration over saturated air.

10.1.2.1. Refer to the manufacturer's recommended procedure for the BOD Magic calibration over saturated air.

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 Procedure

11.3.1. Assemble the BOD tray protocol according to the preferred calibration method.

11.3.1.1. Test an aliquot of sample for chlorine following the test procedures in the Hach test kit. If chlorine is present, add sodium sulfite solution drop by drop to the colored aliquot until pink color disappears. Note the number of drops used.

To another aliquot of sample add the same proportion of sodium sulfite (ex: 5 drops to 25 mL = 40 drops to 200 mL). Mix well. Test again after 20 minutes.

11.3.2. **NOTE:** Addition of sodium sulfite must be performed in a drop wise fashion to prevent the accidentally depletion of dissolved oxygen.

11.3.3. Check the pH of the sample. Adjust pH (if necessary) to 6.5 – 7.5 using 1 N NaOH or 1 N H₂SO₄.

11.3.4. Sample temperature adjustment – Before making dilutions, bring samples to 20°C±1 °C. Add the appropriate volume of sample into labeled bottles. Dilutions of 10, 50, 150, and 300 mL may be set up to cover all ranges, but greater dilutions may be necessary if the sample seems to be high in organic material.

11.3.5. For CBOD samples only: Add approximately 0.1 gram of nitrification inhibitor to each sample bottle (including any associated QC samples.)

11.3.6. Add the appropriate volume of seed to each sample bottle (including seeded blanks and standards), either manually or by using the BOD Magic seed dilution pump. (Recommendation: 2-5 mL of seed to ensure an oxygen depletion of the seed blanks of 0.5-1.0 mg/L).

11.3.7. Add buffered dilution water to fill each bottle, either manually or by using the BOD Magic dilution water pump.

11.4. Sample Analysis Procedure

11.4.1. Follow operating instruction in the instrument manual for the BOD Magic.

11.4.2. Determine the initial DO on the bottles. The initial DO reading for all of the samples and associated QC should be between 7-9 mg/L.

11.4.3. Samples containing more than 9 mg of DO at 20 °C initially should be reduced. To prevent loss of oxygen during the incubation of such samples, reduce DO by vigorously shaking/agitating or by aerating with clean, filtered air until it is below 9 mg/L.

11.4.4. Replace any displaced contents of the bottles with sample dilution to fill the bottle. Stopper tightly and incubate for 5 days. (or other recommended number of days upon request) at 20°C.

11.4.5. After the appropriate number of days, remove the samples and follow the operating instructions for the BOD Magic to analyze the final oxygen concentration.

11.4.6. Record the results or print the BOD run.

11.5. Analytical Documentation

11.5.1. Record all analytical information on the analytical logsheet which may be in an electronic format, including the analytical data from standards, blanks, duplicates, and LCSs and any corrective actions or modifications to the method. The BOD Magic spreadsheet may be used.

11.5.2. All standards are logged into a departmental 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 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. Biochemical Oxygen Demand, $mg/L = ([A - B] - C) \times D$

Where:

A = Initial O₂, mg/L

B = Incubated O₂, mg/L

C = Seeded Blk (Initial O₂, mg/L - Incubated O₂ mg/L)

D = 300 / Volume of sample used, ml

12.2. LCS % Recovery = BOD (from 12.1) $\frac{\text{mg/L/2}}{198 (\text{true})} \times 100$

12.3. Final Biochemical Oxygen Demand

12.3.1. Calculate all the dilutions prepared for each sample.

12.3.2. Average those values, which do not fall below 1 mg/L, incubated O₂ and drop at least 2 mg/L from initial O₂ to incubated O₂. If no sample dilutions drop at least 2 mg/L then report ND. If all sample dilutions fall below 1 mg/L, flag the data appropriately. Prewritten narratives are in the LIMS system.

NOTE: CBOD's have the same calculation as BOD's. Result should be equal to or less than BOD should.

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 Qualification:

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.

13.2.2. Method validation information (where applicable) in the form of laboratory demonstrations of capabilities is maintained for this method in the laboratory QA files.

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. All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

15.2. Waste Streams Produced by the Method

15.2.1. The following waste streams are produced when this method is carried out.

15.2.1.1. Aqueous waste can be poured down the drain if the pH is between 4 and 10. Any sample waste generated that is not in this pH range must be collected and disposed in the container identified "Acid Waste" located in the Metals Lab.

15.3. Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices of STL North Canton. 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. EPA 600, Methods for Chemical Analysis of Water and Wastes, Biochemical Oxygen Demand, Method 405.1

16.1.2. Standard Methods, Eighteenth Edition, Oxygen Demand (Biochemical), Method 5210B.

16.1.3. STL North Canton Laboratory Quality Manual (LQM), current version.

16.1.4. Corporate Quality Management Plan (QMP), current version.

16.2. Associated SOPs

16.2.1. Chlorine, Total (Residual) and Free (NC-WC-0021)

16.2.2. Statistical Evaluation of Data and Development of Control Charts, NC-QA-0018.

16.2.3. QA Policy, QA-003.

16.2.4. Glassware Washing, NC-QA-0014.

16.2.5. Navy/Army SOP, NC-QA-0016.

17. MISCELLANEOUS (TABLES, APPENDICES, ETC...)

17.1. Reporting Limits

17.1.1. The reporting limit (RL) is 2 mg/L.

17.1.2. If samples require dilutions or smaller volumes than specified in this method, the RL will be elevated.

APPENDIX A

QC SUMMARY TABLE

SUMMARY OF INTERNAL QUALITY CONTROL

Method Blank

Frequency:	One Per Batch
Acceptance Criteria:	• Instrument response <RL. • The amount of contaminant in the blank is <u>NOT</u> subtracted from the sample, but is reported with the data and the associated samples are flagged.
Corrective Action:	• Reanalyze blank if it will identify or correct the problem. • Due to method limitations and holding time considerations, samples associated with a contaminated blank are not normally reprocessed. • Document all corrective actions taken.

Laboratory Control Sample(LCS)

Frequency:	One every batch.
Acceptance Criteria:	Recovery is evaluated against accuracy acceptance limits.
Corrective Action:	• If the recovery exceeds the established recovery limits, contact the client to determine if the data is to be redone outside holding time. If the data is to be reported with the failed LCS, a narrative must be written. Include a narrative if the decision is to rerun the data outside of holding time.

APPENDIX B

DETERMINATION OF SAMPLE VOLUMES

CHART 1

Sample Type	Expected BOD (mg/L)
Surface Water	0-10
Polluted Surface	10-50
Treated Sewage	10-100
Raw Sewage	100-500
Industrial Waste	10-500
Strong Industrial Waste	500-5,000

CHART 2

mL of Sample in BOD Bottle	Acceptable Range of BOD value
300	1.0 to 6.5
100	3.0 to 19.5
50	6.0 to 40
25	12 to 80
10	30 to 200
5	60 to 400
2	150-1000
1.0	300 to 2000
0.5	600 to 4000

APPENDIX C

TROUBLESHOOTING and MAINTENANCE

TROUBLESHOOTING

- The probe membrane must be inspected daily and replaced if any tears, defects, or air bubbles appear in or on the membrane. The membrane should be replaced every two weeks for best results. Record membrane replacement in Maintenance logbook.

MAINTENANCE

- See manufacture's instructions for line flushing instructions and tip replacement instructions.

DO Meter Batteries (If applicable)

- If the low battery signal comes on, the batteries are low and need replaced.
- Replace all batteries by removing the back cover and changing them.
- Note battery replacements in the maintenance logbook.

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Implementation Date 6/13/06

SOP No. NC-WC-0010

Revision No. 7

Revision Date: 03/23/06

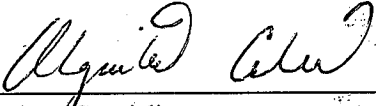
Page 1 of 11

STL NORTH CANTON STANDARD OPERATING PROCEDURE

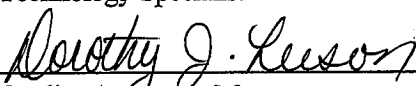
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(SUPERSEDES: REVISION 6, DATED 10/27/04)

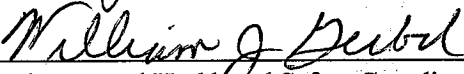
Reviewed by:

 6/8/06
Technology Specialist Date

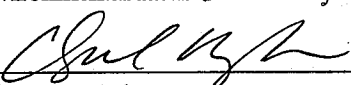
Approved by:

 5/16/06
Quality Assurance Manager Date

Approved by:

 3-27-06
Environmental Health and Safety Coordinator Date

Approved by:

 6/13/06
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 Laboratory Quality Manual (LQM), latest 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. Employees must abide by the policies and procedures in the Corporate Safety Manual and this document.
- 5.2. There are no materials used in this method that have a serious or significant hazard rating.
NOTE: This list does not include all materials used in the method. A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.
- 5.3. Eye protection that protects against splash, 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.

- 5.4. 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. 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 involved solvents such as methylene chloride} should be conducted in a fume hood with the sash closed as far as the operations will permit.
- 5.7. Standards in solution may be diluted in the open laboratory when syringes and the like are utilized.
- 5.8. All work must be stopped in the event of a known or potential compromise to the health and safety of an STL North Canton associate. The situation must be reported **immediately** to the EH&S Coordinator and the 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
- 6.6. Autotitrator
- 6.7. Centrifuge tubes

7. REAGENTS AND STANDARDS

7.1. Standards

7.1.1. Target Calibration Standards

7.1.1.1. pH 2, 4, 7, 10, and 12 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 $4^{\circ}\text{C} \pm 2^{\circ}\text{C}$.

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 and Sample Duplicate) 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. Sample Duplicate

9.2.1. 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.

9.2.2. Sample duplicates are performed at a frequency of 10% per matrix, and must meet laboratory-specific limits for precision.

9.3. Laboratory Control Sample (LCS)

9.3.1. One aqueous LCS must be processed with each analytical batch. The LCS must be carried through the entire analytical procedure. 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.

9.3.2. A commercially available (Environmental Resource Associates or equivalent) control standard will be analyzed. Recovery must be within +/- 2% of true value.

9.3.3. Corrective Action for LCS

9.3.3.1. If the pH is outside the established control limits the system is out of control and corrective action must occur.

9.3.3.2. Corrective action consists of identification and correction of the cause for the out of control situation and reanalysis of all effected samples.

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 Orion 250 pH meter.

10.1.2.1. Rinse the electrodes with reagent water and place in the pH 4.0 buffer. Press "Cal". Allow the value to stabilize and then, using the arrow keys, adjust the value up or down to read 4.00. Press Enter.

10.1.2.2. Rinse the electrodes and place in the pH 7.0 buffer. Allow the value to stabilize and then, using the arrow keys, adjust the value up or down to read 7.00. Press Enter.

10.1.2.3. Calibration Check: Rinse the electrodes and place in the pH 10.0 buffer. Allow value to stabilize. The pH should be between 9.95 and 10.05 or recalibration is necessary.

NOTE: When analyzing drinking water samples, calibrate as described in section 10.1.2, using the pH 7.0 and pH 10.0 buffers for calibration and the pH 4.0 buffer for the calibration check.

10.1.3 The pH meter should be calibrated daily. The calibration is recorded on the analytical logsheet.

10.1.4 If the pH meter has been turned off, it must be calibrated prior to use.

10.2. 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 $\pm 2\%$. 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 ($\pm$ 0.5 g) of sample in a beaker or other suitable container.

11.3.2.2. Add 20 mL 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. Manual Procedure

11.4.1.1. Waters

11.4.1.1.1. 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 logsheet. Remove the electrodes from the sample. Rinse and gently dab off the electrodes between each measurement. Store the electrodes in pH 7 buffer when not in use.

11.4.1.1.2. For 9040B – Continuously stir the sample while obtaining a stable reading.

11.4.1.2. Solids

11.4.1.2.1. 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 logsheet. Remove and rinse the electrodes between each measurement. Store electrodes in the pH 7.0 buffer.

NOTE: If the sample contains oil or other substances that will coat or damage the electrodes, the pH should be analyzed following SOP# NC-WC-0009, pH - Paper Method.

11.4.2. Automated Procedure

11.4.2.1. Load the appropriate schedule on the autotitrator, starting with the pH calibration.

11.4.2.2. Pour a homogenized sample into the centrifuge tubes and place the tubes in the appropriate position on the autosampler. Remember to include a pH 7 buffer check after every ten positions.

11.4.2.3. Start the autotitrator.

11.5. Analytical Documentation

11.5.1. Record all analytical information in the analytical logbook/logsheet, 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 an 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.

13.2.2. Method validation information (where applicable) in the form of laboratory demonstrations of capabilities is maintained for this method in the laboratory QA files.

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. All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

15.2. Waste Streams Produced by the Method

- 15.2.1. The following waste streams are produced when this method is carried out.

15.2.1.1. Acidic and alkaline sample waste and exhausted buffer solutions poured down the drain if the pH is between 4 and 10. Any sample waste generated that is not in this pH range is collected in a designated container identified as "Acid Waste".

15.2.1.2. Exhausted soil or oil samples analyzed by the method. The liquid layer is decanted and disposed of in a designated container identified as "Acid Waste". The remaining solid layer is disposed of by placing it in a container identified as "Solid Waste".

- 15.3. Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices of STL North Canton. 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 North Canton Laboratory Quality Manual (LQM), current version

16.1.5. Corporate Quality Management Plan (QMP), current version.

16.1.6. STL Corporate Safety Manual, M-E-0001 and STL North Canton Facility Addendum and Contingency Plan, current version.

16.2. Associated SOPs and Policies, latest version

16.2.1. QA Policy, QA-003

16.2.2. Glassware Washing, NC-QA-0014

16.2.3. Statistical Evaluation of Data and Development of Control Charts, NC-QA-0018

16.2.4. Method Detection Limits and Instrument Detection Limits, NC-QA-0021

16.2.5. Navy/Army SOP, NC-QA-0016

17. MISCELLANEOUS (TABLES, APPENDICES, ETC...)

17.1. Reporting limits

17.1.1. A minimum reporting limit is not listed in LIMS. Units are reported as No Units.

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Implementation Date 12/29/04

SOP No. NC-WC-0017

Revision No. 2.3

Revision Date: 12/16/04

Page 1 of 15

**STL North Canton
STANDARD OPERATING PROCEDURE**

TITLE: TOTAL ORGANIC CARBON (TOC)

(SUPERSEDES: REVISION 2.2, DATED 01/24/03)

Prepared by: Rebecca L. Nolan 12/28/04
Date

Reviewed by: Angela Sura 12/28/04
Technology Specialist Date

Approved by: Beckham 12/29/04
Quality Assurance Manager Date

Approved by: William J. Derbel 12-16-04
Environmental Health and Safety Coordinator Date

Approved by: Paul M. Cole 12/29/04
Laboratory Director Date

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17. MISCELLANEOUS (TABLES, APPENDICES, ETC...).....15

1. SCOPE AND APPLICATION

- 1.1. This method is applicable to the determination of Total Organic Carbon (TOC) 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. QuantIMS method codes Fare DA (415.1) and FM (9060).
- 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. Organic Carbon is converted to carbon dioxide (CO₂) using chemical oxidation. The CO₂ is then measured by an infrared detector. The samples are purged prior to analysis such that only non-purgable organic carbon is being measured.

3. DEFINITIONS

- 3.1. Refer to the glossary in the Laboratory Quality Manual (LQM), latest 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. Employees must abide by the policies and procedures in the Corporate Safety Manual and this document.
- 5.2. The auto sampler has a probe that is sharp; use caution not to stick yourself.
- 5.3. The furnace is very hot and can cause severe burns if touched.

- 5.4. The Sodium Persulfate is a strong oxidizer. Avoid contact with combustible materials, organic materials, strong reducing agents, and excess heat.
- 5.5. The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Sulfuric Acid	Corrosive Oxidizer Dehydra-dator	1 mg/m ³	This material will cause burns if comes into contact with the skin or eyes. Inhalation of vapors will cause irritation of the nasal and respiratory system.
Phosphoric Acid	Corrosive	1 Mg/M3 TWA	Inhalation is not an expected hazard unless misted or heated to high temperatures. May cause redness, pain, and severe skin burns. May cause redness, pain, blurred vision, eye burns, and permanent eye damage.
Sodium Persulfate	Oxidizer Corrosive	0.1 Mg/M3- TWA as Persulfates	Causes irritation to the respiratory tract. Symptoms may include sore throat, shortness of breath, inflammation of nasal passages, coughing, and wheezing. Causes severe irritation or burns to the skin and eyes. Symptoms include redness, itching, pain and burns. May cause allergic skin reactions. Can cause eye damage.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

- 5.6. Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Cut resistant gloves must be worn doing any other task that presents a strong possibility of getting cut. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.
- 5.7. 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, where possible. All samples with pink stickers that read "Caution/Use Hood!" **must** be opened in the hood. Contact the EH&S Coordinator if this is not possible. Solvent and waste containers will be kept closed unless transfers are being made.

- 5.8. The preparation of standards and reagents will be conducted in a fume hood with the sash closed as far as the operation will permit.
- 5.9. It is recommended that neat standards be purchased only as a last resort. The preparation of standards from neat materials and reagents should be conducted in a fume hood with the sash closed as far as the operations will permit.
- 5.10. Standards in solution may be diluted in the open laboratory when syringes and the like are utilized.
- 5.11. 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 the EH&S Coordinator and 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 ($\text{Na}_2\text{S}_2\text{O}_8$) 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

7.2.3. Primary and secondary sources are needed.

7.2.3.1. TOC 1000 mg/L

7.2.3.1.1. Dilute 1.06 g KHP (potassium acid phthalate) to volume in a 500 mL volumetric flask. A commercially prepared solution may also be used.

7.2.3.2. Prepare every six months.

7.2.4. TOC Calibration Standards

7.2.5. Prepare the following standards from the primary stock standard described in Section 7.2.3.1.1.

Concentration (mg/L)	Volume (mL)	Stock Concentration (mg/L)	Final Volume (mL)
50	5	1000	100
25 (MS/MSD) (LCS)	12.5	1000	500
10	1	1000	100
1	0.1	1000	100

7.2.6. TOC Verification Standard (LCS)

7.2.6.1. A commercially prepared solution is used.

8. **SAMPLE COLLECTION, PRESERVATION AND STORAGE**

8.1 Samples are preserved to a pH <2 with sulfuric acid (H₂SO₄) 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, Method Blank, MS, MSD) 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. Method Blank

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 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 addressed in the project narrative.

9.3. Laboratory Control Sample (LCS)

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 purchased LCS 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.

9.3.3.2.The only exception is that if the LCS recoveries are biased high and the associated sample is ND for the parameter(s) of interest, the batch is acceptable. **This must be addressed in the project narrative.**

9.3.3.3.Corrective action will be reparation 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 reparation 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 "amount" MSB. The Exception Code is changed to NC. The following two footnotes will appear on the report page "NC The recovery and/or RPD were not calculated." "MSB The recovery and RPD were not calculated because the sample amount was greater than four times the spike amount."

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. Control Limits

9.5.1. Control limits are established by the laboratory as described in SOP, NC-QA-0018.

9.5.2. Laboratory control limits are internally generated and updated periodically unless method specified. Control limits are listed in the Laboratory Quality Manual (LQM) and the latest version is easily accessible via the LIMs (QC Browser program).

9.6. Method Detection Limits (MDLs) and MDL Checks

9.6.1. MDLs and MDL Checks are established by the laboratory as described in SOP, NC-QA-0021 and S-Q-003..

9.6.2. MDLs are listed in the Laboratory Quality Manual (LQM) and the latest version is easily accessible via the LIMs (QC Browser program).

9.7. Nonconformance and Corrective Action

- 9.7.1. Any deviations from QC procedures must be documented as a nonconformance, with applicable cause and corrective action approved by the facility QA Manager.

10. CALIBRATION AND STANDARDIZATION

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.
- 10.1.2 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 "Calibration". Start a new file with the current date.
- 10.1.3.2. Choose "Sequences" from the "databases" menu option, open up the calibration template.
- 10.1.3.3. Confirm all information. If blanking is required, it is best if done before calibration. Enter the desired number of blanks (no less than five) in the "reagent blanks before" field.
- 10.1.3.4. Analyze an ICV/ICB
- 10.1.3.5. Save the file using the current date as the filename.
- 10.1.3.6. Update data file information.

10.1.3.6.1. Choose the setup menu option, go into win TOC output, change the log fill name and prefix counter.

10.1.3.7. When analysis is complete, print the run from “/utilities/view run log”

10.1.3.8. Evaluate the data. The correlation coefficient of the original curve must be ≥ 0.995 or recalibration is required.

10.2. Continuing Calibration

10.6.1. The run is checked at the beginning, after every ten samples, and at the end of the run of the same species using a midrange CCV made from a primary source (Section 7.2.4. or 7.2.7.) to verify continued linearity. A CCV cannot vary from the original curve by more than $\pm 10\%$, or recalibration is required.

10.6.2. System cleanliness is checked every ten samples and at the end of the run using Continuing Calibration Blank (CCB). A CCB cannot contain the analyte of interest above the reporting limit, or recalibration is required.

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. Sample Preparation Procedure

11.2.1. If excess particulate matter exists, filter an aliquot of sample through a Whatman #4 filter into a TOC vial or decant.

11.3. Preparation Documentation

11.3.1. Record any sample preparation on the analytical logsheet.

11.4. Analytical Documentation

11.4.1 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.

- 11.4.2 All standards are logged into a department standard logbook. All standards are assigned a unique number for identification. The supervisor or designee reviews logbooks.
- 11.4.3 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.
- 11.4.4 Sample results and associated QC are entered into the Laboratory Information Management System (LIMS) after final technical review.
- 11.4.5 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. 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/win TOC output.
- 12.1.2. 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.
- 12.1.3. For method 415.1 only one analysis is required. The single analysis is reported directly from the instrument printout.
- 12.1.4. 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.
- 12.1.5. Be sure the samples are loaded on the sampler, the first one positioned under the needle.
- 12.1.6. Click the "Start" button.
- 12.1.7. Samples that fall outside the linear range (>50 mg/L) of the instrument must be diluted and reanalyzed.
 - 12.1.7.1. Samples following a high sample should be re-analyzed if carryover is a concern.

12.1.8. Print the run from “utilities/view run log”.

12.1.9. When analysis is complete, properly dispose of or put away samples and standards.

12.2. Calculations for 9060 only

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.*

$$12.2.2. \quad LCS \% Recovery = \frac{\text{Instrument values}^*}{\text{True Value}} \times 100$$

12.2.3. MS/MSD % recovery

$$\left(\frac{(\text{Instrument values}^* \text{ MS or MSD}) - (\text{Avg sample instrument value}^* \div 2)}{12.5} \right) \times 100$$

*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 this procedure is performed by an associate who has been properly trained in its use and has the required experience.

13.2.2. Method validation information (where applicable) in the form of laboratory demonstrations of capabilities is maintained for this method in the laboratory QA files.

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. All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

15.2. Waste Streams Produced by the Method

15.2.1. The following waste streams are produced when this method is carried out.

15.2.1.1. Acidic waste from the auto-analyzer. This waste is disposed of in a designated container identified as "Acid Waste."

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, 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. Corporate Quality Management Plan (QMP), current version.

16.1.4. STL Laboratory Quality Manual Plan (LQMP), current version.

16.1.5. STL Corporate Safety Manual, M-E-0001 and STL North Canton Facility Addendum and Contingency Plan, current version.

16.2. Associated SOPs and Policies, latest version

16.2.1. QA Policy, QA-003

16.2.2. Glassware Washing, NC-QA-0014

16.2.3. Statistical Evaluation of Data and Development of Control Charts, NC-QA-0018

16.2.4. Method Detection Limits, NC-QA-0021 and S-Q-003

16.2.5. Navy/Army SOP, NC-QA-0016

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. Method deviations

17.3.1. A blender is not used to homogenize samples.

17.3.2. For Method 9060, the calibration must be verified with an independently prepared check standard every 15 samples. The laboratory is verifying the calibration every 10 samples.

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SOP No NC-WC-0019

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Revision Date: 11/8/04

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STL NORTH CANTON STANDARD OPERATING PROCEDURE

TITLE: CHEMICAL OXYGEN DEMAND, COLORIMETRIC

(SUPERSEDES: REVISION 5.1, 02/03/03)

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Proprietary Information Statement:

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1. SCOPE AND APPLICATION

- 1.1. This method is applicable to the determination of Chemical Oxygen Demand in waters, wastewaters, and leachates. It is based on Standard Methods 5220D and EPA 410.4. The working linear range is 20 to 800 mg/L, with a reporting limit of 20 mg/L.
- 1.2. The applicable QuantIMS method codes are GT (5220D) and VO (410.4). The preparation code is 21.
- 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. Organic matter is oxidized by a boiling mixture of chromic and sulfuric acid and then the solution is analyzed colorimetrically at 600 nm against digested standards.

3. DEFINITIONS

- 3.1. Refer to the glossary in the STL North Canton Laboratory Quality Manual (LQM), latest version.

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. Specific selection of reagents may be required to avoid introduction of contaminants.
- 4.2. Halides such as chloride, bromide, and iodide interfere causing negative biased results, but can be eliminated by the addition of mercuric sulfate. Concentration of chloride greater than 2000 mg/L cannot be eliminated without dilution.
- 4.3. Reduced inorganic species such as ferrous iron, sulfide, and manganese may also interfere.

5. SAFETY

- 5.1. Employees must abide by the policies and procedures in the Corporate Safety Manual and this document.
- 5.2. **The disposable glass COD digestion tubes used in this analysis contain Mercuric Sulfate. A compound composed of Mercuric Oxide Red, which may affect the central nervous system, and Sulfuric acid**
- 5.3. The following is a list of the materials used in this method, which have a serious or significant hazard rating. NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table. A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Mercuric Oxide, Red	Oxidizer Corrosive Poison	0.1 Mg/M3 Ceiling (Mercury Compound s)	Extremely toxic. Causes irritation to the respiratory tract. Causes irritation. Symptoms include redness and pain. May cause burns. May cause sensitization. Can be absorbed through the skin with symptoms to parallel ingestion. May affect the central nervous system. Causes irritation and burns to eyes. Symptoms include redness, pain, and blurred vision; may cause serious and permanent eye damage.
Potassium Dichromate	Oxidizer Corrosive Carcinogen	0.1 Mg/M3 TWA as CrO3	Extremely destructive to tissues of the mucous membranes and upper respiratory tract. May cause ulceration and perforation of the nasal septum. Symptoms of redness, pain, and severe burn can occur. Dusts and strong solutions may cause severe irritation. Contact can cause blurred vision, redness, pain and severe tissue burns. May cause corneal injury or blindness.
Sulfuric Acid	Corrosive Oxidizer Dehydrator Poison Carcinogen	1 Mg/M3-TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.

1 – Always add acid to water to prevent violent reactions.

2 – Exposure limit refers to the OSHA regulatory exposure limit.

- 5.4. Eye protection that protects from splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Cut resistant

gloves must be worn doing any other task that presents a strong possibility of getting cut. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

- 5.5. 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 where possible. All samples with a pink stickers that read "Caution/Use Hood!" **must** be opened in the hood. Contact the EH&S co-ordinator if this is not possible. 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 operation will permit.
- 5.7. It is recommended that neat standards be purchased only as a last resort. The preparation of standards from neat materials and reagents should be conducted in a fume hood with the sash closed as far as the operations will permit.
- 5.8. Standards in solution may be diluted in the open laboratory when syringes and the like are utilized.
- 5.9. All work must be stopped in the event of a known or potential compromise to the health and safety of a STL North Canton associate. The situation must be reported **immediately** to the EH&S Coordinator and to a laboratory supervisor.

6. EQUIPMENT AND SUPPLIES

- 6.1. Culture Tubes: Borosilicate Glass 16 x 100 mm (10mL) with TFE caps
- 6.2. Chemical Oxygen Demand Reactor (HACH): Operate at 150°C ($\pm 2^\circ\text{C}$)
- 6.3. Autopipettor and disposable tips
- 6.4. Test tube rack
- 6.5. Spectrophotometer: set at 600 nm
- 6.6. Volumetric flasks: various
- 6.7. Analytical balance: capable of accurately weighing ± 0.0001 g

7. REAGENTS AND STANDARDS

7.1. Reagent

7.1.1. Bioscience prepared COD vials (20 - 900 mg/L range)

7.1.2. Mercuric Sulfate (HgSO_4): reagent grade7.1.3. Sulfuric Acid (H_2SO_4): concentrated, reagent grade7.1.4. Potassium Dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$): primary standard grade7.1.5. Potassium Dichromate Solution: Add 10.216 g of pre-dried $\text{K}_2\text{Cr}_2\text{O}_7$, 167 mL concentrated H_2SO_4 and 33.3 g HgSO_4 to 500 mL reagent water, mix, cool and dilute to 1000 mL in a volumetric flask. Stable for one year.7.1.6. Silver Sulfate (AgSO_4): reagent grade7.1.7. Sulfuric Acid Solution: Add 22 g silver sulfate to a full 2.5 L bottle of concentrated H_2SO_4 . Mix and label well.

7.1.8. Potassium Acid Phthalate (KHP): primary standard grade

7.2. Standards

7.2.1. 1000 mg/L Chemical Oxygen Demand Standard, HACH Primary Standard.

7.2.1.1. Calibration Standards: Add the following suggested volumes to each vial using primary standard.

Concentration (mg/L)	1000 mg/L (mL)	Reagent Water (mL)
0	0	2.50
20	0.05	2.45
80	0.20	2.30
200	0.50	2.00
400	1.00	1.50
800	2.00	0.50

7.2.1.2. 1000 mg/L Chemical Oxygen Demand Standard, Hach Secondary Standard or add 0.850 g Potassium Acid Phthalate (KHP) to 800 mL reagent water, mix and dilute to 1000 mL in a volumetric flask. Stable for one year.

7.2.1.3. Verification standards: Add the following suggested volumes to each vial using secondary standard.

QC	Concentration (mg/L)	1000 mg/L (mL)	Reagent Water (mL)	Sample (mL)
LCS (may be purchased)	100	0.25	2.25	0
CCV	200	0.50	2.00	0
MS	250	0.50	0	2.00

8. SAMPLE PRESERVATION AND STORAGE

- 8.1. Samples are preserved to a pH < 2 with H₂SO₄ 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, Method Blanks) 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. 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 reagent water blank consisting of 2.5 mL of reagent water must be digested with each analytical batch of samples. This may also be used as a continuing calibration blank.

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 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 addressed in the project narrative.**

9.3. Laboratory Control Samples (LCS)

9.3.1. 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. 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.

9.3.2. A midrange LCS consisting of 0.25 mL of the secondary 1000 mg/L standard and 2.25 mL of reagent water is digested with each analytical batch of samples. A purchased standard may be used.

9.3.3. Corrective Action for LCSs

9.3.3.1. If any analyte is outside established control limits, the system is out of control and corrective action must occur.

9.3.3.2. The only exception is that if the LCS recoveries are biased high and the associated sample is ND for the parameter(s) of interest, the batch is acceptable. **This must be addressed in the project narrative.**

9.3.3.3. Corrective action will be reparation and reanalysis of the batch unless the client agrees that other corrective action is acceptable.

9.4. Matrix Spike (MS)

9.4.1. One MS sample must be analyzed every 10 samples. A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added. Some client specific data quality objectives (DQOs) may require the use of sample duplicates in place of or in addition to an MS. The MS result is 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 analysis.

9.4.2. An MS consisting of 2.0 mL of sample and 0.5 mL of 1000 mg/L standard (either source) is digested with each analytical batch of samples.

9.4.3. Corrective action for MSs

9.4.3.1. If any 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 reparation and reanalysis of the batch.

9.4.3.2. If the native analyte concentration in the MS exceeds 4x the spike level for that analyte, the recovery data is reported as "amount" MSB. The Exception Code is changed to NC. The following two footnotes will appear on the report page "NC The recovery and/or RPD were not calculated." "MSB The recovery and RPD were not calculated because the sample amount was greater than four times the spike amount."

9.4.3.3. If an MS 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 laboratory limits matrix spike RPD limits.

9.4.3.4. If client program requirements specify to confirm matrix interference's, reparation and reanalysis of the MS may be necessary.

9.5. Control Limits

9.5.1. Control limits are established by the laboratory as described in SOP, NC-QA-0018.

9.5.2. Laboratory control limits are internally generated and updated periodically unless method specified. Control limits are listed in the Laboratory Quality Manual (LQM) and the latest version is easily accessible via the LIMs (QC Browser program).

9.6. Method Detection Limits (MDLs) and MDL Checks

9.6.1. MDLs and MDL Checks are established by the laboratory as described in SOP, NC-QA-0021amd S-Q-0003.

9.6.2. MDLs are listed in the Laboratory Quality Manual (LQM) and the latest version is easily accessible via the LIMs (QC Browser program).

9.7. Nonconformance and Corrective Action

9.7.1. Any deviations from QC procedures must be documented as a nonconformance, with applicable cause and corrective action approved by the facility QA Manager.

10. CALIBRATION AND STANDARDIZATION

10.1. Colorimetric Method

10.1.1. Prepare standards as in Section 7.2.1.1 and then follow Sections 11 and 12. The correlation coefficient of the standard curve must be ≥ 0.995 or recalibration is required.

10.2. Continuing Calibration: valid sample results must be bracketed by acceptable CCVs and CCBs.

10.2.1. A CCV should be analyzed at the beginning, every 10 readings, and at the end to ensure that linearity is maintained. A CCV cannot vary by more than $\pm 10\%$ of the true value or recalibration and reanalysis of all readings following the last acceptable CCV is required.

10.2.2. A CCB should be analyzed at the beginning, every 10 readings, and at the end to ensure system cleanliness. A CCB cannot contain the analyte of interest above the reporting limit or recalibration and reanalysis of all readings following the last acceptable CCB is required.

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 Procedure (Prepared Bioscience Vials)
 - 11.3.1. Turn on COD reactor to 150°C at least fifteen minutes prior to digestion.
 - 11.3.2. Add 2.5 mL of sample to a prepared COD vial, or, if dilution is needed, an aliquot brought up to 2.5 mL.
 - 11.3.3. Tightly cap the vial and invert to mix. If any samples turn a darker color (green/blue) than the 800mg/L standard, a dilution is needed.
 - 11.3.4. Place the vials from Section 11.3.2 including QC (calibration curve, ICV/CCV, LCS, Method Blank, and MS) in the COD reactor for two hours.
 - 11.3.5. Remove the vials from the reactor, invert several times, and place in the test tube rack to cool for at least fifteen minutes.
 - 11.3.6. Continue with sample analysis (Section 11.6).
- 11.4. Sample Preparation Procedure (Unprepared Vials)
 - 11.4.1. Turn on the COD reactor to 150°C at least fifteen minutes prior to digestion.
 - 11.4.2. Add 2.5 mL of sample, blank standard (see Section 7) or an aliquot brought up to 2.5 mL to a 10 mL vial and label.

11.4.3. Add approximately 0.1 g of HgSO_4 to the vial (for samples known to be high in chloride).

11.4.4. Add 1.5 mL of potassium dichromate solution.

11.4.5. Slowly, add 3.5 mL sulfuric acid reagent.

11.4.6. Tightly cap the vial and invert to mix. If any of the samples turn a darker color than the 1000 mg/L standard, a dilution is necessary. Refer to 11.4.2 for repreparation.

CAUTION: Wear safety glasses with side shields and protect hands from the heat produced when the contents of the tubes are mixed. Mix thoroughly before applying heat to prevent local heating of vessel bottom and explosive reaction.

11.4.7. Place the vial in the COD reactor for two hours.

11.4.8. Remove the vial from the reactor, invert several times, and place in the test tube rack to cool for at least fifteen minutes.

11.4.9. Continue with sample analysis (Section 11.6).

11.5. Summary

11.5.1. The digested sample is analyzed against a standard curve on a spectrophotometer at 600 nm.

11.6. Sample Analysis Procedure

11.6.1. Colorimetric Method

11.6.1.1. Allows vial to cool and precipitate to settle.

11.6.1.2. Set the spectrophotometer to 600 nm in the absorbance mode.

11.6.1.3. Zero the spectrophotometer with the "O" calibration standard. Be sure to wipe off any residue on the outside of the vials.

NOTE: Scratches or marks on the vial may cause erroneously high results. It may be necessary to turn the vial while in the spectrophotometer chamber to achieve the lowest absorbance value possible.

11.6.1.4. Analyze the remaining calibration standards and derive the correlation coefficient of the linear regression calibration curve. The correlation coefficient must be ≥ 0.995 to continue.

11.7. Analyze the samples and associated QC. Be sure to analyze a CCV and CCB at a minimum of every 10 readings (section 10.2). Record all absorbencies on the analytical logsheet.

11.8. Analytical Documentation

11.8.1. Record all analytical information in the analytical logbook/logsheet which may be in an electronic format, including the analytical data from standards, blanks, LCSs, MSs, and any corrective actions or modifications to the method.

11.8.2. All standards are logged into a departmental standard logbook. All standards are assigned a traceable number for identification. Logbooks are reviewed by the supervisor or designee.

11.8.3. 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.

11.8.4. Sample results and associated QC are entered into the LIMs after final technical review.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Using calibration curve information from 11.6.1.4, calculate as follows, or derive the corresponding concentration values from their absorbance values.

$$\frac{\text{Absorbance} - A}{B} \times \text{Dilution} = \text{COD, mg / L}$$

Where: $A = \text{Intercept}$

$B = \text{Slope}$

$$\frac{\text{COD, mg/L (from 12.1)} \times 100}{100 (\text{True})} = \text{LCS \% Recovery}$$

$$\frac{A-B}{250} \times 100 = MS \% Recovery$$

250

Where: A = MS Concentration, mg/L

 B = Native Sample Concentration, mg/L

$$\frac{COD, mg / L (from 12.1)}{200(True)} \times 100 = CCV \% Recovery$$

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.

13.2.2. Method validation information (where applicable) in the form of laboratory demonstrations of capabilities is maintained for this method in the laboratory QA files.

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. All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

15.2. The following waste streams are produced when this method is carried out.

15.2.1. Acidic COD reagent and sample generated by the analysis. All COD digestates must be collected in a container labeled "COD Waste."

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 annual refresher training.

16. REFERENCES

16.1. References.

16.1.1. USEPA 600 Method 410.4

16.1.2. Standard Methods for Examination of Water and Wastewater, Eighteenth Edition and Nineteenth Edition. Closed Reflux Colorimetric Method, Method 5220D.

16.1.3. STL North Canton Laboratory Quality Manual (LQM), latest version

16.1.4. Corporate Quality Management Plan (QMP), current version.

16.1.5. STL Corporate Safety Manual, M-E-0001, current version with STL North Canton Facility Addendum and Contingency Plan, current version.

16.2. Associated SOP

16.2.1. Statistical Evaluation of Data and Development of Control Charts, NC-QA-0018.

16.2.2. QA Policy, QA-003

16.2.3. Glassware Washing, NC-QA-0014

16.2.4. Method Detection Limits and Instrument Detection Limits, S-Q-003 and NC-QA-0021

16.2.5. Navy/Army SOP, NC-QA-0016

17. MISCELLANEOUS (TABLES, APPENDICES, ETC...)

17.1. Reporting limits

17.1.1. The Reporting limit for Standard Method 5220D and EPA Method 410.4 is 20 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. Mercuric sulfate is added to remove chloride from the samples. Samples containing greater than 2000 mg/L of chloride should be analyzed using alternate methods.

17.2.2. Samples that contain high levels of chloride may be cloudy and difficult to analyze photometrically. These should be prepared and analyzed by COD Method 5220B or 5220D in Standard Methods.

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Implementation Date: 10/27/04

SOP No. NC-WC-0024

Revision No. 3.3

Revision Date: 10/08/04

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STL NORTH CANTON STANDARD OPERATING PROCEDURE

TITLE: CHROMIUM, HEXAVALENT (COLORIMETRIC)

(SUPERSEDES: REVISION 3.2, DATED 06/12/02)

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1. SCOPE AND APPLICATION

- 1.1. This method is used to determine the concentration of Hexavalent Chromium (Cr[VI]) in groundwaters and waters. This method may also be applicable to certain domestic and industrial wastes, provided that no interfering substances are present. It is based on SW846 Methods 7196A, and Standard Methods 3500-CR.-D The working linear range is 0.02 - 0.5 mg/L for waters. The working linear range is 0.8-40 mg/kg for solid samples.
- 1.2. The associated method codes are EA (7196A) and H4 (3500-CR-D).
- 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 by the laboratory.

2. SUMMARY OF METHOD

- 2.1. Hexavalent Chromium, in the absence of interfering amounts of substances such as molybdenum, vanadium, and mercury, is determined colorimetrically by reaction with diphenylcarbazide in acid solution and measuring the resulting red-violet color at 540 nm.

3. DEFINITIONS

- 3.1. Refer to the glossary in the STL North Canton Laboratory Quality Manual (LQM), latest version.

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. Specific selection of reagents may be required to avoid introduction of contaminants.
- 4.2. The Chromium reaction with diphenylcarbazide is usually free from interferences. However, certain substances may interfere if the Chromium concentration is relatively low. Hexavalent molybdenum and mercury salts also react to form color with the reagent; however, the red-violet intensities produced are much lower than those for Chromium at the specified pH. Concentrations of up to 200 mg/L of molybdenum and mercury can be tolerated. Vanadium interferes strongly, but concentrations up to ten times that of Chromium will not cause trouble.
- 4.3. Iron in concentrations greater than 1 mg/L may produce a yellow color, but the ferric iron color is not strong and no difficulty is encountered normally if the absorbance is measured photometrically at the appropriate wavelength.

5. SAFETY

- 5.1. Employees must abide by the policies and procedures in the Corporate Safety Manual and this document.
- 5.2. Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Cut resistant gloves must be worn doing any other task that presents a strong possibility of getting cut. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.
- 5.3. Samples that contain high concentrations of carbonates or organic material or samples that are at elevated pH can react violently when acids are added.
- 5.4. The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Sulfuric Acid	Corrosive Oxidizer Dehydrator Poison Carcinogen	1 Mg/M3-TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.
Acetone	Flammable	1000 ppm-TWA	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.

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Potassium Dichromate	Oxidizer Corrosive Carcinogen	0.1 Mg/M3 TWA as CrO3	Extremely destructive to tissues of the mucous membranes and upper respiratory tract. May cause ulceration and perforation of the nasal septum. Symptoms of redness, pain, and severe burn can occur. Dusts and strong solutions may cause severe irritation. Contact can cause blurred vision, redness, pain and severe tissue burns. May cause corneal injury or blindness.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

- 5.5. 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, where possible. Solvent and waste containers will be kept closed unless transfers are being made. All samples with a pink stickers that read "Caution/Use Hood!" **must** be opened in the hood. Contact the EH&S co-ordinator if this is not possible. 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 operation will permit.
- 5.7. 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 involved solvents such as methylene chloride} should be conducted in a fume hood with the sash closed as far as the operations will permit.
- 5.8. Standards in solution may be diluted in the open laboratory when syringes and the like are utilized.
- 5.9. All work must be stopped in the event of a known or potential compromise to the health and safety of a STL North Canton associate. The situation must be reported **immediately** to a laboratory supervisor.

6. EQUIPMENT AND SUPPLIES

- 6.1. Spectrophotometer for use at 540 nm. Specific instrumentation is listed in the LQM, current version.
- 6.2. 1 cm Spectrophotometer Cell
- 6.3. Beakers: glass, plastic
- 6.4. Volumetric flasks: various
- 6.5. Pipettes: various
- 6.6. Autopipettor with disposable tips
- 6.7. Funnels: various
- 6.8. Snapseal containers

6.9. Graduated cylinders: various

7. REAGENTS AND STANDARDS

7.1. Reagents

7.1.1. Sulfuric Acid (H_2SO_4): concentrated

7.1.2. Acetone: reagent grade. Avoid material that comes in containers with metal or metal-lined caps.

7.1.3. 1, 5 Diphenylcarbazide: reagent grade

7.1.4. Diphenylcarbazide Solution: Dissolve 0.25 g phenylcarbazide in 50 mL acetone. Store in a brown bottle. The solution is stable for 30 days unless a marked color change is noted. If this occurs, a new solution should be prepared. This solution is commercially available.

7.1.5. Potassium Dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$): primary standard grade

7.2. Standards

7.2.1. Primary Chromium Stock Solution, 50 mg/L: Dissolve 0.1414 g of dried potassium dichromate in 800 mL reagent water. Dilute to 1 liter in a volumetric flask with reagent water. Stable 6 months.

7.2.1.1. Calibration Standards: Add the indicated volume of the appropriate standard and dilute to volume with reagent water.

<u>Conc., mg/L</u>	<u>mLs</u>	<u>Source, mg/L</u>	<u>Final Vol., mL</u>
0.5	0.5	50	50
0.25	0.25	50	50
0.1	0.10	50	50
0.02	0.02	50	50

7.2.1.2. Secondary Chromium Stock Solution, 50 mg/L: Dissolve 0.1414 g dried potassium dichromate secondary source, in 800 mL reagent water. Dilute 1 liter in a volumetric flask with reagent water. Stable 6 months.

7.2.1.3. Verification Standards: Add the indicated volume of the appropriate standard and dilute to volume with reagent water.

<u>Use</u>	<u>Conc., mg/L</u>	<u>mLs</u>	<u>Source, mg/L</u>	<u>Final Vol., mL</u>
MS/MSD (waters)	0.25	0.25	50	50
CCV	0.25	0.25	50	50
LCS (waters)	0.25	0.25	50	50

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

- 8.1. To retard the chemical activity of Hexavalent Chromium, the samples and extracts should be stored at $4^{\circ}\text{C} \pm 2^{\circ}\text{C}$ until analyzed.
- 8.2. The maximum holding time prior to analysis for water samples is one day.
- 8.3. The holding time for solid samples is 30 days prior to digestion and 168 hours after digestion.

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, MS, MSD) 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. Method Blank

- 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. Project specific method blank requirements are listed in SOP NC-QA-0016, SUPPLEMENTAL PRACTICES FOR NAVY AND ARMY PROJECT WORK.

9.2.2. A reagent water blank consisting of 10 mL reagent water must be prepared and analyzed with each analytical batch of samples.

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 addressed in the project narrative.**

9.2.3.2. The only exception is that if the LCS recoveries are biased high and the associated sample is ND for the parameter(s) of interest, the batch is acceptable. **This must be addressed in the project narrative.**

9.2.3.3. 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 (LCS)

9.3.1. One aqueous LCS must be processed with each preparation batch. The LCS must be carried through the entire analytical procedure. 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. Acceptance limits are listed in the LQM, current version.

9.3.2. An LCS for waters, consisting of 10 mL of the 0.25 mg/L standard, is analyzed with each analytical 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.

9.3.3.2. Corrective action will be reparation 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. Acceptance limits are listed in the LQM, current version.

9.4.2. A MS/MSD consisting of 50 mL of sample and 0.25 mL of 50 mg/L secondary standard should be prepared and analyzed with every 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 reparation 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.

9.4.3.4. If client program requirements specify to confirm matrix interference's, reparation and reanalysis of the MS/MSD may be necessary.

9.5. Control Limits

9.5.1. Control limits are established by the laboratory as described in SOP, NC-QA-0018.

9.5.2. Laboratory control limits are internally generated and updated periodically unless method specified. Control limits are listed in the Laboratory Quality Manual (LQM) and the latest version is easily accessible via the LIMs (QC Browser program).

9.6. Method Detection Limits (MDLs) and MDL Checks

9.6.1. MDLs and MDL Checks are established by the laboratory as described in SOP, NC-QA-0021.

9.6.2. MDLs are listed in the Laboratory Quality Manual (LQM) and the latest version is easily accessible via the LIMs (QC Browser program).

9.7. Nonconformance and Corrective Action

9.7.1. Any deviations from QC procedures must be documented as a nonconformance, with applicable cause and corrective action approved by the facility QA Manager.

10. CALIBRATION AND STANDARDIZATION

10.1. Summary

10.1.1. A calibration curve is prepared monthly prior to the analysis of the samples.

10.2. Initial Calibration

10.2.1. See Section 11.4.3.6 for calibration procedure.

10.3. Continuing Calibration

10.3.1. The calibration is verified at the beginning, every ten samples and at the end of the run using a midrange CCV to verify continued linearity. It cannot vary from the original curve by more than $\pm 10\%$ or recalibration is required.

10.3.2. The system cleanliness is verified at the beginning, every ten samples and at the end of the run using a CCB. The CCB is 50 mL of reagent water which is processed through all corresponding preparation and analysis steps like a method blank. It cannot contain the analyte of interest above the reporting limit or recalibration is required.

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. Water samples require minimal sample preparation. Solid samples require an alkaline digestion procedure after which the sample can be treated as a water throughout the remainder of the analysis.

11.3.1.1. Solids – Refer to SOP NC-WC-0086, Alkaline Digestion for Hexavalent Chromium.

11.3.1.2. Water Samples

11.3.1.2.1. No preparation is necessary.

11.4. Sample Analysis

11.4.1. An aliquot of prepared sample is acidified to a pH of < 2 and colorized with diphenylcarbazide solution. The samples are then analyzed on a spectrophotometer at 540 nm.

11.4.2. Recommended Instrument Conditions

11.4.2.1. Turn on the spectrophotometer and adjust the wavelength to 540 nm. Set the instrument to the absorbance mode.

11.4.3. Preliminary Evaluation

11.4.3.1. Preliminary evaluation can consist of visual determination by comparison to the standards to determine if dilutions are required.

11.4.3.2. Transfer 10 mL, or aliquot diluted to 10 mL with reagent water, of calibration standards, CCV, CCB, LCS's blanks, and water samples or solid digestion solution to suitable containers.

11.4.3.3. Method SM3500 Cr-D

11.4.3.3.1. Add concentrated sulfuric acid (drop by drop) to each flask until the pH is 1.0 ± 0.3 . Measure the pH by placing a drop of sample or digestate on narrow range pH paper ($0 - 3 \pm 0.25$). Solid digests should take approximately 1 mL and all other samples (standards and

waters) should take approximately 5 - 10 drops.

NOTE: For samples that may cause color interferences, a second acidified aliquot should be analyzed without the diphenylcarbide solution. Record the absorbance on the analytical logsheet.

11.4.3.3.2. Add 0.1 mL diphenylcarbide solution to each flask and swirl to mix.

11.4.3.4. Method 7196A

11.4.3.4.1. Add 0.1 mL diphenylcarbide solution to each flask and swirl to mix.

11.4.3.4.2. Add concentrated sulfuric acid (drop by drop) to each flask until the pH is 2.0 ± 0.5 . Measure the pH by placing a drop of sample or digestate on narrow range pH paper ($0 - 3 \pm 0.25$). Solid digests should take approximately 1 mL and all other samples (standards and waters) should take approximately 5 - 10 drops.

NOTE: For samples that may cause color interferences, a second acidified aliquot should be analyzed without the diphenylcarbide solution. Record the absorbance on the analytical logsheet.

11.4.3.5. Allow 10 minutes for color development.

11.4.3.6. Zero the instrument. Analyze initial calibration standards for both water and solid matrices as needed and record all absorbances on the analytical logsheet. Derive the correlation coefficient (r), slope (a), and y-intercept (b). The correlation coefficient must be ≥ 0.995 to continue or reanalysis is required.

11.4.3.7. Analyze each sample on absorbance and record the value on the analytical logsheet.

11.4.3.8. A CCV and CCB are analyzed at the beginning and end of the run and every ten samples to verify linearity. The CCV must be $\pm 10\%$ or recalibration is required. The CCB must be less than the reporting limit.

11.4.3.9. Absorbance values greater than the highest calibration standard must be diluted and reanalyzed. Follow procedures 11.4.3.2 - 11.4.3.5.

11.5. Analytical Documentation

11.5.1. Record all analytical information in the analytical logbook/logsheet, including the analytical data from standards, blanks, LCSs, MS/MSDs, analysis time, 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. Use linear regression or the following equation to calculate sample results.

$$\frac{\text{Absorbance} - a}{b} = \text{mg} / \text{L Cr}^{6+}$$

Where:

a = y-intercept

$$b = \text{slope}$$

12.2. $\text{Waters, mg/L Cr}^{+6} = (A - B) \times C$

$$\text{Solids, mg/kg Cr}^{+6} = (A - B) \times C \times D$$

Where:

$$A = \text{mg/L of sample colorized}$$

$$B = \text{mg/L of non-colorized sample}$$

$$C = \text{Dilution Factor} = \frac{\text{Final Volume}}{\text{Initial Volume}}$$

$$D = \text{Weight/Volume Factor} = \frac{\text{Final Volume}}{\text{Sample Weight}}$$

12.3. $\text{LCS Recovery} = \frac{\text{mg/L}}{0.25 \text{ (true)}} \times 100$

12.4. $\text{CCV Recovery} = \frac{\text{mg/L}}{0.25 \text{ (true)}} \times 100$

12.5. $\text{MS / MSD Recovery} = \frac{E - F}{0.25 \text{ (true)}} \times 100$

Where:

$$E = \text{MS/MSD, mg/L}$$

$$F = \text{Sample, mg/L}$$

13. METHOD PERFORMANCE

- 13.1. Each laboratory must have initial demonstration of performance data on file and corresponding method detection limit files. Method detection limit studies are performed on an annual basis and are listed in the LQM, current version.

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.

13.2.2. Method validation information (where applicable) in the form of laboratory demonstrations of capabilities is maintained for this method in the laboratory QA files.

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 Streams Produced by the Method

15.1.1. The following waste streams are produced when this method is carried out.

15.1.1.1. Acidic waste generated by the analysis. This waste is disposed of in designated acid waste containers located in the lab.

15.2. Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices of STL North Canton. 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, Third Edition, Chromium, Hexavalent (Colorimetric), Method 7196A.

16.1.2. Standard Methods 3500-CR, 18th Edition

16.1.3. STL North Canton Laboratory Quality Manual (LQM), current version.

16.1.4. SW846 Test Method for Evaluating Solid Waste, Third Edition, Method 7000A, Section 8.7

16.1.5. Corporate Quality Management Plan (QMP), current version.

16.1.6. Alkaline Digestion for Hexavalent Chromium, SOP NC-WC-0086.

16.2. Associated SOPs and Policies, latest version

16.2.1. QA Policy, QA-003

16.2.2. Glassware Washing, NC-QA-0014

16.2.3. Statistical Evaluation of Data and Development of Control Charts, NC-QA-0018

16.2.4. Method Detection Limits and Instrument Detection Limits, NC-QA-0021

16.2.5. Navy/Army SOP, NC-QA-0016

16.2.6. Corporate Safety Manual and Facility Appendix

17. MISCELLANEOUS (TABLES, APPENDICES, ETC...)

17.1. Reporting limits

17.1.1. The lower reporting limit (RL) is 0.02 mg/L for waters.

17.1.2. If samples require dilution or smaller volumes than specified in this method, the RL will be elevated.

17.2. Method deviations

17.2.1. SW-846 Method 7196A and Standard Methods 3500-CR, 18th edition, specify different pH requirements for the sample prior to color development (Section 11.4.3.3). The pH requirement from 7196A (2.0 ± 0.5) was selected for implementation in this SOP rather than the 3500-CR requirement (1.0 ± 0.3).

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Implementation Date: 11/22/04

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Page 1 of 28

STL NORTH CANTON STANDARD OPERATING PROCEDURE

TITLE: CYANIDE AUTOMATED, PYRIDINE-BARBITURIC ACID METHOD

(SUPERSEDES: REVISION 7 DATED 05/31/01)

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Proprietary Information Statement:

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1. SCOPE AND APPLICATION

- 1.1. This method is applicable to the determination of Total, Amenable, and Free Inorganic Cyanide in solids, liquids, and waters. It is based on CLP ILM03.0, CLP ILM04.0, SW846 Method 9012A, 335.2, 335.4 and Standard Method 4500-CN-E. The working linear range is 0.005 - 0.2 mg/L for waters and 0.25 to 10 mg/kg for solids.
- 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. The associated method codes are CLP ILM03.0 (DV), CLP ILM04.0 (OU), SW846 Method 9012A (QP), EPA 335.1(CF), 335.2 (CG), EPA 335.4 (O2), and Standard Method 4500-CN-E (A4).

2. SUMMARY OF METHOD

- 2.1. The 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 colormetrically on an autoanalyzer using the pyridine-barbituric acid method.

3. DEFINITIONS

- 3.1. Refer to the glossary in the Laboratory Quality Manual (LQM), latest version.

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. Specific selection of reagents may be required to avoid introduction of contaminants.
- 4.2. Sulfides interfere, but can be eliminated by treating the sample with cadmium carbonate prior to analysis.

5. SAFETY

- 5.1. Employees must abide by the policies and procedures in the Corporate Safety Manual and this document.
- 5.2. Ensure cooling water is turned on to the distillation unit. Otherwise the samples may boil over and come into contact with the heating plates.
- 5.3. Preparation of sodium hydroxide solutions produces considerable amounts of heat. Use plastic containers to mix this solution if possible. If glass containers are used, they must be free of any cracks or irregularities.
- 5.4. The acidification of samples prior to extraction/preparation can result in the release of a highly toxic gas, hydrogen cyanide.
- 5.5. If samples are identified with cyanide concentrations equal to or greater than 200 mg/L, immediately notify the department manager and personnel responsible for hazardous waste shipping. Those samples must be identified as extremely hazardous for other chemists and must receive special attention during disposal.
- 5.6. Potassium cyanide and sodium cyanide will give off Hydrogen Cyanide (HCN) gas if combined with strong acids. Inhalation of CN gas can cause irritation, dizziness, nausea, unconsciousness and potentially death.
- 5.7. Cyanide and cyanide salts are extremely toxic. Addition of acid can generate Hydrogen Cyanide gas, which can be extremely dangerous.
- 5.8. The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure

Potassium Cyanide	Poison Corrosive	5 Mg/M3 TWA as CN	This material will form Hydrogen Cyanide (HCN) gas when combined with strong acids. Breathing HCN gas may result in death. Corrosive to the respiratory tract. May cause headache, weakness, dizziness, labored breathing nausea and vomiting, which can be followed by weak and irregular heart beat, unconsciousness, convulsions, coma and death. Solutions are corrosive to the skin and eyes, and may cause deep ulcers, which heal slowly. May be absorbed through the skin, with symptoms similar to those noted for inhalation. Symptoms may include redness, pain, blurred vision, and eye damage.
Pyridine	Flammable Irritant	5 ppm-TWA	Inhalation causes severe irritation to the respiratory tract. Symptoms of overexposure include headache, dizziness, nausea, and shortness of breath. Causes severe irritation possibly burns, to the skin. Symptoms include redness and severe pain. Absorption through the skin may occur, resulting in toxic effects similar to inhalation. May act as a photosensitizer. Vapors cause eye irritation. Splashes cause severe irritation, possible corneal burns and eye damage.
Bismuth Nitrate	Oxidizer	None	May cause irritation to the respiratory tract, skin and eyes.
Sodium Hydroxide	Corrosive Poison	2 ppm, 5 mg/m ³ 2 Mg/M3- Ceiling	This material will cause burns if comes into contact with the skin or eyes. Severe irritant. Effects from inhalation of dust or mist vary from mild irritation to serious damage of the upper respiratory tract, depending on severity of exposure. Symptoms may include sneezing, sore throat or runny nose. Contact with skin can cause irritation or severe burns and scarring with greater exposures. Causes irritation of eyes, and with greater exposures it can cause burns that may result in permanent impairment of vision, even blindness.
Potassium Phosphate	Flammable	None	Inhalation causes severe irritation to the respiratory tract. Causes severe irritation possibly burns, to the skin. Symptoms include redness and severe pain. .

Sodium Phosphate		None	Inhalation may cause respiratory tract irritation. Can produce delayed pulmonary edema. Causes mild skin and eye irritation. Ingestion may cause gastrointestinal irritation.
Hydrochloric Acid	Corrosive Poison	5 ppm- Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Cadmimum Carbonate	Probable carcinogen	0.01 mg/ m ³ as Cd	Ingestion causes increated salivation, choking, vomiting, stomach pains and diahrrhea. Inhalation may cause respiratory irritation, nausea and dyspnea.
Sulfuric Acid	Corrosive Oxidizer Dehydrator Poison Carcinogen	1 Mg/M3- TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.
Barbituric Acid	Irritant	Not established	Limited information. Inhalation may irritate respiratory tract. Causes skin and eye irritation. Should be treated as potential health hazard; do not ingest.
Potassium Hydroxide	Poison Corrosive Reactive	2 mg/m ³ – Ceiling	Inhalation symptoms may include coughing, sneezing, damage to the nasal or respiratory tract. High concentrations can cause lung damage. Swallowing may cause severe burns of mouth, throat and stomach. Other symptoms may include vomiting, diarrhea. Severe scarring of tissue and death may result. Contact with skin can cause irritation or severe burns and scarring. Causes irritation of eyes with tearing, redness, swelling. Greater exposures cause severe burns with possible blindness.

Sodium Cyanide	Poison Corrosive	5 mg/m ³ TWA as CN (skin)	This material will form Hydrogen Cyanide (HCN) gas when combined with strong acids. Breathing HCN gas may result in death. Corrosive to the respiratory tract. May cause headache, weakness, dizziness, labored breathing nausea and vomiting, which can be followed by weak and irregular heartbeat, unconsciousness, convulsions, coma and death. Solutions are corrosive to the skin and eyes, and may cause deep ulcers, which heal slowly. May be absorbed through the skin, with symptoms similar to those noted for inhalation. Symptoms may include redness, pain, blurred vision, and eye damage.
Chloramine T Hydrate	Poison		May be harmful by inhalation, ingestion, or skin absorption. This material is irritating to mucous membranes and upper respiratory tract. Avoid contact and inhalation.
Zinc Acetate	Irritant	None Listed	Symptoms of skin or eye contact include redness, itching and pain.
Silver Nitrate	Corrosive Poison Oxidizer	0.01 mg/m ³ (TWA) for silver metal dust and fume as 0.02 Ag	This is a corrosive, poisonous material. It will cause burns to any area of contact and is harmful if inhaled. Ingestion may cause death. Contact with other material may cause fire. Inhalation symptoms may include burning sensation, coughing, wheezing, laryngitis, shortness of breath, headache, nausea, and vomiting. May be absorbed into the body following inhalation. Swallowing can cause severe burns of the mouth, throat and stomach. Can cause sore throat, vomiting, and diarrhea. Poison. Symptoms include pain and burning in the mouth, blackening of the skin and mucous membranes, throat, and abdomen, salivation, vomiting of black material, diarrhea, collapse, shock, coma and death. Skin contact can cause redness, pain and severe burns. Eye contact can cause blurred vision, redness, pain, severe tissue burns and eye damage.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

- 5.9. Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Cut resistant gloves must be worn doing any other task that presents a strong possibility of getting cut. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned.
- 5.10. 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.
- 5.11. 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 involved solvents such as methylene chloride} should be conducted in a fume hood with the sash closed as far as the operations will permit.
- 5.12. Standards in solution may be diluted in the open laboratory when syringes and the like are utilized.
- 5.13. 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 the EH&S Coordinator and to a laboratory supervisor.

6. EQUIPMENT AND SUPPLIES

- 6.1. Traacs 800 autoanalyzer or discrete autoanalyzer (Konelab)
- 6.2. Probe 0.016"
- 6.3. Flowcell 10nm
- 6.4. Wavelength cell 570nm
- 6.5. Manifold-Multitest cartridge with cyanide tubing
- 6.6. 4mL Cuvettes
- 6.7. 100 mL, 250 mL, 1000 mL volumetric flasks

- 6.8. Volumetric pipettes: various
- 6.9. Top loading balance: capable of accurately weighing $\pm 0.01\text{g}$.

7. REAGENTS AND STANDARDS

7.1. Reagents

- 7.1.1. Cadmium carbonate: powder
- 7.1.2. 1.25 N sodium hydroxide: Add 50 g of sodium hydroxide pellets (NaOH) to a 1 liter volumetric flask and dilute to volume with reagent water.
- 7.1.3. Phosphate buffer: Add 136 g of potassium phosphate - monobasic (KH_2PO_4) and 2.8 g of sodium phosphate – dibasic anhydrous (Na_2HPO_4) to 800 mL of reagent water in a 1 liter volumetric flask. Mix, bring to volume with reagent water. Add 3-5 drops of Brij-35 to 100 mL of Buffer prior to using.
- 7.1.4. Chloramine-T reagent: Add 1.0 g of chloramine-T to a 250 mL volumetric flask and dilute to volume with reagent water. Prepare fresh daily.
- 7.1.5. Pyridine reagent: Add 15.0 g of barbituric acid to a 1 liter volumetric flask. Add 75 mL of pyridine and 15 mL of concentrated hydrochloric acid (HCl) and mix. Bring to volume with reagent water and store at $4^\circ\text{C} \pm 2^\circ\text{C}$ in an amber glass bottle.

Note: the pyridine barbituric acid may be purchased commercially. Filter 50 ml of the pyridine barbituric acid and bring up to 250 ml with DI water.

- 7.1.6. 0.25 N sodium hydroxide: Add 200 mL of 1N NaOH to a 1 liter volumetric flask and dilute to volume with reagent water.

Note: 0.25 N NaOH may be purchased instead.

- 7.1.7. Brij-35
- 7.1.8. 30% Brij solution: Add 2 mL Brij-35 to 1000 mL reagent water.
- 7.1.9. Rhodanine indicator, purchased.
- 7.1.10. 0.0192 N silver nitrate, purchased

7.2. Standards

- 7.2.1. Primary Source Cyanide Stock Standard, 1000 mg/L: Add 2.51 g of potassium cyanide (KCN) and 2.0 g of potassium hydroxide (KOH) to a 1000 mL volumetric flask and dilute to volume with reagent water. Mix well and store in glass amber container. Stable for 1-3 months.

Note: This stock standard may also be purchased.

Note: This stock standard must be standardized prior to use. See Appendix I.

- 7.2.2. Secondary Source Cyanide Standard, 1000 mg/L: Follow 7.2.1 using an alternate source of Potassium Cyanide (KCN).

Note: This stock standard may also be purchased.

Note: This stock standard must be standardized prior to use. See Appendix I.

7.2.3. Calibration Standards (Water and Solid Matrices)

- 7.2.3.1. If using the 1.25 N NaOH: pipet the appropriate amount of cyanide standard into 100 mL volumetric and add 20 mL 1.25N NaOH to each calibration standard (except the 1.0 mg/L) and bring to volume with reagent water.

If using the purchased 0.25N NaOH: pipet the appropriate amount of cyanide standard into 100 mL volumetric and bring to volume with 0.25N NaOH.

Prepare weekly.

<u>Concentration CN-</u>	<u>mL CN-</u>	<u>Final Volume</u>
10 mg/L	1 mL of 1000 mg/L	100 mL
1.0 mg/L (secondary only)	10 mL of 10 mg/L	100 mL
*0.2 mg/L	2 mL of 10 mg/L	100 mL
*0.1 mg/L	1 mL of 10 mg/L	100 mL
*0.05 mg/L	0.5 mL of 10 mg/L	100 mL

*0.025 mg/L	0.25 mL of 10 mg/L	100 mL
*0.01 mg/L	0.1 mL of 10 mg/L	100 mL
*0.005 mg/L	0.05 mL of 10 mg/L	100 mL

*Denotes calibration standards

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

- 8.1. Solid samples are not chemically preserved. Water samples are preserved with NaOH to a pH > 12. All samples are stored at 4°C ± 2°C in plastic or glass containers.
- 8.2. The holding time for **non-CLP** samples is fourteen days from sampling to analysis.
- 8.3. The holding time for **CLP** samples is twelve days from receipt to analysis.

9. QUALITY CONTROL

9.1. Batch Definition

9.1.1. **Non –CLP:**

- 9.1.1.1. A batch is a group of no greater than 20 samples excluding QC samples (LCS, Method Blank, MS, MSD) 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.

9.1.2. **CLP**

- 9.1.2.1. A batch is a group of no greater than 20 samples excluding QC samples (LCS/ICV, Method Blank, Sample Duplicate and Matrix Spike) 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.

- 9.1.2.2. A Chain of Custody (COC) is needed for each SDG.

9.2. Method Blank

9.2.1. Non-CLP

9.2.1.1. One method blank (MB) must be processed with each preparation batch. The method blank consists of reagent water or 0.25N NaOH 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.

9.2.1.2. A method blank consists of 50 mL 0.25N NaOH for Total Cyanide analysis or 50 mL reagent water for Free and Amenable Cyanide analysis and must be distilled and analyzed with each analytical batch of samples. See SOP NC-WC-0032 for distillation instructions.

9.2.2. CLP

9.2.2.1. Each SDG (sample delivery group) must have one method blank (MB) processed per matrix and per twenty samples. If the SDG is distilled over multiple “racks”, the method blanks must be distilled with the samples. If more than one SDG is on one rack, process one method blank per SDG and per matrix. The solid method blank is called “PBS” (prep blank solid) and the water method blank is called “PBW” (prep blank water).

NOTE: A “rack” is one setup of cyanide samples and QC, and can encompass 1-3 of the midi-distillation units.

9.2.2.2. A method blank (PBW/PS) consisting of 50 mL 0.25N NaOH must be distilled and analyzed with each analytical batch of samples. See SOP NC-WC-0032 for distillation instructions.

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 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 (LCS)

9.3.1. One LCS from an independent source must be processed with each preparation batch. The LCS must be carried through the entire analytical procedure. 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.

9.3.2. Non-CLP

9.3.2.1. A midrange LCS consisting of a 0.04 mg/L (2.0 mL of 1.0 mg/L to 50 mL) must be distilled and analyzed with each analytical batch of samples for Total, Amenable, and Free cyanide analysis. See SOP NC-WC-0032 for distillation instruction.

NOTE: A purchased complex cyanide solution may be used instead as the midrange LCS for **Total Cyanide** analysis only.

9.3.2.2. The acceptance limits for drinking water samples, Method 335.4, is 90 – 110%.

9.3.3. CLP

9.3.3.1. A LCS (which doubles as an ICV) is processed with each batch or each SDG, whichever is more frequent. Even if multiple SDG's are on the "rack", only one LCS (ICV) needs to be distilled for up to a maximum of 20 samples.

NOTE: A "rack" is one setup of cyanide samples and QC, and can encompass 1 – 3 of the midi-distillation units.

9.3.3.2. For CLP waters: the LCS is 4.0 mL of 1.0 ppm secondary source in 50 mL (TV = 80ug/L).

9.3.3.3. For CLP solids, a solid LCS must be processed per SDG or per batch, whichever is more frequent. Weigh out 0.05g of the solid LCS sample. If more than one SDG is processed on a “rack”, process a solid LCS for each one. If a SDG has solid sample distilled on a different “rack”, then additional solid LCS’s will need to be distilled. The value for this LCS changes as the solid lot number changes each time a new one is ordered. The value is noted on the product certification.

9.3.3.4. If more than one SDG is distilled on one rack, they may be analyzed together (however, each SDG **must** be **analyzed separately with a separate PBW**). It is also **preferred** that each SDG have its own method blank(s), its own ICV (LCS), its own LCS-S (if samples are solids), and its own sample duplicate and matrix spike. If the SDG has been split over multiple distillation “racks”, then you may not have a sample duplicate and matrix spike for each rack. However, an ICV (LCS) is distilled with each “rack”. If more than one SDG is distilled on a “rack”, then the ICV (LCS) distilled with that rack must be analyzed with each SDG.

9.3.4. Corrective Action for LCS

9.3.4.1. If any analyte is outside established control limits the system is out of control and corrective action must occur.

9.3.4.2. Corrective action will be reparation 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. Non-CLP

9.4.1.1. 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.

9.4.1.2. A MS/MSD consisting of 50 mL or 1.0 g sample and 0.04 mg/L spike (2.0 mL of 1.0 mg/L to 50 mL) will be distilled and analyzed with every batch. See SOP NC-WC-0032 for distillation instructions. This is also the same value for CLP.

9.4.1.3. The acceptance limits for drinking water samples, Method 335.4, is 90 – 110%.

9.4.2. **CLP**

9.4.2.1. Each SDG must have a sample duplicate and a matrix spike processed per matrix. Sometimes this requirement is waived by the client or PM but, if uncertain, make sure that these are done. Usually, the sample to be spiked is assigned, but not always. If a MS/MSD is created in receiving, either batch the MSD and “N/A” the result or have the MSD deleted. In either case, create a sample duplicate for the sample that is spiked when batching. If processing a SDG over more than one “rack”, then there is no need to process additional matrix spikes and sample duplicates (unless specifically requested). Typically, only one sample duplicate and matrix spike is required per SDG.

9.4.2.2. Matrix spike for CLP consists of 50 mL or 1.0 g of sample and 100 µg/L spike (5.0 mL of 1.0 mg/L secondary standard).

NOTE: see corrective action section 9.4.3.4 for A-spike

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 reparation 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 "amount" MSB. The Exception Code is changed to NC. The A-spike is not needed in this case.

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.

9.4.3.4. A-spike corrective action: if matrix spike recovery fails criteria, then spike the sample at two times the reporting limit or 2 times the sample concentration, which ever is greater. Examples are shown below.

*A-spike = 2 mL of sample + 2mL of A-spike solution

A-spike solution = 0.8 mL .25N NaOH, +3.2 mL 0.05 ppm 1° standard

9.5. QC Acceptance Criteria

9.5.1. Control limits are established by the laboratory as described in NC-QA-0018.

9.5.2. Laboratory control limits are internally generated and updated periodically unless method specified. Control limits are listed in the Laboratory Quality Manual (LQM) and the latest is version easily accessible via the LIMs (QC Browser program.).

9.6. Method Detection Limits (MDLs) and MDL Checks

9.6.1. MDLs and MDL Checks are established by the laboratory as described in SOPs S-Q-003 and NC-QA-0021.

9.6.2. MDLs are listed in the Laboratory Quality Manual (LQM) and the latest version is easily accessible via the LIMs (QC Browser program).

9.7. Nonconformance and Corrective Action

9.7.1. Any deviations from QC procedures must be documented as a nonconformance, with applicable cause and corrective action approved by the facility QA Manager.

10. CALIBRATION AND STANDARDIZATION

10.1. Summary

10.1.1. The instrument is calibrated using six cyanide standards and a blank at the time of analysis. Non- CLP samples are processed in mg/L and CLP samples are in ug/L.

10.2. Initial Calibration

10.2.1. Non-CLP

10.2.1.1. The instrument is calibrated at the beginning of each run and is verified at the beginning of the run by using a midrange ICV. The ICV is composed of the 0.1 ppm secondary standard. The ICV must not vary from the original curve by more than $\pm 15\%$ or recalibration is required. For drinking water samples, Method 335.4, the criteria is $\pm 10\%$. The correlation coefficient of the original curve must be ≥ 0.995 or recalibration is required.

10.2.2. CLP

10.2.2.1. The instrument is calibrated at the beginning of each run and is verified at the beginning of the run by analyzing the ICV/LCS. The ICV is composed of 4.0 mL of 1.0 ppm secondary standard (TV = 80 ug/L). The correlation coefficient of the original curve must be ≥ 0.995 or recalibration is required.

10.3. Continuing Calibration

10.3.1. The run is checked every ten samples and at the end of the run using a midrange CCV to verify continued linearity. It cannot vary from the original curve by more than $\pm 15\%$ or recalibration is required. For drinking water samples, Method 335.4, the criteria is $\pm 10\%$. The previous 10 samples must be reanalyzed and bracketed by a CCV that passes criteria. The CCV is composed of the 0.1 mg/L primary standard for non-CLP runs and the 100 ug/L for CLP runs.

10.3.2. System cleanliness is checked every ten samples and at the end of the run using a CCB. It cannot contain the analyte of interest above the reporting limit or recalibration is required. The previous 10 samples must be reanalyzed and bracketed by a CCB that passes criteria. The CCB is 0.25N NaOH.

NOTE: Base and gain values may change with new reagents, standards, tubing changes, or board cleaning. These values are for reference only.

10.4. High and Low Standard

10.4.1. The distillation technique is checked by distilling a high and low standard and comparing the values obtained to the standard curve. The method recommends that the HI/LO standards be compared to the curve with a +/-10% agreement. The HI/LO standards are evaluated against all applicable batch QC.

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. See cyanide distillation SOP: NC-WC-0032.

11.3.1.1. Non-CLP

11.3.1.1.1. The sample is distilled/refluxed under acidic conditions for one hour. The released HCN is trapped in 50 mL of 0.25 N NaOH solution. EPA Method 335.4 says to reflux for one and a half hours.

11.3.1.2. CLP

11.3.1.2.1. The sample is distilled/refluxed under acidic conditions for one and a half hours. The released HCN is trapped in 50 mL of 0.25 N NaOH solution.

11.3.2. Sample Preparation Procedure

All Samples: Test each sample for the presence of sulfides using lead acetate paper. If sulfides are present, treat the sample with powdered cadmium carbonate. Yellow cadmium sulfide precipitates if the sample contains sulfide. Repeat this operation until a drop of the treated sample solution does not darken the lead acetate test paper. Filter the solution. Avoid a large excess of

cadmium carbonate and long contact time in order to minimize loss by complexation or occlusion of cyanide on the precipitated material.

NOTE: Water should be tested prior to distillation

11.4. Sample Analysis

11.4.1. Summary

11.4.1.1. The sample distillates are analyzed on the autoanalyzer for cyanide using the automated pyridine-barbituric method.

11.4.2. Recommended Instrument Conditions

11.4.2.1. See Manufacturer's information for operation instructions.

11.4.2.2. Start Up Solutions (and Wash Solutions)

11.4.2.2.1. All lines in 0.25N NaOH solution:

11.4.2.2.2. Then all lines in 30% Brij solution.

11.4.2.3. Running Solutions

11.4.2.3.1. Two DI water lines (orange/green) in 30% Brij solution

11.4.2.3.2. Red/Red in pyridine reagent

11.4.2.3.3. Orange/red in chloramine-T reagent

11.4.2.3.4. White/white in phosphate buffer solution

11.4.2.4. Base and Gain

11.4.2.4.1. Performed on the 0.2 mg/L standard

11.4.2.4.2. Approximate values: Base = 75 Gain = 150

*These values are for reference only and may change with new reagent or standard preparations.

11.4.2.5. Trouble shooting for poor Base and Gain or baseline noise

11.4.2.5.1. Place reagent lines 1-3 back in Brig solution and run on high for five minutes. Place all 5 lines (1-5) and probe line in 1.25 N NaOH solution and run on high for five minutes. Place lines back in appropriate “start-up” solutions and run on high for five minutes or make fresh new reagents.

Place lines back in reagents and perform another base and gain when the baseline has stabilized.

11.4.3. Sample Analysis Procedure

11.4.3.1. See Manufacturer’s information for operating instructions.

11.4.3.2. A calibration curve is analyzed at the beginning of each run. The correlation coefficient must be > 0.995 to continue.

11.4.3.3. The ICV (from the secondary source) and the ICB is analyzed at the beginning of every run. CCV’s (from the primary source) and CCB’s are analyzed at the end and between every 10 samples.

11.4.3.4. Sample distillates higher than the highest calibration standard (0.2 mg/L) must be diluted with 0.25 N NaOH and re-analyzed.

11.4.3.5. Any samples analyzed after a high sample must be re-analyzed if carryover is suspected.

11.5. Tray Protocol (Run Order)

Normal Tray Protocol

1. Calibration
2. MRL
3. ICV (secondary source)
4. ICB (CCB)

5. Prep Blank
6. LCS
7. LOW
8. HI
9. UP to 6 more samples
10. MRL
11. CCV
12. CCB
13. Up to 10 samples
14. MRL
15. CCV
16. CCB

CLP Tray Protocol-Water

1. Calibration
2. Distilled ICV/LCS
3. ICB
4. CCV
5. CCB
6. PBW
7. Sample

8. Sample duplicate
9. Sample MS
10. Up to 6 more samples
11. CCV
12. CCB
13. Up to ten more samples
14. CCV
15. CCB

CLP Tray Protocol-Solid

1. Calibration standards
2. Distilled ICV
3. ICB
4. CCV
5. CCB
6. PBS
7. LCSS
8. Sample
9. Sample duplicate
10. Matrix Spike
11. Up to 5 more samples

12. CCV

13. CCB

14. Up to ten more samples

15. CCV

16. CCB

11.6. Analytical Documentation

11.6.1. Record all analytical information in the analytical logbook/logsheets, including the analytical data from standards, blanks, LCSs, MS/MSDs, and any corrective actions or modifications to the method.

11.6.2. All standards and reagents are logged into a department standard logbook. All standards are assigned a unique number for identification. Logbooks are reviewed by the supervisor or designee.

11.6.3. 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.

11.6.4. Sample results and associated QC are entered into the LIMs after final technical review.

12. DATA ANALYSIS AND CALCULATIONS

$$12.1. \text{ Total Cyanide, mg / L } = \frac{\text{mg / L CN}^- \text{ from printout} \times 50}{\text{mL of sample distilled}} \times D$$

$$12.2. \text{ Total Cyanide, mg / kg } = \frac{\text{mg / L CN}^- \text{ from printout} \times 50}{\text{g of sample distilled.}} \times D$$

$$12.3. \text{ Amenable Cyanide, mg / L } = \text{Total CN}^- \text{ (mg / L) } - \text{Chlorinated CN}^- \text{ (mg / L)}$$

Where:

mg/L = *can also be mg/kg*

D = **Dilution Factor** = $\frac{\text{Final Volume of Dilution}}{\text{Volume of Sample Distillate Used}}$

NOTE: *Free cyanide has the same calculations as Total cyanide*

12.4. LCS Recovery:

$$\frac{\text{Instrument Value}}{0.04(\text{true})} \times 100 = \% \text{ Recovery}$$

12.5. CCV Recovery:

$$\frac{\text{Instrument Value}}{0.025(\text{true})} \times 100 = \% \text{ Recovery}$$

NOTE: *CCV recovery must be between 85 - 115% for data to be acceptable. If CCV recovery is not within these limits, reanalysis is required 335.4 says 10%.*

12.6. **MS/MSD Recovery for Waters and solids:**

$$\frac{A - B}{0.040(\text{true})} \times 100 = \% \text{ Recovery}$$

Where:

A = *Instrument value MS/MSD*

B = *Sample instrument value*

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.

13.2.2. Method validation information (where applicable) in the form of laboratory demonstrations of capabilities is maintained for this method in the laboratory QA files.

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. All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

15.2. Waste Streams Produced by the Method

15.2.1. The following waste streams are produced when this method is carried out.

15.2.2. Alkaline material from the auto-analyzer. This waste is collected in the lab in a container labeled "Pyridine Waste".

15.2.3. Acidic waste This waste is collected in the lab in a container labeled "Acid Waste".

15.2.4. Caustic waste containing Pyridine. This waste is collected in the lab in a containers labeled "Pyridine Waste".

15.2.5. Wastewater contaminated with Pyridine. This waste is collected in the lab in a containers labeled "Pyridine Waste".

15.2.6. Wastewater containing 1.5% Pyridine This waste is collected in the lab in a containers labeled "Pyridine Waste".

- 15.2.7. Aqueous analytical waste, neutral to slightly basic, contaminated with 3% pyridine. This waste is collected in the lab in a container labeled "Pyridine Waste".
- 15.2.8. Filter paper contaminated with lead sulfide This waste is placed in a container labeled "Solid Waste".
- 15.2.9. Aqueous rinsates from distillation tube clean up This waste is collected in the lab and disposed of in a container labeled "Acid Waste".
- 15.2.10. Miscellaneous solid waste contaminated with sample residue, acids, caustics and reagents used in this SOP. A weigh tin is the only type of this waste generated. The tin is rinsed with water and disposed of in a container labeled "Solid Waste".
- 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 Method 9012 A, and its updates
- 16.1.2. EPA 600; Cyanide, Total and Cyanide, Amenable to Chlorination; Methods 335.2, March 1983
- 16.1.3. EPA 600; Determination of Total Cyanide by Semi-Automated Colorimetry, 335.4, Revision 1.0, August 1993.
- 16.1.4. Standard Methods for the Examination of Water and Wastewater, Eighteenth Edition: Weak and Dissociable Cyanide; Method 4500-CN-E
- 16.1.5. USEPA CLP SOW ILM03.0 and ILM04.0, Section D - Cyanide Midi Distillation
- 16.1.6. Corporate Quality Management Plan (QMP), current version.
- 16.1.7. STL Laboratory Quality Manual (LQM), current version

16.1.8. STL Corporate Safety Manual, M-E-0001 and STL North Canton Facility Addendum and Contingency Plan, current version.

16.2. Associated SOPs and Policies, latest version

16.2.1. QA Policy, QA-003

16.2.2. Glassware Washing, NC-QA-0014

16.2.3. Statistical Evaluation of Data and Development of Control Charts, NC-QA-0018

16.2.4. Method Detection Limits and Instrument Detection Limits, S-Q-003 and NC-QA-0021

16.2.5. Navy/Army SOP, NC-QA-0016

16.2.6. NC-WC-0032, Cyanide Preparation Method

17. MISCELLANEOUS (TABLES, APPENDICES, ETC...)

17.1. Reporting limits

17.1.1. The reporting limit (RL) is 0.01 mg/L for waters (50 mL used) and 0.50 mg/kg for solids (1.0 g used). The reporting limit for solid samples performed only under the Michigan program is 200 µg/kg for solids (2.5 g used). The lowest level of the calibration curve can be used as the reporting limit upon request.

17.1.2. If samples require dilution or smaller volumes than specified in this method, the RL will be elevated.

17.2. Troubleshooting guide for poor Base and Gain or baseline noise

17.2.1. Place reagent lines 1-3 back in Brig solution and run on high for five minutes. Place all 5 lines (1-5) and probe line in 1.25 N NaOH solution and run on high for five minutes. Place lines back in appropriate "start-up" solutions and run on high for five minutes.

Place lines back in reagents and perform another base and gain when the baseline has been stabilized.

17.3. Method Deviation (9012A/335.2)

17.3.1. Method of Standard Addition is not performed for samples with matrix interference (sulfides).

Appendix I - Cyanide Standardization

1. Pipet 10.0 mL of the 1000 ppm stock cyanide standard into a 250 mL Erlenmeyer flask and add 90 mL of reagent water.
2. Add 0.5 mL (10 drops) of Rhodanine indicator.
3. Titrate with 0.0192 N silver nitrate (using a micro burette) until the color changes from yellow to pink/orange.
4. Titrate a blank (100 mL reagent water) following steps 2 and 3.
5. Calculation:

$$\text{Cyanide, mg / L} = \frac{(A - B) (1000)}{\text{mL Cyanide Solution (10)}}$$

Where:

A = mL titrant for standard

B = mL titrant for blank

6. If the cyanide concentration is not 1000 ppm, adjust concentration accordingly.

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Implementation Date: 1/3/05

SOP No.: NC-WC-0032

Revision No.: 8.4

Revision Date: 12/08/04

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STL STANDARD OPERATING PROCEDURE

TITLE: CYANIDE PREPARATION METHOD

(SUPERSEDES: REVISION 8.3, DATED 06/17/03)

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1. SCOPE AND APPLICATION

- 1.1. This method is applicable to the determination of Total, Amenable, and Free Cyanide in solids, liquids, and waters. It is based on CLP ILM03.3, CLP ILM04.0, SW 846 Method 9012A, EPA 335.1, 335.2, 335.4, Standard Method 4500-CN-I and ASTM D 4282-83. The working linear range is 0.005 - 0.2 mg/L for waters and 0.25 to 10 mg/kg for solids.
- 1.2. The associated method codes are CLP ILM03.0 (DV), CLP ILM04.0 (OU), SW846 Method 9012A (QP), EPA 335.1 and 335.2 (CG), EPA 335.4 (O2), Standard Method 4500-CN-E (A4), Free Cyanide 4500CN-I (HF) and Amenable Cyanide 9012A (N4).
- 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 by the laboratory QA department.

2. SUMMARY OF METHOD

- 2.1. The Cyanide, as HCN, is released by distilling/refluxing the sample with strong acid and is trapped in a sodium hydroxide solution.

3. DEFINITIONS

- 3.1. Refer to the glossary in the Laboratory Quality Manual (LQM), latest version.

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. Specific selection of reagents may be required to avoid introduction of contaminants.
- 4.2. Oxidizing agents such as chlorine will decompose most cyanides. Sulfide will distill over with the cyanide and could affect colorimetric, titrimetric, and electrode procedures. Refer to the preparation section on how to screen and treat samples appropriately.
- 4.3. Aldehydes convert cyanide to cyanohydrin which could result in the loss of cyanide. If the presence of aldehydes are suspected, stabilize the sample with NaOH at the time of collection and add 2 mL 3.5% ethylenediamine solution per 100 mL of sample.

- 4.4. Refer to Standard Methods for further information on possible interferences and associated treatments.

5. SAFETY

- 5.1. Employees must abide by the policies and procedures in the Corporate Safety Manual the Waste Management SOP, and this document.
- 5.2. In the event the sample begins to react unexpectedly during distillation, remove entire apparatus from heat source, set aside, and allow to cool. **DO NOT ATTEMPT TO DISASSEMBLE GLASSWARE.** Doing so may result in a sudden release of pressure with spraying of the sample.
- 5.3. Ensure cooling water is turned on to the distillation unit. Otherwise the samples may boil over and come into contact with the heating plates.
- 5.4. Latex, vinyl, Nitrile or similar gloves may be used.
- 5.5. Preparation of sodium hydroxide solutions produces considerable amounts of heat. Use plastic containers to mix this solution if possible. If glass containers are used, they must be free of any cracks or irregularities.
- 5.6. The acidification of samples prior to extraction/preparation can result in the release of a highly toxic gas, hydrogen cyanide.
- 5.7. If samples are identified with cyanide concentrations equal to or greater than 200 mg/L, immediately notify the department manager and personnel responsible for hazardous waste shipping. Those samples must be identified as extremely hazardous for other chemists and must receive special attention during disposal. **Potassium cyanide and sodium cyanide will give off Hyrdogen Cyanide (HCN) gas if combined with strong acids. Inhalation of CN gas can cause irritation, dizziness, nausea, unconsciousness and potentially death.**
- 5.8. Cyanide and cyanide salts are extremely toxic. Addition of acid can generate Hydrogen Cyanide gas, which can be extremely dangerous.
- 5.9. The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in

the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Potassium Cyanide	Poison Corrosive	5 Mg/M3 TWA as CN	This material will form Hydrogen Cyanide (HCN) gas when combined with strong acids. Breathing HCN gas may result in death. Corrosive to the respiratory tract. May cause headache, weakness, dizziness, labored breathing nausea and vomiting, which can be followed by weak and irregular heart beat, unconsciousness, convulsions, coma and death. Solutions are corrosive to the skin and eyes, and may cause deep ulcers, which heal slowly. May be absorbed through the skin, with symptoms similar to those noted for inhalation. Symptoms may include redness, pain, blurred vision, and eye damage.
Pyridine	Flammable Irritant	5 ppm- TWA	Inhalation causes severe irritation to the respiratory tract. Symptoms of overexposure include headache, dizziness, nausea, and shortness of breath. Causes severe irritation possibly burns, to the skin. Symptoms include redness and severe pain. Absorption through the skin may occur, resulting in toxic effects similar to inhalation. May act as a photosensitizer. Vapors cause eye irritation. Splashes cause severe irritation, possible corneal burns and eye damage.
Acetic Acid (1)	Corrosive Poison Flammable	10 ppm- TWA	Contact with concentrated solution may cause serious damage to the skin and eyes. Inhalation of concentrated vapors may cause serious damage to the lining of the nose, throat, and lungs. Breathing difficulties may occur.
Acetone	Flammable	1000 ppm- TWA	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.
Bismuth Nitrate	Oxidizer	None	May cause irritation to the respiratory tract, skin and eyes.

Sodium Hydroxide	Corrosive Poison	2 ppm, 5 mg/m ³ 2 Mg/M3- Ceiling	This material will cause burns if comes into contact with the skin or eyes. Severe irritant. Effects from inhalation of dust or mist vary from mild irritation to serious damage of the upper respiratory tract, depending on severity of exposure. Symptoms may include sneezing, sore throat or runny nose. Contact with skin can cause irritation or severe burns and scarring with greater exposures. Causes irritation of eyes, and with greater exposures it can cause burns that may result in permanent impairment of vision, even blindness.
Potassium Phosphate	Flammable	None	Inhalation causes severe irritation to the respiratory tract. Causes severe irritation possibly burns, to the skin. Symptoms include redness and severe pain. .
Hydrochloric Acid	Corrosive Poison	5 ppm- Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Lead Carbonate	Poison Neurotoxin Irritant Probable carcinogen Reproductive hazard	0.05mg/m3 TWA as Lead	Inhalation can cause local irritation of bronchia and lungs and can cause symptoms such as metallic taste in the mouth, chest and abdominal pain. Skin contact can cause local irritation, redness and pain. Can be absorbed through the skin.

Sulfuric Acid	Corrosive Oxidizer Dehydrator Poison Carcinogen	1 Mg/M3-TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.
Phosphoric Acid	Corrosive	1 mg/m ³ TWA	Inhalation is not an expected hazard unless misted or heated to high temperatures. May cause redness, pain, and severe skin burns. May cause redness, pain, blurred vision, eye burns, and permanent eye damage.
Barbituric Acid	Irritant	Not established	Limited information. Inhalation may irritate respiratory tract. Causes skin and eye irritation. Should be treated as potential health hazard; do not ingest.
Potassium Hydroxide	Poison Corrosive Reactive	2 mg/m ³ – Ceiling	Inhalation symptoms may include coughing, sneezing, damage to the nasal or respiratory tract. High concentrations can cause lung damage. Swallowing may cause severe burns of mouth, throat and stomach. Other symptoms may include vomiting, diarrhea. Severe scarring of tissue and death may result. Contact with skin can cause irritation or severe burns and scarring. Causes irritation of eyes with tearing, redness, swelling. Greater exposures cause severe burns with possible blindness.
Sodium Cyanide	Poison Corrosive	5 mg/m ³ TWA as CN (skin)	This material will form Hydrogen Cyanide (HCN) gas when combined with strong acids. Breathing HCN gas may result in death. Corrosive to the respiratory tract. May cause headache, weakness, dizziness, labored breathing nausea and vomiting, which can be followed by weak and irregular heartbeat, unconsciousness, convulsions, coma and death. Solutions are corrosive to the skin and eyes, and may cause deep ulcers, which heal slowly. May be absorbed through the skin, with symptoms similar to those noted for inhalation. Symptoms may include redness, pain, blurred vision, and eye damage.

Chloramine T Hydrate	Poison		May be harmful by inhalation, ingestion, or skin absorption. This material is irritating to mucous membranes and upper respiratory tract. Avoid contact and inhalation.
Zinc Acetate	Irritant	None Listed	Symptoms of skin or eye contact include redness, itching and pain.
Silver Nitrate	Corrosive Poison Oxidizer	0.01mg/m ³ (TWA) for silver metal dust and fume as 0.02 Ag	This is a corrosive, poisonous material. It will cause burns to any area of contact and is harmful if inhaled. Ingestion may cause death. Contact with other material may cause fire. Inhalation symptoms may include burning sensation, coughing, wheezing, laryngitis, shortness of breath, headache, nausea, and vomiting. May be absorbed into the body following inhalation. Swallowing can cause severe burns of the mouth, throat and stomach. Can cause sore throat, vomiting, and diarrhea. Poison. Symptoms include pain and burning in the mouth, blackening of the skin and mucous membranes, throat, and abdomen, salivation, vomiting of black material, diarrhea, collapse, shock, coma and death. Skin contact can cause redness, pain and severe burns. Eye contact can cause blurred vision, redness, pain, severe tissue burns and eye damage.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

- 5.10 Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Cut resistant gloves must be worn doing any other task that presents a strong possibility of getting cut. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.
- 5.11 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. All samples with pink stickers that read "Caution/Use Hood!" **must** be opened in the hood. Contact the EH&S Coordinator if this is not possible. Solvent and waste containers will be kept closed unless transfers are being made.

- 5.12 The preparation of standards and reagents will be conducted in a fume hood with the sash closed as far as the operation will permit.
- 5.13 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 the EH&S Coordinator and the Laboratory Supervisor.

6. EQUIPMENT AND SUPPLIES

- 6.1. Cyanide Distillation Apparatus
- 6.2. Analytical balance, capable of accurately weighing ± 0.0001 g
- 6.3. Vacuum pump
- 6.4. Graduated cylinders: various
- 6.5. Volumetric flasks: various
- 6.6. Volumetric pipets: various
- 6.7. Balance: Top loading, capable of accurately weighing ± 0.01 g
- 6.8. Lead Acetate Indicator Paper
- 6.9. Potassium Iodide (KI) Indicator Paper
- 6.10. Erlenmeyer flasks: various
- 6.11. Buret: Class A 10 mL
- 6.12. pH strips
- 6.13. Boiling stones or chips
- 6.14. Beakers: various
- 6.15. Snap seal containers: 120 mL
- 6.16. Plastic bottles with lids: 250mL or 500mL

7. REAGENTS AND STANDARDS

7.1. Reagents

- 7.1.1. Sulfamic Acid: reagent grade (not used for CLP ILM03.0)
- 7.1.2. Sulfamic Acid Solution: Add 100 g of sulfamic acid to 800 mL reagent water and dilute to 1 liter with reagent water (not used for CLP ILM03.0)
- 7.1.3. Ascorbic Acid: reagent grade
- 7.1.4. Sodium Hydroxide: (NaOH), high purity grade.
- 7.1.5. Sodium Hydroxide, 1.25 N: Add 50 g of NaOH to 900 mL and dilute to 1 liter with reagent water.
- 7.1.6. Sodium Hydroxide, 0.25 N: Add 10 g of NaOH to 900 mL reagent water and dilute to 1 liter with reagent water. Purchased reagent may also be used.
- 7.1.7. Sulfuric Acid: (H₂SO₄), concentrated
- 7.1.8. Acetic Acid Solution: Add 10 mL of glacial acetic acid to 90 mL of reagent water.
- 7.1.9. Magnesium Chloride: (MgCl₂•6H₂O), reagent grade
- 7.1.10. Magnesium Chloride Solution: Add 510 g MgCl₂•6H₂O to 500 mL reagent water and dilute to 1 liter with reagent water. Purchased reagent may also be used.
- 7.1.11. Calcium Hypochlorite: [Ca (OC1)₂], reagent grade
- 7.1.12. Calcium Hypochlorite Solution: Add 5 g of Ca(OC1)₂ to 100 mL of reagent water.
- 7.1.13. Methyl Red Indicator: Add 0.05 g of methyl red to 50 mL of glacial acetic acid and dilute to 100 mL with reagent water.
- 7.1.14. Methyl red reagent grade glacial
- 7.1.15. Acetic Acid: (CH₃COOH), glacial reagent grade
- 7.1.16. Zinc Acetate: [Zn(C₂H₃O₂)], reagent grade
- 7.1.17. Zinc Acetate Solution: Add 100 g zinc acetate to 800 mL reagent water and dilute to 1 liter with reagent water.
- 7.1.18. Sodium Acetate: [NaC₂H₃O₂•3H₂O] reagent grade

7.1.19. Sodium Acetate Buffer: Add 410 g of sodium acetate to 500 mL of reagent water. Adjust the pH to 4.5 using glacial acetic acid and dilute to 1 liter with reagent water.

7.1.20. Rhodanine: reagent grade

7.1.21. 0.0192 N Silver Nitrate: reagent grade

7.1.22. Bismuth nitrate [$\text{Bi}(\text{NO}_3)_3$]: Dissolve 30 g of $\text{Bi}(\text{NO}_3)_3$ in 100 mL of reagent water. While stirring, add 250 mL of glacial acetic acid. Stir until dissolved. Dilute to 1 L with reagent water.

7.1.23. Cadmium chloride [CdCl_2] – anhydrous : Dissolve 1.0 g CdCl_2 in 90 mL of reagent water. Dilute to 100 mL with reagent water to produce a 10 g/L CdCl_2 solution.

7.2. Standards

7.2.1. Primary Source Cyanide Stock Standard, 1000 mg/L: Add 2.51 g of potassium cyanide (KCN) and 2.0 g of potassium hydroxide (KOH) to a 1000 mL volumetric flask and dilute to volume with reagent water. Mix well and store in glass amber container. Stable for 1-3 months.

Note: This stock standard may also be purchased.

Note: This stock standard must be standardized prior to use. See SOP NC-WC-0031 Appendix I

7.2.2. Secondary Source Cyanide Standard, 1000 mg/L: Follow 7.2.1 using an alternate source of Potassium Cyanide (KCN).

Note: This stock standard may also be purchased.

Note: This stock standard must be standardized prior to use. See SOP NC-WC-0031 Appendix I.

7.2.3. Calibration Standards (Water and Solid Matrices)

7.2.3.1. If using the 1.25 N NaOH: pipet the appropriate amount of cyanide standard into 100 mL volumetric and add 20 mL 1.25N NaOH to each calibration standard (except the 1.0 mg/L) and bring to volume with reagent water.

If using the purchased 0.25N NaOH: pipet the appropriate amount of cyanide standard into 100 mL volumetric and bring to volume with 0.25N NaOH. Prepare weekly.

<u>Concentration CN-</u>	<u>mL CN-</u>	<u>Final Volume</u>
100 mg/L	10 mL of 1000 mg/L	100 mL
10 mg/L	10 mL of 100 mg/L	100 mL
1.0 mg/L	10 mL of 10 mg/L	100 mL
*0.2 mg/L	20 mL of 1 mg/L	100 mL
*0.1 mg/L	10 mL of 1 mg/L	100 mL
*0.05 mg/L	5 mL of 1 mg/L	100 mL
*0.025 mg/L	25 mL of 0.1 mg/L	100 mL
*0.01 mg/L	10 mL of 0.1 mg/L	100 mL
*0.005 mg/L	10 mL of 0.05 mg/L	100 mL

*Denotes calibration standards

8. SAMPLE PRESERVATION AND STORAGE

- 8.1. Solid and liquid samples are not chemically preserved. Water samples are preserved with NaOH to a pH>12. All samples are stored at 4° C ± 2°C in plastic or glass containers.
- 8.2. The holding time for **non-CLP** samples is fourteen days from sampling to analysis.
- 8.3. The holding time for **CLP** samples holding time is twelve days from receipt to analysis.

9. QUALITY CONTROL

- 9.1. Batch Definition
 - 9.1.1. **Non-CLP**

A batch is a group of no greater than 20 samples excluding QC samples (LCS, Method Blank, MS, MSD) 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 process.

9.1.2. CLP:

A batch is a group of no greater than 20 samples excluding QC samples (LCS/ICV, Method Blank, Sample Duplicate and Matrix Spike) 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. Method Blank (MB)

9.2.1. Non-CLP

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.

9.2.1.1. A method blank consists of 50 mL 0.25N NaOH for Total Cyanide analysis or 50 mL reagent water for Free and Amenable Cyanide analysis. The blank must be distilled and analyzed with each analytical batch of samples.

9.2.2. CLP:

Each SDG (sample delivery group) must have one method blank processed per matrix and per twenty samples. If the SDG is distilled over multiple “racks”, the method blanks must be distilled with the samples. If more than one SDG is on one rack, process one method blank per SDG and per matrix. The solid method blank is called “PBS” (prep blank solid) and the water method blank is called “PBW” (prep blank water).

9.2.2.1. A method blank (PBW/PBS) consisting of 50 mL 0.25N NaOH must be distilled and analyzed with each analytical batch of samples.

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 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 (LCS)

9.3.1. One LCS must be processed with each preparation batch. The LCS must be carried through the entire analytical procedure. 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.

9.3.2. **Non-CLP:**

A midrange LCS consisting of a 0.04 mg/L (2.0 mL of 1.0 mg/L secondary source to 50 mL) must be distilled and analyzed with each analytical batch of samples for Total, Amenable, and Free cyanide analysis.

NOTE: A purchased complex cyanide solution may be used instead as the midrange LCS for **Total Cyanide** analysis only.

9.3.2.1. The acceptance limits for drinking water samples is 90 – 110%.

9.3.3. **CLP:**

9.3.3.1.A LCS (which doubles as an ICV) is processed with each batch or each SDG, which ever is more frequent. Even if multiple SDG's are on the "rack", only one LCS (ICV) needs to be distilled for up to a maximum of 20 samples.

NOTE: A "rack" is one setup of cyanide samples and QC, and can encompass 1 – 3 of the midi-distillation units.

9.3.3.2.For CLP waters: the LCS is 4.0 mL of 1.0 ppm secondary source in 50 mL (TV = 80ug/L).

9.3.3.3.For CLP solids: a solid LCS must be processed per SDG or per batch, which ever is more frequent. If more than one batch is processed on a "rack", process a solid LCS for each one. If a SDG has solid samples distilled on a different "rack", then additional solid LCSs will need to be distilled. The value for the LCS changes as the solid lot numbers change each time a new one is ordered. The value is noted on the product certification.

9.3.3.4. If more than one SDG is distilled on one rack, they may be analyzed together (however, it is **preferred** that each SDG be **analyzed separately**). It is also **preferred** that each SDG have its own method blank(s), its own ICV (LCS), its own LCS-S (if samples are solids), and its own sample duplicate and matrix spike. If the SDG has been split over multiple distillation "racks", then you may not have a sample duplicate and matrix spike for each rack. However, an ICV (LCS) is distilled with each "rack". If more than one SDG is distilled on a "rack", then the ICV (LCS) distilled with that rack must be analyzed with each SDG.

9.3.4. Corrective Action for Laboratory Control Samples

9.3.4.1.If any analyte is outside established control limits the system is out of control and corrective action must occur.

9.3.4.2.Corrective action will be reparation and reanalysis of the batch unless the client agrees that other corrective action is acceptable.

9.4. Matrix Spike/Matrix Spike Duplicate (MS/MSD)

9.3.1. **Non-CLP**

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.

9.4.1.1.A MS/MSD consisting of 50 mL or 1.0 g of sample brought up to 50 mL with reagent water and 2.0 mL of the 1.0 mg/L standard (either source) must be distilled with each analytical batch of samples.

9.4.1.2.The acceptance limits for drinking water samples is 90 – 110%.

9.4.2. CLP:

Each SDG must have a sample duplicate and a matrix spike processed per matrix. Sometimes this requirement is waived by the client or PM but, if uncertain, make sure that these are done. Usually, the sample to be spiked is assigned, but not always. If a MS/MSD is created in receiving, either batch the MSD and "N/A" the result or have the MSD deleted. In either case, create a sample duplicate for the sample that is spiked when batching. If processing a SDG over more than one "rack", then there is no need to process additional matrix spikes and sample duplicates (unless specifically requested). Typically, only one sample duplicate and matrix spike is required per SDG.

9.4.2.1.Matrix spike for CLP consists of 50 mL or 1.0 g of sample and 100 µg/L spike (5.0 mL of 1.0 mg/L secondary standard).

NOTE: see corrective action section 9.4.3.4 for A-spike

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 reparation 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 MSB and NC for the exception code. The A-spike is not needed in this case.

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.

9.4.3.4.A-spike corrective action: if spike recovery fails criteria, then spike the sample at two times the reporting limit or 2 times the sample concentration, which ever is greater. Examples are shown below.

*A-spike = 2 mL of sample + 2mL of A-spike solution

A-spike solution = 0.8 mL .25N NaOH, +3.2 mL 0.05 ppm 1° standard.

9.5 Control Limits

9.5.1 Control limits are established by the laboratory as described in SOP, NC-QA-0018.

9.5.2 Laboratory control limits are internally generated and updated periodically unless method specified. Control limits are listed in the Laboratory Quality Manual (LQM) and the latest is version easily accessible via the LIMs (QC Browser program).

9.6 Method Detection Limits (MDLs) and MDL Checks

9.6.1 MDLs and MDL Checks are established by the laboratory as described in SOP, NC-QA-0021 and S-Q-003.

9.6.2 MDLs are listed in the Laboratory Quality Manual (LQM) and the latest version is easily accessible via the LIMs (QC Browser program).

9.7 Nonconformance and Corrective Action

9.7.1 Any deviations from QC procedures must be documented as a nonconformance, with applicable cause and corrective action approved by the facility QA Manager.

10. CALIBRATION AND STANDARDIZATION

10.1. Non-CLP:

A Low and High standard are distilled from the same source as the calibration curve each day. Prepare the Low standard (0.025mg/L) by diluting 0.125 mL of 10 ppm standard with reagent water to a final volume of 50 mL. Prepare the High standard (0.075 mg/L) by diluting 0.375 mL of 10 ppm standard with reagent water to a final volume of 50 mL. The distilled standards are evaluated against all applicable batch QC.

10.2. CLP:

The Low and High standards do not have to be evaluated for CLP.

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

11.3Summary

11.3.1 Non-CLP

For all non-CLP methods, the sample is distilled/refluxed under acidic conditions for one hour. The released HCN is trapped in 50 mL of 0.25 N NaOH solution.

11.3.2 For CLP and Drinking Water (EPA 335.4) methods, the samples are distilled for one and a half hours. The released HCN is trapped in 0.25 N NaOH solution.

11.4. Sample Preparation Procedure applicable for use with the Midi distillation unit.

11.4.1. Checking for Interferences (For non-CLP samples)

11.4.1.1. Using pH paper strips, check the pH of the sample and record it as >12 or <12 on the analytical logsheet. If pH is <12, the deviation **must be addressed in the project narrative.**

11.4.1.2. For **ALL samples** (non-CLP and CLP samples): Test each sample for the presence of sulfides using lead acetate paper. If sulfides are present, treat the sample with powdered cadmium carbonate. Yellow cadmium sulfide precipitates if the sample contains sulfide. Repeat this operation until a drop of the treated sample solution does not darken the lead acetate test paper. Filter the solution. Avoid a large excess of cadmium carbonate and long contact time in order to minimize loss by complexation or occlusion of cyanide on the precipitated material.

11.4.1.3. **All Samples:** Test each sample for the presence of chlorine using potassium iodide test strips. Document this on the analytical logsheet.

11.4.2. Complex Cyanide Preparation Procedure [THIS PROCESS IS PERFORMED ONLY WHEN REQUESTED BY THE CLIENT]: Add 100 mL of water sample or 2.0 g of solid sample and 100 mL reagent water to a plastic, sealable container. Add 10 g NaOH pellets. Mix or tumble for 12-16 hours. Allow solids to settle out. Transfer 50 mL of the solution to the distillation tube. Distill sample (See section 11.4.4.1).

Note: If the sample requires an MS/MSD or MS/Dup, double or triple the volumes as stated above. A blank and LCS should be prepared and analyzed with samples using 10 g NaOH and 100 mL reagent water.

11.4.3. Amenable Cyanide (Chlorinated Aliquot) [THIS PROCESS IS PERFORMED ONLY WHEN REQUESTED BY THE CLIENT]

11.4.3.1. Place 50 mL (waters) or 1.0 g (solids/liquids) into a beaker. Add 50 mL of reagent water to non-waters. Place the beaker on a stir plate and begin mixing. Test the pH of the solution, if less than 12 add 1.25 N NaOH, drop by drop until $\text{pH} \geq 12$. Drop by drop, add calcium hypochlorite until an excess of chlorine is reached. Test for chlorine excess using KI paper. Allow the sample to chlorinate for one hour. At the end of the chlorination period, add about 0.1 to 0.5 g of ascorbic acid to destroy excess chlorine. Test using KI paper. Keep the addition of ascorbic acid to a minimum. Pour the sample into a distillation flask and follow the total cyanide preparation method (Section 11.4.4). Also set up an unchlorinated aliquot of sample (50 mL or 1.0 g) following the total cyanide method.

11.4.4. Total Cyanide

11.4.4.1. Add 50 mL or 1.0 g of the sample and 2 - 3 boiling chips to the distillation tube. Bring the final volume to 50 mL with reagent water. Add 50 mL of 0.25 N NaOH solution to the absorber tube and assemble the scrubber. Assemble the cyanide distillation apparatus.

NOTE: If solid samples are being prepared under the Michigan program, the initial solid weight is 2.5 g

11.4.4.2. Turn on the cooling water to "60". Turn on the vacuum source and adjust the flow such that even stream of air bubbles are in the scrubber tube approximately $\frac{1}{4}$ " of foam or 1-2 bubbles per second. At this time add any spiking solutions to the LCS or MS/MSDs samples directly into the inlet tube.

11.4.4.3. In the order stated, add 2.0 mL sulfamic acid solution (not for CLP ILM03.0 samples), 2.5 mL of concentrated sulfuric acid and 2.0 mL of magnesium chloride solution to the distillation tube. Be sure to rinse the inlet tube sparingly with reagent water between and after reagent additions.

Note: Complex cyanide samples require an additional 2.5 mL of sulfuric acid. Be sure the pH is < 2.

11.4.4.4. Flip the heater switch to "on" and turn the dial to an appropriate setting (according to manufacturer's instructions) to allow the apparatus to warm up. Be sure to adjust the air flow and water as necessary. Heat for one hour. After the heating period, the heater will turn off automatically. Allow to cool for fifteen minutes. Keep the vacuum and cooling water on.

11.4.4.5. Disconnect the absorber. Pour solution into a 120 mL snap seal container. Do not rinse the scrubber tube or dilute NaOH in the snap seal. Be sure to properly label the bottles "total" or "amenable" along with sample ID, position and date.

11.4.5. Free Cyanide (Weak and Dissociable) [THIS PROCESS IS PERFORMED ONLY WHEN REQUESTED BY THE CLIENT]

11.4.5.1. Add 50 mL or 1.0 g of sample to the distillation tube. Bring all volumes up to 50 mL with reagent water. Add 50 mL of 0.25 N NaOH to the absorber tube and assemble.

11.4.5.2. Turn on cooling water to "60". Turn on the vacuum source. Add any spiking standards to the appropriate LCS or MS/MSDs at this time. Through the inlet tube, add 1.0 mL of sodium acetate buffer, 1.0 mL of zinc acetate, and 0.25 mL of methyl red indicator. Rinse the inlet tube sparingly with reagent water between and after reagent additions. If the sample is not red, carefully add 1:9 acetic acid dropwise until the sample

does turn red. Check the sample color periodically throughout the distillation hour to ensure the sample stays red.

Reminder: Do not use the complex purchased cyanide solution standard as the LCS for Free cyanide analysis.

11.4.5.3. Flip on the heater switch and turn the dial to “10.5” (This allows the apparatus to warm up). Adjust the air flow and water as needed. Heat for 1 hour. After the heating period, the heater will shut off automatically. Allow the sample to cool for fifteen minutes with the air and water on.

11.4.5.4. Pour the scrubber contents into a 120 mL snap seal bottle. Do not rinse the scrubber. Label the bottle well and be sure to denote that it is a “free” sample distillate.

11.4.6. CLP Cyanide distillation

11.4.6.1. Add 50 mL or 1.0 g of sample to the distillation tube. Bring all volumes up to 50 mL with reagent water. Add 50 mL of 0.25 N NaOH to the absorber tube and assemble.

11.4.6.2. Turn on cooling water to “60”. Turn on the vacuum source and adjust the flow such that even stream of air bubbles are in the scrubber tube approximately $\frac{1}{4}$ “ of foam or 1 –2 bubbles per second. At this time add any spiking solutions to the LCS or MS samples directly into the inlet tube.

11.4.6.3. In the order stated, add 2.5 mL of concentrated sulfuric acid and 2.0 mL of magnesium chloride solution to the distillation tube. Be sure to rinse the inlet tube sparingly with reagent water between and after reagent additions.

11.4.6.4. Flip the heater switch to “on” and turn the dial to an appropriate setting to allow the apparatus to warm up. Be sure to adjust the air flow and water as necessary. Heat for one and a half hours. After the heating period, allow to cool for fifteen minutes. Keep the vacuum and cooling water on.

11.4.6.5. Disconnect the absorber. Pour solution into a snap seal container. Do not rinse the scrubber tube or dilute NaOH in the snap seal. Be sure the properly label the snap seals with the sample ID.

11.4.7 Cyanide Unit Clean-up

- 11.4.7.1 Cyanide distillation unit glassware is very fragile and expensive. It must be handled with care at all times.
- 11.4.7.2 Disassemble each set-up and rinse the sample down the drain with large amounts of water. Be sure to collect the solids in a screen and dispose of properly.
- 11.4.7.3 Wash each set-up with soap and hot water. Rinse several times with reagent water. **After preparing samples found to be extremely high in cyanide, a subsequent rinse with 1.0N NaOH, followed by further rinsing with reagent water can help rinse away any residual cyanide. If contamination is suspected, distill 1.0N NaOH through the system.
- 11.4.7.4 Re-assemble the set-up.
- 11.4.7.5 Be sure to wash each set up as a separate unit and replace in the same position.
- 11.4.7.6 If a sample of known high cyanide concentration was distilled in a certain position, be sure to change the appropriate tubing on that position.

11.5 Analytical Documentation

- 11.5.1 Record all analytical information in the analytical logbook/logsheets, including the analytical data from standards, blanks, LCSs, MS/MSDs, 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.

13.2.2. Method validation information (where applicable) in the form of laboratory demonstrations of capabilities is maintained for this method in the laboratory QA files

14. POLLUTION PREVENTION

14.1. Using a Midi Cyanide distillation unit saves time and requires less sample and reagents for use.

15. WASTE MANAGEMENT

15.1 All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

15.2 Waste Streams Produced by the Method

15.2.1 The following waste streams are produced when this method is carried out.

15.2.1.1 Acidic waste. This waste is disposed of in the designated container labeled "Acid Waste".

15.2.1.2 Caustic waste containing Pyridine. This waste is disposed of in a designated container identified as "Pyridine Waste".

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, Third Edition, Total and Amenable Cyanide, Automated UV; Method 9012A.
- 16.1.2. EPA 600; Cyanide, Total and Cyanide, Amenable to Chlorination; Methods 335.1, 335.4, and 335.2
- 16.1.3. Standard Methods for the Examination of Water and Wastewater, Eighteenth Edition; Weak and Dissociable Cyanide; Method 4500-CN-I
- 16.1.4. Standard Methods for the Examination of Water and Wastewater, Eighteenth Edition; Complex Cyanide; Method 4500-CN-E
- 16.1.5. USEPA CLP SOW ILM03.0 Section D-Cyanide Midi Distillation
- 16.1.6. Corporate Quality Management Plan (QMP), current version
- 16.1.7. STL Laboratory Quality Manual (LQM), current version
- 16.1.8 STL Corporate Safety Manual, M-E-0001 and STL North Canton Facility Addendum and Contingency Plan, current version.
- 16.2. Associated SOPs and Policies, latest version
 - 16.2.1. QA Policy, QA-003
 - 16.2.2 Glassware Washing, NC-QA-0014
 - 16.2.3 Statistical Evaluation of Data and Development of Control Charts, NC-QA-0018
 - 16.2.4 Method Detection Limits and Instrument Detection Limits, NC-QA-0021 and S-Q-003
 - 16.2.5 Navy/Army SOP, NC-QA-0016
 - 16.2.6 Cyanide, Automated Method NC-WC-0031
- 17. MISCELLANEOUS (TABLES, APPENDICES, ETC...)**
 - 17.1. BASF RFI Requirements

17.1.1. Amendments to this SOP to satisfy BASF RCRA Facility Investigation (RFI) requirements are based on comments from US EPA upon review of site requirements and laboratory procedures.

17.1.2. Amendment to the preparation of **all** samples

17.1.2.1. **Section 7.2.1:** Change 2.51 g of potassium cyanide to 2.11g potassium ferricyanide.

17.1.2.2. **Section 9.4:** The matrix spike/duplicate frequency has been increased from one per batch to one per 7 samples. Consult with the project manger for specific samples to be spiked. The goal is to spike each sampling area at the site at least once.

17.1.3. Amendment to the preparation of **Prussian blue area** samples

17.1.3.1. **Section 7.1.22:** Sodium thiocyanate (reagent grade): Prepare a spiking solution at a concentration 100X greater than the measured cyanide for the appropriate Prussian blue area samples.

17.1.3.2. **Section 9.5:** Three Prussian blue area samples will be spiked with 1 mL of the sodium thiocyanate solution (Section 17.1.3.1) in order to assess the potential impact of thiocyanate in the original samples on the measured cyanide concentration. These matrix spikes do not replace the cyanide matrix spikes mentioned above (Section 17.1.2.2). The increase (if any) in measured cyanide concentration relative to the original sample shall be reported as “percentage increase” using the following equation:

$$\%CN_{increase} = \frac{Conc_{SCN\_spike} - Conc_{unspiked}}{Conc_{unspiked}} \times 100$$

where

$\frac{Conc_{SCN\_spike}}{\text{[redacted]}}$ = cyanide concentration measured in the thiocyanate
spiked sample

$\frac{Conc_{unspiked}}{\text{[redacted]}}$ = cyanide concentration measured in the unspiked sample

Note: Section 11.3.2.1 of NC-WC-0031 addresses sulfide testing and precipitation.

17.2. Method Deviation (9012A, 335.1, 335.2)

17.2.1. The reflux distillation apparatus used is the midi distillation.

17.2.2. The volume of sample used is reduced to 50 mL vs. 500 mL using the midi-distillation apparatus.

17.2.3. Method of Standard Addition is not performed for samples with matrix interference (sulfides)

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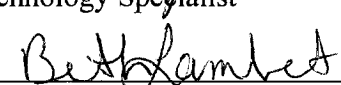
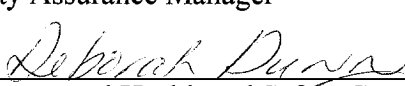
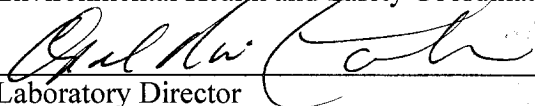
Implementation Date 10/6/03

SOP No. NC-WC-0034
Revision No. 1
Revision Date: 09/25/03
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STL NORTH CANTON STANDARD OPERATING PROCEDURE

TITLE: FLASHPOINT CLOSED CUP

(SUPERSEDES: REVISION 0, REVISION DATE 10/24/97)

Prepared by:	<u></u>	<u>9/30/03</u>
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1. SCOPE AND APPLICATION

- 1.1. This method is applicable to the determination of Flashpoint by Pensky-Martens closed cup tester in a variety of wastes and liquids. It is based on ASTM D93-90 and SW846 Method 1010. Although the approximate working range is 20 - 200 °F, the test is generally considered complete when the temperature reaches 180°F without a measurable Flashpoint.
- 1.2. The associated LIMS method codes are AE (Method 1010) and GG (Method D93-90-Waste Matrix only).
- 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 sample is heated at a slow constant rate with continual stirring if it is a liquid or water. A small test flame is directed into the sample cup at regular intervals. The Flashpoint is the lowest temperature at which the test flame causes the vapor above the sample to ignite.

3. DEFINITIONS

- 3.1. Refer to the glossary in the STL North Canton Laboratory Quality Manual (LQM), latest version.

4. INTERFERENCES

- 4.1. Not Applicable

5. SAFETY

- 5.1. Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual, the facility addendum to the CSM, and this document.
- 5.2. Eye protection that protects against splash, 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 following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the**

method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table. A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Methylene Chloride	Carcinogen Irritant	25 ppm-TWA 125 ppm-STEL	Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting and headache. Causes irritation, redness and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degrades the skin. May be absorbed through skin.
Xylene	Flammable Irritant	100 ppm-TWA	Inhalation of vapors may be irritating to the nose and throat. Inhalation of high concentrations may result in nausea, vomiting, headache, ringing in the ears, and severe breathing difficulties, which may be delayed in onset. High vapor concentrations are anesthetic and central nervous system depressants. Skin contact results in loss of natural oils and often results in a characteristic dermatitis. May be absorbed through the skin. Vapors cause eye irritation. Splashes cause severe irritation, possible corneal burns and eye damage.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

- 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. It is recommended that neat standards be purchased only as a last resort. The preparation of standards from neat materials and reagents should be conducted in a fume hood with the sash closed as far as the operations will permit.
- 5.7. Standards in solution may be diluted in the open laboratory when syringes and the like are utilized.

- 5.8. All work must be stopped in the event of a known or potential compromise to the health and safety of a STL North Canton associate. The situation must be reported **immediately** to a laboratory supervisor.
- 5.9. In the event a sample ignites in the test apparatus do not attempt to remove the sample. Turn off the apparatus and flame. The flame should go out when the cup is closed. If this does not happen the flame may be extinguished by covering the sample with a non-flammable material. After the apparatus has cooled the sample may be removed.

6. EQUIPMENT AND SUPPLIES

- 6.1. Pensky-Martens closed cup tester with stirrer and stirring motor
- 6.2. Flash point sample cup
- 6.3. Thermometer: 20 - 200°F range (made for the Pensky-Martens) or Thermocouple
- 6.4. Barometer

7. REAGENTS AND STANDARDS

- 7.1. Reagents
 - 7.1.1. p-Xylene

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

- 8.1. Samples are not chemically preserved.
- 8.2. Samples are stored in glass containers at 4°C ± 2°C. Samples are not to be stored in plastic containers since volatile materials may diffuse through the walls of the enclosure.

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 and Method Blank) 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. 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.

9.2.2. Sample duplicates are performed at a minimum frequency of 10% per matrix (or one per analytical batch) and must meet laboratory-specific limits for precision. Soil and Waste matrices may be combined for batching purposes.

9.3. Control Limits

9.3.1. Control limits are established by the laboratory as described in SOP, NC-QA-0018.

9.3.2. Laboratory control limits are internally generated and updated periodically unless method specified. Control limits are listed in the Laboratory Quality Manual (LQM) and the latest version is easily accessible via the LIMs (QC Browser program).

9.4. Nonconformance and Corrective Action

9.4.1. Any deviations from QC procedures must be documented as a nonconformance, with applicable cause and corrective action approved by the facility QA Manager.

10. CALIBRATION AND STANDARDIZATION

10.1. Calibration of tester

10.1.1. Determine the flash point of p-xylene following the procedures outlined in 11.4

10.1.2. The tester is operating properly when a value of $81 \pm 2^{\circ}\text{F}$ is obtained.

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 Procedure

- 11.3.1. Not Applicable

11.4. Sample Analysis Procedure

- 11.4.1. Operate the Pensky-Martens tester according to the manufacturer's specifications, in a well-ventilated area away from flammable materials and significant air movement. Performing this analysis under a hood is the best approach - ensure that the air intake and hood lights are turned off. Fill the sample cup to the designated line with sample and assemble the tester as directed.

- 11.4.2. A flash check must be analyzed with each analytical batch of samples. The compound p-Xylene is used to provide the analyst a reference true flash. The flash temperature is recorded on the analytical logsheet. The true flash temperature for p-Xylene is 81°F.

- 11.4.3. Pour the sample into the cup and record the initial temperature. Record the temperature at which the flash occurred on the analytical logsheet. If the temperature reaches 180°F and no flash occurs, select appropriate method.(See manual) turn off flashpoint, record > 180°F as the Flashpoint on the analytical logsheet.

- 11.4.4. Record the barometric pressure.

- 11.4.5. If solvents are used to clean sample cups, be sure to clean thoroughly with reagent water to prevent contamination.

NOTE:Some samples may burn, but not flash. Record the initial temperature at which it burns and reanalyze for confirmation. Note this as a footnote when reporting.

Some samples have a Flashpoint below room temperature. If this is known, the sample should be chilled to just above freezing and then analyzed promptly to confirm a true Flashpoint.

11.5. Analytical Documentation

- 11.5.1. Record all analytical information in the analytical logsheet, which may be in electronic format, 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 an 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. If the sample did not flash, report > 180°F
- 12.2. Use the following equation to calculate the flashpoint:

$$\text{Flash} = F = [0.6 (76 - \text{BP})]$$

Where: F = Observed Flash

B = Barometric Pressure

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.
 - 13.2.2. Method validation information (where applicable) in the form of laboratory demonstrations of capabilities is maintained for this method in the laboratory QA files.

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. Solvent waste must be disposed of in clearly labeled waste cans.
- 15.2. Solid materials (gloves, soiled paper products, etc.) 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 STL North Canton. They must have training on the hazardous waste disposal practices upon initial assignment to these tasks, followed by an annual refresher training.
- 15.5. All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."
- 15.6. Waste Streams Produced by the method
- 15.6.1. The following waste streams are produced when this method is carried out.
- 15.6.1.1. **Solid samples.** Solids are put into the red can for the debris waste stream
- 15.6.1.2. **Liquid samples and waste solvents** Flammable wastes including the xylene standard are disposed of in the solvent waste stream located in the red can in the hood. Adding water to the solvent waste stream should be avoided.

16. REFERENCES

- 16.1. References
- 16.1.1. Annual Book of ASTM Standards, ASTM Method D93-90, Flashpoint by Pensky-Martens Closed Tester.

16.1.2. SW846, Test Methods for Evaluating Solid Waste, Third Edition, Pensky-Martens Closed Cup Method for Determining Ignitability, Method 1010

16.1.3. Corporate Quality Management Plan (QMP), current version.

16.1.4. STL Laboratory Quality Manual (LQM), current version.

16.2. Associated SOPs and Policies, latest version

16.2.1. QA Policy, QA-003

16.2.2. Glassware Washing, NC-QA-0014

16.2.3. Statistical Evaluation of Data and Development of Control Charts, NC-QA-0018

16.2.4. Navy/Army SOP, NC-QA-0016

17. MISCELLANEOUS (TABLES, APPENDICES, ETC...)

17.1. Troubleshooting guide

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Implementation Date: 11-23-04

SOP No. NC-WC-0036

Revision No. 3.1

Revision Date: 11/06/04

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STL NORTH CANTON STANDARD OPERATING PROCEDURE

TITLE: TOTAL HARDNESS (MG/L CaCO_3), TITRIMETRIC

(SUPERSEDES: REVISION 3.0, DATED 04/19/99)

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1. SCOPE AND APPLICATION

- 1.1. This method is applicable to the determination of Hardness in waters and wastewaters. It is based on EPA Method 130.2. The approximate working range is 2 to 400 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. The applicable LIMs method code is AD. The preparation code for aqueous samples is 88.

2. SUMMARY OF METHOD

- 2.1. Calcium and magnesium ions in the sample are sequestered upon the addition of magnesium ethylenediamine tetraacetate (MgEDTA). The end point of the reaction is detected using Eriochrome Black T indicator, which has a red color in the presence of calcium and magnesium and a blue color when the cations are sequestered.

3. DEFINITIONS

- 3.1. Refer to the glossary in the STL North Canton Quality Manual (LQM), current version.

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. Specific selection of reagents may be required to avoid introduction of contaminants.

5. SAFETY

- 5.1. Employees must abide by the policies and procedures in the Corporate Safety Manual and this document.
- 5.2. The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Ammonium Hydroxide	Corrosive Poison	50 ppm-TWA	Vapors and mists cause irritation to the respiratory tract. Causes irritation and burns to the skin and eyes.
Hydrochloric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

- 5.3. Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Cut resistant gloves must be worn doing any other task that presents a strong possibility of getting cut. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.
- 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 where possible. All samples with a pink stickers that read "Caution/Use Hood!" **must** be opened in the

hood. Contact the EH&S co-ordinator if this is not possible. 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. It is recommended that neat standards be purchased only as a last resort. The preparation of standards from neat materials and reagents should be conducted in a fume hood with the sash closed as far as the operations will permit.
- 5.7. Standards in solution may be diluted in the open laboratory when syringes and the like are utilized.
- 5.8. All work must be stopped in the event of a known or potential compromise to the health and safety of a STL North Canton associate. The situation must be reported **immediately** to the EH&S Coordinator and to a laboratory supervisor.

6. EQUIPMENT AND SUPPLIES

- 6.1. Stir plate and stir bars
- 6.2. Erlenmeyer flasks: various
- 6.3. Graduated cylinders: various
- 6.4. Autopipettor and disposable tips
- 6.5. Class A Microburet: 10 mL
- 6.6. Volumetric flasks: various
- 6.7. Plastic bottles: various
- 6.8. Analytical balance: Capable of accurately weighing ± 0.0001 g

7. REAGENTS AND STANDARDS

- 7.1. Reagents
 - 7.1.1. Ammonium Chloride (NH₄Cl): reagent grade

- 7.1.2. Ammonium Hydroxide (NH₄OH): reagent grade
- 7.1.3. Magnesium EDTA: reagent grade
- 7.1.4. EDTA Buffer Solution: Dissolve 16.9 g of NH₄Cl in 143 mL of NH₄OH. Add 1.25 g of magnesium salt of EDTA and dilute to 250 mL with reagent water. Mix well and store in a plastic bottle. This solution is stable for one month. Alternatively, use purchased hardness buffer.
- 7.1.5. Buffer for Water Hardness: Ammonium Chloride-Hydroxide Buffer with Magnesium EDTA.
- 7.1.6. Eriochrome Black T Indicator: reagent grade
- 7.1.7. Sodium Chloride (NaCl): reagent grade
- 7.1.8. Indicator: Mix together 0.5 g of Eriochrome Black T and 100 g of NaCl. Alternatively, use purchased indicator (such as Calamagite).
- 7.1.9. 1 N Ammonium Hydroxide: Dilute 7 mL of NH₄OH to 100 mL with reagent water and mix well.
- 7.1.10. Disodium EDTA Dihydrate: Primary standard grade
- 7.1.11. 0.02 N EDTA Titrant: Purchased. Alternatively, prepare titrant by dissolving 3.723 g of disodium EDTA dihydrate in about 400 mL of reagent water in a 1000 mL volumetric flask. Dilute to 1 liter with reagent water and mix well. This solution is stable for six months. Calibrate weekly against standard calcium solution by titration. Store in polyethylene bottle.
- 7.1.11.1. Standardization Titration Procedure: Place 5.0 mL of 1000 ppm standard calcium solution in a vessel containing about 50 mL of reagent water. Add 1 mL of buffer solution. Add about 0.5 - 1 g of dry indicator. Titrate slowly with continuous stirring until the last reddish tinge disappears, adding the last few drops at 3 - 5 second intervals. At the end point, the color is blue. Repeat the standardization procedure two more times and average the values.

$$\text{N of EDTA} = \frac{0.1}{\text{mL of EDTA}}$$

7.2. Standards

7.2.1. Calcium Carbonate Standard Solution, 1000 mg/L: Purchased standard (Hach or other supplier). Alternately, a standard may be made: Place 1.0 g of anhydrous calcium carbonate (primary standard grade) in a 500 mL Erlenmeyer flask. Slowly add 6 N HCl until all the CaCO₃ has dissolved. Add 200 mL of reagent water and boil for five minutes. Cool the solution and add several drops of methyl red indicator. Adjust the solution to an intermediate orange color with 3 N NH₄ OH or 6 N HCl as required. Quantitatively transfer the solution to a 1 liter volumetric flask and dilute to volume with reagent water. This solution is stable for six months.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Samples are preserved to a pH < 2 with concentrated nitric acid.

8.2. Samples are stored in plastic or glass containers at 4°C ± 2°C.

8.3. The holding time is six months from sampling to the completion of 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, Method Blank, MS, MSD) 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. Method Blank

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 reagent water blank consisting of 50 mL of reagent water and all other reagents added to samples must be analyzed with each analytical batch of samples.

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 holding time considerations, the corresponding sample data **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 addressed in the project narrative.**

9.3. Laboratory Control Sample (LCS)

9.3.1. One aqueous LCS from an independent source must be processed with each preparation batch. The LCS must be carried through the entire analytical procedure. 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.

9.3.2. A midrange LCS must be analyzed with each analytical batch of samples. The LCS is made of 45 mL reagent water and 5.0 mL 1000 ppm CaCO₃ standard. Alternatively, use 25mL water and 25mL purchased hardness standard.

9.3.3. Corrective Active 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.

9.3.3.2.The only exception is that if the LCS recoveries are biased high and the associated sample is ND for the parameter(s) of interest, the batch is acceptable. **This must be addressed in the project narrative.**

9.3.3.3.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 must be analyzed per analytical batch. The MS/MSD is composed of 25 mL reagent water, 25 mL sample, and 0.5 mL 10,000 ppm CaCO₃. Alternatively, use 20mL sample, 25mL reagent water, and 5mL 1000ppm CaCO₃.
- 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 reparation 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 "amount" MSB. The Exception Code is changed to NC. The following two footnotes will appear on the report page "NC The recovery and/or RPD were not calculated." "MSB The recovery and RPD were not calculated because the sample amount was greater than four times the spike amount."
- 9.4.3.3.In 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 laboratory matrix spike RPD limits.
- 9.4.3.4.If client program requirements specify to confirm matrix interference's, reparation and reanalysis of the MS/MSD may be necessary.

9.5. Sample Duplicates

- 9.5.1. 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.
- 9.5.2. If samples are analyzed for NPDES work or drinking waters, a duplicate sample is prepared and analyzed per batch of 10 samples processed.
- 9.5.3. Sample duplicates are performed at a frequency of 10% and must meet laboratory-specific limits for precision.

9.6. Control Limits

- 9.6.1. Control limits are established by the laboratory as described in NC-QA-0018.
- 9.6.2. Laboratory control limits are internally generated and updated periodically unless method specified. Control limits are listed in the Laboratory Quality Manual (LQM) and the latest is version easily accessible via the LIMs (QC Browser program).

9.7. Method Detection Limits (MDLs) and MDL Checks

- 9.7.1. MDLs and MDL Checks are established by the laboratory as described in SOP, NC-QA-0021 and S-Q-003.
- 9.7.2. MDLs are listed in the Laboratory Quality Manual (LQM) and the latest version is easily accessible via the LIMs (QC Browser program).

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.

10. CALIBRATION AND STANDARDIZATION

- 10.1. Not applicable

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 documents as a nonconformance, with a cause and corrective action described.
- 11.3. Sample Preparation - Not Applicable
- 11.4. Sample Analysis Procedure
 - 11.4.1. All reagents and samples must be at ambient temperature prior to analysis.
 - 11.4.2. Rinse the burette with reagent water once and with EDTA titrant once. Fill with EDTA titrant and be sure all air bubbles are removed.
 - 11.4.3. Place 25 mL of sample and 25 mL of reagent water in an Erlenmeyer flask. Add approximately 1 to 2 mL of 1N NH₄OH, approximately 1 to 2 mL of EDTA buffer, (or add 3-4mL of the purchased buffer) and approximately 0.5 to 1 g of Indicator. Titration should be completed within 5 minutes of the addition of the buffer.
 - 11.4.4. While stirring, slowly titrate with EDTA titrant until the last reddish tint disappears. The end point is blue. Record the volume of titrant used and its true normality on the analytical logsheet.
- NOTE:** Samples requiring more than 10 mL of titrant must be diluted. An aliquot is diluted to a final volume of 50 mL with reagent water.
- 11.5. Analytical Documentation
 - 11.5.1. Record all analytical information in the analytical logbook/logsheet which may be in an electronic format, including the analytical data from standards, blanks, LCSs, MS/MSDs, 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 an 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

$$12.1.1. \quad \text{Hardness, mg/L CaCO}_3 = \frac{(A - B) \times N \times 50,000}{C} \times D$$

Where:

A = Volume of EDTA titrant used for sample, mL

B = Volume of EDTA titrant used for blank, mL

C = Volume of sample used, mL (not total volume after addition of DI water)

D = Dilution Factor = $\frac{\text{Final Dilution Volume, mL}}{\text{Initial Sample Volume Used For Dilution, mL}}$

N = Normality of EDTA titrant

50,000 = 50 (Equivalent weight of Calcium) x 1000 mg/g

12.1.2. LCS Recovery:

$$\text{LCS \% Recovery} = \frac{\text{mL titrant} \times N \times 50,000}{(25)(200)} \times 100$$

Where:

N = Normality of EDTA titrant

12.1.3. MS/MSD Calculation:

$$\text{MS / MSD \% Recovery} = \frac{(A - B)}{200} \times 100$$

Where:

A = MS/MSD concentration (from 12.1.1)

B = Sample concentration (from 12.1.1)

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.

13.2.2. Method validation information (where applicable) in the form of laboratory demonstrations of capabilities is maintained for this method in the laboratory QA files.

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. All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

15.2. Waste Streams Produced by the Method

15.2.1. The following waste streams are produced when this method is carried out.

15.2.1.1. **Aqueous waste generated by the analysis.** Aqueous waste can be poured down the drain if the pH is between 4 and 10. Any sample waste generated that is not in this pH range must be collected and disposed of in the acid waste drum labeled as "Acid Waste" located in the metals lab.

- 15.3. Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices of STL North Canton. 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. EPA 600, Methods for Chemical Analysis of Water and Wastes, Hardness, Total (Mg/L as CaCO₃, Titrimetric, EDTA), Method 130.2
- 16.1.2. Corporate Quality Management Plan (QMP), current version.
- 16.1.3. STL Laboratory Quality Manual (LQM), current version.
- 16.1.4. STL Corporate Safety Manual, M-E-0001 and STL North Canton Facility Addendum and Contingency Plan, current version.

16.2. Associated SOPs

- 16.2.1. Statistical Evaluation of Data and Development of Control Charts, NC-QA-0018.
- 16.2.2. QA Policy, QA-003
- 16.2.3. Glassware Washing, NC-QA-0014
- 16.2.4. Method Detection Limits and Instrument Detection Limits, NC-QA-0021 and S-Q-003.
- 16.2.5. Navy/Army SOP, NC-QA-0016

17. MISCELLANEOUS (TABLES, APPENDICES, ETC...)

17.1. Reporting Limits

- 17.1.1. The lower reporting limit (RL) for undiluted samples is 5 mg/L CaCO₃.
- 17.1.2. If samples require dilution or smaller volumes than specified in this method, the RL will be elevated.

17.2. Deviation from EPA Method 130.2

17.2.1. Wastewater samples are not digested.

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Implementation Date 9/8/04

SOP No. NC-WC-0060
Revision No. 4
Revision Date: 09/02/04
Page 1 of 22

STL NORTH CANTON STANDARD OPERATING PROCEDURE

TITLE: SULFIDE

(SUPERSEDES: REVISION 3; DATED 06/17/03)

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1. SCOPE AND APPLICATION

- 1.1. This method is applicable to the determination of the concentration of Sulfide in waters, liquids, solids, and sludges. It is based on SW846 Method 9030B, Methods for Chemical Analysis of Water and Wastes (MCAWW) 376.1, and SM 4500-S2-D. The working range is 1 to 30 mg/L for waters and 10-650 mg/kg for solids and sludges.
- 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 by the laboratory QA department.
- 1.3. The associated QuantIMS method codes are TV (9030B), OG (4500-S2-D), and CT (376.1).

2. SUMMARY OF METHOD

- 2.1. For acid soluble sulfide samples, separation of sulfide from the sample matrix is accomplished by the addition of sulfuric acid to the sample. The sample is heated to 70⁰C and the hydrogen sulfide (H₂S) which is formed, is distilled under acidic conditions and carried by a nitrogen stream into zinc acetate scrubbing bottles where it is precipitated as zinc sulfide.
- 2.2. For acid-insoluble sulfide samples, separation of sulfide from the sample matrix is accomplished by suspending the sample in concentrated hydrochloric acid by vigorous agitation. Tin (II) chloride is present to prevent oxidation of sulfide to sulfur by the metal ion (as in copper (II)), by the matrix, or by dissolved oxygen in the reagents. The prepared sample is distilled under acidic conditions at 100⁰C under a stream of nitrogen. Hydrogen sulfide gas is released from the sample and collected in gas scrubbing bottles containing zinc(II) and a strong acetate buffer. Zinc sulfide precipitates.
- 2.3. An excess of iodine is added to a sample which oxidizes the Sulfide to sulfur under acidic conditions. The excess iodine is back titrated with sodium thiosulfate.

3. DEFINITIONS

- 3.1. Refer to the glossary in the STL North Canton Laboratory Quality Manual (LQM), latest version.

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. Specific selection of reagents may be required to avoid introduction of contaminants.

- 4.2. Reducing substances such as thiosulfite, sulfites, and various organic compounds cause interferences, but treatment with zinc acetate solution will eliminate some of these interferences. (Use approximately 15 drops of 2 N zinc acetate per 500 mL of sample if not already preserved with it.)
- 4.3. Samples that contain strong oxidizers or reducers will interfere with this method.

5. SAFETY

- 5.1. Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual and this document.
- 5.2. Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Cut resistant gloves must be worn doing any other task that presents a strong possibility of getting cut. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.
- 5.3. Sodium Sulfide will form Hydrogen Sulfide (HS) gas if combined with water moisture or strong acids. Inhalation of HS gas may be fatal.
- 5.4. The following is a list of the materials used in this method, which have a serious or significant hazard rating. NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table. A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

5.5.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Hydrochloric Acid	Corrosive Poison	5 ppm- Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Formaldehyde	Poison	260 Mg/M3 TWA	Inhalation of vapors may cause respiratory irritation leading to frequent bronchial infection. Eye contact causes redness, watering, and itching. Skin contact causes itching, scaling, and reddening or blistering.
Iodine	Poison Corrosive Oxidizer	0.1 ppm- Ceiling	Vapors severely irritate and can burn the mucous membranes and respiratory tract. Liquid contact may cause blistering burns, irritation, and pain. Vapors may be severely irritating to the skin. Vapors are severely irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Potassium Dichromate	Oxidizer Corrosive Carcinogen	0.1 Mg/M3 TWA as CrO3	Extremely destructive to tissues of the mucous membranes and upper respiratory tract. May cause ulceration and perforation of the nasal septum. Symptoms of redness, pain, and severe burn can occur. Dusts and strong solutions may cause severe irritation. Contact can cause blurred vision, redness, pain and severe tissue burns. May cause corneal injury or blindness.

Sodium Hydroxide	Corrosive	2 Mg/M3-Ceiling	Severe irritant. Effects from inhalation of dust or mist vary from mild irritation to serious damage of the upper respiratory tract, depending on severity of exposure. Symptoms may include sneezing, sore throat or runny nose. Contact with skin can cause irritation or severe burns and scarring with greater exposures. Causes irritation of eyes, and with greater exposures it can cause burns that may result in permanent impairment of vision, even blindness.
Sulfuric Acid	Corrosive Oxidizer Dehydrator Poison Carcinogen	1 Mg/M3-TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose, throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.
Sodium Sulfide	Corrosive	10 ppm-TWA 15 ppm-STEL	Will form Hydrogen Sulfide (HS) gas if combined with strong acids. Inhalation of HS gas may be fatal. Symptoms include painful conjunctivitis, headache, nausea, dizziness, coughing and, in extreme cases, pulmonary edema and possible death. Irritant. Contact with skin can produce serious caustic burns with painful inflammation and possible destruction of tissue. Inflammation, tearing and pain may be expected. Severe contact can cause destruction of tissue.
1 – Always add acid to water to prevent violent reactions.			
2- Exposure limit refers to the OSHA regulatory exposure limit.			

- 5.6. 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.
- 5.7. The preparation of standards and reagents will be conducted in a fume hood with the sash closed as far as the operation will permit.
- 5.8. It is recommended that neat standards be purchased only as a last resort. The preparation of standards from neat materials and reagents should be conducted in a fume hood with the sash closed as far as the operations will permit.
- 5.9. Standards in solution may be diluted in the open laboratory when syringes and the like are utilized.
- 5.10. All work must be stopped in the event of a known or potential compromise to the health and safety of a STL North Canton associate. The situation must be reported **immediately** to a laboratory supervisor.

6. EQUIPMENT AND SUPPLIES

- 6.1. Volumetric pipettes: various
- 6.2. Buret: 25 mL Class A
- 6.3. Erlenmeyer flasks: 500 mL
- 6.4. Graduated cylinder: 250 mL
- 6.5. Top loading balance: capable of accurately weighing ± 0.01 g
- 6.6. Volumetric flasks: various
- 6.7. Vacuum pump, filter and flask
- 6.8. Whatman 934-AH filters
- 6.9. Distillation apparatus containing: 250 mL addition funnel, 500 mL – 3-neck reaction flask, sparging tube and 1 – 500 mL Erlenmeyer Flask.
- 6.10. Stirring / Hot Plates

6.11. Crystallizing dishes

7. REAGENTS AND STANDARDS

7.1. Reagents

- 7.1.1. (1:1) Hydrochloric Acid: Add 250 mL concentrated hydrochloric acid (HCl) to 250 mL of reagent water.
- 7.1.2. Starch Indicator: Add 10 mL of reagent water to 5 g starch (potato) and mix. Add starch mixture to 500 mL of boiling reagent water. Mix, cool, and store in a well-labeled squirt bottle. Alternately, use purchased starch solution.
- 7.1.3. 0.025 N Sodium Thiosulfate (stored in dessicator): Add 0.4 g NaOH and 6.205 g of sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$) to 500 mL of reagent water in a 1 liter volumetric. Dilute to volume with reagent water. Store in a dark container. Also available commercially.
- 7.1.3.1. Standardization of 0.025 N Sodium Thiosulfate Solution: *To make 0.025N Biodate Solution, dissolve 0.462 g $\text{KH}(\text{IO}_3)_2$ in 500 mL with reagent water. Weigh 2 g KI in a 500 mL Erlenmeyer flask. Add 100 to 150 mL reagent water, 5 drops H_2SO_4 and 20 mL biodate solution using a volumetric pipet. Dilute to 200 mL with reagent water. Titrate with Sodium Thiosulfate. When a pale straw yellow color is reached, add 1-2 mL starch. Continue titrating from a blue to a clear end point.

*Note: Biodate Solution may be purchased.

Calculation

$$\text{Na}_2\text{S}_2\text{O}_3 \text{ Normality} = \frac{(a)(b)}{c}$$

a = mLs Biodate (20 mL)

b = Normality Biodate (0.025N)

c = mLs of $\text{Na}_2\text{S}_2\text{O}_3$ used to titrate Repeat two more times

- 7.1.4. 0.0282 N Iodine Solution: Add 20 g KI (potassium iodide) and 3.2 g iodine to a 1 liter volumetric flask. Add 500 - 700 mL of reagent water and dissolve. Dilute to

volume with reagent water. Store in a dark container. Also available commercially.

- 7.1.4.1. Standardization 0.025 N Iodine Solution: Perform three method blanks daily. Refer to method blank section in SOP.

Calculation

$$\text{Normality Iodine} = \frac{(\text{Normality Na}_2\text{S}_2\text{O}_3)(\text{mL of titrant Na}_2\text{S}_2\text{O}_3)}{20 \text{ mL Iodine}}$$

- 7.1.5. 2N Zinc Acetate: Dissolve 220 g of zinc acetate in 870 mL of reagent water and dilute to 1 liter with reagent water.
- 7.1.6. Formaldehyde (37% solution), CH₂O. This solution is commercially available.
- 7.1.7. Zinc Acetate for the Erlenmeyer flasks:
- 7.1.7.1. For acid-soluble Zinc: Zinc acetate solution (approximately 0.5M). Dissolve 110g Zinc acetate, dihydrate NaC₂H₃O₂, in 800 mL of reagent water. Add 1 mL concentrated hydrochloric acid and dilute to 1 liter.
- 7.1.7.2. For acid-insoluble sulfides: Zinc acetate/sodium acetate buffer. Dissolve 100 g sodium acetate, NaC₂H₃O₂, and 11 g zinc acetate dihydrate in 800 mL of reagent water. Add 1 mL concentrated hydrochloric acid and dilute to 1 liter. The resulting pH should be 6.8
- 7.1.8. Sulfuric acid – 50%. Place 450 mL of reagent water in a volumetric flask. **Slowly** add 500 mL concentrated Sulfuric Acid (H₂SO₄). **Use extreme caution – this is an exothermic reaction and will create excess heat.** This solution is commercially available.
- 7.1.9. Hydrochloric Acid, 9.8N, for **acid-insoluble sulfides**: Place 200 mL of reagent water in a 1-liter beaker. Slowly add concentrated HCl to bring the total volume to 1 liter.
- 7.1.10. Tin (II) chloride, SnCl₂, granular

7.2. Standards

7.2.1. Laboratory Control Sample

- 7.2.1.1. 2000 ppm Sulfide: Add 3.5 g of sodium sulfide to 100 mL of reagent water in a 250mL volumetric flask. Dilute to volume with reagent water. The sulfide standard must be verified each working day. If the resulting value is <75% of the original standard, a new solution must be prepared.

7.2.2. Matrix Spike Standard

- 7.2.2.1. Prepare a midrange matrix spike standard as described in 7.2.1 for use as a MS/MSD.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

- 8.1. Waters are preserved to a pH > 9 with NaOH and zinc acetate. Non-water samples are unpreserved. All matrices are stored at $4^{\circ}\text{C} \pm 2^{\circ}\text{C}$ in plastic or glass containers.
- 8.2. The holding time is seven days from sampling to analysis. Samples must be analyzed immediately if arrived in the laboratory without proper chemical preservation.

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, MS, MSD) 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. Method Blank

- 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 reagent water blank consisting of 250 mL of reagent water must be analyzed with each analytical batch of samples.

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 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 addressed in the project narrative.**

9.3. Laboratory Control Sample (LCS)

9.3.1. One aqueous LCS must be processed with each preparation batch. The LCS must be carried through the entire analytical procedure. 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.

9.3.2. A midrange LCS is prepared by adding 2.5 mL for Methods 376.1 and SM 4500-S2-D and 1.0 mL for Method 9030B (water samples) or 1.0 mL (solid samples) of 2000ppm sulfide standard to a flask. This standard must be analyzed with each analytical 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.

9.3.3.2. The only exception is that if the LCS recoveries are biased high and the associated sample is ND for the parameter(s) of interest, the batch is acceptable. **This must be addressed in the project narrative.**

9.3.3.3. 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. A MS/MSD consisting of 30 g or 250 mL of the sample and 2.5 mL for Methods 376.1 and SM 4500-S2-D or 1.0 mL for Method 9030B of 2000 ppm sulfide standard should be analyzed with every 20 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 "amount" MSB. The Exception Code is changed to NC. The following two footnotes will appear on the report page "NC The recovery and/or RPD were not calculated." "MSB The recovery and RPD were not calculated because the sample amount was greater than four times the spike amount."
- 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 laboratory limits.

9.5. Control Limits

- 9.5.1. Control limits are established by the laboratory as described in SOP, NC-QA-0018.

9.5.2. Laboratory control limits are internally generated and updated periodically unless method specified. Control limits are listed in the Laboratory Quality Manual (LQM) and the latest is version easily accessible via the LIMs (QC Browser program).

9.6. Method Detection Limits (MDLs) and MDL Checks

9.6.1. MDLs and MDL Checks are established by the laboratory as described in SOP, NC-QA-0021.

9.6.2. MDLs are listed in the Laboratory Quality Manual (LQM) and the latest version is easily accessible via the LIMs (QC Browser program).

9.7. Nonconformance and Corrective Action

9.7.1. Any deviations from QC procedures must be documented as a nonconformance, with applicable cause and corrective action approved by the facility QA Manager.

10. CALIBRATION AND STANDARDIZATION

10.1. Not Applicable

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. Aqueous Sample Method 9030B

11.3.1.1. For an efficient distillation, the mixture in the distillation flask must be of such a consistency that the motion of the stirring bar is sufficient to keep the solids from settling. The mixture must be free of

solid objects that could disrupt the stirring bar. Prepare the sample using one of the procedures in this section then proceed with the distillation step.

11.3.1.2. If the sample is aqueous, shake the sample container to suspend any solids, then quickly decant the appropriate volume (250 mL) of the sample to a graduated cylinder. Transfer the contents of the graduated cylinder into the reaction flask.

11.3.1.3. If the sample is aqueous, but contains a large proportion of solids, the sample may be roughly separated by phase and the amount of each phase measured and weighed to the nearest milligram into the distillation flask in proportion to their abundance in the sample. Reagent water may be added up to a total volume of 250 mL.

11.3.2. Solids and Waste Samples, Method 9030B

11.3.2.1. Weigh out 30 g +/- 0.1 g of homogenized sample and put into the reaction flask.

11.3.2.2. Samples that are not water miscible (oils, various solvents) cannot be analyzed using this method.

11.3.3. 9030B Distillation

11.3.3.1. Acid Soluble Sulfides:

11.3.3.1.1. Add 30g +/- 0.1g of solid sample plus 200 mL of reagent water or 250 mL of aqueous sample and a stir bar to the reaction flask

11.3.3.1.2. Attach the reaction flask to the distillation apparatus such that the bottom of the reaction flask does not touch the bottom of the crystallizing dish (submerge approximately 1/3 of the flask in the warm water).

11.3.3.1.3. Add 100 mL of 50% H₂SO₄ (7.1.8) to the addition flask and place in the center neck of the reaction flask. Attach the nitrogen flow line to the top of the addition flask.

11.3.3.1.4. Prepare one (1) gas trap bottles for each distillation setup by adding 200 mL of reagent water, 40 mL of zinc acetate buffer (7.1.7.1) and 10 mL of formaldehyde (7.1.6) to each trap.

11.3.3.1.5. Connect the trap and insert the trap arm into the right neck of the reaction flask. Turn on the nitrogen to approximately 5 psi and adjust the flow to 3 – 5 bubbles per second and purge for 15 minutes.

11.3.3.1.6. Add spike and LCS solution by removing the trap arm and pipetting the spike solution, below the surface of the water. Replace the trap arm and re-establish the flow of nitrogen, purge for 5 minutes.

11.3.3.1.7. Open the addition funnel to add the sulfuric acid (7.1.8) drop by drop. Do not open the stop cock fully. Distill the sample for 90 minutes, maintaining 70°C in the water bath.

11.3.3.1.8. Fill the crystallizing dish with 650 – 700 mL of reagent water and place on the hotplate/stirrer. Turn on the hotplate to a setting of “6” for approximately 15 – 20 minutes. Turn down to a setting of “4” to maintain a temperature of 70°C, +/- 5°C.

11.3.3.2. Acid-Insoluble Sulfide:

11.3.3.2.1. As the concentration of HCl during distillation must be within a narrow range for successful distillation of H₂S, the water content must be controlled. It is imperative that the final concentration of HCl in the distillation flask be about 6.5N and that the sample is mostly suspended in the fluid by the action of the stirring bar. This is achieved by adding 50 mL of reagent water, including water in the sample, 100 mL of 9.8N HCl, and the sample to the distillation flask. Solids which absorb water and swell will restrict fluid motion and, therefore, lower recovery will be obtained. Such samples should be limited to 25 g dry weight.

11.3.3.2.2. If the matrix is aqueous, then a maximum of 50 g of the sample may be used. No additional water may be added.

11.3.3.2.3. If the matrix is dry solid, use 30 g +/- 0.1 g of the sample and add 50 mL of reagent water.

11.3.3.2.4. Add 5 g SnCl to each distillation flask

11.3.3.2.5. Assemble the distillation apparatus. Place 200 +/- 4.0 mL of zinc acetate/sodium acetate buffer solution and 10.0 mL +/- 2.0

mL of 37% formaldehyde in each Erlenmeyer flask. Add 40 mL DI water.

- 11.3.3.2.6. Add 100 +/- 1.0 mL of 9.8N HCL to the addition funnel. Connect the nitrogen line to the top of the funnel and turn the nitrogen on to pressurize the dropping funnel headspace.
- 11.3.3.2.7. Set the nitrogen flow at 25 mL/min. The nitrogen in the Erlenmeyer flask should bubble at about five (5) bubbles per second. Purge the oxygen from the system for about 15 minutes.
- 11.3.3.2.8. Turn on the magnetic stirrer. Set the stirring bar to spin as fast as possible. The fluid should form a vortex. If not, the distillation will exhibit poor recovery. Add all the HCl from the dropping funnel to the flask.
- 11.3.3.2.9. Heat the water bath to the boiling point (100⁰C). the sample may or may not be boiling. Allow the purged distillation to proceed for 90 minutes at 100⁰C.

*Note: Watch water dishes so they don't go dry!

11.4. Sample Analysis

11.4.1. Summary

- 11.4.1.1. Excess iodine is added to a sample and under acidic conditions is back titrated with sodium thiosulfate from a blue to a clear color.

11.4.2. Sample Analysis Procedure

11.4.2.1. Method 376.1

- 11.4.2.1.1. Place 250mL of homogenized sample in a 500 mL Erlenmeyer flask. At this time, add any spiking solutions if necessary for the filtered water samples.
- 11.4.2.1.2. Add 20.0 mL .028 N Iodine solution and 1-2 mL 1:1 HCl solution (watch for fumes). Check the pH prior to titration to make sure it is less than 2. If the pH is not <2, add additional acid. Add 250 mL reagent water only for the water samples and mix.

11.4.2.1.3. Add 1 squirt (1-2 mL) of starch indicator and mix. Titrate from blue to clear with .025 N sodium thiosulfate titrant. Record the amount of titrant used on the analytical logsheet.

Note: Some matrices may be turbid or colored and the color change from blue to clear may not be easily seen. In this case, look for a shade change.

11.4.2.2. 9030B/9034 Titrations

11.4.2.2.1. Titrate the scrubber solution in the Erlenmeyer.

11.4.2.2.2. Add 20 mL of 0.028 N iodine solution under the liquid level in the Erlenmeyer, and 1-2 mL of 1:1 HCl solution. (More HCl is needed for insoluble 9030B.) Check the pH prior to titration to make sure it is less than 2.

11.4.2.2.3. Add 1 squirt of starch indicator and mix. Titrate from blue to clear with .025 N sodium thiosulfate titrant.

*Note: Because of the buffer and the formaldehyde, the titration will take between 15 – 30 minutes. Add titrant slowly to allow the reaction to take place. Overtitrating could be an issue if the titrant is added too quickly.

11.4.2.2.4. After adding 20 mL iodine, the color should be orange/red. If the color remains yellow, add additional 10 mL aliquots until the orange/red color persists (adjust the calculation accordingly). If the sample requires more than 60 mL of iodine, the sample must be re-prepped at a smaller dilution. The iodine should turn a yellow-orange color when added to the sample after the addition of the reagent water. If it does not, the sample may be high in sulfide and less sample should be used, or more iodine for 9030B.

11.4.2.3. Method 4500-S2-D Titrations.

11.4.2.3.1. Add 20 mL iodine to a 500mL Erlenmeyer flask.

11.4.2.3.2. Add 2mL HCl.

11.4.2.3.3. Add 250mL of homogenized water sample to the flask.

11.4.2.3.4. Add 1-2mL of starch indicator.

11.4.2.3.5. Titrate from blue to clear with 0.025N sodium thiosulfate.
Record the amount of titrant used on the analytical logsheet.

11.5. Analytical Documentation

- 11.5.1. Record all analytical information in the analytical logbook/logsheets, which may be in electronic format, including the analytical data from standards, blanks, LCSs, MS/MSDs, 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. Calculations

$$\text{Sulfide, mg / L or mg / kg} = \frac{[(A \times B) - (C \times D)] \times 16,000}{\text{mL or g of sample used}}$$

Where:

A = *mL of iodine solution*

B = *Normality of iodine solution*

C = *mL of sodium thiosulfate titrant*

D = *Normality of sodium thiosulfate titrant*

$$\text{Sulfide, mg / L or mg / kg} = \frac{(20 - \text{mL titrant}) \times 400}{\text{mL or g of sample used}}$$

12.1.1.

$$LCS \% \text{ Recovery} = \frac{\text{mg/L (from 12.1.1)}}{20 (\text{true})} \times 100$$

Note: The true value of the standard is determined daily.

12.1.2.

$$\text{MS/MSD \% Recovery} = \frac{A - B}{20 (\text{waters}) \text{ or } 1000 (\text{solids})} \times 100$$

Where:

$$A = (20 - \text{mL titrant for MS/MSD}) \times 400$$

$$B = \text{Concentration from 12.1.1} \times \text{mL or g of sample used}$$

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.

13.2.2. Method validation information (where applicable) in the form of laboratory demonstrations of capabilities is maintained for this method in the laboratory QA files.

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. All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize

the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

- 15.2. Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices of STL North Canton. They must have training on the hazardous waste disposal practices upon initial assignment to these tasks, followed by an annual refresher training.
- 15.3. Waste Streams Produced by the Method
 - 15.3.1. The following waste streams are produced when this method is carried out.
 - 15.3.1.1. Acidic waste generated by sample titration. Waste material is disposed of in acid waste containers located in the lab.
 - 15.3.1.2. Aqueous acidic material from the distillation double-necked flask is collected in 5-gallon containers and taken to the neutralization area for neutralization.
 - 15.3.1.3. Aqueous sample waste containing formaldehyde, sodium thiosulfate, and iodate. Waste is disposed of in waste containers specific to this test method located in the laboratory.

16. REFERENCES

16.1. References

- 16.1.1. SW846, Test Methods of Evaluating Solid Waste, Third Edition, Sulfide, Method 9030B.
- 16.1.2. EPA 600, Methods for Chemical Analysis of Waters and Wastes, Sulfide (Titrimetric, Iodine), Method 376.1
- 16.1.3. Standard Methods Eighteenth Edition, Sulfide Method 4500-S2-D.
- 16.1.4. STL North Canton Laboratory Quality Manual (LQM), current version.
- 16.1.5. STL Quality Management Plan (QMP), current version.
- 16.1.6. SW846, Test Methods of Evaluating Solid Waste, Third Edition, Titrimetric Procedure for Acid-soluble and Acid-insoluble Sulfides, Method 9034.

16.2. Associated SOPs and Policies, latest version

16.2.1. QA Policy, QA-003

16.2.2. Glassware Washing, NC-QA-0014

16.2.3. Statistical Evaluation of Data and Development of Control Charts, NC-QA-0018

16.2.4. Method Detection Limits and Instrument Detection Limits, NC-QA-0021

16.2.5. Navy/Army SOP, NC-QA-0016

17. MISCELLANEOUS (TABLES, APPENDICES, ETC...)

17.1. Reporting limits

17.1.1. The lower reporting limits (RL) are 1 mg/L for waters and 50 mg/kg for solids.

17.1.2. If samples require dilution or smaller volumes than specified in this method, the RL will be elevated.

17.2. Method Deviations

17.2.1. The lab does not perform the distillation procedure described in Method SW846 9030A.

17.2.2. The laboratory uses one collection flask instead of two.

17.2.3. The laboratory does not titrate the sample in the original container as specified in Method 376.1

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STL STANDARD OPERATING PROCEDURE

TITLE: DETERMINATION OF INORGANIC ANIONS BY ION CHROMATOGRAPHY

(SUPERSEDES: REVISION 4, REVISION DATE 11/06/04)

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1. SCOPE AND APPLICATION

- 1.1. This method covers the determination of fluoride, chloride, nitrite, bromide, nitrate, ortho-phosphate and sulfate in drinking water, surface water, mixed domestic and industrial wastewaters, groundwater, reagent waters, solids (after extraction 11.7) and leachates (when no acetic acid is used). This SOP is based on Method 300.0A and 9056A.
- 1.2. A listing of associated LIMs method codes is located in Section 8.2.
- 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. A 25 uL volume of sample is introduced into the ion chromatograph. The sample is pumped through three different ion exchange columns and into a conductivity detector. The first two columns, a precolumn or guard column and a separator column, are packed with low-capacity, strongly basic anion exchange resin. Ions are separated into discrete bands based on their affinity for the exchange sites of the resin. The last column is a suppresser column that reduces the background conductivity of the eluent to a low or negligible level and converts the anions in the sample to their corresponding acids. The separated anions in their acid form are measured using an electrical conductivity cell. Anions are identified based on their retention times compared to known standards. Quantitation is accomplished by measuring the peak height or area and comparing it to a calibration curve generated from known standards.

3. DEFINITIONS

- 3.1. Refer to the glossary in the Laboratory Quality Manual (LQM).

4. INTERFERENCES

- 4.1. Interferences can be caused by substances with retention times that are similar to and overlap those of the anion of interest. Large amounts of an anion can interfere with the peak resolution of an adjacent anion. Sample dilution and/or fortification can be used to solve most interference problems associated with retention times.
- 4.2. The water dip or negative peak that elutes near, and can interfere with, the fluoride peak can usually be eliminated by the addition of concentrated eluent to each standard and sample.

- 4.3. Method interferences may be caused by contaminants in the reagent water, reagents, glassware and other sample processing apparatus that lead to discrete artifacts or an elevated baseline in the ion chromatograms.
- 4.4. Any anion that is not retained by the column or only slightly retained will elute in the area of fluoride and interfere. Known coelution is caused by carbonate and other small organic anions. At concentrations of fluoride above 1.5 mg/L, this interference may not be significant; however, it is the responsibility of the user to generate precision and accuracy information in each sample matrix.
- 4.5. The acetate anion elutes early during the chromatographic run. The retention times of the anions also seem to differ when large amounts of acetate are present. Therefore, this method is not recommended for leachates of solid samples when acetic acid is used for pH adjustment.

5. SAFETY

- 5.1. Employees must abide by the policies and procedures in the Corporate Safety Manual and this document.
- 5.2. Exercise caution when using syringes with attached filter assemblies. Application of excessive force has, upon occasion, caused a filter disc to burst during the process.
- 5.3. The following is a list of the materials used in this method, which have a serious or significant hazard rating. NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table. A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Potassium Nitrate	Oxidizer	None	Causes irritation to the respiratory tract, skin and eyes. Symptoms may include coughing, shortness of breath. Symptoms include redness, itching, and pain.

Sodium Fluoride	Poison	2.5 Mg/M3-TWA as F	Highly Toxic. Causes severe irritation to the respiratory tract, symptoms may include coughing, sore throat, and labored breathing. Causes irritation, with redness and pain. Solutions are corrosive. Eye irritant! May cause irritation and serious eye damage. Effects may not appear immediately.
Sulfuric Acid	Corrosive Oxidizer Dehydrator Poison Carcinogen	1 Mg/M3-TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

- 5.4. Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Cut resistant gloves must be worn doing any other task that presents a strong possibility of getting cut. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.
- 5.5. 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 when possible. All samples with a pink stickers that read "Caution/Use Hood!" **must** be opened in the hood. Contact the EH&S co-ordinator if this is not possible. 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 operation 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 the EH&S Coordinator and to a laboratory supervisor.

6. EQUIPMENT AND SUPPLIES

- 6.1. Balance -- Analytical, capable of accurately weighing to the nearest 0.0001 g.
- 6.2. Ion Chromatograph -- Analytical system complete with ion chromatograph and all required accessories including analytical columns, compressed gases and detectors.
 - 6.2.1. Anion guard column: A protector of the separator column. If omitted from the system the retention times will be shorter. Usually packed with same substrate as the separator column. 4 x 50 mm, Dionex IonPac AG14 P/N 46134, or equivalent.
 - 6.2.2. Anion separator column: The separation shown in Figure 1 was generated using a Dionex IonPac AS14 column (P/N 46134). Equivalent column may be used if comparable resolution is obtained, and the requirements of Sect. 9.2 can be met.
 - 6.2.3. Anion suppresser device: Dionex anion micro membrane suppresser (P/N 37106) or ASRS-Ultra Self-Regenerating Suppressor (4mm) P/N 53946 or equivalent.
 - 6.2.4. Detector -- Conductivity cell: approximately 1.25 uL internal volume, Dionex, or equivalent.
 - 6.2.5. Dionex --PeakNet 5.1Data Chromatography Software or equivalent.
- 6.3. Assorted laboratory glassware (pipettes, volumetric flasks, etc.).

7. REAGENTS AND STANDARDS

- 7.1. Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.
- 7.2. Reagent water: Distilled or deionized water, free of the anions of interest. Water should contain particles no larger than 0.20 microns.
- 7.3. Eluent solution: sodium bicarbonate (CASRN 144-55-8) 1.0 mM, sodium carbonate (CASRN 497-19-8) 3.5 mM. Dissolve 1.680 g sodium bicarbonate (NaHCO_3) and 7.417 g of sodium carbonate (Na_2CO_3) in reagent water (7.2) and dilute to 100 mL in a volumetric flask. Take 10 mL of this concentrated eluent solution and dilute to 2 L for use as the working eluent solution or dissolve the entire bicarbonate/carbonate amount in 20 L of reagent water.

7.4. Stock solutions (1,000 mg/L): All stocks are purchased from commercial sources. Primary and secondary sources are required for each target analyte.

7.4.1. Commercial stock solution A: F^- - 25 mg/L, Cl^- - 500 mg/L, Br^- - 100 mg/L, NO_3^- - N- 25 mg/L, $PO_4 - P$ - 25 mg/L, SO_4^{2-} - 500 mg/L. The stock solution may also be at the following concentrations: F^- - 125 mg/L, Cl^- - 2500 mg/L, Br^- - 500 mg/L, NO_3^- - N- 125 mg/L, $PO_4 - P$ - 125 mg/L, SO_4^{2-} - 2500 mg/L.

7.4.2. Commercial stock solution B: NO_2^- - N- 25 mg/L. The spike solution may also be at 125 mg/L.

7.4.3. Commercial IC Spike solution A: : F^- - 125 mg/L, Cl^- - 2500 mg/L, Br^- - 500 mg/L, NO_3^- - N- 125 mg/L, $PO_4 - P$ - 125 mg/L, SO_4^{2-} - 2500 mg/L

7.4.4. Commercial IC Spike solution B: NO_2^- - N- 125 mg/L

7.5. Working standards: Prepare calibration standard #5 in a 10 mL volumetric flask and transfer to a vial. Adjust the amount of stock solution used to prepare the working standards if the stock concentration differs from 1000 mg/L as assumed. Alternatively prepare Cal standard #5 by mixing 4.0 mL commercial stock A, 4.0 mL commercial stock B and 2.0 mL of eluent or, if the more concentrated solution is used, by mixing 0.8 mL A, 0.8 mL B, and 8.4 mL of eluent.

Calibration Standard #5

Analyte	mL of Stock	Final Conc.
Fluoride	0.10mL	10.0 mg/L
Chloride	2.0 mL	200. mg/L
Nitrite	0.10 mL	10.0 mg/L
Bromide	0.40 mL	40.0 mg/L
Nitrate	0.10 mL	10.0 mg/L
Ortho-Phosphate	0.10 mL	10.0 mg/L
Sulfate	2.0 mL	200. mg/L

7.5.1. In 5 mL PolyVials prepare the following calibration standards in reagent grade water. Final concentrations of working standards are shown below.

Calibration Standard #4: take 2.50 mL of calibration standard #5 and add 2.50 mL of eluent.

Calibration Standard #2: take 250 μ L of calibration standard #5 and add 4.75 mL of eluent.

Calibration Standard #1: take 25.0 μ L of calibration standard #5 and add 4.95 mL of eluent.

Calibration Standard #3: take 1.25 mL of calibration standard #5 and add 3.75 mL of eluent.

Calibration Standard #1

Analyte	25.0 mL of Cal Std #5	Final Conc
Fluoride		0.05 mg/L
Chloride		1.0 mg/L
Nitrite		0.05 mg/L
Bromide		0.20 mg/L
Nitrate		0.05 mg/L
Ortho-Phosphate		0.05 mg/L
Sulfate		1.0 mg/L

Calibration Standard #2

Analyte	250 mL of Cal Std #5	Final Conc.
Fluoride		0.5 mg/L
Chloride		10. mg/L
Nitrite		0.5 mg/L
Bromide		2.0 mg/L
Nitrate		0.5 mg/L
Ortho-Phosphate		0.5 mg/L
Sulfate		10. mg/L

Calibration Standard #3

Analyte	1.25 mL of Cal Std #5	Final Conc.
Fluoride		2.5 mg/L
Chloride		50. mg/L
Nitrite		2.5 mg/L
Bromide		10. mg/L
Nitrate		2.5 mg/L
Ortho-Phosphate		2.5 mg/L
Sulfate		50. mg/L

Calibration Standard #4

Analyte	2.5 mL of Cal Std #5	Final Conc.
Fluoride		5.0 mg/L
Chloride		100 mg/L
Nitrite		5.0 mg/L
Bromide		40. mg/L
Nitrate		5.0 mg/L
Ortho-Phosphate		5.0 mg/L
Sulfate		100 mg/L

- 7.5.2. Prepare or purchase a secondary stock standard(s) using a standards source other than that used for the primary standards as described in Section 7.5. Dilute these stock standards to as indicated in the table below to prepare the mixture to be used for the LCS and CCV solution. The CCV/LCS solution may be prepared by mixing 20 mL of A and 20 mL of B and diluting to 200 mL. A higher dilution solution may also be prepared by taking 5mL of A (5X) and 4 mL of B (5X) and diluting to 200 mL.

LCS & Continuing Calibration Verification Solution

Analyte	Final Conc. (V _f =5ml)
Fluoride	2.5 mg/L
Chloride	50. mg/L
Nitrite	2.5 mg/L
Bromide	10. mg/L
Nitrate	2.5 mg/L
Ortho Phosphate	2.5 mg/L
Sulfate	50. mg/L

- 7.5.3. Prepare or purchase a secondary stock standard(s) using a standards source other than that used for the primary standards as described in Section 7.5. Dilute these stock standards to prepare the mixture to be used for the Matrix Spike solution. Alternatively purchase these mixes (ready to use) from a commercial source. Add 100 uL of each IC Spike solution to 5 mL of sample when preparing the MS. Dilute as needed after spiking the sample.

Matrix Spike “True” Values

Analyte	Final Conc.
Fluoride	2.5 mg/L
Chloride	50. mg/L
Nitrite	2.5 mg/L
Bromide	10. mg/L
Nitrate	2.5 mg/L
Ortho Phosphate	2.5 mg/L
Sulfate	50. mg/L

NOTE: Stock standards, calibration standard #5 and LCS standard should be stored in the dark at 4° ± 2°C. Replace these standards when instrument response indicates target analyte degradation may have occurred or after the standard has expired (12 months commercial mix or

6 months in house mix), which ever occurs first. Nitrite and ortho-phosphate are particularly light and oxygen sensitive.

8 SAMPLE COLLECTION, PRESERVATION AND STORAGE

- 8.1. Samples should be collected in plastic or glass bottles. All bottles must be thoroughly cleaned and rinsed with reagent water. The volume collected should be sufficient to ensure a representative sample, allow for replicate analysis, if required, and minimize waste disposal.
- 8.2. Sample preservation and holding times for the anions that can be determined by this method for water samples are as follows:

QuanTIMs Method Code		Analyte	Preservation	Holding Time
EPA 300.0A	SW846 9056A	Fluoride	4° ± 2°C	28 days
C8	3C			
CX	3D	Chloride	4° ± 2°C	28 days
GO	3E	Nitrite	4° ± 2°C	48 hours
GM	3F	Bromide	4° ± 2°C	28 days
C9	3G	Nitrate	4° ± 2°C	48 hours
DO	3H	Ortho Phosphate	4° ± 2°C	48 hours
CY	3I	Sulfate	4° ± 2°C	28 days

Note: Soil leachates will follow the same preservation and holding times as the water samples; starting from the time of extraction.

9. QUALITY CONTROL

- 9.1. The STL QC Program document provides further details of the QC and corrective action guidelines presented in this SOP. Refer to this document if additional guidance is required.

- 9.2. Table I provides a summary of quality control requirements including type, frequency, acceptance criteria and corrective action.
- 9.3. Initial Demonstration of Capability
- 9.3.1. Prior to the analysis of any samples by Ion Chromatography, the following requirements must be meet:
- 9.3.1.1. Method Detection Limit (MDL): An MDL must be determined prior to analysis of any samples. The MDL is determined using seven replicates of eluent spiked with the anions of interest that has been carried through the entire analytical procedure. MDLs must be redetermined on an annual basis. The spike level must be greater than the calculated MDL but less than or equal to 10x the MDL. The result of the MDL determination must be below the STL reporting limit.
- 9.4. Batch definition: Preparation and QC batch definitions are provided in the STL QC Policy.
- 9.5. Method Blank (MB): One method blank must be processed with each preparation batch. The method blank consists of eluent that has been taken through the entire preparation and analytical process. 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 above the reporting limit.
- 9.6. Laboratory Control Sample (LCS): One LCS must be processed with each preparation batch and must be carried through the entire analytical procedure. 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 the result is outside established control limits the system is out of control and corrective action must occur. Until in-house limits are established, a control limit of 90 - 110% recovery must be applied. Corrective action will be repreparation and reanalysis of the batch unless the client agrees that other corrective action is acceptable. The LCS is prepared from a separate stock standard, or neat material, of a different manufacturer than the stock, or neat material, used to prepare the calibration standard.
- 9.7. Matrix Spike/Matrix Spike Duplicate (MS): One MS sample must be analyzed every 10 samples. A matrix spike (MS) is a field sample to which a known concentration of target analyte has been added. Some client specific DQO's may require the use of sample duplicates in place of or in addition to MS's. The MS result is 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. Spiking levels will be the same as the LCS values.

- If the MS recovery or RPD falls outside the acceptance range, the recovery of the analyte must be in control for the LCS. Until in-house control limits are established, a control limit of 80-120% recovery and 20% RPD must be applied to the MS.
- If the native analyte concentration in the MS exceeds 4x the spike level for that analyte, the recovery data is reported as "amount" MSB. The Exception Code is changed to NC. The following two footnotes will appear on the report page "NC The recovery and/or RPD were not calculated." "MSB The recovery and RPD were not calculated because the sample amount was greater than four times the spike amount."
- 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 the limits, corrective action must be taken. Corrective action will include reparation and reanalysis of the batch.
- If an MS is not possible due to limited sample volume then a LCS duplicate must be analyzed. The RPD of the LCS and LCSD must be compared to the matrix spike limits.

9.8. Continuing Calibration Verification (CCV/CCB): Continuing calibration is verified by analyzing the calibration standard after every ten (10) samples. The CCV must fall within +/- 10% of the true value for each target analyte. A CCB is analyzed immediately following the CCV to monitor low level accuracy and system cleanliness. The CCB result must be below the reporting limit for that analyte. If either the CCV or CCB fail to meet criteria, the analysis must be terminated, the problem corrected and reparation and analysis of all samples following the last CCV and CCB which were in control.

9.9. Reporting Limit Check – Drinking Water Samples. A reporting limit check must be analyzed every day drinking water samples are analyzed. The acceptance criteria is $\pm 30\%$ for the check.

9.10. Control Limits

9.10.1. Control limits are specified in the method.

9.10.2. Control limits are listed in the Laboratory Quality Manual (LQM) and the latest version is easily accessible via the LIMs (QC Browser program).

9.11. Method Detection Limits (MDLs) and MDL Checks

9.11.1. MDLs and MDL Checks are established by the laboratory as described in SOPs S-Q-003 and NC-QA-0021.

9.11.2. MDLs are listed in the Laboratory Quality Manual (LQM) and the latest version is easily accessible via the LIMs (QC Browser program).

9.12. Nonconformance and Corrective Action

9.12.1. Any deviations from QC procedures must be documented as a nonconformance, with applicable cause and corrective action approved by the facility QA Manager.

10. CALIBRATION AND STANDARDIZATION

10.1. Establish ion chromatographic operating parameters equivalent to those indicated in table 2. Refer to Table 3 for typical standard run retention times. Other than the presence of the analytical column the instrument conditions are the same.

10.2. For each analyte of interest, prepare a **minimum** of 3 calibration standards and a blank by adding accurately measured volumes of one or more stock standards to a volumetric flask and dilution to volume with eluent. If a sample analyte concentration exceeds the calibration range the sample may be diluted to fall within the range. If this is not possible then three new calibration concentrations must be chosen, two of which must bracket the concentration of the sample analyte of interest. Each attenuation range of the instrument used to analyze a sample must be calibrated individually.

10.3. Using an injection volume of 25 uL of each calibration standard, tabulate peak height or area responses against the concentration. The results are used to prepare a calibration curve for each analyte. During this procedure, retention times must be recorded. All analytes will be calibrated using a quadratic regression forced through the origin. Correlation coefficients (R^2) must be 0.995 or better.

10.3.1. For Drinking Water samples, a linear curve, that is not forced through the origin, is used.

10.3. Initial Calibration Verification (ICV) – The Initial Calibration is verified at the start of each day following calibrating prior to sample analysis. The acceptance criteria is $\pm 10\%$ of the true value. If this criteria is not met, the instrument must be re-calibrated.

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. Table 2 summarizes the recommended operating conditions for the ion chromatograph. Included in this table are estimated retention times that can be achieved by this method. Other columns, chromatographic conditions, or detectors may be used if the requirements of Sect. 9.2 are met.
- 11.4. Check system calibration daily as outlined in Table 1 and, if required, recalibrate as described in Sect 10.
- 11.5. Load and inject a fixed amount (25 uL) of settled & filtered sample. If the sample is cloudy then it should be filtered prior to loading into the autosampler polyvial. Flush injection loop thoroughly, using each new sample. Use the same size loop for standards and samples. Record the resulting peak size in area or peak height units. An automated constant volume injection system may also be used.
- 11.6. The width of the retention time window used to make identifications should be based upon measurements of actual retention time variations of various concentration. Three times the standard deviation of a retention time can be used to calculate a suggested window size for each analyte. However, the experience of the analyst should weigh heavily in the interpretation of chromatograms since retention time is concentration dependent for most analytes..
- 11.7. If the response for the peak exceeds the working range of the system, dilute the sample with an appropriate amount of eluent and reanalyze.
- 11.8. If the resulting chromatogram fails to produce adequate resolution, or if identification of specific anions is questionable, fortify the sample with an appropriate amount of standard and reanalyze.

NOTE: Retention time is affected by concentration. Nitrate and sulfate exhibit the greatest amount of change, although all anions are affected to some degree. See Table 3. In some cases this peak migration may produce poor resolution or identification.

- 11.9. The following extraction should be used for solid materials: Add an amount of reagent water equal to ten times the weight of dry solid material taken as a sample. This slurry is mixed for one hour using a magnetic stirring device or tumbler. Filter the resulting slurry before injecting using a 0.45 um membrane type filter. This can be the type that attaches directly to the end of the syringe

11.10. Should more complete resolution be needed between peaks the eluent (7.3) can be diluted. This will spread out the run but will also cause the later eluting anions to be retained longer. The analyst must determine to what extent the eluent is diluted. This dilution should not be considered a deviation from the method.

11.11. Analytical Documentation

11.11.1. Record all analytical information in the analytical logbook/logsheets which may be in an electronic format, including the analytical data from standards, blanks, LCSs, MSs, and any corrective actions or modifications to the method.

11.11.2. All standards are logged into a department standard logbook. All standards are assigned an unique number for identification. Logbooks are reviewed by the supervisor or designee.

11.11.3. 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.

11.11.4. Sample results and associated QC are entered into the LIMs after final technical review.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Prepare a calibration curve for each analyte by plotting instrument response against standard concentration. Compute sample concentration by comparing sample response with the standard curve. Multiply answer by appropriate dilution factor.

12.2. Report only those values that fall between the lowest and the highest calibration standards. Samples exceeding the highest standard should be diluted and reanalyzed.

12.3. Report results in mg/L for aqueous samples and mg/Kg for 1 hour leachates and mg/L for 18 hour leachates of solid samples.

12.4. Report NO_2^- as N, NO_3^- as N, $\text{HPO}_4^{=}$ as P

13. METHOD PERFORMANCE

13.1. The reporting limits for the following analytes are based on a 25 uL injection volume:

Analyte	Water RL	Soil RL
Fluoride	1.0 mg/L	10 mg/kg
Chloride	1.0 mg/L	10 mg/kg
Nitrite	0.5 mg/L	5 mg/kg
Bromide	0.5 mg/L	5 mg/kg
Nitrate	0.05 mg/L	0.5 mg/kg
O-Phosphate	0.5 mg/L	5 mg/kg
Sulfate	1.0 mg/L	10 mg/kg

13.2. 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 analyst must be given two blind performance samples to analyze or process for analysis. Upon successful completion of the performance evaluation (PE) samples, these analyses will be documented as initial qualification,. Requalification must be performed annually thereafter for this procedure. The group/team leader must document the training and PE performance and submit the results to the QA Manager for inclusion in the associate's training files.

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. All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

15.2. Waste Streams Produced by the Method

15.2.1. The following waste streams are produced when this method is carried out.

15.2.1.1. Spent samples. Solid samples are disposed of as solid debris waste in the container labeled "Solid Waste."

15.2.1.2. Alkaline and/or acidic waste generated by the analysis. Aqueous waste can be poured down the drain if the pH is between 4 and 10. Any sample waste generated that is not in this pH range must be collected and disposed of in the designated acid waste drum located in the lab. This waste is collected in the laboratory in a designated container identified as "Acid Waste".

15.2.1.3. Contaminated plastic materials such as IC syringes, filters, caps and vials utilized for sample preparation. This waste is disposed of in containers labeled "Solid Waste."

16. REFERENCES

16.1. References

16.1.1. Method 300.0, "Determination of Inorganic Anions by Ion Chromatography", Environmental Monitoring Systems Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Cincinnati, Ohio, Revision 2.1, August 1993.

16.1.2. Method 9056A, "Determination of Inorganic Anions by Ion Chromatography", SW846, Test Methods for Evaluating Solid Waste, Third Edition, Draft Revision 1, September 1999.

16.1.3. STL North Canton Laboratory Quality Manual (LQM), current version.

16.1.4. Corporate Quality Management Plan (QMP), current version.

16.1.5. STL Corporate Safety Manual, M-E-0001 and STL North Canton Facility Addendum and Contingency Plan, current version.

16.2. Associated SOPs and Policies, latest version

16.2.1. QA Policy, QA-003

16.2.2. Glassware Washing, NC-QA-0014

16.2.3. Statistical Evaluation of Data and Development of Control Charts, NC-QA-0018

16.2.4. Method Detection Limits and Instrument Detection Limits, NC-QA-0021 and S-Q-003.

16.2.5. Navy/Army SOP, NC-QA-0016

17. MISCELLANEOUS (TABLES, APPENDICES, ETC...)

17.1. Reporting limits

17.1.1. If samples require dilution or smaller volumes than specified in this method, the RL will be elevated.

17.2. Attachment #1, method Flow Chart

17.3. Table 1, Quality Control Samples

17.4. Table 2, Standard Instrument Operating Parameters

17.5. Table 3, Retention Time Matrix

17.6. Figure 1, Example Chromatogram

Determination Of Inorganic Anions By Ion Chromatography

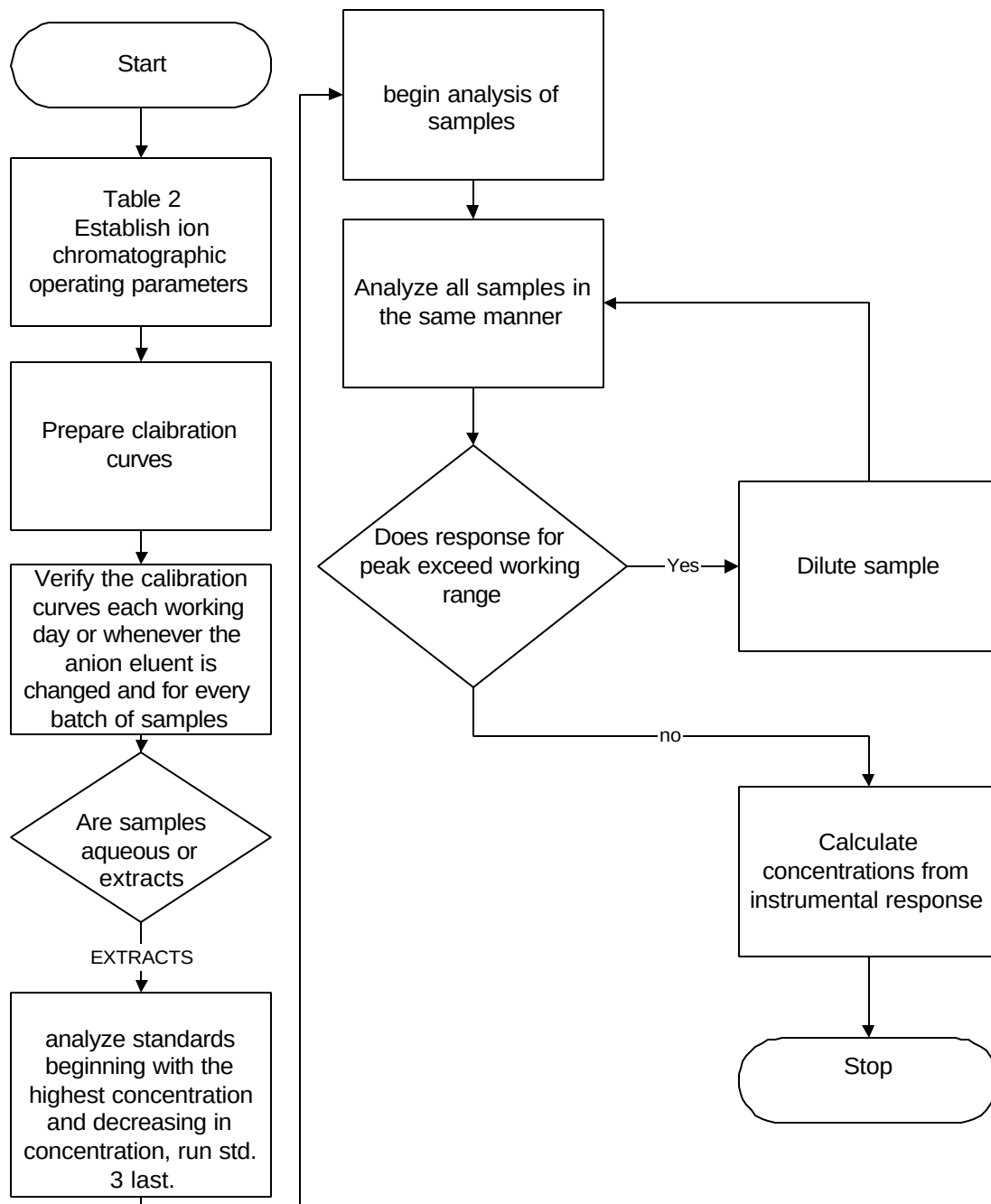


TABLE 1
QUALITY CONTROL SAMPLES

QC Samples	Frequency	Acceptance Criteria	Corrective Action
Initial Calibration Verification (ICV)	At the start of each day following calibrating prior to sample analysis	+/- 10% of true value	Recalibrate and reanalyze
Initial Calibration Blank (ICB)	After Initial Calibration Verification and prior to sample analysis	< the Reporting Limit	Reprepare and reanalyze
Laboratory Control Sample (LCS)	1 per batch of 20 samples	Meets laboratory historical limits	Reanalyze all samples associated with unacceptable LCS
Matrix Spike Sample (MS)	1 MS per every 10 samples	Meets laboratory historical limits	Supervisor's technical judgment
Continuing Calibration Verification (CCV)	Between each group of 10 injections and at the end of the analytical sequence	+/- 10% of true value	Recalibrate and reanalyze all samples since the last acceptable CCV
Continuing Calibration Blank (CCB)	Between each group of 10 injections and at the end of the analytical sequence	< the Reporting Limit	Recalibrate and reanalyze all samples since the last acceptable CCB

TABLE 2

Standard Instrument Operating Parameters

Standard Conditions:

Eluent Pump Rate:	1.20 mL/min (DX-120 and DX-320)
Sample Loop:	25 uL
Eluent:	1.0mM sodium bicarbonate, 3.5mM sodium carbonate
Detector output	Baseline conductivity should be 15 - 20 uS prior to sample analysis.

TABLE 3

Standard Run Retention Time Matrix (minutes)*

Analyte	Concentration (mg/L)													RT window
	0.05	0.2	0.5	1	2	2.5	5	10	20	40	50	100	200	
F ⁻	2.75	2.75				2.75	2.75	2.75						
Cl ⁻				3.97				3.98			4.03	4.08	4.17	
NO ₂ ⁻	4.80	4.80				4.78	4.78	4.80						
Br ⁻		6.15			6.13			6.10	6.08	6.07				
NO ₃ ⁻	7.33	7.27				7.17	7.13	7.07						
o-PO ₄ ²⁻	9.53	9.53				9.52	9.50	9.48						
SO ₄ ²⁻				11.50				11.48			11.43	11.38	11.27	

* Analyte retention time is concentration dependent for most anions. Retention time increases with increasing concentration for chloride. Retention time decreases with increasing concentration for bromide, nitrate, ortho-phosphate and sulfate.

EXAMPLE ION CHROMATOGRAM

cal std 4 IC stds 9001/9002

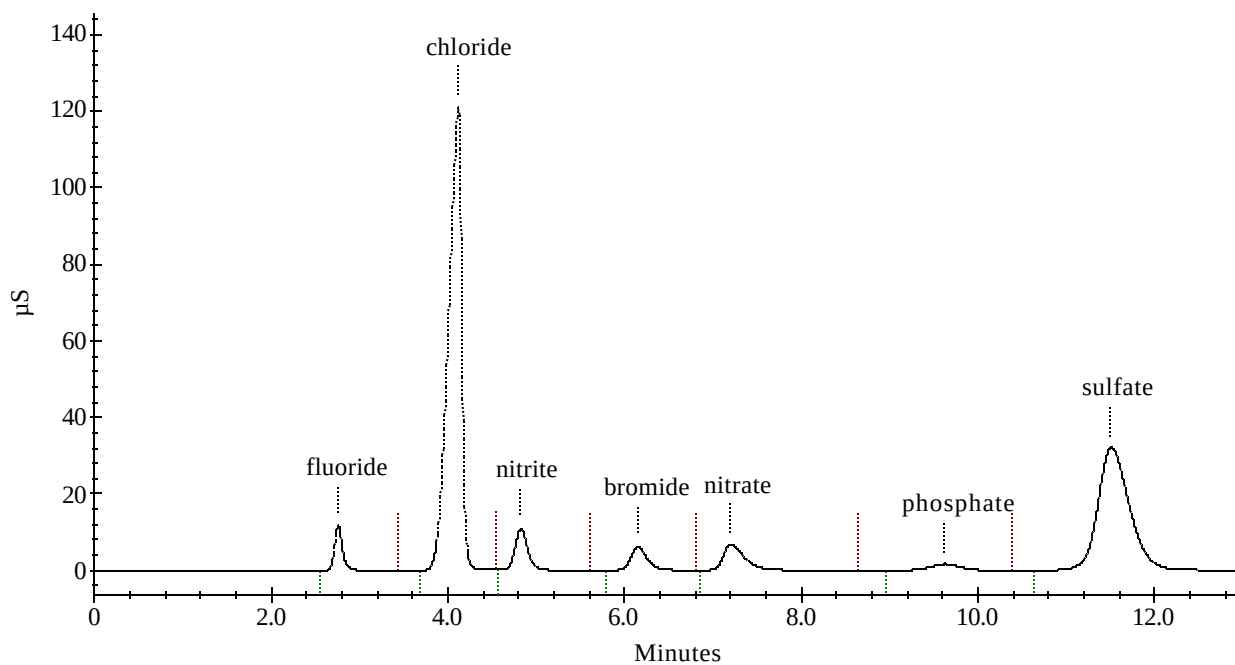


Figure #1

Controlled Copy

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Implementation Date 1/3/05

SOP No. NC-WC-0086

Revision No. 1.1

Revision Date: 12/06/04

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**STL North Canton
STANDARD OPERATING PROCEDURE**

TITLE: ALKALINE DIGESTION FOR HEXAVALENT CHROMIUM

(SUPERSEDES: REVISION 1, REVISION DATE 09/07/01)

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1. SCOPE AND APPLICATION

- 1.1. This method is used to determine the concentration of dissolved Hexavalent Chromium (Cr[VI]) in solids. This method may also be applicable to certain domestic and industrial wastes, provided that no interfering substances are present. It is based on SW846 Methods 3060A and ASTM Method D1498. The working linear range is 0.8-80 mg/kg for solids.
- 1.2. The associated method code is EA. The preparation code for solid samples is DW.
- 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 by the laboratory.

2. SUMMARY OF METHOD

- 2.1. This method uses an alkaline digestion to solubilize both water insoluble (with the exception of partial solubility of barium chromate in some soil matrices) and water soluble Cr(VI) compounds in solid waste samples.
- 2.2. The sample is digested using 0.28M Na₂CO₃/0.5M NaOH solution and heating at 90-90°C for 180 minutes to dissolve the Cr(VI) and stabilize it against reduction to Cr(III).

3. DEFINITIONS

- 3.1. Refer to the glossary in the STL North Canton Laboratory Quality Manual (LQM).

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. Specific selection of reagents may be required to avoid introduction of contaminants.
- 4.2. When analyzing a sample digest for total Cr(VI), it is appropriate to determine the reducing/oxidizing tendency of each sample matrix. This can be accomplished by characterization of each sample for additional analytical parameters, such as pH (Method 9045), ferrous iron (ASTM Method D3872-86), sulfides (Method 9030), and Oxidation Reduction Potential (ORP) (ASTM Method D 1498-94-aqueous samples). Method 9045 (Section 7.2 of Method 9045) is references as the preparatoy method for soil samples. The ORP probe is inserted directly into the soil slurry. The displayed ORP value is allowed to equilibrate and the resulting measurement is recorded. Other indirect

indicators of reducing/oxidizing tendency include Total Organic Carbon (TOC), Chemical Oxygen Demand (COD), and Biological Oxygen Demand (BOD). Analysis of these additional parameters establishes the tendency of Cr(VI) to exist or not exist in the unspiked sample(s) and assists in the interpretation of QC data for matrix spike recoveries outside conventionally accepted criteria for total metals.

- 4.3. Certain substances, not typically found in the alkaline digests of soils, may interfere in the analytical methods for Cr(VI) following alkaline extraction if the concentrations of these interfering substances are high and the Cr(VI) concentration is low. Refer to Method 7196A for a discussion of the specific agents that may interfere with Cr(VI) quantification. Analytical techniques that reduce bias caused by co-extracted matrix components may be applicable in correcting these biases after validation of their performance effectiveness.
- 4.4. For waste materials or soils containing soluble Cr(III) concentrations greater than four times the laboratory Cr(VI) reporting limit, Cr(VI) results obtained using this method may be biased high due to method induced oxidation. The addition of Mg and a phosphate buffer to the alkaline extraction solution has been shown to suppress this oxidation. The presence of soluble Cr(III) can be approximated by extracting the sample with deionized water (ASTM methods D4646-87, D5233-92, or D3987-85) and analyzing the resultant leachate for both Cr(VI) and total Cr. The difference between the two values approximates soluble Cr(III). Iron in concentrations greater than 1 mg/L may produce a yellow color, but the ferric iron color is not strong and no difficulty is encountered normally if the absorbance is measured photometrically at the appropriate wavelength.

5. SAFETY

- 5.1. Employees must abide by the policies and procedures in the Corporate Safety Manual and this document.
- 5.2. Samples that contain high concentrations of carbonates or organic material or samples that are at elevated pH can react violently when acids are added.
- 5.3. The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Nitric Acid	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Potassium Dichromate	Oxidizer Corrosive Carcinogen	0.1 Mg/M3 TWA as CrO3	Extremely destructive to tissues of the mucous membranes and upper respiratory tract. May cause ulceration and perforation of the nasal septum. Symptoms of redness, pain, and severe burn can occur. Dusts and strong solutions may cause severe irritation. Contact can cause blurred vision, redness, pain and severe tissue burns. May cause corneal injury or blindness.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

- 5.4. Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Cut resistant gloves must be worn doing any other task that presents a strong possibility of getting cut. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.
- 5.5. 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, where possible. All samples with pink stickers that read "Caution/Use Hood!" **must** be opened in the hood. Contact the EH&S Coordinator if this is not possible. 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 to the optimum level.
- 5.7. It is recommended that neat standards be purchased only as a last resort. The preparation of standards from neat materials and reagents should be conducted in a fume hood with the sash closed as far as the operations will permit.
- 5.8. Standards in solution may be diluted in the open laboratory when syringes and the like are utilized.
- 5.9. 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 the EH&S coordinator and to a laboratory supervisor.

6. EQUIPMENT AND SUPPLIES

- 6.1. Hot Block: Environmental Express
- 6.2. Thermometer (NIST traceable) & plastic beaker to monitor hot block temperature.
- 6.3. Beakers: glass, plastic (with snap on lids)
- 6.4. Autopipettes with disposable tips
- 6.5. Funnels: various
- 6.6. Analytical balance capable of accurately weighing $\pm 0.0001\text{g}$
- 6.7. Top load balance capable of accurately weighing $\pm 0.01\text{g}$
- 6.8. Snapseal containers
- 6.9. Graduated cylinders: various
- 6.10. Filter Paper: Whatman 4

7. REAGENTS AND STANDARDS

- 7.1. Reagents
 - 7.1.1. Sulfuric Acid (H_2SO_4): concentrated

7.1.2. Nitric Acid (HNO_3): concentrated (do not use if tinted yellow). (A yellow color indicates a change from NO_3 to NO_2 . This is a reducing agent for Hexavalent Chromium.)

7.1.2.1. 5M HNO_3 – 330mL concentrated nitric acid diluted to 1L. Stable at six months or until yellow tint develops which ever is less.

7.1.2.1.1. Start with about 500 mL of water in 1 L bottle, add acid, dilute to volume

7.1.3. Magnesium Chloride (MgCl_2): anhydrous, reagent grade

7.1.4. Phosphate Buffer

7.1.4.1. Potassium Hydrogen Phosphate, K_2HPO_4 : reagent grade

7.1.4.2. Potassium Dihydrogen Phosphate, KH_2PO_4 : reagent grade

7.1.4.3. 0.5M K_2HPO_4 /0.5M KH_2PO_4 buffer at pH 7: dissolve 8.71 g KH_2PO_4 and 6.80 g K_2HPO_4 in 70mL reagent water. Dilute to 100mL in a Snapseal vial. Expires at six months.

7.1.5. Sodium Hydroxide (NaOH): reagent grade

7.1.6. Sodium Carbonate (Na_2CO_3): reagent grade

7.1.7. Alkaline Digestion Solution: Dissolve $20.0 \pm 0.5\text{g}$ of sodium hydroxide and $30.0\text{g} \pm 0.5\text{g}$ of sodium carbonate in water. Dilute to 1000mL. Prepare fresh monthly. Check pH with pH paper, must be ≥ 11.5 , if not discard.

7.1.8. Potassium Dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$): primary standard grade

7.1.9. Lead Chromate (PbCrO_2): reagent grade, 10-20mg for insoluble MS/MSD

7.2. Standards

7.2.1. Primary Chromium Stock Solution, 50mg/L: Dissolve 0.1414 g of dried potassium dichromate in 800mL reagent water. Dilute to 1 liter in volumetric flask with reagent water. Stable 6 months.

7.2.1.1. Calibration Standards: Add the indicated volume of the appropriate standard to a beaker, add 50mL of digestion solution. Process the same as samples:

Conc		mLs	Source, mg/L	Final Vol, mL (after complete sample prep)
mg/L	mg/kg*			
2.0	80	4.0	50	100
1.0	40	2.0	50	100
0.5	20	1.0	50	100
0.25	10	0.5	50	100
0.10	4.0	0.2	50	100
0.02	0.8	0.04	50	100

*assuming 2.5 g solid to 100mL final volume

7.2.2. Secondary Chromium Stock Solution, 50mg/L: Dissolve 0.1414g dried potassium dichromate secondary source, in 800 mL reagent water. Dilute 1liter in a volumetric flask with reagent water. Stable 6 months

7.2.2.1. Verification Standards: Add the indicated volume of the appropriate secondary standard to a beaker (LCS) or sample (MS/MSD), add 50mL of digestion solution. Process the same as samples.

Use	Conc. mg/kg	mLs	Source, mg/L	Final Vol, mL (after complete sample prep)
CCV/LCS	20	1.0	50	100

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. To retard the chemical activity of Hexavalent Chromium, the samples and extracts should be stored at $4^{\circ}\text{C} \pm 2^{\circ}\text{C}$ until analyzed.

8.2. The holding time for solid samples is 30 days prior to digestion and 168 hours after digestion.

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, MS, MSD) 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. Method Blank

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. Corrective Action for Blanks

9.2.2.1. 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 addressed in the project narrative.**

9.2.2.2. 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 addressed in the project narrative.**

9.3. Laboratory Control Sample (LCS)

9.3.1. Two LCS samples must be processed with each preparation batch. The LCS must be carried through the entire analytical procedure. 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.

9.3.2. A soluble LCS for solids, consisting of 1.0mL of the 50mg/L secondary standard diluted to 50mL with digestion solution is prepared and analyzed with each analytical batch of samples.

9.3.3. An insoluble LCS for solids is analyzed with each analytical batch of samples. Use the calibrated disposable micropipette to put ~10mg of PbCrO_4 on 2.5 g sample of Kaolin. Record the actual amount added and use in the %R calculation. (Section 12.5)

9.3.4. Corrective Action for LCS

9.3.4.1. If any analyte is outside established control limits the system is out of control and corrective action must occur.

9.3.4.2. The only exception is that if the LCS recoveries are biased high and the associated sample is ND for the parameter(s) of interest, the batch is acceptable. **This must be addressed in the project narrative.**

9.3.4.3. Corrective action will be reparation and reanalysis of the batch unless the client agrees that other corrective action is acceptable.

9.4. Control Limits

9.4.1. Control limits are established by the laboratory as described in SOP, NC-QA-0018.

9.4.2. Laboratory control limits are internally generated and updated periodically unless method specified. Control limits are listed in the Laboratory Quality Manual (LQM) and the latest version is easily accessible via the LIMs (QC Browser program).

9.5. Method Detection Limits (MDLs) and MDL Checks

9.5.1. MDLs and MDL Checks are established by the laboratory as described in SOPs NC-QA-0021 and S-Q-003.

9.5.2. MDLs are listed in the Laboratory Quality Manual (LQM) and the latest version is easily accessible via the LIMs (QC Browser program).

9.6. Nonconformance and Corrective Action

9.6.1. Any deviations from QC procedures must be documented as a nonconformance, with applicable cause and corrective action approved by the facility QA Manager.

10. CALIBRATION AND STANDARDIZATION

10.1. All calibration standards are prepared and digested by the same procedure used for the samples.

10.2. Refer to 11.4 of SOP NC-WC-0024 for analysis.

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. Solid samples require an alkaline digestion procedure after which the sample can be analyzed as a water sample via SOP NC-WC-0024.

11.3.2. Homogenize the sample and weigh $2.5 \pm 0.1\text{g}$ of sample into a plastic vessel. record sample weight in the 3060A spreadsheet. Add matrix spike standards as appropriate. (Section 7.2.2 and 7.2.3). Add $50 \pm 1\text{mL}$ of digestion solution. Add approximately 400mg of magnesium chloride. Add 0.5mL of phosphate buffer. Cover with lid.

11.3.3. Move the covered vessel to a hot block and heat at $90\text{-}95^{\circ}\text{C}$ for at least 3 hours.

11.3.4. After the digestion is complete cool the vessel to room temperature. Filter through a Whatman #4 filter into a beaker of Snapseal container. Quantitatively transfer the entire contents of the digestion beaker to the filter.

11.3.5. Stir the digestate while adding 5M nitric acid (dropwise) until the pH is 7.5 ± 0.5 . If the pH goes below 7.0 discard the digestate and reprepare the sample or analyze the sample digestate within 8 hours. Monitor the pH with a pH meter. If a precipitate forms filter through a Whatman #4 filter into a Snapseal container. Transfer quantitatively and dilute to a final volume of 100mL in a Snapseal container.

Note: Standards and QC samples without solid matrices should not require the second filtration step. Many environmental solids will require the second filtration.

11.3.6. Analyze the digested standards and samples as described in Section 11.4 of SOP NC-WC-0024.

11.4. Method of Standard Addition

11.4.1. Prepare three (3) additional sample aliquots as described in section 11.3. Spike each aliquot according to the following table:

Conc.		mLs	Source, mg/L	Final Vol., mL (after complete sample prep).
mg/L	mg/kg*			
0.02	0.8	0.04	50	100
0.25	10	0.5	50	100
1.0	40	2.0	50	100

11.5. Analytical Documentation

11.5.1. Record all analytical information in the analytical logbook or computer spreadsheet, including the analytical data from standards, blanks, LCD, MS/MSS, sample duplicates, analysis dates 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. The supervisor or designee reviews logbooks.

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.

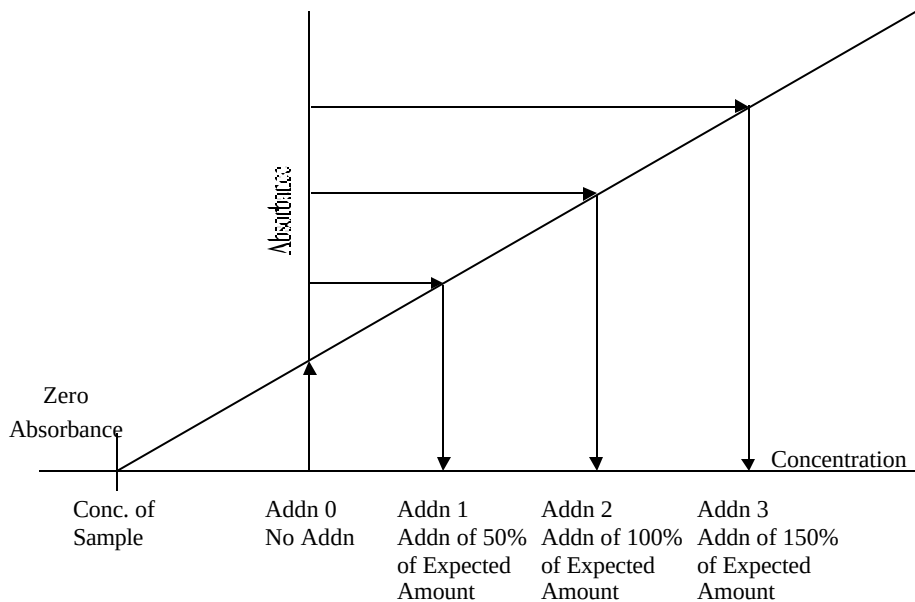
11.5.4. Sample results and associated QC are entered into the Limas after final technical review.

12. DATA ANALYSIS AND CALCULATIONS

12.1. 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 absorbency, 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.

$$12.2. \quad \text{LCS Recovery} = \frac{\text{mg/kg}}{20(\text{true})} \times 100 = \% \text{ Recovery}$$

$$12.3. \quad \text{CCV Recovery} = \frac{\text{mg/kg}}{20 \text{ (true)}} \times 100 = \% \text{ Recovery}$$

$$12.4. \quad \text{Soluble LCS Recovery} = \frac{\text{mg/kg}}{20 \text{ (true)}} \times 100 = \% \text{ Recovery}$$

$$12.5. \quad \text{Insoluble LCS Recovery} = \frac{\text{mg/kg}}{G \bullet H/I} \times 100 = \% \text{ Recovery}$$

G = mg of PbCrO₄ spiked

H = 0.16 (fraction of Cr in PbCrO₄)

I = kg of sample spiked

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.

13.2.2. Method validation information (where applicable) in the form of laboratory demonstrations of capabilities is maintained for this method in the laboratory QA files.

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. All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."
- 15.2. Waste Streams Produced by the Method
- 15.2.1. The following waste streams are produced when this method is carried out.
- 15.2.1.1. Acidic waste generated by the analysis. This waste is disposed of in waste containers located in the lab which are identified as "Waste Acid".
- 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, Third Edition, Alkaline Digestion for Hexavalent Chromium, Method 3060A.
- 16.1.2. ASTM D1498, Standard Practice for Oxidation-Reduction Potential of Water.
- 16.1.3. SOP NC-WC-0010 pH ELECTROMETRIC METHOD
- 16.1.4. SOP NC-WC-0024 CHROMIUM, HEXAVALENT (COLORIMETRIC)
- 16.1.5. Corporate Quality Management Plan (QMP), current version.
- 16.1.6. STL Laboratory Quality Manual (LQM), current version.
- 16.1.7. STL Corporate Safety Manual, M-E-0001 and STL North Canton Facility Addendum and Contingency Plan, current version.
- 16.2. Associated SOPs and Policies, latest version
- 16.2.1. QA Policy, QA-003

16.2.2. Glassware Washing, NC-QA-0014

16.2.3. Statistical Evaluation of Data and Development of Control Charts, NC-QA-0018

16.2.4. Method Detection Limits and Instrument Detection Limits, NC-QA-0021 and S-Q-003.

16.2.5. Navy/Army SOP, NC-QA-0016

17. MISCELLANEOUS (TABLES, APPENDICES, ETC...)

17.1. Reporting limits

17.1.1. The lower reporting limit (RL) is 1.0 mg/kg for solids.

17.1.2. If samples require dilution or smaller volumes than specified in this method, the RL will be elevated.

17.2. Method deviations

17.2.1. SW-846 Method 3060A describes a stirred 1 hour digestion. a 3 hour nonstired hot block digestion has been substituted.

17.2.2. SW-846 Method 3060A describes single matrix spikes used to control QC acceptability. If the initial MS fails reparation of the entire batch is necessary to demonstrate matrix effect. This SOP uses the standard MS/MSD approach to demonstrating matrix effect.

17.2.3. ASTM Standard D1498 describes repeat measurements of the ORP from multiple aliquots of the sample until they differ by no more than 10 mV. In adapting this water method for solid samples, a single sample aliquot is measured until the ORP reading stabilized within 10mV.

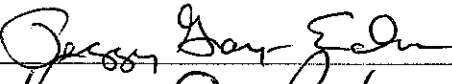
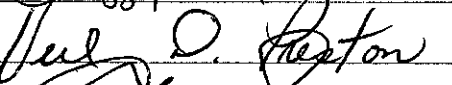
STL Buffalo
LABORATORY STANDARD OPERATING PROCEDURES

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TITLE: **HEAT OF COMBUSTION**

Supercedes: **NA**

REVIEWED & APPROVED BY:	SIGNATURE	DATE
Peggy Gray-Erdmann, Supervisor		12/14/05
Verl D. Preston, Quality Manager		12/14/05
Christopher A. Spencer, Laboratory Director		12/14/05

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1.0 IDENTIFICATION OF TEST METHOD

- 1.1 Heat of Combustion is based on ASTM D240-87 and E 144-64. Percent sulfur is based on ASTM D129-64 and percent chlorine is based on ASTM E 442-74.

2.0 APPLICABLE MATRIX

- 2.1 This method is used to determine the heat of combustion of liquid, oil and soil samples.

3.0 REPORTING LIMIT

- 3.1 Reporting limit = 1000 Btu/lb.

4.0 SCOPE AND APPLICATION

- 4.1 This procedure outlines the steps used to determine the gross heat of combustion of liquid, solid and oil matrices. The gross heat of combustion is expressed as British Thermal Units per pound (BTU/LB).

5.0 SUMMARY OF THE TEST METHOD

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- 5.1 Heat of combustion is determined in this test method by burning a weighed sample in an oxygen bomb calorimeter under controlled conditions. The heat of combustion is computed from temperature observations before, during and after combustion, with proper allowance for thermochemical and heat transfer corrections.

6.0 DEFINITIONS

- 6.1 Standard definitions are used in this document as defined by section 3.0 of STL Buffalo Laboratory Quality manual (LQM).

7.0 INTERFERENCES NA

8.0 SAFETY

Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual and this document.

8.1 *SAFETY CONCERNS OR REQUIREMENTS*

Oxygen vigorously accelerates combustion. Keep all oil and greases away, do not use on regulators or gages. Keep all combustibles away from oxygen and eliminate ignition sources. Use common safety practices for handling gas cylinders and ensure cylinder is secured at all times.

8.2 *PRIMARY MATERIALS USED*

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Oxygen, Compressed	Oxidizer	NA	Exposure to Oxygen will not result in exposure symptoms unless the individual is exposed to high levels for more than 17 hours. However, exposure of flammable or combustible materials to Oxygen can create an extremely dangerous situation and result in an explosion,
1- Always add acid to water to prevent violent reactions.			
2-Exposure limit refers to the OSHA regulatory exposure limit.			

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9.0 EQUIPMENT AND SUPPLIES

Mineral Oil
Oxygen Bomb Calorimeter – Parr model 1341
Oxygen Bomb – Parr model 1108
Calorimeter water bucket
Analytical balance
Oxygen tank
Sample bomb cups
Fuse wire
Thermometer reading lens
Mercury bomb thermometer
Bomb head support stand
White cotton string
2 liter graduated cylinder

10.0 REAGENTS AND STANDARDS

- 10.1 Benzoic acid tablets – commercially prepared- standardized annually.
- 10.2 Oxygen – free of combustible material and sulfur compounds, at a pressure of 30-40 psi.
- 10.3 Deionized (DI) water
- 10.4 Sodium Carbonate (Na_2CO_3)/Sodium Bicarbonate (NaHCO_3) Solution– add 2.5440g sodium carbonate and 2.520 g sodium bicarbonate to 1 liter DI water.
- 10.5 Mineral Oil – commercially prepared- standardized annually.

11.0 SAMPLE COLLECTION, PRESERVATION, SHIPMENT AND STORAGE

- 11.1 There are no published regulatory compliance parameters concerning container, preservation or holding times for this procedure. The laboratory defaults to storage at 4 +/- 2 degrees Celsius and analyzes within 28 days of sampling.

12.0 QUALITY CONTROL

- 12.1 Laboratory Control Sample (LCS): For every 20 or fewer samples a LCS should be done using a purchased Benzoic Acid tablet.
- 12.2 Sample Duplicate (MD): In every group of 20 or fewer samples there should be a sample duplicate. It is not applicable to add a sample spike or a method blank to this test.

13.0 CALIBRATION AND STANDARDIZATION

- 13.1 Benzoic Acid Bomb Calibration: To determine the energy equivalent of the calorimeter as the average of not less than six tests using standard benzoic acid tablets. These tests should be spaced over a period of not less than three days. Use not less than 0.9g or more than 1.1g of standard benzoic acid (Attachment 22.3).

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- 13.2 Mineral Oil Calibration: Determine the heat of combustion of the mineral oil using 0.5g of the oil as if it's a normal sample. Repeat the procedure at least three times. Average the three trials to standardize (Attachment 22.4).

14.0 PROCEDURE

- 14.1 Weigh out 1.0 grams sample on a tared analytical balance. Record the sample identity and sample weight into the BTU run log.
- 14.1.1 If poor combustion is expected add several drops of mineral oil. Make sure that the total weight is still 1.0 grams or less.
- 14.2 Add 2-liters of water using a flask into the calorimeter bucket. Place bucket into the calorimeter jacket on the pins.
- 14.3 Place the head of the oxygen bomb onto the stand and place the combustion capsule with the known amount of sample into the loop electrode.
- 14.4 Cut a 10cm length of fuse wire. Insert the wire into the electrode eyelets, push the wire caps down to pinch the wire into place. Have a loop of wire down as close to the sample as possible without actually touching the sample. You may add a short piece of fine cotton thread over the fuse loop having the other end touching the sample
- 14.5 If percent chlorine or percent sulfur is required then add 10mls of the sodium carbonate/sodium bicarbonate solution (10.4) to the bomb cylinder instead of the DI water.
- 14.6 With a small amount of water moisten the sealing ring.
- 14.7 With the oxygen release valve open, gently push the bomb head down into the bomb cylinder. Take care not to disturb the sample. Push the bomb head down as far as it will go. Then screw the cap down until you come to a solid stop.
- 14.8 Close the release valve and slowly add oxygen until you reach 30 psi.
- 14.9 Using the lifting handle place the bomb into the water. Make sure the bomb is centered on the circular impression. Insert the ignition wires into the terminal sockets on the bomb head.

**** NOTE**** Look for air bubbles, there will be some small bubbles when the bomb is initially submersed but these should subside within about 5 seconds. Any additional bubbles are indicators that the seal is not complete and the bomb must be removed and reset.

- 14.10 Place the cover on the calorimeter, attach belt and turn on the stirrer, make sure that it is turning easily.
- 14.11 Let the calorimeter run for 5 minutes or until a stable temperature is reached. Record this temperature in the logbook.
- 14.12 After a stable initial temperature is reached ignite the bomb by pressing down the ignition button, the red light should glow for no more then one second upon firing. If no glow is noted then the connection is not correct and the sample needs to be redone.
- 14.13 Monitor the temperature every minute until a stable temperature is maintained for at least three minutes. Record that Temperature.
- 14.14 Stop the stirrer, remove the pulley belt, remove the top and remove the ignition wires. Take the bomb out using lifting handle.
- 14.15 In a ventilation hood VERY SLOWLY release the oxygen from the bomb. This should take at least one minute.

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- 14.16 If preparing sample for percent sulfur or percent chlorine analysis, rinse bomb head and cylinder thoroughly with DI water to 100mL total volume, then dry with clean paper towels.
- 14.17 Scrub the combustion capsule with soap and water, rinse with DI water and bake for 4 hours in oven.

15.0 CALCULATIONS

Benzoic Acid Bomb Calibration

$$\frac{\Delta T}{\text{Benzoic Acid (grams)}} \times \frac{6318}{x} = \text{Calorimeter Constant (Cal / } ^\circ \text{C)}$$

where:

ΔT = Change in temperature

Benzoic Acid in grams

x = result of temperature divided by grams of Benzoic acid used

6318 = cal/gal of benzoic acid –this value is a constant

Mineral Oil Calibration

$$\frac{\Delta T \times \text{Calorimeter Constant}}{\text{Mineral Oil (grams)}} \times 1.8 = \text{Mineral Oil Calibration Constant (BTU/lb)}$$

where :

ΔT = Change in temperature

Mineral Oil in grams

Calorimeter Constant: Constant derived from Benzoic Acid Bomb Calibration

1.8: factor derived from converting cal/g to BTU/lb

BTU/lb

$$\frac{[(\text{Cal. Constant}) (\text{Temp. change})] - [(\text{g. Oil}) (\text{oil constant})]}{\text{Sample volume (grams)}} \times 1.8 = \text{BTU/lb.}$$

BTU/Gal.

$$(8.34)(\text{Density})(\text{Btu/lb.}) = \text{BTU/Gal.}$$

Percent Sulfur

$$\frac{(\text{mg/l SO}_4\text{-Dry Weight Corrected}) (\text{bomb washing volume}) (.333758)}{\text{Weight of sample used in the bombing} \times 10,000} = \% \text{ Sulfur}$$

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Percent Chlorine

$$\frac{(\text{mg/l Cl- Dry Weight Corrected}) (\text{bomb washing volume}) (.333758)}{\text{Weight of sample used in the bombing} \times 10,000} = \% \text{ Chlorine}$$

Dry Weight of Sample:

Sample conc. (µg/kg) as dry weight = [sample conc. µg/kg]/D

where:

D = (100 - % moisture)/100

16.0 METHOD PERFORMANCE

- 16.1. Method Detection Limit: A valid method detection limit for each analyte of interest must be generated. 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. See STL SOP S-Q-003, "Method Detection Limit Studies," current revision, for further guidance. Current STL Buffalo MDLs are maintained the QA department and are easily viewed in the laboratory LIMs system.
- 16.2. A one-time initial demonstration of performance for each individual method for both soils and water matrices must be generated.
 - 16.2.1. This requires quadruplicate analysis of a mid-level check standard containing all of the standard analytes for the method using the same procedures used to analyze samples, including sample preparation.
 - 16.2.2. Calculate the average recovery and standard deviation of the recovery for each analyte of interest.
 - 16.2.3. Compare these results with the acceptance criteria given in the Method or to laboratory historical limits (if available).
 - 16.2.4. Repeat the test for any analyte that does not meet the acceptance criteria. Repeated failure for any analyte indicates the need for the laboratory to evaluate the analytical procedure and take corrective action.
- 16.3. Training Qualifications
- 16.4. The supervisor 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.
- 16.5. The following analyst validation information is maintained for this method in the laboratory QA files.

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- 16.6. The analyst must complete the laboratory safety orientation training that includes, but is not limited to, chemicals, PPE requirements, and electrical safety.
- 16.7. The analyst must read and understand this SOP.
- 16.8. The analyst must read and understand the Method used as reference for this SOP.
- 16.9. The analyst must complete a DOC or successfully analyze PT samples annually.
- 16.10. The analyst must complete the STL Quality Assurance Training.

17.0 DATA ASSESSMENT AND ACCEPTANCE CRITERIA FOR QUALITY CONTROL MEASURES

- 17.1 Each batch must include a lab control standard (LCS) and a sample duplicate. It is not applicable to the test to include a method blank.
- 17.2 Determine the energy equivalent of the calorimeter as the average of not less than six tests using standard benzoic acid tablets. These tests should be done within a period of not less than three days. Do not use less than 0.9g or more than 1.1g of benzoic acid.
- 17.3 Standardization tests should be repeated after changing any part of the calorimeter, re-finishing the calorimeter, any new batch of oil or benzoic acid, or at least once a year. Average the determinations together. This procedure must be repeated at least annually.

18.0 CORRECTIVE ACTION FOR OUT-OF-CONTROL DATA

- 18.1 If acceptance criteria are exceeded, all related samples and check standards must be re-analyzed.

19.0 CONTINGENCIES FOR HANDLING OUT-OF-CONTROL DATA OR UNACCEPTABLE DATA

- 19.1 A Job Exception Form must be completed and filed with the Project Manager and QA Manager for any of the following conditions:
 - 19.1.1 Holding times exceeded
 - 19.1.2 Insufficient sample volume for re-analysis
 - 19.1.3 In the event of unknown positives or sample matrix which present the analyst with questionable data, the project manager shall be notified so the client may be contacted and involved in the decision process and course of action

20.0 WASTE MANAGEMENT AND POLLUTION PREVENTION

All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for

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pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

20.1 WASTE STREAMS PRODUCED BY THE METHOD

- Alkaline sample waste generated by the analysis is to be disposed of in the "D" waste containers.
- Acidic sample waste generated by the analysis is to be disposed of in the "A" waste containers.

21.0 REFERENCE

Heat of Combustion is based on ASTM D240-87 and E 144-64. Percent sulfur is based on ASTM D129-64 and percent chlorine is based on ASTM E 442-74. Also the instruction pamphlet that is included with the bomb calorimeter.

22.0 TABLES, DIAGRAMS, FLOWCHARTS AND VALIDATION DATA

- 22.1 Analytical Run Sequence
- 22.2 Analytical Batch
- 22.3 Benzoic Acid Bomb Calibration Log
- 22.4 Mineral Oil Calibration Log
- 22.5 Wet Chemistry Batch Summary

23.0 CHANGES FROM PREVIOUS REVISION NA

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22.1 Analytical Sequence

LCS
Sample
Sample
Sample
Sample
Sample
Sample
Sample
Sample
Sample
Sample dup.
LCS

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Laboratory Bench Sheet
Heat of Combustion - Method D-240

BTU_Template
Revision 0
May, 2005

[illegible]

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22.3 Benzoic Acid Bomb Calibration

Benzoic Acid Bomb Calibration

cal/gal of benzoic acid = 6318

Formula=	$\frac{\Delta T}{\text{Benzoic Acid (grams)}}$	=	result	$\frac{6318}{\text{result}}$	=	
Date						
5/16/2005	$\frac{2.58}{0.9527}$	=	2.708	=		2333.01
5/16/2005	$\frac{2.55}{0.899}$	=	2.836	=		2227.40
5/18/2005	$\frac{2.42}{0.994}$	=	2.435	=		2595.08
5/18/2005	$\frac{2.6}{0.909}$	=	2.860	=		2208.87
5/21/2005	$\frac{2.52}{0.9085}$	=	2.774	=		2277.74
5/21/2005	$\frac{2.61}{0.9108}$	=	2.866	=		2204.76
				average	=	2307.81
				New Calorimeter Constant	=	2308

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22.4 Mineral Oil Calibration

Mineral Oil Calibration

Calorimeter Constant= 2308.00 cal / ° C

Formula=
$$\frac{\Delta T \text{ (Bomb Calorimeter Constant)}}{\text{mineral oil (grams)}}$$

Date:

6/8/2005	$\frac{0.7}{0.1826}$	Mineral Oil Constant= 8847.75 cal/g	x 1.8 =	15925.96 BTU/lb

6/8/2005	$\frac{0.62}{0.1572}$	Mineral Oil Constant= 9102.80 cal/g	x 1.8 =	16385.04 BTU/lb

6/8/2005	$\frac{0.44}{0.1558}$	Mineral Oil Constant= 6518.10 cal/g	x 1.8 =	11732.58 BTU/lb

Average = 8156.22 cal/g Average = **14681.19 BTU/lb**

1.8 is factor derived from converting cal/g to BTU/lb

1 calorie= 0.0039693 btu
1 gram= 0.0022046 lb

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22.5 Wet Chemistry Batch Summary

WET CHEMISTRY BATCH SUMMARY

PARAMETER _____ METHOD _____ BATCH _____

COMMENTS	JOB NUMBER
WC Reporting Limit < STL Quant Limit	
WC Historical confirms within Hold Time	
WC Historical NO confirm & RE outside of HT	
WC Hold Time Exceedance-Dilution required	
WC Hold Time Exceedance-Instrument Failure	
WC Holding Time Exceedance by Date	
WC Holding Time Exceedance by Hours	
WC LCS within ERA limits outside internal	
WC LCS high recovery, sample ND	
WC MBLK hit but samples > 10X blank value	
WC RPD Exceedance for MS / SD	
WC Spike Failure HIGH MS only	
WC Spike Failure LOW MS only	
WC Spike Failure MS and SD	
WC BOD HT met- Oxygen depleted-RE out HT	
WC Carbonate Alkalinity, LCS/MBLK	
WC Reactivity Qualification	
WC TDS/Conductivity ratio outside of range	
WC TOX Breakthrough- no volume for redo	
WC TOX samples were centrifuged	
Other	

DILUTION CODES	REASON
002	Sample matrix effects
003	Excessive foaming
004	High levels of non-target compounds
008	High concentration of target analytes
009	Sample turbidity
010	Sample color
011	Insufficient volume for lower dilution
012	Sample viscosity
013	other

ICAL Compliant?	YES	NO	NA	IF NO, Why?	_____
LCS/CCV Compliant?	YES	NO	NA	IF NO, Why?	_____
CCB Compliant?	YES	NO	NA	IF NO, Why?	_____
RPD Compliant?	YES	NO	NA	IF NO, Why?	_____
ERA Compliant?	YES	NO	NA	IF NO, Why?	_____

NUMBER of REANALYSIS FOR THIS BATCH: _____

Analyst _____ Date _____

Time Critical Batch Review _____ Date _____

Secondary Review & Closure _____ Date _____

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TITLE: DENSITY

Supersedes: Revision 2

REVIEWED & APPROVED BY:	Signature	Date
Verl D. Preston, Quality Manager	<i>Verl D. Preston</i>	11/21/05
Christopher Spencer, Laboratory Director	<i>Chris Spencer</i>	11/21/05
Peggy Gray-Erdmann, Supervisor	<i>Peggy Gray Erdmann</i>	11/21/05

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1.0 IDENTIFICATION OF TEST METHODS

1.1 This method is taken from ASTM method D 1429-87.

2.0 APPLICABLE MATRIX

2.1 This method is applicable to waters or oils.

3.0 REPORTING LIMIT NA

4.0 SCOPE AND APPLICATION

4.1 Density is the ratio of the masses of equal volumes of a sample and distilled water.

5.0 SUMMARY OF TEST METHOD

5.1 A sample is weighed out and then divided by the actual amount used to determine the density of the sample.

6.0 DEFINITIONS

6.1 Standard definitions are in section 3.0 of the Laboratory Quality Manual.

7.0 INTERFERENCES NA

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8.0 SAFETY

Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual and this document.

8.1 SPECIFIC SAFETY CONCERNS OR REQUIREMENTS

None

8.2 PRIMARY MATERIALS USED

There are no materials used in this method that have a serious or significant hazard rating. A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

9.0 EQUIPMENT AND SUPPLIES

9.1 Analytical balance checked daily.

9.2 10ml disposable pipettes

9.3 100ml disposable beakers

10.0 REAGENTS AND STANDARDS

10.1 DiH₂O

11.0 SAMPLE COLLECTION, PRESERVATION, SHIPMENT AND STORAGE

11.1 Collect samples in a cleaned glass or plastic container and refrigerate at 4 degrees C.

12.0 QUALITY CONTROL

12.1 A duplicate should be run for every batch of twenty or fewer samples.

12.2 A Method Blank (MBLK) must be analyzed at the beginning and end of every analytical batch.

13.0 CALIBRATION AND STANDARDIZATION

13.1 Analytical balances are calibrated every 6 months and checked daily to ensure calibration is maintained.

14.0 PROCEDURE

14.1 Tare a clean 100ml disposable beaker.

14.2 Weigh out 10mls of the sample and record weight in logbook.

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15.0 CALCULATIONS

15.1

$$\text{Density} = \frac{\text{Weight of sample}}{\text{Volume used}}$$

16.0 METHOD PERFORMANCE NA

17.0 DATA ASSESSMENT AND ACCEPTANCE CRITERIA FOR QUALITY CONTROL MEASURES

17.1 Obtained MBLK values must be within 90-110% of the true value (1.0g/ml).

17.2 Sample duplicates are required to have a calculated RPD ≤ 20 .

18.0 CORRECTIVE ACTIONS FOR OUT-OF-CONTROL DATA

18.1 If acceptance criteria are not met, all related samples must be repeated.

19.0 CONTINGENCIES FOR HANDLING OUT-OF-CONTROL OR UNACCEPTABLE DATA

19.1 Job exception forms are filled out and submitted to the appropriate project manager for client input.

20.0 WASTE MANAGEMENT/ POLLUTION PREVENTION

All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

Waste Streams Produced by the Method

- Excess non-flammable samples. Aqueous samples are pH tested using wide-range pH paper. Acidic samples are discarded as the "A-waste" and alkaline samples as the "D-waste".
- Excess flammable samples and waste solvents: Solvent and oil samples as well as the LCS waste are discarded as the "C-waste" container.
- All spent soil samples are discarded in the soil collection tray for later disposal.

21.0 REFERENCE

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21.1 Annual Book of ASTM Standards, Volume 11.01 (1987), pages 292-298, method D 1429-87.

22.0 TABLES, DIAGRAMS, FLOWCHARTS AND VALIDATION DATA

22.1 Analytical run sequence

22.2 Analytical batch

22.3 Wet Chem. Batch summary sheet

23.0 CHANGES FROM PREVIOUS REVISION

23.1 Laboratory Director change, signature updated.

23.2 Updated attachment 22.3.

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22.1 Analytical run sequence

CCB
Sample
Sample
Sample
Sample
Sample
Sample
Sample
Sample
Sample
Sample Duplicate
CCB

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22.4 Wet Chemistry Batch Summary

WET CHEMISTRY BATCH SUMMARY

PARAMETER _____ METHOD _____ BATCH _____

COMMENTS	JOB NUMBER
WC Reporting Limit < STL Quant Limit	
WC Historical confirms within Hold Time	
WC Historical NO confirm & RE outside of HT	
WC Hold Time Exceedance-Dilution required	
WC Hold Time Exceedance-Instrument Failure	
WC Holding Time Exceedance by Date	
WC Holding Time Exceedance by Hours	
WC LCS within ERA limits outside internal	
WC LCS high recovery, sample ND	
WC MBLK hit but samples > 10X blank value	
WC RPD Exceedance for MS / SD	
WC Spike Failure HIGH MS only	
WC Spike Failure LOW MS only	
WC Spike Failure MS and SD	
WC BOD HT met- Oxygen depleted-RE out HT	
WC Carbonate Alkalinity, LCS/MBLK	
WC Reactivity Qualification	
WC TDS/Conductivity ratio outside of range	
WC TOX Breakthrough- no volume for redo	
WC TOX samples were centrifuged	
Other	

DILUTION CODES	REASON
002	Sample matrix effects
003	Excessive foaming
004	High levels of non-target compounds
008	High concentration of target analytes
009	Sample turbidity
010	Sample color
011	Insufficient volume for lower dilution
012	Sample viscosity
013	other

ICAL Compliant?	YES	NO	NA	IF NO, Why?	_____
LCS/CCV Compliant?	YES	NO	NA	IF NO, Why?	_____
CCB Compliant?	YES	NO	NA	IF NO, Why?	_____
RPD Compliant?	YES	NO	NA	IF NO, Why?	_____
ERA Compliant?	YES	NO	NA	IF NO, Why?	_____

NUMBER of REANALYSIS FOR THIS BATCH: _____

Analyst _____ Date _____

Time Critical Batch Review _____ Date _____

Secondary Review & Closure _____ Date _____

WC Summary Rev 4 / 5-2005

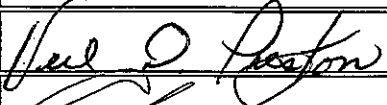
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TITLE: VISCOSITY

Supersedes: Revision 2

REVIEWED & APPROVED BY:	Signature	Date
Verl D. Preston, Quality Manager		12/2/05
Christopher Spencer, Laboratory Director		12/2/05
Peggy Gray-Erdmann, Supervisor		12/2/05

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1.0 IDENTIFICATION OF TEST METHODS

1.1 ASTM Method D2983-87, Brookfield Viscosity

2.0 APPLICABLE MATRIX

2.1 This method is valid for any viscous fluid.

3.0 REPORTING LIMIT N/A

4.0 SCOPE AND APPLICATION

4.1 This test method describes the use of the Brookfield viscometer for the determination of the low-shear-rate viscosity of fluids. The viscometer is able to measure over a number of ranges since, for a given drag, the actual viscosity is proportional to the spindle speed, and is also related to the size and shape of the spindle. This is accomplished by driving the spindle through a beryllium copper spring. The degree to which the spring is wound is proportional to the viscosity of the fluid for any given speed and spindle.

4.2 The test method uses the centipose (cP) as the unit of viscosity.

5.0 SUMMARY OF TEST METHOD

5.1 A viscous sample is allowed to warm to approximately 20C. Using a Brookfield viscometer, with various spindles, the Brookfield viscosity is measured.

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6.0 DEFINITIONS

- 6.1 Brookfield Viscosity – the viscosity determined by this test method. It is expressed in centipose. Its value may vary with the spindle speed (shear rate).
- 6.2 Standard definitions can be found in section 3.0 of the STL Buffalo Laboratory Quality Manual.

7.0 INTERFERENCES N/A

8.0 SAFETY

- 8.1 Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual and this document.

8.2 SPECIFIC SAFETY CONCERNS OR REQUIREMENTS

None

8.3 PRIMARY MATERIALS USED

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Acetone	Flammable	1000 ppm-TWA	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

9.0 EQUIPMENT AND SUPPLIES

- 9.1 Brookfield viscometer and stand
- 9.2 Various sized spindles - included with viscometer
- 9.3 Factor Finder – included with viscometer. This card is used to obtain the viscosity of the test material using the different speeds and spindles.
- 9.4 Test cell - A 600ml low form Griffin beaker

10.0 REAGENTS AND STANDARDS

- 10.1 Viscosity Standard – purchased from VWR Scientific or similar vendor.

11.0 SAMPLE COLLECTION, PRESERVATION, SHIPMENT AND STORAGE

- 11.1 Samples are collected in glass containers and shipped at 4C. Samples are stored under refrigeration at 4C. No further preservative is needed.

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12.0 QUALITY CONTROL

- 12.1 Laboratory Control Sample (LCS): The viscosity standard must be analyzed prior to the analysis of any samples. After every ten samples, the standard is analyzed again. The analysis is also ended with the viscosity standard.
- 12.2 Sample Duplicate (MD): A sample duplicate must be analyzed in every group of twenty samples. If less than twenty samples are to be analyzed, then one duplicate must also be analyzed.

13.0 CALIBRATION AND STANDARDIZATION

- 13.1 The instrument is calibrated to Bureau of Standards values on the basis of immersion in an infinite body with the spindle guard attached. They are accurate to within 1% of full scale.
- 13.2 The viscosity standard is used to check the calibration of the instrument.

14.0 PROCEDURE

- 14.1 Assemble the viscometer according to the instruction manual.
 Insert the spindle into the test material until the fluid's level is at the immersion groove cut in the spindle's shaft.
- 14.2 Level the viscometer using the bubble level that is on the top of the viscometer.
 Depress the clutch and turn on the motor. Release the clutch and allow the dial to rotate until the pointer stabilizes at a fixed point on the dial. It is possible to observe the pointer's position and stability at low speeds as the dial rotates, but at higher speeds it will be necessary to depress the clutch and snap the motor switch to stop the instrument with the pointer in view. The viscosity of the test material can be obtained by using the Factor Finder card which is supplied with the viscometer.

15.0 CALCULATIONS

- 15.1 **Relative Percent Difference (RPD):**

$$RPD = \frac{|x_1 - x_2|}{\left(\frac{x_1 + x_2}{2}\right)} \times 100$$

where:

- x_1 = analytical % recovery
 x_2 = replicate % recovery

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15.2 Percent Recovery for LCS:

$$\% \text{ Recovery (LCS)} = 100 \left(\frac{E}{C} \right)$$

where:

E = obtained (experimental) value
 C = true value

16.0 METHOD PERFORMANCE

- 16.1. Method Detection Limit: A valid method detection limit for each analyte of interest must be generated. 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. See STL SOP S-Q-003, "Method Detection Limit Studies," current revision, for further guidance. Current STL Buffalo MDLs are maintained the QA department and are easily viewed in the laboratory LIMs system.
- 16.2. A one-time initial demonstration of performance for each individual method for both soils and water matrices must be generated.
- 16.2.1. This requires quadruplicate analysis of a mid-level check standard containing all of the standard analytes for the method using the same procedures used to analyze samples, including sample preparation.
- 16.2.2. Calculate the average recovery and standard deviation of the recovery for each analyte of interest.
- 16.2.3. Compare these results with the acceptance criteria given in the Method or to laboratory historical limits (if available).
- 16.2.4. Repeat the test for any analyte that does not meet the acceptance criteria. Repeated failure for any analyte indicates the need for the laboratory to evaluate the analytical procedure and take corrective action.
- 16.3. Training Qualifications
- 16.3.1. The supervisor 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.
- 16.3.2. The following analyst validation information is maintained for this method in the laboratory QA files.
- 16.3.2.1. The analyst must complete the laboratory safety orientation training that includes, but is not limited to, chemicals, PPE requirements, and electrical safety.

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- 16.3.2.2. The analyst must read and understand this SOP.
- 16.3.2.3. The analyst must read and understand the Method used as reference for this SOP.
- 16.3.2.4. The analyst must complete a DOC or successfully analyze PT samples annually.
- 16.3.2.5. The analyst must complete the STL Quality Assurance Training.

17.0 DATA ASSESSMENT AND ACCEPTANCE CRITERIA FOR QUALITY CONTROL MEASURES

- 17.1 The viscosity standard must be read within 90-110% of the true value.
- 17.2 Sample duplicates must have an RPD of <20.0.

18.0 CORRECTIVE ACTIONS FOR OUT-OF-CONTROL DATA

- 18.1 Any quality control analysis that does not fall within the acceptable range must be repeated until it is acceptable. Any samples that are attached to that quality check must also be repeated.

19.0 CONTINGENCIES FOR HANDLING OUT-OF-CONTROL OR UNACCEPTABLE DATA

- 19.1 A Job Exception Form must be completed and filed with the Project Manager and QA Manager for any of the following conditions:
 - 19.1.1. Holding times exceeded
 - 19.1.2. Insufficient sample volume for re-analysis
 - 19.1.3. In the event of unknown positives or sample matrix which present the analyst with questionable data, the project manager shall be notified so the client may be contacted and involved in the decision process and course of action

20.0 WASTE MANAGEMENT / POLLUTION PREVENTION

- 20.1 All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."
- 20.2 Any sample that may contain hazardous or volatile components should be handled and tested in a ventilated fume hood.
- 20.3 Waste Streams Produced by the Method
 - Acidic samples are disposed of in the "A" waste.
 - Alkaline samples are disposed of in the "D" waste.

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- Oil samples are disposed of in the "C" waste.

21.0 REFERENCES

- 21.1 Annual Book of ASTM Standards, Vol. 05.01, method D2983-87.
- 21.2 Brookfield Synchro-lectric Viscometer Instruction Manual, Brookfield Engineering Laboratories Inc., July 1983.

22.0 TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

- 22.1 Analytical Sequence
- 22.2 Analytical Batch
- 22.3 Wet Chemistry Batch Summary

23.0 CHANGES FROM PREVIOUS REVISION

- 23.1 Laboratory Director change, signature updated.
- 23.2 Updated attachments 22.1, 22.2 and 22.3.
- 23.3 Updated sections 15.0, 16.0 and 19.0.
- 23.4 Removed section 8.4 and re-placed as section 20.3

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22.1 Analytical Sequence

LCS
Sample
Sample
Sample
Sample
Sample
Sample
Sample
Sample
Sample
Sample
LCS
Sample
Sample
Sample
Sample
Sample
Sample
Sample
Sample
Sample Duplicate
LCS

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22.2 Analytical Batch:

STL BUFFALO
VISCOSITY LOGBOOK
Logbook# A03-4-15

ASB14983 LVF

DATE	ANALYST	JOB #	SAMPLE I.D.	SPINDLE #	TIME (MIN.)	Temperature	SPEED (RPM)	READING	VISCOSITY (CENTIPOISE)	MODEL FACTOR	COMMENTS
7/29/05	Kg	ICV	47.9 CP	1	1	20.0	60	45.5	45.5	1	
		AB39	01	1	1			7.0	7.0	1	94.9.1
		AB40	01	1	1			6.0	6.0	1	
			02	1	1			6.5	6.5	1	
			04	1	1			2.0	7.0	1	
			05	1	1			7.0	7.0	1	
			06	1	1			6.5	6.5	1	
			06 dup	1	1			6.5	6.5	1	
		LCS	47.9 CP	1	1			6.5	6.5	1	
				1	1			46.0	46.0	1	94.0.1

Start Time 1715 Reviewed By _____
 End Time 1800 Date _____
 Solutions (CHA-98-F)
47.9 CP
84.1

000015

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22.3 Wet Chemistry Batch Summary

WET CHEMISTRY BATCH SUMMARY

PARAMETER _____ METHOD _____ BATCH _____

COMMENTS	JOB NUMBER
WC Reporting Limit < STL Quant Limit	
WC Historical confirms within Hold Time	
WC Historical NO confirm & RE outside of HT	
WC Hold Time Exceedance-Dilution required	
WC Hold Time Exceedance-Instrument Failure	
WC Holding Time Exceedance by Date	
WC Holding Time Exceedance by Hours	
WC LCS within ERA limits outside internal	
WC LCS high recovery, sample ND	
WC MBLK hit but samples > 10X blank value	
WC RPD Exceedance for MS / SD	
WC Spike Failure HIGH MS only	
WC Spike Failure LOW MS only	
WC Spike Failure MS and SD	
WC BOD HT met- Oxygen depleted-RE out HT	
WC Carbonate Alkalinity, LCS/MBLK	
WC Reactivity Qualification	
WC TDS/Conductivity ratio outside of range	
WC TOX Breakthrough- no volume for redo	
WC TOX samples were centrifuged	
Other	

DILUTION CODES	REASON
002	Sample matrix effects
003	Excessive foaming
004	High levels of non-target compounds
008	High concentration of target analytes
009	Sample turbidity
010	Sample color
011	Insufficient volume for lower dilution
012	Sample viscosity
013	other

ICAL Compliant? YES NO NA IF NO, Why? _____
 LCS/CCV Compliant? YES NO NA IF NO, Why? _____
 CCB Compliant? YES NO NA IF NO, Why? _____
 RPD Compliant? YES NO NA IF NO, Why? _____
 ERA Compliant? YES NO NA IF NO, Why? _____

NUMBER of REANALYSIS FOR THIS BATCH: _____

Analyst _____ Date _____

Time Critical Batch Review _____ Date _____

Secondary Review & Closure _____ Date _____

WC Summary Rev 4 / 5-2005

ATTACHMENT 3

LABORATORY REFERENCE DATA

STL Reference Data Summary

Target Analyte List: NC: OLM03.1/4.2 Volatile List

Matrix: WATER
Extraction: PURGE AND TRAP - 25 mL purge (Waters)
Method: Volatile Organics, GC/MS (8260B)
QC Program: MICHIGAN DEQ
Location: STL North Canton

Target List 4121					Check List 1630					Spike List 1631					
Compound	RL	Detection Units	MDL	Units	Run Date	Amt	Units	LCL	UCL	RPD	Amt	Units	LCL	UCL	RPD
Acetone	25	ug/L	0.74	ug/L	20040108	20	ug/L	22	200	95	10	ug/L	45	128	30
Benzene	1	ug/L	0.22	ug/L	20040210	20	ug/L	80	116	20	10	ug/L	78	118	20
Bromodichloromethane	1	ug/L	0.14	ug/L	20040210	20	ug/L	87	130	30	10	ug/L	80	146	30
Bromoform	1	ug/L	0.17	ug/L	20040114	20	ug/L	76	150	30	10	ug/L	58	176	30
Bromomethane	1	ug/L	0.36	ug/L	20040108	20	ug/L	64	129	30	10	ug/L	55	145	30
2-Butanone	25	ug/L	0.39	ug/L	20040217	20	ug/L	28	237	65	10	ug/L	71	123	30
Carbon disulfide	5	ug/L	0.28	ug/L	20040210	20	ug/L	73	139	30	10	ug/L	69	138	41
Carbon tetrachloride	1	ug/L	0.19	ug/L	20040210	20	ug/L	75	149	30	10	ug/L	63	176	30
Chlorobenzene	1	ug/L	0.2	ug/L	20040210	20	ug/L	76	117	20	10	ug/L	76	117	20
Dibromochloromethane	1	ug/L	0.19	ug/L	20040210	20	ug/L	81	138	30	10	ug/L	71	158	30
Chloroethane	1	ug/L	0.24	ug/L	20040108	20	ug/L	66	126	30	10	ug/L	59	142	30
Chloroform	1	ug/L	0.16	ug/L	20040210	20	ug/L	84	128	30	10	ug/L	83	141	30
Chloromethane	1	ug/L	0.14	ug/L	20040210	20	ug/L	48	123	30	10	ug/L	40	137	39
Cyclohexane	1	ug/L	0.12	ug/L	20040217			70	130	30			70	130	30
1,2-Dibromo-3-chloropropane	1	ug/L	0.28	ug/L	20040210			70	130	30			70	130	30
1,2-Dibromoethane	1	ug/L	0.24	ug/L	20040210			70	130	30			70	130	30
1,2-Dichlorobenzene	1	ug/L	0.2	ug/L	20040210			70	130	30			70	130	30
1,3-Dichlorobenzene	1	ug/L	0.18	ug/L	20040210			70	130	30			70	130	30
1,4-Dichlorobenzene	1	ug/L	0.22	ug/L	20040210			70	130	30			70	130	30
Dichlorodifluoromethane	1	ug/L	0.25	ug/L	20040210			70	130	30			70	130	30
1,1-Dichloroethane	1	ug/L	0.21	ug/L	20040210	20	ug/L	86	123	30	10	ug/L	88	127	30
1,2-Dichloroethane	1	ug/L	0.16	ug/L	20040210	20	ug/L	79	136	30	10	ug/L	71	160	30
cis-1,2-Dichloroethene	1	ug/L	0.21	ug/L	20040210	20	ug/L	85	113	30	10	ug/L	87	114	30
trans-1,2-Dichloroethene	1	ug/L	0.16	ug/L	20040217	20	ug/L	80	120	30	10	ug/L	85	116	30
1,1-Dichloroethene	1	ug/L	0.18	ug/L	20040210	20	ug/L	63	130	20	10	ug/L	62	130	20
1,2-Dichloropropane	1	ug/L	0.15	ug/L	20040114	20	ug/L	82	115	30	10	ug/L	87	114	30
cis-1,3-Dichloropropene	1	ug/L	0.12	ug/L	20040114	20	ug/L	84	130	30	10	ug/L	82	130	30
trans-1,3-Dichloropropene	1	ug/L	0.17	ug/L	20040210	20	ug/L	84	130	30	10	ug/L	73	147	30
Ethylbenzene	1	ug/L	0.19	ug/L	20040114	20	ug/L	86	116	30	10	ug/L	86	132	30
2-Hexanone	50	ug/L	0.35	ug/L	20040108	20	ug/L	35	200	52	10	ug/L	81	128	30
Isopropylbenzene	5	ug/L	0.15	ug/L	20040116			70	130	30			70	130	30
Methyl acetate	10	ug/L	0.52	ug/L	20040217			70	130	30			70	130	30
Methylcyclohexane	1	ug/L	0.5	ug/L	20040210			70	130	30			70	130	30
Methylene chloride	5	ug/L	0.19	ug/L	20040210	20	ug/L	78	118	30	10	ug/L	82	115	30
4-Methyl-2-pentanone	50	ug/L	0.32	ug/L	20040217	20	ug/L	78	141	32	10	ug/L	82	135	30
Methyl tert-butyl ether	5	ug/L	0.18	ug/L	20040210			70	130	30			70	130	30
Styrene	1	ug/L	0.13	ug/L	20040114	20	ug/L	85	117	30	10	ug/L	83	120	30

Target Analyte List: NC: OLM03.1/4.2 Volatile List

Matrix: WATER
 Extraction: PURGE AND TRAP - 25 mL purge (Waters)
 Method: Volatile Organics, GC/MS (8260B)
 QC Program: MICHIGAN DEQ
 Location: STL North Canton

Target List 4121					Check List 1630					Spike List 1631					
Compound	RL	Units	MDL	Units	Run Date	Amt	Units	LCL	UCL	RPD	Amt	Units	LCL	UCL	RPD
1,1,2,2-Tetrachloroethane	1	ug/L	0.22	ug/L	20040210	20	ug/L	85	118	30	10	ug/L	88	116	30
Tetrachloroethane	1	ug/L	0.19	ug/L	20040114	20	ug/L	88	113	30	10	ug/L	85	121	30
Toluene	1	ug/L	0.17	ug/L	20040210	20	ug/L	74	119	20	10	ug/L	70	119	20
1,2,4-Trichlorobenzene	5	ug/L	0.19	ug/L	20040114			70	130	30			70	130	30
1,1,1-Trichloroethane	1	ug/L	0.21	ug/L	20040210	20	ug/L	78	140	30	10	ug/L	71	162	30
1,1,2-Trichloroethane	1	ug/L	0.22	ug/L	20040114	20	ug/L	83	122	30	10	ug/L	86	129	30
Trichloroethene	1	ug/L	0.28	ug/L	20040210	20	ug/L	75	122	20	10	ug/L	62	130	20
Trichlorofluoromethane	1	ug/L	0.16	ug/L	20040114			70	130	30			70	130	30
1,1,2-Trichloro-1,2,2-trifluoroethane	1	ug/L	0.26	ug/L	20040210			70	130	30			70	130	30
Vinyl chloride	1	ug/L	0.15	ug/L	20050225	20	ug/L	61	120	30	10	ug/L	88	126	30
Xylenes (total)	2	ug/L	0.44	ug/L	20040210	60	ug/L	87	116	30	30	ug/L	89	121	30
4-Bromofluorobenzene						10	ug/L	74	116	0	10	ug/L	74	116	0
1,2-Dichloroethane-d4						10	ug/L	61	128	0	10	ug/L	61	128	0
Toluene-d8						10	ug/L	76	110	0	10	ug/L	76	110	0
Dibromofluoromethane						10	ug/L	73	122	0	10	ug/L	73	122	0

STL Reference Data Summary

Target Analyte List: NC: OLM03.1/4.2 Semivolatile List

Matrix: WATER
Extraction: LIQ/LIQ, CONT (B/N/A) - Base->Acid
Method: Base/Neutrals and Acids (82/70C)
QC Program: MICHIGAN DEQ
Location: STL North Canton

Target List 4122				Check List 1114				Spike List 1115			
Compound	RL	Detection Units	MDL	Units	Run Date	Amt	Units	LCL UCL RPD	Amt	Units	LCL UCL RPD
Acenaphthene	5	ug/L	0.054	ug/L	20050316	50	ug/L	40 110 30	50	ug/L	36 110 30
Acenaphthylene	5	ug/L	0.054	ug/L	20050316	50	ug/L	43 110 30	50	ug/L	39 110 30
Acetophenone	5	ug/L	0.55	ug/L	20050217						
Anthracene	5	ug/L	0.054	ug/L	20050131	50	ug/L	54 114 30	50	ug/L	46 110 30
Atrazine	5	ug/L	0.65	ug/L	20050316						
Benzaldehyde	10	ug/L	0.75	ug/L	20050316						
Benzo(a)anthracene	1	ug/L	0.052	ug/L	20050316	50	ug/L	55 115 30	50	ug/L	52 110 30
Benzo(b)fluoranthene	2	ug/L	0.049	ug/L	20050131	50	ug/L	43 122 30	50	ug/L	33 114 30
Benzo(k)fluoranthene	5	ug/L	0.049	ug/L	20050201	50	ug/L	43 124 30	50	ug/L	32 121 30
Benzo(ghi)perylene	5	ug/L	0.053	ug/L	20050201	50	ug/L	45 120 30	50	ug/L	34 116 30
Benzo(a)pyrene	2	ug/L	0.048	ug/L	20050316	50	ug/L	43 116 30	50	ug/L	33 110 30
1,1'-Biphenyl	10	ug/L	0.55	ug/L	20050316						
bis(2-Chloroethoxy)methane	5	ug/L	0.49	ug/L	20050316	50	ug/L	39 110 30	50	ug/L	35 110 30
bis(2-Chloroethyl) ether	4	ug/L	0.088	ug/L	20050131	50	ug/L	34 113 30	50	ug/L	27 110 30
bis(2-Ethylhexyl) phthalate	5	ug/L	0.88	ug/L	20050216	50	ug/L	36 163 30	50	ug/L	40 140 30
4-Bromophenyl phenyl ether	5	ug/L	0.52	ug/L	20050316	50	ug/L	51 114 30	50	ug/L	42 113 30
Butyl benzyl phthalate	5	ug/L	0.51	ug/L	20050217	50	ug/L	53 126 30	50	ug/L	51 121 30
Caprolactam	10	ug/L	0.61	ug/L	20050216						
Carbazole	10	ug/L	0.54	ug/L	20050217	50	ug/L	53 120 30	50	ug/L	49 114 30
4-Chloroaniline	20	ug/L	0.56	ug/L	20050316	50	ug/L	10 110 30	50	ug/L	10 110 30
4-Chloro-3-methylphenol	5	ug/L	0.41	ug/L	20050217	50	ug/L	39 110 30	50	ug/L	33 110 30
2-Chloronaphthalene	5	ug/L	0.62	ug/L	20050316	50	ug/L	39 110 30	50	ug/L	34 110 30
2-Chlorophenol	5	ug/L	1.1	ug/L	20050316	50	ug/L	27 110 30	50	ug/L	26 110 30
4-Chlorophenyl phenyl ether	5	ug/L	0.55	ug/L	20050316	50	ug/L	50 115 30	50	ug/L	43 113 30
Chrysene	5	ug/L	0.048	ug/L	20050316	50	ug/L	55 115 30	50	ug/L	52 111 30
Dibenz(a,h)anthracene	2	ug/L	0.039	ug/L	20050316	50	ug/L	46 122 30	50	ug/L	35 118 30
Dibenzofuran	5	ug/L	0.54	ug/L	20050316	50	ug/L	46 111 30	50	ug/L	41 110 30
Di-n-butyl phthalate	5	ug/L	0.61	ug/L	20050217	50	ug/L	55 122 30	50	ug/L	50 117 30
3,3'-Dichlorobenzidine	4	ug/L	0.48	ug/L	20050316	50	ug/L	19 110 30	50	ug/L	10 110 30
2,4-Dichlorophenol	10	ug/L	1.1	ug/L	20050316	50	ug/L	33 110 30	50	ug/L	30 110 30
Diethyl phthalate	5	ug/L	0.63	ug/L	20050316	50	ug/L	33 134 30	50	ug/L	33 130 30
2,4-Dimethylphenol	5	ug/L	0.56	ug/L	20050316	50	ug/L	12 110 30	50	ug/L	11 110 30
Dimethyl phthalate	5	ug/L	0.44	ug/L	20050217	50	ug/L	15 143 30	50	ug/L	36 124 30
4,6-Dinitro-2-methylphenol	20	ug/L	0.27	ug/L	20050217	50	ug/L	28 112 30	50	ug/L	25 110 30
2,4-Dinitrophenol	20	ug/L	3.5	ug/L	20050218	50	ug/L	17 112 30	50	ug/L	11 119 30
2,4-Dinitrotoluene	5	ug/L	0.4	ug/L	20050316	50	ug/L	52 123 30	50	ug/L	46 119 30
2,6-Dinitrotoluene	5	ug/L	0.47	ug/L	20050316	50	ug/L	52 119 30	50	ug/L	48 115 30

Target Analyte List: NC: OLM03.1/4.2 Semivolatile List

Matrix: WATER
 Extraction: LIQ/LIQ, CONT (B/N/A) - Base->Acid
 Method: Base/Neutrals and Acids (8270C)
 QC Program: MICHIGAN DEQ
 Location: STL North Canton

Target List 4122					Check List 1114					Spike List 1115					
Compound	RL	Units	MDL	Units	Run Date	Amt	Units	LCL	UCL	RPD	Amt	Units	LCL	UCL	RPD
Di-n-octyl phthalate	5	ug/L	0.39	ug/L	20050217	50	ug/L	44	128	30	50	ug/L	36	124	30
Fluoranthene	5	ug/L	0.036	ug/L	20050316	50	ug/L	54	122	30	50	ug/L	53	111	30
Fluorene	5	ug/L	0.043	ug/L	20050316	50	ug/L	47	112	30	50	ug/L	43	110	30
Hexachlorobenzene	5	ug/L	0.065	ug/L	20050131	50	ug/L	51	112	30	50	ug/L	40	113	30
Hexachlorobutadiene	5	ug/L	0.51	ug/L	20050316	50	ug/L	13	110	30	50	ug/L	14	110	30
Hexachlorocyclopentadiene	5	ug/L	0.74	ug/L	20050316	50	ug/L	10	110	30	50	ug/L	10	110	30
Hexachloroethane	5	ug/L	0.58	ug/L	20050316	50	ug/L	12	110	30	50	ug/L	10	110	30
Indeno(1,2,3-cd)pyrene	2	ug/L	0.065	ug/L	20050131	50	ug/L	46	121	30	50	ug/L	36	116	30
Isophorone	5	ug/L	0.5	ug/L	20050316	50	ug/L	44	128	30	50	ug/L	34	125	30
2-Methylnaphthalene	5	ug/L	0.061	ug/L	20050316	50	ug/L	35	110	30	50	ug/L	35	110	30
2-Methylphenol	5	ug/L	0.56	ug/L	20050316	50	ug/L	30	110	30	50	ug/L	26	110	30
4-Methylphenol	5	ug/L	0.64	ug/L	20050316	50	ug/L	32	110	30	50	ug/L	25	110	30
Naphthalene	5	ug/L	0.069	ug/L	20050316	50	ug/L	31	110	30	50	ug/L	32	110	30
2-Nitroaniline	20	ug/L	0.43	ug/L	20050316	50	ug/L	43	130	30	50	ug/L	31	129	30
3-Nitroaniline	20	ug/L	0.67	ug/L	20050316	50	ug/L	45	116	30	50	ug/L	23	112	30
4-Nitroaniline	20	ug/L	0.47	ug/L	20050217	50	ug/L	45	120	30	50	ug/L	26	115	30
Nitrobenzene	4	ug/L	0.053	ug/L	20050131	50	ug/L	37	115	30	50	ug/L	26	118	30
2-Nitrophenol	5	ug/L	1.3	ug/L	20050316	50	ug/L	29	110	30	50	ug/L	30	110	30
4-Nitrophenol	20	ug/L	0.63	ug/L	20050316	50	ug/L	12	130	30	50	ug/L	13	127	30
N-Nitrosodiphenylamine	5	ug/L	0.46	ug/L	20050217	50	ug/L	53	113	30	50	ug/L	28	118	30
N-Nitrosodi-n-propylamine	5	ug/L	0.53	ug/L	20050316	50	ug/L	37	121	30	50	ug/L	25	119	30
2,2'-oxybis(1-Chloropropane)	5	ug/L	0.52	ug/L	20050316										
Pentachlorophenol	20	ug/L	0.48	ug/L	20050316	50	ug/L	26	110	30	50	ug/L	23	110	30
Phenanthrene	5	ug/L	0.087	ug/L	20050131	50	ug/L	52	114	30	50	ug/L	47	110	30
Phenol	5	ug/L	0.96	ug/L	20050316	50	ug/L	14	112	30	50	ug/L	16	110	30
Pyrene	5	ug/L	0.048	ug/L	20050316	50	ug/L	55	120	30	50	ug/L	54	115	30
2,4,5-Trichlorophenol	5	ug/L	0.96	ug/L	20050217	50	ug/L	39	110	30	50	ug/L	36	110	30
2,4,6-Trichlorophenol	4	ug/L	1.4	ug/L	20050316	50	ug/L	35	110	30	50	ug/L	34	110	30
2-Fluorobiphenyl						50	ug/L	28	110	0	50	ug/L	28	110	0
2-Fluorophenol						75	ug/L	10	110	0	75	ug/L	10	110	0
2,4,6-Tribromophenol						75	ug/L	22	120	0	75	ug/L	22	120	0
Nitrobenzene-d5						50	ug/L	27	111	0	50	ug/L	27	111	0
Phenol-d5						75	ug/L	10	110	0	75	ug/L	10	110	0
Terphenyl-d14						50	ug/L	37	119	0	50	ug/L	37	119	0

STL Reference Data Summary

Target Analyte List: Q: TCLP MSSemi Standard List

Matrix: WATER
 Extraction: TCLP(1311) -> LIQ/LIQ, SEP FUNNEL - Acid->Base
 Method: Base/Neutrals and Acids (8270C)
 QC Program: STANDARD TEST SET
 Location: STL North Canton

Target List 2105						Check List 1116						Spike List 1117					
Compound	RL	Detection Limits		Units	Run Date	Amt	Units	LCL	UCL	RPD	Amt	Units	LCL	UCL	RPD		
m-Cresol & p-Cresol	0.04	mg/L	0.75	ug/L	20040228	0.4000	mg/L	28	110	30	0.400	mg/L	46	109	32		
1,4-Dichlorobenzene	0.004	mg/L	0.52	ug/L	20050217	0.2000	mg/L	13	110	30	0.200	mg/L	18	110	36		
2,4-Dinitrotoluene	0.02	mg/L	0.4	ug/L	20050316	0.2000	mg/L	45	119	30	0.200	mg/L	31	131	32		
Hexachlorobenzene	0.02	mg/L	0.065	ug/L	20050131	0.2000	mg/L	46	112	30	0.200	mg/L	36	132	22		
Hexachlorobutadiene	0.02	mg/L	0.51	ug/L	20050316	0.2000	mg/L	10	110	30	0.200	mg/L	18	116	32		
Hexachloroethane	0.02	mg/L	0.58	ug/L	20050316	0.2000	mg/L	10	110	30	0.200	mg/L	18	110	33		
o-Cresol	0.004	mg/L	0.56	ug/L	20050316	0.2000	mg/L	23	110	30	0.200	mg/L	33	115	31		
Nitrobenzene	0.004	mg/L	0.053	ug/L	20050131	0.2000	mg/L	29	118	30	0.200	mg/L	19	211	59		
Pentachlorophenol	0.04	mg/L	0.48	ug/L	20050316	0.2000	mg/L	10	116	30	0.200	mg/L	10	140	56		
Pyridine	0.02	mg/L	0.78	ug/L	20050316	0.2000	mg/L	15	110	30	0.200	mg/L	10	148	65		
2,4,5-Trichlorophenol	0.02	mg/L	0.96	ug/L	20050217	0.2000	mg/L	36	110	30	0.200	mg/L	24	143	22		
2,4,6-Trichlorophenol	0.02	mg/L															
2-Fluorobiphenyl		mg/L	1.4	ug/L	20050316	0.2000	mg/L	32	110	30	0.200	mg/L	36	135	27		
2-Fluorophenol								20	110	0			20	110	0		
2,4,6-Tribromophenol								10	110	0			10	110	0		
Nitrobenzene-d5								28	110	0			28	110	0		
Phenol-d5								27	110	0			27	110	0		
								10	110	0			10	110	0		
Terphenyl-d14								44	110	0			44	110	0		

STL Reference Data Summary

Target Analyte List: Q: Aroclors Only Standard List

Matrix: WATER
 Extraction: LIQ/LIQ, CONT w/ACID STRIP (PCB) - Nominal
 Method: PCBs (8082)
 QC Program: MICHIGAN DEQ
 Location: STL North Canton

Target List 2207						Check List 928						Spike List 929					
Compound	RL	Detection Limits		Run Date	Amt			Amt									
		Units	MDL		Units	Units	LCL	UCL	RPD	Units	Units	LCL	UCL	RPD			
Aroclor 1016	0.2	ug/L	0.044	ug/L	20050112	10	ug/L	50	115	30	10	ug/L	10	200	30		
Aroclor 1221	0.2	ug/L	0.045	ug/L	20050112												
Aroclor 1232	0.2	ug/L	0.073	ug/L	20050112												
Aroclor 1242	0.2	ug/L	0.06	ug/L	20050112												
Aroclor 1248	0.2	ug/L	0.061	ug/L	20000229												
Aroclor 1254	0.2	ug/L	0.032	ug/L	20050112												
Aroclor 1260	0.2	ug/L	0.038	ug/L	20050112	10	ug/L	45	112	30	10	ug/L	10	150	30		
Decachlorobiphenyl						0.2	ug/L	10	110	0	0.2	ug/L	10	110	0		
Tetrachloro-m-xylene						0.2	ug/L	35	130	0	0.2	ug/L	35	130	0		

STL Reference Data Summary

Target Analyte List: All Analytes

Matrix: WATER
 Extraction: EXTRACTION, WATER/GAS (MANUAL) -> EQUILIBRATION
 Method: Dissolved Gases in Water - preserved
 QC Program: STANDARD TEST SET
 Location: STL North Canton

Analyte List Compound	RL	Detection Limits			Run Date	Check List 961			Amt	Spike List 961		
		Units	MDL	Units		Amt	Units	LCL UCL RPD		Amt	Units	LCL UCL RPD
Acetylene	1	ug/L	0.19	ug/L	20050315			70 130 30				70 130 30
Ethane	0.5	ug/L	0.16	ug/L	20050315			74 138 30				74 138 30
Ethene	0.5	ug/L	0.16	ug/L	20050315			73 140 30				73 140 30
Methane	0.5	ug/L	0.11	ug/L	20050315			75 127 30				75 127 30

STL Reference Data Summary

Target Analyte List: NC: Michigan 10 Metals (Trace Water)

Matrix: WATER
 Extraction: METALS, TOTAL RECOVERABLE
 Method: Inductively Coupled Plasma (6010B Trace)
 QC Program: MICHIGAN DEQ
 Location: STL North Canton

Target List 4139		Detection Limits		Run Date	Check List 906			Spike List 907		
Compound	RL	Units	MDL		Amt	Units	LCL UCL RPD	Amt	Units	LCL UCL RPD
Arsenic	10	ug/L	4.3	20050128	2000	ug/L	80 120 20	2000	ug/L	75 125 20
Barium	100	ug/L	3.2	20050127	2000	ug/L	80 120 20	2000	ug/L	75 125 20
Chromium	5	ug/L	1.6	20050127	200	ug/L	80 120 20	200	ug/L	75 125 20
Copper	25	ug/L	1.8	20050128	250	ug/L	80 120 20	250	ug/L	75 125 20
Lead	3	ug/L	1.7	20050127	500	ug/L	80 120 20	500	ug/L	75 125 20
Selenium	5	ug/L	2.4	20050127	2000	ug/L	80 120 20	2000	ug/L	75 125 20

STL Reference Data Summary

Target Analyte List: NC: Michigan 10 Metals (ICPMS Water)

Matrix: WATER
 Extraction: METALS, TOTAL - Soils
 Method: Inductively Coupled Plasma Mass Spectrometry(6020)
 QC Program: MICHIGAN DEQ
 Location: STL North Canton

Target List 4138 Compound	Detection Limits			Run Date	Check List 932			Spike List 933		
	RL	Units	MDL		Amt	Units	LCL UCL RPD	Amt	Units	LCL UCL RPD
Cadmium	0.5	ug/L	0.086	20050112	100	ug/L	82 116 20	100	ug/L	70 130 20
Silver	0.5	ug/L	0.047	20050112	100	ug/L	70 115 20	100	ug/L	70 130 20
Zinc	10	ug/L	2.3	20050112	100	ug/L	90 127 20	100	ug/L	70 130 20

STL Reference Data Summary

Matrix:	WATER
Extraction:	METALS, FILTERED (DISS) -> TOTAL RECOVERABLE
Method:	Inductively Coupled Plasma (6010B Trace)
QC Program:	MICHIGAN DEQ
Location:	STL North Canton

Target Analyte List: NC: Michigan 10 Metals (Trace Water)

Target List 4139				Check List 906						Spike List 907					
Compound	RL	Detection Limits		Units	Run Date	Amt			Amt						
		Units	MDL			Units	LCL	UCL	RPD	Units	LCL	UCL	RPD		
Arsenic	10	ug/L	4.3	ug/L	20050128	2000	ug/L	80	120	20	2000	ug/L	75	125	20
Barium	100	ug/L	3.2	ug/L	20050127	2000	ug/L	80	120	20	2000	ug/L	75	125	20
Chromium	5	ug/L	1.6	ug/L	20050127	200	ug/L	80	120	20	200	ug/L	75	125	20
Copper	25	ug/L	1.8	ug/L	20050128	250	ug/L	80	120	20	250	ug/L	75	125	20
Lead	3	ug/L	1.7	ug/L	20050127	500	ug/L	80	120	20	500	ug/L	75	125	20
Selenium	5	ug/L	2.4	ug/L	20050127	2000	ug/L	80	120	20	2000	ug/L	75	125	20

STL Reference Data Summary

Target Analyte List: NC: OLM 4.2 TCL + 2-Methylnaphthlene (Michigan)

Matrix: SOLID
Extraction: PURGE AND TRAP - Field MEOH Ext. (Solids or Wastes)
Method: Volatile Organics, GC/MS (8260B)
QC Program: MICHIGAN DEQ
Location: STL North Canton

Target List 4125				Detection Limits				Check List 924				Spike List 925			
Compound	RL	Units	MDL	Units	Run Date	Amt	Units	LCL	UCL	RPD	Amt	Units	LCL	UCL	RPD
Acetone	600	ug/kg	99	ug/kg	20040223	20	ug/kg	58	130	30	50	ug/kg	10	200	66
Benzene	40	ug/kg	6.4	ug/kg	20040223	20	ug/kg	75	129	20	50	ug/kg	55	138	20
Bromodichloromethane	80	ug/kg	12	ug/kg	20040223	20	ug/kg	72	125	30	50	ug/kg	47	131	51
Bromoform	80	ug/kg	13	ug/kg	20040224	20	ug/kg	43	149	30	50	ug/kg	26	141	64
Bromomethane	200	ug/kg	25	ug/kg	20040223	20	ug/kg	24	152	30	50	ug/kg	15	152	72
2-Butanone	600	ug/kg	49	ug/kg	20040223	20	ug/kg	27	200	46	50	ug/kg	21	195	60
Carbon disulfide	200	ug/kg	20	ug/kg	20040224	20	ug/kg	50	137	30	50	ug/kg	27	149	73
Carbon tetrachloride	40	ug/kg	12	ug/kg	20040223	20	ug/kg	57	137	30	50	ug/kg	32	143	68
Chlorobenzene	40	ug/kg	6.3	ug/kg	20040223	20	ug/kg	75	127	22	50	ug/kg	49	139	22
Dibromochloromethane	40	ug/kg	6.9	ug/kg	20040223	20	ug/kg	49	135	30	50	ug/kg	44	135	61
Chloroethane	200	ug/kg	65	ug/kg	20040224	20	ug/kg	31	144	30	50	ug/kg	32	140	66
Chloroform	40	ug/kg	12	ug/kg	20040223	40	ug/kg	73	115	30	50	ug/kg	59	128	46
Chloromethane	200	ug/kg	5.2	ug/kg	20040223	20	ug/kg	15	136	30	50	ug/kg	28	130	81
Cyclohexane	960	ug/kg	7.7	ug/kg	20040223										
1,2-Dibromo-3-chloropropane	200	ug/kg	60	ug/kg	20040224										
1,2-Dibromoethane	200	ug/kg	9.9	ug/kg	20040223										
1,2-Dichlorobenzene	80	ug/kg	17	ug/kg	20040224										
1,3-Dichlorobenzene	80	ug/kg	7.2	ug/kg	20040223										
1,4-Dichlorobenzene	80	ug/kg	7.9	ug/kg	20040223										
Dichlorodifluoromethane	80	ug/kg	5.4	ug/kg	20040223										
1,1-Dichloroethane	40	ug/kg	7.3	ug/kg	20040223	20	ug/kg	77	119	30	50	ug/kg	56	130	54
1,2-Dichloroethane	40	ug/kg	9.3	ug/kg	20040223	20	ug/kg	78	121	30	50	ug/kg	56	126	38
cis-1,2-Dichloroethane	40	ug/kg	14	ug/kg	20040223	20	ug/kg	77	114	30	50	ug/kg	48	127	52
trans-1,2-Dichloroethene	40	ug/kg	11	ug/kg	20040223	20	ug/kg	68	117	30	50	ug/kg	47	127	58
1,1-Dichloroethene	40	ug/kg	8.3	ug/kg	20040223	20	ug/kg	55	142	27	50	ug/kg	43	147	27
1,2-Dichloropropane	40	ug/kg	7.4	ug/kg	20040223	20	ug/kg	78	116	30	50	ug/kg	54	125	43
cis-1,3-Dichloropropene	40	ug/kg	5.5	ug/kg	20040223	20	ug/kg	71	125	30	50	ug/kg	30	138	49
trans-1,3-Dichloropropene	40	ug/kg	5.4	ug/kg	20040223	20	ug/kg	67	125	30	50	ug/kg	34	134	57
Ethylbenzene	40	ug/kg	6.8	ug/kg	20040223	20	ug/kg	79	114	30	50	ug/kg	36	133	72
2-Hexanone	2000	ug/kg	24	ug/kg	20040223	20	ug/kg	29	200	41	50	ug/kg	20	190	70
Isopropylbenzene	200	ug/kg	5.1	ug/kg	20040223										
Methyl acetate	960	ug/kg	52	ug/kg	20040223										
Methylcyclohexane	960	ug/kg	5.7	ug/kg	20040223										
Methylene chloride	200	ug/kg	99	ug/kg	20040224	20	ug/kg	58	130	30	50	ug/kg	45	129	49
2-Methylnaphthalene	264	ug/kg	13	ug/kg	20020213										
4-Methyl-2-pentanone	2000	ug/kg	11	ug/kg	20040223	20	ug/kg	68	142	60	50	ug/kg	42	143	60
Methyl tert-butyl ether	200	ug/kg	10	ug/kg	20040223			70	130	30			70	130	30

Target Analyte List: NC: OLM 4.2 TCL + 2-Methylnaphthlene (Michigan)

Matrix: SOLID
Extraction: PURGE AND TRAP - Field MEOH Ext. (Solids or Wastes)
Method: Volatile Organics, GC/MS (8260B)
QC Program: MICHIGAN DEQ
Location: STL North Canton

Target List 4125				Detection Limits						Check List 924						Spike List 925					
Compound	RL	Units	MDL	Units	Run Date	Amt	Units	LCL	UCL	RPD	Amt	Units	LCL	UCL	RPD						
Styrene	40	ug/kg	28	ug/kg	20040224	20	ug/kg	80	114	30	50	ug/kg	23	136	65						
1,1,2,2-Tetrachloroethane	80	ug/kg	8.2	ug/kg	20040223	20	ug/kg	70	133	30	50	ug/kg	33	162	90						
Tetrachloroethane	40	ug/kg	9	ug/kg	20040223	20	ug/kg	72	120	30	50	ug/kg	31	137	81						
Toluene	80	ug/kg	9.1	ug/kg	20040223	20	ug/kg	71	130	24	50	ug/kg	46	147	24						
1,2,4-Trichlorobenzene	200	ug/kg	12	ug/kg	20040223																
1,1,1-Trichloroethane	40	ug/kg	9.5	ug/kg	20040223	20	ug/kg	67	123	30	50	ug/kg	48	132	57						
1,1,2-Trichloroethane	40	ug/kg	9.9	ug/kg	20040223	20	ug/kg	82	116	30	50	ug/kg	58	128	52						
Trichloroethene	40	ug/kg	12	ug/kg	20040223	20	ug/kg	70	131	23	50	ug/kg	46	143	23						
Trichlorofluoromethane	80	ug/kg	8.3	ug/kg	20040223																
1,1,2-Trichloro-1,2,2-trifluoroethane	200	ug/kg	10	ug/kg	20040223																
Vinyl chloride	80	ug/kg	16	ug/kg	20040224	20	ug/kg	24	152	30	50	ug/kg	30	136	80						
4-Bromofluorobenzene						50	ug/kg	47	158	0	50	ug/kg	47	158	0						
1,2-Dichloroethane-d4						50	ug/kg	61	130	0	50	ug/kg	61	130	0						
Toluene-d8						50	ug/kg	60	143	0	50	ug/kg	60	143	0						
Dibromofluoromethane						50	ug/kg	59	138	0	50	ug/kg	59	138	0						

STL Reference Data Summary

Target Analyte List: NC: OLM03.1/4.2 Volatile List

Matrix: SOLID
Extraction: PURGE AND TRAP - Field MECH Ext. (Solids or Wastes)
Method: Volatile Organics, GC/MS (8260B)
QC Program: MICHIGAN DEQ
Location: STL North Canton

Compound	RL	Detection Limits			Run Date	Check List 924				Spike List 925			
		Units	MDL	Units		Amt	Units	LCL UCL	RPD	Amt	Units	LCL UCL	RPD
Acetone	600	ug/kg	99	ug/kg	20040223	20	ug/kg	58 130	30	50	ug/kg	10 200	66
Benzene	40	ug/kg	6.4	ug/kg	20040223	20	ug/kg	75 129	20	50	ug/kg	55 138	20
Bromodichloromethane	80	ug/kg	12	ug/kg	20040223	20	ug/kg	72 125	30	50	ug/kg	47 131	51
Bromoform	80	ug/kg	13	ug/kg	20040224	20	ug/kg	43 149	30	50	ug/kg	26 141	64
Bromomethane	200	ug/kg	25	ug/kg	20040223	20	ug/kg	24 152	30	50	ug/kg	15 152	72
2-Butanone	600	ug/kg	49	ug/kg	20040223	20	ug/kg	27 200	46	50	ug/kg	21 195	60
Carbon disulfide	200	ug/kg	20	ug/kg	20040224	20	ug/kg	50 137	30	50	ug/kg	27 149	73
Carbon tetrachloride	40	ug/kg	12	ug/kg	20040223	20	ug/kg	57 137	30	50	ug/kg	32 143	68
Chlorobenzene	40	ug/kg	6.3	ug/kg	20040223	20	ug/kg	75 127	22	50	ug/kg	49 139	22
Dibromochloromethane	40	ug/kg	6.9	ug/kg	20040223	20	ug/kg	49 135	30	50	ug/kg	44 135	61
Chloroethane	200	ug/kg	65	ug/kg	20040224	20	ug/kg	31 144	30	50	ug/kg	32 140	66
Chloroform	40	ug/kg	12	ug/kg	20040223	40	ug/kg	73 115	30	50	ug/kg	59 128	46
Chloromethane	200	ug/kg	5.2	ug/kg	20040223	20	ug/kg	15 136	30	50	ug/kg	28 130	81
Cyclohexane	960	ug/kg	7.7	ug/kg	20040223								
1,2-Dibromo-3-chloropropane	200	ug/kg	60	ug/kg	20040224								
1,2-Dibromoethane	200	ug/kg	9.9	ug/kg	20040223								
1,2-Dichlorobenzene	80	ug/kg	17	ug/kg	20040224								
1,3-Dichlorobenzene	80	ug/kg	7.2	ug/kg	20040223								
1,4-Dichlorobenzene	80	ug/kg	7.9	ug/kg	20040223								
Dichlorodifluoromethane	80	ug/kg	5.4	ug/kg	20040223								
1,1-Dichloroethane	40	ug/kg	7.3	ug/kg	20040223	20	ug/kg	77 119	30	50	ug/kg	56 130	54
1,2-Dichloroethane	40	ug/kg	9.3	ug/kg	20040223	20	ug/kg	78 121	30	50	ug/kg	56 126	38
cis-1,2-Dichloroethane	40	ug/kg	14	ug/kg	20040223	20	ug/kg	77 114	30	50	ug/kg	48 127	52
trans-1,2-Dichloroethene	40	ug/kg	11	ug/kg	20040223	20	ug/kg	68 117	30	50	ug/kg	47 127	58
1,1-Dichloroethene	40	ug/kg	8.3	ug/kg	20040223	20	ug/kg	55 142	27	50	ug/kg	43 147	27
cis-1,3-Dichloropropene	40	ug/kg	7.4	ug/kg	20040223	20	ug/kg	78 116	30	50	ug/kg	54 125	43
trans-1,3-Dichloropropene	40	ug/kg	5.5	ug/kg	20040223	20	ug/kg	71 125	30	50	ug/kg	30 138	49
Ethylbenzene	40	ug/kg	5.4	ug/kg	20040223	20	ug/kg	67 125	30	50	ug/kg	34 134	57
2-Hexanone	2000	ug/kg	6.8	ug/kg	20040223	20	ug/kg	79 114	30	50	ug/kg	36 133	72
Isopropylbenzene	200	ug/kg	24	ug/kg	20040223	20	ug/kg	29 200	41	50	ug/kg	20 190	70
Methyl acetate	960	ug/kg	5.1	ug/kg	20040223								
Methylcyclohexane	960	ug/kg	5.7	ug/kg	20040223								
Methylene chloride	200	ug/kg	99	ug/kg	20040224	20	ug/kg	58 130	30	50	ug/kg	45 129	49
4-Methyl-2-pentanone	2000	ug/kg	11	ug/kg	20040223	20	ug/kg	68 142	60	50	ug/kg	42 143	60
Methyl tert-butyl ether	200	ug/kg	10	ug/kg	20040223			70 130	30		70 130	30	
Styrene	40	ug/kg	28	ug/kg	20040224	20	ug/kg	80 114	30	50	ug/kg	23 136	65

Target Analyte List: NC: OLM03.1/4.2 Volatile List

Matrix: SOLID
 Extraction: PURGE AND TRAP - Field MEOH Ext. (Solids or Wastes)
 Method: Volatile Organics, GC/MS (8260B)
 QC Program: MICHIGAN DEQ
 Location: STL North Canton

Target List 4121				Detection Limits				Check List 924				Spike List 925			
Compound	RL	Units	MDL	Units	Run Date	Amt	Units	LCL	UCL	RPD	Amt	Units	LCL	UCL	RPD
1,1,2,2-Tetrachloroethane	80	ug/kg	8.2	ug/kg	20040223	20	ug/kg	70	133	30	50	ug/kg	33	162	90
Tetrachloroethene	40	ug/kg	9	ug/kg	20040223	20	ug/kg	72	120	30	50	ug/kg	31	137	81
Toluene	80	ug/kg	9.1	ug/kg	20040223	20	ug/kg	71	130	24	50	ug/kg	46	147	24
1,2,4-Trichlorobenzene	200	ug/kg	12	ug/kg	20040223										
1,1,1-Trichloroethane	40	ug/kg	9.5	ug/kg	20040223	20	ug/kg	67	123	30	50	ug/kg	48	132	57
1,1,2-Trichloroethane	40	ug/kg	9.9	ug/kg	20040223	20	ug/kg	82	116	30	50	ug/kg	58	128	52
Trichloroethene	40	ug/kg	12	ug/kg	20040223	20	ug/kg	70	131	23	50	ug/kg	46	143	23
Trichlorofluoromethane	80	ug/kg	8.3	ug/kg	20040223										
1,1,2-Trichloro-1,2,2-trifluoroethane	200	ug/kg	10	ug/kg	20040223										
Vinyl chloride	80	ug/kg	16	ug/kg	20040224	20	ug/kg	24	152	30	50	ug/kg	30	136	80
Xylenes (total)	120	ug/kg	15	ug/kg	20040223	60	ug/kg	80	114	30	150	ug/kg	33	135	78
4-Bromofluorobenzene						50	ug/kg	47	158	0	50	ug/kg	47	158	0
1,2-Dichloroethane-d4						50	ug/kg	61	130	0	50	ug/kg	61	130	0
Toluene-d8						50	ug/kg	60	143	0	50	ug/kg	60	143	0
Dibromofluoromethane						50	ug/kg	59	138	0	50	ug/kg	59	138	0

STL Reference Data Summary

Target Analyte List: Q: TCLP MSVOA Standard List

Matrix: SOLID
Extraction: TCLP(1311-ZHE/filter) -> PURGE-AND-TRAP (Low Level)
Method: Volatile Organics, GC/MS (8260B)
QC Program: STANDARD TEST SET
Location: STL North Canton

Target List 2006					Check List 996					Spike List 997							
Compound	RL	Detection Limits		Units	Run Date	Amt	Units		LCL	UCL	RPD	Amt	Units		LCL	UCL	RPD
Benzene	0.025	mg/L	0.23	ug/L	20040107	50	ug/L	76	118	30		50	ug/L	76	117	30	
2-Butanone (MEK)	0.05	mg/L	1	ug/L	20040107												
Carbon tetrachloride	0.025	mg/L	0.45	ug/L	20040226	50	ug/L	71	124	30		50	ug/L	72	124	30	
Chlorobenzene	0.025	mg/L	0.28	ug/L	20040226	50	ug/L	76	113	30		50	ug/L	72	114	30	
Chloroform	0.025	mg/L	0.4	ug/L	20040226	50	ug/L	82	117	30		50	ug/L	82	117	30	
1,2-Dichloroethane	0.025	mg/L	0.48	ug/L	20040107	50	ug/L	78	122	30		50	ug/L	80	120	30	
1,1-Dichloroethylene	0.07	mg/L	0.6	ug/L	20040107												
Tetrachloroethylene	0.07	mg/L	0.83	ug/L	20040107												
Trichloroethylene	0.05	mg/L	0.41	ug/L	20040107												
Vinyl chloride	0.025	mg/L	0.44	ug/L	20040226	50	ug/L	47	123	30		50	ug/L	54	118	30	
4-Bromofluorobenzene						50	ug/L	84	125	0		50	ug/L	84	125	0	
1,2-Dichloroethane-d4						50	ug/L	80	122	0		50	ug/L	80	122	0	
Toluene-d8						50	ug/L	90	122	0		50	ug/L	90	122	0	
Dibromofluoromethane						50	ug/L	86	124	0		50	ug/L	86	125	0	

STL Reference Data Summary

Target Analyte List: All Analytes

Matrix: SOLID
Extraction: SONICATION - Low Level
Method: Base/Neutrals and Acids (82/70C)
QC Program: MICHIGAN DEQ
Location: STL North Canton

Analyte List Compound	RL	Detection Limits			Run Date	Check List 1114				Spike List 1115								
		Units	MDL	Units		Amt	Units	LCL	UCL	RPD	Amt	Units	LCL	UCL	RPD			
a,a-Dimethylphenethylamine	1280	ug/kg	110	ug/kg	20050119													
Acenaphthene	264	ug/kg	1.3	ug/kg	20050317	1700	ug/kg	46	110	30	1700	ug/kg	10	200	30			
Acenaphthylene	264	ug/kg	1.2	ug/kg	20050127	1700	ug/kg	47	110	30	1700	ug/kg	10	200	30			
Acetophenone	264	ug/kg	26	ug/kg	20050317													
2-Acetylaminofluorene	2640	ug/kg	120	ug/kg	20050113													
4-Aminobiphenyl	1280	ug/kg	97	ug/kg	20050119													
Aniline	264	ug/kg	15	ug/kg	20050317													
Anthracene	264	ug/kg	1.3	ug/kg	20050127	1700	ug/kg	56	111	30	1700	ug/kg	10	200	30			
Aramite	528	ug/kg	4.8	ug/kg	20050119													
Atrazine	264	ug/kg	21	ug/kg	20050127													
Azobenzene	264	ug/kg	20	ug/kg	20030429													
Benzaldehyde	264	ug/kg	21	ug/kg	20050317													
Benz(a)anthracene	264	ug/kg	0.95	ug/kg	20050127													
Benzenethiol	264	ug/kg	5.2	ug/kg	20050314													
Benzdline	2640	ug/kg	140	ug/kg	20050317													
Benzo(a)anthracene	264	ug/kg	0.95	ug/kg	20050127	1700	ug/kg	58	111	30	1700	ug/kg	10	200	30			
Benzo(b)fluoranthene	264	ug/kg	1.2	ug/kg	20050127	1700	ug/kg	43	124	30	1700	ug/kg	10	200	30			
Benzo(k)fluoranthene	264	ug/kg	1.7	ug/kg	20050127	1700	ug/kg	38	122	30	1700	ug/kg	10	200	30			
Benzoic acid	1280	ug/kg	240	ug/kg	20050317	1700	ug/kg	10	124	30	1700	ug/kg	10	200	30			
Benzo(ghi)perylene	264	ug/kg	1.3	ug/kg	20050317	1700	ug/kg	44	120	30	1700	ug/kg	10	200	30			
Benzo(a)pyrene	264	ug/kg	1.3	ug/kg	20050317	1700	ug/kg	44	115	30	1700	ug/kg	10	200	30			
Benzothiazole	0.264	mg/kg	69	ug/kg	20050314													
Benzyl Mercaptan	0.264	mg/kg	110	ug/kg	19980518													
o-Benzyl Phenol	0.264	mg/kg	70	ug/kg	20050314													
Benzyl alcohol	264	ug/kg	140	ug/kg	20050128													
1,1'-Biphenyl	264	ug/kg	23	ug/kg	20050317													
bis(2-Chloroethoxy)ethane	264	ug/kg	25	ug/kg	20020212													
bis(2-Chloroethoxy)methane	264	ug/kg	22	ug/kg	20050317	1700	ug/kg	42	110	30	1700	ug/kg	36	110	30			
bis(2-Chloroethyl) ether	264	ug/kg	2	ug/kg	20050317	1700	ug/kg	41	110	30	1700	ug/kg	32	118	30			
bis(2-Chloroisopropyl) ether	264	ug/kg	26	ug/kg	20050317	1700	ug/kg	36	116	30	1700	ug/kg	25	124	30			
bis(2-Chloro-1-methylethyl) ether	264	ug/kg	26	ug/kg	20050317													
bis(2-Ethylhexyl) phthalate	264	ug/kg	18	ug/kg	20050127	1700	ug/kg	56	123	30	1700	ug/kg	10	200	30			
4-Bromophenyl phenyl ether	264	ug/kg	21	ug/kg	20050317	1700	ug/kg	53	112	30	1700	ug/kg	44	120	30			
2,3-Butanedithiol	0.264	mg/kg	240	ug/kg	19980518													
1,4-Butanedithiol	0.264	mg/kg	110	ug/kg	19980518													
Butyl benzyl phthalate	264	ug/kg	19	ug/kg	20050127	1700	ug/kg	57	121	30	1700	ug/kg	43	138	30			
Caprolactam	264	ug/kg	37	ug/kg	20050127													

Target Analyte List: All Analytes

Matrix: SOLID
Extraction: SONICATION - Low Level
Method: Base/Neutrals and Acids (82/70C)
QC Program: MICHIGAN DEQ
Location: STL North Canton

Analyte List Compound	RL	Detection Limits			Run Date	Check List 1114				Spike List 1115					
		Units	MDL	Units		Amt	Units	LCL	UCL	RPD	Amt	Units	LCL	UCL	RPD
Carbazole	264	ug/kg	19	ug/kg	20050317	1700	ug/kg	56	115	30	1700	ug/kg	10	162	30
p-Chloroaniline	1360	ug/kg	17	ug/kg	20050317										
4-Chloroaniline	1360	ug/kg	17	ug/kg	20050317	1700	ug/kg	25	110	30	1700	ug/kg	11	110	30
Chlorobenzilate	264	ug/kg	3.4	ug/kg	20050214										
4-Chloro-3-methylphenol	264	ug/kg	21	ug/kg	20050317	1700	ug/kg	42	110	30	1700	ug/kg	32	117	30
p-Chloro-m-cresol	264	ug/kg	21	ug/kg	20050317										
2-Chloronaphthalene	264	ug/kg	22	ug/kg	20050317	1700	ug/kg	46	110	30	1700	ug/kg	40	110	30
2-Chlorophenol	264	ug/kg	26	ug/kg	20050317	1700	ug/kg	39	110	30	1700	ug/kg	32	110	30
4-Chlorophenyl phenyl ether	264	ug/kg	24	ug/kg	20050317	1700	ug/kg	53	110	30	1700	ug/kg	47	116	30
Chrysene	264	ug/kg	0.9	ug/kg	20050317	1700	ug/kg	56	111	30	1700	ug/kg	10	200	30
6-Methylchrysene	264	ug/kg	62	ug/kg	20050314										
m-Cresol	264	ug/kg	4.3	ug/kg	20050119										
p-Cresol	264	ug/kg	22	ug/kg	20050317										
m-Cresol & p-Cresol	528	ug/kg	20	ug/kg	20040303										
Cresols (total)	528	ug/kg	49	ug/kg	20050317										
Cyclohexylamine	1280	ug/kg	640	ug/kg	19980521										
Diallate	528	ug/kg	4.6	ug/kg	20050119										
Dibenz(a,h)acridine	264	ug/kg	72	ug/kg	20050314										
Dibenz(a,i)acridine	264	ug/kg	70	ug/kg	20050314										
Dibenz(a,h)anthracene	264	ug/kg	1.3	ug/kg	20050127	1700	ug/kg	45	122	30	1700	ug/kg	10	200	30
Dibenzofuran	264	ug/kg	20	ug/kg	20050317	1700	ug/kg	50	110	30	1700	ug/kg	10	200	30
1,3-Dibutyl-2-Thiourea	0.264	mg/kg	77	ug/kg	20050314										
Di-n-butyl phthalate	264	ug/kg	19	ug/kg	20050317	1700	ug/kg	57	119	30	1700	ug/kg	31	145	30
1,2-Dichlorobenzene	264	ug/kg	29	ug/kg	20050317	1700	ug/kg	42	110	30	1700	ug/kg	29	110	30
o-Dichlorobenzene	264	ug/kg	29	ug/kg	20050317										
1,3-Dichlorobenzene	264	ug/kg	23	ug/kg	20050317	1700	ug/kg	40	110	30	1700	ug/kg	29	110	30
m-Dichlorobenzene	264	ug/kg	23	ug/kg	20050317										
1,4-Dichlorobenzene	264	ug/kg	21	ug/kg	20050127	1700	ug/kg	38	110	30	1700	ug/kg	26	110	30
p-Dichlorobenzene	264	ug/kg	21	ug/kg	20050127										
3,3'-Dichlorobenzidine	1600	ug/kg	18	ug/kg	20050127	1700	ug/kg	31	110	30	1700	ug/kg	10	110	30
2,4-Dichlorophenol	264	ug/kg	20	ug/kg	20050317	1700	ug/kg	40	110	30	1700	ug/kg	33	110	30
2,6-Dichlorophenol	264	ug/kg	4	ug/kg	20050119										
1,3-Diethyl-2-Thiourea	0.264	mg/kg	58	ug/kg	20050314										
Diethyl phthalate	264	ug/kg	19	ug/kg	20050317	1700	ug/kg	55	114	30	1700	ug/kg	48	118	30
O,O-Diethyl-O-(2-pyrazinyl) phosphor	1280	ug/kg	6.5	ug/kg	20050214										
2,3-Dimercapto-1-Propanol	0.33	mg/kg	0.33	mg/kg	19991202										
Dimethoate	528	ug/kg	130	ug/kg	20050113										
1,3-Dimethyl-2-Thiourea	0.264	mg/kg	56	ug/kg	20050314										
p-Dimethylaminoazobenzene	528	ug/kg	3.4	ug/kg	20050214										

Target Analyte List: All Analytes

Matrix: SOLID
Extraction: SONICATION - Low Level
Method: Base/Neutrals and Acids (8270C)
QC Program: MICHIGAN DEQ
Location: STL North Canton

Analyte List Compound	RL	Detection Limits		Run Date	Check List 1114			Spike List 1115		
		Units	MDL		Amt	Units	LCL UCL RPD	Amt	Units	LCL UCL RPD
7,12-Dimethylbenz(a)anthracene	528	ug/kg	120	20050119						
3,3-Dimethylbenzidine	1280	ug/kg	63	20050119						
2,4-Dimethylphenol	264	ug/kg	20	20050317	1700	ug/kg	28 110 30	1700	ug/kg	19 114 30
Dimethyl phthalate	264	ug/kg	21	20050317	1700	ug/kg	54 112 30	1700	ug/kg	47 116 30
1,2-Dinitrobenzene	264	ug/kg	18	20050127						
m-Dinitrobenzene	264	ug/kg	120	20050119						
1,3-Dinitrobenzene	264	ug/kg	120	20050119						
p-Dinitrobenzene	264	ug/kg	110	20050113						
1,4-Dinitrobenzene	264	ug/kg	110	20050113						
4,6-Dinitro-o-cresol	1360	ug/kg	13	20050317						
4,6-Dinitro-2-methylphenol	1360	ug/kg	13	20050317	1700	ug/kg	21 110 30	1700	ug/kg	10 110 30
2,4-Dinitrophenol	1360	ug/kg	83	20050317	1700	ug/kg	10 110 30	1700	ug/kg	10 110 30
2,4-Dinitrotoluene	264	ug/kg	18	20050127	1700	ug/kg	55 116 30	1700	ug/kg	42 118 30
2,6-Dinitrotoluene	264	ug/kg	21	20050317	1700	ug/kg	54 115 30	1700	ug/kg	28 137 30
2-sec-Buyl-4,6-dinitrophenol	528	ug/kg	110	20050113						
Dinoseb	528	ug/kg	110	20050113						
Di-n-octyl phthalate	264	ug/kg	18	20050317	1700	ug/kg	45 123 30	1700	ug/kg	10 182 30
1,4-Dioxane	264	ug/kg	22	20050317	1700	ug/kg	10 110 30	1700	ug/kg	10 110 30
Diphenyl Thiourea	0.264	mg/kg	31	20050314						
Diphenylamine	264	ug/kg	21	20050317						
1,2-Diphenylhydrazine	264	ug/kg	22	20050317						
Disulfoton	1280	ug/kg	4.1	20050214						
1,2-Ethanedithiol	1.28	mg/kg	310	19980518						
Ethyl methanesulfonate	264	ug/kg	4	20050119						
Famphur	2640	ug/kg	4.6	20050214						
Fluoranthene	264	ug/kg	1.2	20050127	1700	ug/kg	55 118 30	1700	ug/kg	10 200 30
Fluorene	264	ug/kg	1.2	20050127	1700	ug/kg	51 110 30	1700	ug/kg	10 187 30
Hexachlorobenzene	264	ug/kg	2.1	20050127	1700	ug/kg	51 110 30	1700	ug/kg	37 122 30
Hexachlorobutadiene	264	ug/kg	26	20050317	1700	ug/kg	39 110 30	1700	ug/kg	30 110 30
Hexachlorocyclopentadiene	264	ug/kg	16	20050317	1700	ug/kg	10 110 30	1700	ug/kg	10 110 30
Hexachloroethane	264	ug/kg	28	20050317	1700	ug/kg	38 110 30	1700	ug/kg	13 110 30
Hexachloropropene	264	ug/kg	4.6	20050214						
Hexamethylphosphoramide	0.02	mg/kg	0.02	19991202						
Indene	264	ug/kg	38	20050314						
Indeno(1,2,3-cd)pyrene	264	ug/kg	1.5	20050317	1700	ug/kg	45 121 30	1700	ug/kg	10 200 30
Isophorone	264	ug/kg	21	20050317	1700	ug/kg	46 117 30	1700	ug/kg	32 129 30
Isosafrole	528	ug/kg	3.9	20050119						
Methapyrene	1280	ug/kg	120	20050119						
3-Methylcholanthrene	528	ug/kg	120	20050119						

Target Analyte List: All Analytes

Matrix: SOLID
Extraction: SONICATION - Low Level
Method: Base/Neutrals and Acids (8270C)
QC Program: MICHIGAN DEQ
Location: STL North Canton

Analyte List Compound	RL	Detection Limits		Run Date	Check List 1114			Spike List 1115							
		Units	MDL		Units	Amt	Units	LCL	UCL	RPD	Amt	Units	LCL	UCL	RPD
Methyl methanesulfonate	264	ug/kg	4.1	ug/kg	20050119										
2-Methylnaphthalene	264	ug/kg	1.5	ug/kg	20050127	1700	ug/kg	46	110	30	1700	ug/kg	10	200	30
1-Methylnaphthalene	264	ug/kg	2.1	ug/kg	20050317										
2-Methylphenol	264	ug/kg	28	ug/kg	20050317	1700	ug/kg	36	110	30	1700	ug/kg	19	124	30
o-Cresol	264	ug/kg	28	ug/kg	20050317										
3-Methylphenol	264	ug/kg	4.3	ug/kg	20050119										
4-Methylphenol	264	ug/kg	22	ug/kg	20050317	1700	ug/kg	40	110	30	1700	ug/kg	27	116	30
3-Methylphenol & 4-Methylphenol	528	ug/kg	20	ug/kg	20040303										
Methylphenols (total)	528	ug/kg	49	ug/kg	20050317										
Naphthalene	264	ug/kg	1.6	ug/kg	20050127	1700	ug/kg	42	110	30	1700	ug/kg	10	200	30
1,4-Naphthoquinone	1280	ug/kg	110	ug/kg	20050113										
1-Naphthylamine	264	ug/kg	3.6	ug/kg	20050214										
2-Naphthylamine	264	ug/kg	3.7	ug/kg	20050214										
2-Nitroaniline	1360	ug/kg	22	ug/kg	20050127	1700	ug/kg	47	124	30	1700	ug/kg	31	141	30
o-Nitroaniline	1360	ug/kg	22	ug/kg	20050127										
3-Nitroaniline	1360	ug/kg	16	ug/kg	20050127	1700	ug/kg	44	110	30	1700	ug/kg	24	110	30
m-Nitroaniline	1360	ug/kg	16	ug/kg	20050127										
4-Nitroaniline	1360	ug/kg	26	ug/kg	20050127	1700	ug/kg	50	110	30	1700	ug/kg	23	124	30
p-Nitroaniline	1360	ug/kg	26	ug/kg	20050127										
Nitrobenzene	264	ug/kg	2.2	ug/kg	20050127	1700	ug/kg	40	110	30	1700	ug/kg	33	111	30
2-Nitrophenol	264	ug/kg	19	ug/kg	20050317	1700	ug/kg	35	110	30	1700	ug/kg	17	110	30
o-Nitrophenol	264	ug/kg	19	ug/kg	20050317										
4-Nitrophenol	1360	ug/kg	110	ug/kg	20050127	1700	ug/kg	24	117	30	1700	ug/kg	10	125	30
p-Nitrophenol	1360	ug/kg	110	ug/kg	20050127										
4-Nitroquinoline-1-oxide	2640	ug/kg	85	ug/kg	20050113										
N-Nitrosodi-n-butylamine	264	ug/kg	7.5	ug/kg	20050214										
N-Nitrosodietylamine	264	ug/kg	4.3	ug/kg	20050214										
N-Nitrosodimethylamine	264	ug/kg	16	ug/kg	20050317										
N-Nitrosodiphenylamine	264	ug/kg	21	ug/kg	20050317	1700	ug/kg	54	112	30	1700	ug/kg	10	169	30
N-Nitrosodi-n-propylamine	264	ug/kg	23	ug/kg	20050317	1700	ug/kg	40	114	30	1700	ug/kg	30	121	30
N-Nitrosomethylethylamine	264	ug/kg	5.2	ug/kg	20050214										
N-Nitrosomorpholine	264	ug/kg	5.1	ug/kg	20050214										
N-Nitrosopiperidine	264	ug/kg	110	ug/kg	20050113										
N-Nitrosopyrrolidine	264	ug/kg	3.9	ug/kg	20050119										
5-Nitro-o-toluidine	528	ug/kg	4.6	ug/kg	20050214										
2,2'-oxybis(1-Chloropropane)	264	ug/kg	26	ug/kg	20050317										
Pentachlorobenzene	264	ug/kg	5.4	ug/kg	20050119										
Pentachloroethane	1280	ug/kg	4.5	ug/kg	20050119										
Pentachloronitrobenzene	1280	ug/kg	6	ug/kg	20050214										

Target Analyte List: All Analytes

Matrix: SOLID
Extraction: SONICATION - Low Level
Method: Base/Neutrals and Acids (8270C)
QC Program: MICHIGAN DEQ
Location: STL North Canton

Analyte List	RL	Detection Limits			Run Date	Check List 1114				Spike List 1115						
		Units	MDL	Units		Amt	Units	LCL	UCL	RPD	Amt	Units	LCL	UCL	RPD	
Compound																
Pentachlorophenol	640	ug/kg	82	ug/kg	20050317	1700	ug/kg	10	110	30	1700	ug/kg	10	182	30	
Phenacetin	528	ug/kg	6.7	ug/kg	20050214											
Phenanthrene	264	ug/kg	2	ug/kg	20050317	1700	ug/kg	54	110	30	1700	ug/kg	10	200	30	
Phenol	264	ug/kg	25	ug/kg	20050317	1700	ug/kg	39	110	30	1700	ug/kg	10	144	30	
p-Phenylenediamine	2640	ug/kg	61	ug/kg	20050113											
Phenyl ether	0.264	mg/kg	68	ug/kg	20050314											
Phorate	1280	ug/kg	5.9	ug/kg	20050119											
2-Picoline	528	ug/kg	4.9	ug/kg	20050214											
Promamide	528	ug/kg	4.8	ug/kg	20050214											
1,3-Propanedithiol	0.264	mg/kg	140	ug/kg	19980518											
2,2'-Oxybis(1-Chloropropane)	264	ug/kg	26	ug/kg	20050317											
Pyrene	264	ug/kg	1.1	ug/kg	20050127	1700	ug/kg	58	113	30	1700	ug/kg	10	200	30	
Pyridine	528	ug/kg	17	ug/kg	20050317	1700	ug/kg	22	110	30	1700	ug/kg	10	110	30	
Quinoline	264	ug/kg	72	ug/kg	20050314											
Safrole	528	ug/kg	4.3	ug/kg	20050214											
Sulfotepp	1280	ug/kg	4.6	ug/kg	20050214											
1,2,4,5-Tetrachlorobenzene	264	ug/kg	5.3	ug/kg	20050214											
2,3,4,6-Tetrachlorophenol	1280	ug/kg	110	ug/kg	20050113											
2,3,5,6-Tetrachlorophenol	1280	ug/kg	46	ug/kg	20050127											
Tetraethyldithiopyrophosphate	1280	ug/kg	4.6	ug/kg	20050214											
1,1,3,3-Tetramethyl-2-Thiourea	0.264	mg/kg	66	ug/kg	20050314											
Thionazin	1280	ug/kg	6.5	ug/kg	20050214											
Thiourea	1280	ug/kg	670	ug/kg	19980518											
o-Toluidine	528	ug/kg	4.9	ug/kg	20050119											
1,2,4-Trichlorobenzene	264	ug/kg	24	ug/kg	20050317	1700	ug/kg	43	110	30	1700	ug/kg	33	110	30	
2,4,5-Trichlorophenol	264	ug/kg	25	ug/kg	20050127	1700	ug/kg	42	110	30	1700	ug/kg	32	112	30	
2,4,6-Trichlorophenol	264	ug/kg	21	ug/kg	20050317	1700	ug/kg	37	110	30	1700	ug/kg	22	110	30	
O,O,O-Triethyl phosphorothioate	1280	ug/kg	5.5	ug/kg	20050119											
sym-Trinitrobenzene	1280	ug/kg	100	ug/kg	20050113											
1,3,5-Trinitrobenzene	1280	ug/kg	100	ug/kg	20050113											
Zinphos	1280	ug/kg	6.5	ug/kg	20050214											
2-Fluorobiphenyl						1700	ug/kg	34	110	0	1700	ug/kg	34	110	0	
2-Fluorophenol						2500	ug/kg	26	110	0	2500	ug/kg	26	110	0	
2,4,6-Tribromophenol						2500	ug/kg	10	118	0	2500	ug/kg	10	118	0	
Nitrobenzene-d5						1700	ug/kg	24	112	0	1700	ug/kg	24	112	0	
Phenol-d5						2500	ug/kg	28	110	0	2500	ug/kg	28	110	0	
Terphenyl-d14						1700	ug/kg	41	119	0	1700	ug/kg	41	119	0	

STL Reference Data Summary

Target Analyte List: NC: OLM03.1/4.2 Semivolatile List

Matrix: SOLID
Extraction: SONICATION - Low Level
Method: Base/Neutrals and Acids (8270C)
QC Program: MICHIGAN DEQ
Location: STL North Canton

Target List 4122			Detection Limits			Check List 1114					Spike List 1115				
Compound	RL	Units	MDL	Units	Run Date	Amt	Units	LCL	UCL	RPD	Amt	Units	LCL	UCL	RPD
Acenaphthene	264	ug/kg	1.3	ug/kg	20050317	1700	ug/kg	46	110	30	1700	ug/kg	10	200	30
Acenaphthylene	264	ug/kg	1.2	ug/kg	20050127	1700	ug/kg	47	110	30	1700	ug/kg	10	200	30
Acetophenone	264	ug/kg	26	ug/kg	20050317										
Anthracene	264	ug/kg	1.3	ug/kg	20050127	1700	ug/kg	56	111	30	1700	ug/kg	10	200	30
Atrazine	264	ug/kg	21	ug/kg	20050127										
Benzaldehyde	264	ug/kg	21	ug/kg	20050317										
Benzo(a)anthracene	264	ug/kg	0.95	ug/kg	20050127	1700	ug/kg	58	111	30	1700	ug/kg	10	200	30
Benzo(b)fluoranthene	264	ug/kg	1.2	ug/kg	20050127	1700	ug/kg	43	124	30	1700	ug/kg	10	200	30
Benzo(k)fluoranthene	264	ug/kg	1.7	ug/kg	20050127	1700	ug/kg	38	122	30	1700	ug/kg	10	200	30
Benzo(ghi)perylene	264	ug/kg	1.3	ug/kg	20050317	1700	ug/kg	44	120	30	1700	ug/kg	10	200	30
Benzo(a)pyrene	264	ug/kg	1.3	ug/kg	20050317	1700	ug/kg	44	115	30	1700	ug/kg	10	200	30
1,1'-Biphenyl	264	ug/kg	23	ug/kg	20050317										
bis(2-Chloroethoxy)methane	264	ug/kg	22	ug/kg	20050317	1700	ug/kg	42	110	30	1700	ug/kg	36	110	30
bis(2-Chloroethyl) ether	264	ug/kg	2	ug/kg	20050317	1700	ug/kg	41	110	30	1700	ug/kg	32	118	30
bis(2-Ethylhexyl) phthalate	264	ug/kg	18	ug/kg	20050127	1700	ug/kg	56	123	30	1700	ug/kg	10	200	30
4-Bromophenyl phenyl ether	264	ug/kg	21	ug/kg	20050317	1700	ug/kg	53	112	30	1700	ug/kg	44	120	30
Butyl benzyl phthalate	264	ug/kg	19	ug/kg	20050127	1700	ug/kg	57	121	30	1700	ug/kg	43	138	30
Caprolactam	264	ug/kg	37	ug/kg	20050127										
Carbazole	264	ug/kg	19	ug/kg	20050317	1700	ug/kg	56	115	30	1700	ug/kg	10	162	30
4-Chloroaniline	1360	ug/kg	17	ug/kg	20050317	1700	ug/kg	25	110	30	1700	ug/kg	11	110	30
4-Chloro-3-methylphenol	264	ug/kg	21	ug/kg	20050317	1700	ug/kg	42	110	30	1700	ug/kg	32	117	30
2-Chloronaphthalene	264	ug/kg	22	ug/kg	20050317	1700	ug/kg	46	110	30	1700	ug/kg	40	110	30
2-Chlorophenol	264	ug/kg	26	ug/kg	20050317	1700	ug/kg	39	110	30	1700	ug/kg	32	110	30
4-Chlorophenyl phenyl ether	264	ug/kg	24	ug/kg	20050317	1700	ug/kg	53	110	30	1700	ug/kg	47	116	30
Chrysene	264	ug/kg	0.9	ug/kg	20050317	1700	ug/kg	56	111	30	1700	ug/kg	10	200	30
Dibenz(a,h)anthracene	264	ug/kg	1.3	ug/kg	20050127	1700	ug/kg	45	122	30	1700	ug/kg	10	200	30
Dibenzofuran	264	ug/kg	20	ug/kg	20050317	1700	ug/kg	50	110	30	1700	ug/kg	10	200	30
Di-n-butyl phthalate	264	ug/kg	19	ug/kg	20050317	1700	ug/kg	57	119	30	1700	ug/kg	31	145	30
3,3'-Dichlorobenzidine	1600	ug/kg	18	ug/kg	20050127	1700	ug/kg	31	110	30	1700	ug/kg	10	110	30
2,4-Dichlorophenol	264	ug/kg	20	ug/kg	20050317	1700	ug/kg	40	110	30	1700	ug/kg	33	110	30
Diethyl phthalate	264	ug/kg	19	ug/kg	20050317	1700	ug/kg	55	114	30	1700	ug/kg	48	118	30
2,4-Dimethylphenol	264	ug/kg	20	ug/kg	20050317	1700	ug/kg	28	110	30	1700	ug/kg	19	114	30
Dimethyl phthalate	264	ug/kg	21	ug/kg	20050317	1700	ug/kg	54	112	30	1700	ug/kg	47	116	30
4,6-Dinitro-2-methylphenol	1360	ug/kg	13	ug/kg	20050317	1700	ug/kg	21	110	30	1700	ug/kg	10	110	30
2,4-Dinitrophenol	1360	ug/kg	83	ug/kg	20050317	1700	ug/kg	10	110	30	1700	ug/kg	10	110	30
2,4-Dinitrotoluene	264	ug/kg	18	ug/kg	20050127	1700	ug/kg	55	116	30	1700	ug/kg	42	118	30
2,6-Dinitrotoluene	264	ug/kg	21	ug/kg	20050317	1700	ug/kg	54	115	30	1700	ug/kg	28	137	30

Target Analyte List: NC: OLM03.1/4.2 Semivolatile List

Matrix: SOLID
Extraction: SONICATION - Low Level
Method: Base/Neutrals and Acids (8270C)
QC Program: MICHIGAN DEQ
Location: STL North Canton

Target List 4122					Check List 1114					Spike List 1115					
Compound	RL	Units	MDL	Units	Run Date	Amt	Units	LCL	UCL	RPD	Amt	Units	LCL	UCL	RPD
Di-n-octyl phthalate	264	ug/kg	18	ug/kg	20050317	1700	ug/kg	45	123	30	1700	ug/kg	10	182	30
Fluoranthene	264	ug/kg	1.2	ug/kg	20050127	1700	ug/kg	55	118	30	1700	ug/kg	10	200	30
Fluorene	264	ug/kg	1.2	ug/kg	20050127	1700	ug/kg	51	110	30	1700	ug/kg	10	187	30
Hexachlorobenzene	264	ug/kg	2.1	ug/kg	20050127	1700	ug/kg	51	110	30	1700	ug/kg	37	122	30
Hexachlorobutadiene	264	ug/kg	26	ug/kg	20050317	1700	ug/kg	39	110	30	1700	ug/kg	30	110	30
Hexachlorocyclopentadiene	264	ug/kg	16	ug/kg	20050317	1700	ug/kg	10	110	30	1700	ug/kg	10	110	30
Hexachloroethane	264	ug/kg	28	ug/kg	20050317	1700	ug/kg	38	110	30	1700	ug/kg	13	110	30
Indeno(1,2,3-cd)pyrene	264	ug/kg	1.5	ug/kg	20050317	1700	ug/kg	45	121	30	1700	ug/kg	10	200	30
Isophorone	264	ug/kg	21	ug/kg	20050317	1700	ug/kg	46	117	30	1700	ug/kg	32	129	30
2-Methylnaphthalene	264	ug/kg	1.5	ug/kg	20050127	1700	ug/kg	46	110	30	1700	ug/kg	10	200	30
2-Methylphenol	264	ug/kg	28	ug/kg	20050317	1700	ug/kg	36	110	30	1700	ug/kg	19	124	30
4-Methylphenol	264	ug/kg	22	ug/kg	20050317	1700	ug/kg	40	110	30	1700	ug/kg	27	116	30
Naphthalene	264	ug/kg	1.6	ug/kg	20050127	1700	ug/kg	42	110	30	1700	ug/kg	10	200	30
2-Nitroaniline	1360	ug/kg	22	ug/kg	20050127	1700	ug/kg	47	124	30	1700	ug/kg	31	141	30
3-Nitroaniline	1360	ug/kg	16	ug/kg	20050127	1700	ug/kg	44	110	30	1700	ug/kg	24	110	30
4-Nitroaniline	1360	ug/kg	26	ug/kg	20050127	1700	ug/kg	50	110	30	1700	ug/kg	23	124	30
Nitrobenzene	264	ug/kg	2.2	ug/kg	20050127	1700	ug/kg	40	110	30	1700	ug/kg	33	111	30
2-Nitrophenol	264	ug/kg	19	ug/kg	20050317	1700	ug/kg	35	110	30	1700	ug/kg	17	110	30
4-Nitrophenol	1360	ug/kg	110	ug/kg	20050127	1700	ug/kg	24	117	30	1700	ug/kg	10	125	30
N-Nitrosodiphenylamine	264	ug/kg	21	ug/kg	20050317	1700	ug/kg	54	112	30	1700	ug/kg	10	169	30
N-Nitrosodi-n-propylamine	264	ug/kg	23	ug/kg	20050317	1700	ug/kg	40	114	30	1700	ug/kg	30	121	30
2,2'-oxybis(1-Chloropropane)	264	ug/kg	26	ug/kg	20050317	1700	ug/kg	10	110	30	1700	ug/kg	10	182	30
Pentachlorophenol	640	ug/kg	82	ug/kg	20050317	1700	ug/kg	54	110	30	1700	ug/kg	10	200	30
Phenanthrene	264	ug/kg	2	ug/kg	20050317	1700	ug/kg	39	110	30	1700	ug/kg	10	144	30
Phenol	264	ug/kg	25	ug/kg	20050317	1700	ug/kg	58	113	30	1700	ug/kg	10	200	30
Pyrene	264	ug/kg	1.1	ug/kg	20050127	1700	ug/kg	42	110	30	1700	ug/kg	32	112	30
2,4,5-Trichlorophenol	264	ug/kg	25	ug/kg	20050127	1700	ug/kg	37	110	30	1700	ug/kg	22	110	30
2,4,6-Trichlorophenol	264	ug/kg	21	ug/kg	20050317	1700	ug/kg	34	110	0	1700	ug/kg	34	110	0
2-Fluorobiphenyl						1700	ug/kg	26	110	0	2500	ug/kg	26	110	0
2-Fluorophenol						2500	ug/kg	10	118	0	2500	ug/kg	10	118	0
2,4,6-Tribromophenol						1700	ug/kg	24	112	0	1700	ug/kg	24	112	0
Nitrobenzene-d5						2500	ug/kg	28	110	0	2500	ug/kg	28	110	0
Phenol-d5						1700	ug/kg	41	119	0	1700	ug/kg	41	119	0
Terphenyl-d14															

STL Reference Data Summary

Target Analyte List: Q: TCLP MSSemi Standard List

Matrix: SOLID
 Extraction: TCLP(1311) -> LIQ/LIQ, CONT - Acid->Base
 Method: Base/Neutrals and Acids (8270C)
 QC Program: STANDARD TEST SET
 Location: STL North Canton

Target List 2105	Compound	RL	Detection Limits		Run Date	Check List 1116			Spike List 1117		
			Units	MDL		Amt	Units	LCL UCL RPD	Amt	Units	LCL UCL RPD
m-Cresol & p-Cresol		0.04	mg/L	0.75	20040228	0.4000	mg/L	27 110 30	0.4000	mg/L	46 109 32
1,4-Dichlorobenzene		0.004	mg/L	0.52	20050217	0.2000	mg/L	16 110 30	0.2000	mg/L	18 110 36
2,4-Dinitrotoluene		0.02	mg/L	0.4	20050316	0.2000	mg/L	45 126 30	0.2000	mg/L	31 131 32
Hexachlorobenzene		0.02	mg/L	0.065	20050131	0.2000	mg/L	47 116 30	0.2000	mg/L	36 132 22
Hexachlorobutadiene		0.02	mg/L	0.51	20050316	0.2000	mg/L	10 110 30	0.2000	mg/L	18 116 32
Hexachloroethane		0.02	mg/L	0.58	20050316	0.2000	mg/L	10 110 30	0.2000	mg/L	18 110 33
o-Cresol		0.004	mg/L	0.56	20050316	0.2000	mg/L	24 110 30	0.2000	mg/L	33 115 31
Nitrobenzene		0.004	mg/L	0.053	20050131	0.2000	mg/L	35 117 30	0.2000	mg/L	19 211 59
Pentachlorophenol		0.04	mg/L	0.48	20050316	0.2000	mg/L	12 110 30	0.2000	mg/L	10 140 56
Pyridine		0.02	mg/L	0.78	20050316	0.2000	mg/L	10 110 30	0.2000	mg/L	10 148 65
2,4,5-Trichlorophenol		0.02	mg/L	0.96	20050217	0.2000	mg/L	35 111 30	0.2000	mg/L	24 143 22
2,4,6-Trichlorophenol		0.02	mg/L	1.4	20050316	0.2000	mg/L	32 110 30	0.2000	mg/L	36 135 27
2-Fluorobiphenyl								22 110 0			22 110 0
2-Fluorophenol								10 110 0			10 110 0
2,4,6-Tribromophenol								17 117 0			17 117 0
Nitrobenzene-d5								29 111 0			29 111 0
Phenol-d5								10 110 0			10 110 0
Terphenyl-d14								40 119 0			40 119 0

STL Reference Data Summary

Target Analyte List: Q: Aroclors Only Standard List

Matrix: SOLID
Extraction: SONICATION w/ACID STRIP (PCB)
Method: PCBs (8082)
QC Program: MICHIGAN DEQ
Location: STL North Canton

Target List 2207				Detection Limits				Check List 928				Spike List 929			
Compound	RL	Units	MDL	Units	Run Date	Amt	Units	LCL	UCL	RPD	Amt	Units	LCL	UCL	RPD
Aroclor 1016	264	ug/kg	6.7	ug/kg	20040120	333	ug/kg	41	130	30	333	ug/kg	10	200	30
Aroclor 1221	264	ug/kg	9.9	ug/kg	20040120										
Aroclor 1232	264	ug/kg	5.2	ug/kg	20040120										
Aroclor 1242	264	ug/kg	10	ug/kg	20040120										
Aroclor 1248	264	ug/kg	4.8	ug/kg	20040120										
Aroclor 1254	264	ug/kg	4.3	ug/kg	20040120										
Aroclor 1260	264	ug/kg	8	ug/kg	20040120	333	ug/kg	42	130	30	333	ug/kg	10	200	30
Decachlorobiphenyl						6.67	ug/kg	40	138	0	6.67	ug/kg	40	138	0
Tetrachloro-m-xylene						6.67	ug/kg	10	127	0	6.67	ug/kg	10	127	0

STL Reference Data Summary

Target Analyte List: NC: TAL List - Hg for Michigan

Matrix: SOLID
Extraction: METALS, TOTAL - Soils
Method: Inductively Coupled Plasma (6010B Trace)
QC Program: MICHIGAN DEQ
Location: STL North Canton

Target List 4136				Detection Limits				Check List 906				Spike List 907			
Compound	RL	Units	MDL	Units	Run Date	Amt	Units	LCL	UCL	RPD	Amt	Units	LCL	UCL	RPD
Aluminum	16	mg/kg	5	mg/kg	20050127	200	mg/kg	80	120	20	200	mg/kg	75	125	20
Antimony	0.5	mg/kg	0.33	mg/kg	20050128	50	mg/kg	80	120	20	50	mg/kg	75	125	20
Arsenic	0.4	mg/kg	0.34	mg/kg	20050127	200	mg/kg	80	120	20	200	mg/kg	75	125	20
Barium	0.8	mg/kg	0.2	mg/kg	20050128	200	mg/kg	80	120	20	200	mg/kg	75	125	20
Beryllium	0.16	mg/kg	0.029	mg/kg	20050128	5	mg/kg	80	120	20	5	mg/kg	75	125	20
Cadmium	0.08	mg/kg	0.027	mg/kg	20050128	5	mg/kg	80	120	20	5	mg/kg	75	125	20
Calcium	400	mg/kg	8.4	mg/kg	20050127	5000	mg/kg	80	120	20	5000	mg/kg	75	125	20
Chromium	0.4	mg/kg	0.13	mg/kg	20050127	20	mg/kg	80	120	20	20	mg/kg	75	125	20
Cobalt	0.4	mg/kg	0.34	mg/kg	20050128	50	mg/kg	80	120	20	50	mg/kg	75	125	20
Copper	0.8	mg/kg	0.33	mg/kg	20050128	25	mg/kg	80	120	20	25	mg/kg	75	125	20
Iron	8	mg/kg	1.9	mg/kg	20050128	100	mg/kg	73	137	20	100	mg/kg	75	125	20
Lead	0.24	mg/kg	0.24	mg/kg	20050127	50	mg/kg	80	120	20	50	mg/kg	75	125	20
Magnesium	80	mg/kg	2.1	mg/kg	20050128	5000	mg/kg	80	120	20	5000	mg/kg	75	125	20
Manganese	0.8	mg/kg	0.042	mg/kg	20050128	50	mg/kg	80	120	20	50	mg/kg	75	125	20
Nickel	0.8	mg/kg	0.28	mg/kg	20050127	50	mg/kg	80	120	20	50	mg/kg	75	125	20
Potassium	400	mg/kg	3.1	mg/kg	20050127	5000	mg/kg	80	120	20	5000	mg/kg	75	125	20
Selenium	0.4	mg/kg	0.3	mg/kg	20050128	200	mg/kg	80	120	20	200	mg/kg	75	125	20
Silver	0.4	mg/kg	0.29	mg/kg	20050128	5	mg/kg	80	120	20	5	mg/kg	75	125	20
Sodium	80	mg/kg	33	mg/kg	20050128	5000	mg/kg	80	120	20	5000	mg/kg	75	125	20
Thallium	0.8	mg/kg	0.53	mg/kg	20050128	200	mg/kg	80	120	20	200	mg/kg	75	125	20
Vanadium	0.8	mg/kg	0.097	mg/kg	20050128	50	mg/kg	80	120	20	50	mg/kg	75	125	20
Zinc	1.6	mg/kg	0.56	mg/kg	20050127	50	mg/kg	80	120	20	50	mg/kg	75	125	20

STL Reference Data Summary

Target Analyte List: NC: Michigan 10 Metals (ICPMS Water)

Matrix: SOLID
 Extraction: METALS, TOTAL - Soils
 Method: Inductively Coupled Plasma Mass Spectrometry(6020)
 QC Program: MICHIGAN DEQ
 Location: STL North Canton

Target List 4138		Detection Limits			Check List 932					Spike List 933					
Compound	RL	Units	MDL	Units	Run Date	Amt	Units	LCL	UCL	RPD	Amt	Units	LCL	UCL	RPD
Cadmium	0.04	mg/kg	0.0071	mg/kg	20050112	10	mg/kg	75	110	20	10	mg/kg	70	130	20
Silver	0.08	mg/kg	0.023	mg/kg	20050112	10	mg/kg	71	110	20	10	mg/kg	70	130	20
Zinc	0.8	mg/kg	0.39	mg/kg	20050112	10	mg/kg	73	114	20	10	mg/kg	70	130	20

STL Reference Data Summary

Target Analyte List: NC: Michigan 10 Metals (Trace Water)

Matrix: SOLID
 Extraction: METALS, TOTAL - Soils
 Method: Inductively Coupled Plasma (6010B Trace)
 QC Program: MICHIGAN DEQ
 Location: STL North Canton

Target List 4139		Detection Limits			Check List 906				Spike List 907			
Compound	RL	Units	MDL	Units	Run Date	Amt	Units	LCL UCL RPD	Amt	Units	LCL UCL RPD	
Arsenic	0.4	mg/kg	0.34	mg/kg	20050127	200	mg/kg	80 120 20	200	mg/kg	75 125 20	
Barium	0.8	mg/kg	0.2	mg/kg	20050128	200	mg/kg	80 120 20	200	mg/kg	75 125 20	
Chromium	0.4	mg/kg	0.13	mg/kg	20050127	20	mg/kg	80 120 20	20	mg/kg	75 125 20	
Copper	0.8	mg/kg	0.33	mg/kg	20050128	25	mg/kg	80 120 20	25	mg/kg	75 125 20	
Lead	0.24	mg/kg	0.24	mg/kg	20050127	50	mg/kg	80 120 20	50	mg/kg	75 125 20	
Selenium	0.4	mg/kg	0.3	mg/kg	20050128	200	mg/kg	80 120 20	200	mg/kg	75 125 20	

STL Reference Data Summary

Matrix: SOLID				Extraction: METALS, TOTAL (Method Exclusive) - Solids			
Target Analyte List: All Analytes				Method: Mercury (7471A, Cold Vapor) - Solids			
				QC Program: MICHIGAN DEQ			
				Location: STL North Canton			

Analyte List Compound	Detection Limits				Check List 1021				Spike List 1026						
	RL	Units	MDL	Units	Run Date	Amt	Units	LCL	UCL	RPD	Amt	Units	LCL	UCL	RPD
Mercury	0.08	mg/kg	0.013	mg/kg	20050114	.833333	mg/kg	73	123	20	0.1666	mg/kg	10	199	50

STL Reference Data Summary

Target Analyte List: All Analytes

Matrix: SOLID
 Extraction: TCLP -> Filtrate -> Waste Dilution
 Method: Inductively Coupled Plasma (6010B)
 QC Program: MICHIGAN DEQ
 Location: STL North Canton

Analyte List Compound	RL	Detection Limits			Check List 906				Spike List 907						
		Units	MDL	Units	Run Date	Amt	Units	LCL	UCL	RPD	Amt	Units	LCL	UCL	RPD
Boron	8	mg/kg	16	ug/L	20050128	100	mg/kg	80	120	20	100	mg/kg	75	125	20

Boron	8	mg/kg	16	ug/L	20050128	100	mg/kg	80	120	20	100	mg/kg	75	125	20

STL Reference Data Summary

Target Analyte List: Q: TCLP Metals ICP Standard List

Matrix: SOLID
 Extraction: TCLP(1311) -> METALS, TOTAL
 Method: Inductively Coupled Plasma (6010B)
 QC Program: STANDARD TEST SET
 Location: STL North Canton

Target List 2804 Compound	RL	Detection Limits		Run Date	Check List 1900			Spike List 1901		
		Units	MDL		Amt	Units	LCL UCL RPD	Amt	Units	LCL UCL RPD
Arsenic	0.5	mg/L	0.0043	20050128	2	mg/L	50 150 20	5	mg/L	50 150 20
Barium	10	mg/L	0.0032	20050127	2	mg/L	50 150 20	50	mg/L	50 150 20
Cadmium	0.1	mg/L	0.00042	20050128	.05	mg/L	50 150 20	1	mg/L	50 150 20
Chromium	0.5	mg/L	0.0016	20050127	.2	mg/L	50 150 20	5	mg/L	50 150 20
Lead	0.5	mg/L	0.0017	20050127	.5	mg/L	50 150 20	5	mg/L	50 150 20
Selenium	0.25	mg/L	0.0024	20050127	2	mg/L	50 150 20	1	mg/L	50 150 20
Silver	0.5	mg/L	0.0021	20050128	.05	mg/L	50 150 20	1	mg/L	50 150 20

STL Reference Data Summary

Target Analyte List: All Analytes

Matrix: SOLID
 Extraction: TCLP(1311) -> METALS, TOTAL (Method exclusive)
 Method: Mercury (7470A, Cold Vapor) - Liquid
 QC Program: STANDARD TEST SET
 Location: STL North Canton

Analyte List Compound	Detection Limits			Run Date	Check List 1900			Spike List 1901		
	RL	Units	MDL		Amt	Units	LCL UCL RPD	Amt	Units	LCL UCL RPD

Mercury	0.002	mg/L	0.00009	mg/L	20050113	5	ug/L	50	150	20	5	ug/L	50	150	20

STL Reference Data Summary

Target Analyte List: NC: OLM03.1/4.2 Volatile List

Matrix: WASTE
Extraction: PURGE AND TRAP, MeOH EXTRACTION (Solids or Waste)
Method: Volatile Organics, GC/MS (8260B)
QC Program: STANDARD TEST SET
Location: STL North Canton

Target List 4121			Detection Limits			Check List 924				Spike List 925					
Compound	RL	Units	MDL	Units	Run Date	Amt	Units	LCL	UCL	RPD	Amt	Units	LCL	UCL	RPD
Acetone	2500	ug/kg	99	ug/kg	20040223	58		130	30		10		200	66	
Benzene	620	ug/kg	6.4	ug/kg	20040223	75		129	20		55		138	20	
Bromodichloromethane	620	ug/kg	12	ug/kg	20040223	72		125	30		47		131	51	
Bromoform	620	ug/kg	13	ug/kg	20040224	43		149	30		26		141	64	
Bromomethane	1200	ug/kg	25	ug/kg	20040223	24		152	30		15		152	72	
2-Butanone	2500	ug/kg	49	ug/kg	20040223	27		200	46		21		195	60	
Carbon disulfide	620	ug/kg	20	ug/kg	20040224	50		137	30		27		149	73	
Carbon tetrachloride	620	ug/kg	12	ug/kg	20040223	57		137	30		32		143	68	
Chlorobenzene	620	ug/kg	6.3	ug/kg	20040223	75		127	22		49		139	22	
Dibromochloromethane	620	ug/kg	6.9	ug/kg	20040223	49		135	30		44		135	61	
Chloroethane	1200	ug/kg	65	ug/kg	20040224	31		144	30		32		140	66	
Chloroform	620	ug/kg	12	ug/kg	20040223	73		115	30		59		128	46	
Chloromethane	1200	ug/kg	5.2	ug/kg	20040223	15		136	30		28		130	81	
Cyclohexane	2500	ug/kg	7.7	ug/kg	20040223										
1,2-Dibromo-3-chloropropane	1200	ug/kg	60	ug/kg	20040224										
1,2-Dibromomethane	620	ug/kg	9.9	ug/kg	20040223										
1,2-Dichlorobenzene	1200	ug/kg	17	ug/kg	20040224										
1,3-Dichlorobenzene	1200	ug/kg	7.2	ug/kg	20040223										
1,4-Dichlorobenzene	1200	ug/kg	7.9	ug/kg	20040223										
Dichlorodifluoromethane	1200	ug/kg	5.4	ug/kg	20040223										
1,1-Dichloroethane	620	ug/kg	7.3	ug/kg	20040223	77		119	30		56		130	54	
1,2-Dichloroethane	620	ug/kg	9.3	ug/kg	20040223	78		121	30		56		126	38	
cis-1,2-Dichloroethene	310	ug/kg	14	ug/kg	20040223	77		114	30		48		127	52	
trans-1,2-Dichloroethene	310	ug/kg	11	ug/kg	20040223	68		117	30		47		127	58	
1,1-Dichloropropane	620	ug/kg	8.3	ug/kg	20040223	55		142	27		43		147	27	
1,2-Dichloropropane	620	ug/kg	7.4	ug/kg	20040223	78		116	30		54		125	43	
cis-1,3-Dichloropropene	620	ug/kg	5.5	ug/kg	20040223	71		125	30		30		138	49	
trans-1,3-Dichloropropene	620	ug/kg	5.4	ug/kg	20040223	67		125	30		34		134	57	
Ethylbenzene	620	ug/kg	6.8	ug/kg	20040223	79		114	30		36		133	72	
2-Hexanone	2500	ug/kg	24	ug/kg	20040223	29		200	41		20		190	70	
Isopropylbenzene	1200	ug/kg	5.1	ug/kg	20040223										
Methyl acetate	1200	ug/kg	52	ug/kg	20040223										
Methylcyclohexane	620	ug/kg	8.92	ug/kg	20020213										
Methylene chloride	620	ug/kg	99	ug/kg	20040224	58		130	30		45		129	49	
4-Methyl-2-pentanone	2500	ug/kg	11	ug/kg	20040223	68		142	30		42		143	60	
Methyl tert-butyl ether	2500	ug/kg	10	ug/kg	20040223	70		130	30						
Styrene	620	ug/kg	28	ug/kg	20040224	80		114	30		23		136	65	

Target Analyte List: NC: OLM03.1/4.2 Volatile List

Matrix: WASTE
 Extraction: PURGE AND TRAP, MeOH EXTRACTION (Solids or Waste)
 Method: Volatile Organics, GC/MS (8260B)
 QC Program: STANDARD TEST SET
 Location: STL North Canton

Target List 4121				Detection Limits				Check List 924				Spike List 925			
Compound	RL	Units	MDL	Units	Run Date	Amt	Units	LCL	UCL	RPD	Amt	Units	LCL	UCL	RPD
1,1,2,2-Tetrachloroethane	620	ug/kg	8.2	ug/kg	20040223			70	133	30			33	162	90
Tetrachloroethane	620	ug/kg	9	ug/kg	20040223			72	120	30			31	137	81
Toluene	620	ug/kg	9.1	ug/kg	20040223			71	130	24			46	147	24
1,2,4-Trichlorobenzene	1200	ug/kg	12	ug/kg	20040223										
1,1,1-Trichloroethane	620	ug/kg	9.5	ug/kg	20040223			67	123	30			48	132	57
1,1,2-Trichloroethane	620	ug/kg	9.9	ug/kg	20040223			82	116	30			58	128	52
Trichloroethene	620	ug/kg	12	ug/kg	20040223			70	131	23			46	143	23
Trichlorofluoromethane	1200	ug/kg	8.3	ug/kg	20040223										
1,1,2-Trichloro-1,2,2-trifluoroethane	2500	ug/kg	10	ug/kg	20040223										
Vinyl chloride	1200	ug/kg	16	ug/kg	20040224										
Xylenes (total)	620	ug/kg	15	ug/kg	20040223			24	152	30			30	136	80
4-Bromofluorobenzene								80	114	30			33	135	78
1,2-Dichloroethane-d4								47	158	0	50	ug/kg	47	158	0
Toluene-d8								61	130	0			61	130	0
								60	143	0			60	143	0
Dibromofluoromethane								59	138	0			59	138	0

STL Reference Data Summary

Target Analyte List: Q: TCLP MSVOA Standard List

Matrix: WASTE
 Extraction: TCLP -> Filtrate -> Waste Dilution
 Method: Volatile Organics, GC/MS (8260B)
 QC Program: STANDARD TEST SET
 Location: STL North Canton

Target List 2006 Compound	RL	Detection Limits			Run Date	Check List 924			Spike List 925		
		Units	MDL	Units		Amt	Units	LCL UCL RPD	Amt	Units	LCL UCL RPD
Benzene	0.025	mg/L	0.23	ug/L	20040107			75 129 20			55 138 20
2-Butanone (MEK)			1	ug/L	20040107						
Carbon tetrachloride	0.025	mg/L	0.45	ug/L	20040226			57 137 30			32 143 68
Chlorobenzene	0.025	mg/L	0.28	ug/L	20040226			75 127 22			49 139 22
Chloroform	0.025	mg/L	0.4	ug/L	20040226			73 115 30			59 128 46
1,2-Dichloroethane	0.025	mg/L	0.48	ug/L	20040107			78 121 30			56 126 38
1,1-Dichloroethylene	0.025	mg/L	0.6	ug/L	20040107						
Tetrachloroethylene	0.025	mg/L	0.83	ug/L	20040107						
Trichloroethylene	0.025	mg/L	0.41	ug/L	20040107						
Vinyl chloride	0.025	mg/L	0.44	ug/L	20040226						
4-Bromofluorobenzene								24 152 30			30 136 80
1,2-Dichloroethane-d4								47 158 0	50	ug/kg	47 158 0
Toluene-d8								61 130 0			61 130 0
Dibromofluoromethane								60 143 0			60 143 0
								59 138 0			59 138 0

STL Reference Data Summary

Target Analyte List: Q: TCLP MSSemi Standard List

Matrix: WASTE
Extraction: TCLP -> Filtrate -> Waste Dilution
Method: Base/Neutrals and Acids (8270C)
QC Program: STANDARD TEST SET
Location: STL North Canton

Target List 2105 Compound	RL	Detection Limits		Run Date	Check List 1116			Spike List 1117		
		Units	MDL		Amt	Units	LCL UCL RPD	Amt	Units	LCL UCL RPD
m-Cresol & p-Cresol	0.04	mg/L	0.75	20040228	0.4000	mg/L	31 110 30	0.4000	mg/L	46 109 32
1,4-Dichlorobenzene	0.004	mg/L	0.52	20050217	0.2000	mg/L	15 122 30	0.2000	mg/L	18 110 36
2,4-Dinitrotoluene	0.02	mg/L	0.4	20050316	0.2000	mg/L	51 117 30	0.2000	mg/L	31 131 32
Hexachlorobenzene	0.02	mg/L	0.065	20050131	0.2000	mg/L	47 115 30	0.2000	mg/L	36 132 22
Hexachlorobutadiene	0.02	mg/L	0.51	20050316	0.2000	mg/L	14 126 30	0.2000	mg/L	18 116 32
Hexachloroethane	0.02	mg/L	0.58	20050316	0.2000	mg/L	10 164 30	0.2000	mg/L	18 110 33
o-Cresol	0.004	mg/L	0.56	20050316	0.2000	mg/L	33 110 30	0.2000	mg/L	33 115 31
Nitrobenzene	0.004	mg/L	0.053	20050131	0.2000	mg/L	37 127 30	0.2000	mg/L	19 211 59
Pentachlorophenol	0.04	mg/L	0.48	20050316	0.2000	mg/L	15 110 30	0.2000	mg/L	10 140 56
Pyridine	0.02	mg/L	0.78	20050316	0.200	mg/L	12 120 30	0.2000	mg/L	10 148 65
2,4,5-Trichlorophenol	0.02	mg/L	0.96	20050217	0.2000	mg/L	42 110 30	0.2000	mg/L	24 143 22
2,4,6-Trichlorophenol	0.02	mg/L	1.4	20050316	0.2000	mg/L	41 110 30	0.2000	mg/L	36 135 27
2-Fluorobiphenyl							29 114 0			29 114 0
2-Fluorophenol							10 114 0			10 114 0
2,4,6-Tribromophenol							20 126 0			20 126 0
Nitrobenzene-d5							33 123 0			33 123 0
Phenol-d5							10 115 0			10 115 0
Terphenyl-d14							42 124 0			42 124 0

STL Reference Data Summary

Target Analyte List: NC: OLM03.1/4.2 Semivolatile List

Matrix: WASTE
Extraction: WASTE DILUTION
Method: Base/Neutrals and Acids (8270C)
QC Program: STANDARD TEST SET
Location: STL North Canton

Target List 4122				Check List 1114				Spike List 1115			
Compound	RL	Detection Units	Limits MDL	Units	Run Date	Amt	Units	LCL UCL RPD	Amt	Units	LCL UCL RPD
Acenaphthene	20000	ug/kg	55.2	ug/kg	20040219	1700	ug/kg	52 110 30	1700	ug/kg	10 200 30
Acenaphthylene	20000	ug/kg	84	ug/kg	20040219	1700	ug/kg	56 110 30	1700	ug/kg	10 200 30
Acetophenone	20000	ug/kg	330	ug/kg	20040218						
Anthracene	20000	ug/kg	138	ug/kg	20040219	1700	ug/kg	59 110 30	1700	ug/kg	10 200 30
Atrazine	20000	ug/kg	660	ug/kg	20040218						
Benzaldehyde	20000	ug/kg	414	ug/kg	20040218						
Benzo(a)anthracene	20000	ug/kg	84	ug/kg	20040219	1700	ug/kg	54 110 30	1700	ug/kg	10 200 30
Benzo(b)fluoranthene	20000	ug/kg	138	ug/kg	20040107	1700	ug/kg	50 110 30	1700	ug/kg	10 200 30
Benzo(k)fluoranthene	20000	ug/kg	138	ug/kg	20040107	1700	ug/kg	46 110 30	1700	ug/kg	10 200 30
Benzo(ghi)perylene	20000	ug/kg	108	ug/kg	20040107	1700	ug/kg	49 110 30	1700	ug/kg	10 200 30
Benzo(a)pyrene	20000	ug/kg	138	ug/kg	20040219	1700	ug/kg	45 110 30	1700	ug/kg	10 200 30
1,1'-Biphenyl	20000	ug/kg	432	ug/kg	20040228						
bis(2-Chloroethoxy)methane	20000	ug/kg	960	ug/kg	20040218	1700	ug/kg	54 110 30	1700	ug/kg	36 110 30
bis(2-Chloroethyl) ether	20000	ug/kg	246	ug/kg	20040218	1700	ug/kg	41 124 30	1700	ug/kg	32 118 30
bis(2-Ethylhexyl) phthalate	20000	ug/kg	960	ug/kg	20040218	1700	ug/kg	52 113 30	1700	ug/kg	10 200 30
4-Bromophenyl phenyl ether	20000	ug/kg	282	ug/kg	20040218	1700	ug/kg	59 110 30	1700	ug/kg	44 120 30
Butyl benzyl phthalate	20000	ug/kg	222	ug/kg	20040218	1700	ug/kg	58 110 30	1700	ug/kg	43 138 30
Caprolactam	20000	ug/kg	468	ug/kg	20031213						
Carbazole	20000	ug/kg	558	ug/kg	20040218	1700	ug/kg	59 110 30	1700	ug/kg	10 162 30
4-Chloroaniline	20000	ug/kg	312	ug/kg	20031213	1700	ug/kg	24 110 30	1700	ug/kg	11 110 30
4-Chloro-3-methylphenol	20000	ug/kg	3060	ug/kg	20040108	1700	ug/kg	51 110 30	1700	ug/kg	32 117 30
2-Chloronaphthalene	20000	ug/kg	378	ug/kg	20040228	1700	ug/kg	56 110 30	1700	ug/kg	40 110 30
2-Chlorophenol	20000	ug/kg	216	ug/kg	20040108	1700	ug/kg	51 110 30	1700	ug/kg	32 110 30
4-Chlorophenyl phenyl ether	20000	ug/kg	216	ug/kg	20040218	1700	ug/kg	59 110 30	1700	ug/kg	47 116 30
Chrysene	20000	ug/kg	59.4	ug/kg	20040228	1700	ug/kg	54 110 30	1700	ug/kg	10 200 30
Dibenz(a,h)anthracene	20000	ug/kg	90	ug/kg	20040107	1700	ug/kg	47 110 30	1700	ug/kg	10 200 30
Dibenzofuran	20000	ug/kg	49.8	ug/kg	20040219	1700	ug/kg	57 110 30	1700	ug/kg	10 200 30
Di-n-butyl phthalate	20000	ug/kg	300	ug/kg	20031213	1700	ug/kg	60 110 30	1700	ug/kg	31 145 30
3,3'-Dichlorobenzidine	96000	ug/kg	294	ug/kg	20040108	1700	ug/kg	36 110 30	1700	ug/kg	10 110 30
2,4-Dichlorophenol	20000	ug/kg	318	ug/kg	20031213	1700	ug/kg	52 110 30	1700	ug/kg	33 110 30
Diethyl phthalate	20000	ug/kg	372	ug/kg	20031213	1700	ug/kg	57 110 30	1700	ug/kg	48 118 30
2,4-Dimethylphenol	20000	ug/kg	408	ug/kg	20040108	1700	ug/kg	44 110 30	1700	ug/kg	19 114 30
Dimethyl phthalate	20000	ug/kg	384	ug/kg	20040218	1700	ug/kg	59 110 30	1700	ug/kg	47 116 30
4,6-Dinitro-2-methylphenol	96000	ug/kg	2820	ug/kg	20040109	1700	ug/kg	35 110 30	1700	ug/kg	10 110 30
2,4-Dinitrophenol	96000	ug/kg	2460	ug/kg	20040301	1700	ug/kg	10 148 30	1700	ug/kg	10 110 30
2,4-Dinitrotoluene	20000	ug/kg	342	ug/kg	20031213	1700	ug/kg	61 110 30	1700	ug/kg	42 118 30
2,6-Dinitrotoluene	20000	ug/kg	348	ug/kg	20040228	1700	ug/kg	60 110 30	1700	ug/kg	28 137 30

Target Analyte List: NC: OLM03.1/4.2 Semivolatile List

Matrix: WASTE
Extraction: WASTE DILUTION
Method: Base/Neutrals and Acids (8270C)
QC Program: STANDARD TEST SET
Location: STL North Canton

Target List 4122						Check List 1114						Spike List 1115					
Compound	RL	Units	MDL	Units	Run Date	Amt	Units	LCL	UCL	RPD	Amt	Units	LCL	UCL	RPD		
Di-n-octyl phthalate	20000	ug/kg	660	ug/kg	20031213	1700	ug/kg	55	110	30	1700	ug/kg	10	182	30		
Fluoranthene	20000	ug/kg	55.8	ug/kg	20040219	1700	ug/kg	58	110	30	1700	ug/kg	10	200	30		
Fluorene	20000	ug/kg	78	ug/kg	20040228	1700	ug/kg	54	110	30	1700	ug/kg	10	187	30		
Hexachlorobenzene	20000	ug/kg	84	ug/kg	20040219	1700	ug/kg	58	110	30	1700	ug/kg	37	122	30		
Hexachlorobutadiene	20000	ug/kg	150	ug/kg	20040218	1700	ug/kg	59	110	30	1700	ug/kg	30	110	30		
Hexachlorocyclopentadiene	96000	ug/kg	174	ug/kg	20040228	1700	ug/kg	31	110	30	1700	ug/kg	10	110	30		
Hexachloroethane	20000	ug/kg	294	ug/kg	20040218	1700	ug/kg	60	110	30	1700	ug/kg	13	110	30		
Indeno(1,2,3-cd)pyrene	20000	ug/kg	120	ug/kg	20040107	1700	ug/kg	44	110	30	1700	ug/kg	10	200	30		
Isophorone	20000	ug/kg	210	ug/kg	20040218	1700	ug/kg	52	128	30	1700	ug/kg	32	129	30		
2-Methylnaphthalene	20000	ug/kg	59.4	ug/kg	20031213	1700	ug/kg	61	110	30	1700	ug/kg	10	200	30		
2-Methylphenol	20000	ug/kg	402	ug/kg	20040108	1700	ug/kg	50	110	30	1700	ug/kg	19	124	30		
4-Methylphenol	20000	ug/kg	348	ug/kg	20040108	1700	ug/kg	53	110	30	1700	ug/kg	27	116	30		
Naphthalene	20000	ug/kg	53.4	ug/kg	20040219	1700	ug/kg	55	110	30	1700	ug/kg	10	200	30		
2-Nitroaniline	96000	ug/kg	306	ug/kg	20031213	1700	ug/kg	55	110	30	1700	ug/kg	31	141	30		
3-Nitroaniline	96000	ug/kg	192	ug/kg	20040108	1700	ug/kg	47	110	30	1700	ug/kg	27	110	30		
4-Nitroaniline	96000	ug/kg	216	ug/kg	20040108	1700	ug/kg	53	110	30	1700	ug/kg	23	124	30		
Nitrobenzene	20000	ug/kg	384	ug/kg	20040218	1700	ug/kg	50	115	30	1700	ug/kg	33	111	30		
2-Nitrophenol	20000	ug/kg	204	ug/kg	20031213	1700	ug/kg	48	110	30	1700	ug/kg	17	110	30		
4-Nitrophenol	96000	ug/kg	4860	ug/kg	20040301	1700	ug/kg	43	110	30	1700	ug/kg	10	125	30		
N-Nitrosodiphenylamine	20000	ug/kg	246	ug/kg	20040218	1700	ug/kg	59	110	30	1700	ug/kg	10	169	30		
N-Nitrosodi-n-propylamine	20000	ug/kg	456	ug/kg	20040218	1700	ug/kg	42	131	30	1700	ug/kg	30	121	30		
2,2-oxybis(1-Chloropropane)			312	ug/kg	20040218												
Pentachlorophenol	20000	ug/kg	2700	ug/kg	20040109	1700	ug/kg	42	110	30	1700	ug/kg	10	182	30		
Phenanthrene	20000	ug/kg	66	ug/kg	20031213	1700	ug/kg	58	110	30	1700	ug/kg	10	200	30		
Phenol	20000	ug/kg	342	ug/kg	20040218	1700	ug/kg	47	110	30	1700	ug/kg	10	144	30		
Pyrene	20000	ug/kg	60	ug/kg	20040219	1700	ug/kg	56	110	30	1700	ug/kg	10	200	30		
2,4,5-Trichlorophenol	20000	ug/kg	294	ug/kg	20031213	1700	ug/kg	49	110	30	1700	ug/kg	32	112	30		
2,4,6-Trichlorophenol	20000	ug/kg	408	ug/kg	20031213	1700	ug/kg	51	110	30	1700	ug/kg	22	110	30		
2-Fluorobiphenyl						1700	ug/kg	44	110	0	1700	ug/kg	44	110	0		
2-Fluorophenol						2500	ug/kg	49	110	0	2500	ug/kg	49	110	0		
2,4,6-Tribromophenol						2500	ug/kg	16	124	0	2500	ug/kg	16	124	0		
Nitrobenzene-d5						1700	ug/kg	53	110	0	1700	ug/kg	53	110	0		
Phenol-d5						2500	ug/kg	47	110	0	2500	ug/kg	47	110	0		
Terphenyl-d14						1700	ug/kg	36	128	0	1700	ug/kg	36	128	0		

STL Reference Data Summary

Target Analyte List: Q: Aroclors Only Standard List

Matrix: WASTE
Extraction: WASTE DILUTION w/ACID STRIP (PCB)
Method: PCBs (8082)
QC Program: STANDARD TEST SET
Location: STL North Canton

Target List 2207 Compound	RL	Detection Limits		Run Date	Check List 928			Spike List 929		
		Units	MDL		Amt	Units	LCL UCL RPD	Amt	Units	LCL UCL RPD
Aroclor 1016	1000	ug/kg	190	20040217			45 133 30			26 144 39
Aroclor 1221	1000	ug/kg	220	20040220						
Aroclor 1232	1000	ug/kg	170	20040219						
Aroclor 1242	1000	ug/kg	290	20040219						
Aroclor 1248	1000	ug/kg	200	20040217						
Aroclor 1254	1000	ug/kg	120	20040220						
Aroclor 1260	1000	ug/kg	130	20040217						
Decachlorobiphenyl							42 128 30			37 138 33
Tetrachloro-m-xylene							40 145 0			40 145 0
							40 145 0			34 197 0

STL Reference Data Summary

Target Analyte List: All Analytes

Matrix: WASTE
 Extraction: WASTE DILUTION
 Method: Hydrocarbons, Extractable Petroleum (8015B)
 QC Program: STANDARD TEST SET
 Location: STL North Canton

Analyte List Compound	RL	Detection Limits			Run Date	Check List 1801				Spike List 1802					
		Units	MDL	Units		Amt	Units	LCL	UCL	RPD	Amt	Units	LCL	UCL	RPD
TPH C10-C32	1000	mg/kg	48	mg/kg	20040109	16.7	mg/kg	43	185	30	16.7	mg/kg	70	130	50
TPH (as Diesel)	1000	mg/kg	48	mg/kg	20040109	1.33	mg/kg	10	110	0	1.33	mg/kg	10	110	0
C9 (nonane)															

STL Reference Data Summary

Target Analyte List: Q: Aroclors Only Standard List

Matrix: WPE
 Extraction: EXTRACTION, SOLID/SOLVENT (Auto shaker) w/ACID ST
 Method: PCBs (8082)
 QC Program: STANDARD TEST SET
 Location: STL North Canton

Target List 2207					Check List 928					Spike List 929					
Compound	RL	Units	MDL	Units	Run Date	Amt	Units	LCL	UCL	RPD	Amt	Units	LCL	UCL	RPD
Aroclor 1016	4	ug	4	ug	20001222	10	mg/kg	79	141	30			10	200	30
Aroclor 1221	4	ug	4	ug	20001222										
Aroclor 1232	4	ug	4	ug	20001222										
Aroclor 1242	4	ug	4	ug	20001222										
Aroclor 1248	4	ug	4	ug	20001222										
Aroclor 1254	4	ug	4	ug	20001222										
Aroclor 1260	4	ug	4	ug	20001222	10	mg/kg	71	136	30			37	138	33
Decachlorobiphenyl						0.2	mg/kg	39	187	0	0.2	mg/kg	39	187	0
Tetrachloro-m-xylene						0.2	mg/kg	52	171	0	0.2	mg/kg	52	171	0

STL Reference Data Summary

Target Analyte List: Q: CLP ICP Metals TAL Standard List

Matrix: WASTE
Extraction: METALS, TOTAL - Soils
Method: Inductively Coupled Plasma (6010B)
QC Program: STANDARD TEST SET
Location: STL North Canton

Target List 2600				Check List 906				Spike List 907			
Compound	RL	Detection Units	Limits MDL	Units	Run Date	Amt	Units	LCL UCL RPD	Amt	Units	LCL UCL RPD
Aluminum	20	mg/kg	5	mg/kg	20050127	200	mg/kg	80 120 20	200	mg/kg	75 125 20
Antimony	6	mg/kg	0.33	mg/kg	20050128	50	mg/kg	80 120 20	50	mg/kg	75 125 20
Barium	20	mg/kg	0.2	mg/kg	20050128	200	mg/kg	80 120 20	200	mg/kg	75 125 20
Beryllium	0.5	mg/kg	0.029	mg/kg	20050128	5	mg/kg	80 120 20	5	mg/kg	75 125 20
Cadmium	0.5	mg/kg	0.027	mg/kg	20050128	5	mg/kg	80 120 20	5	mg/kg	75 125 20
Calcium	500	mg/kg	8.4	mg/kg	20050127	5000	mg/kg	80 120 20	5000	mg/kg	75 125 20
Chromium	1	mg/kg	0.13	mg/kg	20050127	20	mg/kg	80 120 20	20	mg/kg	75 125 20
Cobalt	5	mg/kg	0.34	mg/kg	20050128	50	mg/kg	80 120 20	50	mg/kg	75 125 20
Copper	2.5	mg/kg	0.33	mg/kg	20050128	25	mg/kg	80 120 20	25	mg/kg	75 125 20
Iron	10	mg/kg	8.7	mg/kg	20050127	100	mg/kg	73 137 20	100	mg/kg	75 125 20
Magnesium	500	mg/kg	2.1	mg/kg	20050128	5000	mg/kg	80 120 20	5000	mg/kg	75 125 20
Manganese	1.5	mg/kg	0.042	mg/kg	20050128	50	mg/kg	80 120 20	50	mg/kg	75 125 20
Nickel	4	mg/kg	0.28	mg/kg	20050127	50	mg/kg	80 120 20	50	mg/kg	75 125 20
Potassium	500	mg/kg	3.1	mg/kg	20050127	5000	mg/kg	80 120 20	5000	mg/kg	75 125 20
Silver	1	mg/kg	0.29	mg/kg	20050128	5	mg/kg	80 120 20	5	mg/kg	75 125 20
Sodium	500	mg/kg	33	mg/kg	20050128	5000	mg/kg	80 120 20	5000	mg/kg	75 125 20
Vanadium	5	mg/kg	0.097	mg/kg	20050128	50	mg/kg	80 120 20	50	mg/kg	75 125 20
Zinc	2	mg/kg	0.56	mg/kg	20050127	50	mg/kg	80 120 20	50	mg/kg	75 125 20

STL Reference Data Summary

Target Analyte List: Q: SW846 Method 7000 Series GFAA & CVAA Re List

Matrix: WASTE
 Extraction: METALS, TOTAL (Method Exclusive) - Solids
 Method: Mercury (7471A, Cold Vapor) - Solids
 QC Program: STANDARD TEST SET
 Location: STL North Canton

Target List 1700						Check List 1021					Spike List 1026				
Compound	RL	Detection Limits		Run Date	Amt			Amt							
		Units	MDL		Units	Units	LCL	UCL	RPD	Units	LCL	UCL	RPD		
Arsenic				0											
Lead				0											
Mercury	0.1	mg/kg	0.013	20050114	.833333	mg/kg	73	123	20	0.166	mg/kg	10	199	50	
Selenium				0											
Thallium				0											

STL Reference Data Summary

Target Analyte List: Q: TCLP MSVOA Standard List

Matrix: AIR
Extraction: TCLP(1311-ZHE/filter) -> PURGE-AND-TRAP (Low Level)
Method: Volatile Organics, GC/MS (8260B)
QC Program: STANDARD TEST SET
Location: STL North Canton

Target List 2006 Compound	RL	Detection Limits		Units	Run Date	Check List 996			Spike List 997		
		MDL				Amt	Units	LCL UCL RPD	Amt	Units	LCL UCL RPD
Benzene		0.23		ug/L	20040107						
2-Butanone (MEK)		1		ug/L	20040107						
Carbon tetrachloride		0.45		ug/L	20040226						
Chlorobenzene		0.28		ug/L	20040226						
Chloroform		0.4		ug/L	20040226						
1,2-Dichloroethane		0.48		ug/L	20040107						
1,1-Dichloroethylene		0.6		ug/L	20040107						
Tetrachloroethylene		0.83		ug/L	20040107						
Trichloroethylene		0.41		ug/L	20040107						
Vinyl chloride		0.44		ug/L	20040226						

STL Reference Data Summary

Target Analyte List: All Analytes

Matrix: AIR
Extraction: NO SAMPLE PREPARATION PERFORMED / DIRECT INJ
Method: Volatile Organics by GC/MS (TO-15) ppb(v/v)
QC Program: STANDARD TEST SET
Location: STL Knoxville

Analyte List Compound	RL	Detection Limits			Check List 83027				Spike List 83027			
		Units	MDL	Units	Run Date	Amt	Units	LCL UCL RPD	Amt	Units	LCL UCL RPD	
Acetone	5.0	ppb(v/v)	0.51	ppb(v/v)	20060130	10	ppb(v/v)	60 140 25	10	ppb(v/v)	60 140 25	
Acetonitrile	1.0	ppb(v/v)	0.24	ppb(v/v)	20060201	10	ppb(v/v)	60 140 25	10	ppb(v/v)	60 140 25	
Acrolein	0.80	ppb(v/v)	0.19	ppb(v/v)	20060204	10	ppb(v/v)	60 140 25	10	ppb(v/v)	60 140 25	
Acrylonitrile	2.0	ppb(v/v)	0.11	ppb(v/v)	20060204	10	ppb(v/v)	60 140 25	10	ppb(v/v)	60 140 25	
alpha-Methylstyrene	0.40	ppb(v/v)	0.032	ppb(v/v)	20060204	10	ppb(v/v)	70 130 25	10	ppb(v/v)	70 130 25	
Benzene	0.20	ppb(v/v)	0.049	ppb(v/v)	20060204	10	ppb(v/v)	70 130 25	10	ppb(v/v)	70 130 25	
Benzyl chloride	0.40	ppb(v/v)	0.065	ppb(v/v)	20060204	10	ppb(v/v)	70 130 25	10	ppb(v/v)	70 130 25	
Bromodichloromethane	0.20	ppb(v/v)	0.036	ppb(v/v)	20060204	10	ppb(v/v)	70 130 25	10	ppb(v/v)	70 130 25	
Vinyl bromide	0.20	ppb(v/v)	0.034	ppb(v/v)	20060201	10	ppb(v/v)	60 140 25	10	ppb(v/v)	60 140 25	
Bromoform	0.20	ppb(v/v)	0.047	ppb(v/v)	20060204	10	ppb(v/v)	70 130 25	10	ppb(v/v)	70 130 25	
Bromomethane	0.20	ppb(v/v)	0.10	ppb(v/v)	20060204	10	ppb(v/v)	70 130 25	10	ppb(v/v)	70 130 25	
1,3-Butadiene	0.40	ppb(v/v)	0.10	ppb(v/v)	20060204	10	ppb(v/v)	70 130 25	10	ppb(v/v)	70 130 25	
n-Butane	0.40	ppb(v/v)	0.038	ppb(v/v)	20060201	10	ppb(v/v)	70 130 25	10	ppb(v/v)	70 130 25	
1-Butanol	2.0	ppb(v/v)	0.15	ppb(v/v)	20060204	10	ppb(v/v)	60 140 25	10	ppb(v/v)	60 140 25	
2-Butanone (MEK)	1.0	ppb(v/v)	0.18	ppb(v/v)	20060204	10	ppb(v/v)	60 140 25	10	ppb(v/v)	60 140 25	
tert-Butyl alcohol	2.0	ppb(v/v)	0.19	ppb(v/v)	20060204	10	ppb(v/v)	60 140 25	10	ppb(v/v)	60 140 25	
n-Butylbenzene	0.40	ppb(v/v)	0.059	ppb(v/v)	20060204	10	ppb(v/v)	70 130 25	10	ppb(v/v)	70 130 25	
sec-Butylbenzene	0.40	ppb(v/v)	0.055	ppb(v/v)	20060204	10	ppb(v/v)	70 130 25	10	ppb(v/v)	70 130 25	
Carbon disulfide	0.50	ppb(v/v)	0.031	ppb(v/v)	20060204	10	ppb(v/v)	70 130 25	10	ppb(v/v)	70 130 25	
Carbon tetrachloride	0.20	ppb(v/v)	0.036	ppb(v/v)	20060204	10	ppb(v/v)	70 130 25	10	ppb(v/v)	70 130 25	
Chlorobenzene	0.20	ppb(v/v)	0.047	ppb(v/v)	20060204	10	ppb(v/v)	70 130 25	10	ppb(v/v)	70 130 25	
Dibromochloromethane	0.20	ppb(v/v)	0.033	ppb(v/v)	20060204	10	ppb(v/v)	70 130 25	10	ppb(v/v)	70 130 25	
Chlorodifluoromethane	0.20	ppb(v/v)	0.053	ppb(v/v)	20060204	10	ppb(v/v)	70 130 25	10	ppb(v/v)	70 130 25	
Chloroethane	0.20	ppb(v/v)	0.040	ppb(v/v)	20060201	10	ppb(v/v)	70 130 25	10	ppb(v/v)	70 130 25	
Chloroform	0.20	ppb(v/v)	0.049	ppb(v/v)	20060204	10	ppb(v/v)	70 130 25	10	ppb(v/v)	70 130 25	
Chloromethane	0.50	ppb(v/v)	0.17	ppb(v/v)	20060204	10	ppb(v/v)	70 130 25	10	ppb(v/v)	70 130 25	
3-Chloropropene	0.20	ppb(v/v)	0.061	ppb(v/v)	20060204	10	ppb(v/v)	60 140 25	10	ppb(v/v)	60 140 25	
2-Chlorotoluene	0.40	ppb(v/v)	0.067	ppb(v/v)	20060204	10	ppb(v/v)	70 130 25	10	ppb(v/v)	70 130 25	
Cyclohexane	0.50	ppb(v/v)	0.086	ppb(v/v)	20060201	10	ppb(v/v)	70 130 25	10	ppb(v/v)	70 130 25	
n-Decane	1.0	ppb(v/v)	0.058	ppb(v/v)	20060204	10	ppb(v/v)	70 130 25	10	ppb(v/v)	70 130 25	
1,2-Dibromoethane (EDB)	0.20	ppb(v/v)	0.045	ppb(v/v)	20060204	10	ppb(v/v)	70 130 25	10	ppb(v/v)	70 130 25	
Dibromomethane	0.40	ppb(v/v)	0.041	ppb(v/v)	20060204	10	ppb(v/v)	70 130 25	10	ppb(v/v)	70 130 25	
1,2-Dichlorobenzene	0.20	ppb(v/v)	0.063	ppb(v/v)	20060204	10	ppb(v/v)	70 130 25	10	ppb(v/v)	70 130 25	
1,3-Dichlorobenzene	0.20	ppb(v/v)	0.063	ppb(v/v)	20060204	10	ppb(v/v)	70 130 25	10	ppb(v/v)	70 130 25	
1,4-Dichlorobenzene	0.20	ppb(v/v)	0.054	ppb(v/v)	20060204	10	ppb(v/v)	70 130 25	10	ppb(v/v)	70 130 25	
Dichlorodifluoromethane	0.20	ppb(v/v)	0.036	ppb(v/v)	20060204	10	ppb(v/v)	70 130 25	10	ppb(v/v)	70 130 25	
1,1-Dichloroethane	0.20	ppb(v/v)	0.056	ppb(v/v)	20060204	10	ppb(v/v)	70 130 25	10	ppb(v/v)	70 130 25	

Target Analyte List: All Analytes

Matrix: AIR
 Extraction: NO SAMPLE PREPARATION PERFORMED / DIRECT INJ
 Method: Volatile Organics by GC/MS (TO-15) ppb(v/v)
 QC Program: STANDARD TEST SET
 Location: STL Knoxville

Analyte List		Detection Limits				Check List 83027				Spike List 83027					
Compound	RL	Units	MDL	Units	Run Date	Amt	Units	LCL	UCL	RPD	Amt	Units	LCL	UCL	RPD
1,2-Dichloroethane	0.20	ppb(v/v)	0.057	ppb(v/v)	20060204	10	ppb(v/v)	70	130	25	10	ppb(v/v)	70	130	25
cis-1,2-Dichloroethene	0.20	ppb(v/v)	0.11	ppb(v/v)	20060204	10	ppb(v/v)	70	130	25	10	ppb(v/v)	70	130	25
trans-1,2-Dichloroethene	0.20	ppb(v/v)	0.14	ppb(v/v)	20060204	10	ppb(v/v)	70	130	25	10	ppb(v/v)	70	130	25
1,1-Dichloroethene	0.20	ppb(v/v)	0.084	ppb(v/v)	20060204	10	ppb(v/v)	70	130	25	10	ppb(v/v)	70	130	25
1,2-Dichloropropane	0.20	ppb(v/v)	0.038	ppb(v/v)	20060204	10	ppb(v/v)	70	130	25	10	ppb(v/v)	70	130	25
cis-1,3-Dichloropropene	0.20	ppb(v/v)	0.040	ppb(v/v)	20060204	10	ppb(v/v)	70	130	25	10	ppb(v/v)	70	130	25
trans-1,3-Dichloropropene	0.20	ppb(v/v)	0.16	ppb(v/v)	20060204	10	ppb(v/v)	70	130	25	10	ppb(v/v)	70	130	25
1,2-Dichloro-1,1,2,2-tetrafluoroethane	0.20	ppb(v/v)	0.047	ppb(v/v)	20060204	10	ppb(v/v)	70	130	25	10	ppb(v/v)	70	130	25
n-Dodecane	1.0	ppb(v/v)	0.051	ppb(v/v)	20060204	10	ppb(v/v)	70	130	25	10	ppb(v/v)	70	130	25
Ethylbenzene	0.20	ppb(v/v)	0.059	ppb(v/v)	20060204	10	ppb(v/v)	70	130	25	10	ppb(v/v)	70	130	25
Ethyl ether	2.0	ppb(v/v)	0.11	ppb(v/v)	20060204	10	ppb(v/v)	60	140	25	10	ppb(v/v)	60	140	25
4-Ethyltoluene	0.40	ppb(v/v)	0.040	ppb(v/v)	20060204	10	ppb(v/v)	70	130	25	10	ppb(v/v)	70	130	25
n-Heptane	0.50	ppb(v/v)	0.047	ppb(v/v)	20060204	10	ppb(v/v)	70	130	25	10	ppb(v/v)	70	130	25
Hexachlorobutadiene	1.0	ppb(v/v)	0.097	ppb(v/v)	20060204	10	ppb(v/v)	70	130	25	10	ppb(v/v)	70	130	25
n-Hexane	0.50	ppb(v/v)	0.039	ppb(v/v)	20060204	10	ppb(v/v)	70	130	25	10	ppb(v/v)	70	130	25
2-Hexanone	0.50	ppb(v/v)	0.12	ppb(v/v)	20060204	10	ppb(v/v)	60	140	25	10	ppb(v/v)	60	140	25
Isopropylbenzene	0.40	ppb(v/v)	0.052	ppb(v/v)	20060204										
Cumene	0.40	ppb(v/v)	0.052	ppb(v/v)	20060204	10	ppb(v/v)	70	130	25	10	ppb(v/v)	70	130	25
4-Isopropyltoluene	0.20	ppb(v/v)	0.065	ppb(v/v)	20060204										
p-Cymene	0.20	ppb(v/v)	0.065	ppb(v/v)	20060204										
Methanol	10	ppb(v/v)	0.76	ppb(v/v)	20060204	10	ppb(v/v)	60	140	25	10	ppb(v/v)	60	140	25
Methylene chloride	0.50	ppb(v/v)	0.030	ppb(v/v)	20060204	10	ppb(v/v)	70	130	25	10	ppb(v/v)	70	130	25
4-Methyl-2-pentanone (MIBK)	0.50	ppb(v/v)	0.12	ppb(v/v)	20060204	10	ppb(v/v)	60	140	25	10	ppb(v/v)	60	140	25
Methyl tert-butyl ether	1.0	ppb(v/v)	0.10	ppb(v/v)	20060204	10	ppb(v/v)	60	140	25	10	ppb(v/v)	60	140	25
Naphthalene	0.50	ppb(v/v)	0.036	ppb(v/v)	20060204	10	ppb(v/v)	70	130	25	10	ppb(v/v)	70	130	25
Nonane	0.50	ppb(v/v)	0.052	ppb(v/v)	20060204	10	ppb(v/v)	70	130	25	10	ppb(v/v)	70	130	25
n-Octane	0.40	ppb(v/v)	0.048	ppb(v/v)	20060204	10	ppb(v/v)	70	130	25	10	ppb(v/v)	70	130	25
Pentane	1.0	ppb(v/v)	0.11	ppb(v/v)	20060204	10	ppb(v/v)	70	130	25	10	ppb(v/v)	70	130	25
n-Propylbenzene	0.40	ppb(v/v)	0.077	ppb(v/v)	20060204	10	ppb(v/v)	70	130	25	10	ppb(v/v)	70	130	25
Styrene	0.20	ppb(v/v)	0.039	ppb(v/v)	20060204	10	ppb(v/v)	70	130	25	10	ppb(v/v)	70	130	25
1,1,2,2-Tetrachloroethane	0.20	ppb(v/v)	0.056	ppb(v/v)	20060204	10	ppb(v/v)	70	130	25	10	ppb(v/v)	70	130	25
Tetrachloroethene	0.20	ppb(v/v)	0.032	ppb(v/v)	20060204	10	ppb(v/v)	70	130	25	10	ppb(v/v)	70	130	25
Toluene	0.20	ppb(v/v)	0.052	ppb(v/v)	20060204	10	ppb(v/v)	70	130	25	10	ppb(v/v)	70	130	25
1,2,4-Trichlorobenzene	1.0	ppb(v/v)	0.068	ppb(v/v)	20060204	10	ppb(v/v)	70	130	25	10	ppb(v/v)	70	130	25
1,1,1-Trichloroethane	0.20	ppb(v/v)	0.038	ppb(v/v)	20060204	10	ppb(v/v)	70	130	25	10	ppb(v/v)	70	130	25
1,1,2-Trichloroethane	0.20	ppb(v/v)	0.049	ppb(v/v)	20060204	10	ppb(v/v)	70	130	25	10	ppb(v/v)	70	130	25
Trichloroethene	0.20	ppb(v/v)	0.033	ppb(v/v)	20060204	10	ppb(v/v)	70	130	25	10	ppb(v/v)	70	130	25
Trichlorofluoromethane	0.20	ppb(v/v)	0.031	ppb(v/v)	20060204	10	ppb(v/v)	70	130	25	10	ppb(v/v)	70	130	25
1,2,3-Trichloropropane	0.50	ppb(v/v)	0.093	ppb(v/v)	20060201	10	ppb(v/v)	60	140	25	10	ppb(v/v)	60	140	25

Target Analyte List: All Analytes

Matrix: AIR
 Extraction: NO SAMPLE PREPARATION PERFORMED / DIRECT INJ
 Method: Volatile Organics by GC/MS (TO-15) ppb(v/v)
 QC Program: STANDARD TEST SET
 Location: STL Knoxville

Analyte List				Detection Limits				Check List 83027				Spike List 83027			
Compound	RL	Units	MDL	Units	Run Date	Amt	Units	LCL	UCL	RPD	Amt	Units	LCL	UCL	RPD
1,1,2-Trichlorotrifluoroethane	0.20	ppb(v/v)	0.024	ppb(v/v)	20060204	10	ppb(v/v)	70	130	25	10	ppb(v/v)	70	130	25
1,1,2-Trichloro-1,2,2-trifluoroethane	0.20	ppb(v/v)	0.024	ppb(v/v)	20060204	10	ppb(v/v)	70	130	25	10	ppb(v/v)	70	130	25
1,2,4-Trimethylbenzene	0.20	ppb(v/v)	0.042	ppb(v/v)	20060204	10	ppb(v/v)	70	130	25	10	ppb(v/v)	70	130	25
1,3,5-Trimethylbenzene	0.20	ppb(v/v)	0.057	ppb(v/v)	20060204	10	ppb(v/v)	70	130	25	10	ppb(v/v)	70	130	25
2,2,4-Trimethylpentane	0.50	ppb(v/v)	0.040	ppb(v/v)	20060204	10	ppb(v/v)	70	130	25	10	ppb(v/v)	70	130	25
n-Undecane	1.0	ppb(v/v)	0.046	ppb(v/v)	20060204	10	ppb(v/v)	70	130	25	10	ppb(v/v)	70	130	25
Vinyl acetate	1.0	ppb(v/v)	0.13	ppb(v/v)	20060204	10	ppb(v/v)	60	140	25	10	ppb(v/v)	60	140	25
Vinyl chloride	0.20	ppb(v/v)	0.051	ppb(v/v)	20060204	10	ppb(v/v)	70	130	25	10	ppb(v/v)	70	130	25
m-Xylene & p-Xylene	0.20	ppb(v/v)	0.053	ppb(v/v)	20060204	20	ppb(v/v)	70	130	25	20	ppb(v/v)	70	130	25
o-Xylene	0.20	ppb(v/v)	0.048	ppb(v/v)	20060204	10	ppb(v/v)	70	130	25	10	ppb(v/v)	70	130	25
4-Bromofluorobenzene						8	ppb(v/v)	70	130	0	8	ppb(v/v)	70	130	0
1,2-Dichloroethane-d4						8	ppb(v/v)	70	130	0	8	ppb(v/v)	70	130	0
Toluene-d8						8	ppb(v/v)	70	130	0	8	ppb(v/v)	70	130	0

STL Reference Data Summary

Target Analyte List: Q: TCLP MSVOA Standard List

Matrix: AIR
Extraction: TCLP(1311-ZHE/filler) -> PURGE-AND-TRAP (Low Level)
Method: Volatile Organics, GC/MS (8260B)
QC Program: STANDARD TEST SET
Location: STL North Canton

Target List 2006 Compound	RL	Detection Limits		Run Date	Check List 996			Spike List 997		
		Units	MDL		Amt	Units	LCL UCL RPD	Amt	Units	LCL UCL RPD
Benzene		ug/L	0.23	20040107						
2-Butanone (MEK)		ug/L	1	20040107						
Carbon tetrachloride		ug/L	0.45	20040226						
Chlorobenzene		ug/L	0.28	20040226						
Chloroform		ug/L	0.4	20040226						
1,2-Dichloroethane		ug/L	0.48	20040107						
1,1-Dichloroethylene		ug/L	0.6	20040107						
Tetrachloroethylene		ug/L	0.83	20040107						
Trichloroethylene		ug/L	0.41	20040107						
Vinyl chloride		ug/L	0.44	20040226						

STL Reference Data Summary

Target Analyte List: COI: Standard TO-14A/TO-15 list

Matrix: AIR
Extraction: NO SAMPLE PREPARATION PERFORMED / DIRECT INJ
Method: Volatile Organics by GC/MS TO-15 (Medium Level) ug
QC Program: STANDARD TEST SET
Location: STL City of Industry

Target List 5700					Check List 5700					Spike List 0				
Compound	RL	Units	MDL	Run Date	Amt	Units	LCL	UCL	RPD	Amt	Units	LCL	UCL	RPD
Acetone	24	ug/m3	4.7	20060111		0	0	30						
Benzene	6.4	ug/m3	2.6	20060111		70	130	30						
Benzyl chloride	130	ug/m3	41	20060112		0	0	30						
Bromodichloromethane	13	ug/m3	5.4	20060111		0	0	30						
Bromoform	21	ug/m3	5.2	20060706		0	0	30						
Bromomethane	7.8	ug/m3	3.9	20060111		0	0	30						
2-Butanone (MEK)	29	ug/m3	5.9	20060111		0	0	30						
Carbon disulfide	31	ug/m3	6.2	20060111		0	0	30						
Carbon tetrachloride	13	ug/m3	3.1	20060706		0	0	30						
Chlorobenzene	9.2	ug/m3	2.3	20060111		70	130	30						
Dibromochloromethane	17	ug/m3	8.5	20060706		0	0	30						
Chloroethane	10	ug/m3	2.1	20060111		0	0	30						
Chloroform	7.8	ug/m3	3.9	20060706		70	130	30						
Chloromethane	8.2	ug/m3	2.1	20060111		0	0	30						
1,2-Dibromoethane (EDB)	15	ug/m3	3.8	20060111		0	0	30						
1,2-Dichlorobenzene	12	ug/m3	5.4	20060111		70	130	30						
1,3-Dichlorobenzene	12	ug/m3	4.8	20060111		0	0	30						
1,4-Dichlorobenzene	12	ug/m3	4.8	20060111		0	0	30						
Dichlorodifluoromethane	9.9	ug/m3	2.5	20060505		0	0	30						
1,1-Dichloroethane	8.1	ug/m3	2.0	20060111		70	130	30						
1,2-Dichloroethane	8.1	ug/m3	3.2	20060111		0	0	30						
cis-1,2-Dichloroethene	7.9	ug/m3	3.2	20060111		0	0	30						
trans-1,2-Dichloroethene	7.9	ug/m3	2.0	20060111		0	0	30						
1,1-Dichloroethene	7.9	ug/m3	2.0	20060111		70	125	30						
1,2-Dichloropropane	9.2	ug/m3	3.7	20060111		70	130	30						
cis-1,3-Dichloropropene	9.1	ug/m3	2.3	20060111		0	0	30						
trans-1,3-Dichloropropene	9.1	ug/m3	4.5	20060111		0	0	30						
1,2-Dichloro-1,1,2,2-tetrafluoroethane	14	ug/m3	5.6	20060111		0	0	30						
Ethylbenzene	8.7	ug/m3	4.3	20060706		0	0	30						
4-Ethyltoluene	9.8	ug/m3	3.4	20060111		0	0	30						
Hexachlorobutadiene	43	ug/m3	14	20060111		0	0	30						
2-Hexanone	41	ug/m3	4.1	20060112		0	0	30						
Methylene chloride	6.9	ug/m3	2.8	20060111		75	120	30						
4-Methyl-2-pentanone (MIBK)	41	ug/m3	8.2	20060112		0	0	30						
Styrene	8.5	ug/m3	4.2	20060706		0	0	30						
1,1,2,2-Tetrachloroethane	14	ug/m3	3.4	20060111		65	130	30						
Tetrachloroethene	14	ug/m3	4.1	20060111		70	130	30						

Target Analyte List: COI: Standard TO-14A/TO-15 list

Matrix: AIR
Extraction: NO SAMPLE PREPARATION PERFORMED / DIRECT INJ
Method: Volatile Organics by GC/MS TO-15 (Medium Level) ug
QC Program: STANDARD TEST SET
Location: STL City of Industry

Compound	RL	Detection Limits		Run Date	Check List 5700				Spike List 0			
		Units	MDL		Amt	Units	LCL	UCL	RPD	Amt	Units	LCL
Toluene	7.5	ug/m3	1.9	20060111			75	125	30			
1,2,4-Trichlorobenzene	37	ug/m3	9.6	20060706			0	0	30			
1,1,1-Trichloroethane	11	ug/m3	2.7	20060111			70	130	30			
1,1,2-Trichloroethane	11	ug/m3	3.3	20060111			0	0	30			
Trichloroethene	11	ug/m3	2.7	20060111			70	125	30			
Trichlorofluoromethane	11	ug/m3	2.8	20060111			0	0	30			
1,1,2-Trichloro-1,2,2-trifluoroethane	15	ug/m3	3.8	20060111			0	0	30			
1,2,4-Trimethylbenzene	15	ug/m3	6.4	20060111			70	130	30			
1,3,5-Trimethylbenzene	15	ug/m3	5.4	20060706			0	0	30			
Vinyl acetate	35	ug/m3	7.0	20060111			0	0	30			
Vinyl chloride	5.1	ug/m3	2.0	20060111			0	0	30			
m-Xylene & p-Xylene	8.7	ug/m3	4.3	20060111			70	130	30			
o-Xylene	8.7	ug/m3	2.6	20060111			70	130	30			
Xylenes (total)	8.7	ug/m3	2.6	20060111			0	0	30			
4-Bromofluorobenzene							70	130	0			
1,2-Dichloroethane-d4							70	130	0			
Toluene-d8							70	130	0			

STL Reference Data Summary

Target Analyte List: COI: Standard TO-14A/TO-15 list

Matrix: AIR
Extraction: NO SAMPLE PREPARATION PERFORMED / DIRECT IN/LI
Method: Volatile Organics by GC/MS TO-15 (Medium Level)
QC Program: STANDARD TEST SET
Location: STL City of Industry

Target List 5700		Detection Limits			Check List 5700				Spike List 0						
Compound	RL	Units	MDL	Units	Run Date	Amt	Units	LCL	UCL	RPD	Amt	Units	LCL	UCL	RPD
Acetone	10	ppb(v/v)	2.0	ppb(v/v)	20060111			0	0	30					
Benzene	2.0	ppb(v/v)	0.8	ppb(v/v)	20060111			70	130	30					
Benzyl chloride	25	ppb(v/v)	8	ppb(v/v)	20060112			0	0	30					
Bromodichloromethane	2.0	ppb(v/v)	0.80	ppb(v/v)	20060111			0	0	30					
Bromoform	2.0	ppb(v/v)	0.5	ppb(v/v)	20060706			0	0	30					
Bromomethane	2.0	ppb(v/v)	1.0	ppb(v/v)	20060111			0	0	30					
2-Butanone (MEK)	10	ppb(v/v)	2.0	ppb(v/v)	20060111			0	0	30					
Carbon disulfide	10	ppb(v/v)	2.0	ppb(v/v)	20060111			0	0	30					
Carbon tetrachloride	2.0	ppb(v/v)	0.5	ppb(v/v)	20060706			0	0	30					
Chlorobenzene	2.0	ppb(v/v)	0.5	ppb(v/v)	20060111			70	130	30					
Dibromochloromethane	2.0	ppb(v/v)	1.0	ppb(v/v)	20060706			0	0	30					
Chloroethane	4.0	ppb(v/v)	0.8	ppb(v/v)	20060111			0	0	30					
Chloroform	2.0	ppb(v/v)	0.8	ppb(v/v)	20060706			70	130	30					
Chloromethane	4.0	ppb(v/v)	1.0	ppb(v/v)	20060111			0	0	30					
1,2-Dibromoethane (EDB)	2.0	ppb(v/v)	0.5	ppb(v/v)	20060111			0	0	30					
1,2-Dichlorobenzene	2.0	ppb(v/v)	0.9	ppb(v/v)	20060111			70	130	30					
1,3-Dichlorobenzene	2.0	ppb(v/v)	0.8	ppb(v/v)	20060111			0	0	30					
1,4-Dichlorobenzene	2.0	ppb(v/v)	0.8	ppb(v/v)	20060111			0	0	30					
Dichlorodifluoromethane	2.0	ppb(v/v)	0.5	ppb(v/v)	20060505			0	0	30					
1,1-Dichloroethane	2.0	ppb(v/v)	0.5	ppb(v/v)	20060111			70	130	30					
1,2-Dichloroethane	2.0	ppb(v/v)	0.8	ppb(v/v)	20060111			0	0	30					
cis-1,2-Dichloroethene	2.0	ppb(v/v)	0.8	ppb(v/v)	20060111			0	0	30					
trans-1,2-Dichloroethene	2.0	ppb(v/v)	0.5	ppb(v/v)	20060111			0	0	30					
1,1-Dichloroethene	2.0	ppb(v/v)	0.5	ppb(v/v)	20060111			70	125	30					
1,2-Dichloropropane	2.0	ppb(v/v)	0.8	ppb(v/v)	20060111			70	130	30					
cis-1,3-Dichloropropene	2.0	ppb(v/v)	0.5	ppb(v/v)	20060111			0	0	30					
trans-1,3-Dichloropropene	2.0	ppb(v/v)	1.0	ppb(v/v)	20060111			0	0	30					
1,2-Dichloro-1,1,2,2-tetrafluoroethane	2.0	ppb(v/v)	0.8	ppb(v/v)	20060111			0	0	30					
Ethylbenzene	2.0	ppb(v/v)	1.0	ppb(v/v)	20060706			0	0	30					
4-Ethyltoluene	2.0	ppb(v/v)	0.7	ppb(v/v)	20060111			0	0	30					
Hexachlorobutadiene	4.0	ppb(v/v)	1.3	ppb(v/v)	20060111			0	0	30					
2-Hexanone	10	ppb(v/v)	1.0	ppb(v/v)	20060112			0	0	30					
Methylene chloride	2.0	ppb(v/v)	0.8	ppb(v/v)	20060111			75	120	30					
4-Methyl-2-pentanone (MIBK)	10	ppb(v/v)	2.0	ppb(v/v)	20060112			0	0	30					
Styrene	2.0	ppb(v/v)	1.0	ppb(v/v)	20060706			0	0	30					
1,1,2,2-Tetrachloroethane	2.0	ppb(v/v)	0.5	ppb(v/v)	20060111			65	130	30					
Tetrachloroethene	2.0	ppb(v/v)	0.6	ppb(v/v)	20060111			70	130	30					

Target Analyte List: COL: Standard TO-14A/TO-15 list

Matrix: AIR
Extraction: NO SAMPLE PREPARATION PERFORMED / DIRECT INJ
Method: Volatile Organics by GC/MS TO-15 (Medium Level)
QC Program: STANDARD TEST SET
Location: STL City of Industry

Target List 5700						Check List 5700						Spike List 0			
Compound	RL	Units	MDL	Units	Run Date	Amt	Units	LCL	UCL	RPD	Amt	Units	LCL	UCL	RPD
Toluene	2.0	ppb(v/v)	0.5	ppb(v/v)	20060111			75	125	30					
1,2,4-Trichlorobenzene	5.0	ppb(v/v)	1.3	ppb(v/v)	20060706			0	0	30					
1,1,1-Trichloroethane	2.0	ppb(v/v)	0.5	ppb(v/v)	20060111			70	130	30					
1,1,2-Trichloroethane	2.0	ppb(v/v)	0.6	ppb(v/v)	20060111			0	0	30					
Trichloroethene	2.0	ppb(v/v)	0.5	ppb(v/v)	20060111			70	125	30					
Trichlorofluoromethane	2.0	ppb(v/v)	0.5	ppb(v/v)	20060111			0	0	30					
1,1,2-Trichloro-1,2,2-trifluoroethane	2.0	ppb(v/v)	0.5	ppb(v/v)	20060111			0	0	30					
1,2,4-Trimethylbenzene	3.0	ppb(v/v)	1.3	ppb(v/v)	20060111			70	130	30					
1,3,5-Trimethylbenzene	3.0	ppb(v/v)	1.1	ppb(v/v)	20060706			0	0	30					
Vinyl acetate	10	ppb(v/v)	2.0	ppb(v/v)	20060111			0	0	30					
Vinyl chloride	2.0	ppb(v/v)	0.8	ppb(v/v)	20060111			0	0	30					
m-Xylene & p-Xylene	2.0	ppb(v/v)	1.0	ppb(v/v)	20060111			70	130	30					
o-Xylene	2.0	ppb(v/v)	0.6	ppb(v/v)	20060111			70	130	30					
Xylenes (total)	2.0	ppb(v/v)	0.60	ppb(v/v)	20060111			0	0	30					
4-Bromofluorobenzene								70	130	0					
1,2-Dichloroethane-d4								70	130	0					
Toluene-d8								70	130	0					

ATTACHMENT 4

FIELD AUDIT CHECKLIST

ATTACHMENT 4

FIELD AUDIT CHECKLIST

Briefing with Project Manager

SIGNATURE OF AUDITOR _____ DATE OF AUDIT _____

PROJECT MANAGER _____ PROJECT NO. _____

PROJECT LOCATION _____

TYPE OF INVESTIGATION _____
(authority, agency)

Yes ____ No ____ N/A ____

1. Was a project plan prepared? If yes, what items are addressed in the Plan?

Yes ____ No ____ N/A ____

2. Were additional instructions given to project participants (i.e., changes in the project plan)? If yes, describe these changes.

Yes ____ No ____ N/A ____

3. Is there a written list of sampling locations and descriptions? If yes, describe where documents are.

Yes ____ No ____ N/A ____

4. Is there a map of sampling locations? If yes, where is the map.

APPENDIX E

FIELD AUDIT CHECKLIST

Field Observations

Yes ____ No ____ N/A ____

1. Are the number, frequency and types of field measurements and observations taken as specified in the project plan or as directed by the project manager? If yes, where are they recorded?

Yes ____ No ____ N/A ____

2. Are samples collected in the types of containers specified for each type of analysis? If no, what kind of sample containers are used?

Yes ____ No ____ N/A ____

3. Are samples preserved as required? If no or N/A, explain.

Yes ____ No ____ N/A ____

4. Are the number, frequency and types of samples collected as specified in the project plan or as directed by the project manager? If no, explain why not.

Yes ____ No ____ N/A ____

5. Are samples packed for preservation when required (i.e., packed in ice, etc.)? If no or N/A, explain why.

Yes ____ No ____ N/A ____

6. Is sample custody maintained? How?

APPENDIX E

FIELD AUDIT CHECKLIST

Document Control

Yes ____ No ____ N/A ____

1. Are samples identified with sample labels? If no, how are samples identified?

Yes ____ No ____ N/A ____

2. Are sample labels completed (e.g., station no., location, date, time, analyses, signatures on samples, type, preservatives, etc.)? If yes, describe types of information recorded.

Yes ____ No ____ N/A ____

3. Are samples collected listed on a chain-of-custody record? If yes, describe the type of chain-of-custody record used and what information is recorded.

Yes ____ No ____ N/A ____

4. If used, are sample tag numbers recorded on chain-of-custody documents?

Yes ____ No ____ N/A ____

5. Does information on sample labels and chain-of-custody records match?

Yes ____ No ____ N/A ____

6. Does the chain-of-custody record indicate the method of sample shipment?

Yes _____ No _____ N/A _____

7. Is the chain-of-custody record included with the samples in the shipping container?

Yes _____ No _____ N/A _____

8. If used, do the sample traffic reports agree with the sample labels?

Yes _____ No _____ N/A _____

9. If used, are blank samples identified?

Yes _____ No _____ N/A _____

10. If collected, are duplicate samples identified on sample labels and chain-of-custody records?

Yes _____ No _____ N/A _____

11. If used, are spiked samples identified?

Yes _____ No _____ N/A _____

12. Are logbooks signed by the individual who checked out the logbook from the project coordinator?

Yes _____ No _____ N/A _____

13. Are logbooks dated upon receipt from the project coordinator?

Yes _____ No _____ N/A _____

14. Are logbooks project-specific (by logbook or by page)?

Yes _____ No _____ N/A _____

15. Are logbook entries dated and identified by the author?

Yes _____ No _____ N/A _____

16. Are photographs documented in logbooks (e.g., time, date, description of subject, photographer, etc.)?

Yes _____ No _____ N/A _____

17. If film from a self-developing camera is used, are photos matched with logbook documentation?

Yes _____ No _____ N/A _____

18. Are sample tag numbers recorded? If yes, describe where they are recorded?

Yes _____ No _____ N/A _____

19. Are calibration of pH meters, conductivity meters, etc., documented? If yes, describe where this is documented.

Yes _____ No _____ N/A _____

20. Are amendments to the project plan documented? If yes, describe where the amendments are documented.

APPENDIX E

FIELD AUDIT CHECKLIST

Debriefing with Project Manager

Yes ____ No ____ N/A ____

1. Was a debriefing held with project manager and/or other participants?

Yes ____ No ____ N/A ____

2. Were any recommendations made to the project participants during the debriefing? If yes, list recommendations.

ATTACHMENT 5

LABORATORY AUDIT CHECKLIST

ATTACHMENT 5

LABORATORY AUDIT CHECKLIST

SIGNATURE OF AUDITOR _____ DATE OF AUDIT _____

PROJECT MANAGER _____ PROJECT NO. _____

PROJECT LOCATION _____

TYPE OF INVESTIGATION _____
(authority, agency)

The enclosed laboratory audit checklists are organized into the categories by laboratory functional area. The attached audit checklists have been numbered according to the following outline:

- 1.0 Sample Management
- 2.0 Organic Sample Preparation
- 3.0 Gas Chromatography
- 4.0 Mass Spectrometry
- 5.0 Metals Preparation
- 6.0 Metals Analysis
- 7.0 Wet Chemistry
- 8.0 Report Generation
- 9.0 Computer Systems

Special Checklists

- Form A Laboratory Temperature Monitoring Checklist
- Form B Laboratory Notebook Checklist
- Form C Laboratory Balance Checklist
- Form D Reagent and Analytical Standards Checklist
- Form E Laboratory Safety Checklist

ATTACHMENT 5

LABORATORY AUDIT CHECKLIST

1.0 Sample Management

Shipment of Sample Bottles and Coolers

Check off which of the following items are utilized in this area and complete the associated forms.

☐	☐	Refrigerators, freezers, ovens,	Complete Form A
☐	☐	Logbooks	Complete Form B
☐	☐	Laboratory Balances	Complete Form C
☐	☐	Reagents and Standards	Complete Form D
☐	☐	Safety Equipment	Complete Form E

Y	N	Item	Comments
☐	☐	Is there a SOP describing preparation and shipment of sample coolers?	
☐	☐	Are sample bottles precleaned and is cleaning documented?	
☐	☐	Are cooler shipment records maintained?	
☐	☐	Are coolers and bottles sent out under chain-of-custody?	
☐	☐	Are preservatives provided with the cooler?	
☐	☐	Are sample collectors supplied with preservatives and sampling instructions for their use?	
☐	☐	Is there a SOP describing the amount and concentration of preservation agents added to bottles?	
☐	☐	Are chain of custody forms provided along with instructions for proper completion?	
☐	☐	Are trip blanks included with the cooler?	
☐	☐	If so, is the purity of the trip blank water checked before shipment and can it be documented?	
☐	☐	Does the laboratory only utilize new sample containers?	
☐	☐		
☐	☐		

ATTACHMENT 5

LABORATORY AUDIT CHECKLIST

1.0 Sample Management (continued)

Receipt and Storage of Samples

Check off which of the following items are utilized in this area and complete the associated forms.

☐	☐	Refrigerators, freezers, ovens,	Complete Form A
☐	☐	Logbooks	Complete Form B
☐	☐	Laboratory Balances	Complete Form C
☐	☐	Reagents and Standards	Complete Form D
☐	☐	Safety Equipment	Complete Form E

Y	N	Item	Comment
		Do the laboratory personnel indicate a familiarity with the requirements set forth in the laboratory QA program?	
		Is there a written SOP readily available to the login personnel?	
		Is the SOP followed as written?	
		If discrepancies are noted between COC records and the samples, are they documented and appropriate personnel notified?	
		Is the pH checked on all appropriate incoming samples and documented?	
		Is the pH check done in such a manner that avoids sample contamination?	
		Is HCl preservation utilized for volatile sample preservation? If not, is a 7-day hold time being applied?	
		Are incoming volatile vials checked for the presence of air bubbles?	
		If air bubbles are detected, is the client notified?	
		If there a mechanism to receive samples after normal work hours and weekends?	
		Is the filing system for original custody forms and paperwork traceable?	
		Is a fume hood available for opening of hazardous samples?	
		Are eyewashes and/or showers available in the immediate area?	
		Is there a central log-in notebook and is it document controlled?	
		Are unique laboratory sample identification numbers assigned and properly recorded on sample container labels and sample log-in documentation?	

ATTACHMENT 5

LABORATORY AUDIT CHECKLIST

1.0 Sample Management (continued)

Y	N	Item	Comment
		Is there a SOP describing how the lab handles samples with short holding times?	
		Are samples checked for proper preservation upon receipt? (Required by NJ)	
		If samples are not properly preserved, is there a SOP describing how it is handled?	
		Are files maintained for log-in documentation?	
		Are all samples and extracts stored in a secure manner? (Locked refrigerators and freezers)	
		Are all samples and extracts stored in separate storage units?	
		Is there limited access to sample and extract storage areas?	
		Is there an internal custody procedure for samples and extracts and is it documented in a SOP? If so, where are records filed?	
		Is there a procedure for documenting where samples and extracts are stored?	
		Are volatile samples stored separately from other samples or extracts?	
		Are volatile water samples stored separately from soil volatile samples?	
		Are refrigerator holding blanks utilized to monitor potential sample contamination in each volatile sample storage unit?	
		Are standards or reagents stored with samples or extracts?	
		Are samples maintained in a cooled condition until holding time expires?	
		Are archived samples stored in a secure manner?	
		Is there a policy describing how long samples are held after a report is issued?	
		Are samples being held after report issuance maintained in a cooled condition?	
		Is there a SOP describing the archival and disposal of samples and sample extracts?	

ATTACHMENT 5

LABORATORY AUDIT CHECKLIST

1.0 Sample Management (continued)

Y	N	Item	Comment
		Does the disposal SOP describe how the lab disposes of samples of unknown content?	
		Is there a record of when every sample has been discarded?	
		Do supervisory personnel review the paperwork in the dept. and is this review documented?	

ATTACHMENT 5

LABORATORY AUDIT CHECKLIST

2.0 Organic Sample Preparation

Check off which of the following items are utilized in this area and complete the associated forms.

☐	☐	Refrigerators, freezers, ovens,	Complete Form A
☐	☐	Logbooks	Complete Form B
☐	☐	Laboratory Balances	Complete Form C
☐	☐	Reagents and Standards	Complete Form D
☐	☐	Safety Equipment	Complete Form E

Y	N	Item	Comment
☐	☐	Are SOPs available detailing the procedures used in this area?	Obtain a listing of all procedures performed in the area. Compare the list with available SOPs and estimate a percentage complete below. Percent Compliance _____

Are the following QC samples processed with each analytical batch?

☐	☐	Method Blank	
☐	☐	QC Check Sample	
☐	☐	Matrix Spike	
☐	☐	Matrix Spike Duplicate	
☐	☐	Are the solvent storage cabinets properly vented as appropriate to avoid possible laboratory contamination?	
☐	☐	Are gas lines checked for leaks each time a tank is changed?	
☐	☐	If the lab utilizes desiccators, do they appear to be properly maintained?	
☐	☐	Is there an SOP for glassware washing and is it posted in the washing area?	
☐	☐	Are operating manuals available to the analysts for all major equipment?	
☐	☐	Is there a record of instrument servicing maintained in a logbook and is it document controlled?	
☐	☐	Is appropriate corrective action taken if a surrogate is outside of acceptable limits?	
☐	☐	Are boiling chips kept to a minimum size to prevent volumetric distortion and minimize sample contamination potential? (only 1 boiling chip, the size of a grain of salt should be used)	
☐	☐	Are graduated cylinders utilized for measuring out sample volumes for water extractions?	

ATTACHMENT 5

LABORATORY AUDIT CHECKLIST

2.0 Organic Sample Preparation (continued)

Y	N	Item	Comment
		Are amber screw cap vials utilized for solvent extracts? (screw cap vials prevent solvent losses associated with crimp top vials)	
		If the volume of solvent extracts is reduced utilizing gas blowdown systems, do the gas lines contain molecular sieves to remove contaminants from the gas supply?	
		Are surrogates added to samples utilizing class A pipets in a manner to ensure quantitative transfer of the surrogates?	
		Are various dry reagents such as florisil, sodium sulfate and glass wool or thimbles, preextracted prior to use?	
		Is florisil PR 60/100 mesh utilized and is it stored in a dark glass bottle with foil lined cap and initially activated at 676 deg. C and at 130 ° C before use?	
		Is anhydrous sodium sulfate used which is dried at 400 ° C for 4 hours and stored at 130 ° before use?	
		Are only approved solvent lot numbers being utilized by the laboratory?	
		Is laboratory glassware rotated so that method blanks are truly representative of the effectiveness of routine glassware cleaning procedures? (dedicated glassware must not be used for QC samples) and only 1 blank can be extracted per batch.	
		When utilizing liquid/liquid continuous extractors is <u>all</u> the solvent remaining after extraction in both the extractor and the boiling flask concentrated down to the final volume?	
		Do the laboratory personnel indicate a familiarity with the requirements set forth in the corporate QA program?	

ATTACHMENT 5

LABORATORY AUDIT CHECKLIST

3.0 Gas Chromatography

Check off which of the following items are utilized in this area and complete the associated forms.

☐	☐	Refrigerators., freezers, ovens,	Complete Form A
☐	☐	Logbooks	Complete Form B
☐	☐	Laboratory Balances	Complete Form C
☐	☐	Reagents and Standards	Complete Form D
☐	☐	Safety Equipment	Complete Form E

Y	N	Item	Comment
☐	☐	Do the laboratory personnel indicate a familiarity with the requirements set forth in the laboratory QA program?	
☐	☐	Are SOPs available detailing the procedures used in this area?	Obtain a listing of all procedures performed in the area. Compare the list with available SOPs and estimate a percentage complete below. Percent Compliance _____
☐	☐	Are gas lines checked for leaks each time a tank is changed?	
☐	☐	Are instruments properly vented or are appropriate traps in place?	
☐	☐	Can the lab demonstrate the absence of volatile organics in the lab reagent water?	
☐	☐	Are SOPs available detailing the procedures used in this area?	
☐	☐	Are the solvent storage cabinets properly vented as appropriate to avoid possible laboratory contamination?	
☐	☐	Are operating manuals available to the analysts for all major equipment?	
☐	☐	Is there a record of instrument servicing maintained in a logbook and is it document controlled?	
☐	☐	Are volatile analysis being conducted using the appropriate packed or capillary columns as specified by the particular method?	
☐	☐	Is there a policy in place concerning carryover prevention in the event a high level sample precedes a relatively low level sample?	
☐	☐	Is quantitation correct for the method? (based upon the average RF of a calibration curve or the RF from a continuing calibration standard)	

ATTACHMENT 5

LABORATORY AUDIT CHECKLIST

3.0 Gas Chromatography (continued)

Y	N	Item	Comment
		Is the initial calibration conducted at five or three concentrations as appropriate for the method?	
		Are all reported results within the calibration range of the highest and lowest standard?	
		Are calibrations performed at the required frequency specified in the methods?	
		Is appropriate corrective action taken if a calibration is out of criteria?	
		Is a method blank run with every batch of samples?	
		Is there specified acceptance limits for the method blank?	
		Is there a policy stating that the laboratory does not "blank correct" sample data?	
		Is appropriate corrective action taken if a surrogate is outside of acceptance limits?	
		Is appropriate corrective action taken if internal standard area is outside of acceptance limits?	
		Is a run log maintained for all instrumentation?	
		Are GC identifications confirmed on a second dissimilar column?	
		Are PCB identifications performed by manual pattern recognition?	
		Are a sufficient number of peaks used to calculate a PCB result? (minimum of 3)	
		Are various extract cleanup techniques such as copper, florisil, alumina, sulfuric acid, used routinely?	
		Do gas lines contain molecular sieves or other filters to remove contaminants from the gas supply?	
		If 25 ml purge vessels are utilized for methods normally requiring a 5 ml purge, have MDL studies been performed to verify that required MDLs are achieved?	

ATTACHMENT 5

LABORATORY AUDIT CHECKLIST

4.0 Mass Spectrometry

Volatile GC/MS Area

Check off which of the following items are utilized in this area and complete the associated forms.

☐	☐	Refrigerators., freezers, ovens,	Complete Form A
☐	☐	Logbooks	Complete Form B
☐	☐	Laboratory Balances	Complete Form C
☐	☐	Reagents and Standards	Complete Form D
☐	☐	Safety Equipment	Complete Form E

Y	N	Item	Comment
☐	☐	Do the laboratory personnel indicate a familiarity with the requirements set forth in the laboratory QA program?	
☐	☐	Are SOPs available detailing the procedures used in this area?	Obtain a listing of all procedures performed in the area. Compare the list with available SOPs and estimate a percentage complete below. Percent Compliance _____
Are the following QC samples processed with each analytical batch?			
☐	☐	Method Blank	
☐	☐	QC Check Sample	
☐	☐	Matrix Spike	
☐	☐	Matrix Spike Duplicate	
☐	☐	Are gas lines checked for leaks each time a tank is changed?	
☐	☐	Are the instruments properly vented or are appropriate traps in place?	
☐	☐	Can the lab demonstrate the absence of volatile organics in the lab reagent water?	
☐	☐	Are the solvent storage cabinets properly vented as appropriate to avoid possible laboratory contamination?	
☐	☐	Is the laboratory utilizing the most recent version of the EPA/NIH mass spectral database? If not what version is being used?	
☐	☐	Are operating manuals available to the analysis for all major equipment?	
☐	☐	Is there a record of instrument servicing maintained in a logbook and is it document controlled?	
☐	☐	Are volatile analyses being conducted using the appropriate packed or capillary columns as specified by the particular method?	
☐	☐	Is there a policy in place concerning carryover prevention in the event a high level sample	

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LABORATORY AUDIT CHECKLIST

		precedes a relatively low level sample?	

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LABORATORY AUDIT CHECKLIST

4.0 Mass Spectrometry (continued)

Volatile GC/MS Area			
Y	N	Item	Comment
		Is the initial calibration conducted at five or three concentrations as appropriate for the method?	
		Is quantitation correct for the method? (based upon the average RF of a calibration curve or the RF from a continuing calibration standard)	
		Are calibrations and tuning performed according to the required frequency specified in the methods?	
		Is appropriate corrective action taken if a calibration is out of criteria?	
		Is appropriate corrective action taken if a continuing calibration is out of criteria?	
		Is a method blank run with every batch of samples?	
		Is there specified acceptance limits for the method blank?	
		Is there a policy stating that the laboratory does not "blank correct" sample data?	
		Is the appropriate corrective action taken if a surrogate is outside of acceptance limits?	
		Is the appropriate corrective action taken if internal standard area is outside of acceptance limits?	
		Are library searches examined by the mass spectrometry expert before results are reported and is there documentation of this review?	
		Is a run log maintained for all instrumentation and is it documented controlled?	
		Is raw data stored in a secure manner under appropriate conditions to prevent loss of data?	
		Are the reported results within the calibration range of the highest and lowest standard?	
		Are appropriate dilutions performed?	
		Do gas lines contain molecular sieves or other filters to remove contaminants in gas supply?	
		If 25-ml purge vessels are utilized for methods normally requiring a 5-ml purge, have MDL studies been performed to verify that required MDLs are achieved?	

ATTACHMENT 5

LABORATORY AUDIT CHECKLIST

4.0 Mass Spectrometry (continued)

Semi-Volatile GC/MS Area

Check off which of the following items are utilized in this area and complete the associated forms.

☐	☐	Refrigerators., freezers, ovens,	Complete Form A
☐	☐	Logbooks	Complete Form B
☐	☐	Laboratory Balances	Complete Form C
☐	☐	Reagents and Standards	Complete Form D
☐	☐	Safety Equipment	Complete Form E

Y	N	Item	Comment
☐	☐	Do the laboratory personnel indicate a familiarity with the requirements set forth in the laboratory QA program?	
☐	☐	Are SOPs available detailing the procedures used in this area?	Obtain a listing of all procedures performed in the area. Compare the list with available SOPs and estimate a percentage complete below. Percent Compliance _____
☐	☐	Are gas lines checked for leaks each time a tank is changed?	
☐	☐	Are the instruments properly vented or are appropriate traps in place?	
☐	☐	Can the lab demonstrate the absence of volatile organics in the lab reagent water?	
☐	☐	Are the solvent storage cabinets properly vented as appropriate to avoid possible laboratory contamination?	
☐	☐	Is the laboratory utilizing the most recent version of the EPA/NIH mass spectral database? If not what version is being used?	
☐	☐	Are operating manuals available to the analysis for all major equipment?	
☐	☐	Is there a record of instrument servicing maintained in a logbook and is it document controlled?	
☐	☐	Are volatile analyses being conducted using the appropriate packed or capillary columns as specified by the particular method?	
☐	☐	Is there a policy in place concerning carryover prevention in the event a high level sample precedes a relatively low-level sample?	
☐	☐	Is the initial calibration conducted at five or three concentrations as appropriate for the method?	

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LABORATORY AUDIT CHECKLIST

4.0 Mass Spectrometry (continued)

Semi-Volatile GC/MS Area			
Y	N	Item	Comment
		Is quantitation correct for the method? (based upon the average RF of a calibration curve or the RF from a continuing calibration standard)	
		Are calibrations and tuning performed according the required frequency specified in the methods?	
		Is appropriate corrective action taken if a calibration is out of criteria?	
		Is appropriate corrective action taken if a continuing calibration is out of criteria?	
		Is a method blank run with every batch of samples?	
		Is there specified acceptance limits for the method blank?	
		Is there a policy stating that the laboratory does not "blank correct" sample data?	
		Is the appropriate corrective action taken if a surrogate is outside of acceptance limits?	
		Is the appropriate corrective action taken if internal standard area is outside of acceptance limits?	
		Are library searches examined by the mass spectrometry expert before results are reported and is there documentation of this review?	
		Is a run log maintained for all instrumentation and is it documented controlled?	
		Is raw data stored in a secure manner under appropriate conditions to prevent loss of data?	
		Are the reported results within the calibration range of the highest and lowest standard?	
		Are appropriate dilutions performed?	
		Do gas lines contain molecular sieves or other filters to remove contaminants in gas supply?	

ATTACHMENT 5

LABORATORY AUDIT CHECKLIST

5.0 Metals Preparation

Check off which of the following items are utilized in this area and complete the associated forms.

☐	☐	Refrigerators, freezers, ovens,	Complete Form A
☐	☐	Logbooks	Complete Form B
☐	☐	Laboratory Balances	Complete Form C
☐	☐	Reagents and Standards	Complete Form D
☐	☐	Safety Equipment	Complete Form E

Y	N	Item	Comment
☐	☐	Is the storage area for acids properly ventilated?	
☐	☐	Do the laboratory personnel indicate a familiarity with the requirements set forth in the laboratory QA program?	
Are the following QC samples processed with each analytical batch?			
☐	☐	Method Blank	
☐	☐	QC Check Sample	
☐	☐	Matrix Spike	
☐	☐	Matrix Spike Duplicate or Matrix Duplicate	
☐	☐	Are SOPs available detailing the procedures used in this area?	Obtain a listing of all procedures performed in the area. Compare the list with available SOPs and estimate a percentage complete below. Perent Compliance _____
☐	☐	Is there a SOP for glassware washing and is it posted in the washing area?	
☐	☐	Are high purity trace metal grade acids utilized for preservation and digestion of samples for metals?	
☐	☐	Is glassware for metals analysis acid washed?	
☐	☐	If automatic dispensers are utilized for acids, are they properly maintained?	
☐	☐	Does the lab ensure that powder free gloves are used to avoid possible zinc contamination of samples?	
☐	☐	Are operating manuals available to the analysts for all major equipment?	

ATTACHMENT 5

LABORATORY AUDIT CHECKLIST

5.0 Metals Preparation (continued)

Y	N	Item	Comment
		Is there a record of instrument servicing maintained in a logbook and is it document controlled?	
		Is a digestion log maintained for all samples and is it document controlled?	
		Is an acid digestion performed for drinking water samples requiring total metals?	
		Are samples for dissolved metals digested after filtration?	EPA required, except for DW where turbidity is below a certain level.

ATTACHMENT 5

LABORATORY AUDIT CHECKLIST

6.0 Metals Analysis

Check off which of the following items are utilized in this area and complete the associated forms.

☐	☐	Refrigerators., freezers, ovens,	Complete Form A
☐	☐	Logbooks	Complete Form B
☐	☐	Laboratory Balances	Complete Form C
☐	☐	Reagents and Standards	Complete Form D
☐	☐	Safety Equipment	Complete Form E

Y	N	Item	Comment
☐	☐	Do the laboratory personnel indicate a familiarity with the requirements set forth in the laboratory QA program?	
☐	☐	Are SOPs available detailing the procedures used in this area?	Obtain a listing of all procedures performed in the area. Compare the list with available SOPs and estimate a percentage complete below. Percent Compliance _____
☐	☐	Are gas lines checked for leaks each time a tank is changed?	
☐	☐	Are vents above AA units functioning properly (200 ft ³ /min.)?	
☐	☐	Are SOPs available detailing the procedures used in this area?	
☐	☐	Are operating manuals available to the analysis for all major equipment?	
☐	☐	Is there a record of instrument servicing maintained in a logbook and is it document controlled?	
☐	☐	Is there a policy in place concerning carryover prevention in the event a high level sample precedes a relatively low-level sample?	
☐	☐	Are calibrations performed according the required frequency specified in the methods?	
☐	☐	Is appropriate corrective action taken if a calibration is out of criteria?	
☐	☐	Are continuing calibrations run at an adequate frequency?	

ATTACHMENT 5

LABORATORY AUDIT CHECKLIST

6.0 Metals Analysis (continued)

Y	N	Item	Comment
		Is appropriate corrective action taken if a continuing calibration is out of criteria?	
		Is a method blank run with every batch of samples?	
		Is there specified acceptance limits for the method blank?	
		Is there a policy stating that the laboratory does not "blank correct" sample data?	
		Is a run log maintained for all instrumentation and is it documented controlled?	
		Are post-digestion spikes performed for graphic furnace analyses?	
		Is there a corrective action when PDS fail? Is it to flag results or perform standard additions?	
		Are ICP interference standards run at the required frequency specified in the method?	
		Are serial dilutions performed?	
		Are check standards run at a frequency of 10% for graphite furnace to monitor when the furnace should be changed?	
		For mercury analysis, is the mercury vapor safely removed from the lab atmosphere?	
		Are all reported results within the calibration range of the highest and lowest standard?	

ATTACHMENT 5

LABORATORY AUDIT CHECKLIST

7.0 Wet Chemistry

Check off which of the following items are utilized in this area and complete the associated forms.

☐	☐	Refrigerators., freezers, ovens,	Complete Form A
☐	☐	Logbooks	Complete Form B
☐	☐	Laboratory Balances	Complete Form C
☐	☐	Reagents and Standards	Complete Form D
☐	☐	Safety Equipment	Complete Form E

Y	N	Item	Comment
☐	☐	Are SOPs available detailing the procedures used in this area?	Obtain a listing of all procedures performed in the area. Compare the list with available SOPs and estimate a percentage complete below. Percent Compliance _____
Are the following QC samples processed with each analytical batch?			
☐	☐	Method Blank	
☐	☐	QC Check Sample	
☐	☐	Matrix Spike	
☐	☐	Matrix Spike Duplicate or Matrix Duplicate	
☐	☐	If the lab utilizes dessicators, do they appear to be properly maintained?	
☐	☐	Is there a SOP for glassware washing and is it posted in the washing area?	
☐	☐	Are operating manuals available to the analysts for all major equipment?	
☐	☐	Is there a record of instrument servicing maintained in a logbook and is it document controlled?	
☐	☐	Is there a policy in place concerning carryover prevention in the event a high level sample precedes a relatively low-level sample?	
☐	☐	Are calibrations performed according the required frequency specified in the methods?	
☐	☐	Is appropriate corrective action taken if a calibration is out of criteria?	

ATTACHMENT 5

LABORATORY AUDIT CHECKLIST

7.0 Wet Chemistry (continued)

Y	N	Item	Comment
		Is a method blank run with every batch of samples?	
		Is there specified acceptance limits for the method banks?	
		Is there a policy stating that the laboratory does not "blank correct" sample data?	
		Is a dedicated analysis log maintained for all parameters determined and are they document controlled?	
		Is the pH meter checked daily, or before use, by setting the meter to pH 7.0, then measuring pH at 4 and 10?	
		Is the conductivity meter calibrated daily against a 0.001MKCl solution and the data recorded in a logbook?	
		Is the turbidometer calibrated daily, or before use, with 40 NTU formazine standard and the data recorded in a logbook?	
		Is the dissolved oxygen meter calibrated weekly against the Winkler method and data recorded in a logbook?	
		Are all reported results within the calibration range of the highest and lowest standard?	

ATTACHMENT 5

LABORATORY AUDIT CHECKLIST

8.0 Report Generation

Check off which of the following items are utilized in this area and complete the associated forms.

☐	☐	Logbooks	Complete Form B
☐	☐	Safety Equipment	Complete Form E

Y	N	Item	Comment
☐	☐	Do the laboratory personnel indicate a familiarity with the requirements set forth in the laboratory QA program?	
☐	☐	Are SOPs available detailing the procedures used in this area?	Obtain a listing of all procedures performed in the area. Compare the list with available SOPs and estimate a percentage complete below. Percent Compliance _____
☐	☐	Is there a document describing in detail the contents and order of deliverables provided with various types of reporting levels or packages?	
☐	☐	Do all reports contain a cover letter and case narrative?	
☐	☐	Is chain of custody provided with all reports?	
☐	☐		
☐	☐		
☐	☐		

ATTACHMENT 5

LABORATORY AUDIT CHECKLIST

9.0 Computer Systems

Check off which of the following items are utilized in this area and complete the associated forms.

		Logbooks	Complete Form B
		Safety Equipment	Complete Form E
Y	N	Item	Comment
		Do the laboratory personnel indicate a familiarity with the requirements set forth in the laboratory QA program?	
		Are SOPs available detailing the procedures used in this area?	Obtain a listing of all procedures performed in the area. Compare the list with available SOPs and estimate a percentage complete below. Percent Compliance _____
		Are computer programs validated before use?	
		Are operating manuals available to the computer specialists for all computer equipment?	
		Is there a record of computer servicing maintained in a logbook and is it document controlled?	
		Is the computer system backed up at a regular frequency and if so, what is the frequency? Backup copy maintained off Site?	
		Is the system protected from unauthorized access utilizing a password system?	
		Are backup power supplied utilized to prevent loss of information in the event of a power failure?	
		Is the system protected from a lightning strike?	
		If an in-house information management system is utilized, are instructions available to the users?	
		Is there a formal training program for new users?	
		Is there any mechanism to prevent computer clocks from being altered to reflect incorrect dates and times?	
		If such alteration would occur, is there a mechanism to detect it in a <u>very</u> timely fashion?	
		Are computer specialists at the facility familiar with the EPA computer requirements set forth in the GALP manual (good automated lab practices)?	

ATTACHMENT 5

LABORATORY AUDIT CHECKLIST

Form A - Laboratory Temperature Monitoring Checklist			
Identify the Laboratory Area under Review:			
Identify the number of units in this laboratory area:			Refrigerators: Freezers: Ovens:
Y	N	Item	Comment
		Do the laboratory personnel indicate a familiarity with the requirements set forth in the laboratory SOP for temperature monitoring?	
		Are temperatures of all lab temperature units such as refrigerators, ovens, freezers and incubators monitored daily and documented in a logbook?	
		Are all units individually identified with a unique identification number on the outside of the unit?	
		Have thermometers been calibrated against NIST within the last year and documented?	
		Are temperature excursion noted and appropriate action taken?	
		Does all laboratory equipment contain thermometers, which are uniquely identified?	
		Are all thermometers immersed in appropriate media?	
		Is the laboratory aware of whether the temperature has been checked routinely?	

ATTACHMENT 5

LABORATORY AUDIT CHECKLIST

Form B - Laboratory Notebook Checklist			
Identify the Laboratory Area under Review:			
Identify the Number of Notebooks in this Area:			
Y	N	Item	Comment
		Do the logbooks comply with GLP standards for logbooks?	
		Are the contents of the notebook clearly identified?	
		Are lab notebooks maintained in black ink?	
		Are notebooks permanently bound and contain preprinted and consecutively numbered pages?	
		Are lab notebooks neat, orderly and legible?	
		Are entries noting anomalies routinely recorded?	
		Are mistakes in notebooks crossed out with one line signed and dated?	
		Do all notebooks have a unique document control number?	
		Is there evidence of secondary review of the notebook?	
		Are unused portions of pages struck out with a line or Z'd out?	

ATTACHMENT 5

LABORATORY AUDIT CHECKLIST

Form C - Laboratory Balance Checklist			
Identify the Laboratory Area under Review:			
Identify the Number of Balances in this Area:			
Y	N	Item	Comment
		Are all balances being calibrated at the correct frequency?	
		Have the calibrations been conducted at the correct level?	
		Are the acceptance limits presented in the logbook?	
		Are balances and S weights maintained in a clean environment?	
		Does each balance have a unique identification number?	
		Has each balance been serviced in the past year and is a sticker affixed to the balance?	

ATTACHMENT 5

LABORATORY AUDIT CHECKLIST

Form D – Laboratory Reagents and Standards Checklist			
Identify the Laboratory Area under Review:			
Y	N	Item	Comment
		Is there a SOP describing how reagents and standards are prepared and stored?	
		Is there a mechanism for verifying a prepared standard or purchased commercial standard prior to its use in the lab?	
		Is a standards notebook maintained for all areas, which describes the preparation and standardization of standard solutions and is it document controlled?	
		Are stock standards traceable to their source?	
		Are standards and reagents properly labeled with received date, concentration, date prepared, preparer's initials and expiration date?	
		Are standards stored separately from samples or sample extracts?	
		Are all sources of reagent water checked daily?	
		Does water meet the conductance requirements outlined in the SOP and is it documented?	
		Are the water quality records document controlled?	
		Are reagent grade or higher-grade chemicals used to prepare standards?	
		Is there evidence that all reagents and standards are within their expiration dates?	
		Are chemicals being used in analyses tested to ensure they contain no contaminants, which may interfere with the analyses, prior to use?	

ATTACHMENT 5

LABORATORY AUDIT CHECKLIST

Form E - Laboratory Safety Checklist			
Identify the Laboratory Area under Review:			
Y	N	Item	Comment
		Is there sufficient safety equipment in this area such as fume hoods, shower, eyewash, first aid kit, etc.?	
		Is there an emergency spill kit available in the vicinity?	
		Are lab fume hoods checked monthly for proper airflow and is it documented?	
		Is there a cutoff level for determining airflow (100fpm)?	
		Is the interior of fume hoods maintained in a clutter free manner?	
		Are safety glasses worn in the laboratory areas?	
		Are appropriate gloves worn suitable for the reagents used in the laboratory?	
		Are the storage areas and benchtops maintained in an orderly manner such that safety hazards are avoided?	
		Have fire extinguishers, safety showers, eyewashes been checked for proper operation?	
		Are self-contained breathing apparatus available for use in emergency situations?	
		Is all standards preparation performed in a fume hood?	
		Are material safety data sheets (MSDS) accessible and up to date?	
		Are all instruments properly vented?	
		Have all personnel participated in formal safety training?	