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QUALITY ASSURANCE PROJECT PLAN FOR THE EMD CHEMICALS INC. FACILITY RCRA VOLUNTARY CORRECTIVE ACTION

NORWOOD, OHIO
OHD 086 438 538

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QUALITY ASSURANCE PROJECT PLAN (QAPP)

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LIST OF ACRONYMS

AOCs ..... Areas of Concern
ASL ..... Analytical Support Levels
CLP ..... Contract Laboratory Program
Corrective Action ..... Corrective Action
DQO ..... Data Quality Objectives
EMD Chemicals ..... EMD Chemicals Inc.
GC ..... Gas Chromatograph
GC/MS ..... Gas Chromatograph/Mass Spectrometer
LCS/LCSD ..... Laboratory Control Sample/Laboratory Control Sample Duplicates
MS ..... Mass Spectrometer
MSL ..... Mean Sea Level
MS/MSD ..... Matrix Spike/Matrix Spike Duplicate
NIST ..... National Institute of Standards and Technology
Ohio EPA ..... Ohio Environmental Protection Agency
PA/VSI ..... Preliminary Assessment/Visual Site Inspection
ppbv ..... Parts Per Billion By Volume
QA ..... Quality Assurance
QAPP ..... Quality Assurance Project Plan
QC ..... Quality Control
RAS ..... Routine Analytical Services
%R ..... Percent Recover
RCRA ..... Resource Conservation and Recovery Act
RFA ..... RCRA Facility Assessment
RPD ..... Relative Percent Difference
RPD ..... Relative Difference
SOP ..... Standard Operating Procedure
SOW ..... Statement of Work
STL ..... Severn-Trent Laboratories, Inc.
SVOCs ..... Semi-Volatile Organic Compounds
SWMUs ..... Solid Waste Management Units
TPF ..... The Payne Firm Inc.
U.S. EPA ..... United States Environmental Protection Agency
VOC ..... Volatile Organic Compounds

1.0 INTRODUCTION

This Quality Assurance Project Plan (QAPP) presents the organization, objectives, functional activities and specific quality assurance (QA) and quality control (QC) activities associated with the voluntary Resource Conservation and Recovery Act (RCRA) Corrective Action (Corrective Action) at the EMD Chemicals Inc. (EMD Chemicals) facility in Norwood, Ohio (Facility). The voluntary Corrective Action is being conducted in accordance with an agreement (Corrective Action Agreement) between EMD Chemicals and the United States Environmental Protection Agency (U.S. EPA).

This QAPP was prepared in accordance with the U.S. EPA Region 5 RCRA QAPP Policy (U.S. EPA, 1998), as appropriate for the Facility. The sampling and analysis procedures and protocols identified in this QAPP are sufficient to identify, characterize, and delineate the nature and extent of all releases at the Facility, and to determine the need for, and design of, any corrective measures for the Facility. QAPPs specifically needed during construction, operation, and maintenance of corrective measures will be prepared separately.

The data collected during Corrective Action sampling efforts are expected to be quantitatively comparable to the data collected by EMD Chemicals during a previous Ohio Environmental Protection Agency (Ohio EPA) remedial investigation and feasibility study (RI/FS) at the Facility. The RI/FS was completed in April 2004. Based on a review of the RI/FS QAPP (Payne Firm, 1993) and other procedures utilized in developing data during the previous RI/FS, the U.S. EPA concurs that existing RI/FS data developed by EMD Chemicals meets the QAPP requirements set forth in Section V.D.7 of the Corrective Action Agreement. Data collection efforts implemented after the completion of the RI/FS will follow the pertinent requirements set forth in the Corrective Action Agreement, as outlined in this QAPP.

The following elements are addressed in this QAPP:

1. **Data Collection**

   It is anticipated that the Corrective Action will involve the collection of soil and ground water for chemical laboratory analysis, and the collection of soil samples for geotechnical engineering laboratory analysis. Soil samples will be collected from native soil and fill material from soil boring locations. Ground water samples will be collected from monitoring wells and from ground water seeps in storm sewers and the Duck Creek concrete box culvert.

   The rationale used to assure that the data accurately and precisely represent a characteristic of a population, variation of physical or chemical parameters, a process condition or an environmental condition, are provided in Section 2.0 of this QAPP.

The methods and procedures to assess the precision, accuracy and completeness of the measurement data are provided in Sections 4.0 and 13.0 of this QAPP. The description of the measures to quantitatively and qualitatively compare data sets is also found in Section 4.0.

The details relating to the schedule and information to be provided in quality assurance reports are provided in Section 15.0.

2. Sample Analysis

Specific information concerning chain-of-custody and sample storage procedures, sample preparation and analytical procedures, calibrative procedures, data reduction, validation and reporting, internal quality control checks, audits, preventive maintenance, and corrective actions are provided in Sections 6.0, 7.0, 8.0, 9.0, 10.0, 11.0, 12.0, and 14.0, respectively. The data will be reported in the format provided in Section 10.0 of this QAPP. Field and laboratory data and assessment of results will be presented in tabular and graphical formats.

2.0 PROJECT OBJECTIVES

2.1 Facility Description

The EMD Chemicals Facility is comprised of nine acres in the Northern 1/2, Northwest 1/4, Section 28, Fractional Range 2, Township 4, Miami Purchase, Cities of Norwood and Cincinnati, Hamilton County, Ohio with latitude 39° 9' 55" and longitude 84° 26' 10". As shown on Figure 1, the Facility is located northwest of the intersection of Interstate 71 (I-71) and State Route 562 (also referred to as S.R. 562 or "Norwood Lateral"). The Facility is bounded by Highland Avenue on the north, the Norwood Lateral on the south, Shepherd Chemical Company on the west, and a Norfolk Southern railroad embankment on the east. The western portion of the property lies within the City of Norwood and occupies approximately 6.62 acres. The eastern portion of the Facility is located within the City of Cincinnati and occupies approximately 2.38 acres. Most of the plant operations through the years have been conducted on the Norwood portion of the property. The Facility is almost entirely paved with concrete or asphalt except for some gravel covered areas in the central and southern portions of the facility, and a grassy area east of Building 14 (Figure 2).

The Facility is located in a mixed commercial/industrial/residential setting. The areas west and north of the facility consist predominantly of industrial manufacturing, warehousing, chemical production, and service companies. Immediately beyond the Norfolk Southern railroad embankment, the topography east of the Facility steeply slopes to a lower parking lot belonging to Duramed Pharmaceutical, Inc. South of the Facility, the Norwood Lateral and associated on and off-ramps separate the facility from I-71 and a residential area located 500 feet southwest of the property.

The original topography of the property included two ravines associated with the Duck Creek drainage system (referred to as the former East Ravine and former West Ravine). Duck Creek is situated in a concrete channel box located approximately 600 feet southeast of the Facility. The East and West Ravines have been filled to present grade which slopes from an elevation of 614 feet above mean sea level (MSL) on the western perimeter of the property to approximately 598 feet MSL along the eastern property boundary. South of the Facility, the surface slopes abruptly (a 2:1 engineered slope developed during the construction of the Norwood Lateral in the late 1960s) from an elevation of approximately 606 feet MSL to 580 feet MSL along the Norwood Lateral.

2.2 Facility History and Background

The EMD Chemicals Facility has been used for the manufacturing, storage and distribution of organic and inorganic chemicals. The Facility has served in this capacity before being purchased by EMD Chemicals in 1977 (at that time known as EM Science, Inc., a division of EM Industries, Inc., Hawthorne,

New York), dating back to the late 1940s. During the 1950s to the early 1970s, chemical discharges occurred from process buildings, sewage systems and other structures involved in the operation of the Facility. Between 1952 and 1971, construction debris and chemical wastes were buried in a ravine (the West Ravine), which is located near the center of the property. In April of 1960, a chemical warehouse burned on the property, and the remaining debris was buried in the West Ravine. Another ravine (the East Ravine) also existed on the eastern portion of the property. It was filled with soil and construction debris from off site sources between 1938 and the early 1970s. There is no record of chemical disposal in the East Ravine. Both ravines are currently filled to grade.

EMD Chemicals has performed remedial investigations and actions for over 20 years. The U.S. EPA and the Ohio EPA conducted several site inspections at the Facility during the 1980s. In addition, EMD Chemicals has conducted several voluntary environmental investigations at the Facility between 1981 and 1990, for various scopes of work and objectives. These investigations were conducted with Ohio EPA's knowledge but without an Ohio EPA Administrative Consent Order. The activities led to the implementation of several interim measures by EMD Chemicals to mitigate the off-site migration of hazardous wastes and constituents. These interim measures include the construction of Sump 562 at the mouth of the West Ravine (1983), the initiation of a storm water management program to collect and redirect storm water from process areas and contaminated areas (1987), the construction of a french drain to intercept and collect contaminated perched ground water migrating beneath the eastern property boundary (1988), and the implementation of a hydraulic gradient control pumping well to prevent the eastward migration of contaminated ground water located at a greater depth than the french drain (1992). In 1992, EMD Chemicals and the Ohio EPA Superfund program entered into an Administrative Order on Consent to prepare a work plan and conduct a Remedial Investigation/Feasibility Study (RI/FS) for the Facility. Ohio EPA approved the RI/FS Work Plan in 1994. The RI report was approved by Ohio EPA in 1996. The FS was submitted to Ohio EPA on January 21, 2000, for review and comment. In 2004, Ohio EPA drafted a modified FS which was acceptable to the State on April 20, 2004.

The Facility was given U.S. EPA Identification Number OHD 086 438 538. On December 3, 1990, the U.S. EPA prepared a Preliminary Assessment/Visual Site Inspection (PA/VSI) Report as part of a RCRA Facility Assessment (RFA), which identified solid waste management units (SWMUs) and areas of concern (AOCs). The PA/VSI Report also recommended corrective action for certain SWMUs and AOCs.

In July 2004, the U.S. EPA and EMD established a RCRA Voluntary Corrective Action Agreement for EMD Chemicals to work independently and voluntarily to investigate, and as necessary, stabilize and remediate releases of hazardous wastes or hazardous constituents at or from the Facility.

2.3 Project Objectives

The overall objective of the Corrective Action Agreement is for EMD Chemicals to work independently and voluntarily to investigate, and as necessary, stabilize and remediate releases of hazardous waste or hazardous constituents at or from the Facility. To date, EMD Chemicals has completed several activities to identify the nature and extent of releases of hazardous waste and hazardous constituents at and from the Facility, as discussed above. To demonstrate that the U.S. EPA's Contaminated Ground Water Environmental Indicator (CA750) has been met and to support the evaluation and design of corrective measures, supplemental investigations to the aforementioned nature and extent activities were also completed.

Future monitoring and measurement data will be collected to verify the effectiveness of existing interim actions, and that the migration of contaminated ground water is controlled. Specific objectives include:

- Achieve an appropriate "Corrective Action Complete" determination from U.S. EPA and to restore the Facility to beneficial use and to emphasize results-based corrective action over process, maximize procedural and program flexibility, and implement recent RCRA Corrective Action policy reforms.

- For EMD Chemicals to perform corrective action in accordance with RCRA and to provide all information necessary for U.S. EPA to make the "Environmental Indicator" determinations required by the Government Performance and Results Act for the control of human exposures and the migration of contaminated ground water.

- For EMD Chemicals to use the protection standards and processes relevant to the Federal RCRA Corrective Action program.

2.3.1 Data Quality Objectives

Data quality objectives (DQOs) have been developed and present a strategy that meets these overall objectives. DQOs are qualitative and quantitative statements that specify the quality of the data required to support decisions made during investigation activities, and are based on the end uses of the data to be collected. As such, different data uses may require different levels of data quality. There are five analytical levels (defined below) which address various data uses and the QA/QC effort and methods required to achieve the desired level of quality.

DQOs for the project have been established in accordance with the U.S. EPA guidance documents, which ensure that the database developed during the facility investigation activities meets the objectives and quality necessary for its intended use (U.S. EPA 1987; 1991; 1998). The DQOs for the project are shown on Table 1.

DQOs can be classified for the measurement data by defining the level of analytical support assigned to each type of data measurement.

The following defines the different DQO analytical support levels (ASL).

i. ASL I – Field screening or analysis using portable instruments.

ii. ASL II – Field screening analyses using more sophisticated portable analytical instruments.

iii. ASL III – All analyses performed in off-facility analytical laboratories using U.S. EPA procedures other than the Contract Laboratory Program (CLP) Routine Analytical Services (RAS).

iv. ASL IV – CLP-RAS performed in a CLP analytical laboratory using CLP procedures.

v. Level V – Non-standard analytical methods performed in an off-facility laboratory (e.g. geotechnical engineering laboratory analyses).

The level of DQO analytical support for each group of media and parameters is presented in Table 2. The levels of analytical support have been chosen to provide data quality that is consistent with the end use of data, which is primarily to characterize the nature and extent of contamination at the Facility, perform evaluations of risks to human health, complete environmental indicator reports, evaluate contaminant fate and transport, and to perform corrective measure evaluations.

A Data Quality Objective Summary Form will be prepared prior to each sampling event. An example is depicted in Appendix I. The purpose of this form is to integrate the DQO process into the planning phase of the RCRA Corrective Action. Completed forms will be approved by The Payne Firm Inc.'s (TPF) project manager and placed in the project files.

2.4 Target Parameter List and Screening Levels

The target parameter list consists of 40 CFR Appendix IX List volatile organic compounds (VOCs); a modified Appendix IX List semi-volatile organic compounds (SVOCs); and, arsenic, chromium, and nickel. The specific laboratory methods needed to analyze for these constituents are presented in Section 8.0. EMD will use appropriate U.S. EPA Region 5 screening levels to determine if further investigation is required.

3.0 PROJECT ORGANIZATION AND RESPONSIBILITY

The Payne Firm will have responsibility of data collection phases of the RCRA Corrective Action that are not related to construction of the corrective measures (e.g. data collected for the nature and extent of contamination, EI purposes, evaluation and design of corrective measures, and operations and maintenance of on-going interim measures). CH2M Hill will have responsibility for data collected as part of the construction of corrective measures. Those measures will be addressed under a separate QAPP prepared as part of the CH2M Hill's construction documents.

All samples collected for chemical analysis by the Payne Firm will be transported to Severn-Trent Laboratories, Inc. (STL) in North Canton, Ohio. Chain-of-custody documentation will be maintained during this process as described in Section 6.0. Samples collected for geotechnical engineering analyses will be shipped directly to Bowser-Morner, Inc., in Dayton, Ohio. TPF will maintain a file copy of all laboratory deliverables. All final validated laboratory data will be distributed by the Payne Firm.

Individuals within TPF and STL that are responsible for implementing the QAPP are presented below.

Kevin D. Kallini, P.G. – Project Manager – TPF

- Management of project team;
- Review and approval of data validation reports;
- Approval of QAPP amendments and revisions;
- Review and approval of Field Task Statement of Works;

Angela L. Hurley – Project Field Coordinator – TPF

- Management of field activities and field QA/QC;
- Management of laboratory activities and analyses;
- Review of data validation reports;
- Data review assessment and management;
- Technical representation of project activities;
- Project file custodian;
- Preparation of Field Task Statement of Works;
- Quality Assurance Officer; and
- Field Safety Officer.

Mark E. Berkich – Data Validation Coordinator – TPF

- Data validation and assessment;
- Advise on data corrective action procedures;
- Preparation and review of data validation reports; and
- QA/QC representation of project activities.

Geoffrey S. King, L.G. – Database Manager – TPF

- Overview of analytical databases.

Beth Lambert – Laboratory QA Manager – Severn Trent Laboratories (North Canton, Ohio)

- Overview of laboratory quality assurance; and
- Overview QA/QC documentation.

Roger Toth – Project and Client Manager – Severn Trent Laboratories (North Canton, Ohio)

- Laboratory quality assurance;
- Laboratory QA/QC documentation;
- Project specific quality assurance; and
- Coordinator with TPF's project manager.

The Payne Firm's Project Manager has the primary responsibility for project quality. Independent quality assurance will be provided by the laboratory's Project Managers and QA Officers prior to release of all data to the Payne Firm. The U.S. EPA Project Manager will be responsible for overview of the corrective action.

During sampling phases of the project, telephone and e-mail contact between the field sampling personnel and the laboratory subcontractors will occur as needed. The laboratory will provide status updates by means of preliminary data telefacsimiles or electronic e-mail. Should unexpected delays or other problems with the laboratory analyses occur, the laboratory project manager will communicate directly to the Payne Firm's Project Manager for resolution.

4.0 QUALITY ASSURANCE OBJECTIVES FOR MEASUREMENT DATA

The overall QA objective is to develop and implement procedures for field sampling, chain-of-custody, laboratory analyses and reporting that will provide data of known quality. Specific procedures for sampling, chain-of-custody, laboratory instrument calibration, laboratory analysis, reporting of data, internal quality control, audits, routine maintenance of field equipment and corrective action are described in other sections of this QAPP. The purpose of this section is to address the specific objectives for accuracy, precision, completeness, representativeness and comparability for the RCRA Corrective Action.

4.1 Level of Effort

Field blank, trip blank, field equipment rinseate, field duplicate and matrix spike samples will be analyzed to assess the quality of the data resulting from the field sampling program. Field and trip blanks consist of analyte-free water and will be submitted to the analytical laboratory to provide the means to assess the quality of the data resulting from the field sampling program. Field blank samples are analyzed to check for procedural contamination at the Facility which may cause sample contamination. Trip blanks are used to assess the potential for contamination of samples due to contaminant migration during sample shipment and storage. Field equipment rinseate samples are analyzed to check that equipment decontamination procedures are adequate. Field duplicate samples are analyzed to check for sampling and analytical precision. Matrix spikes provide information about the effect of the sample matrix on the preparation and measurement methodology. All matrix spikes are performed in duplicate. One matrix spike/matrix spike duplicate (MS/MSD) will be collected for every 20 or fewer investigative samples.

The general level of the QC effort will consist of one field duplicate, one field equipment rinseate, and one field blank per 20 investigative samples. One VOC trip blank sample will be prepared by the laboratory and will be included along with each shipment of aqueous VOC samples. VOC trip blanks will be preserved by the laboratory in the same manner as the investigative samples.

MS/MSD samples are investigative samples. MS/MSD water samples must be collected at triple volume for VOC and double the volume for extractable organics. No additional volume is required for solid samples. The number of duplicate and field blank samples to be collected will be provided on a Data Quality Summary Form as shown in Appendix I. A new form will be prepared for each phase of sampling.

4.2 Accuracy, Precision and Sensitivity of Analyses

The fundamental QA objective with respect to accuracy, precision, and sensitivity of laboratory analytical data is to achieve the QC acceptance criteria of the analytical protocols.

Accuracy will be determined by assessing the percent recoveries of matrix spike samples and QC check samples. Precision will be determined by assessing the relative difference (RPD) determined from the percent recoveries of MS/MSD samples. The equations for determining percent recovery and RPD are presented in Section 13.0.

The targeted quantitation limits, as presented in Table 4, represent the level of sensitivity for the analyses. The units of measure for soil/sediment and water samples will be mg/kg or ug/kg and mg/L or ug/L, respectively. The units of measure for geological property testing will be consistent with the referenced methods.

Tables 5 and 6 present the accuracy and precision requirements for the analyses in terms of MS/MSD recovery and RPD control limits and surrogate compound control limits.

4.3 Completeness, Representativeness, and Comparability

Completeness is a measure of the amount of valid data obtained from a measurement system compared to the amount that was expected to be obtained under normal conditions. It is expected that the project laboratory will provide data meeting QC acceptance criteria for 90 percent or more of all samples tested using the specified methods.

Following completion of the analytical testing, the percent completeness will be determined by the following equation:

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

The completeness goal for the investigation will be 90 percent or greater.

Representativeness expresses the degree to which data accurately and precisely represent a characteristic of a population, parameter variation at a sampling point, process condition or an environmental condition. Representativeness is a qualitative parameter which is dependent upon the proper design and implementation of the sampling program and the proper laboratory analysis. The sampling network will be designed to provide data that is representative of Facility conditions. During development of this network, consideration will be given to Facility operations, existing analytical data, and physical setting. The rationale underlying the sampling network design is discussed on Table 1. The development of representative data will be undertaken by using proper sampling techniques, following proper analytical procedures, and ensuring that holding times of the samples are not exceeded.

Comparability expresses the confidence with which one data set can be compared with another. The extent to which existing and planned analytical data will be comparable depends on the similarity of sampling and analytical methods. The analytical data, collected as part of the RCRA Corrective Action, are expected to be directly comparable to existing data because the same procedures and QA objectives will be used.

Compliance of precision, accuracy, representativeness, completeness, comparability and sensitivity objectives will be evaluated by the Data Validation Coordinator. Should the quality assurance objectives not be fully compliant with those specified in the QAPP, the impact on the data set will be evaluated and corrective actions (as discussed on Section 14.0) will be implemented, as necessary.

4.4 Field Measurements

Measurement data will be generated during field activities. These activities may include, but are not limited, to the following.

i. Documenting time and weather conditions.
ii. Determining pH, specific conductance, turbidity and temperature of ground water samples.
iii. Verifying well development and pre-sampling purge volume.
iv. Monitoring well slug tests and pumping tests.
v. Determining ground water elevations.
vi. Determining the presence of non-aqueous liquids and depth, if present.
vii. Soil organic vapor measurements.
viii. Soil VOC screening.

The general QA objective for such measurement data is to obtain reproducible and comparable measurements to a degree of accuracy that is possible with the use of standardized procedures. The QA objectives for the field measurements are presented in the Payne Firm's field Standard Operating Procedures (SOPs) provided in Appendix II. Accuracy and precision for the field measurements will be monitored by analyzing calibration check solutions and duplicate sample or duplicate calibration check solution measurements. Evaluation of field quality assurance objective compliance will be the responsibility of the Project Field Coordinator. Should the QA objectives not be met, corrective actions will be implemented as necessary.

5.0 SAMPLING PROCEDURES

Required sampling containers, sample preservation methods, maximum holding times, collection instructions, and sample preparation methods are presented on Table 7. Presented on Table 8 is a list of the site-specific SOPs that may be used for field sampling and related activities. The listed SOPs are presented in detail in Appendix II.

Prior to each sampling event or sampling phase, the Project Field Coordinator will have the responsibility of preparing a Field Task Statement of Work (SOW). The Field Task SOW will detail the field work activities that will be completed by the field team, including at a minimum:

- Sampling objectives and purpose;
- Sample locations;
- Sample numbering and labeling;
- Pertinent SOPs to follow;
- QA/QC samples;
- Any special holding time requirements; and
- Any task-specific QAPP or QA/QC procedures to follow.

The Field Task SOW will be reviewed and approved by the Project Manager. Prior to the sampling event or sampling phase, the Project Manager will meet with the Field Team to review the Field Task SOW. Completed Field Task SOWs will be retained in Appendix IV of the QAPP and electronically in the project's network file.

6.0 SAMPLE CUSTODY AND DOCUMENT CONTROL

The chain-of-custody protocols can be segregated into three parts: 1) Sample collection; 2) laboratory analysis; and 3) project files. Project files, including all originals of laboratory reports, are maintained under document control in a secure area.

A sample or project file is under your custody if it:

i. Is in your possession;
ii. Is in your view, after being in your possession;
iii. Is in your possession and you place them in a secured location; or
iv. Is in a designated secure area.

6.1 Field Chain-of-Custody Procedures

The sample packaging and shipment procedures summarized below will ensure that the samples will arrive at the laboratory with the chain-of-custody intact.

6.1.1 Field Procedures

1. The field sampler is personally responsible for the care and custody of the samples until they are transferred or properly dispatched. As few people as possible should handle the samples.

2. All bottles will be labeled with unique sample numbers.

3. Sample labels are to be completed for each sample using waterproof ink unless prohibited by weather conditions.

6.1.2 Field Logbooks/Documentation

A field logbook will provide the means of recording data collecting activities performed. As such, entries will be described in as much detail as possible so that persons going to the Facility could reconstruct a particular situation without reliance on memory. The use of field notebooks is described in SOP 1-1.

6.1.3 Transfer of Custody and Shipment Procedures

Field chain-of-custody procedures are provided in SOP 1-3. Example chain-of-custody documents and shipping labels are provided in the SOP.

6.2 Laboratory Chain-of-Custody Procedures

The sample custodian will assign a unique number to each incoming sample for use in the laboratory. The unique number and customer number will then be entered into the sample receiving log. The laboratory date of receipt will also be recorded.

Laboratory custody procedures and document control for those samples analyzed by the project laboratory will be carried out using the laboratory's SOPs (Appendix III).

6.3 Storage of Samples

After the sample custodian has prepared the log book, the chain-of-custody will be checked to ensure that all samples are stored in the appropriate location(s). All samples will be stored within an access-controlled location and will be maintained properly preserved until completion of all analytical work or, at a minimum, for at least 30 days after receipt of the final report, or as specified in the laboratory's SOPs (Appendix III).

6.4 Project Files

Files maintained by the Payne Firm will consist of the following, as appropriate:

i. Project plan;
ii. Project log books;
iii. Field data records;
iv. Sample identification documents;
v. Chain-of-custody records;
vi. Correspondence;
vii. References, literature;
viii. Final data packages (electronic and/or paper copy);
ix. Miscellaneous – phone notes, maps, drawings, etc.; and
x. Final data validation report (electronic and/or paper copy).

Project file materials will be the responsibility of the Project Manager with respect to maintenance and document removal and will be stored in a secured, access-controlled area.

The project laboratory will be responsible for maintaining analytical log books and laboratory data. Raw electronic laboratory data files will be inventoried and maintained by the laboratories for a period of at least five years, at which time the laboratories will notify the Payne Firm regarding the need for additional storage. Each laboratory's document control personnel will be responsible for document control.

7.0 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.

7.1 Field Instruments/Equipment

Instruments and equipment used to gather, generate, or measure environmental data will be calibrated with sufficient frequency and in such a manner that accuracy and reproducibility of results are consistent with the manufacturer's specification and QAPP requirements noted herein.

Field instrument calibration procedures are provided in each specific instrument SOP.

7.2 Laboratory Instruments

Calibration of laboratory equipment will be based on the project laboratory's SOPs. Records of calibration, repairs, or replacement will be filed and maintained by the designated laboratory personnel performing quality control activities. These records will be filed at the location where the work is performed and will be subject to QA audit. For all instruments, the laboratory will maintain an adequately trained repair staff with in-house spare parts or will maintain service contracts with vendors.

The records of calibration will typically be kept as follows:

1. If possible, each instrument will have a record of calibration permanently affixed with an assigned record number.
2. A label will be affixed to each instrument or a notebook available showing description, manufacturer, model numbers, date of last calibration and by whom calibrated (signature), due date of next calibration, where appropriate, and compensation or correction figures, as appropriate.
3. A written calibration procedure will be available for each piece of test and measurement equipment.
4. Any instrument that is not calibrated within the manufacturer's original specification will display an appropriate warning tag.

All standard materials will be traceable to U.S. EPA or National Institute of Standards and Technology (NIST) reference standards, if available. Each calibration standard will receive a reference number that is traceable to the lot number of the reference standard from which it was prepared.

In addition to the above, specific calibration procedures are detailed in the laboratory-specific SOPs, which are available at anytime to the Payne Firm, if needed. A summary of calibration procedures and acceptance criteria is provided on Table 9. Failure of instrument calibration to meet the acceptance criteria will result in instrument recalibration.

8.0 ANALYTICAL PROCEDURES

The samples collected for chemical analyses will be analyzed using the methods listed in Table 10. Laboratory-specific SOPs for the methods are presented in Appendix III.

Geotechnical engineering and waste characterization laboratory analyses will be performed using the standard methods also presented in Table 10.

9.0 INTERNAL QUALITY CONTROL

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

9.1 Field QC

Quality control procedures for field measurements will be limited to checking the reproducibility of the measurement in the field by obtaining multiple readings and by calibrating the instruments as specified in the Field SOPs provided in Appendix II.

Additional field QC procedures include: collecting field duplicate samples to determine the overall precision of the sampling event; collecting field blanks to determine bias of samples due to field conditions; collecting field equipment rinseate samples to ensure that the sampling and equipment decontamination procedures are consistent with the SOPs; and the sample preservation, packaging, and shipping procedures are consistent with this QAPP.

9.2 Laboratory QC

Specific procedures related to internal laboratory QC samples (i.e. matrix spikes, surrogate spikes, blanks, QC check samples and matrix spike duplicates) are detailed in the following subsections.

The internal QC checks for the analytical parameters will follow the appropriate methods specified in Table 10 and the laboratory's SOPs presented in Appendix III.

9.2.1 Initial and Continuing Calibration Checks

The compliance requirements for satisfactory instrument calibration are established to ensure that the instrument is capable of producing acceptable quantitative data. The initial calibration demonstrates that the instrument is capable of acceptable performance at the beginning of an analysis run. The continuing calibration checks document that the initial calibration is still valid. Also documented is the satisfactory maintenance and adjustment of the instrument on a day-to-day basis. The specific control criteria and corrective action requirements for these calibrations will be as specified by the respective methods presented in Table 10 and the applicable SOPs in Appendix III.

9.2.2 Internal Standards Performance

The internal standards performance criteria ensure that gas chromatograph/mass spectrometer (GC/MS) sensitivity and response is stable during every run. Acceptance criteria are as specified by the referenced methods and the SOPs in Appendix III.

9.2.3 Method Blank Samples

A method blank sample will be analyzed by the laboratory at a frequency of one blank per twenty sample analyses or, in the event that an analytical round consists of less than twenty samples, one method blank sample will be analyzed. The method blank sample, an aliquot of analyte-free water or suitable solid material (sodium, sulfate, Ottawa sand) will be carried through the entire analytical procedure.

9.2.4 Matrix Spike/Matrix Spike Duplicates

A MS/MSD sample set will be analyzed at a minimum frequency of one per twenty investigative water samples. A matrix spike sample will be analyzed at a minimum frequency of one per twenty investigative soil samples. Percent spike recoveries will be used to evaluate analytical accuracy while the relative percent difference between the spike and duplicate will be used to assess analytical precision.

9.2.5 Surrogates

Surrogates are used in all GC and GC/MS analyses. Every blank, standard, and environmental sample including MS/MSD samples will be spiked with surrogate compounds prior to purging volatiles or extracting semi-volatiles.

Surrogates will be spiked into samples according to the appropriate analytical methods. Surrogate spike recoveries will fall within the control limits specified by the method for all analyte concentrations that are within the quantitation limits without dilution. Dilution of samples to bring the analyte concentration into the linear range of calibration may dilute the surrogates out of the quantitation limit; assessment of analytical accuracy in these cases will be based on the quality control information embodied by the check, matrix spike and matrix spike duplicate samples.

9.2.6 Calibration Standards

All primary standard materials will be traceable to U.S. EPA or NIST reference standards, if possible. Each calibration standard will receive a reference number that is traceable to the lot number from the primary reference standard from which it was prepared. The procedures for preparing calibration standards are contained within the applicable SOPs in Appendix III.

9.2.7 Reagent Checks

Reagents prepared for instrumental methods of analysis will be monitored by method blank samples and QC check samples, where appropriate.

9.2.8 QC Check Samples

QC check samples will be analyzed to determine the accuracy of the analytical methods. QC check samples are generally prepared from standards that are from a different source than the calibration standards or are standard reference materials. The percent recoveries will be calculated and compared to the acceptance criteria in the SOPs in Appendix III.

10.0 DATA REDUCTION, VALIDATION AND REPORTING

The project laboratory will perform analytical data reduction and review in-house under the direction of the laboratory QA officer. The laboratory QA officer will be responsible for assessing data quality and advising of any data which were rated "preliminary" or "unacceptable" or other qualifications based on the established QC criteria. The project laboratory will provide analytical support Level (ASL) IV "CLP-like" deliverables. At a minimum, one complete "CLP-like" data package will be delivered. Data reduction, review and reporting by the laboratory is typically conducted as outlined in the following procedure. However, the laboratory may perform data reduction, review and reporting in a slightly different manner.

1. Raw data produced and checked by the responsible analyst is turned over for independent review by another analyst.

2. The area supervisor reviews the data for attainment of quality control criteria established by the QAPP.

3. The area supervisor will decide whether any sample re-analysis is required.

4. Upon completion of all review and acceptance of the raw data by the supervisor, a report will be generated and sent to the laboratory Project Manager.

5. The laboratory Project Manager will complete a thorough inspection of all reports.

6. Upon acceptance of the preliminary reports by the Project Manager, final reports will be generated and signed by the laboratory manager or his designee.

7. A thorough review is performed for all data packages by the Laboratory Quality Assurance Officer, or his designee.

Field data from direct-reading instruments (pH, conductance, turbidity, temperature) will not require reduction. Laboratory data reduction will be performed using the equations in the SOPs provided in Appendix III and the ASTM Standards applied to chemical and geotechnical engineering laboratory analyses, respectively.

The Payne Firm's Data Validation Coordinator will conduct an evaluation of data reduction and reporting by the laboratory. These evaluations will consider the finished data sheets, field blank data and recovery data for surrogate and matrix spikes. The material will be checked for legibility, completeness,

correctness and the presence of requisite dates, initials, and signatures. The results of these checks will be assessed and reported to the Project Manager and the Project Field Coordinator noting any discrepancies upon the acceptability of the data. All information for QA/QC checks will be discussed in the Data Validation report. The Project Manager will review and approve all validation reports. The reports will be retained in the project file.

Validation of the analytical data will be performed by the Data Validation Coordinator based on the evaluation criteria outlined in the National Functional Guidelines for Organic and Inorganic Data Review (U.S. EPA, 1999). The assessment of analytical field data will include checks for adherence to laboratory QA procedures and accuracy and precision criteria and also the presence of transmittal errors and anomalously high or low parameter values. The results of these data validations will be reported to the Project Manager and the Project Field Coordinator, noting any problems and the effect upon the acceptability of the data. The manner in which the analytical data will be handled by the Payne Firm once it is received from the project laboratory is presented in Appendix V.

Data produced from field measurements and sample collection activities that are used in the project reports will be appropriately identified and appended to the report. Where data have been reduced or summarized, the method of reduction will be documented in the report. In addition, field data will be audited by the Project Field Coordinator for anomalously high or low values that may appear to be inconsistent with other data.

The Data Validation Coordinator will review items listed on the Data Validation Checklist, which is presented in Appendix VI. In addition, the overall completeness of the data package deliverable will be evaluated. One-hundred percent of the analytical data will be validated.

Laboratory data packages for chemical analyses will consist of ASL IV "CLP-Like" deliverables. The package shall include, at a minimum, the following:

1. Case Narrative

   i. Data of issuance
   ii. Laboratory analysis performed
   iii. Any deviations from intended analytical strategy
   iv. Laboratory batch number
   v. Numbers of samples and respective matrices
   vi. QC procedures utilized and also references to the acceptance criteria
   vii. Laboratory report contents
   viii. Project name and number
   ix. Condition of samples "as-received"

x. Discussion of whether or not sample holding times were met
xi. Discussion of technical problems or other observations which may have created analytical difficulties
xii. Discussion of any laboratory QC checks which failed to meet project criteria
xiii. Signature of Laboratory QA Manager

2. Chemistry Data Package

i. Case narrative for each analyzed batch of samples
ii. Summary page indicating dates of analyses for samples and laboratory QC checks
iii. Cross referencing of laboratory sample to project sample identification numbers
iv. Description of data qualifiers to be used
v. Sample preparation and analyses for samples
vi. Sample results
vii. Raw data for sample results and laboratory QC samples
viii. Results of (dated) initial and continuing calibration checks, and GC/MS turning results
ix. MS/MSD recoveries, laboratory control samples, method blank results, calibration check compounds, and system performance check compound results
x. Labeled (and dated) chromatograms/spectra of sample results and laboratory QC checks
xi. Results of tentatively identified compounds

Data packages for geotechnical engineering laboratory analyses will present the data in tabular format with graphical displays for grain size distributions.

The data packages will be stored with the project files as described in Section 6.0. Modeling of data for graphical displays such as concentration isopleths, ground water contours, and contaminant fate and transport modeling may be performed using validated data.

All laboratory reports, data, chain-of-custody forms, laboratory QA/QC summaries, photographs, field notes, and other information produced during the corrective action will be submitted to the U.S. EPA. The information will be attached to quarterly progress reports required by the Corrective Action Agreement (prepared by the 15th day of the month following each quarter), or under a separate cover.

11.0 PERFORMANCE AND SYSTEM AUDITS

Performance and system audits of both field and laboratory activities may be conducted to verify that sampling and analysis are performed in accordance with the procedures established in Section 5.0. Performance audits consist of sending performance evaluation samples to the laboratories for analysis and evaluation while system audits determine whether the requirements of the QAPP are being followed. The audits of field and laboratory activities include two separate, independent parts, internal and external audits.

11.1 Field Audits

Internal audits of field activities (sampling and measurements) will be conducted by the Payne Firm's Project Field Coordinator. The audits will include examination of field sampling records, field instrument operating records, sample collection, handling and packaging in compliance with the established procedures, maintenance of QA procedures, chain-of-custody, etc. These audits will be conducted to verify that QA procedures are maintained throughout the investigation and to correct deficiencies, if identified. The audits will involve review of field measurement records, instrumentation calibration records and sample documentation.

At the request of the U.S. EPA, EMD and the Payne Firm will provide or allow a U.S. EPA representative to take split or duplicate samples of all samples collected by EMD and the Payne Firm under the Corrective Action Agreement.

11.2 Laboratory Audits

The internal performance and system audits of the project laboratory may be conducted by the Payne Firm's Data Validation Coordinator. The system audits, which may be conducted prior to project commencement (and as necessary thereafter based on the results of performance evaluation samples routinely analyzed by the laboratory), will include examination of laboratory documentation of sample receipt, sample log-in, sample storage, chain-of-custody procedures, sample preparation and analysis, instrument operating records, etc. Blind QC samples may be prepared and submitted along with project samples to the laboratory for analysis throughout the project. The laboratory QC officer will evaluate the analytical results of these blind performance samples to ensure the laboratory maintains acceptable performance.

The U.S. EPA may audit the project laboratory, or require EMD to purchase and have analyzed Performance Evaluation samples selected by the U.S. EPA for compounds of concern.

12.0 PREVENTIVE MAINTENANCE

All analytical instruments to be used by the project laboratory will be serviced by the laboratory personnel at regularly-scheduled intervals in accordance with the manufacturer's recommendations. Instruments may also be serviced at other times due to failure. Requisite servicing beyond the abilities of the laboratory personnel will be performed by the equipment manufacturer or its designated representative(s).

Daily checks of each instrument will be completed by the laboratory analyst who has been assigned responsibility for that instrument. This will include changing GC inlet liners, tuning GC/MS, checking operation of data systems, checking for leaks, etc. Manufacturer's recommended procedures will be followed in every case. All maintenance will be recorded in a bound logbook kept with each instrument.

13.0 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.

13.1 Field Measurements

Field data will be assessed by the Project Field Coordinator who will review the field results for compliance with the established QC criteria that are specified in the QAPP. The accuracy of field measurements will be assessed using daily instrument calibration, calibration check, and blank data. Precision will be assessed on the basis of the reproducibility of multiple readings of a single sample. Data completeness will be calculated using the following equation:

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

The required minimum level of completeness will be 90 percent.

13.2 Laboratory Data

Laboratory results will be assessed for compliance with required precision, accuracy, completeness, and sensitivity as follows:

13.2.1 Precision

The precision of laboratory analysis will be assessed by comparing the analytical results between MS/MSD for organic analysis. The relative percent difference (RPD) will be calculated for each pair of duplicate analysis using the equation below:

$$\text{RPD} = \frac{S - D}{(S + D)/2} \times 100$$

Where:
S = First sample value (original or matrix spike value)
D = Second sample value (duplicate or matrix spike duplicate value)

13.2.2 Accuracy

The accuracy of laboratory results will be assessed for compliance with the established QC criteria that are described in Section 4.0 and 9.0 of the QAPP using the analytical results of method blanks,

reagent/preparation blank, check samples and MS/MSD samples. The percent recover (%R) of matrix spike samples and check samples will be calculated as indicated below:

$$\%R = \frac{A - B}{C} \times 100$$

Where:
A = The analyte concentration determined experimentally from the spiked sample
B = The background level determined by a separate analysis of the unspiked sample
C = The amount of spike added

13.2.3 Completeness

Completeness will be assessed by comparing the number of valid (usable) results (as determined by the Data Validation Coordinator) to the total possible number of results using the formula presented below. The required level of completeness for laboratory analyses will be 90 percent or greater.

$$\text{Percent Completeness} = \frac{\text{(number of valid measurements)}}{\text{(number of measurements planned)}} \times 100$$

13.2.4 Sensitivity

The achievement of targeted quantitation limits depends on instrumental sensitivity and matrix effects. Therefore, to ensure the data quality, it is important to monitor the instrumental sensitivity by means of constant instrument performance. The instrumental sensitivity will be monitored through the analysis of method blank, calibration check and laboratory control samples.

13.3 Statistical Evaluations

To evaluate large numbers of samples, or to evaluate sample matrix interference and its effect on final data results, statistical analysis and/or hypothesis testing may be required. Guidance on procedures, methods, rationale, and equations for evaluating data of this type is found in U.S. EPA, 1996.

14.0 CORRECTIVE ACTION

Corrective action is the process of identifying, recommending, approving and implementing measures to counter unacceptable procedures or out of quality control performance which can affect data quality. Corrective action can occur during field activities, laboratory analyses, data validation and data assessment. All corrective action proposed and implemented will be documented.

14.1 Field Corrective Action

Corrective action in the field may be necessary when the sample network is changed (i.e. more/less samples or sampling locations other than those specified in the QAPP) or sampling procedures and/or field analytical procedures require modification, due to unexpected conditions. In general, the field sampling team may identify the need for corrective action. The field sampling team, in consultation with the Field Quality Assurance (QA) Officer, will recommend a corrective action. The Project Manager will approve the corrective action which will be implemented by the field team. It will be the responsibility of the Field QA Officer to ensure the corrective action has been implemented.

Corrective action resulting from internal field audits will be implemented if data are adversely affected due to unapproved or improper use of approved methods. The Payne Firm's Project Field Coordinator will identify deficiencies and recommend corrective action to the Project Manager. The Project Manager will approve the corrective action(s) which will be implemented by the field team. Corrective action will be documented in the field log book.

14.2 Laboratory Corrective Action

Corrective action in the laboratory may occur prior to, during, and after initial analyses. A number of conditions (i.e. broken sample containers, multiple phases, low/high pH readings, potentially high concentration samples) may be identified during sample log-in or just prior to analysis. Following consultation with analysts and section leaders, it may be necessary for the laboratory QA Officer to approve the implementation of corrective action. The laboratory's submitted SOPs specify some conditions, during or after analysis, that may automatically trigger corrective action or optional procedures. These conditions may include dilution of samples, additional sample extract cleanup, automatic re-injection/re-analysis when certain QC criteria are not met.

The calibration acceptance/rejection criteria presented in Table 9 presents examples of situations requiring corrective action for each analytical instrument. In addition, the laboratory SOPs in Appendix III each provide a section on corrective action requirements.

The bench chemist will identify the need for corrective action. The laboratory supervisor will approve the required corrective action to be implemented by the laboratory staff. The laboratory QA Officer will ensure implementation and documentation of the corrective action.

These corrective actions are performed prior to release of the data from the laboratory. The corrective action will be documented in both the laboratory's corrective action report and the narrative data report sent to TPF.

The need for corrective action may also be identified during systems or performance audits. In these cases, the need for corrective action will be identified by the auditor. The corrective action taken to resolve the problem will be documented by the laboratory QA Manager. The corrective action taken will depend upon the QA/QC criteria which were violated.

14.3 Corrective Action During Data Validation and Data Assessment

The Payne Firm's Data Validation Coordinator may identify the need for corrective action during either the data validation or data assessment. Potential types of corrective action may include re-sampling by the field team or re-injection/re-analysis of samples by the laboratory.

These potential corrective actions are dependent upon the ability to mobilize the field team and whether the data to be collected are necessary to meet the required quality assurance objectives (e.g. the holding time for samples is not exceeded). When the Payne Firm's Data Validation Coordinator identifies a correction action situation, the Project Manager will be responsible for approving the implementation of corrective action (including re-sampling) during data assessment.

15.0 QUALITY ASSURANCE REPORTS TO MANAGEMENT

The Project Manager may receive an update from field team leaders on the performance of the measurement system and data quality following each sampling round and at the conclusion of the project.

These updates may include:

1. Assessment of data quality objectives (i.e. data accuracy, precision, sensitivity, and completeness);
2. Results of system and performance audits;
3. Amendments to the QAPP; and
4. QA problems, action taken, and resolutions.

16.0 REFERENCES

The Payne Firm, Inc., 1993, Work Plan for the Remedial Investigation/Feasibility Study of the EM Science Site, Volume 3 of 4---Quality Assurance Project Plan, Parts 1 and 2, Project No. 100.37.04.

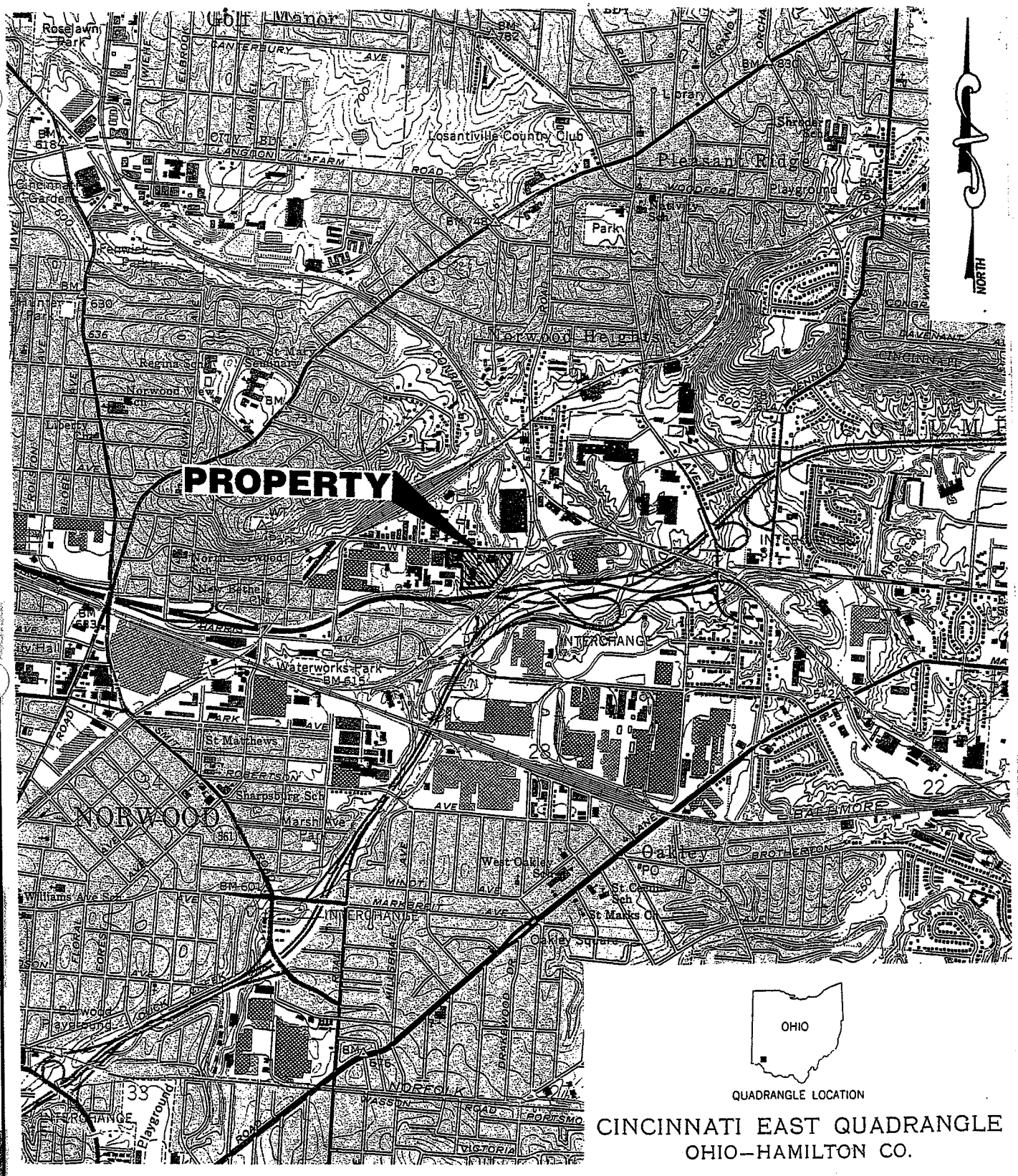
U.S. EPA, 1987; Data Quality Objectives for Remedial Response Activities; Office of Emergency and Remedial Response, Washington, D.C.; EPA/540/G-87/004.

U.S. EPA, 1991; Preparation Aids for the Development of Category I Quality Assurance Project Plans, Risk Reduction Engineering Laboratory, Office of Research and Development, Cincinnati, Ohio; EPA/600/8-91/003.

U.S. EPA, 1996; Guidance for Data Quality Assessment – Practical Method for Data Analysis; EPA-2A-G9; QA96, July 1996.

U.S. EPA, 1998; RCRA QAPP Instructions, U.S. EPA Region 5, Revision: April 1998; U.S. EPA Region 5 Waste Pesticides and Toxics Division, Chicago, Illinois.

U.S. EPA 1999; U.S. EPA Contract Laboratory National Functional Guidelines for Organic and Inorganic Data Review; EPA-540/R-94-012 and EPA-540/R-94-013.



QUADRANGLE LOCATION

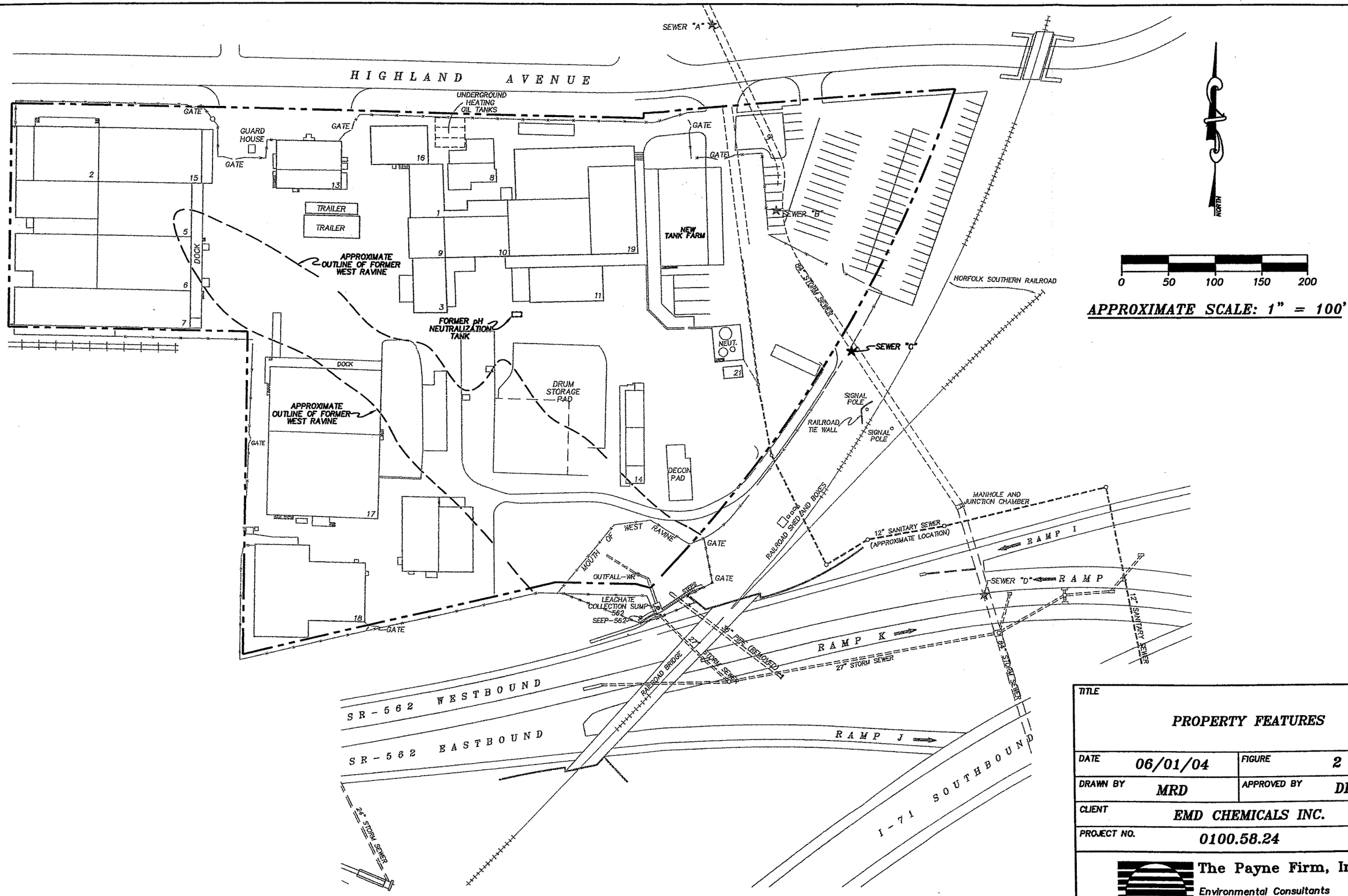
CINCINNATI EAST QUADRANGLE
OHIO–HAMILTON CO.

DRAWN BY	APPROVED BY	PROJECT NO.	DATE	FIGURE
WJH	DCC	100.58.24	06/01/04	1

CLIENT: EM SCIENCE

The Payne Firm, Inc.
Environmental Consultants
Cincinnati, Ohio 45242

TITLE: PROPERTY LOCATION



TITLE	PROPERTY FEATURES
DATE 06/01/04	FIGURE 2
DRAWN BY MRD	APPROVED BY DDW
CLIENT	EMD CHEMICALS INC.
PROJECT NO.	0100.58.24

The Payne Firm, Inc.
Environmental Consultants
Cincinnati, Ohio 45242

EMD Chemicals Inc.
Norwood, Ohio
Project No. 0100.58.19

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TABLE 1: Data Quality Objectives

FACILITY INVESTIGATION	DECISION TO SAMPLE	INPUTS CONSIDERED	CONTROL UNCERTAINTY
1. **Nature and Extent of Contamination:** Define the nature and extent of vertical contamination such that informed decisions can be made with respect to completing the migration of contaminated ground water under control, environmental indicator report (ground water EI), and evaluating corrective measures.	• Sample and analyze soil, ground water and surface water, as appropriate. • Obtain additional nature and extent of contamination data to support the ground water EI and the design of corrective measures. • Determine the horizontal and vertical extent of contamination.	• Previous investigations at the Facility indicate that VOCs, SVOCs, and metals are the constituents of concern. • Mobility and seasonality were considered requiring single (soil) and multiple (ground water and surface water) sampling events. • Biased sampling towards locations known to have contamination.	• Biased data set to confirm nature and extent of contamination. • Sample list consists of Appendix IX VOCs, SVOCs, and site-specific metals. • Analysis uses SW-846 standard methods at lowest detection limits achievable. • Laboratory analyses will be reported with a "CLP-Like" data package. • Analyses at ASL IV. • Uncertainty limited by close spatial and temporal coordination between soil and ground water observations, and adherence to QAPP.

TABLE 1: Data Quality Objectives (cont.)

FACILITY INVESTIGATION	DECISION TO SAMPLE	INPUTS CONSIDERED	CONTROL UNCERTAINTY
2. **Define Physical and Hydrogeological System:** Continue to define the site geologic/hydrogeologic model and identify the potential routes of contaminant migration.	• Perform additional stratigraphic and geotechnical engineering sampling, as needed. • Perform surface water sampling to confirm ground water infiltration pathways to sewer systems. • Conduct fate and transport modeling as necessary to support decisions. • Semi-annual sampling of ground water monitoring wells.	• Establishing the overall boundary conditions for the geologic/hydrogeologic model. • Use existing boring log and hydraulic data to confirm geological information.	• Uncertainty controlled by use of standard geological property testing methods and ASL V for non-standard methods. • Biased geotechnical samples to determine geological conditions in geological units ensure model consistency. • Ground water wells correlated to initial stratigraphic borings increase certainty in the model and will increase confidence in contaminant migration routes.
3. **Human Health/Ecological Risks:** Characterize human health risks and environmental impacts necessary to complete the ground water EI report.	• Confirm potential exposure pathways and receptors. • Sample soil, surface water, and ground water media, as appropriate, for VOCs, SVOCs, and metals.	• Detected concentrations of contaminants in on-property soil and ground water media. • Contaminants in storm sewers.	• Multiple ground water sampling locations and events provide less uncertainty in the evaluation of mobility and fate of contaminants. • Sufficient characteristics of soil source area and ground water contamination provides assurances for the level of significance of human health risks. • ASL IV analyses performed using SW-846 methods for VOCs, SVOCs, and metals. Data reported using "CLP-Like" data packages.

TABLE 1: Data Quality Objectives (cont.)

FACILITY INVESTIGATION	DECISION TO SAMPLE	INPUTS CONSIDERED	CONTROL UNCERTAINTY
4. **Ground Water Environmental Indicator Determination**	• Sample and analyze ground water and surface water, as appropriate. • Obtain sufficient data to support ground water plume stabilization and to assess current human exposures to contamination.	• Mobility and seasonality were considered requiring multiple (ground water) sampling events. • Detected concentrations of contaminants in on-property soil and ground water media. • Detected concentrations of contaminants in storm sewers.	• At a minimum, conduct semi-annual sampling events. • Collect QA/QC samples consistent with the QAPP. • ASL IV Analyses performed using SW-846 methods for VOCs, SVOCs, and metals. • Data reported use "CLP-Like" data packages.
5. **Contaminant Fate and Transport:** If necessary, determine estimates on the rate of migration of contaminants in environmental media to support the ground water EI report corrective measures evaluation.	• Define relationship between contaminant concentrations and the physical hydrogeological system. • Using existing information, and data to be collected from the proposed sampling program. • Obtain, through hydrogeologic sampling, significant transport routes and site physical parameters, such as permeability and hydraulic conductivity.	• Physical parameters related to air, surface water, and ground water transport including gradient and hydraulic conductivity. • Results of ground water transport modeling.	• Uncertainty in estimated future potential for contamination migration could be large; therefore, conservative estimates will be used for transport factors. • Comparisons with actual observations will reduce inherent uncertainties to the maximum extent practical.
6. **Evaluation of Corrective Measures:** Use on- and off-property data to develop and evaluate an applicable range of corrective measures.	• Sample relevant media to assess toxicity, mobility, and volume. • Sample for geotechnical engineering to characterize all geologic units. • Conduct ground water transport and fate transport modeling, as necessary.	• Existing information and knowledge. • Collection of additional data prior to design will assist in corrective action decision-making. • Geological property analyses augment evaluation of key physical parameters. • Existing information derived from ongoing interim measures.	• Uncertainty reduced through development of site geologic/hydrogeologic model, nature and extent of contamination definition, and determination of key physical parameters (addressed in Parts 1 through 4 above).

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Norwood, Ohio
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TABLE 2: Levels of Data Quality Objective Analytical Support

Matrix	Analysis	DQO Analytical Support
Soil	VOCs*	Level IV with "CLP-Like" Data Package
	Metals (As, Cr, Ni)	Level IV with "CLP-Like" Data Package
	SVOCs*	Level IV with "CLP-Like" Data Package
	TOC	Level IV with "CLP-Like" Data Package
Ground Water	VOCs *	Level IV with "CLP-Like" Data Package
	SVOCs*	Level IV with "CLP-Like" Data Package
	Metals (As, Cr, Ni)	Level IV with "CLP-Like" Data Package
Surface Water	VOCs*	Level IV with "CLP-Like" Data Package
Geotechnical Engineering Properties	Various properties (e.g. grain size, permeability, moisture content, etc.)	Level V

*40 CFR 264 Appendix IX List

EMD Chemicals Inc.
Norwood, Ohio
Project No. 0100.58.19

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TABLE 4: Target Quantitation Limits

Volatile Organic Compounds-SW846 8260B Water			
Compound	**Reporting Limit**	**Method Detection Limit**	**Units**
Acetone	10	0.74	ug/L
Acetonitrile	20	1.5	ug/L
Acrolein	20	7.3	ug/L
Acrylonitrile	20	1.6	ug/L
Benzene	1	0.22	ug/L
Bromodichloromethane	1	0.14	ug/L
Bromoform	1	0.17	ug/L
Bromomethane	1	0.36	ug/L
2-Butanone	10	0.39	ug/L
Carbon disulfide	1	0.28	ug/L
Carbon tetrachloride	1	0.19	ug/L
Chlorobenzene	1	0.2	ug/L
Chloroprene	2	0.2	ug/L
Chloroethane	1	0.24	ug/L
Chloroform	1	0.16	ug/L
Chloromethane	1	0.14	ug/L
3-Chloropropene	2	0.21	ug/L
Dibromochloromethane	1	0.19	ug/L
1,2-Dibromo-3-chloropropane	2	0.28	ug/L
Dibromomethane	1	0.21	ug/L
1,2-Dibromoethane	1	0.24	ug/L
trans-1,4-Dichloro-2-butene	1	0.62	ug/L
Dichlorofluoromethane	2.0	0.25	ug/L
1,1-Dichloroethane	1	0.21	ug/L
1,2-Dichloroethane	1	0.16	ug/L
1,1-Diclhloroethene	1	0.18	ug/L
1,2-Dichloroethene (Total)	1	0.16	ug/L
cis-1,2-Dichloroethene	1.0	0.21	ug/L
trans-1,2-Dichloroethene	1.0	0.16	ug/L
1,2-Dichloropropane	1	0.15	ug/L
cis-1,3-Dichloropropene	1	0.12	ug/L
trans-1,3-Dichloropropene	1	0.17	ug/L
1,4-Dioxane	50	12	ug/L
Ethylbenzene	1	0.19	ug/L

TABLE 4: Target Quantitation Limits

Volatile Organic Compounds-SW846 8260B Water			
Compound	**Reporting Limit**	**Method Detection Limit**	**Units**
Ethyl methacrylate	1	0.13	ug/L
2-Hexanone	10	0.35	ug/L
Iodomethane	1	0.19	ug/L
Isobutanol	50	4.6	ug/L
Methacrylonitrile	2	0.17	ug/L
Methylene chloride	1	0.19	ug/L
Methyl methacrylate	2	0.14	ug/L
4-Methyl-2-pentanone	10	0.32	ug/L
Ethyl cyanide	4	0.78	ug/L
Styrene	1	0.13	ug/L
1,1,2,2-Tetrachloroethane	1	0.22	ug/L
1,1,1,2-Tetrachloroethane	1	0.12	ug/L
Tetrachloroethene	1	0.19	ug/L
Toluene	1	0.17	ug/L
1,1,1-Trichloroethane	1	0.21	ug/L
1,1,2-Trichloroethane	1	0.22	ug/L
Trichloroethene	1	0.28	ug/L
Trichlorofluoromethane	1	0.16	ug/L
1,2,3-Trichloropropane	1	0.36	ug/L
Vinyl acetate	2	0.14	ug/L
Vinyl chloride	1	0.36	ug/L
Xylenes (total)	1	0.44	ug/L

Volatile Organic Compounds-SW846 8260B Solid			
Compound	**Reporting Limit**	**Method Detection Limit**	**Units**
Acetone	20.0	2.7	ug/kg
Acetonitrile	100	5.6	ug/kg
Acrolein	100	4.8	ug/kg
Acrylonitrile	100	2.5	ug/kg
Benzene	5.0	0.23	ug/kg
Bromodichloromethane	5.0	0.48	ug/kg
Bromoform	5.0	0.65	ug/kg
Bromomethane	5.0	0.61	ug/kg
2-Butanone	20.0	1	ug/kg
Carbon disulfide	5.0	0.2	ug/kg
Carbon tetrachloride	5.0	0.45	ug/kg
Chlorobenzene	5.0	0.28	ug/kg
Chloroprene	5	0.21	ug/kg
Chloroethane	5.0	0.54	ug/kg
Chloroform	5.0	0.4	ug/kg
Chloromethane	5.0	0.25	ug/kg
3-Chloropropene	10	0.78	ug/kg
Dibromochloromethane	5.0	0.36	ug/kg
1,2-Dibromo-3-chloropropane	10.0	1.4	ug/kg
Dibromomethane	5	0.57	ug/kg

TABLE 4: Target Quantitation Limits

Volatile Organic Compounds-SW846 8260B Solid			
Compound	**Reporting Limit**	**Method Detection Limit**	**Units**
1,2-Dibromoethane	5.0	0.37	ug/kg
trans-1,4-Dichloro-2-butene	5	0.75	ug/kg
Dichlorodifluoromethane	5.0	0.4	ug/kg
1,1-Dichloroethane	5.0	0.32	ug/kg
1,2-Dichloroethane	5.0	0.48	ug/kg
1,1-Diclhloroethene	5	0.6	ug/kg
1,2-Dichloroethene (Total)	5.0	0.35	ug/kg
cis-1,2-Dichloroethene	0.5	0.35	ug/kg
trans-1,2-Dichloroethene	5.0	0.55	ug/kg
1,2-Dichloropropane	5.0	0.35	ug/kg
cis-1,3-Dichloropropene	5.0	0.35	ug/kg
trans-1,3-Dichloropropene	5.0	0.35	ug/kg
1,4-Dioxane	300	29	ug/kg
Ethylbenzene	5.0	0.53	ug/kg
Ethyl methacrylate	5	0.45	ug/kg
2-Hexanone	20.0	0.84	ug/kg
Iodomethane	5	0.44	ug/kg
Isobutanol	200	16	ug/kg
Methacrylonitrile	5	0.76	ug/kg
Methylene chloride	5.0	1.3	ug/kg
Methyl methacrylate	5	0.54	ug/kg
4-Methyl-2-pentanone	20.0	0.54	ug/kg
Propionitrile	20.0	1.8	ug/kg
Styrene	5.0	0.2	ug/kg
1,1,2,2-Tetrachloroethane	5.0	0.46	ug/kg
1,1,1,2-Tetrachloroethane	5	0.42	ug/kg
Tetrachloroethene	5.0	0.83	ug/kg
Toluene	5.0	0.29	ug/kg
1,1,1-Trichloroethane	5.0	0.76	ug/kg
1,1,2-Trichloroethane	5.0	0.41	ug/kg
Trichloroethene	5.0	0.41	ug/kg
Trichlorofluoromethane	5.0	0.41	ug/kg
1,2,3-Trichloropropane	5	0.82	ug/kg
Vinyl acetate	10	0.28	ug/kg
Vinyl chloride	5.0	0.44	ug/kg
Xylenes (total)	10.0	0.76	ug/kg

Semi-Volatile Organic Compounds-SW846 8270C Water			
Compound	**Reporting Limit**	**Method Detection Limit**	**Units**
Acenaphthene	10	0.028	ug/L
Acenaphthylene	10	0.03	ug/L
Acetophenone	10	0.19	ug/L
2-Acetylaminofluorene	100	0.74	ug/L
4-Aminobiphenyl	50	0.92	ug/L
Aniline	10	0.14	ug/L

TABLE 4: Target Quantitation Limits

Semi-Volatile Organic Compounds-SW846 8270C Water			
Compound	**Reporting Limit**	**Method Detection Limit**	**Units**
Anthracene	10	0.03	ug/L
Aramite	10	0.45	ug/L
Benzo(a)anthracene	10	0.028	ug/L
Benzo(b)fluoranthene	10	0.043	ug/L
Benzo(k)fluoranthene	10	0.071	ug/L
Benzo(g,h,i) perylene	10	0.044	ug/L
Benzo(a)pyrene	10	0.022	ug/L
Benzyl alcohol	10	1.1	ug/L
bis(2-Chloroethoxy)methane	10	0.24	ug/L
bis(2-Chloroethyl) ether	10	0.19	ug/L
bis(2-Chloroisopropyl) ether	10	0.21	ug/L
bis(2-Ethylhexyl) phthalate	10	0.36	ug/L
4-Bromophenyl phenyl ether	10	0.29	ug/L
Butyl benzyl phthalate	10	0.14	ug/L
4-Chloroaniline	10	0.31	ug/L
Chlorobenzilate	10	0.6	ug/L
2-Chloronaphthalene	10	0.29	ug/L
4-Chlorophenyl phenyl ether	10	0.21	ug/L
Chrysene	10	0.035	ug/L
Diallate	20	0.59	ug/L
Dibenz(a,h)anthracene	10	0.054	ug/L
Dibenzofuran	10	0.025	ug/L
Di-n-butyl phthalate	10	0.13	ug/L
1,2-Dichlorobenzene	10	0.16	ug/L
1,3-Dichlorobenzene	10	0.11	ug/L
1,4-Dichlorobenzene	10	0.13	ug/L
3,3'-Dichlorobenzidine	50	0.19	ug/L
Diethyl phthalate	10	0.12	ug/L
Thionazin	50	0.57	ug/L
Dimethoate	20	0.28	ug/L
p-(Dimethylamino) azobenzene	20	0.66	ug/L
7,12-Dimethlybenz(a)anthracene	20	0.68	ug/L
3,3-Dimethylbenzidine	50	1.2	ug/L
alpha, aplha-dimethylphenethylamine	50	0.45	ug/L
Dimethyl phthalate	10	0.27	ug/L
1,3-Dinitrobenzene	10	0.11	ug/L
2,4-Dinitrotoluene	10	0.16	ug/L
2,6-Dinitrotoluene	10	0.17	ug/L
Di-n-octylphthalate	10	0.16	ug/L
Dinoseb	20	0.44	ug/L
Diphenylamine	10	0.18	ug/L
Disulfoton	50	0.59	ug/L
Ethyl methanesulfonate	10	0.57	ug/L
Famphur	10	0.86	ug/L
Fluoranthene	10	0.024	ug/L
Fluorene	10	0.035	ug/L

TABLE 4: Target Quantitation Limits

Semi-Volatile Organic Compounds-SW846 8270C Water			
Compound	**Reporting Limit**	**Method Detection Limit**	**Units**
Hexachlorobenzene	10	0.075	ug/L
Hexachlorobutadiene	10	0.11	ug/L
Hexachlorocyclopentadiene	50	1.5	ug/L
Hexachloroethane	10	0.21	ug/L
Hexachloropropene	100	0.47	ug/L
Indeno(1,2,3-cd)pyrene	10	0.081	ug/L
Isophorone	10	0.16	ug/L
Isosafrole	20	0.6	ug/L
Methapyrilene	50	0.81	ug/L
3-Methylcholanthrene	20	0.6	ug/L
Methyl methanesulfonate	10	0.4	ug/L
2-Methylnaphthalene	10	0.028	ug/L
Methyl parathion	10	0.72	ug/L
Naphthalene	10	0.031	ug/L
1,4-Naphthoquinone	50	24	ug/L
1-Naphthylamine	10	0.62	ug/L
2-Naphthylamine	10	0.69	ug/L
2-Nitroaniline	50	0.18	ug/L
3-Nitroaniline	50	0.094	ug/L
4-Nitroaniline	50	0.11	ug/L
Nitrobenzene	10	0.21	ug/L
4-Nitroquinoline-1-oxide	100	0.21	ug/L
N-Nitrosodimethylamine	10	0.23	ug/L
N-Nitrosodiethylamine	10	0.6	ug/L
N-Nitrosodiphenylamine	10	0.18	ug/L
N-Nitrosodi-n-propylamine	10	0.21	ug/L
N-Nitrosodi-n-butylamine	10	0.54	ug/L
N-Nitrosomethylethylamine	10	0.65	ug/L
N-Nitrosomorpholine	10	0.63	ug/L
N-Nitrosopiperidine	10	0.53	ug/L
N-Nitrosopyrrolidine	10	0.49	ug/L
5-Nitro-o-toluidine	20	0.72	ug/L
Parathion	10	0.72	ug/L
Pentachlorobenzene	10	0.55	ug/L
Pentachloroethane	50	8.8	ug/L
Pentachloronitrobenzene	50	0.68	ug/L
Phenacetin	20	0.69	ug/L
Phenanthrene	10	0.044	ug/L
p-Phenylenediamine	100	4	ug/L
Phorate	50	0.7	ug/L
2-Picoline	20	0.62	ug/L
Pronamide	20	0.52	ug/L
Pyrene	10	0.051	ug/L
Pyridine	20	0.13	ug/L
Safrole	20	0.59	ug/L
Tetraethyldithiopyro Phosphate	50	0.57	ug/L

TABLE 4: Target Quantitation Limits

Semi-Volatile Organic Compounds-SW846 8270C Water			
Compound	**Reporting Limit**	**Method Detection Limit**	**Units**
1,2,4,5-Tetrachlorobenzene	10	0.58	ug/L
o-Toluidine	20	0.58	ug/L
1,2,4-Trichlorobenzene	10	0.12	ug/L
O,O,O-Triethyl Phosphorothioate	50	0.66	ug/L
1,3,5-Trinitrobenzene	50	0.23	ug/L
O,O-Dethyl-O-(2-pyrazinyl) phosphorothioate	50.0	0.57	ug/L
Carabozole	10	0.17	ug/L
4-chloro-3-methylphenol	10	0.18	ug/L
2-Chlorophenol	10	0.14	ug/L
2,4-Dichlorophenol	10	0.24	ug/L
2,6-Dichlorophenol	10	0.97	ug/L
2,4-dimethylphenol	10	0.23	ug/L
4,6-Dinitro-2-methylphenol	50	1.8	ug/L
2,4-Dinitrolphenol	50	1.3	ug/L
2-Methylphenol	10	0.15	ug/L
3-Methylphenol	10	0.74	ug/L
4-Methylphenol	10	0.2	ug/L
2-Nitrophenol	10	0.14	ug/L
4-Nitrophenol	50	1	ug/L
Pentachlorophenol	10	2	ug/L
Phenol	10	0.14	ug/L
2,3,4,6-Tetrachlorophenol	50	0.99	ug/L
2,4,5-Trichlorophenol	10	0.13	ug/L
2,4,6-Trichlorophenol	10	0.16	ug/L

Semivolatile Organic Compounds-SW846 8270C Solid			
Compound	**Reporting Limit**	**Method Detection Limit**	**Units**
a,a-Dimethylphenethylamine	1600	59	ug/kg
Acenaphthene	330	0.92	ug/kg
Acenaphthylene	330	1.4	ug/kg
Acetophenone	330	5.5	ug/kg
2-Acetylaminofluorene	3300	26	ug/kg
4-Aminobiphenyl	1600	20	ug/kg
Aniline	330	34	ug/kg
Anthracene	330	2.3	ug/kg
Aramite	660	27	ug/kg
Benzo(a)anthracene	330	1.4	ug/kg
Benzo(b)fluoranthene	330	2.3	ug/kg
Benzo(k)fluoranthene	330	2.3	ug/kg
Benzo(ghi)perylene	330	1.8	ug/kg
Benzo(a)pyrene	330	2.3	ug/kg
Benzyl alcohol	330	140	ug/kg
bis(2-Chloroethoxy)methane	330	16	ug/kg
bis(2-Chloroethyl) ether	330	4.1	ug/kg
bis(2-Chloro-1-methylethyl) ether	330	5.2	ug/kg

TABLE 4: Target Quantitation Limits

Semivolatile Organic Compounds-SW846 8270C Solid			
Compound	**Reporting Limit**	**Method Detection Limit**	**Units**
bis(2-Ethylhexyl) phthalate	330	16	ug/kg
4-Bromophenyl phenyl ether	330	4.7	ug/kg
Butyl benzyl phthalate	330	3.7	ug/kg
4-Chloroaniline	330	5.2	ug/kg
Chlorobenzilate	330	25	ug/kg
4-Chloro-3-methylphenol	330	51	ug/kg
2-Chloronaphthalene	330	6.3	ug/kg
2-Chlorophenol	330	3.6	ug/kg
4-Chlorophenyl phenyl ether	330	3.6	ug/kg
Chrysene	330	0.99	ug/kg
Diallate	660	30	ug/kg
Dibenz(a,h)anthracene	330	1.5	ug/kg
Dibenzofuran	330	0.83	ug/kg
Di-n-butyl phthalate	330	5	ug/kg
1,2-Dichlorobenzene	330	4.1	ug/kg
1,3-Dichlorobenzene	330	4.5	ug/kg
1,4-Dichlorobenzene	330	3.9	ug/kg
3,3'-Dichlorobenzidine	1600	4.9	ug/kg
2,4-Dichlorophenol	330	5.3	ug/kg
2,6-Dichlorophenol	330	30	ug/kg
Diethyl phthalate	330	6.2	ug/kg
Dimethoate	660	25	ug/kg
p-Dimethylaminoazobenzene	660	21	ug/kg
7,12-Dimethylbenz(a)anthracene	660	27	ug/kg
3,3'-Dimethylbenzidine	1600	76	ug/kg
2,4-Dimethylphenol	330	6.8	ug/kg
Dimethyl phthalate	330	6.4	ug/kg
1,3-Dinitrobenzene	330	22	ug/kg
4,6-Dinitro-2-methylphenol	1600	47	ug/kg
2,4-Dinitrophenol	1600	41	ug/kg
2,4-Dinitrotoluene	330	5.7	ug/kg
2,6-Dinitrotoluene	330	5.8	ug/kg
2-sec-Butyl-4,6-dinitrophenol	660	9	ug/kg
Di-n-octyl phthalate	330	11	ug/kg
Diphenylamine	330	4.1	ug/kg
Disulfoton	1600	23	ug/kg
Ethyl methanesulfonate	330	30	ug/kg
Famphur	3300	34	ug/kg
Fluoranthene	330	0.93	ug/kg
Fluorene	330	1.3	ug/kg
Hexachlorobenzene	330	1.4	ug/kg
Hexachlorobutadiene	330	2.5	ug/kg
Hexachlorocyclopentadiene	1600	2.9	ug/kg
Hexachloroethane	330	4.9	ug/kg
Hexachloropropene	3300	21	ug/kg
Indeno(1,2,3-cd)pyrene	330	2	ug/kg

TABLE 4: Target Quantitation Limits

Semivolatile Organic Compounds-SW846 8270C Solid			
Compound	**Reporting Limit**	**Method Detection Limit**	**Units**
Isophorone	330	3.5	ug/kg
Isosafrole	660	27	ug/kg
Methapyrilene	1600	11	ug/kg
3-Methylcholanthrene	660	21	ug/kg
Methyl methanesulfonate	330	19	ug/kg
2-Methylnaphthalene	330	0.99	ug/kg
2-Methylphenol	330	6.7	ug/kg
3-Methylphenol	330	23	ug/kg
4-Methylphenol	330	5.8	ug/kg
Naphthalene	330	0.89	ug/kg
1,4-Naphthoquinone	1600	11	ug/kg
1-Naphthylamine	330	12	ug/kg
2-Naphthylamine	330	15	ug/kg
2-Nitroaniline	1600	5.1	ug/kg
3-Nitroaniline	1600	3.2	ug/kg
4-Nitroaniline	1600	3.6	ug/kg
Nitrobenzene	330	6.4	ug/kg
2-Nitrophenol	330	3.4	ug/kg
4-Nitrophenol	1600	81	ug/kg
4-Nitroquinoline-1-oxide	3300	6.6	ug/kg
N-Nitrosodi-n-butylamine	330	28	ug/kg
N-Nitrosodiethylamine	330	27	ug/kg
N-Nitrosodimethylamine	330	5.4	ug/kg
N-Nitrosodiphenylamine	330	4.1	ug/kg
N-Nitrosodi-n-propylamine	330	7.6	ug/kg
N-Nitrosomethylethylamine	330	22	ug/kg
N-Nitrosomorpholine	330	27	ug/kg
N-Nitrosopiperidine	330	23	ug/kg
N-Nitrosopyrrolidine	330	25	ug/kg
5-Nitro-o-toluidine	330	17	ug/kg
Pentachlorobenzene	330	29	ug/kg
Pentachloroethane	1600	31	ug/kg
Pentachloronitrobenzene	1600	30	ug/kg
Pentachlorophenol	330	45	ug/kg
Phenacetin	660	27	ug/kg
Phenanthrene	330	1.1	ug/kg
Phenol	330	5.7	ug/kg
p-Phenylene diamine	3300	57	ug/kg
Phorate	1600	32	ug/kg
2-Picoline	660	31	ug/kg
Pronamide	660	25	ug/kg
Pyrene	330	1	ug/kg
Pyridine	660	6	ug/kg
Safrole	660	32	ug/kg
1,2,4,5-Tetrachlorobenzene	330	24	ug/kg
2,3,4,6-Tetrachlorophenol	1600	21	ug/kg

TABLE 4: Target Quantitation Limits

Semivolatile Organic Compounds-SW846 8270C Solid			
Compound	**Reporting Limit**	**Method Detection Limit**	**Units**
Tetraethyldithiopyrophosphate	1600	27	ug/kg
Thionazin	1600	26	ug/kg
o-Toluidine	660	33	ug/kg
1,2,4-Trichlorobenzene	330	5.1	ug/kg
2,4,5-Trichlorophenol	330	4.9	ug/kg
2,4,6-Trichlorophenol	330	6.8	ug/kg
O,O,O-Triethyl phosphorothioate	1600	26	ug/kg
1,3,5-Trinitrobenzene	1600	12	ug/kg

Metals-SW846 6010B Water			
Compound	**Reporting Limit**	**Method Detection Limit**	**Units**
Arsenic	0.01	0.0026	mg/L
Chromium	0.005	0.0019	mg/L
Nickel	0.04	0.0025	mg/L

Metals-SW846 6010B Solid			
Compound	**Reporting Limit**	**Method Detection Limit**	**Units**
Arsenic	1	0.4	mg/kg
Chromium	0.5	0.12	mg/kg
Nickel	4	0.17	mg/kg

TOC	10	0.81	mg/kg

EMD Chemicals Inc.
Norwood, Ohio
Project No. 0100.58.19

The Payne Firm, Inc.
Environmental Consultants

TABLE 5: MS/MSD and Laboratory Control Standard Recovery and RPD Control Limits

Volatile Organic Compounds-SW846 8260B Water						
Compound	Laboratory Control Standard			MS/MSD		
	LCL	UCL	RPD	LCL	UCL	RPD
Acetone	22	200	95	45	128	30
Benzene	80	116	20	78	118	20
Bromodichloromethane	87	130	30	80	146	30
Bromoform	76	150	30	58	176	30
Bromomethane	64	129	30	55	145	30
2-Butanone	28	237	65	71	123	30
Carbon disulfide	73	139	30	69	138	41
Carbon tetrachloride	75	149	30	63	176	30
Chlorobenzene	76	117	20	76	117	20
Dibromochloromethane	81	138	30	71	158	30
Chloroethane	66	126	30	59	142	30
Chloroform	84	128	30	83	141	30
Chloromethane	48	123	30	40	137	39
Cyclohexane	0	0	0	0	0	0
1,2-Dibromo-3-chloropropane	0	0	0	0	0	0
1,2-Dibromoethane	0	0	0	0	0	0
1,2-Dichlorobenzene	0	0	0	0	0	0
1,3-Dichlorobenzene	0	0	0	0	0	0
1,4-Dichlorobenzene	0	0	0	0	0	0
Dichlorodifluoromethane	0	0	0	0	0	0
1,1-Dichloroethane	86	123	30	88	127	30
1,2-Dichloroethane	79	136	30	71	160	30
cis-1,2-Dichloroethene	85	113	30	87	114	30
trans-1,2-Dichloroethene	79	120	30	85	116	30
1,1-Dichloroethene	63	130	20	62	130	20
1,2-Dichloropropane	82	115	30	87	114	30
cis-1,3-Dichloropropene	84	130	30	82	130	30
trans-1,3-Dichloropropene	84	130	30	73	147	30
Ethylbenzene	86	116	30	86	132	30
2-Hexanone	35	200	52	81	128	30
Isopropylbenzene	0	0	0	0	0	0
Methyl acetate	0	0	0	0	0	0
Methylcyclohexane	0	0	0	0	0	0

LCL = Lower Control Limit
UCL = Upper Control Limit
RPD = Relative Percent Difference

MS = Matrix Spike
MSD = Matrix Spike Duplicate

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TABLE 5: MS/MSD and Laboratory Control Standard Recovery and RPD Control Limits

Volatile Organic Compounds-SW846 8260B Water						
Compound	Laboratory Control Standard			MS/MSD		
	LCL	UCL	RPD	LCL	UCL	RPD
Methylene chloride	78	118	30	82	115	30
4-Methyl-2-pentanone	78	141	32	82	135	30
Methyl tert-butyl ether	0	0	0	0	0	0
Styrene	85	117	30	83	120	30
1,1,2,2-Tetrachloroethane	85	118	30	88	116	30
Tetrachloroethene	88	113	30	85	121	30
Toluene	74	119	20	70	119	20
1,2,4-Trichlorobenzene	0	0	0	0	0	0
1,1,1-Trichloroethane	78	140	30	71	162	30
1,1,2-Trichloroethane	83	122	30	86	129	30
Trichloroethene	75	122	20	62	130	20
Trichlorofluoromethane	0	0	0	0	0	0
1,1,2-Trichloro-1,2,2-trifluoroethane	0	0	0	0	0	0
Vinyl chloride	61	120	30	88	126	30
Xylenes (total)	87	116	30	89	121	30

Volatile Organic Compounds-SW846 8260B Solid						
Compound	Laboratory Control Standard			MS/MSD		
	LCL	UCL	RPD	LCL	UCL	RPD
Acetone	58	130	30	10	200	66
Benzene	75	129	20	55	138	20
Bromodichloromethane	72	125	30	47	131	51
Bromoform	43	149	30	26	141	64
Bromomethane	24	152	30	15	152	72
2-Butanone	27	200	46	21	195	60
Carbon disulfide	50	137	30	27	149	73
Carbon tetrachloride	57	137	30	32	143	68
Chlorobenzene	75	127	22	49	139	22
Dibromochloromethane	49	135	30	44	135	61
Chloroethane	31	144	30	32	140	66
Chloroform	73	115	30	59	128	46
Chloromethane	15	136	30	28	130	81
Cyclohexane	0	0	0	0	0	0
1,2-Dibromo-3-chloropropane	0	0	0	0	0	0
1,2-Dibromoethane	0	0	0	0	0	0
1,2-Dichlorobenzene	0	0	0	0	0	0
1,3-Dichlorobenzene	0	0	0	0	0	0
1,4-Dichlorobenzene	0	0	0	0	0	0
Dichlorodifluoromethane	0	0	0	0	0	0
1,1-Dichloroethane	77	119	30	56	130	54
1,2-Dichloroethane	78	121	30	56	126	38
cis-1,2-Dichloroethene	77	114	30	48	127	52
trans-1,2-Dichloroethene	68	117	30	47	127	58
1,1-Dichloroethene	55	142	27	43	147	27

LCL = Lower Control Limit
UCL = Upper Control Limit
RPD = Relative Percent Difference

MS = Matrix Spike
MSD = Matrix Spike Duplicate

TABLE 5: MS/MSD and Laboratory Control Standard Recovery and RPD Control Limits

Volatile Organic Compounds-SW846 8260B Solid						
Compound	Laboratory Control Standard			MS/MSD		
	LCL	UCL	RPD	LCL	UCL	RPD
1,2-Dichloropropane	78	116	30	54	125	43
cis-1,3-Dichloropropene	71	125	30	30	138	49
trans-1,3-Dichloropropene	67	125	30	34	134	57
Ethylbenzene	79	114	30	36	133	72
2-Hexanone	29	200	41	20	190	70
Isopropylbenzene	0	0	0	0	0	0
Methyl acetate	0	0	0	0	0	0
Methylcyclohexane	0	0	0	0	0	0
Methylene chloride	58	130	30	45	129	49
4-Methyl-2-pentanone	68	142	60	42	143	60
Methyl tert-butyl ether	0	0	0	0	0	0
Styrene	80	114	30	23	136	65
1,1,2,2-Tetrachloroethane	70	133	30	33	162	90
Tetrachloroethene	72	120	30	31	137	81
Toluene	71	130	24	46	147	24
1,2,4-Trichlorobenzene	0	0	0	0	0	0
1,1,1-Trichloroethane	67	123	30	48	132	57
1,1,2-Trichloroethane	82	116	30	58	128	52
Trichloroethene	70	131	23	46	143	23
Trichlorofluoromethane	0	0	0	0	0	0
1,1,2-Trichloro-1,2,2-trifluoroethane	0	0	0	0	0	0
Vinyl chloride	24	152	30	30	136	80
Xylenes (total)	80	114	30	33	135	78

Semi-Volatile Organic Compounds-SW846 8270C Water						
Compound	Laboratory Control Standard			MS/MSD		
	LCL	UCL	RPD	LCL	UCL	RPD
Acenaphthene	39	118	35	26	118	35
Acenaphthylene	51	110	30	49	111	51
Acetophenone	0	0	0	0	0	0
Anthracene	54	116	33	49	118	51
Atrazine	0	0	0	0	0	0
Benzaldehyde	0	0	0	0	0	0
Benzo(a)anthracene	49	112	34	48	115	51
Benzo(b)fluoranthene	51	115	38	44	123	54
Benzo(k)fluoranthene	52	116	34	46	123	53
Benzo(ghi)perylene	47	118	35	44	122	55
Benzo(a)pyrene	50	116	34	44	122	51
1,1'-Biphenyl	0	0	0	0	0	0
bis(2-Chloroethoxy)methane	54	112	32	57	114	49
bis(2-Chloroethyl) ether	59	114	30	57	120	51
bis(2-Ethylhexyl) phthalate	49	124	39	43	128	84
4-Bromophenyl phenyl ether	56	113	33	51	119	51
Butyl benzyl phthalate	46	121	40	41	127	84
Caprolactam	0	0	0	0	0	0
Carbazole	50	118	34	48	119	53
4-Chloroaniline	21	110	41	10	110	99
4-Chloro-3-methylphenol	29	124	55	21	124	55
2-Chloronaphthalene	50	116	30	51	119	51

LCL = Lower Control Limit
UCL = Upper Control Limit
RPD = Relative Percent Difference

MS = Matrix Spike
MSD = Matrix Spike Duplicate

TABLE 5: MS/MSD and Laboratory Control Standard Recovery and RPD Control Limits

Semi-Volatile Organic Compounds-SW846 8270C Water						
Compound	Laboratory Control Standard			MS/MSD		
	LCL	UCL	RPD	LCL	UCL	RPD
2-Chlorophenol	19	124	43	19	124	43
4-Chlorophenyl phenyl ether	56	112	31	51	118	51
Chrysene	49	118	34	49	118	52
Dibenz(a,h)anthracene	48	124	36	45	127	57
Dibenzofuran	53	112	30	51	117	51
Di-n-butyl phthalate	50	116	36	41	121	53
3,3'-Dichlorobenzidine	10	110	75	10	110	99
2,4-Dichlorophenol	51	118	43	52	121	88
Diethyl phthalate	14	135	47	10	148	81
2,4-Dimethylphenol	10	123	44	10	125	62
Dimethyl phthalate	10	150	51	10	159	99
4,6-Dinitro-2-methylphenol	22	143	79	20	158	99
2,4-Dinitrophenol	10	146	99	10	168	99
2,4-Dinitrotoluene	47	131	32	31	131	32
2,6-Dinitrotoluene	59	125	32	58	127	82
Di-n-octyl phthalate	49	130	42	39	144	89
Fluoranthene	54	118	33	49	122	53
Fluorene	53	114	31	51	119	51
Hexachlorobenzene	54	114	34	48	123	51
Hexachlorobutadiene	36	113	47	35	118	56
Hexachlorocyclopentadiene	10	114	51	10	113	97
Hexachloroethane	29	115	49	31	118	92
Indeno(1,2,3-cd)pyrene	45	120	43	39	126	59
Isophorone	54	111	33	56	112	50
2-Methylnaphthalene	52	110	32	45	119	51
2-Methylphenol	33	115	31	29	115	31
4-Methylphenol	49	110	35	29	122	55
Naphthalene	49	112	35	50	176	52
2-Nitroaniline	53	122	34	48	125	83
3-Nitroaniline	10	140	39	10	140	99
4-Nitroaniline	32	116	49	20	122	99
Nitrobenzene	56	119	32	56	125	81
2-Nitrophenol	46	129	49	51	131	77
4-Nitrophenol	19	144	34	10	145	34
N-Nitrosodiphenylamine	49	117	36	49	117	51
N-Nitrosodi-n-propylamine	30	115	36	18	115	36
2,2'-oxybis(1-Chloropropane)	0	0	0	0	0	0
Pentachlorophenol	10	140	56	10	140	56
Phenanthrene	53	112	32	52	117	51
Phenol	10	131	43	10	131	43
Pyrene	46	130	31	27	138	31
2,4,5-Trichlorophenol	46	122	48	45	125	74
2,4,6-Trichlorophenol	46	118	48	46	122	98

LCL = Lower Control Limit
UCL = Upper Control Limit
RPD = Relative Percent Difference

MS = Matrix Spike
MSD = Matrix Spike Duplicate

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TABLE 5: MS/MSD and Laboratory Control Standard Recovery and RPD Control Limits

Semi-Volatile Organic Compounds-SW846 8270C Solid						
Compound	Laboratory Control Standard			MS/MSD		
	LCL	UCL	RPD	LCL	UCL	RPD
Acenaphthene	44	108	44	13	133	44
Acenaphthylene	55	110	30	43	120	75
Acetophenone	0	0	0	0	0	0
Anthracene	57	116	30	34	137	83
Atrazine	0	0	0	0	0	0
Benzaldehyde	0	0	0	0	0	0
Benzo(a)anthracene	56	110	30	30	136	63
Benzo(b)fluoranthene	54	116	30	31	139	67
Benzo(k)fluoranthene	54	110	36	30	133	84
Benzo(ghi)perylene	48	124	31	23	142	89
Benzo(a)pyrene	56	115	30	28	142	86
1,1'-Biphenyl	0	0	0	0	0	0
bis(2-Chloroethoxy)methane	59	110	30	46	116	97
bis(2-Chloroethyl) ether	62	111	30	49	123	93
bis(2-Ethylhexyl) phthalate	53	115	30	36	131	54
4-Bromophenyl phenyl ether	58	110	30	47	121	95
Butyl benzyl phthalate	54	113	30	34	136	94
Caprolactam	0	0	0	0	0	0
Carbazole	56	117	31	40	130	85
4-Chloroaniline	28	110	33	10	110	99
4-Chloro-3-methylphenol	43	110	55	17	128	55
2-Chloronaphthalene	52	116	30	43	125	75
2-Chlorophenol	43	110	54	17	116	54
4-Chlorophenyl phenyl ether	59	110	30	47	119	74
Chrysene	56	110	30	28	139	63
Dibenz(a,h)anthracene	50	129	33	31	142	99
Dibenzofuran	57	110	30	35	132	58
Di-n-butyl phthalate	58	114	30	44	128	74
3,3'-Dichlorobenzidine	22	110	33	10	110	99
2,4-Dichlorophenol	60	111	30	45	122	85
Diethyl phthalate	57	112	30	45	122	76
2,4-Dimethylphenol	41	110	35	31	119	99
Dimethyl phthalate	60	111	30	48	124	75
4,6-Dinitro-2-methylphenol	37	126	37	10	142	99
2,4-Dinitrophenol	15	131	53	10	149	99
2,4-Dinitrotoluene	48	111	45	10	171	45
2,6-Dinitrotoluene	61	121	30	45	124	99
Di-n-octyl phthalate	47	129	33	34	143	99
Fluoranthene	57	118	30	25	150	92
Fluorene	57	110	30	35	133	80
Hexachlorobenzene	57	111	30	45	123	74
Hexachlorobutadiene	56	113	30	43	126	86
Hexachlorocyclopentadiene	10	113	57	10	110	99
Hexachloroethane	61	110	30	36	134	97

LCL = Lower Control Limit
UCL = Upper Control Limit
RPD = Relative Percent Difference

MS = Matrix Spike
MSD = Matrix Spike Duplicate

TABLE 5: MS/MSD and Laboratory Control Standard Recovery and RPD Control Limits

Semi-Volatile Organic Compounds-SW846 8270C Solid						
Compound	Laboratory Control Standard			MS/MSD		
	LCL	UCL	RPD	LCL	UCL	RPD
Indeno(1,2,3-cd)pyrene	44	128	54	20	147	73
Isophorone	58	110	30	45	116	95
2-Methylnaphthalene	58	110	30	30	137	79
2-Methylphenol	41	102	39	33	113	39
4-Methylphenol	56	110	30	36	123	86
Naphthalene	59	110	30	31	138	65
2-Nitroaniline	58	113	30	42	126	99
3-Nitroaniline	42	110	37	17	113	99
4-Nitroaniline	42	116	40	14	125	99
Nitrobenzene	62	110	30	49	120	99
2-Nitrophenol	55	118	30	44	125	99
4-Nitrophenol	22	128	64	10	148	64
N-Nitrosodiphenylamine	58	113	30	37	135	94
N-Nitrosodi-n-propylamine	38	110	50	12	128	50
2,2'-oxybis(1-Chloropropane)	0	0	0	0	0	0
Pentachlorophenol	10	123	87	10	144	87
Phenanthrene	56	110	30	24	145	81
Phenol	35	110	50	10	148	50
Pyrene	42	122	66	10	218	66
2,4,5-Trichlorophenol	52	115	37	39	123	99
2,4,6-Trichlorophenol	51	112	30	43	123	99

Metals-SW846 6010B Water						
Compound	Laboratory Control Standard			MS/MSD		
	LCL	UCL	RPD	LCL	UCL	RPD
Chromium	80	120	20	75	125	20
Arsenic	80	120	20	75	125	20
Nickel	80	120	20	75	125	20

Metals-SW846 6010B Solid						
Compound	Laboratory Control Standard			MS/MSD		
	LCL	UCL	RPD	LCL	UCL	RPD
Chromium	80	120	20	75	125	20
Arsenic	80	120	20	75	125	20
Nickel	80	120	20	75	125	20
TOC						

LCL = Lower Control Limit
UCL = Upper Control Limit
RPD = Relative Percent Difference

MS = Matrix Spike
MSD = Matrix Spike Duplicate

EMD Chemicals Inc.
Norwood, Ohio
Project No. 0100.58.19

The Payne Firm, Inc.
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TABLE 6: Surrogate Compound Recovery Control Limits

SW846 8260B Water						
Compound	Laboratory Control Standard			MS/MSD		
	LCL	UCL	RPD	LCL	UCL	RPD
4-Bromofluorobenzene	74	116	0	74	116	0
1,2-Dichloroethane-d4	61	128	0	61	128	0
Toluene-d8	76	110	0	76	110	0
Dibromofluoromethane	73	122	0	73	122	0

SW846 8260B Soil						
Compound	Laboratory Control Standard			MS/MSD		
	LCL	UCL	RPD	LCL	UCL	RPD
4-Bromofluorobenzene	47	158	0	47	158	0
1,2-Dichloroethane-d4	61	130	0	61	130	0
Toluene-d8	60	143	0	60	143	0
Dibromofluoromethane	59	138	0	59	138	0

LCL = Lower Control Limit
UCL = Upper Control Limit
RPD = Relative Percent Difference

MS = Matrix Spike
MSD = Matrix Spike Duplicate

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TABLE 6: Surrogate Compound Recovery Control Limits

Semi-Volatile Organic Compounds-SW846 8270C Water						
Compound	Laboratory Control Standard			MS/MSD		
	LCL	UCL	RPD	LCL	UCL	RPD
2-Fluorobiphenyl	30	110	0	30	110	0
2-Fluorophenol	13	110	0	13	110	0
2,4,6-Tribromophenol	21	122	0	21	122	0
Nitrobenzene-d5	32	112	0	32	112	0
Phenol-d5	10	113	0	10	113	0
Terphenyl-d14	10	144	0	10	144	0

Semi-Volatile Organic Compounds-SW846 8270C Solid						
Compound	Laboratory Control Standard			MS/MSD		
	LCL	UCL	RPD	LCL	UCL	RPD
2-Fluorobiphenyl	43	110	0	43	110	0
2-Fluorophenol	11	116	0	11	116	0
2,4,6-Tribromophenol	35	116	0	35	116	0
Nitrobenzene-d5	42	110	0	42	110	0
Phenol-d5	25	115	0	25	115	0
Terphenyl-d14	37	137	0	37	137	0

LCL = Lower Control Limit
UCL = Upper Control Limit
RPD = Relative Percent Difference

MS = Matrix Spike
MSD = Matrix Spike Duplicate

EMD Chemicals Inc.
Norwood, Ohio
Project No. 0100.58.19

The Payne Firm, Inc.
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TABLE 7: Sample Containers, Preservatives, and Holding Times

Analytical Parameters	Matrix	Minimum Sample Size[1]	RCRA (SW846)[2,3]		
			Analytical Method	Sample Preparation Method	Requirements
VOCs	Water	40 mL	8260B	SW-846 5030B	40 mL glass, VOA vial (in triplicate) with Teflon®-lined septa without headspace, Cool, 4° C, Add sodium thiosulfate if residual chlorine, 1:1 HCl to pH £ 2, 14 days with pH £ 2
	Solid[4]	5 g or 25 g	8260B	SW-846 5035	4 or 8 oz glass with Teflon®-lined lid, Cool 4° C, 14 days. Field preserved with sodium bisulfate solution for low level analysis, or with methanol for medium level analysis. Soil sample can also be taken by using three EnCore™ samplers and preserved in the laboratory within 48 hours of sampling. Maximum holding time for Encore Sampler is 48 hours (before the sample is added to methanol or sodium bisulfate). Cool, 4° C[5]
SVOCS	Solid	50 g	SW-846 8270C	SW-846 3550B	4 oz. glass wide mouth with Teflon-lined lid, cool, 4° C, Extraction within 14 days of sample collection, and analysis within 40 days of extraction.
	Water	1000 ml	SW-846 8270C	SW-846 3520C	2X1 liter amber glass with Teflon-lined lid, cool to 4°C, extraction within 7 days of sample collection, and analysis within 40 days of extraction.
Metals[6]	Solid	50 g	SW846-6010B	SW846-3050B	4 oz. glass jar at 4°C, holding time 6 months after sample collection.
	Water	500 ml	SW846-6010B	SW846-3005A	500 mL plastic bottle preserved with HNO3 to pH<2, holding time 6 months after sample collection.
TOC	Solid				

1 = Minimum sample size indicates sample amount needed for a single analysis. Matrix spikes or duplicates will require an additional sample amount of at least this amount for each additional QC sample aliquot required.

2 = Holding times are calculated from the date of collection.

3 = Resource Conservation and Recovery Act, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, Third Edition, September 1986. Contains Final Update I (July 1992), Final Update IIA (August 1993), Final Update II (September 1994), Final Update IIB (January 1995), and Final Update III (December 1996).

4 = Solid matrix type includes soil, sediment, sludge or other solids not classified as waste.

5 = Depending on regulatory programs, EnCore™ samplers may be preserved for up to 14 days from sampling by freezing at -5 to -12° C until analysis. Alternatively the EnCore™ sample may be transferred to a 40-ml VOA vial and preserved by freezing at -5 to -12° C until analysis. Some regulatory agencies may require 4 or 8 oz glass with Teflon®-lined lid, Cool 4° C, 14 days. This technique is not recommended, but will be supported where required. (Preservation and holding times are subject to client specifications.)

6 = Arsenic, chromium, and nickel.

EMD Chemicals Inc.
Norwood, Ohio
Project No. 0100.58.19

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TABLE 8: List of Field Standard Operating Procedures

Field Procedure	The Payne Firm SOP Number[1]
Field Log Books	1-1
Labeling and Custody	1-3
Packaging and Shipping	1-4
Hazard Recognition	1-5
Restoration of Work Site	1-7
Land or Elevation Survey	1-8
Water Level Measurements	2-5
Turbidity Measurements	2-7
Measurement of Specific Conductance and pH	2-9
Measurement of Temperature	2-10
Collection of an Air Sample	2-11
Use of Toxic Vapor Analyzers	2-14
Decontamination of Drilling Equipment	3-1
Observation of Hollow Stem Auger Drilling Activities	3-2
Borehole Logging	3-5
Borehole Abandonment	3-6
Observation of Rotasonic Drilling Activities	3-7
Installation of Monitoring Wells	4-2
Well Abandonment	4-4
Decontamination of Soil Sampling Equipment	5-1
Soil Sampling	5-2
Soil Headspace Organic (HSO) Field Screening	5-3
Decontamination of Water Sampling Equipment	6-1
Well Development	6-2
Well Purging	6-3
Ground Water Sampling	6-4
Field Filtration of Ground Water Samples	6-6
Project Management	8-1
Data Validation	8-2

[1] SOPs are located in Appendix II.

EMD Chemicals Inc.
Norwood, Ohio
Project No. 0100.58.19

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TABLE 9: Laboratory Instrument Maintenance Schedule

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

Daily	Weekly	As Needed	Quarterly	Semi-Annually	Annually
Check for sufficient gas supply. Check for correct column flow and/or inlet pressure.	Check mass calibration (PFTBA or FC-43)	Check level of oil in mechanical pumps and diffusion pump if vacuum is insufficient. Add oil if needed between service contract maintenance.	Check ion source and analyzer (clean, replace parts as needed)	Clean rods	Replace the exhaust filters on the mechanical rough pump every 1-2 years.

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TABLE 9: Laboratory Instrument Maintenance Schedule

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

The Payne Firm, Inc.
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EMD Chemicals Inc.

Norwood, Ohio
Project No. 0100.58.19

TABLE 10: Summary of Analytical Methods

Parameter Group	Water	Solid	Sample Preparation Method	
			Water	Solid
Appendix IX Volatile Organic Compounds	SW-846 8260B	SW-846 8260B	SW-846 5030B	SW-846 5035
Appendix IX Semi-Volatile Organic Compounds (Modified)	SW-846 8270C	SW-846 8270C	SW-846 3520C	SW-846 3550B
Metals	SW-846 6010B	SW-846 6010B	SW-846 3005A	SW-846 3050B
Total Organic Carbon	NA	SW-846 9060	NA	NA
Geotechnical Engineering Properties				
Grain Size	NA	ASTM D422	NA	NA
Unit Weight, Porosity, Void Ratio, Degree of Saturation	NA	ACOE	NA	NA
Moisture Content	NA	ASTM D2216	NA	NA
Specific Gravity	NA	ASTM D854	NA	NA
Atterberg Limits	NA	ASTM D4318	NA	NA
Permeability (Undistributed)	NA	ASTM D5084	NA	NA
Permeability (Distributed)	NA	ASTM D2487	NA	NA
Unified Soil Classification System (USCS)	NA	ASTM D2434	NA	NA
Waste Characterization				
VOC TCLP	NA	SW-846 8260B	NA	SW-846 5035
SVOC TCLP	NA	SW-846 8220C	NA	SW-846 3550
Metals TCLP	NA	SW-846 6010B	NA	SW-846 3050B
Pesticides TCLP	NA	SW-846 8081A	NA	
Herbicides TCLP	NA	SW-846 8151A	NA	
Polychlorinated Biphenyls TCLP	NA	SW-846 8082	NA	
Corrosivity	NA	SW-846 9045C	NA	

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TABLE 10: Summary of Analytical Methods

Parameter Group	Water	Solid	Sample Preparation Method	
			Water	Solid
Ignitability	NA	SW-846 1010	NA	
Reactive Cyanide	NA	SW-846 7.3.3	NA	
Reactive Sulfide	NA	SW-846 7.3.4	NA	
Total % Solids	NA	MCAWW 160.3 MOP	NA	

NA = Not Applicable.
SW-846 = "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods," EPA SW-846, 3rd Edition
ASTM = American Society for Testing Materials
ACOC = "Laboratory Soil Testing," Army Corps of Engineers, EM 1110-2-1906, November 30, 1970.
MCAWW = Method for Chemical Analysis of Water and Waste

THE PAYNE FIRM, INC.
STANDARD OPERATING PROCEDURE

SUBJECT: Use of Field Logbooks

PROCEDURE NO.: SOP 1-1

EFFECTIVE ISSUE DATE:

REVISION NO.: 1

PRIOR EFFECTIVE DATE:

SITE-SPECIFIC AMENDMENTS: None

1.0 PURPOSE

The purpose of this procedure is to detail the minimum requirements for the proper use and maintenance of logbooks during the performance of a field investigation. The Field Logbook is a primary record of information documenting all activities performed during a field project and may be used as legal evidence.

2.0 SCOPE

This procedure provides information for the proper documentation of events, observations and measurements during the course of a field investigation. Information in the Field Logbook should contain sufficient detail to reconstruct past events and data collection activities for the purposes of testimony during legal proceedings. Entries may include information pertaining to personnel, procedures, sampling, measurements, equipment, photographs, health and safety, unusual occurrences and other relevant observations.

3.0 REQUIREMENTS

The logbook is controlled in the field by the Field Operations Leader until being incorporated into the permanent project file. If more than one logbook is required for a site, each logbook must be assigned a sequential number and so indicated on the logbook and in the project file. Each logbook must include a project-information page at the beginning of the book. Information must include Payne Firm and client data. All logbook entries are to be made in black or blue ink unless restricted by weather conditions. Any errors in entry are to be crossed out with a single line and then corrected. Daily entries are to be signed and dated. All logbooks must be secured at the end of each day.

4.0 REFERENCES

United States Environmental Protection Agency, December 1987. *A Compendium of Superfund Field Operations Methods*, EPA/540/P-87/001.

United States Environmental Protection Agency, October 1988. *Guidance for Conducting Remedial Investigations and Feasibility Studies under CERCLA*, Interim Final, EPA/540/G-89/004.

5.0 DEFINITIONS

Logbook - A bound notebook in which significant field activities are described. Entries are made in ink, signed and dated. The logbook becomes part of the permanent project and may be admitted as legal evidence.

6.0 RESPONSIBILITIES

6.1 Project Manager

The Field Logbook is issued by the Project Manager to the Field Operations Leader. The Project Manager shall ensure that Field Logbooks are properly issued and ultimately included in the project file.

6.2 Field Operations Leader

The Field Operations Leader controls Field Logbooks at a site. Logbooks are obtained from the Project Manager and are made available to field personnel as necessary. The Field Operations Leader ensures that a copy of the daily log is placed in the project file. Following the cessation of fieldwork, the Field Logbook is returned to the Project Manager for inclusion in the permanent project files or continued use during subsequent stages of the project.

6.3 Field Geologist/Field Engineer/Field Technician

The Field Geologist, Field Engineer and Field Technician is responsible for obtaining the Field Logbook and documenting significant site activities. A copy of the daily log shall be placed into the project file.

7.0 EQUIPMENT

- Logbook
- Black or blue ink pen, compatible with the logbook paper to make permanent, non-smearing entries

8.0 PROCEDURE

8.1 General

All entries should be made in black or blue ink. No erasures are permitted. If an incorrect entry is made, the data should be crossed out with a single strike mark so as not to be obliterated, then initialed and dated. The logbook must be signed by all individuals recording information in the logbook for that specific day at the end of the last entry for each day.

8.2 Identification

The outside cover of each logbook will contain the Payne Firm project number, the project name and sequential book number if applicable. A project information page will be maintained at the beginning of the logbook. The information page will repeat information on the cover and include the following:

- The Payne Firm's address and phone number;
- Project Manager and Field Operations Leader;
- Client, address, contact and phone number;
- Appropriate subcontractor phone numbers;
- Applicable Agency phone numbers;
- Logbook temporal data; and
- Reward stamp.

8.3 Field Logbook Entries

The Field Logbook is a controlled document which records all major on-site activities during a field investigation. The logbook is kept up-to-date in real time. At a minimum, the following activities or events should be recorded in the logbook pertaining to the project:

- Arrival and departure of visitors;
- Arrival and departure of equipment;
- Sample pick-up (e.g., chain-of-custody form numbers, carrier, time);
- Sampling activities and sample logsheet numbers;
- Start or completion of borehole, trench or monitoring well installation or sampling activities; and
- Health and safety issues.

Daily entries into the logbook may contain a variety of information. At the beginning of each day, the following information must be recorded:

- Date;
- Start time;
- Weather;
- The full names and affiliations of all field personnel present; and
- The full names and affiliations of any visitor present.

During the day, a summary of all site activities and the level of personal protection should be recorded in the logbook. An example of a Field Logbook page is shown in Attachment 9.1. In general, the Field Logbook remains on-site during the project. A Field Logbook is typically used by the Field Geologist or the Field Operations Leader to record specific details of each task.

8.4 Health and Safety Entries

Health and Safety entries are completed in the Field Logbook to document protection levels, health and safety training sessions, and equipment meter readings that substantiate protection levels. The Health and Safety entries may also be used to document unusual occurrences or accidents. A separate Health and Safety Logbook may be required for a project and would be maintained by the Project Health and Safety Officer or his designee.

8.5 Field Equipment Entries

Field equipment entries are used to document the proper use, maintenance, and calibration of field testing equipment. Before using field equipment, field personnel shall inspect and approve the use of the field equipment by initialing the appropriate entry in the logbook. The calibration record shall be maintained for each instrument used on-site. Specific projects may require maintenance of a separate field equipment logbook.

The following items shall be tracked in the logbook:

- Equipment calibration status;
- Equipment decontamination status;
- Equipment nonconformance; and
- Equipment inspection and repair records.

The person using, maintaining or calibrating field equipment shall make an entry in the logbook, documenting the following:

- Names and signatures of persons making entry;
- Date of entry;
- Adjustments made during calibration or maintenance;
- Name of equipment and its identifying number;
- List or reference of procedure(s) used for calibration or maintenance; and
- Standard type, concentration manufacturer, lot number and expiration date of calibration standards.

Entries in the log shall be signed and dated by the person(s) making the entry.

8.6 Decontamination Entries

Decontamination entries are used to document the proper decontamination of equipment used during the field investigation.

Decontamination entries will contain the following:

- Name of person performing decontamination;
- Date of entry;
- Equipment shall be identified as to type and serial number (if applicable);
- Decontamination procedure used;
- Name, manufacturer, lot number and expiration of decontamination solutions used; (if applicable) and
- Record of any organic vapor checks (after decontamination).

Entries in the log shall be signed and dated by the person making the entry.

8.7 Photographic Entries

The record of photographs taken at a site for the purpose of project documentation must be recorded in the Field Logbook. When movies, videos, slides or photographs are taken of a site or any monitoring location, they are to be numbered and numbers recorded in the logbook. The name of the photographer, date, time, site location and weather conditions are to be entered with a description of the photographs as taken. A series or counter entry may be used for rapid-sequence photographs, movies or videos. The photographer is not required to record the aperture settings and shutter speeds for photographs taken within the normal automatic exposure range; however, special lenses, films, filters and other image-enhancement techniques must be noted in the logbook. Such techniques should be avoided if possible, as they can adversely affect the admissibility of photographs as evidence. Chain-of-custody procedures depend on the subject matter, type of film and the processing it requires.

Film used for aerial photography, confidential information or criminal investigations require chain-of-custody procedures. Adequate logbook notations and receipts may be used to account for routine film processing.

After developing the photographic evidence shall be numbered and labeled in conformance with the logbook descriptions. Any negatives shall be retained in the process packaging, which shall be labeled as per the logbook characterization, and placed in the project file.

9.0 ATTACHMENTS

9.1 Typical Field Logbook Entry

TYPICAL FIELD LOGBOOK ENTRY

START TIME: 08:00

DATE: 06/09/90

FIELD LEADER:

PERSONNEL: PFI **DRILLER: EMR/OEPA**

WEATHER: Clear, 68° F, two to five mile per hour (mph) wind from the southeast

ACTIVITIES:

1. Steam jenny set up.

2. Drilling activities at well _____ resumed. Rig geologist was _____. See logbook No. 1, August 19, 1993, for details of drilling activity. Sample No. _____ collected. Drilling activities completed at 11:50 and a four inch stainless steel well installed. See logbook No. 1, August 20, 1993, and well construction details for well _____.

3. Drilling Rig No. 2 steam-cleaned at decontamination pit. Then set up at location of well _____.

4. Well _____ drilled. Rig geologist was _____. See Geologist's Logbook, No. 2, August 20, 1993 for details of drilling activities. Sample Numbers _____, _____ and _____.

5. Well _____ was developed. Seven, 55-gallon drums were filled in the flushing stage. The well was then pumped using the pitcher pump for one hour. At the end of the hour, water pumped from well was "sand-free."

6. Ohio Environmental Protection Agency (OEPA) arrives on-site at 14:25 hours.

7. Large dump truck arrives at 14:45 and is steam-cleaned, backhoe and dump truck set up over test pit _____.

8. Test pit _____ dug with cuttings placed in dump truck. Rig geologist was _____. See Geologist's Logbook No. 1, August 21, 1993, for details of test pit activities. Test pit subsequently filled. No samples taken for chemical analysis. Due to shallow ground water table, filling in of test pit _____ resulted in a very soft and wet area. A mound was developed and the area roped off.

9. Express carrier picked up samples (see Sample Logbook, pages 42 through 45) at 17:50 hrs. Site activities terminated at 18:22 hours. All personnel off-site, gate locked.

Field Operations Leader

THE PAYNE FIRM, INC.
STANDARD OPERATING PROCEDURE

SUBJECT: Labeling and Custody of Samples

PROCEDURE NO.: SOP 1-3

EFFECTIVE ISSUE DATE: February 18, 2000

REVISION NO.: 3

PRIOR EFFECTIVE DATE: July 26, 1999

SITE-SPECIFIC AMENDMENT: None

1.0 PURPOSE

The purpose of this procedure is to describe the steps necessary to properly label and initiate the chain-of-custody for samples to be sent to a laboratory for potential analysis.

2.0 SCOPE

This procedure addresses labeling and chain-of-custody for samples being transferred to a laboratory by Payne Firm personnel. Associated Standard Operating Procedures (SOPs) describe sample collection, packaging and shipping requirements. This SOP may also be used to initiate a chain-of-custody for other purposes, if warranted.

3.0 REQUIREMENTS

Payne Firm personnel must label each sample collected during a project with a unique site-specific designation. Samples that are to be sent to a laboratory must be accompanied by a properly completed chain-of-custody. Documentation must be placed in the project file.

4.0 REFERENCES

American Society for Testing and Materials, 1995. *Standard Guide for Sampling Chain-of-Custody Procedures*, D 4840-95.

Hazardous Waste Consultant, January/February 1999. *Chemical Analysis of Hazardous Wastes and Environmental Media – Practices to Improve Data Quality*, Volume 17, Issue 1, Elsevier Press.

United States Environmental Protection Agency, 1984. *Sampler's Guide to the Contract Laboratory Program*.

United States Environmental Protection Agency, December 1987. *A Compendium of Superfund Field Operations Methods*, EPA/540/P-87/001.

United States Environmental Protection Agency, October 1988. *Guidance for Conducting Remedial Investigations and Feasibility Studies Under CERCLA: Interim Final*, EPA/540/G-89/004.

5.0 DEFINITIONS

Carrier - A person or firm engaged in the transportation of property (e.g., samples).

Chain-of-Custody Record - A printed form that accompanies a sample or group of samples during transfer from one custodian to another. A chain-of-custody is a control document that establishes legal possession.

Custodian - The person responsible for the custody of a sample at a particular time, until custody is formally transferred to another person, who then becomes custodian. Until formally transferring custody by means of chain-of-custody, a sample is in your custody if:

- You collect and possess the sample;
- It is in your care after being in your possession; and
- It has been secured by you after being in your possession.

Sample - Physical evidence collected from a facility or environmental medium that is representative of conditions at the point and time of collection.

6.0 RESPONSIBILITIES

6.1 Project Manager

The Project Manager in conjunction with the Field Operations Leader is responsible for identifying any special considerations for labeling samples or annotating the chain-of-custody. Such considerations may include project-specific sample designations, project-specific analytical protocols, requests for rush analysis or project-specific reporting instructions.

6.2 Field Operations Leader

In addition to assisting the Project Manager in identifying special considerations, the Field Operations Leader is responsible for implementing this SOP and ensuring that field personnel are trained in the use of this procedure.

6.2 Field Geologist/Field Engineer/Field Technician

Field personnel are responsible for understanding and implementing this SOP.

7.0 EQUIPMENT

- Sample Labels (e.g., Attachment 9.1)
- Chain-of-Custody (e.g., Attachment 9.2)
- Custody Seal (e.g., Attachment 9.3)
- Sampling Gloves
- Permanent Marker
- Ink Pen (black or blue ink)
- Shipping Coolers

8.0 PROCEDURE

This procedures picks up from the point after a sample has been collected (e.g., SOP 5-2 or SOP 6-4), placed into a sample container and temporarily stored pending disposition. Certain types of samples (e.g., industrial hygiene) may require project-specific labeling.

8.1 Samples To Be Labeled

Any sample that is to be sent to a laboratory for analysis will be properly labeled. The decision about whether to send a sample for analysis will either be predetermined in the project work plan or determined by field observation or screening procedures. Predetermined samples may be pre-labeled or labeled at the time of collection. Samples requiring field determination prior to selection will be preliminarily labeled by marking unique identification data on the sample container. The identification data is to be cross-referenced in the field logbook, on the field report form, the borehole log form or other project document.

8.2 Labeling

Sample labels (e.g., Attachment 9.1) are to be completed and affixed to the appropriate sample container, as applicable. (Please note that some industrial hygiene samples and other specialized sampling may necessitate alternative labeling procedures, but they still require a unique identification number.) Sample information for the label is predetermined and/or obtained from the field logbook, field report form or borehole log. All label entries are completed with an ink pen or permanent marker and include the following information:

- Project Number;
- Client/Project Name;
- Sampler Affiliation;
- Sample Designation (Section 8.3);
- Sample Type (e.g., grab, composite, etc.);
- Date/Time;
- Requested Analysis;
- Preservative, if applicable; and
- Sampler's Initials.

The completed sample label is affixed to the corresponding sample container by its adhesive backing. If warranted, the label may be protected or affixed with a clear tape covering. (Note: The sample container's surface should have been previously wiped clean in accordance with SOP 5-2 or SOP 6-4.) After labeling, the sample is appropriately stored prior to packaging and shipping.

8.3 Sample Identification

The unique sample identification consists of the designated name and the other information marked on the sample label. The sample designation may be predetermined in the project work plan, generated during the field investigation at the site or include a measured coordinate system.

8.3.1 Site-Generated Sample Name

The sample name consists of three parts: a geographic location acronym; a site sample location acronym; and a depth indicator, if applicable, or date in the case of water samples.

- The geographic location acronym is two to four letters long and consists of initials representing the client/project and the city/state followed by a dash (e.g., Paulding Company's UST Closure in Cincinnati, Ohio may be designated as PUCO).
- The site sample location acronym consists of a two to five letter acronym for the type of sample location and its sequential number followed by a slash or parenthesis, and depth interval or date (e.g., Soil Boring 23 may be designated as SB23/or Monitoring Well 5 as MW5).
- For water samples, the date differentiates the sample from other water samples at the location.
- The depth indicator identifies the sample interval or lowermost depth as which the sample was collected (e.g., 10-12' or 12').

Example: PUCO-SB23/10-12', PUCO-SB23(10-12'), PUCO-SB23/12' or PUCO-MW5

Please note that some analytical laboratories may truncate a sample name to a certain number of digits.

8.3.2 Coordinate System Sample Name

The sample name consists of two parts, a geographic location acronym and the coordinate position of the sample as measured from the site grid. The coordinate system is typically used primarily to identify soil samples. Monitoring well samples are commonly designated as in Section 8.3.1.

- The geographic location acronym is two to four letters long and consists of initials representing the client/project and the city/state followed by a dash (e.g., Paulding Company's UST Closure in Cincinnati, Ohio may be designated as PUCO).
- The coordinate position of the sample is measured within a pre-established grid system and consists of "x, y and z" coordinate numbers, with "z" representing the lower-most depth (e.g., 180,320,6).

Example: PUCU-180,320,6.

8.4 Initiating the Chain-of-Custody

The chain-of-custody is a control document that establishes legal possession of a sample or group of samples during transfer from one custodian to anther. As a control document, the chain-of-custody may be used as evidence in legal proceedings to track the path of a sample from collection to analysis or other disposition. Procedures for consistent and detailed records, such as the chain-of-custody, facilitate the admission of evidence under Rule 803(b) of the Federal Rules of Evidence (P.L. 93-575).

Labeled samples are documented on a pre-printed chain-of-custody (e.g., Attachment 9.2). The chain-of-custody is filled out with an ink pen and includes information from the sample label in addition to following:

- Signature of sampler;
- Numbers of containers associated with the sample;
- Analyses to be performed;
- Pertinent remarks such as:
  - Laboratory contact;
  - Turnaround time;
  - Required detection limits;
  - Where to forward results;
  - Preservatives;
  - Identification of sample, which may contain high concentrations; and
  - Other applicable requirements.
- Custodian transfer signature, time and date; and
- Carrier identification.

Each chain-of-custody is assigned a unique number for quality assurance tracking. The chain-of-custody number is cross-referenced in the field logbook or on the field report form. The number may be specified in the project work plan, previously imprinted on the form, or generated as needed. A typical generated number consists of the date, project number and initials of the Payne Firm.

A copy of the chain-of-custody is placed in the project file. The original chain-of-custody remains with the samples or current custodian.

8.5 Custody Seals

If samples are subject to interim storage before shipment, custody seals (e.g., Attachment 9.3) may be placed over the lids of sample jars or across the opening of the storage container, depending on the project requirements.

8.6 Related Procedures

- SOP 1-1 Use of Field Logbooks
- SOP 1-4 Packaging and Shipment of Samples
- SOP 5-2 Soil Sampling
- SOP 6-4 Ground Water Sampling

9.0 ATTACHMENTS

9.1 Example Sample Label

9.2 Example Chain-of-Custody

9.3 Example Custody Seal

THE PAYNE FIRM, INC.
STANDARD OPERATING PROCEDURE

SUBJECT: Packaging and Shipping Samples

PROCEDURE NO.: SOP 1-4

EFFECTIVE ISSUE DATE: March 3, 2000

REVISION NO.: 2

PRIOR EFFECTIVE DATE: November 19, 1993

SITE-SPECIFIC AMENDMENT: None

1.0 PURPOSE

The purpose of this procedure is to provide instructions to determine the shipping status of samples, to perform the subsequent packaging of samples and to properly ship samples to the intended destination. The relative concentration and source of a sample determines how it is packaged and shipped via carrier. Packaging and shipping regulations have been promulgated by the United States Department of Transportation (DOT), the International Air Transport Association (IATA) and the International Civil Aviation Organization (ICAO). Most international and domestic airlines belong to IATA and require conformance to all applicable regulations. Regulatory agencies with jurisdiction have the authority to levy substantial fines and penalties for violators.

2.0 SCOPE

This procedure applies to the packaging and shipping of samples by Payne Firm personnel.

3.0 REQUIREMENTS

The shipping status of a sample must be determined prior to packaging and shipping. Once determined, the sample must be packaged and shipped in accordance with the appropriate packaging and shipping regulations for the shipping status of the sample.

4.0 REFERENCES

American Society for Testing and Materials, 1995. *Guide for Sampling Chain-of-Custody Procedures*, ASTM D 4840-95.

American Society for Testing and Materials, 1995. *Practices for Preserving and Transporting Soil Samples*, ASTM D 4220-95.

American Society for Testing and Materials, 1996. *Standard Practice for Preparation of Sample Containers and for Preservation of Organic Constituents*, ASTM D 3694-96.

Hazardous Waste Consultant, 1999. *Chemical Analysis of Hazardous Wastes and Environmental Media – Practices to Improve Data Quality*, Volume 17, pp 4.1 – 4.51, Elsevier Science, Inc.

International Air Transport Association, February 1998. *Dangerous Goods Regulations*, 39th Edition.

United States Environmental Protection Agency, July 1991. *Protection of Environment*, 40 CFR 261-263.

United States Environmental Protection Agency, 1996. *Sampler's Guide to the Contract Laboratory Program,* Office of Solid Waste and Emergency Response, EPA/540/R-96/032.

United States Department of Transportation, 1997. *Hazardous Materials Regulations*, 49 CFR 107, 171-180.

5.0 DEFINITIONS

Carrier - A person or firm engaged in the transportation of property.

Chain-of-Custody Record - A form that accompanies a sample or group of samples as custody is transferred from one custodian to another.

Environmental Sample - A low or medium-concentration sample.

Hazardous Sample - A high-concentration sample.

High-Concentration Sample - High-concentration samples are considered to be those samples collected directly from drums, pits, ponds, lagoons, tanks or other areas where no dilution of waste is evident.

Low-Concentration Sample - Low-concentration samples are considered to be those samples collected in areas where immediate hazards are thought to be significantly reduced either by normal environmental processes or because of limited contamination.

Marking - Applying the descriptive name, instruction, cautions and/or specification marks required on the outside of hazardous sample containers.

Medium-Concentration Sample - Medium-concentration samples are considered to be those samples collected from areas of moderate dilution by normal environmental processes. These areas may include soil and ground water contamination source areas.

n.o.i. - Not otherwise indicated.

n.o.s. - Not otherwise specified.

ORM - Other Regulated Material.

Sample - Physical evidence collected at a work site, which is representative of the sample media and conditions at the point and time of collection.

6.0 RESPONSIBILITIES

6.1 Field Operations Leader

The Field Operations Leader is responsible for determining the shipping status of a sample in consultation with the Project Manager, as necessary prior to packaging and shipping. The Field Operations Leader ensures that field personnel are trained in the use of this procedure and that samples are packaged and shipped in accordance with this procedure and applicable regulations.

6.2 Field Geologist/Field Engineer/Field Technician

Field personnel are responsible for understanding this procedure and implementing the proper packaging and shipping of samples.

7.0 EQUIPMENT

The following equipment may be needed:

- Teflon Tape
- Nylon Strapping Tape
- Packaging Tape
- Paper-based (Evidence) Tape
- Styrofoam Packaging Materials
- Bubble Pack
- Resealable Plastic Bags
- Permanent Marker
- Ink Pen (black or blue)
- Shipping Cooler
- Chain-of-Custody Record (Attachment 9.1)
- Custody Seals (Attachment 9.2)
- Ice or Blue Ice
- Shipping Airbill (Attachment 9.3)
- DOT Hazardous Materials Classification (Attachment 9.4)
- DOT List of Class A Poison (Attachment 9.5)
- Labels for Marking
- Flammable Liquids n.o.s. (Attachment 9.6)
- Flammable Solids n.o.s. (Attachment 9.7)
- This End Up (Attachment 9.8)
- Cargo Aircraft Only (Attachment 9.9)
- Vermiculite
- Metal Paint Cans
- Shipper's Certification for Restricted Articles/Dangerous Goods (Attachment 9.10)

8.0 PROCEDURE

40 CFR Section 261.4(d) provides that samples of hazardous waste are exempt from the provisions of Parts 261 – 268, 270, and 124 and the notification requirements of the Resource Conservation and Recovery Act (RCRA) Section 3010. To qualify for this exemption, samples of solid waste, water, soil, or air must be collected only for the purpose of testing to determine characteristic or composition. The exemption applies when the samples are 1) transported to a laboratory for testing; 2) transported back to the collector after testing; 3) stored by the collector prior to transport to the laboratory; 4) stored in the laboratory before or after testing; or 5) stored in the laboratory for a specific purpose, such as awaiting the conclusion of a court case or enforcement action that may required additional testing.

Following analysis and removal from the laboratory, the exemption no longer applies and the possessor of the waste becomes the generator. For example, the facility owner/operator is considered the generator if the waste is returned to the original site. The laboratory becomes the generator if the waste is kept for disposal and any storage or treatment prior to disposal must comply with the hazardous waste regulations. If the sample is collected by a third-party and is returned to him/her, the collector becomes the generator.

A sample collector shipping exempt samples to a laboratory returning exempt samples to a sample collector must comply with DOT, United States Postal Service (USPS), or any other applicable shipping requirements [261.4(d)(2)(i)].

If the sample collector determines that DOT, USPS or other requirements do not apply to the sample shipment, 261.4(d)(2)(ii) requires that the sample be packaged so that is does not leak, spill or vaporize form its packaging. The collector must also include the following information with the sample:

- *The sample collector's name, mailing address and telephone number;*
- *The laboratory's name, mailing address and telephone number;*
- *Sample quantity;*
- *The date of the shipment; and*
- *A description of the sample.*

DOT's hazardous materials transportation requirements, commonly called the Hazardous Materials Regulations (HMR), appear in CFR Title 49, Parts 100 – 180. The requirements contain provisions for classifying, packaging, marking, labeling, placarding and handling hazardous waste shipments of DOT "hazardous materials."

Hazardous materials regulated under DOT include certain RCRA hazardous wastes and Comprehensive Environmental Response Compensation Liability Act (CERCLA) hazardous substances, as well as marine pollutants and elevated-temperature materials. DOT hazardous materials are listed in Appendix A of the Hazardous Materials Table (172.101), which includes all CERCLA hazardous substances, all RCRA hazardous wastes also appear in Appendix A.

A RCRA hazardous waste, however, is a DOT hazardous material only if it is subject to the Environmental Protection Agency (EPA) manifest requirements of 40 CFR Part 262. Because 261.4(d) exempts hazardous waste samples from Part 262 requirements, a sample would not be considered a hazardous material under DOT regulations if the exemption applies. However, if the exemption does not apply and the sample is subject to the manifest requirements of Part 262, the sample would be regulated under DOT as a hazardous material. Similarly, CERCLA hazardous substances are DOT hazardous materials only if they are shipped in quantities that equal or exceed the applicable reportable quantity of the substances as given in 49 CFR 172.101 (Appendix A). Since samples are typically shipped in small quantities, it is unlikely that they would be regulated under DOT as a CERCLA hazardous substance.

8.1 Packaging and Shipping Regulations

Regulations have been promulgated by the DOT and the IATA to be protective of carriers (e.g., Federal Express, Purolator, Airborne Express, UPS), the environment in transit and receivers of goods (e.g., laboratory personnel). Commercial carriers determine the specific regulations they will adhere to and may need to be contacted prior to shipping to ensure that the proper shipping and packaging requirements are met.

Most air transport organizations belong to IATA and require conformance to all applicable regulations. For those who do not belong to IATA, the Field Operations Leader still should conform to IATA policy.

8.2 Shipping Status of Sample

Proper packaging and shipping of samples requires a determination of the shipping status of each sample.

If the sample is exempt as identified in Section 8.0, then it is considered an environmental sample.

An environmental sample is a low-concentration or medium-concentration sample, which requires less stringent minimum packaging and shipping procedures than a hazardous sample.

A hazardous sample is a high-concentration sample, which requires more stringent minimum packaging and shipping requirements than an environmental sample.

8.3 Determination of Shipping Status

The shipping status of each sample is determined by previously available information, observed site conditions, regulatory requirements and/or generator knowledge. In general, media samples for any site characterization activities are considered environmental samples at a minimum. Site characterization samples that are considered to be hazardous are collected only when field personnel are wearing the appropriate level of personal protective equipment, either as specified in the site-specific health and safety plan or as site conditions warrant.

Previously available information, observed site conditions, regulatory requirements and/or generator knowledge are used to evaluate whether samples may be considered high, medium or low concentration.

High concentration samples are considered to be those samples collected directly from drums, pits, ponds, lagoons or other areas where no dilution of waste is evident. Medium concentration samples are considered to be those samples collected from areas of moderate dilution by normal environmental processes and may include soil and ground water contamination source areas. Low concentration samples are considered to be those samples collected in areas where immediate hazards are thought to be significantly reduced either by normal environmental processes or because of limited contamination. Field judgment based on currently known conditions must necessarily be used to establish the appropriate shipping status.

8.4 Environmental Samples

Environmental samples require less-stringent minimum packaging, marking and shipping procedures than hazardous samples. Individual EPA regions may have variations in requirements, which should be determined prior to initiating a project when subject to EPA review.

8.4.1 Environmental Packaging

Environmental samples that have been properly containerized and labeled (SOP 1-3) are packaged as follows:

- Each sample bottle, except 40-milliliter (ml) vials, is placed in a separate resealable plastic bag with the air squeezed out. Up to three 40-ml vials with the same sample designation may be wrapped and included in a single resealable plastic bag.
- A cooler is used to ship samples. The drain plug of the cooler, if present, is taped shut and the bottom of the cooler is lined with bubble wrap, styrofoam or other suitable packaging materials.
- Sample bottles are placed in the cooler with sufficient packaging materials to minimize the potential for breakage.
- A copy of the properly completed chain-of-custody record (e.g., Attachment 9.1) is inserted in a plastic bag and placed inside the cooler for retrieval at the destination.
- The cooler is closed and taped shut with packaging tape.
- If required by site-specific or project-specific protocols, two signed custody seals (e.g., Attachment 9.2) are placed across the opening of the cooler.

8.4.2 Environmental Marking

A cooler containing only environmental samples need not be marked as containing "Environmental Samples" or with arrows identifying which end of the cooler is up. Such markings may be done if required by the needs of the project or as a specific contrast when shipping hazardous samples in a separate cooler. Specific marking and labeling of the outside of the cooler is only required for hazardous samples.

8.4.3 Environmental Shipping

A standard Shipping Airbill (e.g., Attachment 9.3) is completed and displayed in a prominent position on the upper surface of the cooler.

8.5 Hazardous Samples

Hazardous samples require more-stringent minimum packaging, marking and shipping procedures than environmental samples. Both individual sample containers and shipping coolers require a specific hazardous shipping classification, which must be determined prior to preparing sample packaging. No EPA regional variations are in place.

8.5.1 Determination of Hazardous Shipping Classification

A sample considered to be a high-concentration sample containing a known substance is shipped according to the specific instructions for that material in the DOT Hazardous Materials Table from 49 CFR 172.101.

A sample considered to be a high-concentration sample containing unknown constituents is shipped according to a DOT Hazardous Materials Classification selection procedure using a priority system of categories. Categories are eliminated beginning with the most protective until the appropriate shipping category is identified. The following sequence is used:

- Are the constituents considered to be radioactive?
- Are the constituents considered to be a Class A poison (refer to Attachment 9.5)?
- Are the constituents considered to be a flammable gas?
- Are the constituents considered to be a non-flammable gas?
- Are the constituents considered to be a flammable liquid?
- Are the constituents considered to be an oxidizer?
- Are the constituents considered to be a flammable solid?

Most high-concentration samples can be shipped as a flammable liquid or solid by a process of elimination. Flashpoint testing may be necessary to determine a lesser shipping classification. A UN or NA identification number is associated with the classification and is required for packaging and marking.

General identification numbers are as follows:

- Compressed Gases, Flammable, n.o.s. - UN 1954
- Compressed Gases, n.o.s. - UN 1956
- Flammable Liquid, n.o.s - UN 1993
- Flammable Solid, n.o.s - UN 1325

8.5.2 Hazardous Packaging

High-concentration samples that have been properly containerized and labeled (SOP 1-3) are packaged as follows:

- The sample bottle is taped around the cap seal with teflon or paper-based tape.
- Each sample bottle, except 40-ml vials, is placed in a separate resealable plastic bag with the air squeezed out. Up to three-40 ml vials with the same sample designation may be wrapped and included in a single resealable plastic bag.
- Each bottle is placed in a separate paint can or other specified suitable container, which is then filled with vermiculite. The paint can is sealed with evidence tape.
- The can is marked with arrows showing which end is up. The proper DOT shipping classification and corresponding UN or NA identification number is marked on the can along with the sample identification.
- A cooler or other specified suitable container is used to ship samples. The drain plug, if present, of the cooler is taped shut.
- The cooler is lined with a plastic liner (e.g., garbage bag) and the bottom of the cooler is cushioned with bubble wrap, styrofoam or other suitable packaging materials.
- One or more cans are placed upright in the cooler.
- A copy of the properly completed chain-of-custody record (e.g., Attachment 9.1) is inserted in a plastic bag and placed inside the cooler for retrieval at the destination.

- The cooler is closed and taped shut with packaging tape.
- If required by site-specific or project-specific protocols, two signed custody seals (Attachment 9.2) are placed across the opening of the cooler.

8.5.3 Hazardous Marking

A cooler containing high concentration samples is marked as follows:

- A label with the proper DOT shipping classification and NA or UN number is placed on top of the cooler.
- The shipper's name and address is placed on top of the cooler.
- A "This End Up" label (e.g., Attachment 9.8) is placed on the side or top of the cooler.
- A "Cargo Aircraft Only" label (e.g., Attachment 9.9) is placed on top of the cooler.

8.5.4 Hazardous Shipping

A Shipper's Certification for Restricted Articles/Dangerous Goods (e.g., Attachment 9.10) is completed and displayed in a prominent position on the top of the cooler. The certification must include the following information in addition to addresses:

- The proper shipping name;
- The shipping classification;
- The UN or NA identification number;
- The quantity and type of packing;
- Whether the samples are radioactive or not;
- Cargo Aircraft Only restriction; and
- Documentation:
  - A copy of the Chain-of-Custody Record (e.g., Attachment 9.1) and Shipping Airbill (e.g., Attachment 9.3) or Shipper's Certification for Restricted Articles/Dangerous (e.g., Attachment 9.10) is included with the shipment and placed in the project files;
  - Related Procedures;
  - SOP 1-1 Use of Field Logbooks;
  - SOP 1-2 Use of Field Equipment Room;
  - SOP 1-3 Labeling and Custody of Samples;

- SOP 5-2 Soil Sampling;
- SOP 6-4 Ground Water Sampling; and
- SOP 6-5 Surface Water Sampling.

9.0 ATTACHMENTS

9.1 Example Chain-of-Custody Record

9.2 Example Custody Seal

9.3 Example Shipping Airbill

9.4 DOT Hazardous Materials Classification

9.5 DOT List of Class A Poison (49 CFR 172.10)

9.6 Flammable Liquids Label

9.7 Flammable Solids Label

9.8 This End Up Label

9.9 Cargo Aircraft Only Label

9.10 Shipper's Certification for Restricted Articles/Dangerous Goods

THE PAYNE FIRM, INC.
STANDARD OPERATING PROCEDURE

SUBJECT: Hazard Recognition

PROCEDURE NO.: SOP 1-5

EFFECTIVE ISSUE DATE: November 19, 1993

REVISION NO.: 0

PRIOR EFFECTIVE DATE: New

SITE-SPECIFIC AMENDMENT: None

1.0 PURPOSE

The purpose of this procedure is to describe the rationale, methods, and sequence of field operations for 1) the recognition/avoidance of unsafe conditions; 2) establishment and maintenance of safe work distances from identified hazards; and 3) the control or elimination of any potential or actual hazards or other exposures, which may cause illness or injury due to field activities at investigation sites.

2.0 SCOPE

This procedure applies to any field activity including, but not limited to, site walks, soil gas sampling, auguring, drilling, monitoring well installation, manhole inspection, pavement coring, excavation activities and third-party observation of such activities.

3.0 REQUIREMENTS

Training, adherence to established rules, staying alert, being observant and careful house keeping can prevent many hazardous situations or accidents arising from physical hazards.

The general rules and preventive measures, as described in Section 8.0, have been developed for use to plan and implement site field investigations.

4.0 REFERENCES

Code of Federal Regulations, Title 29:

- Part 1910.333 (b) (3) (iii) (C)
- Part 1926.137
- Part 1926.150 through .154

- Part 1926.200 through .202
- Part 1926.403 through .408
- Part 1926.416
- Part 1926.600 through .602
- Part 1926.651

5.0 DEFINITIONS

None.

6.0 RESPONSIBILITIES

6.1 Field Operations Leader

The Field Operations Leader is responsible for 1) calling "Call Before You Dig" for tasks involving breaking of the ground surface; 2) monitoring work activities to ensure compliance with the procedures to recognize and avoid unsafe conditions, and maintain safe working distances from hazards;3) documenting the establishment and maintenance of safe working distances in field notes, when applicable; and 4) informing the Payne Firm employees or the Payne Firm subcontractors of unsafe work practices and, if necessary, stopping work activities, with corresponding documentation in field notes.

6.2 Field Geologist/Field Engineer/Field Technician

All field personnel are responsible for 1) implementing the hazard recognition procedures; 2) taking precautions necessary to prevent injury to themselves and other team members; 3) maintaining the minimum safe working distances; and 4) immediately reporting any accidents and unsafe conditions to the Field Operations Leader.

7.0 EQUIPMENT

None specified.

8.0 PROCEDURE

8.1 Accident Prevention

8.1.1 Flammable and Hazardous Materials and Control of Fire and Explosive Hazards

Flammable and hazardous materials, such as gasoline, diesel fuel and decontamination solvents, may be stored, handled and used on a site during the course of an investigation. To reduce the risks of fires and explosions, small quantities (one to five gallons) of flammable liquids will be stored in approved "safety" cans and labeled according to the contents. Very small quantities (one gallon and less) of decontamination solvents will be stored in the vendor supplied shipping containers and cartons until transferred to quart size, plastic spray bottles for use. Bulk storage of flammable materials will be allowed only on service support vehicles for heavy equipment. Open flames will be prohibited within 50 feet of the service support vehicles.

Flammable vapors may be encountered in confined spaces and may produce an explosive atmosphere which can be ignited by a spark or other energy source. Procedures for confined space evaluation will be implemented prior to any proposed entry as presented in Section 8.1.10.

Occupational Safety and Health Administration (OSHA) standards for fire protection and prevention are contained in 29 CFR Subpart F, 1926.154. of particular concern on site investigations are:

- Proper storage of flammables;
- Adequate numbers and types of fire extinguishers; and
- Monitoring for development of an explosive atmosphere.

8.1.2 "Hot Work"

If "Hot Work", as described below, is to be performed, a fully completed Hot Work Permit must be filled out on a daily basis as per SOP 1-9 prior to starting the "Hot Work" activity. "Hot Work" is defined as any one of the following:

- Use of a torch, burning, welding, soldering, brazing or any unit having an open flame;
- Use of any powered tool that could or would have the potential to produce a spark or an ignition source that could evolve into a fire or explosive situation; and
- Use of any hand tool not of spark-proof nature in an area where the potential for accidental fire or

explosion may exist (i.e., hammers, chisels, picks, etc.)

8.1.3 Electrical Hazards

Overhead power lines, downed electrical wires, temporary electric circuits and buried cables can pose a danger of electrical shock and electrocution if workers contact or sever them during field activities. Electrical equipment used during the investigation may also pose a potential electrical shock hazard to workers. To help minimize this hazard, low-voltage equipment and ground-fault circuit interrupters and watertight, corrosion-resistant, connecting cables should be used wherever possible. OSHA standards for electrical safety are contained in 29 CFR Subpart K, 1926.403 through 1926.408 and 1926.416. OSHA regulations given in 29 CFR, Part 1910.137 describe clothing and equipment for protection against electrical hazards. All applicable sections of these regulations will be complied with. The following requirements are particularly relevant:

- Use only ground-fault circuit interrupter (GFCI) outlets for all on-site electrical use other than permanent wiring in buildings or structures;
- Design or specify the use of equipment and installations appropriate to avoid/control hazards associated with electrical hazards of a particular area (e.g., explosion-proof ventilation systems, pumps, etc., will be used for materials handling); and
- Use only heavy duty flexible electrical cords.

8.1.4 Motor Vehicles and Heavy Equipment

Working with motor vehicles and heavy equipment could be a major hazard at a site. Injuries can result from equipment hitting or running over personnel and impacts by flying objects or overturning vehicles. Vehicles and heavy equipment operation will be in accordance with 29 CFR Subpart O, 1926.600 through 1926.602.

8.1.5 Slip, Trip and Fall Hazards

Investigation sites may contain slip, trip and fall hazards for site workers, such as but not limited to:

- Holes, pits or ditches;
- Slippery surfaces;

- Steep grades;
- Uneven grades or surfaces; and
- Sharp objects, such as nails, metal shards and broken glass.

Field Team Members shall constantly be on the lookout for potential safety hazards and immediately inform the Field Operations Leader of any newly identified hazards. If the hazard cannot be immediately removed or controlled, actions must be taken to warn site workers of the hazard or prevent workers from being exposed to the physical hazards. The signs, signals and barricades used to warn and protect site workers from these hazards will be in accordance with OSHA 29 CFR Subpart G, 1926.200 through 1926.202.

8.1.6 Subsurface Hazards

Prior to any drilling or excavation activity, the presence and location of any underground lines and structures such as electric lines, telephone, equipment control lines, natural gas, water, steam, product transfer, sewer (including sanitary, storm and process) and underground storage tanks (USTs) must be determined. Within Ohio, call the Ohio Utilities Protection Service (1-800-362-2764), a consortium of most utility companies which operates a "Call Before You Dig" free utility marking service for member utilities. By Ohio law, this must be contacted at least two working days prior to any excavations. If working in states other than Ohio, consult the local telephone company for underground cable and pipe information number. For private underground lines installed for or by the landowner or facility, contact the site representative for assistance.

Prior to breaking the surface, every drill location or excavation will be visibly marked on the surface and the location approved for drilling or excavation by the site representative.

8.1.7 Excavation Hazards

The walls and faces of all excavations in which personnel are exposed to the danger from moving ground [greater than (>) 3.5 feet deep] must be guarded by a shoring system, sloping of the ground or some other equivalent means. Field Team Members are not permitted to enter into or be located next to an excavation >3.5 feet deep without written approval from the Project Manager and then all OSHA requirements concerning excavation activities in 29 CFR 1926.651 must be followed before entry into the excavation by field personnel.

8.1.8 Drilling Accidents

Workers in the area of drilling equipment are exposed to hazards such as but not limited to falling suspended equipment, moving machinery parts including augers and cables, or moving vehicles or equipment. Accidents of this type are most likely to occur during drilling operations and risks can be reduced by safe operation of drilling equipment, the wearing of protective equipment including a hard hat and safety boots, attentiveness by all personnel and staying a safe working distance from the equipment at all times.

8.1.9 Electrical Line Clearance and Thunderstorms

Extra precautions will be exercised when drilling or operating heavy equipment near overhead electrical lines. The minimum clearance between overhead electrical lines of 50 kilovolts (kV) or less and the equipment and/or the longest conductive object is ten feet. For lines rated over 50 kV, the minimum clearance between the lines and any part of the rig is ten feet plus 0.4 inches for each kV over 50 kV. If the rating of overhead power lines is not known, the minimum safe working distance is 20 feet.

Equipment operations must cease during thunderstorms or if lightening-producing conditions approach the site.

8.1.10 Confined Space Entry

When a confined space is identified at a site, the need to enter the confined space will be evaluated and the requirement for a confined space entry permit will be determined. When entry into a permitted confined space is to be performed, a confined space entry permit will be completed prior to entering the confined space. All investigation personnel must follow the confined space entry program as described in SOP 1-6.

8.2 Establishing and Maintaining Safe Work Distances

Site investigations often require the use of heavy equipment and machinery such as drill rigs and excavation equipment. Investigation workers not operating or assisting in the operation of the equipment must identify and maintain a safe working distance from the equipment while performing their related

activities following the minimum distances established below.

8.2.1 Translocation of Heavy Equipment

When mobile heavy equipment is about to be moved or is moving from one location to another, workers will maintain a minimum distance from the heavy equipment of 20 feet in front and back, and/or ten feet to other sides of the equipment. This minimum distance should be increased if site conditions are adverse (i.e., inclement weather, poor visibility, uneven terrain, reduced avenues of escape and/or blind spots along the path of movement).

8.2.2 Drill Rig Operations

When the drill crew is operating a drill rig, including stationary tools under tension on winch cables, non-operating workers will maintain the following minimum distances:

- Ten feet from the sides of the drill rig;
- 15 feet from the back of the drill rig;
- Ten feet from the drilling tool lay down area; and
- 15 additional feet from any drill rods elevated higher than the drilling mast.

8.2.3 Excavator and Other Heavy Equipment Operations

When working around an excavator or other heavy equipment, a distance of ten feet greater than the swing radius of the equipment will be the minimum work distance while the equipment is operating. If specific investigation duties (i.e., soil sample collection) require approach within this minimum distance, eye contact between the operator of the equipment and the approaching worker must be established prior to approaching and maintained at regular intervals while within the swing radius of the equipment. Working under the bucket or arm of an excavator is never permitted. Riding in the bucket of an excavator is never permitted.

8.2.4 Equipment Capable of being Energized by Electrical Sources

If electrical sources, such as overhead electric lines (see Section 8.1.9), have been identified in or near a work area such that a vehicle or mechanical equipment is capable of having parts of its structure

energized, a minimum distance of 20 feet will be maintained between the Payne Firm worker and the potential energized equipment or the point of grounding of the equipment.

8.2.5 Work Station Location

Any workstation established to perform activities related to the operation of heavy equipment (i.e., soil sampling, soil description, sampling tool decontamination or other activity requiring attention away from the heavy equipment operation) shall maintain a minimum distance of 20 feet from the nearest point of activity.

8.3 Noise-Induced Hearing Loss

Active hazardous waste sites and industrial facilities often involve the use of heavy equipment or machinery such as drill rigs, compressors, generators, earth-moving equipment and process equipment. The unprotected exposure of workers to high intensity noise can result in noise-induced hearing loss. The Payne Firm will ensure that hearing-protection devices are made available to their employees working in the vicinity of the operation of heavy equipment or other sources of high intensity noise.

8.4 Heat Stress and Cold-Related Illness and Injury

Two primary weather conditions, heat and cold, can threaten workers conducting investigations. Exposure to high or low environmental temperatures produces stress on the body. As the body attempts to compensate, physiological strain results. This strain, usually in combination with other strain caused by work and fatigue, may lead to heat stress or cold-related illness and injury. The following subsections delineate preventive measures and methods for heat or cold stress monitoring.

8.4.1 Prevention of Heat Stress

Successful prevention of the adverse effects of heat is dependent on the education of personnel and supervisors, the implementation of procedures to alert all workers to be aware of the dangerous heat stress levels and the reduction or prevention of additional heat loads in active personnel. Heat stress prevention is particularly important because once a person suffers from heat stroke or heat exhaustion, that person may be predisposed to heat-related illnesses.

The Project and Field Health and Safety Officer shall remind all workers about the dangers and recognition of heat stress symptoms. The signs and symptoms of heat stress are as follows:

- Heat rash may result from continuous exposure to heat or humid air.
- Heat cramps are caused by heavy sweating with inadequate fluid and electrolyte replacement and symptoms include a) muscle spasms; and b) pain in the hands, feet and abdomen.
- Heat exhaustion occurs from increased stress on various body organs including inadequate blood circulation due to cardiovascular insufficiency or dehydration and symptoms include a) pale, cool, moist skin; b) heavy sweating; c) dizziness; d) nausea; and e) fainting.
- Heat stroke occurs from failure of the body's temperature regulating system and body temperature rises to critical levels, immediate action must be taken to cool the body before serious injury and death occur, competent medical help must be obtained, symptoms include a) red, hot, usually dry skin; b) lack of or reduced perspiration; c) nausea; d) dizziness and confusion; e) strong, rapid pulse; and f) coma.

The Project and Field Health and Safety Officer can minimize the potential for heat stress by the following:

- Adjusting work schedules by modifying work and rest schedules according to monitoring requirements, mandating work slowdowns as needed, and performing work during cooler hours of the day if possible or at night if adequate lighting can be provided;
- Providing shelter (air-conditioned, if possible) or shaded areas to protect personnel during rest periods; and
- Maintaining worker's body fluids at normal levels.

The maintaining of body fluids at normal levels ensures that the cardiovascular system functions adequately. Daily fluid intake must approximately equal the amount of water lost in sweat. The normal thirst mechanism is not sensitive enough to ensure that enough water will be ingested to replace that lost in sweat. When heavy sweating occurs, encourage workers to drink more fluids. A total of one to 1.6 gallons of fluid per day are recommended, but more may be necessary to replace lost fluids.

8.4.2 Heat Stress Monitoring

Either environmental or physiological monitoring can be used to predict and control workers' heat stress.

For workers who are wearing permeable clothing, environmental monitoring and the suggested work and rest cycles outlined in the current (1992-1993) American Conference of Governmental Industrial Hygienists' (ACGIH) Threshold Limit Values (TLVs) for heat stress should be applied.

The use of personnel protective equipment will increase an individual's heat stress, and the physiological monitoring of personnel wearing semi-permeable or impermeable clothing should commence when the ambient temperature is 70° F or more. Physiological monitoring includes measurements of workers' heart rates and oral temperatures. The suggested frequency for a 15-minute rest period and physiological monitoring is as follows:

Suggested Frequency of 15-Minute Rest Period and Physiological Monitoring for Fit and Acclimatized Workers Performing Strenuous Field Activities[1]

Adjusted Temperature[2]	Normal Work Ensemble[3]	Impermeable Ensemble[4]
90° F (32.2°C) or above	After each 45 minutes of work	After each 15 minutes of work
87.5° to 90° F (30.8° to 32.2° C)	After each 60 minutes of work	After each 30 minutes or work
82.5° to 87.5° F (28.1° to 30.8° C)	After each 90 minutes of work	After each 60 minutes or work
77.5° to 82.5° F (25.3° to 28.1° C)	After each 120 minutes of work	After each 90 minutes of work
72.5° to 77.5° F (22.5°to 25.3° C)	After each 150 minutes of work	After each 120 minutes of work

Source: NIOSH, OSHA, USCG and USEPA, 1985

For heart rate, count the radial or cardial pulse during a 30-second period as early as possible in the rest period. If the heart rate exceeds 110 beats per minute at the beginning of the rest period, shorten the next work cycle by one-third and keep the rest period the same. If the heart rate still exceeds 110 beats per minute at the next rest period, shorten the following work cycle by one-third.

For oral temperature, use a clinical thermometer or similar device to measure the oral temperature at the start of the rest period and before drinking fluids. If the oral temperature exceeds 99.6° F at the

[1] For work levels of 250 kilocalories/hour.
[2] Calculate the adjusted air temperature (ta adj) by using this equation: ta adj °F = ta °F + (13 x % sunshine). Measure air temperature (ta) with a standard mercury-in-glass thermometer, with the bulb shielded from radiant heat. Estimate percent sunshine by judging what percent time the sun is not covered by clouds that are thick enough to produce a shadow. (100 percent sunshine = no cloud cover and a sharp, distinct shadow; 0 percent sunshine = no shadows.)
[3] A normal work ensemble consists of cotton overalls or other cotton clothing with long sleeves and pants.

beginning of the next period, shorten the following cycle by one-third. Do not permit a worker to wear a semi-permeable or impermeable garment when oral temperature exceeds 100.6° F.

8.4.3 Cold-Related Illness

If fieldwork takes place during winter months, thermal injury from cold exposure may be a problem for personnel. Systemic cold exposure is referred to as hypothermia and localized cold exposure is referred to as frostbite.

Frostbite is both a general and medical term given to areas of local cold injury. Unlike systemic hypothermia, frostbite rarely occurs unless the ambient temperature is less than 20° F.

Hypothermia is defined as a decrease in the body core temperature below 96° F. The body temperature is normally maintained by a combination of central nervous system and body activities. Interference with any of these mechanisms can result in hypothermia, even in the absence of what is normally considered a "cold" ambient temperature.

Hypothermia begins when the body loses heat faster than it can be produced. When the body is chilled, it passes through several stages:

- The initial response of a person exposed to cold is to voluntarily exercise in order to generate heat and stay warm; and
- As the body tissue is cooled, the person begins to shiver as a result of an involuntary adjustment by the body to preserve normal temperature in the vital organs.

Up to this point, the person can foresee and take steps to prevent further hypothermia. However, these responses drain the body's dwindling energy reserves. If exposure continues until the victim's energy reserves are exhausted, the following symptoms appear:

- Cold reaches the brain and deprives the victim of judgment and reasoning powers;
- The victim experiences feelings of apathy, listlessness and indifference;
- The victim does not realize what is happening; and

[4] An impermeable ensemble consists of clothing which restricts air circulation to cool the skin.

- The victim loses control of the hands.

Loss of body heat becomes more rapid as the body temperature is lowered. Eventually, the worsening hypothermia will result in the victim entering a stupor, collapsing and then, if unabated, death.

The victim of hypothermia may not recognize the symptoms and even deny that medical attention is needed. Therefore, it is important for others to judge the symptoms rather than follow what the victim says. Even mild symptoms of hypothermia need immediate medical care.

8.4.4 Prevention of Cold-Related Illness

The following steps shall be taken by the Project and Field Health and Safety Officer to prevent cold related illness:

- Educating workers to recognize the symptoms of frostbite and hypothermia;
- Identifying and limiting known risk factors;
- Ensuring the availability of an enclosed, heated environment on-site;
- Ensuring the availability of dry changes of clothes; and
- Ensuring the availability of warm drinks.

8.4.5 Monitoring for Cold-Related Illness

Cold-related illness can be monitored by measuring the oral temperature of the potentially exposed workers. This should be done as follows:

- At the supervisor's discretion when suspicion is based on changes in worker's performance or mental status;
- At the worker's request;
- As a screening measure (two times per shift) when hazardous weather conditions of windchill is less than 20° F or a windchill is less than 30° F with precipitation; and
- As a screening measure whenever any worker on the site develops hypothermia.

Any worker developing moderate hypothermia, defined as a core temperature of 92° F, may not return to

work for 48 hours.

9.0 ATTACHMENTS

None.

THE PAYNE FIRM, INC.
STANDARD OPERATING PROCEDURE

SUBJECT: Restoration of Work Site

PROCEDURE NO.: SOP 1-7

EFFECTIVE DATE: November 19, 1993

REVISION NO.: 1

PRIOR EFFECTIVE DATE: July 15, 1993

SITE-SPECIFIC AMENDMENTS: None

1.0 PURPOSE

The purpose of this procedure is to describe the general requirements for restoration of a work site after Payne Firm field investigation activities.

2.0 SCOPE

This procedure applies to planning for restoration as part of a project scope of work, accomplishing restoration during and at the completion of a project, and documenting the results of restoration.

3.0 REQUIREMENTS

Environmental investigation and remediation routinely alters a site as a result of probing the subsurface, installing equipment, removing site features and penetrating the surface. Project planning must include identification of potential restoration issues, communication of these issues to the client and appropriate resolution. Restoration activities should be performed, as needed, during the investigation, during the day's work, at the end of the workday and at the completion of the project. Restoration should be documented in the field logbook.

4.0 REFERENCES

None.

5.0 DEFINITIONS

None.

6.0 RESPONSIBILITIES

6.1 Project Manager

The Project Manager is responsible for identifying potential restoration issues, communicating these issues to the client and including the agreed upon resolution of restoration issues in the scope of work for the project. The Project Manager shall ensure that restoration is accomplished.

6.2 Field Operations Leader

The Field Operations Leader is responsible for planning and scheduling daily activities to include site restoration. Restoration activities shall be documented in the field logbook.

Unexpected restoration issues that arise during the course of field activities should be addressed promptly by the Field Operations Leader or communicated to the Project Manager for client conferral and resolution, if necessary.

7.0 EQUIPMENT

None specified.

8.0 PROCEDURE

8.1 Planning

Identified work tasks shall be evaluated for potential restoration needs. These potential needs shall be communicated to the client for input and resolution, which shall be incorporated into the scope of work. Common work tasks which require surface restoration may include:

- Borehole Patching
- Soil Gas Survey Patching
- Excavation Patching
- Heavy Equipment Rutting
- Conduit Laying
- Well Installation Monitoring

- Test Pit Patching
- Trenching
- Removal or Abandonment of Monitoring Wells
- Removal of Debris

8.2 Restoration of Work Site

Work tasks requiring restoration shall be performed in accordance with the scope of work. Restoration should occur in a timely manner and may be performed throughout the course of a project, as needed.

Surface holes should be appropriately patched soon after completion. Excavations should be backfilled and patched according to the scope of work. Open holes or excavations should be barricaded and marked until restored.

Heavy equipment rutting, surface welts or soil piles caused by auger drilling should be filled in or leveled.

Unanticipated needs for restoration should be evaluated by the Field Operations Leader. If unable to resolve promptly, the Project Manager should be informed to solicit client input and resolution.

As field activities are completed and areas restored, field inspection of the area shall be performed by the Field Operations Leader to assess the status and any need for further restoration.

During project activities and at the end of each day, all trash and debris will be collected and disposed.

Site cleanup and restoration activities should be entered in the field logbook.

9.0 ATTACHMENTS

None.

THE PAYNE FIRM, INC.
STANDARD OPERATING PROCEDURE

SUBJECT: Arranging a Land or Elevation Survey

PROCEDURE NO.: SOP 1-8

EFFECTIVE ISSUE DATE: November 19, 1993

REVISION NO.: 1

PRIOR EFFECTIVE DATE: July 15, 1993

SITE-SPECIFIC AMENDMENT: None

1.0 PURPOSE

The purpose of this procedure is to identify the general requirements for arranging a land or elevation survey. Survey activities will be performed by a land surveying subcontractor or qualified client and will necessitate the prior determination of specific data needs to present to the surveyor as a scope of work.

2.0 SCOPE

This procedure applies to arranging a survey to establish spatial relations between objects and/or the feature elevation referenced to a benchmark. Pre-existing data may be available at a site and will have to be evaluated within the context of the needs of the project, the desired quality of any new data, and the identified quality and reproducibility of the old data.

3.0 REQUIREMENTS

Sufficient planning must be performed to supply a surveyor with the information necessary to achieve the data needs for the project. Planning will include identifying what spatial and vertical data is needed, the standard of quality this data has to meet, whether there are special requirements to collect the data, and when the data can be collected. All surveying operations shall be performed under the direction of a Licensed Surveyor of the state in which the site is located.

4.0 REFERENCES

Bouchard, H. and F. Moffit, 1982, *Surveying*. Seventh Edition, Harper and Row, New York, New York.

United States Environmental Protection Agency, December 1987. *A Compendium of Superfund Field Operations Methods*, EPA/540/P-87/001.

5.0 DEFINITIONS

Accuracy - The extent to which a set of data represents the "true" value (i.e., is free of measurement error). The accuracy of some equipment can be determined by comparing measurements made using the equipment to a known standard.

Azimuth - The azimuth of a line is the angle between a meridian and the line, and is always measured from the meridian in a clockwise direction.

Baseline - A straight line established in the field by two or more monuments. The baseline is often used as a primary horizontal reference for layout in determining the locations of site activities, features or secondary horizontal surveying stations. For convenience, baselines are also provided with intermediate stationing stakes or hubs at major stations (i.e., 50 or 100 feet) along their length.

Base Map - A detailed site map, often a topographic/boundary map, which is used as a basis to create other site maps by imposing additional information (i.e., sampling locations, boring or test pit locations, planned excavation limits, etc.).

Beachmark/Datum Plane - A level surface serving as a reference from which vertical distances are measured. Unless otherwise specified, all altitudes shall refer to Mean Sea Level, as determined by the 1929 General Adjustment.

Bearing - Bearing of a line is the acute angle a line makes with the four cardinal compass directions (north, east, west, south). A bearing is designated by the original cardinal direction from which it is measured, the acute angle the line makes with the original cardinal direction, and the adjacent cardinal direction toward which the actuate angle is turned.

Licensed Surveyor - A person responsible for the performance of surveying operations who is licensed by the state in which the site is located to perform such surveying activities as a Registered or Licensed Surveyor.

Monument - A permanent point of known horizontal coordinates used to locate various site features or locations with respect to the particular horizontal coordinate system.

Precision - The ability of a measurement to yield an exact, repeatable value.

Survey Party - A crew of specially trained people who perform field survey activities and related office calculations under the overall direction of a Licensed Surveyor.

Transit - A precision engineering measurement device having a sighting telescope and used to measure vertical and horizontal angles.

Traverse - A series of connected transit lines whose lengths and bearings are known. An open traverse forms a segmented line. Usually a traverse is closed to form a polygon, so that measurements may be balanced throughout the traverse survey. Traverses are used as reference baselines for performing other horizontal control surveying operations.

6.0 RESPONSIBILITIES

6.1 Project Manager

The Project Manager is responsible for meeting the planning requirements necessary to achieve a successful survey. This will include informing the surveyor of the scope of work and ensuring that the surveyor can safely access the site. The Project Manager shall ensure that any quality assurance objectives are evaluated.

6.2 Field Operations Leader

The Field Operations Leader is responsible for coordinating site and monitoring well access for the surveying crew and documenting the progress of surveying activities.

6.3 Surveyor

The Surveyor is responsible for meeting the requirements of the scope of work. The Surveyor shall assure that all surveying field operations, office calculations, map preparation and related surveying activities conform with standard professional guidelines and that the specific requirements of the scope of work (including health and safety requirements) are met. All field measurements are to be recorded in a bound field logbook that is to be made available for review by the Project Manager upon request. A surveying report shall be submitted to the Project Manager as specified in the scope of work.

7.0 EQUIPMENT

Appropriate properly operating and calibrated surveying equipment shall be supplied by the surveyor to meet the scope of work.

8.0 PROCEDURE

8.1 Determine Data Needs and Quality

Surveying data needs shall be determined during the planning stages of a project. Commonly needed surveying data are ground surface and casing elevations for monitoring wells, with which are used to

calculate ground water potentiometric elevations. Other horizontal and/or vertical location information may be required for the following categories:

- Wells;
- Piezometers;
- Borings;
- Test Pits;
- Property Boundaries;
- Base Maps;
- Surface Soil Samples;
- Surface Water Samples;
- Air Station Samples;
- Surface Grid; and
- Building Slabs or Surfaces.

The level of accuracy should be determined for any identified data needs. Unless otherwise required, horizontal accuracy is sufficient to the nearest foot. Vertical accuracy for wells and piezometers should be measured to the nearest 0.01 foot. Vertical accuracy for other features may be determined to the nearest 0.1 foot.

8.2 Evaluate Quality of Pre-Existing Survey Data

Pre-existing survey data may be available for a site. When possible, such data should be evaluated for any obvious quality problems. For instance, settling or heaving may be visible at a well and may indicate an alteration in its elevation. The accuracy of previous survey data may be insufficient for the purposes of the present project.

Previous survey data may be quantitatively evaluated by resurveying one or more data points.

8.3 Identify Site-Specific Requirements

The Project Manager shall identify any special requirements which may need to be met in order for the surveying crew to achieve the scope of work. Special requirements may include health and safety issues, special training, temporal constraints and site access restrictions. Identified special requirements shall be included in the scope of work for the surveyor.

8.4 Communication of Scope of Work

The Scope of Work for a project will be communicated to the surveyor prior to scheduling. Communication may be either verbal or written. However, if verbal, detailed documentation of instructions should be included in the project file and confirmed with the surveyor. Any scope of work should include site location instructions.

8.5 Site Access and Documentation

The Field Operations Leader or designee thereof will meet the surveying crew at the site to ensure access and review the scope of work. Pertinent site activities by the surveying screw shall be documented in the field logbook.

8.6 Evaluation of Surveying Results

Upon receipt of surveying results, values will be checked for reasonableness and consistency with other site information. Any unusual or suspect results will be confirmed with the surveyor.

9.0 ATTACHMENTS

None.

THE PAYNE FIRM, INC.
STANDARD OPERATING PROCEDURE

SUBJECT: Use of Water Level Indicators (Solinst and QED Models)

PROCEDURE NO.: SOP 2-5

EFFECTIVE ISSUE DATE: November 19, 1993

REVISION NO.: 1

PRIOR EFFECTIVE DATE: July 15, 1993

SITE-SPECIFIC AMENDMENT: None

1.0 PURPOSE

The purpose of this procedure is to provide information on the operation and maintenance of water level indicators. Water level measurements are frequently conducted in conjunction with ground water sampling and may be used to prepare ground water flow maps or in ground water modeling.

2.0 SCOPE

This procedure applies to the use of Solinst and QED water level indicators and may be used in conjunction with the manufacturers specifications for other water level indicators.

3.0 REQUIREMENTS

Water level indicators must be checked for proper operation prior to departure for the field. The indicator probe and measuring tape that come into contact with target water must be decontaminated after each measurement. All measurements must be documented in the Field Logbook or on the Water Level Data Sheet.

4.0 REFERENCES

United States Environmental Protection Agency, September, 1986, *Resource Conservation and Recovery Act (RCRA) Ground Water Monitoring Technical Enforcement Guidance Document*, OSWER-9950.1.

United States Environmental Protection Agency, December 1987. *A Compendium of Superfund Field Operations Methods*, EPA/540/p-87/001.

5.0 DEFINITIONS

Confined Aquifer - An aquifer bounded above and below by impermeable beds or by beds distinctly less permeable than that of the aquifer itself.
Piezometric Head - The height to which water will rise in a well.
Potentiometric Surface - A surface representing the total pressure head of ground water and defined by the level to which water will rise in a well.
Unconfined (Water Table) Aquifer - An aquifer in which the water table forms the upper boundary.
Water Level Indicator - A device consisting of a weighted probe with electrical-circuit connection attached to a measuring tape. When the probe comes in contact with water, the circuit is closed and triggers a high-toned beep.
Water Table - A surface in an aquifer where ground water pressure is equal to atmospheric pressure and below which all strata are saturated with water.

6.0 RESPONSIBILITIES

6.1 Field Operations Leader

The Field Operations Leader is responsible for ensuring access to all water level measurement locations and that field personnel are properly trained in the use of this procedure.

6.2 Field Geologist/Field Technician

The Field Geologist or Field Technician is responsible for properly operating and maintaining the water level indicator. All measurements are to be recorded in the Field Logbook or on the water level data sheet. Any operating problems should be communicated to the Field Operations Leader for resolution.

7.0 EQUIPMENT

- Solinst or QED
- Water Level Indicator
- Well Access Keys
- Latex Gloves
- Ratchet
- Well Casing Head Fluid Evacuation Devices

- Sponge
- Baster
- Cup
- Ziploc Bag
- Field Logbook
- Water Level Data Sheets (Attachment 9.1)
- Deionized Water
- Methanol Spray Bottle, if necessary
- Garbage Bag
- Spare 9-Volt Battery
- Paper Towels

8.0 PROCEDURE

8.1 Planning

Prior to departure for the work site, field personnel must ensure that equipment is properly operating, know what locations are to be measured and that access is available and identify any special requirements necessary to perform the water level measurements (e.g., higher levels of protection or specific decontamination procedures).

8.2 Arrival at the Measuring Location

Typically water levels are measured in wells.

- The protective cover should be opened as per the specific project requirements, if any.
- If there is standing water, ice or other materials at the head of the well casing, it will need to be evacuating to a level sufficiently beneath the top of the casing to ensure that no material enters the well.
- The well caps should then be removed.
- A sound of air movement or pressure release when removing the well cap may indicate that the well will require pressure stabilization of the water level in the well prior to measurement.
- The water level probe should be rinsed with deionized water prior to measurement.
- If a bailer is dedicated to the well, it should be removed and propped on plastic while measuring the

water level.

8.3 Measurement of Water Levels

The following steps will ensure accurate measurement of a water level under the prevailing conditions.

- Check that the indicator beeps properly. If no sound is heard, check that the instrument is turned on. Change the battery, if necessary.
- Insert the probe into the well and release the measuring tape slowly until the probe reaches water and the instrument begins to beep.
- Read the water level at which the instrument beings to beep at the reference mark on top of the well casing. The water level measurement should be made to the nearest 0.01 feet.
- Reel the tape up a few feet, wait a minimum of ten seconds and then repeat the measurement to verify a stable water level. Repeat this step until a stable water level is achieved.
- Document the stable water level for the well and any pertinent remarks (e.g., evacuation or stabilization).

8.4 Documentation

Water level measurements are to be recorded in the Field Logbook for the project or a water level data sheet. The following water level information should be recorded:

- Water Level Indicator Number
- Well Designation
- 24-Hour Time
- Depth to Water
- Remarks

Field Logbook entries should conform to "Use of Field Logbooks" (SOP 1-1). If the water level data sheet is used, it should be completed to the extent applicable including:

- Client/Project
- Project No.
- Date

- Measurements By
- Signature

8.5 Decontamination of Water Level Indicator

Decontamination of the water level indicator shall be performed after removal from the well. Decontamination mitigates the potential for cross-contamination between wells. This is especially important when water levels are obtained preliminary to sampling.

Decontamination may consist of simply rinsing the probe with deionized water or may require site-specific procedures. This section describes decontamination with deionized water and a combination of methanol or deionized water.

8.5.1 Deionized Water

The probe and any part of the tape which may have come into contact with water in the well shall be thoroughly rinsed with deionized water. If foreign material is visible on the probe or tape after rinsing it can be wiped off with a paper towel and rinsed again.

8.5.2 Methanol and Deionized Water

Methanol and deionized water will be used for decontamination when part of the project requirements. Methanol is available in a spray bottle. It can either be sprayed directly onto the appropriate parts of the water level indicator or sprayed onto a paper towel for wiping. After methanol has been applied, deionized water should be used to rinse the appropriate parts of the instrument.

8.6 Maintenance of Water Level Indicators

Water level indicators are to be properly operated as per this procedure. They will be decontaminated after each measurement and turned off when not in use. The battery will be changed as necessary. Any performance problems are to be evaluated and communicated to the Field Operations Leader for resolution.

8.7 Related Procedures

- SOP 6-2 Well Development
- SOP 6-3 Well Purging - Bailing Method
- SOP 6-4 Well Purging - Pumping Method
- SOP 7-1 Slug Testing

9.0 ATTACHMENTS

9.1 Water Level Data Sheet

THE PAYNE FIRM, INC.
STANDARD OPERATING PROCEDURE

SUBJECT: Use of Turbidity Meters
(LaMotte Turbidimeter Model 2008)

PROCEDURE NO.: SOP 2-7

EFFECTIVE ISSUE DATE: November 19, 1993

REVISION NO.: 1

PRIOR EFFECTIVE DATE: July 15, 1993

SITE-SPECIFIC AMENDMENT: None

1.0 PURPOSE

The purpose of this procedure is to describe the steps necessary for calibration (standardization), operation (standardization) and maintenance of the LaMotte Turbidimeter Model 2008.

2.0 SCOPE

This procedure applies to the LaMotte Turbidimeter Model 2008. It may also be used in conjunction with manufacturer's instructions for other nephelometric turbidity meters.

3.0 REQUIREMENTS

The Model 2008 portable turbidimeter is acceptable for turbidity measurements reportable under either the National Primary Drinking Water Regulations (NPDWR) or the National Pollutant Discharge Eliminating System (NPDES) compliance monitoring program.

Turbidity measurements are to be performed and documented during the development of wells and where required by the project scope of work.

4.0 REFERENCES

Bates, Robert L. and Jackson, Julia A., 1987. *Glossary of Geology, 3rd Edition, American Geological Institute.*

LaMotte Chemical Turbidimeter Model 2008 Operator's Manual, Chestertown, Maryland, January 1990.

Renn, Charles E., October 1992. *Turbidity: Its Meaning and Measurement*, LaMotte Company,

Chestertown, Maryland.

United States Environmental Protection Agency, September 1986. *RCRA Ground Water Monitoring Technical Enforcement Guidance Document*, OSWER-99501.

5.0 DEFINITIONS

Jackson Candle - An apparatus that was used to measure influent and effluent water at treatment plants. Measurement is accomplished by adding or removing water in a long glass tube supported over a standard candle until the image of the candle flame becomes distinct. Jackson turbidity units are read off the calibrated scale on the glass tube.

Nephelometer - An instrument used to measure the amount of cloudiness of a medium. Measurement is accomplished by transmitting light through a fluid and detecting scattered light at a fixed angle (90 degrees) from the light source. Measurement is recorded in nephelometric turbidity units (NTUs).

Secchi Disc - An instrument used to measure surface water transparency or clarity. Measurement is accomplished by lowering a white disc of known diameter into a body of water. The average depth at which the disc disappears and reappears is recorded.

Turbidity - The state, condition or quality of opaqueness or reduced clarity of a fluid due to the presence of suspended matter. Turbidity may be quantified by measuring the ability of suspended matter to disturb or diminish the penetration of light through a fluid. Turbidity has been measured by means of a nephelometer, Secchi Disc or Jackson Candle apparatus.

6.0 RESPONSIBILITIES

6.1 Field Operations Leader

The Field Operations Leader is responsible for ensuring that the necessary equipment and supplies are available for calibration, operation and maintenance of the sampling equipment. Any equipment performance problems should be evaluated and resolved in conformance with the manufacturer's specifications. The Field Operations Leader is also responsible for ensuring that field calibration and operations are consistently applied during a project and that all field personnel have been instructed the turbidity meter.

6.2 Field Geologist/Field Engineer/Field Technician

Field personnel shall calibrate, operate and maintain the LaMotte Model 2008 Turbidimeter in conformance with this SOP. Any equipment performance problems shall be evaluated and communicated to the Field Operations Leader. Turbidity measurements, calibration and performance problems shall be documented in the Field Logbook.

7.0 EQUIPMENT AND SUPPLIES

LaMotte Model 2008 Turbidity Meter Case containing:

- AMCO™ Primary Turbidity Standards
- 0.5 NTU
- 5.0 NTU
- 40-ml standard vial
- 40-ml sample vial
- Deionized Water
- Membrane Filter
- Sample Syringe
- 120V/9VDC 500 mA AC Adaptor
- Model 2008 Turbidity Meter, LaMotte Company, Chestertown, MD
- Latex Gloves
- Lint-Free Paper Towels

8.0 PROCEDURE

The LaMotte Model 2008 turbidimeter is a true nephelometer, measuring the amount of light scattered at right angles from a beam of light passing through the test sample. Test results are read directly in nephelometric turbidity units (NTUs) on a liquid crystal diode (LCD) digital readout. Two ranges of magnitude make the Model 2008 a versatile instrument for testing turbidity in treated waters, natural waters and wastewaters.

The accuracy and repeatability of measurements is a necessary part of equipment operations and is a function of the condition of the standards, the technique and the quality of the glassware.

8.1 Calibration (Standardization)

Two standards are supplied with each Model 2008 turbidimeter, and others are available. The standards are used as a field check to calibrate or Standardize the instrument. Calibration will be performed at each sampling location or when excess variability is observed (see Section 8.3). Since the accuracy of results depends on the condition of the standards, the following observations and precautions are important:

- In an unopened bottle (as supplied) the standards will remain stable indefinitely as long as they are not exposed to excessively hot or cold environments. (Keep between 10° C and 40° C.)
- Once the seal is broken on the standards, the stability is only guaranteed for nine months thereafter, again based on normal environmental conditions.
- To ensure the accuracy of the standard, never transfer anything into the bottle (e.g., don't dilute, don't return standards that have been removed, don't combine with other standards, etc.)
- Do not open the standards in dusty environments, and guard against contaminants entering the bottle while it is open.
- When transferring the standard to a standard vial be certain that the vial is absolutely clean. A reasonable precaution is to rinse out the inside of the vial with the standard before filling the vial. This wastes a few mL of standard, but will minimize the possibility of contamination.
- After transferring the standard, promptly cap both the sample vial and the standards bottle.

8.2 Operation

The handling of the sample vials and the preparation of the sample is of utmost importance. The glassware must be clean and defect-free. Scratches and/or abrasions will permanently affect the accuracy of your readings by further scattering transmitted light.

The following procedure should be performed:

- Use a clean container to obtain a portion of the liquid to be measured. The volume should be sufficiently in excess of 40 ml to ensure rinsing and filling the sample vial. Set the container aside to allow the sample to equilibrate to ambient temperature and degas. Be sure to keep dust and other airborne contaminants from contact with the liquid.
- After the liquid has equilibrated, rinse the sample vial with a portion of the liquid and empty. Then completely, fill the sample vial making sure to avoid creating any air bubbles.
- Cap the vial and wipe the outside surface with a clean, lint-free, absorbent wipe until the vial is dry and smudge-free. Handling the vial only by its cap will avoid light scattering problems due to

fingerprints. Set the vial aside on a clean surface that won't contaminate or scratch the bottom of the vial.

- Select the appropriate range on the turbidimeter and insert a sample vial containing an AMCO™ standard with a value close to what you suspect the sample you are measuring to be.
- Be certain the chamber is capped, and that the vial is seated at the bottom of the chamber. The green front panel LED must be illuminated, indicating that the lamp is on. Adjust the *Standardization* control so that the display reads the known value of the chosen standard.
- Withdraw the standard and insert the vial with the sample to be measured. Again, make sure the chamber is capped and the vial is seated on the bottom. The reading should stabilize within 15 seconds. Make a note of the reading and withdraw the vial.
- If you wish to take repeated measurements or measure several samples in succession, it will not be necessary to readjust the *Standardization* before each reading. Once set it will remain stable as described in Section 8.1 above. Of course you may reinsert the standard at any time to verify the stability of the readings.

8.3 Problems of Variability

8.3.1 Glassware

The variability in the geometry and quality of the glassware is the predominate cause of variability in the readings that will be obtained.

No piece of glassware is ever perfectly cylindrical (or perfectly like any other). You will notice that if the vial is rotated in the chamber slightly (say in 15-degree increments) the reading will also vary somewhat. If the vial were always placed into the chamber with the same orientation this source of variability could be eliminated. This can be accomplished if the cap is marked in some way and always used with the same vial. When inserting the vial with its paired cap you can observe the mark on the cap and always insert it with the same orientation. It is especially useful to do this with the vial used for the AMCO™ standards; any variability in the standardization will affect all subsequent readings.

Once the rotational variability is compensated for, the residual uncertainty is a result of how well the vials match. If absolute accuracy is necessary in your readings, it is possible to calibrate the set of vials supplied with the turbidimeter. The procedure entails filling all the vials with the same sample, preferably a sample with a turbidity at the upper end of the range you will normally use, and recording the readings for each vial. The value of the readings are irrelevant, but they can be used to derive a

correction factor for each vial relative to any other vial. However, if monitoring trends and following small changes is more of a concern, the simple precaution of always using the same vial (in the same orientation) will effectively eliminate the ±2 percent uncertainty.

Following these precautions can allow the precision and repeatability of your readings to approach ±.01 NTU. Do not forget, however, that since the standardization procedure is based on the AMCO™ standard used, no reading can be considered to be more accurate than ±1 percent in an absolute sense.

8.3.2 Dilution of Samples

If the sample has a turbidity reading greater than 200 NTUs, it is necessary to dilute the sample with turbidity-free deionized water if a reading within the range of the instrument is desired. Turbidity-free deionized water may be prepared as described below. The following calculation is required if the sample is diluted:

$$\frac{A(B+C)}{C}=D$$

where: A = NTU found in diluted sample;
B = Volume of deionized dilution water used, mL;
C = Sample volume taken for dilution, mL; and
D = NTU of original, undiluted sample.

For example: If 10 mL of sample water is diluted with 90 mL of turbidity-free water to a total volume of 100 mL and the resulting solution measures 40 NTU, the turbidity of the original undiluted sample is:

$$\frac{40(90+10)}{10}=400\,NTU$$

Dilution increases the variability of a measurement due to volume uncertainty factors and the introduction of prepared turbidity-free water.

8.3.3. Preparation of Turbidity-Free Water

The preparation of turbidity-free water for the purposes of sample dilution requires careful technique. Introduction of any foreign matter will affect the turbidity reading. A filtering device with a special membrane filter is used to prepare turbidity-free water. The filter, filter holder, and syringe must be conditioned by forcing at least two syringe loads of deionized water through the filtering mechanism to remove foreign matter from the filtering apparatus. The first and second rinses are discarded. Turbidity-free water as prepared below may be stored in the dark at room temperature in a clear glass bottle with screw cap or in a turbidity vial (Code 0273) and used as required. The storage vessels should be rinsed thoroughly with filtered deionized water. Periodically inspect the water for foreign matter in bright light.

Note: The membrane filters are white and packaged between two blue protective disks. Handle membrane filter with extreme care.

Procedure:

- Unscrew the top of the filter holder and place a white membrane filter on the screen inside. The filter disc should be positioned carefully so that it covers the entire surface of the screen. Replace the top of the filter holder and screw on securely.
- Remove the plunger from the syringe, then attach the filter holder to the bottom of the syringe.
- Pour approximately 50 mL of deionized water into the barrel of the syringe. Replace plunger into barrel and exert pressure on the plunger to slowly force the water through the filter. Collect the water in a decontaminated container.
- Remove filter holder from syringe, then remove plunger from barrel. This step is required to prevent rupturing the membrane filter by vacuum as the plunger is removed from the barrel.
- Replace filter holder and repeat Steps 3 and 4 until the desired amount of turbidity-free water is collected. Periodically examine the membrane filter to ensure no holes or cracks are evident.
- Depending upon the nature of the unfiltered water, it is possible to prepare a liter or more of turbidity-free water using a single filter. The membrane filter may be stored in the holder for an indefinite period of time and used as required.

8.4 Quality Control

Duplicate turbidity measurements will be taken at each sampling location by retesting the sample. Both results shall be recorded. If the results differ by more than 2.0 percent of the previous reading, the meter shall be recalibrated and the sample retested.

8.5 Maintenance

No periodic maintenance is required. The most important considerations in assuring long life and accurate readings are:

- Keep the instrument clean and dry, especially the sample chamber. Keep the chamber capped except while inserting or removing sample vial. If the chamber needs to be cleaned, the best first choice is compressed gas. Photo-supply outlets sell an "aerosol" can of clean and dry gas for cleaning lenses - this is ideal. Hold the turbidimeter upside down while "squirting" it so that the particles will fall out and not be forced further into the bottom of the chamber.
- Be aware that the lamp will eventually "burn out", though its estimated service life in normal use is in excess of ten years. It is not user serviceable because the type of lamp used is not commonly available and its placement critically effects the calibration and so it is best replaced at the LaMotte Service Laboratory where the necessary calibration equipment is available. But also note that the lamp may become unstable and/or excessively dim well before it actually fails. A good test of lamp stability is to observe the display with a clean, dry and empty sample vial in the chamber. The actual value under these conditions is unpredictable (it will probably be between 1.50 and 3.00 NTU) but it should be stable (±0.02 NTU). As long as the display is stable the lamp is useable.
- Likewise the battery life is finite, though it is harder to estimate, since it is a function of use history and environmental conditions. As a rule, if AC power is available, use it instead of the battery. If the instrument is used occasionally (once a month or less), it will maximize battery life, if the function switch is left in the "Charge" position. Another useful practice is to continue using battery power only, once the instrument had been disconnected from the AC adaptor, until the battery low indicator is visible. Recharging from the fully discharged condition (Bat low indicator visible) to the fully charged condition (red LED extinguished) should take four to five hours. If it takes notably less than that, it is a sign of diminished battery capacity. Note that the turbidimeter may be used with the AC adaptor even with the totally exhausted and/or "worn out" batteries. If the battery capacity diminishes to the extent that they are no longer able to make as many measurements as you need between charging cycles, return the instrument for battery replacement.

8.6 Related Procedures

- SOP 6-2 Well Development
- SOP 4-7 Surface Water Sampling

9.0 ATTACHMENTS

None.

THE PAYNE FIRM, INC.
STANDARD OPERATING PROCEDURE

SUBJECT: Use of pH/Conductivity Meters (Presto-Tek Model DspH-1)

PROCEDURE NO.: SOP 2-9

EFFECTIVE ISSUE DATE: November 19, 1993

REVISION NO.: 1

PRIOR EFFECTIVE DATE: July 15, 1993

SITE-SPECIFIC AMENDMENT: None

1.0 PURPOSE

The purpose of this procedure is to describe the steps necessary for the proper calibration, operation and maintenance of the Presto-Tek Model DspH-1 combined pH/conductivity meter. Routinely, specific conductivity and pH measurements are taken for purge water prior to sampling to assess the stabilized condition of the water.

2.0 SCOPE

This procedure applies to all personnel who may use the Presto-Tek Model DspH-1 pH/conductivity meter and may be used for the same meter name-plated by other suppliers or for similar meters in conjunction with the manufacturer's instructions and specifications.

3.0 REQUIREMENTS

The pH/conductivity meter must be properly calibrated prior to each day's use and when there is reason to believe the instrument has been adversely affected by ambient site conditions. Calibration must be documented in the Equipment Logbook and noted in the Field Logbook prior to use at a site. The instrument must be properly operated and maintained as per this SOP. Any equipment malfunctions must be reported to the Field Operations Leader for resolution. The pH/conductivity meter must be cleaned, returned to its case and stored in the equipment room after use.

4.0 REFERENCES

Cole-Parmer Instrument Company, 1991/1992. *Hand-Held pH/Conductivity and pH/TDS Meters*. p. 179.

Operating and Calibration Instructions for Presto-Tek pH/Conductivity Meter Model DspH-1.

5.0 DEFINITIONS

pH - The negative $\log_{10}$ of the hydrogen-ion activity in solution; a measure of the acidity or basicity of a solution in dimensionless pH units.
pH/Conductivity Meter - A combined meter with two different electrode probes that measure the relative ion activity and electrical conductance via a weak, battery-induced current.
Specific Conductivity - The ability of water to transmit an electrical current, which is related to the concentration and charge of ions present in the water. Specific conductivity is measured in micromhos.

6.0 RESPONSIBILITIES

6.1 Field Operations Leader

The Field Operations Leader is responsible for ensuring that all field personnel have been trained in the use of this procedure and that the necessary equipment is available for calibration, operation and maintenance.

6.2 Field Geologist/Field Technician

Field personnel are responsible for understanding this procedure, properly calibrating, operating and maintaining the pH/conductivity meter and documenting the calibration and operation of the instrument.

7.0 EQUIPMENT

- Presto-Tek Model DspH-1 pH/Conductivity Meter (or same meter from different supplier)
- pH Calibration Standards (neutral 7, and acidic 4 or basic 10)
- Conductivity Calibration Standard (1,000 micromhos solution)
- Distilled Water
- Water Container
- Equipment Logbook
- Field Logbook
- Small Screwdriver (1/16-inch or smaller flat head)
- Latex Gloves
- 9-Volt Battery

8.0 PROCEDURE

8.1 General Information

The pH scale ranges from 0 to 14 pH units; 7 being neutral, >7 being basic and <7 being acidic. A properly calibrated meter will be able to measure pH accurately to ±0.1 pH units with a precision of 0.01. For best results, the instrument should be calibrated with a non-neutral standard that is within 3 pH units of the expected value for the test sample. Manufacturer's specifications indicate that the instrument has a built-in temperature compensation mechanism allowing use between 0 to 100° C (freezing and boiling points) water temperature.

This instrument is capable of measuring specific conductivity within a range of 0 to 20,000 micromhos. A properly calibrated conductivity meter will be able to measure specific conductance accurately to within ±2 % with a precision of 0.05 %. For best results a calibration standard that is close to the expected value should be used. Manufacturer's specifications indicate that the instrument has a built-in temperature compensation mechanism allowing use between 0 to 50° C water temperature.

8.2 Storage

When not in use, the pH/conductivity meter is stored in its case in the metal cabinet in the equipment room. The instrument should be signed out and in on the equipment log sheet. The instrument calibrated prior to use in the field.

8.3 Calibration

The pH/conductivity meter must be calibrated to both neutral and non-neutral pH standards and a conductivity standard.

8.3.1 pH Standards

The pH electrode is calibrated to a neutral standard to establish a reference point and to a non-neutral standard (typically 4.01 pH units) to control the measurement of any departure from neutral, which is referred to as slope. A properly calibrated instrument will have a consistent slope between the neutral and a specific non-neutral reference standard from one use to the next. An instrument that has not been

properly calibrated may have a slope, which has not been determined, that is steeper or flatter than it should be and consequently results in measurements that are above or below the true pH value. The following calibrations steps should be performed with reference to Attachment 9.1.

- Slide back the battery compartment cover exposing the adjustment potentiometers.
- Press the On switch and make sure the pH display is visible.
- Remove the protective pH cap-bottle from the pH electrode and the protective cap from the conductivity electrode.
- Rinse the probes in distilled water.
- Insert the probes in a fresh 7.00 pH standard solution.
- Allow the pH display value to equilibrate. This may take several minutes.
- Adjust the calibration (Cal) potentiometer until the display value stabilizes at 7.00.
- Remove the probes from the solution and rinse with distilled water.
- Insert the probes into a fresh 4.01 pH standard solution.
- Allow the pH display value to equilibrate. This may take several minutes.
- Adjust the slope potentiometer until the display value stabilizes at 4.01.
- Remove the probes from the solution and rinse with distilled water.
- Calibrate the conductivity electrode as described below.

8.3.2 Conductivity Standard

The conductivity electrode is zeroed and calibrated to a reference standard (typically 1,000 micromhos). Zero conductivity serves as the point of departure from which to measure test samples. Measurements are controlled by calibration to a known standard, which establishes a span. A properly calibrated instrument will have a consistent span from zero to the reference standard from one use to the next. An instrument that has not been properly calibrated may have a span, which has not been determined, that is greater or less than it should be and consequently results in measurements that are above or below the true specific conductivity value. The following calibrations steps should be performed with reference to Attachment 9.1 after pH has been calibrated.

- Rinse the probes thoroughly by agitating in distilled water.
- Wipe off the conductivity probe and allow to dry.
- Change the display readout to conductivity mode.
- Allow the conductivity display to equilibrate. This should take less than 30 seconds.

- Adjust the zero potentiometer until the display value stabilizes at 0000.
- Insert the probes into a fresh 1,000 micromhos conductivity solution.
- Allow the conductivity display to equilibrate. This should take less than 30 seconds.
- Adjust the span potentiometer until the display value stabilizes at 1,000 micromhos.
- Remove the probes from the solution and rinse with distilled water.
- Replace the protective caps and turn the instrument off.

8.4 Operation

After the pH/conductivity meter has been calibrated, it is ready for use at a work site. The following steps should be performed with reference to Attachment 9.1.

- Deploy the probes from the unit in either the 90 or 180-degree measurement position.
- Turn on the instrument by pressing the on/off switch.
- Remove the protective covers from the ends of the probes.
- Insert the probes into the test sample. The probes should be immersed no more than halfway into the test sample. Over-immersion risks introducing water to the internal circuits and damaging the instrument.
- Measure either the pH or specific conductivity by allowing the display value to stabilize. It does not matter which measurement is made first, although for the sake of consistency you may want to establish a sequence of operations which would lead to measuring specific conductance earlier since it tends to stabilize quickly, and pH later since it usually takes longer to stabilize.
- Measure the other parameter by changing the display mode.
- Remove the probes from the test sample and rinse thoroughly with distilled water.
- Replace the protective covers on the probes and return the instrument to its case.

8.5 Documentation

All calibrations of the pH/conductivity meter should be documented in the Equipment Logbook located in the equipment room. Calibrations should be noted in the Field Logbook or full documented if calibrated in the field. If calibration occurs in the field, the calibration information should also be entered in the Equipment Logbook. Equipment operations should be recorded in the Field Logbook.

8.6 Maintenance

Routine maintenance will extend the lifetime of the instrument and ensure that a properly operating instrument is available for use. The following procedures should be followed.

- The pH/conductivity meter should be calibrated prior to each day's use and on a regular schedule (monthly) when not in use.
- The 9-volt battery should be replaced periodically and an extra battery should be available in the field.
- The tip of the pH electrode should be kept moist at all times by immersion in distilled water with the protective cap-bottle.
- Dirt, oil, moisture or foreign materials should be wiped from the instrument with a soft cloth or paper towel.
- Care should be taken to not immerse the instrument housing in water, since this will damage the internal circuitry.

If instrument malfunctions are identified, the instrument should be sent to an authorized repair dealer for servicing.

9.0 ATTACHMENTS

9.1 DspH-1 pH/Conductivity Meter Parts Identification

THE PAYNE FIRM, INC.
STANDARD OPERATING PROCEDURE

SUBJECT: Use of Thermometers

PROCEDURE NO.: SOP 2-10

EFFECTIVE ISSUE DATE: November 19, 1993

REVISION NO.: 1

PRIOR EFFECTIVE DATE: July 15, 1993

SITE-SPECIFIC AMENDMENT: None

1.0 PURPOSE

The purpose of this procedure is to describe the operation and maintenance of thermometers. In combination with other parameters, temperature can be a useful indicator of the likelihood of physical, chemical or biological action in surface or ground water.

2.0 SCOPE

This procedure applies to the use of a thermometer to measure temperature of a ground water sample.

3.0 REQUIREMENTS

Temperature measurements are taken of *in situ* water or water measurements must be taken within one to two minutes of collection to record the water temperature before equilibration with ambient air temperatures. Temperature measurements must be documented in the field logbook or on the Ground Water Sampling form.

4.0 REFERENCES

Driscoll, F.G., 1986. *Ground Water and Wells*, Johnson Division, St. Paul, Minnesota, pg. 92-94.

5.0 DEFINITIONS

None.

6.0 RESPONSIBILITIES

6.1 Field Operations Leader

The Field Operations Leader is responsible for ensuring that the necessary equipment is available for use and that field personnel have been trained in the performance of this procedure.

6.2 Field Geologist/Field Technician

Field personnel shall properly operate and maintain thermometers and document measurements.

7.0 EQUIPMENT

- Thermometer
- Sample Container
- Latex Gloves
- Field Logbook
- Ground Water Sampling Form (Attachment 9.1)
- Deionized Water

8.0 PROCEDURE

8.1 The Situation

Temperature measurements are being taken as one of a set of ground water parameters prior to sampling.

8.2 Measurement

Temperature is commonly one of several parameters measured for ground water prior to sampling. Collected water samples may rapidly equilibrate with the temperature of their surroundings. Temperature should be measured within one to two minutes of collection. The following steps are generally performed.

- Water is collected into a container.
- The thermometer is immersed in the sample until temperature equilibrium is obtained (one to two minutes) with the instrument. To avoid the possibility of contamination, the thermometer shall not be inserted into samples which will undergo subsequent chemical analysis.
- The temperature is recorded in the field logbook or sample log sheet.

8.3 Maintenance

The thermometer shall be rinsed and returned to its sleeve after use. Broken thermometers shall be disposed and reported to the Field Technician for replacement.

8.4 Related Procedures

- SOP 6-3 Well Purging-Bailing Methods
- SOP 6-4 Well Purging-Pumping Method
- SOP 6-5 Ground Water Sampling

9.0 ATTACHMENTS

9.1 Ground Water Sampling Form

THE PAYNE FIRM, INC.
STANDARD OPERATING PROCEDURE

SUBJECT: Collection of an Air Sample (Summa® Passivated Canister)

PROCEDURE NO.: SOP 2-11

EFFECTIVE ISSUE DATE: November 19, 1993

REVISION NO.: 0

PRIOR EFFECTIVE DATE: New

SITE-SPECIFIC AMENDMENT: None

1.0 PURPOSE

The purpose of this procedure is to describe a method for sampling ambient or headspace air for laboratory analysis. The method utilizes a Summa® Passivated Canister to collect an air sample, which is subsequently analyzed for volatile organic compounds (VOCs) with gas chromatography by Environmental Protection Agency (EPA) Method TO-14.

2.0 SCOPE

This procedure applies to the collection of an air sample from either ambient air or headspace air associated with enclosed spaces or partially enclosed spaces. This procedure may also be used to sample air associated with soil, water or other restricted areas.

3.0 REQUIREMENTS

Air sampling must be planned during project scoping and include details such as sample location, restrictions upon sample collection (ambient air conditions such as temperature, wind speed, humidity, etc.) and duration of sampling (grab sample or time composited sample).

Air sampling details must be recorded in the field logbook and/or on a Summa® Canister Sampling Field Data Sheet.

4.0 REFERENCES

United States Environmental Protection Agency, May 1988. *Compendium Method TO-14, The Determination of Volatile Organic Compounds (VOCs) in Ambient Air Using Summa® Passivated Canister Sampling and Gas Chromatographic Analysis*, Quality Assurance Division Environmental

Monitoring Systems Laboratory, United States Environmental Protection Agency, Research Triangle Park, North Carolina.

5.0 DEFINITIONS

Summa® Canister - A stainless steel air sampling canister with a capacity of six liters which has been treated by the Summa® passivation process and is capable of sustaining a vacuum of 0.05 mm Hg. Valves are fitted with special "valve-saver" handles which allow the valve to be closed to a sufficient torque but then slip to prevent over-tightening and damage to the valve. For time composite samples, a vacuum flow regulator is mounted on the side valve. This regulator is preset by the contract laboratory to a rate corresponding to the total anticipated sample time. Attached to the regulator is a particulate filter to prevent clogging of the fine passages in the vacuum flow regulator.

6.0 RESPONSIBILITIES

6.1 Project Manager

The Project Manager is responsible for determining the need to sample ambient air associated with a ground water seep or other restricted area and incorporating the need into the project work plan.

6.2 Field Operations Leader

The Field Operations Leader is responsible for ensuring that field personnel have been trained in the use of this procedure and that the necessary air sampling equipment is available for use.

6.3 Field Geologist/Field Technician

The Field Geologist/Technician is responsible for performing the field collection and documenting the activity in the field logbook and on the chain-of-custody record.

7.0 EQUIPMENT

- Field Logbook
- Scope of Work
- Summa® Passivated Canister evacuated and supplied by the analyzing laboratory

- Teflon tubing
- Portable vacuum pump and valve with T-connector
- Watch with second hand
- Temporary air barricade (i.e., plywood sheeting, cardboard, plastic sheeting, tyvek or sand bags)

8.0 PROCEDURE

8.1 Planning

Air sampling is planned during project scoping. Planning should include an assessment of the data needs and objectives of the air sample in order to determine specific sampling parameters. Planning considerations may include whether the sample is to represent a source emission for a dispersion model or to represent previously dispersed contaminants. Source emission samples require collection immediately adjacent to the source and may require a temporary air barricade to restrict interference with ambient air.

The type of sample to be collected, either a grab or time composite, must also be specified to the analytical laboratory at the time of ordering the Summa® canister. If a time composite sample is required, the laboratory mounts a preset vacuum flow regulator corresponding to the total sample time specified (by the user) to fill the six-liter canister.

8.2 Scope of Work

A scope of work is formulated by the Field Operations Leader based on the project work plan and is communicated to field personnel. Scoping details are also communicated to the laboratory so that the Summa® canister can be prepared and shipped to the site for sampling.

8.3 Set Up

Prior to establishing the exact location for the collection of the air sample, field screening is performed utilizing a direct reading instrument [i.e., photo-ionization detector or flame-ionization detector (PID/FID)]. The general area being considered for air sampling is screened to determine potential "hot spots."

When collecting a sample from an enclosed or partially enclosed space, a field assessment is made

regarding whether temporary barricading is needed to limit the mixing of ambient air and the air to be sampled. This temporary barricading may be constructed out of plywood sheeting, cardboard, plastic sheeting, tyvek and/or sand bags. The construction of the barricade should limit the movement of air into and out of the space.

8.4 Sample Collection

The air sample is collected in accordance with the following protocols and information is recorded on the Summa® Canister Sampling Field Data Sheet (Attachment 9.1).

- Check the vacuum integrity of the canister by reading the vacuum gauge. The vacuum gauge should show approximately 30 inches Hg. If the vacuum is less than 28 inches, the canister should not be used.
- Attach the pre-evacuated, six-liter Summa® canister and a portable vacuum pump with a T-connector to an intake probe (tubing) with the valves on the probe and canister closed.
- The intake probe is evacuated for a sufficient time to remove the probe volume of gas at standard temperature and pressure.
- After purging is completed but prior to shutting off the vacuum pump, the valve between the pump and the T-connector is closed. The vacuum pump can then be shut off.
- With the probe valve open and the canister valve shut, the probe is allowed to equilibrate to ambient pressure.
- After the vacuum gauge on the probe has read zero vacuum for one minute, the valve on the Summa® Canister is gradually opened to allow a slow, even flow rate for the collection of the sample. If a preset regulator is used, open the valve two turns. The maximum-minimum thermometer on the canister is reset to the current temperature.
- Sampling is completed after the vacuum gauge on the probe has read zero vacuum for one minute.
- The valves on the canister and the probe are then closed. The sampling probe equipment is disconnected from the canister;
- The canister tag is labeled according to SOP 1-3, "Labeling and Custody of Samples," with the project number, client/project name, sample ID, date, time, sample type, sampler's initials and analysis/remarks. **DO NOT ATTACH ADHESIVE LABELS DIRECTLY TO CANISTERS. ATTACH LABELS TO THE TAGS PROVIDED.**
- The sample is shipped to the laboratory, within 24 hours of collection according to SOP 1-4, "Packaging and Shipping of Samples."

8.5 Documentation

The Field Geologist/Technician records and documents all air sampling activities and measurements. At a minimum, the information must be sufficient to complete the Summa® Canister Sampling field Data Sheet (Attachment 9.1) and Sample Labels (SOP 1-3).

8.6 Related Procedure

- SOP 1-1 Use of Field Logbooks
- SOP 1-3 Labeling and Custody of Samples
- SOP 1-4 Packaging and Shipping of Samples
- SOP 2-1 Use of Flame-Ionization Detectors
- SOP 2-2 Use of Photo-Ionization Detectors

9.0 ATTACHMENTS

9.1 Summa® Canister Sampling Field Data Sheet

THE PAYNE FIRM, INC.
STANDARD OPERATING PROCEDURE

SUBJECT: Use of Toxic Vapor Analyzers (TVA-1000) **Procedure No.:** 2-14

EFFECTIVE ISSUE DATE: March 19, 1996 **Revision No.:** 0

PRIOR EFFECTIVE DATE: New

SITE SPECIFIC AMENDMENTS: None

1.0 PURPOSE

The purpose of this procedure is to describe the steps necessary for the proper calibration, operation, and maintenance of the Foxboro Toxic Vapor Analyzer (TVA), Model TVA-1000. The TVA is used as an individual or concurrent photo ionization detector (PID) and flame ionization detector (FID) for monitoring or field screening organic compounds present in ambient air or soil and water offgas.

2.0 SCOPE

This procedure applies to all personnel who may use the TVA and/or data resulting from its operation. It may also be used in conjunction with the manufacturer's instructions and specifications for other TVAs.

3.0 REQUIREMENTS

- **Calibration** - prior to each day's use and when there is reason to believe the instrument has been affected by ambient site conditions.
- **Operation** - as per this SOP and the manufacturer's specifications.
- **Maintenance** - as per this SOP and the manufacturer's specifications.
- **Recharge** - by connection to battery charger for period not greater than 96 hours.
- **Log In/Log Out** - in equipment logbook for each use.
- **Documentation** - of calibration and use in equipment and field logbooks.
- **Prompt Notification of Malfunction** - to Equipment Technician and Senior Geologist.

4.0 REFERENCES

- **Foxboro Company, August 31, 1993.** Instruction Book 3455, TVA1000A, Toxic

Vapor Analyzer.

- **Foxboro Company, February 1995.** TVA1000 - Response Factor Information: Photoionization and Flame Ionization Detectors.
- **United States Environmental Protection Agency, December 1987.** A Compendium of Superfund Field Operations Methods, EPA/540/P-87/001.

5.0 DEFINITIONS

Calibration - Prior to each day's use and when there is a reason to believe the instrument has been affected by ambient site conditions.

Flame Ionization Detector (FID) - An organic vapor detector which ionizes gases and vapors in a hydrogen flame to detect and measure organic compounds. An electrical field drives the ions to an electrode generating a current corresponding to the rate of collection. The current is calibrated to a standard for relative response.

Ionization Potential (IP) - The energy required to completely remove the outermost electron from its ground state in an atom or molecule. Measured in electron-volts (eV).

Photo Ionization Detector (PID) - An organic vapor detector in which gas molecules are ionized by ultraviolet light. An electrical field drives the ions to an electrode generating a current corresponding to the rate of collection. The current is calibrated to a standard for relative response.

Relative Response Factor - A percent or a ratio of a compound's response to that of the calibration gas.

6.0 RESPONSIBILITIES

6.1 Project Manager

The Project Manager shall determine specific monitoring or field screening requirements employing the TVA and incorporate its use into the project work plan or scope of work.

6.2 Field Operations Leader

The Field Operations Leader is responsible for ensuring that all field personnel have been trained in the use of this procedure and that the necessary equipment is available for calibration, operation and maintenance.

6.3 Field Geologist/Field Technician/Equipment Technician

Field personnel are responsible for understanding the use of this procedure, properly calibrating, operating, and maintaining the TVA, documenting the calibration and operation of the instrument, and reporting any instrument malfunctions for resolution.

7.0 EQUIPMENT

- Foxboro TVA-1000
- Foxboro Carrying Case
- Foxboro TVA Battery Charger
- Hydrogen Gas with Compressed-Gas Bottle Wrench and Regulator
- Methane Calibration Gas with Regulator
- Total Organic Vapor Probe
- Probe with Activated Carbon Filter Pack
- Activated Carbon Granules
- Water Trap Probe
- Permanent Marker
- Equipment Logbook
- Field Logbook

8.0 PROCEDURES

Attachments 9.1 through 9.5 depict physical parts of the TVA for reference.

8.1 General Information

The TVA has been approved as intrinsically safe by CENELEC, CSA, and FM testing laboratories for specific hazardous situations. The Foxboro Instruction Book (p. 7) identifies

the product safety specifications. Further details can be obtained from the Foxboro Company at 508-543-8750.

The FID portion of the instrument is fueled by a detachable pressurized hydrogen cylinder. If the hydrogen cylinder is shipped to a site by commercial carrier, it must conform with procedures for the shipment of dangerous goods (Section 8.9).

Operational settings for the instrument must be reviewed and documented prior to use to ensure that the desired data collection mode is set and that subsequent interpretation of the data is accurate. Setting options are discussed in Section 8.5.2.

The sensitivity of the TVA to numerous chemicals is presented in the Foxboro Response Factor Information (February 1995) document in the equipment room. Selected chemical information from that document is presented in Section 8.1.4.

8.1.1 Theory of Instrument Detection and Measurement

Attachment 9.1 shows a schematic for the gas flow to the FID and PID.

The FID mode utilizes the principle of hydrogen flame ionization for the detection and measurement of organic vapors. Organic vapor concentrations are determined by measuring the response of a sample of unknown organic vapor concentration relative to a standard. Organic vapors are continuously drawn through a probe assembly to a detector chamber via an internal pumping system. Inside the detector chamber, the sample stream is exposed to a hydrogen flame which ionizes the organic vapors. An electrical field drives the ions to a collecting electrode. A current corresponding to the collection rate is generated and displayed on the front panel liquid crystal display (LCD) as well as the probe assembly LCD display. Readout is displayed in both measured values and as a logarithmic bargraph. The current is proportional to the organic vapor concentration of the calibration standards.

The PID mode utilizes the principle of photo ionization for the detection and measurement of organic vapors. Photo ionization occurs when an atom or molecule absorbs a photon of sufficient energy to release an electron and become a positive ion. The source of photons is an ultra violet lamp with an energy of 10.6 or 11.8 eV. Unknown organic vapors are drawn, via a positive displacement pump, through a probe attached at the side surface of the

analyzer. Inside the chamber, the sample gas is exposed to photons emanating from the ultraviolet light. Ionization occurs for those molecules having an ionization potential near to or less than that of the lamp. A positive-biased electrode causes the ions (which are positively charged) to travel to a collector electrode where the ions create an electrical current which is amplified and displayed on an LCD readout as measured values and as a logarithmic bargraph. The display can be read off both the sampling probe and the main data display.

8.1.2 TVA Specifications

Unless otherwise noted, the following specifications apply to the TVA assuming that the PID is calibrated to 100 ppm of isobutylene and the FID is calibrated to 100 ppm of methane.

CATEGORY	PID	FID
Accuracy	± 25% or ± 2.5 ppm, whichever is greater	± 25% or ± 2.5 ppm, whichever is greater
Repeatability	± 1%	± 2%
Dynamic Range	0.5 to 200 ppm	1.0 to 50,000 ppm
Linear Range	0.5 to 500 ppm	1.0 to 10,000 ppm
Minimum Detection Level	100 ppb of benzene	300 ppb of hexane
Response Time - Total	<3.5 seconds for 90% of final value	<3.5 seconds for 90% of final value*
Recovery Time - Charcoal	<20 seconds to return to 10% of original	<20 seconds to return to 10% of original*
Sample Flow Rate	1 liter/minute	1 liter/minute
Primary Power	Internal Battery	Internal Battery
Fuel Supply	NA	Hydrogen
Max Fuel Pressure	NA	2200 psi
Operating Time	8 hours	8 hours
Operating Temperature	32 to 104 degrees F	32 to 104 degrees F
Relative Humidity	20 to 90%	20 to 90%

*FID using 10,000 ppm of methane

8.1.3 TVA Limitations

The following limitations apply to the use of the TVA as an FID and/or PID.

- The FID will not detect inorganic volatiles. However, the PID will detect certain inorganic volatiles such as ammonia, carbon disulfide, hydrogen sulfide, and nitric oxide, using the appropriate lamp.
- The PID will not detect methane due to the high ionization potential of methane.
- The current PID lamp in the TVA is 10.6 eV and will not ionize (and thereby detect) compounds with a higher ionization potential (e.g., Chloroform, Methanol, Methyl Chloride, Methylene Chloride, 1,1,1-TCA).
- Low oxygen levels affect the characteristics of the hydrogen flame (FID) and may cause readings to be artificially elevated or the flame to be extinguished.
- Relative humidities outside of the operating range may cause inaccurate or unstable responses.
- Temperatures outside of the operating ranges may cause slow, inaccurate or unstable responses.
- Actual contaminant concentrations are measured relative to the calibration gases used. Specific contaminants and concentrations are not identified.
- The TVA responds differently to different compounds. Selected response factors are presented in Section 8.1.4.

8.1.4 Relative Response Factors

Detailed response factor information for the TVA and its ability to measure volatile vapors may be found in Foxboro (1995). The reference lists information for both PID and FID operation, with PID calibration to isobutylene and FID calibration to methane. Response factor information may be used to evaluate whether the TVA is capable of detecting volatile compounds of interest. Selected relative response factors of chemicals to PID and FID operation are listed below. Responses for other chemicals may be found in Foxboro (1995).

COMPOUND	USING PID LAMP eV	FOXBORO TVA PID RELATIVE RESPONSE	FOXBORO TVA FID RELATIVE RESPONSE	PUBLISHED IONIZATION POTENTIALS eV
Acetone	10.6	59	124	9.69
Ammonia	10.6	13	NR	10.15
Ammonia	11.8	17	NR	10.15
Benzene	10.6	132	356	9.25
Bromoform	11.8	123	15	10.50
Butane	11.8	50	181	10.63
Butanone,2- (MEK)	10.6	77	189	9.53
CFC-12	11.8	NR	21	12.91
Chlorobenzene	10.6	135	327	9.10
Chloroform	11.8	27	41	11.37
Dichloroethylene, trans-1,2	10.6	117	108	10.00
Ethyl Benzene	10.6	114	370	8.76
Hexane	10.6	12	250	10.18
Hexane	11.8	91	262	10.18
Methanol	11.8	19	27	10.85
Methyl Chloride	11.8	63	76	11.28
Methylene Chloride	11.8	49	78	11.40
Methyl-2-Pentanone,4 (MIBK)	10.6	64	184	9.30
Styrene	10.6	148	344	8.47
Tetrachloroethylene	10.6	108	106	11.10
Tetrachloroethylene	11.8	168	106	11.10

COMPOUND	USING PID LAMP eV	FOXBORO TVA PID RELATIVE RESPONSE	FOXBORO TVA FID RELATIVE RESPONSE	PUBLISHED IONIZATION POTENTIALS eV
Toluene	10.6	125	297	8.82
Trichloroethane,1,1,1-	11.8	48	132	11.25
Trichloroethylene	10.6	112	94	9.45
Vinyl Chloride	10.6	39	87	10.00
Xylenes	10.6	127	293	8.56

NR - No Response

- Lamp Not Currently In Stock

8.1.5 TVA Warning Displays

The TVA may display the following WARNINGS that require appropriate responses.

- BATTERY POWER IS LOW
- PUMP MUST BE ON TO SELECT MODE
- LOGGER MEMORY IS ALREADY FULL
- FID FLAMEOUT! IGNITE AGAIN
- PID LAMP NOT OPERATING
- BAD CALIBRATION PARAMETERS
- HARDWARE FAILURE
- PID LAMP MUST BE ON TO CONTINUE
- ENTRY IS INVALID!
- LOG RATE TOO SLOW FOR PC STEL CALC
- LOG RATE INVALID!

8.2 Storage and Fueling

When not in use, the TVA is kept in the field equipment room. The instrument should be signed out and in on the equipment log sheet and calibration should be performed prior to use in the field. The instrument requires two hours of charge for each hour of use.

Each TVA has a detachable 85cc hydrogen gas cartridge that requires periodic refueling (Attachment 9.2). Each cartridge is rated to be filled to a maximum pressure of 2,200 psi at 77° F. However, the cartridge should not be filled greater than 2,000 psi.

The hydrogen supply tank is located in the locked utility cage located at the rear of the Payne Firm offices. When refueling is necessary the following procedure should be performed with reference to Attachments 9.1 and 9.2.

- Obtain the hydrogen cage key (#54) from the equipment room.
- Transport the TVA hydrogen cartridge to the utility cage and unlock the gate.
- Make sure the supply tank valve is OFF.
- Attach the TVA hydrogen cartridge to the tank fill adapter. (Note left hand thread - *do not overtighten.*)
- Open supply valve. Slowly move fill adapter to FILL position.
- Wait for TVA cartridge to fill. This may take 2 to 3 minutes because of flow restrictors in the tank and fill adapter.
- Close the fill adapter valve.
- Remove the TVA cartridge.
- Close the supply tank valve.

Note: Always remove the hydrogen cartridge from the instrument after use or when not begin used further during the day.

8.3 Instrument Display and Menus

The TVA is operated by a series of menu-driven setup procedures that are initiated through the keypad on the face of the instrument. Attachment 9.3 shows the instrument keypad. Functions for the keys are presented in the following table.

Key	Function
ON	Enables power from the battery
OFF	Enables power from the battery
CONTROL	Turn pump and PID on or off and ignite FID
EXIT	Clears entry made in error or bypasses information
ENTER	Responds to a menu question, records data when making manual VOC measurements
Left/Right Arrows	Move character entry position
Up/Down Arrows	Make page selection or switch from PPM, PPB, or %
Alphanumeric	Enables typing characters into menus

The Main Menu consists of the following selections.

Menu Selection	Function
1 = RUN	Assign tags to specific surveys and view the real time analysis of organic/inorganic compounds
2 = SETUP	Configuration procedures and menu structure for performing calibrations, entering ID numbers, setting alarm levels, setting log rate, and entering time/date information
3 = INFO	Displays most SETUP parameters previously entered
4= PCLink/Memory	Download information to a PC, perform a remote SETUP from a PC, or clear memory

Attachment 9.6 shows the complete menu structure for the TVA.

8.4 Calibration

To provide the specified accuracy, the TVA must be calibrated prior to each day's use.

Note: Prior to performing calibration, the TVA must be ON and warmed up for approximately 30 minutes. Throughout the warmup period, the pump must also be ON and the FID flame ignited. For STARTUP, proceed to Section 8.5.1.

Calibration of the TVA consists of four basic steps: 1) establishing a zero or background reference point; 2) measuring a volatile gas reference point, termed span; 3) defining the actual concentration of the span gas; and 4) setting the relative response factor.

- From the MAIN menu, select 2=SETUP, then 1=CALIBRATION.

Calibration may proceed with the FID, PID or both, which requires selection at each step of the process. Be sure to have calibration gases readily available. Zero of background calibration may be done for the PID and FID simultaneously. Span calibration uses separate gases for the PID and FID and is done consecutively.

- From the CALIBRATION menu, select either 1=ZERO or 2=BACKGRND.

Follow instructions on the display. Apply the zero gas or ambient background to the probe (Attachment 9.4) and press ENTER=START. The TVA will display that it is calibrating and indicate ACCEPTED when done. The CALIBRATION menu will then appear automatically.

- From the CALIBRATION menu, select 3=SPAN
- From the PID/FID SPAN CAL menu, select 2=PID (or 3=FID)

Follow instructions on the display. Apply the span gas (isobutylene for PID; methane for FID) and press ENTER=START. The TVA will display that it is calibrating and indicate ACCEPTED when done. The CALIBRATION menu will then appear automatically. The gas concentration will then need to be defined to the TVA.

- From the CALIBRATION menu, select 4=GASCONC.

- From the PID/FID SPAN GAS menu, select 2=PID (or 3=FID).
- Input the concentration of the span gas and press ENTER

Note: The span gas concentration may be entered as a percent, parts per million, or part per billion. The display can be changed to the desired entry unit by pressing the UP/DOWN keys. A unit of parts per million units is the standard setting.

- Press EXIT to return to the Calibration menu.

Repeat the span calibration and definition steps for the FID (or PID).

The response factor setting should be 1.00 for both the PID and FID unless otherwise required for a project. The setting should be verified before use.

- From the CALIBRATION menu, select 5=RESPONSE FACTOR.

The settings for both the PID and FID will be displayed. If either is different than 1.00, then select the appropriate mode (PID or FID), input 1.00, and press ENTER.

Zero and span calibration dates are stored in memory for later access. The most recent calibration date may be viewed by selecting 3=INFO, from the MAIN menu. Calibration information should be documented in the Calibration and Field Logbooks.

8.5 Operation

Operation of the TVA involves specific startup, operational settings, and shutdown steps. Prior to use in the field, the instrument must be calibrated (Section 8.4) and sufficient fuel must be present in the hydrogen cartridge (Section 8.2), if the FID is to be used. The following discussion assumes that both the FID and PID functions will be used. If only the PID function is used, then instructions pertaining to the hydrogen cartridge and the FID may be disregarded. The following steps should be performed with reference to Attachments 9.2 through 9.5 Steps are discussed with reference to facing the instrument keypad.

8.5.1 Startup

- Install the hydrogen cartridge in the instrument (upper left side).
- Connect the sample probe (two connections at top).
- Press the ON key. The status of the BATTERY, NV RAM, and DATE/TIME will be displayed. The TVA will perform a 15 second internal diagnostic SELF TEST after which the MAIN menu will appear. If the status is OK, then proceed.
- Press the CONTROL key.
- From the CONTROL menu, select 1=TURN PUMP ON. The pump will turn on and the MAIN menu will reappear.
- Turn the red hydrogen supply valve (top) to the ON position and let the instrument pump for at least 30 seconds.
- Press the CONTROL key.
- From the CONTROL menu, select 2=IGNITE. The hydrogen flame will ignite and the MAIN menu will reappear.

Note: The PID function will be ON unless turned OFF from the CONTROL menu.

Note: Prior to performing calibration or operation, the TVA must be ON and warmed up for approximately 30 minutes. Throughout the warmup period, the pump must also be ON and the FID flame ignited. Field operation must also account for this warmup period.

If CALIBRATION is being performed, proceed to Section 8.4. For OPERATION:

- From the MAIN menu, select 1=RUN.

The instrument is now functioning as per the operational setting.

8.5.2 Operational Settings

Operational parameters should be set or verified prior to using the TVA. Parameters include:

- **Calibration** (see Section 8.4)

- Alarm Levels (only if required by project for health and safety monitoring)
- Time of Day and Date (to be reset only after seasonal time change or February 29)
- **Logging Methods** (discussed below)
- Reader Port Initialization (only if used to download stored information)
- User Identification Number (Payne Firm Instrument #)
- Other Optional Settings (optional, see manual)

Instrument logging options include: 1=NONE; 2=AUTO; and 3=VOC.

The NONE option registers information digitally in the same manner as the analog OVA (SOP 2-1), the analog HNu (SOP 2-2), and the digital OVM (SOP 2-3). In this mode the vapor reading on the display (Attachment 9.2) and the probe readout (Attachment 9.5) is observed to fluctuate and is not stored in memory. The AUTO and VOC options provide a means to record results on the display and store results in memory, if the mode is properly initialized. The AUTO sampling mode records vapor readings at a periodic interval when this setting is initialized **and provides a means to reduce measuring error resulting from visual observation of the readout while in the NONE mode. VOC mode is the preferred option.** The VOC mode records the highest reading during a ten second interval when this setting is initialized. To set the LOGGING METHOD:

- From the MAIN menu, select 2=SETUP.
- From the SETUP menu, select 3=LOG.
- From the LOG MODE menu, select 1=NONE, 2=AUTO, or 3=VOC.

If AUTO mode is selected, then a prompt for the automatic logging rate will be displayed. A rate between 1 second and 999 minutes may be typed and entered.

Data collection can then proceed in RUN mode.

AUTO and VOC modes are initialized to record and store vapor readings by: 1) typing a tag identifier using the alphanumeric character keys; 2) pressing the ENTER key to record the tag identifier; and then 3) pressing the LOG key on the probe or the ENTER key on keypad to initialize the data recording process. Pressing the EXIT key will end the AUTO mode initialization. Each VOC log must be done manually and individually. **If the AUTO or VOC mode is not initialized, then the instrument operates as if it were in NONE mode.**

8.5.3 Background Readings

When screening samples, background readings for PID and FID (both total and "methane" probes) operation should be measured and recorded periodically. These readings serve as a point of departure to adjust the measured values for samples. For instance, the following table shows hypothical background and sample readings and the resulting adjustment.

	PID	FID	
Readings		Total	Methane
Background	0.16	-0.92	-1.08
Sample	0.40	0.21	-0.94
Adjusted	0.24	1.13	0.14

8.5.4 Shutdown

- Press and hold the OFF key.
- Turn the red hydrogen supply valve to the OFF position.
- Remove the hydrogen cartridge if no further use is planned for the day.

8.6 Maintenance

Instrument maintenance consists of routine, periodic, and supplier responsibilities.

Note: The user must not open the instrument housing for any reason. Opening the TVA housing may void the warranty. A seal is present on the right side of the instrument.

8.6.1 Routine Maintenance

Routine maintenance is performed by the user before and after use. This maintenance

includes:

- Charging the battery
- Refilling the hydrogen cartridge
- Refilling the charcoal filter adapter
- Cleaning the instrument housing and case.

8.6.2 Periodic Maintenance

Periodic maintenance is performed monthly or as needed by the Equipment Technician. This maintenance may include:

- Removing and cleaning the PID (blue) and/or FID (red) cartridge (right side)
- Cleaning the PID and/or FID cavity
- Cleaning or replacing the sintered metal filter in the sampler assembly (probe) and sidepack assembly (top)
- Removing and cleaning the FID end cap and flame arrestor (right side)
- Replacing the sample line tubing (probe)

The manual should be consulted for specific procedures.

8.6.3 Supplier Maintenance

The instrument supplier or an authorized dealer will perform specialized maintenance of the TVA on an annual basis or as needed. This maintenance includes:

- Cleaning
- Testing
- Calibration

8.7 Quality Assurance/Quality Control

Quality Assurance/Quality Control is achieved by:

- properly calibrating, operating, and maintaining the instrument

- documenting calibration and maintenance events in the Calibration and Equipment Logbooks
- documenting ambient conditions during use in the Field Logbook
- obtaining background readings of ambiant air for PID and FID (both total and "methane" probes) operation

8.8 Documentation

Use of the TVA requires the following documentation:

- Sign In/Sign Out in the Equipment Logbook
- Calibration details entered in the Calibration Logbook
- Ambient conditions during use noted in the Field Logbook
- Any problems encountered during use entered in the Field and Equipment Logbooks
- Resolution of equipment problems kept in the Equipment Logbook

8.9 Shipping

The FID portion of the instrument is fueled by a detachable pressurized hydrogen cartridge. If the hydrogen cartridge is shipped to a site by commercial carrier, it must conform with procedures for the shipment of dangerous goods (SOP 1-4). The following steps must be taken:

- A Shipper's Certification for Dangerous Goods form must accompany the hydrogen cartridge (Attachment 9.7).
- A Cargo Aircraft Only label (Attachment 9.8) must be placed on the hydrogen cartridge container.
- A Flammable Gas label (Attachment 9.9) must be placed on the hydrogen cartridge container.
- The UN identification number for the dangerous goods must be visible on the hydrogen cartridge container. The hydrogen gas ID is UN 1049.
- A copy of the Shipper's Certification for Dangerous Goods form should be kept with the cartridge at all times while on the project, and must be included in the project file at the conclusion of use.

Civil and criminal penalties can result from improper shipment of the hydrogen cartridge.

9.0 ATTACHMENTS

9.1 TVA Gas Flow Schematic

9.2 TVA Face, Side, Top and Bottom Views

9.3 TVA Keypad

9.4 TVA Probe

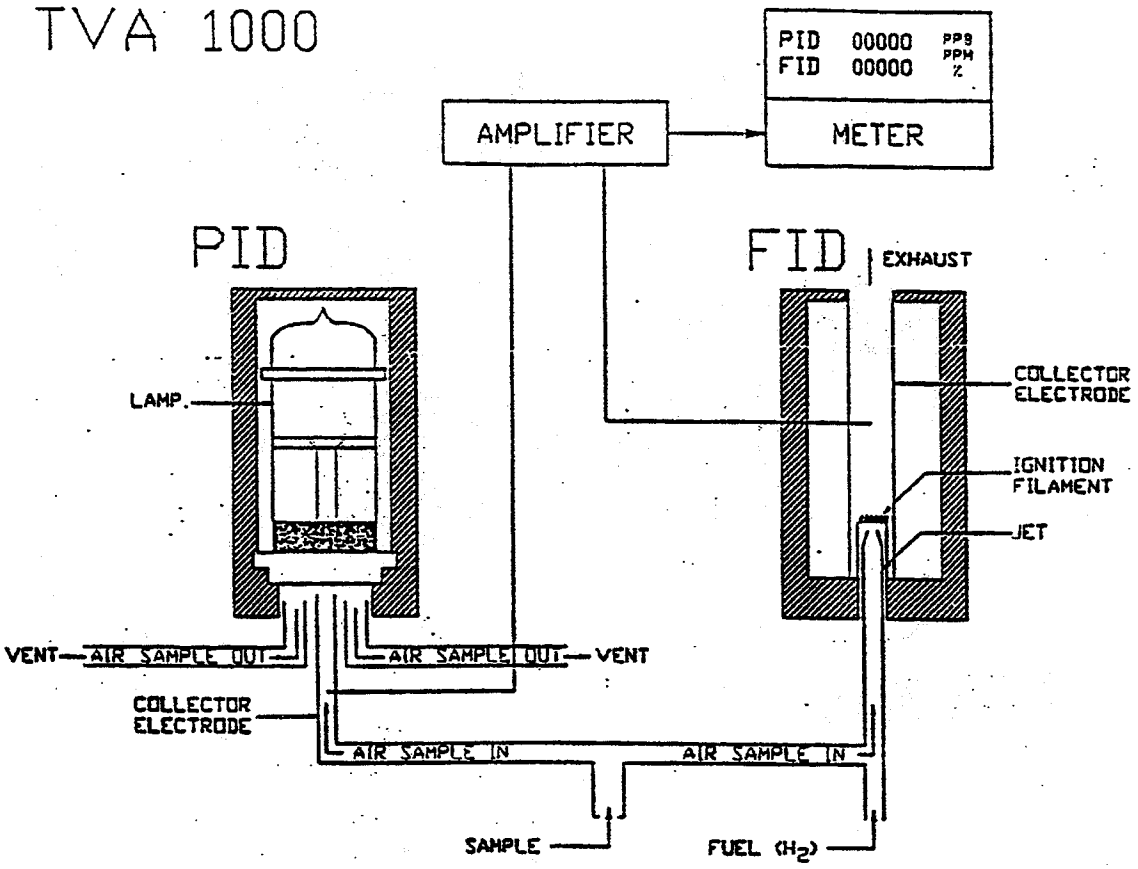
9.5 TVA Probe Face

9.6 TVA Menu Structure

9.7 Example Shipper's Certification for Dangerous Goods

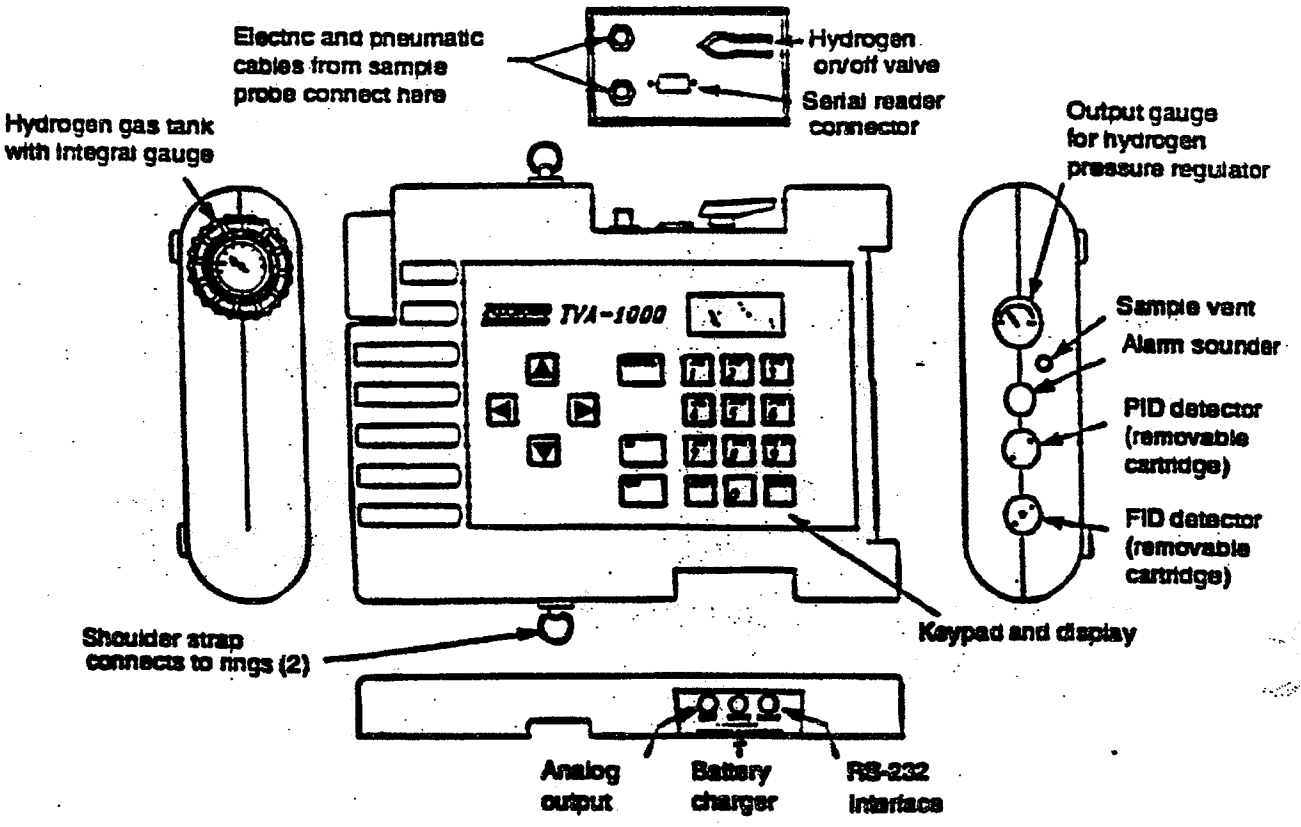
9.8 Example Cargo Aircraft Only Label

9.9 Example Flammable Gas Label



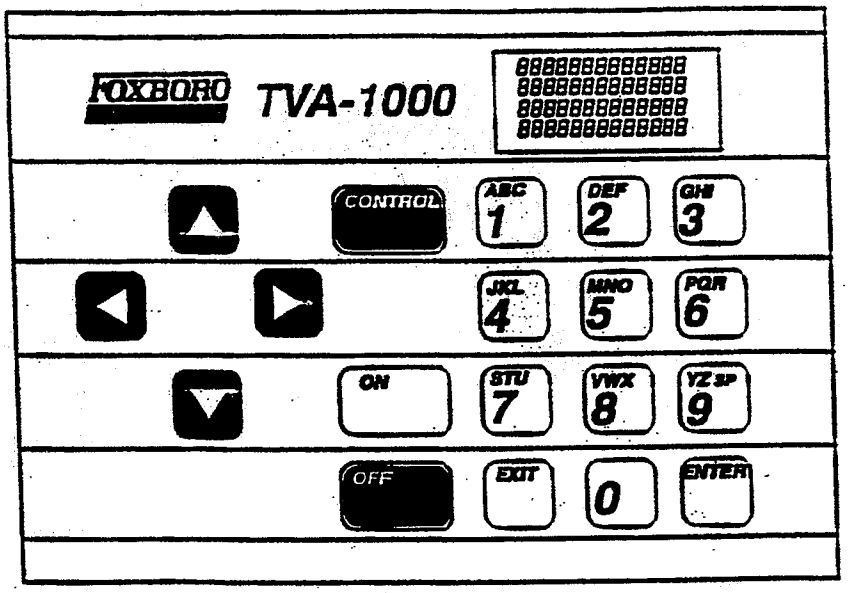
ATTACHMENT 9.1

TVA GAS FLOW SCHEMATIC



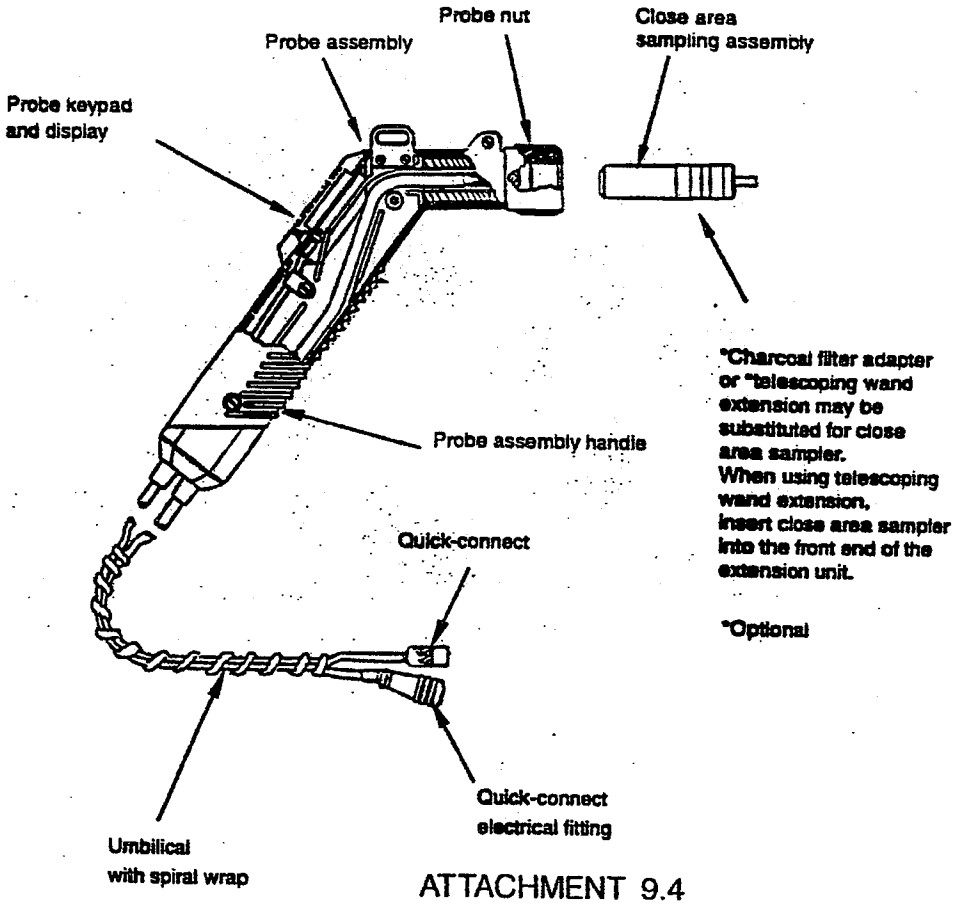
ATTACHMENT 9.2

TVA FACE, SIDE, TOP AND BOTTOM VIEWS



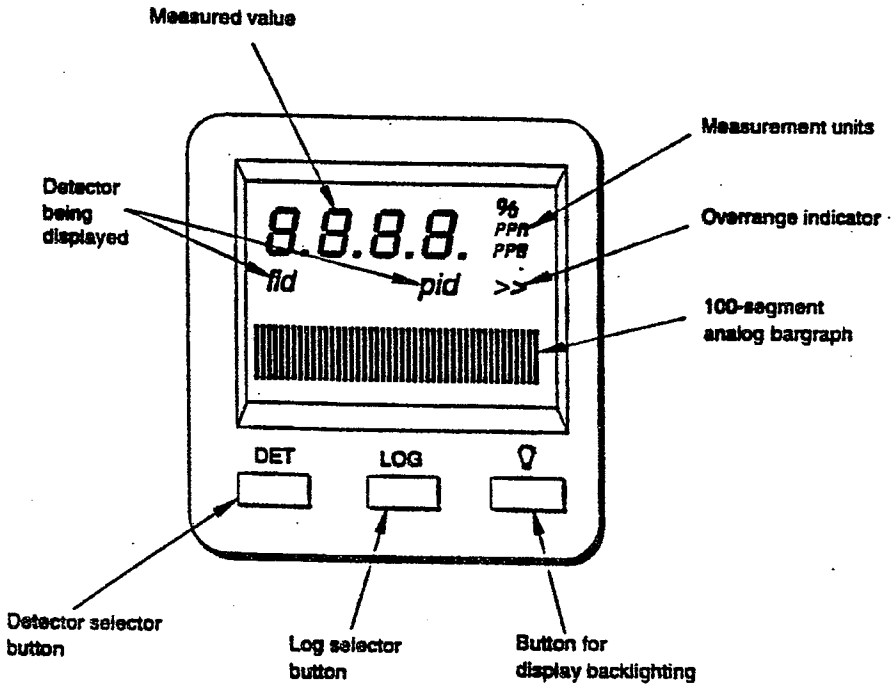
ATTACHMENT 9.3

TVA KEYPAD



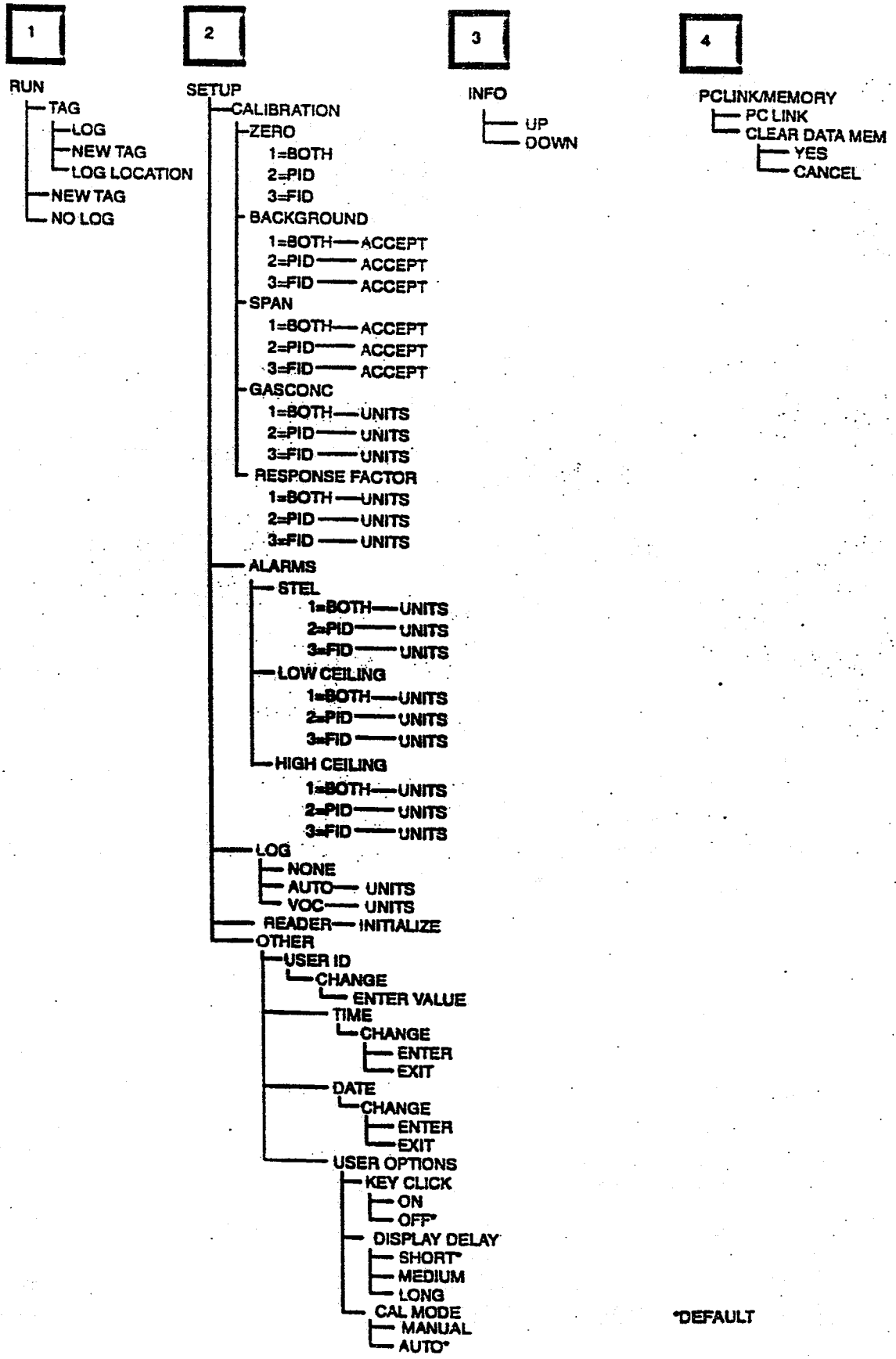
ATTACHMENT 9.4

TVA PROBE



ATTACHMENT 9.5

TVA PROBE FACE



ATTACHMENT 9.6

TVA MENU STRUCTURE

FEDERAL EXPRESS

USE THIS AIRBILL FOR DANGEROUS GOODS SHIPMENTS ONLY WITHIN THE CONTINENTAL U.S.A., ALASKA AND HAWAII
USE THE INTERNATIONAL AIR WAYBILL FOR SHIPMENTS TO PUERTO RICO AND ALL NON U.S. LOCATIONS
QUESTIONS? CALL 800-238-5355 TOLL FREE.

AIRBILL PACKAGE TRACKING NUMBER 9763211743

48 1057M 9763211743

ORIGIN COPY

Sender's Federal Express Account Number: 1096-3133-7
Date: 09/22/93

From (Your Name) Please Print: Joe Geologist
Your Phone Number (Very Important): (513-489-2255
Company: The Payne Firm, Inc.
Department/Floor No:
Street Address: 11231 CORNELL PARK DR
City: CINCINNATI
State: OH
ZIP Required: 45242

To (Recipient's Name) Please Print:
Recipient's Phone Number (Very Important):
Company:
Department/Floor No:
Exact Street Address (We Cannot Deliver to P.O. Boxes or P.O. Zip+4 Codes):
City:
State:
ZIP Required:

YOUR INTERNAL BILLING REFERENCE INFORMATION (First 24 characters will appear on invoice.)
500.00.00

IF HOLD FOR PICK-UP, Print FEDEX Address Here (Not available at all locations)
Street Address:
City:
State:
ZIP Required:

PAYMENT 1 [X] Bill Sender 2 [ ] Bill Recipient's FedEx Acct. No. 3 [ ] Bill 3rd Party FedEx Acct. No. 4 [ ] Bill Credit Card
5 [ ] Cash/Check
Acct./Credit Card No.
Exp. Date

SERVICES (Check only one box)
- Priority Overnight Service (Delivery by next business afternoon) 1 [X]
- Standard Overnight Service (Delivery by next business afternoon) 5 [ ]
- Economy Two-Day Service (Delivery by second business day) 30 [ ]
- Heavyweight Service (for Extra Large or Extra Heavy packages over 150 lbs.) 70 [ ] HEAVYWEIGHT* 80 [ ] EXPRESS HEAVYWEIGHT*
- *Call for delivery schedule.

DELIVERY AND SPECIAL HANDLING (Check services required)
1 [ ] HOLD FOR PICK-UP
2 [ ] DELIVER WEEKDAY
3 [ ] DELIVER SATURDAY
4 [X] DANGEROUS GOODS
6 [ ] DRY ICE
- Dangerous Goods Shipper's Declaration not required
- Dry Ice, 9, UN 1845, kg
7 [ ] OTHER SPECIAL SERVICE
11 [ ]
12 [ ] HOLIDAY DELIVERY

Packages	Weight	Value Declared (Dollars)
1	35	
Total	Total	Total

DIM SHIPMENT (Dimensions / Weight) [ ] lbs.

Payment By
1 [ ] Regular Stop 3 [ ] Drop Box
2 [ ] On-Call Stop 4 [ ] 95C
5 [ ] Station
FedEx Emp No
Date/Time

INSTRUCTIONS (Check only one box)
- Dangerous Goods as per attached Shipper's Declaration [ ]
- Dangerous Goods Shipper's Declaration not required [ ]
- Cargo Aircraft only [X]

SERVICE CONDITIONS, DECLARED VALUE AND LIMIT OF LIABILITY

Use of this airbill constitutes your agreement to the service conditions in our current Service Guide, available upon request. See back of sender's copy of this airbill for minimums.

We will not be responsible for any claim in excess of $100 per package, whether the result of loss, damage, delay, non-delivery, misdelivery, or misinformation, unless you declare a higher value, pay an additional charge, and document your actual loss at time of shipment. Maximum amount transportation found in the current Federal Express Service Guide apply. Your right to recover from Federal Express for any loss, including intrinsic value of the package, loss of sales, income interest, profit, attorney's fees, costs, and other forms of damages whether direct, incidental, consequential, or special is limited to the greater of $100 or the declared value specified in (4). Recovery cannot exceed actual documented loss. The maximum Declared Value for FedEx Letter and FedEx Pak packages is $100.00.

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Declared Value Charge
Other 1
Other 2
Total Charges
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043
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9763211743 AIRBILL NUMBER

SHIPPER'S CERTIFICATION FOR RESTRICTED ARTICLES/DANGEROUS GOODS (TYPE OR PRINT)
CHECK ONE ▶ [ ] 49 CFR [ ] IATA/ICAO

DANGEROUS GOODS IDENTIFICATION: PROPER SHIPPING NAME	CLASS OR DIVISION	UN OR ID NO	SUBSIDIARY RISK	QUANTITY AND TYPE OF PACKING	PACKING INST	AUTHORIZATION
Hydrogen, Compressed	Flammable Gas	UN 1049		2 x 1 pound cylinders		

ADDITIONAL HANDLING INFORMATION
Cargo Aircraft Only

TRANSPORT DETAILS	THIS SHIPMENT IS WITHIN THE LIMITATIONS PRESCRIBED FOR ▶	XPASSENGER X AIRCRAFT	CARGO AIRCRAFT ONLY	(DELETE-NONAPPLICABLE)
AIRPORT OF DEPARTURE	AIRPORT OF DESTINATION / SHIPMENT TYPE ▶	NON-RADIOACTIVE	XXXXXXXX	(DELETE-NONAPPLICABLE)

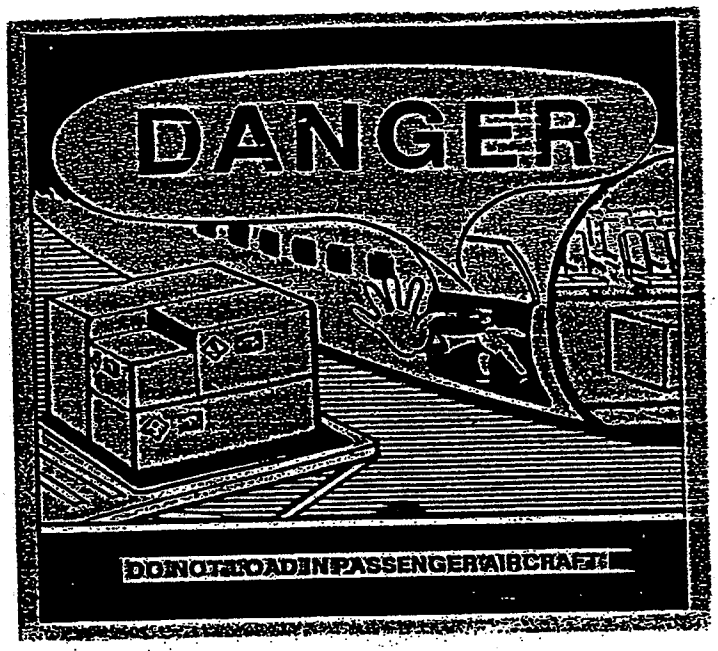
IF ACCEPTABLE FOR PASSENGER AIRCRAFT, THIS SHIPMENT CONTAINS RADIOACTIVE MATERIAL INTENDED FOR USE IN, OR INCIDENT TO, RESEARCH, MEDICAL DIAGNOSIS OR TREATMENT.

I HEREBY DECLARE THAT THE CONTENTS OF THIS CONSIGNMENT ARE FULLY AND ACCURATELY DESCRIBED ABOVE BY PROPER SHIPPING NAME AND ARE CLASSIFIED, PACKED, MARKED, AND LABELED, AND ARE IN ALL RESPECTS IN PROPER CONDITION FOR TRANSPORT BY AIR ACCORDING TO THE APPLICABLE INTERNATIONAL AND NATIONAL GOVERNMENT REGULATIONS.

NAME AND TITLE OF SHIPPER
PLACE AND DATE
EMERGENCY TELEPHONE NUMBER: 513-489-2255
SIGNATURE OF SHIPPER
SEE WARNING ON BACK

ATTACHMENT 9.7

EXAMPLE SHIPPER'S CERTIFICATION FOR DANGEROUS GOODS



ATTACHMENT 9.8

EXAMPLE CARGO AIRCRAFT ONLY LABEL

ATTACHMENT 9.9

EXAMPLE FLAMMABLE GAS LABEL

THE PAYNE FIRM, INC.
STANDARD OPERATING PROCEDURE

SUBJECT: Observation of Drilling Equipment Decontamination **PROCEDURE NO.:** SOP 3-1

EFFECTIVE ISSUE DATE: November 19, 1993 **REVISION NO.:** 1

PRIOR EFFECTIVE DATE: July 15, 1993

SITE-SPECIFIC AMENDMENT: None

1.0 PURPOSE

The purpose of this procedure is to describe the kinds of observations made and recorded as necessary to document the proper decontamination of drilling equipment by the drilling subcontractor in conformance with a scope of work during a field investigation.

2.0 SCOPE

This procedure applies to the observation and documentation of drilling equipment decontamination activities by the drilling subcontractor prior to initiating borehole drilling. This procedure may also apply to decontamination of other heavy equipment.

3.0 REQUIREMENTS

Proper decontamination of drilling equipment minimizes the potential for cross-contamination between sampling locations and the transfer of contamination off-site. Decontamination must be included in project planning. Projects that require drilling activities must have the decontamination need identified. The decontamination needs should be communicated to the client, accounted for in the project work plan, and included in the scope of work to the drilling subcontractor. Decontamination practices must be standard in the field, verified with the scope of work and consistent with the needs of the project.

4.0 REFERENCES

United States Environmental Protection Agency, September 1986. *Resource Conservation and Recovery Act (RCRA) Ground Water Monitoring Technical Enforcement Guidance Document, OSWER-9950.1.*

United States Environmental Protection Agency, November 1986. *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*, EPA-SW-846, Third Edition.

United States Environmental Protection Agency, December 1987, *A Compendium of Superfund field Operations Methods*, EPA/540/P-87/001.

5.0 DEFINITIONS

Cross-Contamination - Is a type of positive contamination caused by the introduction of part of one sample into a second sample during sampling, storage or analysis.
Negative Contamination - Occurs when the measured concentration of an analyte is artificially low as a result of volatilization, adsorption dilution or related losses.
Positive Contamination - Occurs when the measured concentration of the analyte is artificially high due to the introduction of foreign contaminated matter into the sample.
Tap or Potable Water - Shall be water from a public, treated water supply system.

6.0 RESPONSIBILITIES

6.1 Project Manager

The Project Manager is responsible for incorporating decontamination needs into the project work plan and ensuring the decontamination procedures for all drilling equipment are established prior to the actual field effort.

6.2 Field Operations Leader

The Field Operations Leader is responsible for ensuring that the drilling scope of work includes the project-required decontamination procedures, the drilling subcontractor complies with the scope of work, an appropriate decontamination area is set up and that field personnel properly document decontamination procedures.

6.3 Field Geologist

The Field Geologist is responsible for observing decontamination procedures by the drilling subcontractor and documenting the activity in the Field Logbook.

7.0 EQUIPMENT

- Field Logbook
- Drilling Scope of work

The drilling subcontractor should supply:

- Portable High-Pressure Steam or Hot Water Generator
- Sheet Plastic
- Decontamination Containment, as required

8.0 PROCEDURE

8.1 Planning

Decontamination needs should be assessed and included as part of the project work plan or scope of work. Any special requirements should be identified and communicated to the drilling subcontractor as part of a drilling scope of work. The scope of work shall be communicated to the drilling subcontractor verbally or in writing. If verbally, details must be noted and placed in the project file, and the scope of work must be confirmed with the driller prior to initiation of work.

8.2 Decontamination Set-Up

After arrival on-site, the Field Operations Leader shall identify the decontamination area for the drilling subcontractor. If pre-arranged, the decontamination area location should be described in the project work plan. The location should be away from investigation areas and should have sufficient space to be able to decontaminate applicable parts of the drill rig or other heavy equipment and to store decontamination equipment and structures. Assistance with access to potable water and electricity will be supplied to the subcontractor, if necessary.

The required decontamination set-up, as specified in the scope of work, will be assembled by the subcontractor. The decontamination set-up may consist of all or any part of the following (as specified by the project needs):

- Plastic Sheeting
- Saw Horses

- Metal Trough
- Constructed Decontamination Containment

8.3 Equipment Decontamination

Drilling equipment should be decontaminated at the subcontractor's shop prior to arrival to prevent cross-contamination from another site. After arrival on-site, prior to each new borehole and at the end of the project, the back of the drill rig, applicable tools, downhole equipment and other heavy equipment used to penetrate the ground surface (e.g., backhoe, trackhoe, etc.) should be decontaminated as per the scope of work. At a minimum, decontamination should consist of cleaning with high-pressure steam or hot water generator. Non-phosphate detergent washing and potable water rinsing may be used as necessary.

8.4 Specific Observations

The following kinds of decontamination details by the drilling subcontractor are to be looked for:

- Decontamination in the designated area only
- Control of decontamination wastes as per the scope of work
- Complete decontamination of external surface of tools and downhole equipment
- Decontamination of internal surface of casing and hollow stem augers
- Placement of plastic sheeting as necessary
- Maintenance of decontaminated equipment in a decontaminated condition

9.0 ATTACHMENTS

None.

THE PAYNE FIRM, INC.
STANDARD OPERATING PROCEDURE

SUBJECT: Observation of Hollow Stem Auger Drilling Activities **PROCEDURE NO.:** SOP 3-2

EFFECTIVE ISSUE DATE: November 19, 1993 **REVISION NO.:** 1

PRIOR EFFECTIVE DATE: July 15, 1993

SITE-SPECIFIC AMENDMENT: None

1.0 PURPOSE

The purpose of this procedure is to establish the minimum requirements for recording field observations pertinent to document continuous flight hollow stem auger drilling activities.

2.0 SCOPE

This procedure applies to the observation of hollow stem auger drilling activities by a subcontractor to advance a borehole. These drilling activities result in the collection of samples to determine the type, thickness and certain physical and chemical properties of the soil, water and/or rock strata which underlie the site.

3.0 REQUIREMENTS

Hollow stem auger drilling activities must be planned for and incorporated into the project work plan and drilling scope of work. Appropriate documentation of drilling activities must be performed and maintained on file to record borehole locations, ensure proper drilling of the borehole, provide a framework for recording physical and chemical data, and verify compliance with the scope of work by the drilling subcontractor.

4.0 REFERENCES

United States Environmental Protection Agency, *Manual of Water Well Construction Practices*, Office of Water Supply, USEPA, Washington, D.C.

United States Environmental Protection Agency, September 1986. *Resource Conservation and Recovery Act (RCRA) Ground Water Monitoring Technical Enforcement Guidance Document*, OSWER-9950.1.

United States Environmental Protection Agency, December 1987. *A Compendium of Superfund Field Operations Methods*, EPA/540/P-87/001.

5.0 DEFINITIONS

Hollow Stem Auger Drilling - Consists of screwing augers with an open center into the ground. Cuttings are brought to the surface by the rotating action of the auger. Soil samples can be taken using split-spoon (split-barrel) or thin wall tube samplers inserted through the hollow stem and driven into the substrata in advance of the auger.

6.0 RESPONSIBILITIES

6.1 Project Manager

The Project Manager is responsible for incorporating any required hollow stem auger drilling activities into the project work plan.

6.2 Field Operations Leader

The Field Operations Leader is responsible for ensuring that field personnel have been trained in the use of this procedure and for verifying that auger drilling activities are being performed in compliance with the project work plan and the drilling scope of work. The Field Operations Leader in conjunction with the project manager should determine the appropriate disposal methods for soil cuttings generated by drilling and identify any specialized supplies or logistical support required for the activities. These activities should be documented in the Field Logbook. The Field Operations Leader may use the Field Logbook entries to verify subcontractor invoicing for materials or hourly rate work.

6.3 Field Geologist

The Field Geologist is responsible for observing drilling activities and recording observations made during drilling in the Field Logbook. A copy of the logbook entries will be provided to the Field Operations Leader for review and inclusion in the project files.

7.0 EQUIPMENT

- Field Logbook
- Drilling Scope of Work

8.0 PROCEDURE

8.1 Planning

A scope of work shall be formulated and communicated to the drilling subcontractor. Communication may be written or verbal. If verbal details must be noted and placed in the project file and the scope of work must be confirmed with the driller prior to arrival on-site.

Prior to arriving at the site drilling location, the Field Geologist and Field Operations Leader will confer regarding pertinent aspects of the drilling scope of work related to the day's drilling activities.

8.2 The Situation

All preparatory activities including Hazard Recognition (SOP 1-5) have been accomplished so that drilling can commence.

8.3 Documentation

Hollow stem auger drilling activities will be documented in the Field Logbook as per SOP 1-1 "Use of Field Logbooks."

Specific information and observations relative to hollow stem auger drilling will include the following as applicable:

- Drilling company
- Drill crew names
- Type of drill rig
- Internal diameter of auger
- Borehole identification
- Borehole location
- Borehole diameter
- Start and finish of drilling activities

- Types of drilling activities (e.g., augering, reaming, etc.)
- Delays in drilling
- Sampling devices
- Relevant footages including:
  - total depth
  - ground water depth
  - sampling intervals
  - auger refusal
  - sampler refusal
- Application of lubricants to downhole equipment - only vegetable-based, petroleum-free lubricants (specific brand name) to be used

8.4 Related Activities

During the course of monitoring hollow stem auger drilling, related activities will be performed and documented as specified in the project work plan or other SOPs. These activities may include:

- Health and safety monitoring (as per the site-specific Health and Safety Plan)
- SOP 1-5 Recognition of Physical Hazards
- SOP 3-1 Observation of Drilling Equipment Decontamination
- SOP 3-5 Borehole Logging
- SOP 3-6 Borehole Abandonment
- SOP 4-2 Installation of Monitoring Wells
- SOP 4-3 Installation of Injection Wells
- SOP 4-4 Installation of Piezometers
- SOP 4-6 Well Abandonment
- SOP 5-2 Soil Sampling

8.5 Verification

Documentation of hollow stem auger drilling activities will be used to verify that the needs of the work plan have been met, the drilling scope of work has been complied with and that invoicing matches what has been recorded.

9.0 ATTACHMENTS

SUBJECT: Observation of Hollow Stem Auger Drilling Activities **PROCEDURE NO.:** SOP 3-2

EFFECTIVE ISSUE DATE: November 19, 1993 **REVISION NO.:** 1

PRIOR EFFECTIVE DATE: July 15, 1993

SITE-SPECIFIC AMENDMENT: None

None.

THE PAYNE FIRM, INC.
STANDARD OPERATING PROCEDURE

SUBJECT: Borehole Logging

PROCEDURE NO.: SOP 3-5

EFFECTIVE ISSUE DATE: November 19, 1993

REVISION NO.: 1

PRIOR EFFECTIVE DATE: July 15, 1993

SITE-SPECIFIC AMENDMENT: None

1.0 PURPOSE

The purpose of this procedure is to establish uniform guidelines and minimum requirements for describing soil on a Log of Boring under field conditions using visual and manual methods. The visual and manual methods discussed herein provide information that may approximate laboratory determinations but are not intended to replace geotechnical or analytical testing. This procedure incorporates the main elements of the Unified Soil Classification System, which are grain size and cohesiveness, but is not intended to require generation of the group symbols of that system.

2.0 SCOPE

This procedure applies to describing soil from drilled or hand-augered boreholes and excavations or trenches where the vertical soil profile can be observed. The principles discussed herein can also be applied to other soil samples in which borehole logging is not required.

3.0 REQUIREMENTS

Uniform soil description methods are essential to accurate characterization of subsurface soil conditions at a site. Soil description must include estimation of the relative concentration of particle sizes, characterization of color, soil moisture conditions, unusual odors and an indication of cohesiveness. Additional information may include a characterization of the shape and angularity of sand or gravel and the consistency, cementation or hardness fine-or coarse-grained soils. Soil structures must be described, if present. Soil samples must be described on a Log of Boring form prior to sampling.

4.0 REFERENCES

American Society of Testing and Materials, June 1990. *Standard Practice for Description and Identification of Soils (Visual-Manual Procedure)*, D2488-90.

United States Environmental Protection Agency, December 1987. *A Compendium of Superfund Field Operations Methods*, EPA/540/P-87/001.

5.0 DEFINITIONS

Angularity - Description of the surface of coarse sand and larger particle sizes. Specific descriptors include angular, subangular, subrounded and rounded.

Cohesiveness - The capacity to stick or adhere together.

Consistency - Description of the cohesiveness of fine-grained soils. Specific descriptors include very soft, soft, medium stiff, firm, stiff and hard.

Fabric - The physical nature of a soil with respect to the spatial arrangement of its components, such as grain size, structure and void spaces.

Friable - Description of cohesiveness of coarse-grained soils referring to easily crumbled nature.

Grading - A trend in grain size moving up or down within a stratified unit. Descriptors include fining upward and coarsening upward.

Grain Size - Size of particles comprising soil or rock. Sizes include clay, silt, sand, gravel, cobbles and boulders.

Plasticity - Description of the ability of a soil to undergo permanent deformation without appreciable volume change, elastic rebound and rupture.

Relative Density - Description of the relative hardness of penetrating non-cohesive soils. Specific descriptors include very loose, loose, medium dense, dense and very dense.

Shape - Description of the shape of gravel, cobbles and boulders. Specific descriptors include flat, elongated or both.

Slickensided - Description of soil structure referring to fracture planes that appear polished or glossy.

Soil - For the purposes of this SOP, soil is considered to include the following materials: 1) loose unconsolidated surface sediments; 2) topsoil; 3) unconsolidated material above bedrock; 4) fill material; 5) stream sediments; and 6) deposits in sediment traps.

Sorting - The degree of similarity of particles in soil. Descriptors include well-sorted and poorly-sorted.

Structure - Description of the fabric of intact soils. Specific descriptors include stratified, laminated, fissured, slickensided, blocky, lensed and homogenous.

Texture - The physical nature of soil with respect to the relative proportions of grain sizes.

6.0 RESPONSIBILITIES

6.1 Field Operations Leader

The Field Operations Leader is responsible for ensuring that field personnel have been trained in the use of this procedure, that the minimum requirements and any project-specified additional characteristics of soil are logged in a consistent manner, and that computer-generated logs of boring are consistent with the field logs.

6.2 Field Geologist/Field Technician

Field personnel are responsible for understanding and implementing this procedure, completing applicable parts of the Log of Boring, and checking the field log against any computer-generated facsimiles.

7.0 EQUIPMENT

- Clipboard
- Log of Boring forms (Attachment 9.1)
- Field Logbook
- Tape Measure
- Knife or Spatula (Stainless Steel)
- Particle Size Gauge
- Color Gauge

- Ink Pen (Blue or Black)
- Acid Bottle
- Hand Lens
- Pocket Penetrometer

8.0 PROCEDURES

8.1 Log of Boring

Soil is collected from a borehole by one of the methods discussed in the "Soil Sampling Procedure" (SOP 5-2). Prior to containerizing samples, soil is described on the Log of Boring form (Attachment 9.1). The boring log includes the following basic identifying information for the borehole:

- Borehole Identification
- Client
- Project Location
- Project No.
- Driller
- Geologist
- Date

Other pertinent information regarding the method of sampling, decontamination procedures, drilling procedures including size of augers or casing (if applicable) and specific location are identified in the Field Logbook or on-site plans as necessary.

Information that is generated during the course of borehole logging is recorded directly on the Log of Boring. This information may include but need not be limited to the following items:

- Total Depth
- Headspace Organic (HSO) Vapor Measurements
- HSO Instrument
- Blow Counts (when driving split-barrel samplers)
- Soil Sampling Interval
- Soil Recovery in the Sampling interval

- Sample Number
- Initial Ground Water Level

Refer to the Boring Log Legend for details (Attachment 9.2)

8.2 Soil Description Components

Soil description always includes an estimate of the percent range of grain size concentrations, color, moisture content and cohesiveness. Additional parameters may include unusual odors, the recognition of fill, angularity, shape, structure, sorting, grading and evidence of organic content.

8.3 Grain Size

The size of particles comprising soil is typically defined by the ability of the particle to pass through or be trapped by a sieve of a certain mesh. Field practicality requires an alternative classification scheme. The following table identifies grain size ranges corresponding in part to sieve definitions.

Particle	Exact Size Limits (mm)	Approximate Inches	Sieve Size
Boulders	> 300	> 11.8	
Cobbles	75 - 300	2.9 - 11.8	
Coarse Gravel	19 - 75	0.75 - 2.9	
Fine Gravel	4.8 - 19	0.19 - 0.75	4
Coarse Sand	2.0 - 4.8	0.08 - 0.19	4 - 10
Medium Sand	0.43 - 2.0	0.02 - 0.08	10 - 40
Fine Sand	0.08 - 0.43	0.003 - 0.02	40 - 200
Silt and Clay	< 0.08	< 0.0003	< 200

The relative abundance of the component grain sizes is indicated in the soil description by associating key words with the identified particle sizes in order from most abundant to least. The following key words are used to indicate estimated percentages:

Key Word	Estimated Percent of Sample
And	30 - 50
Some	12 - 30
Little	5 - 12
Trace	< 5

Soil components with an estimated percent greater than 30 are considered the primary constituents of the soil and are capitalized in the description. The following examples illustrate this method.

- GRAVEL AND SAND, little silt, trace clay
- SILT AND CLAY, little sand
- CLAY, some silt, trace gravel, trace sand
- SILT, SAND AND GRAVEL, trace clay

Grain size and cohesiveness are primary components of the Unified Soil Classification System (Attachment 9.3).

8.4 Color

Soil color is described using a single color descriptor preceded by a modifier to denote variations in shade or color mixtures. Colors must be described from broken or split soil while the sample is fresh and moist. The term "mottled" is used to indicate soils irregularly marked with spots of different colors. The following examples illustrate the description of color:

- light gray
- mottled gray-brown
- dark brown
- greenish-gray

Color is identified immediately after grain size.

8.5 Moisture Content

A description of moisture content is critical to the evaluation of potential water-bearing horizons in the subsurface. Moisture content is described as dry, moist or wet. A qualifying adjective may be appended to moist as necessary. Moisture content is identified immediately after color.

8.6 Cohesiveness

Soil cohesiveness is evaluated by the consistency of fine-grained soils or the relative density of coarse-grained soils. Consistency may be determined by blow counts per foot when driving split-barrel samplers or by thumb penetration. Relative density is gauged by blow counts per foot or otherwise implied as non-cohesive for coarse-grained soils. The second and third six-inch blow-count intervals are used to evaluate cohesiveness using split-barrel samplers. The following tables identify field criteria for determining the consistency or relative density of soils.

TERM	FIELD TEST (After Cooling, Skempton and Glossip)
Very Soft	Squeezes between fingers when fist is closed.
Soft	Easily molded by fingers.
Firm	Dented by strong pressure of fingers.
Stiff	Dented only slightly by finger pressure.
Hard	Dented only slightly by pencil point.

Consistency of Fine Grained Soils Standard Penetration Test		Relative Density of Sand Standard Penetration Test	
Blows Over One Foot Penetration	Consistency	Blows Over One Foot Penetration	Relative Density
0 – 1	Very Soft	0 – 4	Very Loose
2 – 4	Soft	4 – 10	Loose
4 – 8	Medium Stiff	10 – 30	Medium Dense
8 – 15	Stiff	30 – 50	Dense
15 – 30	Very Stiff	>50	Very Dense
>30	Hard		

8.7 Unusual Odors

Unusual, unidentified and contaminant odors are described when encountered. Unusual odors may be associated with soil discolorations.

Olfactory characteristics of soil samples are noted where they occur in borings. The relative strength and subjective description of the odors are noted when considered appropriate. Olfactory characteristics are subject to field conditions, such as temperature and wind, and individual nasal sensitivities. The following relative descriptions apply:

- Strong Odor - Noticeable at arm's length.
- Slight Odor - Noticeable only when soil vapors are wafted to the nose.

8.8 Structure

Intact soils may show remnant structures and are described when present. Common structures include stratification, laminations, fissures, slickensides, lenses, blockiness and homogeneity. Stratification (greater than six mm) and laminations (less than six mm) are differentiated by the thickness of layers, which should be noted.

8.9 Organic Content

Organic remnants are described specifically, when known or identified as organics, if indeterminate. Typical organic features include roots, fossils and wood.

8.10 Angularity

Angularity refers to the surface shape of a coarse-grained particle. Typical descriptions identify grains as angular, subangular, subrounded and rounded. A range of angularities may be observed in a soil sample and should be noted if present.

8.11 Shape

Shape refers to the spatial appearance of gravel particles and includes identifiers, such as flat and elongated.

8.12 Sorting

Sorting is a gauge of the predominance of a particular type or size of grain in the soil. Typically, sorting is used to describe sand with greater or lesser quantities of fines. A well-sorted medium sand is composed of mostly medium sand size particles with little else. A poorly-sorted sand may have a wide range of sand sizes in addition to the presence of finer material and gravel. Sorting can also refer to lag concentrations of a type of grain in soil, such as rock fragments.

8.13 Grading and Gradation

Soil may exhibit fining upward or coarsening upward grain size trends in stratified units. These trends indicate depositional processes which may preferentially affect water movement and should be recorded if observed.

Soil gradation is a descriptive term which refers to the distribution and size of grains in soil. A grain size analysis or field estimate is used to characterize the ranges of grain sizes. A soil is said to be well-graded when there is a good representation of all particle sizes. A poorly-graded soil exists when there is an excess or deficiency of a certain particle size within the range of particle sizes present.

8.14 Genetic Judgment

As soil is being described, an evaluation of how the soil was deposited is made by the Field Geologist. The determination of depositional genesis is a judgment based on physical characteristics and experience. Such a determination is valuable for later geologic and hydrogeologic analysis. The genetic judgment determination is placed in parentheses at the end of the description of a soil unit. Depositional categories include, but are not limited to, the following:

8.14.1 Fill

Soil that has been imported to a site or from another location at a site is identified as such, if possible. Fill typically has different geotechnical properties from natural in-place soil and may be critical to an understanding of the movement of fluids in the subsurface. Fill may be easily recognized when man-made constituents are embedded in the soil or sorted backfill is encountered. However, the difference between fill and slump failure sediments may be more difficult to evaluate.

8.14.2 Backfill

Cavities and piping runs are commonly backfilled with coarse sediments. Backfill typically consists of sand, gravel or a combination.

8.14.3 Slumpage

Slopes are subject to landslides, soil creep and soil slump. As soil moves downslope under the force of gravity, soil components mix together creating a heterogeneous assemblage similar to that of some types of fill. Water flow associated with slumpage tends to preferentially move along interfaces. Slope or former slope areas should be suspected of having slumpage.

8.14.4 Paleosols

Former surface soils encountered at depth indicate past topography. Paleosols are recognized by evidence of a horizon that supported organic growth (topsoil).

8.14.5 Tills

Tills are glacially-deposited materials consisting of a heterogeneous assemblage of clay, silt, sand, gravel and boulders that are unconsolidated, unsorted and unstratified. Tills may vary widely in specific characteristics between locales and within a till body. Typically, the till matrix is fine-grained with coarse-grained clasts. The till body typically has a very stiff to hard consistency and very low permeability.

8.14.6 Lacustrine Deposits

Lacustrine deposits refer to sediments deposited in a lake or dammed body of water. Lacustrine sediments consist primarily of clay, silt and sand components that were transported and deposited on the lake bottom. Coarser sediments are deposited near stream influxes as the energy of the stream is dissipated by the standing body of water. Fine sediments tend to be suspended in the water column for a longer period of time before settling to the bottom. Suspension and settling may be cyclic with daily, seasonal or periodic runoff. This temporal variation results in the formation of laminae, which is a

distinctive characteristic of lacustrine sediments. Seasonal variation in floral and faunal communities in the lake and potential temperature stratification of the water column result in greater or lesser organic contributions to the sediments during the course of deposition and may result in varves.

8.14.7 Outwash Deposits

Outwash sediments are deposited by melt-water streams at the margins of glaciers. Deposits typically are dominated by sand and gravel components with lesser quantities of silts and clays. Locally and at certain horizons within a sequence, fine-grained components may be extensive. Outwash deposits typically contain water-bearing horizons of variable magnitude and may be prolific aquifers.

8.14.8 Loess

Loess is a windblown deposit that blankets the area where it occurs. Loess tends to be homogenous and consists primarily of silt with lesser clay and fine sand components. Deposits are typically thin (less than ten feet), homogeneous, non-stratified, porous and slightly cohesive to friable. Loess may be suspected downwind of glaciated areas, outwash deposits and desert areas.

9.0 ATTACHMENTS

9.1 Log of Boring

9.2 Boring Log Legend

9.3 Unified Soil Classification System

THE PAYNE FIRM, INC.
STANDARD OPERATING PROCEDURE

SUBJECT: Borehole Abandonment

PROCEDURE NO.: SOP 3-6

EFFECTIVE ISSUE DATE: November 19, 1993

REVISION NO.: 1

PRIOR EFFECTIVE DATE: July 15, 1993

SITE-SPECIFIC AMENDMENTS: None

1.0 PURPOSE

The purpose of this procedure is to describe the steps necessary to abandon a borehole. Boreholes are properly abandoned to minimize the potential that the borehole may become a contaminant transport pathway.

2.0 SCOPE

This procedure applies to the abandonment of drilled and hand-augured boreholes by a drilling subcontractor or Payne Firm representative. For the purposes of this procedure, soil gas survey holes are included and considered to be small-diameter holes to be treated the same as those produced by a screw auger.

3.0 REQUIREMENTS

Borehole abandonment must be accounted for in the project work plan and included within the scope of work. Abandonment and the need for patching the surface of boreholes must be identified, communicated to the client and appropriately resolved. If abandonment is to be performed by the drilling subcontractor, the necessary materials must be specified and communicated in the drilling scope of work. Borehole abandonment must be performed according to the project work plan and/or scope of work and documented in the Field Logbook.

Notification to regulatory agencies of borehole abandonment is not required.

4.0 REFERENCES

Aller, Linda, et al., June, 1989. *Handbook of Suggested Practices for the Design and Installation of Ground Water Monitoring Wells*, National Water Well Association.

Ohio Administrative Code 3701-28-07. *Abandonment of Test Holes, Wells and Cisterns*, Ohio Department of Health.

Ohio Administrative Code 3745-9-10. *Abandonment of Test Holes and Wells*, Ohio Environmental Protection Agency.

5.0 DEFINITIONS

Abandonment - The complete sealing of a well or borehole with grout or other impermeable materials to restore the original hydrogeologic conditions and/or to prevent the borehole from becoming a pathway for contamination of the aquifer.

Bentonite - A commercial term applied to any of numerous clay products containing montmorillonite (smectite) as the essential mineral and presenting a very large total surface area, characterized by the ability to swell in water. Bentonite is available in a variety of forms (powder, granular flakes, chips, and pellets), which have different settling characteristics through water and within a borehole.

Bridging - A borehole process in which the natural formation or introduced material incompletely collapses or descends within the borehole, thereby creating a void space (i.e., potential conduit) of unknown magnitude beneath the material. Bridging may prevent the introduction of material below the point of bridging.

Grout - A slurry of neat cement, bentonite, inert natural materials, drilling mud or concrete that is impervious to and capable of preventing movement of water.

6.0 RESPONSIBILITIES

6.1 Project Manager

The Project Manager is responsible for determining the borehole abandonment requirements for the project and incorporating those requirements into the work plan and/or scope of work with appropriate input from the client.

6.2 Field Operations Leader

The Field Operations Leader is responsible for communicating the scope of work to the drilling subcontractor and Field Geologist/Field Technician, ensuring that the necessary supplies are available and training field personnel in the use of this procedure.

6.3 Field Geologist/Field Technician

Field personnel are responsible for understanding this procedure, performing or ensuring proper abandonment by the drilling subcontractor and documenting the procedure.

7.0 EQUIPMENT

- Grout
- Bentonite (powder, granular flakes, chips and/or pellets)
- Potable Water
- Field Logbook
- Borehole Abandonment Details form (Attachment 9.1)

8.0 PROCEDURE

8.1 Planning

Boreholes, which will not be converted to monitoring wells, must be evaluated for the appropriate abandonment procedures. Consideration must be given to what contaminants may be encountered in the borehole, how the soil should be controlled, whether ground water may be encountered, applicable regulations and client needs. Borehole conditions may differ between holes; therefore, contingencies should be addressed to account for multiple methods of abandonment. Borehole abandonment resolution must be part of the project work plan.

8.2 Scope of Work

A scope of work will be formulated by the Field Operations Leader based on the project work plan and communicated to the drilling subcontractor and/or field personnel as appropriate. Communication of the drilling scope of work may be written or verbal. If verbal, details must be noted and placed in the project file and the scope of work must be confirmed with the driller prior to arrival at the work site.

8.3 Field Abandonment Considerations

The following considerations should be used as a guideline to identifying the appropriate method of abandonment in conformance with the requirements of the project work plan and/or scope of work.

- Can the borehole be considered clean based on field determinations?
- How close is the borehole to known or potential contaminant sources?
- Has ground water been encountered in the borehole?
- Is there standing water in the borehole?
- Are there wells nearby and are the function and construction of the wells known?
- What predominant soil textures are present and at what depth?
- How deep is the borehole?
- Where is the borehole location?
- Will remediation take place at the borehole location?
- How is the borehole to be capped?

Appropriate abandonment for the purpose of minimizing the potential for a borehole to become a contaminant transport pathway will depend on the answers to these kinds of questions. Judgment and, if necessary, consultation with the Field Operations Leader or Project Manager must be used to determine the proper abandonment procedure for a borehole under situations not specified in the project work plan and/or scope of work.

8.4 Borehole Abandonment

Borehole abandonment shall be performed in accordance with the project work plan, scope of work and requirements of the actual field conditions.

The most protective means of abandoning a borehole is considered to be grouting to the surface with a tremie pipe and capping with concrete. Abandonment by other methods is performed to save time and money when additional steps are unwarranted by field conditions. For instance, grouting to the surface with a tremie pipe is not required for a two-foot hand auger hole. Justification must be in place for less protective means of abandonment.

Due to the endless number of potential field situations, this procedure will not attempt to address every situation for abandoning a borehole. General approaches to performing borehole abandonment are identified with the methods discussed below. Important associated considerations for abandonment include how soil cutting are to be disposed and how the surface is to be restored. Borehole abandonment may include but need not be limited to the following methods.

8.4.1 Tremie-Grouting

Tremie-grouting involves the injection of grout through a pipe within downhole equipment into the subsurface media. This method is performed utilizing a drill rig by the drilling subcontractor. Grout is introduced to the borehole from the bottom up as downhole equipment is being removed. Soil cuttings may be mixed into the grout, if appropriate, through the augers or casing at the discretion of the drilling subcontractor. Due to the nature of the method, introduced soil cuttings may bridge within the auger or casing and therefore not mix with the grout.

This method is appropriate for deep (greater than ten feet) boreholes and boreholes containing standing water.

Careful consideration about using this method must be made when wells are within ten feet of the borehole, since grout may interfere with the function of the nearby well.

8.4.2 Grouting

Grouting involves the spraying of grout through a hose into the open borehole or through the downhole equipment as it is removed from the hole. This method is performed utilizing a drill rig by the drilling subcontractor. The point of introduction of the grout is at or near the surface of the borehole. Soil cuttings may be mixed into the grout, if appropriate, through the open borehole, augers or casing with input from the drilling subcontractor. The nature of the soil cuttings and their careless mixture with the grout may lead to bridging within the borehole and/or downhole equipment.

This method is appropriate for deep (greater than ten feet) boreholes without standing water, boreholes with less than two feet of standing water, boreholes with saturated zones, open boreholes that do not readily collapse and shallow boreholes.

Grout may spread to and interfere with the function of nearby wells within ten feet.

8.4.3 Plugging With Bentonite

Bentonite may be used to plug the borehole. This method consists of introducing bentonite, in one of its forms (powder, granular flakes, chips, pellets), into the open borehole or downhole equipment from the surface and may be performed by the drilling subcontractor or Field Geologist/Field Technician. The introduced bentonite is hydrated as necessary. Soil cuttings may be mixed with the bentonite prior to hydration. Care must be taken to ensure that bentonite/soil mixture adequately seals the borehole. This can best be done by achieving a bentonite to soil cuttings ratio of at least 1:1. Bentonite expands significantly upon hydration (2+ times) and should provide a sufficient seal if this ratio is achieved or surpassed. Bridging must be guarded against and can be minimized or avoided by slowly introducing small quantities of material to the borehole.

This method is appropriate for deep or shallow boreholes created with a drill rig and shallow open boreholes advanced by hand auger. Bentonite chips and pellets can fall through water if slowly and evenly introduced. The use of bentonite flakes and powder should be restricted to boreholes without standing water unless mixed as part of a slurry for grouting.

The slow introduction of bentonite pellets or chips may be preferred in situations where wells are present within ten feet.

8.4.4 Plugging With Soil Cuttings

Soil cuttings may be used to plug very shallow (less than five feet) boreholes in certain situations. This method consists entirely of returning soil cuttings from the borehole back into the hole and compacting it.

Plugging with soil cuttings is appropriate when the:

- Borehole is less than two feet deep;
- Surrounding surface soil is highly permeable;
- Borehole is in an area that will be remediated;
- Borehole is considered to be clean, is distant from potential contaminant source areas and will be appropriately patched.

8.5 Documentation

Borehole abandonment shall be documented in the Field Logbook. If required for the project, a Borehole Abandonment Details form (Attachment 9.1) should also be completed and included in the project file.

8.6 Related Procedures

- SOP 1-7 Restoration of Work Site
- SOP 3-2 Observation of Hollow Stem Auger Drilling Activities
- SOP 3-3 Observation of Cable Tool Drilling Activities
- SOP 3-5 Hand Auger Boring Installation
- SOP 4-6 Well Abandonment

9.0 ATTACHMENTS

9.1 Borehole Abandonment Details

THE PAYNE FIRM, INC.
STANDARD OPERATING PROCEDURE

SUBJECT: Observation of Rotasonic Drilling Activities

PROCEDURE NO.: SOP 3-7

EFFECTIVE ISSUE DATE: April 18, 1994

REVISION NO.: 0

PRIOR EFFECTIVE DATE: New

SITE-SPECIFIC AMENDMENT: None

1.0 PURPOSE

The purpose of this procedure is to establish the minimum requirements for recording field observations to document rotasonic drilling activities.

2.0 SCOPE

This procedure applies to the observation of rotasonic drilling activities performed by a subcontractor to advance a borehole and drive casing. These drilling activities will result in the collection of samples to determine the type, thickness, and certain physical and chemical properties of the soil, water and/or rock strata which underlie the site.

3.0 REQUIREMENTS

Project planning must include identifying the need for rotasonic drilling activities and incorporating that need into the project work plan and drilling scope of work. Appropriate documentation of drilling activities must be performed and maintained on file to record borehole locations, maintain proper drilling of the borehole, record casing emplacement and removal procedures, provide a framework for recording physical and chemical data, and verify compliance with the scope of work by the drilling subcontractor.

4.0 REFERENCES

Alliance Environmental Inc., "Rotasonic Drilling" Video.

Engineering Sciences, June 1990, *Monitoring Rotosonic Drilling Activities; in Project Plan for Remedial Investigations and Feasibility Studies at Wright Patterson Air Force Base, Ohio, Volume 2, Appendix C, Quality Assurance Project Plan*, United States Department of Energy, Oak Ridge, Tennessee, Contract DE-AL05-840R21400.

5.0 DEFINITIONS

Casing - Heavy steel pipe driven into the borehole during drilling to seal unwanted fluids and solid material from the borehole. It may be temporary or made permanent by cementing in place.
Rotasonic Drilling - A method of drilling in which employs simultaneous high frequency resonance vibrations and low speed rotational drive to advance casing and a continuous core sampler through the subsurface.

6.0 RESPONSIBILITIES

6.1 Project Manager

The Project Manager is responsible for incorporating any need to rotasonic drilling activities into the project work plan.

6.2 Field Operations Leader

The Field Operations Leader is responsible for ensuring that field personnel have been trained in the use of this procedure and for verifying that rotasonic drilling activities are being performed in compliance with the project work plan and the drilling scope of work. The Field Operations Leader in conjunction with the Project Manager will determine the appropriate disposal methods for soil cuttings and saturated sediments generated by the drilling, and will identify any specialized supplies or logistical support required for the activities. These activities will be documented in the Field Logbook. The Field Operations Leader may use the Field Logbook entries to verify subcontractor invoicing for materials or hourly rate work.

6.3 Field Geologist

The Field Geologist is responsible for monitoring drilling activities and recording observations made during drilling in the Field Logbook. A copy of the logbook entries will be provided to the Field Operations Leader for inclusion in the project files.

7.0 EQUIPMENT

- Field Logbook
- Drilling Scope of Work
- Hot Work Permit, if necessary

8.0 PROCEDURE

Any need for rotasonic drilling is identified and incorporated into the project work plan.

8.1 Planning

A scope of work is formulated and communicated to the drilling subcontractor. Communication may be written or verbal. If verbal, details must be noted and placed in the project file and the scope of work must be confirmed with the driller prior to arrival on-site.

Prior to arriving at the drilling location, the Field Geologist and Field Operations Leader will confer regarding the pertinent aspects of the drilling scope of work related to the day's drilling activities.

8.2 The Situation

All preparatory activities including Hazard Recognition (SOP 1-5) have been accomplished so that drilling can commence.

8.3 Documentation

Rotasonic drilling activities will be documented in the Field Logbook as per SOP 1-1 "Use of Field Logbooks."

Specific information and observations relative to rotasonic drilling will include the following items, as applicable:

- Drilling company
- Drill crew names
- Type of drill rig
- Internal diameter of initial casing
- Borehole identification

- Borehole location
- Relevant borehole and casing diameters
- Start and finish of drilling activities
- Type of drilling activities
- Delays in drilling
- Sampling devices
- Nested casings
- Whether casing is permanent or temporary
- How casing is emplaced or cemented
- Relevant footage including:
  - Total depth
  - Depth of ground water
  - Sample intervals
  - Depth of casings
  - Casing refusal
  - Sampler refusal
- The quantity and frequency of any water that is added to or removed from the borehole - only potable water is to be added.
- Any application of lubricants to downhole equipment - only vegetable-based, petroleum-free lubricants (specific brand name) are to be used.
- Any need to weld together sections of casing being driven into the borehole. Welding will require a hot work permit as per SOP 1-5 "Hazard Recognition" and SOP 1-9 "Hot Work."

8.4 General Activities

A rotasonic drill rig advances a four-inch diameter core barrel for sampling and can advance up to a 12-inch diameter drive casing for the construction of standard and telescoped monitoring wells. The core barrel is advanced ahead of the drive casing, generally in five to ten feet increments. Once a new interval has been cored, the core barrel is left in place, detached from the drill head and sealed. Next, the drive casing is advanced to just above the leading edge of the core barrel and the cuttings are flushed out with potable water and containerized. After the core barrel has been backed out of the bore hole, the core is extruded into a plastic sleeve and placed on a metal trough.

8.5 Casing Observations

Casing is driven to seal fluids and unconsolidated sediments from the borehole. The casing seal may have varying degrees of effectiveness with respect to formation fluids based on the sealing method. Nested casings may also be used. Particular care must be given to identifying water-bearing horizons during the emplacement of casing. At the conclusion of the borehole or as part of monitoring well installation, casing is removed and/or grouted in place depending on the needs of the project.

8.5.1 Casing Removal

At the conclusion of the borehole or during monitoring well installation, casing is removed. The casing will be removed by using the sonic aspect of the drill rig and pulling the casing upward. The borehole is abandoned as per SOP 3-6.

8.6 Related Activities

During the course of monitoring the rotasonic drilling, related activities will be performed and documented as specified in the project work plan or other SOPs. These activities may include:

- Health and safety monitoring (as per site specific Health and Safety Plan)
- SOP 1-5 Recognition of Physical Hazards
- SOP 1-9 Hot Work
- SOP 3-1 Observation of Drilling Equipment Decontamination
- SOP 3-5 Borehole Logging
- SOP 3-6 Borehole Abandonment
- SOP 4-2 Installation of Monitoring Wells
- SOP 4-3 Installation of Injection Wells
- SOP 4-4 Installation of Piezometers
- SOP 4-6 Well Abandonment
- SOP 5-2 Soil Sampling

8.7 Verification

Documentation of rotasonic drilling activities will be used to verify that the needs of the work plan have been met, the drilling scope of work has been complied with, and that invoicing matches what has been recorded.

9.0 ATTACHMENTS

None.

THE PAYNE FIRM, INC.
STANDARD OPERATING PROCEDURE

SUBJECT: Installation of Monitoring Wells

PROCEDURE NO.: SOP 4-2

EFFECTIVE ISSUE DATE: November 19, 1993

REVISION NO.: 1

PRIOR EFFECTIVE DATE: July 15, 1993

SITE-SPECIFIC AMENDMENT: None

1.0 PURPOSE

The purpose of this procedure is to establish the minimum requirements for the installation of monitoring wells, including recommended installation procedures and measurements to be taken to verify construction results.

2.0 SCOPE

This procedure applies to the construction of all monitoring wells. Most monitoring wells will be installed by licensed or certified subcontractors, such as water well drillers. The resulting monitoring well will provide a means of obtaining representative and repeatable water samples from the ground water formation. A properly installed monitoring well can also serve as a piezometer for taking ground water level measurements and as means of testing aquifer characteristics.

3.0 REQUIREMENTS

Monitoring well construction must be planned during project scoping and include details, such as the screen length, casing material, casing diameter, filter pack, seal, ground and well protection materials. Actual construction details are usually dependent on field conditions. Successful installation of a monitoring well requires field judgment.

Well construction details must be recorded in the Field Logbook and/or on a Monitoring Well Construction Log.

4.0 REFERENCES

American Society for Testing and Materials, October 1990. *Standard Practice for Design and Installation of Ground Water Monitoring Wells in Aquifers*, D5092-90.

United States Environmental Protection Agency, September 1986. *Resource Conservation and Recovery Act (RCRA) Technical Enforcement Guidance Document*, OSWER-9950.1.

United States Environmental Protection Agency, December 1987. *A Compendium of Superfund Field Operations Methods*. EPA/540/P-87/001.

5.0 DEFINITIONS

Annular Space (Annulus) - The space between two concentric tubes or casings, or between the casing and the borehole wall. This would include the space(s) between multiple strings of tubing/casings in a borehole installed either concentrically or multi-cased adjacent to each other.
Aquifer - A geologic formation, group of formations or part of a formation that is saturated and capable of providing a significant quantity of water.
Borehole - A circular open or uncased subsurface hole created by drilling.
Bridge - An obstruction within the annulus which may prevent circulation or proper emplacement of annular materials.
Centralizer - A device that assists in the centering of a casing or riser within a borehole or another casing.
Filter Pack - A clean silica sand or sand and gravel mixture of selected grain size and gradation that is installed in the annular space between the borehole wall and the well screen, extending an appropriate distance above the screen, for the purpose of retaining and stabilizing the particles from the adjacent strata.
Grout - A low permeability material placed in the annulus between the well casing or riser pipe and the borehole wall (that is, in a single-cased monitoring well) or between the riser and casing (that is, in a multi-cased monitoring well) to maintain the alignment of the casing and riser and to prevent movement of ground water or surface water within the annular space.
Neat Cement - A mixture of Portland cement (ASTM Specification 150) and water.
Protective Casing - A section of larger diameter pipe that is emplaced over the upper end of a smaller diameter monitoring well riser or casing to provide structural protection to the well and restrict unauthorized access into the well.
Riser - The pipe extending from the well screen to or above the ground surface.
Tremie Pipe - A pipe or tube lowered into the annular space that is used to transport filter pack materials and annular sealant materials from the ground surface into the borehole annulus or between casings and casings to riser pipe of a monitoring well.

Weep Hole - A small diameter hole (usually 0.25 inches) drilled into the protective casing above the ground surface that serves as a drain hole for water that may enter the protective casing annulus.
Well Screen - A filtering device used to retain the primary or natural filter pack; usually a cylindrical pipe with openings of a uniform width, orientation and spacing.

6.0 RESPONSIBILITIES

6.1 Project Manager

The Project Manager is responsible for determining monitoring well needs for the project. Any special construction requirements or materials are identified and incorporated in the work plan.

6.2 Field Operations Leader

The Field Operations Leader is responsible for developing and communicating a field scope of work based on the project requirements. Specific monitoring well construction materials are identified and arranged prior to site work. The Field Operations Leader ensures that field personnel have been trained in the use of this procedure and for verifying that monitoring wells have been constructed according to the project work plan. The Field Operations Leader may use the Field Logbook entries to verify subcontractor invoicing for materials or hourly rate work.

6.3 Field Geologist

The Field Geologist is responsible for observing and recording the installation and construction of the monitoring well in the Field Logbook and/or on the Monitoring Well Construction Log. A copy of the logbook entries will be provided to the field operations leader for review and inclusion in the project files.

7.0 EQUIPMENT

- Field Logbook
- Scope of Work
- Monitoring Well Construction Log (Attachment 9.1)
- Weighted Fiberglass Measuring Tape

8.0 PROCEDURE

8.1 Planning

Monitoring well construction is planned during project scoping. The planning of monitoring wells should assess the objectives in sampling the ground water. The objectives should consider the aquifer interval to be sampled, the hydrologic characteristics of the aquifer, contaminants that may be present and possible reactivity with well material and the client and property owner's site specific requirements.

Each state has its own regulations regarding proper monitoring well construction. The regulations or guidance documents must be reviewed for specific requirements during the initial planning stages.

Planning considerations may include the following items:

- Choice of screen and riser materials
- Length of screen
- Part of water-bearing interval being screened
- Diameter of screen and riser
- Choice of filter pack material and interval above screen
- Slot size of screen
- Type and installation of annular seal above filter pack
- Grout
- Borehole drilling method
- Choice of protective casing

NOTE: Monitoring well design must <u>not</u> cross different hydrostratigraphic units (i.e., aquitards).

8.1.1 Diameter

- Standard well diameters are two, four, six or eight inches. For most monitoring programs, a two- or four-inch diameter well is preferred. Smaller wells have a smaller volume of standing water, well construction costs are lower and the water level stabilizes readily.
- In specifying well diameter, sampling requirements must be considered. A total of up to four gallons of water may be required for a single sample to account for full organic and inorganic analyses and split samples. Also, the standing water in the monitoring well available for sampling after complete

recharge is dependent on the well diameter as follows:

Casing Inside Diameter, Inches	Standing Water Depth to Obtain One Gallon of Water (ft)	Total Depth of Standing Water for Four Gallons (ft)
2	6.13	25
4	1.53	6
6	0.68	3

- The borehole should be at least four inches larger than the well riser pipe diameter.

8.1.2 Riser Pipe and Screen Materials

- Schedule 40 PVC or Type 304 stainless steel materials are used depending on project requirements.
- Threaded, flush joint casing is required. No glues or solvents will be used in well construction.
- For deep wells, the screen must be chosen to withstand the column weight without collapsing. The screen shall pass no more than ten percent of pack materials or *in situ* aquifer materials. The selection is based on the ASTM recommended screen slot sizes are as follows.

RECOMMENDED (ACHIEVABLE) FILTER PACK CHARACTERISTICS FOR COMMON SCREEN SLOT SIZES					
Size of Screen Opening mm (in)	Slot No.	Sand Pack Mesh Size Name(s)	1% Passing Size (D-1) mm	Effective Size (D-10) mm	30% Passing Size (D-30) mm
0.125 (0.005)	5	100	0.09 - 0.12	0.14 - 0.17	0.17 - 0.21
0.25 (0.010)	10	20 - 40	0.24 - 0.35	0.4 - 0.5	0.5 - 0.6
0.50 (0.020)	20	10 - 20	0.7 - 0.9	1.0 - 1.2	1.2 - 1.5

8.1.3 Screen Length

Standard screen lengths are ten feet long, except where the water-bearing formation to be examined is less than ten feet thick or where a particular contaminant layer is being screened. A screen length less than ten feet long will be installed in these instances. Longer screens may be used in situations where an unconfined aquifer is present with a potential for a widely varying seasonal fluctuation in the top of the water table.

8.1.4 Annular Materials

- Material placed in the annular space between the borehole and well riser pipe includes a filter pack, and a bentonite seal and/or cement bentonite grout.
- The filter pack is usually a fine to medium grained uniform sand. The quantity of sand placed in the annular space is dependent upon the borehole diameter and the length of the screened interval but should extend one to three feet above the top of the screen. A one-foot filter pack is necessary above the screened interval when bentonite pellets are used to form the bentonite seal. A minimum three-foot filter pack is necessary above the screened interval when a bentonite slurry is used to form the seal.
- A bentonite pellet seal is a minimum of two feet thick.
- A bentonite or neat cement grout may be used to seal the annular space above the bentonite seal.
- A bentonite slurry seal may be used in place of bentonite pellets (with three feet of filter pack above the screen) and then is installed completely to the surface, if used.

8.2 Scope of Work

A scope of work is formulated by the Field Operations Leader based on the project work plan and communicated to the drilling subcontractor and/or field personnel as appropriate. The scope of work includes identification of well construction materials and specific requirements as necessary. Communication of the drilling scope of work may be written or verbal. If verbal, details must be noted and placed in the project file, and the scope of work must be confirmed with the driller prior to arrival at the work site.

8.3 The Situation

This procedure covers the installation of the monitoring well materials in an existing borehole with drilling augers or cable-tool drive pipe in place in unconsolidated soil or incompetent rock. Related procedures (Section 8.6) account for steps proceeding and following this SOP.

8.4 Monitoring Well Installation Procedure

Monitoring well installation after the borehole has been completed includes confirming the bottom of the borehole, inserting the screen and riser, constructing the filter pack, placing the bentonite seal, grouting

and securing the protective casing.

8.4.1 Confirming the Bottom of the Borehole

The initial step is to verify that the borehole is open to the bottom and has reached the proper depth. To check, the driller or Field Geologist lowers the clean weighted tape measure into the open augers or borehole until the weight reaches the bottom. The depth is measured from the ground surface.

If the proper depth has been reached, monitoring well construction may begin. If the borehole is too shallow, the drilling must continue. If the borehole depth is too deep, it may be adjusted by pouring clean sand or bentonite pellets into the borehole depending on the circumstances. If bentonite is used, a sandpack must be placed below the screen to keep the bentonite from entering the well screen. The depth should be rechecked with the augers or drive pipe raised above the fill placed at the bottom of the borehole.

8.4.2 Inserting the Screen and Riser

The end cap, well screen and riser pipe are connected as it is lowered into the open borehole. The well screen length, material and diameter are measured to confirm compliance with scope of work prior to installation. The distance between the bottom of the well screen and the bottom of the end cap also is measured and recorded. The connections between sections of well screen and riser pipe must be threaded with an o-ring type gasket at the thread end. Under no circumstances may glue be used in the construction of the monitoring well. The well screen should be constructed with assorted screen lengths (i.e., 1 foot, 2 feet, 5 feet) or cut to adjust to the borehole depth before placing it in the well so that the cut can be as smooth and even as possible.

The well screen and riser should be centered in the borehole. Centralizers may be used if necessary to keep the casing in the center of the borehole during construction.

8.4.3 Constructing the Filter Pack

Once the well screen and riser pipe are in place, a sand pack is placed in the borehole around the well screen. The sand used in the sand pack must be clean washed sand from a supplier. It is usually supplied in bags and is manually poured into the augers or drive casing. The augers are raised as the sandpack is poured into the annulus around the well screen. This procedure must be done cautiously to prevent bridging in the augers and to allow the sand to settle to the bottom of any standing water in the borehole. A weighted tape should be used periodically to check the sandpack depth on all sides of the screen.

The sandpack usually extends one to three feet above the top of the well screen to keep any bentonite or grout from entering the well screen.

8.4.4 Placing the Bentonite Seal

After the sand pack is in place, a bentonite plug is installed above the sand pack. The bentonite plug is used to form a water tight seal above the sandpack and the well screen. The bentonite plug is constructed by pouring bentonite pellets or chips into the augers or drive pipe as it is retracted. The bentonite plug is usually at a minimum one foot thick, but may be required to be at least two feet thick.

8.4.5 Grouting

The remaining borehole is filled with a grout consisting of bentonite or neat cement slurry. The placement of this material forms a seal in the borehole to prevent it from acting as a passage way for contaminants or water from the surface. The grout is pumped into the augers using a hose or tremie pipe as the augers or drive pipe is retracted. The grout should extend to at least within two feet of the ground surface.

8.4.6 Securing the Protective Casing

After the grout has solidified sufficiently to support weight, the protective cover should be installed. The protective cover is a steel cover that has a locking or bolted closure to prevent tampering. If a protective cover with a bolt type closure is used, a locking cap must be use to seal the riser pipe to prevent tampering. The protective cover must be cemented in place using concrete mix. The protective cover should be slightly elevated above the ground surface to keep surface water out of the well.

8.5 Documentation

The Field Geologist records and documents all monitoring well installation activities and measurements. At a minimum the information must be sufficient to complete the Monitoring Well Construction Log (Attachment 9.1).

8.6 Related Activities

- SOP 1-1 Use of Field Logbooks
- SOP 1-5 Hazard Recognition
- SOP 1-7 Restoration of Work Site
- SOP 1-8 Arranging a Land or Elevation Survey
- SOP 3-2 Observation of Hollow Stem Drilling Activities
- SOP 3-3 Observation of Cable Tool Drilling Activities
- SOP 4-1 Decontamination of Well Construction Materials
- SOP 4-3 Installation of PrePack Monitoring Wells
- SOP 4-4 Well Abandonment
- SOP 6-2 Well Development

9.0 ATTACHMENTS

9.1 Monitoring Well Construction Log

THE PAYNE FIRM, INC.
STANDARD OPERATING PROCEDURE

SUBJECT: Well Abandonment

PROCEDURE NO.: SOP 4-4

EFFECTIVE ISSUE DATE: November 19, 1993

REVISION NO.: 1

PRIOR EFFECTIVE DATE: July 15, 1993

SITE-SPECIFIC AMENDMENT: None

1.0 PURPOSE

The purpose of this procedure is to establish guidelines and methods for the proper abandonment of wells. State regulations specify minimum requirements for abandoning wells in order to seal the aquifer to prevent contaminants from entering ground water. The requirements of a project may necessitate more stringent means of abandonment than required by the State of Ohio regulations.

2.0 SCOPE

This procedure applies to abandoning monitoring wells, injection wells, temporary wells, hydropunch points, and piezometers.

3.0 REQUIREMENTS

Well abandonment must be planned and incorporated into the project work plan or scope of work. Pertinent state regulations must be reviewed and complied with in project plans. The drilling scope of work must be communicated to the subcontractor and include the appropriate method and list of supplies. Abandonment must be performed according to the project requirements and documented in the Field Logbook and/or on the Well Abandonment Details form.

4.0 REFERENCES

Aller, Linda, et. al., June 1989. *Handbook of Suggested Practices for the Design and Installation of Ground Water Monitoring Wells*, National Water Well Association.

Ohio Department of Health. *Abandonment of Test Holes, Wells, and Cisterns*, Ohio Administrative Code 3701-28-07.

Ohio Environmental Protection Agency. *Abandonment of Test Holes and Wells*, Ohio Administrative Code 3745-9-10.

5.0 DEFINITIONS

Abandonment - The complete sealing of a well or borehole with grout or other impermeable materials to restore the original hydrogeologic conditions and/or to prevent the well from being a pathway for contamination of the aquifer.
Grout - A slurry of neat cement, bentonite, inert natural materials, drilling mud or concrete that is impervious to and capable of preventing movement of water.

6.0 RESPONSIBILITIES

6.1 Project Manager

The Project Manager is responsible for determining the well abandonment requirements for a project and incorporating those requirements into the work plan or scope of work.

6.2 Field Operations Leader

The Field Operations Leader is responsible for communicating the scope of work to the drilling subcontractor and Field Geologist/Field Technician, ensuring that the necessary equipment and supplies are available, and training field personnel in the use of this procedure.

6.3 Field Geologist/Field Technician

Field personnel are responsible for understanding this procedure, ensuring that the proper well abandonment method is successfully completed and documenting abandonment.

7.0 EQUIPMENT

- Drilling Subcontractor Equipment
- Tremie Pipe
- Grout Pump

- Grout
- Bentonite
- Potable Water
- Field Logbook
- Well Abandonment Details (Attachment 9.1)

8.0 PROCEDURE

8.1 Planning

Well abandonment must be planned during project scoping. The need to abandon wells typically arises toward the end of a project after investigation and/or remediation has been completed. Abandonment may also be necessary during the performance of a project, if wells are determined to be a potential pathway for contamination of an aquifer.

Each state has its own regulations regarding proper well abandonment. Well abandonment regulations are reviewed for specific requirements during the initial planning stages. This SOP addresses the State of Ohio requirements specifically.

Planning includes a determination of the method and materials of abandonment. The method of abandonment is contingent upon whether one or more hydrostratigraphic intervals are determined to be screened by the well. If more than one hydrostratigraphic interval is screened by the well, then it must be abandoned by the overdrilling method, since grouting can not be known to ensure sealing of the filter pack.

Abandonment methods include tremie-grouting an in-place well to the surface or over-augering and removing the well and then tremie-grouting the borehole to the surface. If the well is to be over-augered, then disposition of the well materials must be determined.

The material of abandonment is the type of grout that is used to seal the well. Materials may include PureGold brand bentonite grout or a mixture of neat cement and two to six percent by weight bentonite.

8.2 Scope of Work

A scope of work is formulated by the Field Operations Leader based on the project work plan and communicated to the drilling subcontractor and field personnel prior to arrival at the work site. Communication of the drilling scope of work may be written or verbal. If verbal, details must be noted and placed in the project file, and the scope of work must be confirmed with the driller prior to arrival at the work site.

8.3 Grout

Grout materials consist of either PureGold brand bentonite grout or a mixture of neat cement and two to six percent by weight bentonite.

8.3.1 PureGold

PureGold brand bentonite grout is produced by the Colloid Environmental Technologies Company (CETCO). PureGold brand consists of a blend of pure dried bentonite clays and contains no polymers or organic additives.

8.3.2 Mixture of Neat Cement and Grout

A mixture of neat cement and two to six percent by weight bentonite may be used for abandonment when specified by the needs of the project.

8.4 Well Abandonment In-Place

In-place well abandonment is accomplished by grouting the well from the bottom to the surface through a tremie pipe. The well cover protection cylinder is removed from the ground and the surface of the well location is patched with cement and pavement if applicable.

8.5 Well Abandonment Over-Drilling

Well abandonment by over-drilling is performed with large diameter hollow stem augers. The size of the hollow stem augers should be sufficient to thoroughly ream the entire diameter of the borehole. The well construction materials are reamed by the screwing action of the augers and well casing is removed from the borehole.

After the borehole has been reamed and well casing has been removed, the borehole is grouted from the bottom to the surface through a tremie pipe. The surface of the well location is patched with cement and pavement if applicable. Well materials are disposed as determined in the scope of work.

8.6 Documentation

Well abandonment materials and methods are documented in the Field Logbook and/or on a Well Abandonment Details form.

Some states require notification of proper well abandonment prior to or immediately after completion. Pertinent state regulations should be reviewed and complied with.

9.0 ATTACHMENTS

9.1 Well Abandonment Details

THE PAYNE FIRM, INC.
STANDARD OPERATING PROCEDURE

SUBJECT: Decontamination of Soil Sampling Equipment

PROCEDURE NO.: SOP 5-1

EFFECTIVE ISSUE DATE: November 19, 1993

REVISION NO.: 1

PRIOR EFFECTIVE DATE: July 15, 1993

SITE-SPECIFIC AMENDMENT: None

1.0 PURPOSE

The purpose of this procedure is to describe methods for decontaminating soil sampling equipment. Proper decontamination of soil sampling equipment is essential to preventing cross-contamination of subsurface soil intervals and soil samples. One or more methods may be applicable to a work site depending on the objectives of the project and the types of analytical data that may be required.

2.0 SCOPE

This procedure applies to the decontamination of split-barrel (split-spoon) samplers, hand augers, stainless steel hand tools, shovels and post-hole diggers that come into direct contact with soil that is to be sampled.

3.0 REQUIREMENTS

Soil sampling is an integral part of a field investigation and proper decontamination of soil sampling equipment must be achieved to prevent potential cross-contamination of site soils and collected samples. Decontamination must be planned and incorporated into the project work plan or scope of work. The necessary decontamination equipment and solutions must be identified and made available. Disposition of decontamination wastes must be arranged. Proper decontamination must be performed in accordance with this SOP and the requirements of the project. Decontamination methods, solutions and disposition of wastes must be recorded in the Field Logbook.

4.0 REFERENCES

American Society for Testing and Materials, June 1990. *Standard Practice for Decontamination of Field Equipment Used at Non-Radioactive Waste Sites*, D5088-90.

United States Environmental Protection Agency, December 1987. *A Compendium of Superfund Field Operations Methods*, EPA/540/P-87/001.

5.0 DEFINITIONS

Acid Rinse - A solution of reagent grade nitric or hydrochloric acid and deionized water used as an inorganic desorbing agent.

Cross-Contamination - The introduction of contamination from one sample, location or vertical interval to another sample, location or vertical interval.

Deionized Water - Ion-free, organic-free reagent grade water.

Detergent - A non-phosphate laboratory grade detergent such as Alconox or Liquinox.

Potable Water - Water from a municipal drinking water system.

Solvent Rinse - Pesticide grade isopropanol, acetone, hexane or methanol used as an organic desorbing agent.

6.0 RESPONSIBILITIES

6.1 Project Manager

The Project Manager is responsible for determining the proper decontamination procedures for a project and incorporating those procedures into the project work plan or scope of work. Planning includes the disposition of decontamination wastes.

6.2 Field Operations Leader

The Field Operations Leader is responsible for formulating the field scope of work and communicating the scope of work to field personnel and the drilling subcontractor, if applicable. The Field Operations Leader ensures that field personnel are trained in the use of this procedure and that the disposition of decontamination wastes has been arranged according to the project work plan.

6.3 Field Geologist/Field Technician

Field personnel are responsible for understanding this procedure and implementing decontamination. Decontamination methods and materials are recorded in the Field Logbook.

7.0 EQUIPMENT

- Non-phosphate Detergent (Alconox or Liquinox)
- Potable Water
- Acid Rinse (Nitric or Hydrochloric Acid ten percent by volume for plastic and Teflon; one percent by volume for stainless steel)
- Solvent Rinse (Methanol or Hexane)
- Deionized Water
- Distilled Water
- Scrub Brushes
- Bottle Brushes
- Plastic Buckets
- Latex Gloves

8.0 PROCEDURE

8.1 Planning

The appropriate decontamination method for soil sampling is determined during project planning. The choice of methods is dependent on the objectives of the investigation, the types of analysis that may be performed and input from the client and regulatory agencies, if applicable.

Three general categories may be addressed when decontaminating soil sampling equipment. Equipment is washed in a detergent solution to remove soil residue. Potential inorganic cross-contamination may be addressed with an acid rinse. Potential organic cross-contamination may be addressed with a solvent rinse.

The following considerations affect the choice of decontamination method:

- Will the potential for inorganic cross-contamination require an acid rinse to meet the objectives of the project?
- Will the potential for organic cross-contamination require a solvent rinse to meet the objectives of the project?
- How will the results of sampling be used?
  - Determine presence or absence of contaminants
  - Determine remediation goals
  - Verify closure
  - Qualitative assessment
  - Verify compliance

The disposition of decontamination wastes is included in project planning.

8.2 Scope of Work

The Field Operations Leader formulates a scope of work based on project planning. The scope of work includes decontamination methods and the disposition of decontamination wastes and is communicated to field personnel and the drilling subcontractor, as applicable, prior to arrival at the work site. The scope of work communicated to the drilling subcontractor may be verbal or written. If verbal, details are noted and placed in the project file, and the scope of work is confirmed with the subcontractor prior to arrival at the work site.

8.3 Decontamination Methods

Decontamination methods remove soil residues and mitigate the potential for inorganic and organic cross-contamination, if warranted by analysis. At a minimum, soil residues are removed by a detergent wash. If required, an acid rinse and/or a solvent rinse may be applied. The acid rinse, if required, always is performed before the solvent rinse, if required.

8.3.1 Detergent Wash

A solution of laboratory-grade Alconox or Liquinox and potable water is used to wash the sampling equipment. A scrub brush and/or bottle brush is applied to the sampling equipment until soil residue is

removed. The sampling equipment is then thoroughly rinsed with potable water followed by a distilled water rinse. The equipment is subsequently allowed to air dry and if necessary covered with aluminum foil prior to its next use.

8.3.2 Acid Rinse

If it has been determined that the potential for inorganic cross-contamination must be mitigated, then an acid rinse is performed. The acid rinse consists of ten percent nitric acid (for plastic and Teflon-coated equipment) or one percent hydrochloric acid (for low-carbon steel or stainless steel equipment) in deionized water. The acid rinse immediately follows the potable water rinse after detergent washing. The acid rinse is followed by a deionized water rinse and air drying if a solvent rinse is not performed.

8.3.3 Solvent Rinse

If it has been determined that the potential for organic cross-contamination must be mitigated, then a solvent rinse is performed. The solvent rinse consists of a rinse with one or more pesticide-grade organic desorbing agents, such as methanol, hexane, isopropanol and acetone. The solvent rinse follows the acid rinse-deionized water rinse if performed or the potable water rinse after detergent washing. The solvent rinse is followed by a deionized water rinse and air drying.

8.3.3.1 Solvents

The following sequential solvent rinse steps may be used:

- Methanol Only (for organics excluding PCBs)
- Methanol to Methanol to Methanol (for organics including PCBs)
- Hexane to Hexane to Hexane (for PCBs only)

8.3.3.2 Rinse

Solvent is expensive to use and dispose. The manner of rinsing may depend on the volume of sampling to be performed. Rinsing is performed in one of the following ways:

- Immersing the sampling equipment in a volume of solvent
- Pouring solvent on the sampling equipment while draining into a contained area
- Spraying solvent onto the sampling equipment in a contained area

8.4 Decontamination Procedures

Water sampling equipment is decontaminated by one of the following methods.

8.4.1 Detergent Wash - Distilled Water Rinse

The following decontamination procedure is used for sampling equipment when an acid rinse and/or solvent rinse is not required:

- Wash and scrub with non-phosphate detergent.
- Rinse thoroughly with potable water.
- Rinse with distilled water.
- Allow to air dry.
- Wrap in aluminum foil or plastic as necessary for later use.

8.4.2 Detergent Wash - Acid Rinse

The following decontamination procedure is used for sampling equipment when an acid rinse is required during inorganic (metals) sampling.

- Wash and scrub with non-phosphate detergent.
- Rinse thoroughly with potable water.
- Rinse plastic or Teflon-coated equipment with ten percent nitric acid solution; rinse stainless steel equipment with one percent hydrochloric acid solution.
- Rinse with deionized water.
- Allow to air dry.
- Wrap in aluminum foil or plastic as necessary for later use.

8.4.3 Detergent Wash - Solvent Rinse

The following decontamination procedure is used for sampling equipment when a solvent rinse is required during organic sampling, but PCBs are not analyzed for:

- Wash and scrub with non-phosphate detergent.
- Rinse thoroughly with potable water.
- Rinse with methanol.
- Allow to air dry.
- Rinse with deionized water.
- Allow to air dry.
- Wrap in aluminum foil or plastic as necessary for later use.

8.4.4 Detergent Wash - Triple Solvent Rinse

The following decontamination procedures is used for sampling equipment when a solvent rinse is required during organic sampling and PCBs are being analyzed for:

- Wash and scrub with non-phosphate detergent.
- Rinse thoroughly with potable water.
- Rinse with methanol.
- Rinse with methanol.
- Rinse with methanol.
- Allow to air dry.
- Rinse with deionized water.
- Allow to air dry.
- Wrap in aluminum foil or plastic as necessary for later use.

8.4.5 Detergent Wash - Acid Rinse - Solvent Rinse

The following decontamination procedure is used for sampling equipment when inorganic (metals) and organic (excluding PCBs) sampling requires acid and solvent rinses:

- Wash and scrub with non-phosphate detergent.
- Rinse thoroughly with potable water.

- Rinse plastic or Teflon-coated equipment with ten percent nitric acid solution; rinse stainless steel equipment with one percent hydrochloric acid solution.
- Rinse with deionized water.
- Allow to air dry.
- Rinse with methanol.
- Allow to air dry.
- Rinse with deionized water.
- Allow to air dry.
- Wrap in aluminum foil or plastic as necessary for later use.

8.4.6 Detergent Wash - Acid Rinse - Triple Solvent Rinse

The following decontamination procedure is for sampling equipment when inorganic (metals) and organic (including PCBs) sampling requires acid and solvent rinses:

- Wash and scrub with non-phosphate detergent.
- Rinse thoroughly with potable water.
- Rinse plastic or Teflon-coated equipment with ten percent nitric acid; rinse stainless steel equipment with one percent hydrochloric acid.
- Rinse with deionized water.
- Rinse with methanol.
- Rinse with methanol.
- Rinse with methanol.
- Allow to air dry.
- Rinse with deionized water.
- Allow to air dry.
- Wrap in aluminum foil or plastic as necessary for later use.

8.5 Disposition of Decontamination Wastes

Decontamination wastewater is properly disposed of as determined in the project work plan and/or scope of work. Decontamination fluids may be managed in the following ways depending on site considerations and characterization:

- Containerized for subsequent characterization and disposal.
- Approved to an on-site treatment system.
- Permitted to an off-site sanitary sewer system.
- Routed to the on-site sanitary sewer system.

Spent acid and solvent rinses are disposed as previously determined by the project requirements.

8.6 Documentation

Proper decontamination is recorded in the Field Logbook. The method is identified along with particular acid, solvent and water rinses. Disposition of decontamination wastes is identified as applicable.

8.7 Related Procedures

- SOP 1-1 Use of Field Logbooks
- SOP 3-1 Observation of Drilling Equipment Decontamination
- SOP 4-1 Decontamination of Well Construction Materials
- SOP 5-2 Soil Sampling
- SOP 6-1 Decontamination of Water Sampling Equipment

9.0 ATTACHMENTS

None.

THE PAYNE FIRM, INC.
STANDARD OPERATING PROCEDURE

SUBJECT: Soil Sampling

PROCEDURE NO.: SOP 5-2

EFFECTIVE ISSUE DATE: November 19, 1993

REVISION NO.: 0

PRIOR EFFECTIVE DATE: July 15, 1993

SITE-SPECIFIC AMENDMENT: None

1.0 PURPOSE

The purpose of this procedure is to describe methods for sampling soil. Soil sampling is performed to collect a portion of soil (disturbed or undisturbed) that is representative of the horizon sampled to test for chemical, geotechnical, or geologic properties. The method that is used will depend on the objectives of the sampling, the equipment that is used to sample, whether sampling is to be performed at a single horizontal location or in a trench or excavation, whether the sample is to be a grab sample or composite, whether field screening and/or laboratory analyses are to be performed, and which analyses may be performed.

2.0 SCOPE

This procedure applies to sampling soil with the aid of drill rigs or other heavy equipment or by hand tool methods. Soil samples may be obtained by split-barrel (split-spoon) samplers, Shelby tubes, continuous core samplers, hand augers, stainless steel hand tools, shovels, post-hole diggers and backhoe buckets. Soil cuttings may be sampled as they rise from the drill augers, after they have been drummed, or in rolloff boxes or dumpsters.

3.0 REQUIREMENTS

Soil sampling is an integral part of a field investigation and must be planned for and included in a project work plan, scope of work or site reconnaissance. Soil sampling must be performed in conformance with the project work plan or scope of work. Soil sampling with the aid of a drill rig or other heavy equipment must be included within a scope of work to the subcontractor. The method of soil sampling must be recorded in the Field Logbook or on a Field Report form. Whether sampling is for field screening or potential laboratory analysis must be indicated along with how the container was filled. "Decontamination of Soil Sampling Equipment" (SOP 5-1) and the "Restoration of Work Site" (SOP 1-7) must be recorded.

4.0 REFERENCES

American Society for Testing and Materials, June 1980. *Standard Practice for Soil Investigation and Sampling by Auger Borings*, D1452-80 (Reapproved 1990).

American Society for testing and Materials, October 1983. *Standard Practice for Thin Walled Tube Sampling of Soils*, D1587-83

American Society for Testing and Materials, December 1984. *Standard Method for Penetration Test and Split-Barrel Sampling of Soils*, D1586-84.

American Society for Testing and Materials, September 1991. *Standard Guide for Soil Sampling from the Vadose Zone*, D4700-91.

United States Environmental Protection Agency, December 1987. *A Compendium of Superfund Field Operations Methods*, EPA/540/P-87/001.

5.0 DEFINITIONS

Composite Sample - A sample resulting from the combination of two or more samples.

Continuous Sample Tube System - A sampling device that fits within a hollow stem auger column, but is prevented from rotating as the auger column is turned. The assembly consists of a five-foot, split-barrel whose lower end is positioned a short adjustable distance in advance of the lead auger. As the auger is rotated, a continuous core sample is obtained within the split-barrel while soil cuttings are generated external to the split-barrel and auger flight. A plastic catcher may be used to prevent the sample from falling out during retrieval.

Sample - Soil collected from a single location or interval.

Shelby Tube Sampler - A thin-walled metal tube sampling device used to recover relatively-undisturbed soil samples suitable for laboratory testing of geotechnical properties. These tubes are available in various sizes, ranging from two to five inches in outside diameter and 18 to 54 inches in length. The tube is pressed into the *in situ* soil, allowed to set for several minutes so that the soil may equilibrate (expand) to the tube, slowly removed and sealed for shipment to the laboratory.

Soil - For the purposes of this SOP, soil is considered to include the following materials: 1) loose unconsolidated surface sediments; 2) topsoil; 3) unconsolidated material above bedrock; 4) fill material; 5) stream sediments; and 6) deposits in sediment traps.

Soil Cuttings - Soil brought to the surface by the use of hand tools or the action of augers as they are screwed into the ground.

Split-Barrel (Split-Spoon) Sampler - A steel sampling device consisting of two split-barrel halves, a drive shoe, and a sampler head, all of which are threaded together. The most commonly used size has a 2-inch outside diameter and 1.5-inch inside diameter; 2.5-inch to 4.5-inch outside diameters may also be available. A plastic catcher is fitted into the drive shoe to prevent the sample from falling out during retrieval.

6.0 RESPONSIBILITIES

6.1 Project Manager

The Project Manager is responsible for identifying soil sampling requirements and incorporating them into the project work plan or scope of work.

6.2 Field Operations Leader

The Field Operations Leader is responsible for ensuring that all field personnel have been trained in the use of this procedure and that the necessary equipment is available to for sampling soil. If sampling with the aid of a drill rig or other heavy equipment is to be performed, the subcontractor scope of work, including sampling requirements should be communicated to the subcontractor. The Field Operations Leader will ensure that soil sampling procedures conform to the project work plan and this procedure and that methods and other pertinent details are documented and included in the project files.

6.3 Field Geologist/Field Engineer/Field Technician

Field personnel are responsible for sampling soil in conformance with this procedure and recording the methods in the Field Logbook or on a Field Report form (Attachment 9.1).

7.0 EQUIPMENT

- Project Work Plan or Scope of Work
- Split-Barrel (Split-Spoon) Sampler
- Shelby Tube Sampler
- Continuous Sample Tube System
- Bucket Auger (Steel or Stainless Steel)
- Stainless Steel Screw Auger
- Shovel
- Post-Hole Digger
- Stainless Steel Spoons
- Stainless Steel Bowls
- Stainless Steel Knife or Spatula
- Appropriate Sampling Containers
- Latex Gloves
- Tape Measure
- Garbage Bags
- Decontamination Equipment and Supplies
- Field Logbook
- Field Report Form (Attachment 9.1)
- Log of Boring Form (Attachment 9.2)

8.0 PROCEDURE

8.1 Planning

Soil sampling is an integral part of a field investigation and must be planned for and included in a project work plan, scope of work or site reconnaissance. The project requirements and objectives, including applicable regulations and technical and budget issues, will have a fundamental impact on how soil samples are to be obtained. The following considerations need to be evaluated in light of the objectives of the project.

- What kinds of environmental or geotechnical analyses are needed to meet the requirements of the project?
- Are specific sampling procedures required for any of the laboratory analyses?

- Will soil sampling be performed with the aid of a drill rig, other heavy equipment or with hand tools?
- Which sampling devices are to be used?
- How is the soil to be handled and placed in a sample container?
- What is to be done with excess soil?
- How are sampling devices to be decontaminated?

8.2 Scope of Work

A scope of work is formulated by the Project Manager and Field Operations Leader based on the project work plan. The scope of work includes sampling methods, soil cuttings disposition and decontamination specifications as applicable and is communicated to the subcontractor and/or field personnel as appropriate. Communication may be written or verbal. If verbal, details are noted and placed in the project file and the scope of work is confirmed with the subcontractor prior to arrival at the work site.

8.3 Decontamination

"Observation of Drilling Equipment Decontamination" (SOP 3-1) and "Decontamination of Soil Sampling Equipment" (SOP 5-1) are performed in conformance with the specific requirements of the project work plan.

8.4 Soil Sampling With the Aid of a Drill Rig

Sampling devices that require the use of a drill rig include split-barrel (split-spoon) samplers, Shelby tube samplers and the continuous sample tube system.

8.4.1 Split-Barrel (Split-Spoon) Samplers

A two-foot long, split-barrel sampler provides a continuous soil sample up to two feet in length. The sampler is driven in advance of augers or casing by the regulated operation of a hammer drop system. Typically, a 140-pound hammer is raised approximately 30 inches and allowed to drop via a hammer fall guide to an anvil attached to the sampling rods at the end of which is the split-barrel sampler.

The number of drops of the hammer (blow counts) in each six-inch interval is recorded on the Log of Boring form for the sample interval. The first six-inch interval is considered to be a seating drive and may include penetration of slough (not-in-place) material in the borehole. The second and third six-inch

intervals combine to form a geotechnical engineering term called the "standard penetration resistance" or "N-value." The N-value can be converted to an approximate field evaluation of the clay consistency or sand density of the soil using a standard geotechnical conversion chart (Attachment 9.3). The fourth six-inch interval is driven for the purpose of cost-effectiveness; the driving of this interval is not identified in the reference material. The split-barrel sampler is typically hammered until a maximum of 50 blows have been applied in any six-inch interval, a total of 100 blows have been applied, no observed advance of the sampler has occurred during the application of ten successive blows of the hammer or until otherwise directed.

The split-barrel sampler is retrieved from the borehole and opened on clean plastic sheeting at the sampling work station. The soil in the split-barrel is described on the Log of Boring as per the "Borehole Logging" (SOP 3-5) procedures. After the sample interval has been logged, soil is apportioned for analytical laboratory and field screening purposes as necessary. If volatile organic compounds may be analyzed for, this potential sample is containerized prior to others by inserting biased core soil into the 40 ml glass vial or two-ounce glass sample jar such that void spaces are minimized. Remaining potential soil samples are homogenized and placed in appropriate sample jars for analytical testing or in Ziploc bags for field screening as per SOP 5-3 ("Headspace Organic Vapor Screening"). Potential analytical samples should have the outside of the container wiped with a paper towel and be inserted into an iced cooler for temporary storage.

Excess soil is included with the soil cuttings for later disposition as per the project work plan. The split-barrel sampler is then decontaminated for reuse as per SOP 5-1.

8.4.2 Shelby Tube Samplers

A Shelby tube sampler provides a relatively undisturbed continuous soil sample up to the dimensions of the tube. The sample is collected for geotechnical and geologic parameters, including but not limited to grain size, moisture content, unit weight, specific gravity, Atterburg Limits, permeability and organic content. Geologic description of the soil profile is not performed in the field, but may be requested from the laboratory. The ends of the tube are sealed upon retrieval to preserve moisture characteristics.

Tube sizes typically range between two and five inches outside diameter and 18 to 54 inches in length. The wall thickness of the tube is directly proportional to the outside diameter. For a three-inch outside diameter, the wall thickness is recommended to be 0.065 inches. The thin walls of the tube make

sampling in hard materials difficult due to the potential to crease or damage the tube. Other sampling devices, such as a Denison core barrel samplers, may be necessary in such cases if the budget and availability will allow.

The Shelby tube sampler is attached to a sampling rod via two to four mounting holes. The borehole is thoroughly reamed to the desired depth. The sampler is then positioned so that its bottom rests at the bottom of the borehole. The sampler is advanced without rotation by a continuous force to the desired depth. Soil is allowed to equilibrate/expand within the Shelby tube for several minutes prior to retrieval. The sampler is then carefully withdrawn from the sampling interval for sealing.

Upon removal of the Shelby tube from the borehole, the length of sample retrieved is recorded on the Log of Boring, in the Field Logbook or on the Field Report. The sampler is then sealed for shipment. Obvious slough material is removed from the top of the sampler. The upper and lower ends are then sealed with impervious disks and a wax plug. The ends are capped and taped. The outside of the sampler should be wiped clean. A sample label is then affixed to the sampler with the project sample labeling information. An arrow showing which end is up (this can also be deduced from the position of the mounting holes) is marked on the sampler. The sampler is stored and transported with the appropriate end up so that minimal disturbance occurs to the sample.

8.4.3 Continuous Sample Tube Systems

A continuous sample tube system is essentially a five-foot split-barrel sampler that fits within and slightly in advance of the lead hollow stem auger. The sampler is not rotated with the augers, but collects soil in advance of the augers. The system that is typically used fits inside of a 4.25-inch internal diameter hollow stem auger and has an outer diameter of 3.5 inches and an internal sampler diameter of three inches. A system for 3.25-inch hollow stem augers is also available. Blow counts are not generated for this sampling method. However, the soil description, sampling procedures and excess soil disposition are the same as that described for the split-barrel sampler.

Due to the size and weight of the sampler, a work station rack may be necessary to facilitate sampling procedures. In addition, the sampler may require decontamination as per other drilling equipment (SOP 3-1), instead of SOP 5-1 ("Decontamination of Soil Sampling Equipment").

8.5 Soil Sampling With the Aid of Other Heavy Equipment

Heavy equipment, such as backhoes or trackhoes, may be used to procure soil from trenches or excavations.

Field personnel direct the heavy equipment operator to a location in the trench or excavation that requires sampling. A quantity of soil is obtained with the bucket under the direct observation of the Field Geologist/Field Technician. The Field person decides whether a representative sample can be obtained that has not come into direct contact with the bucket. A soil sample is then obtained using stainless steel hand tools (Section 8.6.5).

If necessary, the bucket should be appropriately decontaminated prior to and/or following sampling.

8.6 Soil Sampling With Hand Tools

Soil sampling with hand tools is performed by augering or digging into *in situ* or stockpiled soil. Stockpiled soils or surface sampling is recorded on a Field Report or in a Field Logbook with reference to a plan view or map location. For *in situ* soils at depth, a Log of Boring is generated. Bucket augers, screw augers, and posthole diggers are used for "Hand Auger Boring Installation" (SOP 3-4). "Borehole Logging" (SOP 3-5) is performed prior to sampling.

"Decontamination of Soil Sampling Equipment" (SOP 5-1) is completed prior to initiating the borehole or surface sampling point and after each sample interval. Soil procurement is performed with the specified instruments as described below.

Soil is apportioned for analytical laboratory and field screening purposes as necessary. If volatile organic compounds may be analyzed for, this potential sample is containerized prior to others by inserting biased core soil into the 40 ml glass vial or two-ounce glass sample jar such that void spaces are minimized. Remaining potential soil samples are homogenized and placed in appropriate sample jars for analytical testing or in Ziploc bags for field screening as per SOP 5-3 ("Headspace Organic Vapor Screening"). Potential analytical samples have the outside of the container wiped with a paper towel and are inserted into an iced cooler for temporary storage.

Excess soil is piled on plastic for disposition at the completion of the borehole.

8.6.1 Bucket Augers

The bucket auger sample is collected in a six-inch long cylinder that is either entirely enclosed or has two quarter sides open. Soil is extruded from the bucket by hand or spatula and placed on clean plastic sheeting, in a stainless steel bowl, or on aluminum foil for description and sampling. The hand auger boring is advanced until the entire sample interval has been penetrated. This may take more than one advance of the auger and retrieval of soil depending on the designated sample interval (typically one foot). Disturbed soil cuttings are obtained which may show soil structures.

8.6.2 Screw Augers

The screw auger sample is procured along the spiral flight of the screw. Soil is removed from the spiral flight by hand or spatula and is placed on clean plastic sheeting, in a stainless steel bowl or on aluminum foil for description and sampling. The hand auger boring is advanced until the entire sample interval has been penetrated. This may take more than one advance of the auger and retrieval of soil depending on the designated sample interval (typically one foot). Disrupted soil cuttings are obtained which do not show soil structures. This sampling method by its nature produces little soil; therefore, sampling plans must recognize that a limited volume of soil will be available with this method.

8.6.3 Post-Hole Diggers

The posthole digger sample is procured through the pincer action of opposed metal scoops. Soil is released from the scoops onto clean plastic sheeting, in a stainless steel bowl or on aluminum foil for description and sampling. This may take more than one advance of the digger and corresponding release of soil, depending on the designated sample interval (typically one foot). Disturbed soil cuttings are obtained which may show soil structures.

8.6.4 Shovel

A shovel is used to either clear surface material to sample fresh soil or to directly sample soil. Typically, soil is placed on clean plastic sheeting or in a clean plastic bucket.

8.6.5 Stainless Steel Spoons

Stainless steel spoons are used to directly sample fresh soil. Fresh soil is obtained by scraping away dried soil crust that has been exposed to the atmosphere for a period of time, scraping away the surface of newly-exposed soil that has been exposed by a non-decontaminated tool or piece of heavy equipment or scraping away the surface of soil that has been stockpiled beneath plastic or in rolloff boxes. Typically, fresh soil can be exposed with the handle end of the stainless spoon. Soil is then procured with the spoon end.

8.7 Composite Sampling

Composite sampling is performed by combining samples from discrete horizons or locations. Compositing may be performed in the field or by the analytical laboratory. If compositing is performed by the laboratory, then field sampling follows the procedures for the specific soil procurement method. If compositing is to be performed in the field, then the manner of compositing will depend on how the samples are to be procured and which analyses may be performed.

In general, field composite sampling may be performed in two distinct ways. Individual samples may be collected into discrete sample containers (such as stainless steel bowls or Ziploc bags) and then subsequently apportioned from the sample containers into a transfer container for homogenization and final compositing. Samples may also be placed directly into a transfer container for homogenization and final compositing.

The number of samples comprising the composite may be determined by the spatial dimensions of the soil being characterized, the type of analyses to be performed, the requirements of a regulatory agency and/or the requirements of the disposal facility.

Transfer containers are typically stainless steel bowls, but may be a clean plastic bucket, plastic bag or plastic sheeting, depending on the analysis to be performed.

Analysis for volatile organic compounds should involve minimal and rapid compositing due to the nature of the target analytes. Metals sampling does not include rapid temporal considerations, but may require specific decontamination procedures.

Composite sampling is most commonly used to identify the presence or absence of target analytes. Quantitative values are viewed to represent qualitative data due to the mixing of samples. Specific regulatory agencies may or may not allow the use of composite data.

8.8 Containers of Soil Cuttings or Stockpiles

Soil may be generated as borehole cuttings or excavation materials that require containerization as specified in the needs of the project work plan or scope of work. This material may subsequently require sampling to determine appropriate disposal methods. The following situations may occur.

8.8.1 Soil Cutting Drums

Soil cuttings may be drummed as part of the project scope of work. For most field projects, the nature of the drummed material is not known to be hazardous and must be determined for disposal. Individual drums may be sampled and analyzed separately or as a composite.

Only drums that are clearly labeled as soil cuttings may be sampled as per this procedure. Drums that are not labeled and whose contents are unknown must not be approached.

Drummed soil cuttings are sampled with a screw or bucket auger. The auger is advanced to the volumetric center of the soil within the drum for the sample. The sample should be procured from soil that is not in contact with the sides of the drum or at the top of the drum. The soil should immediately be placed in the appropriate sample container(s) for laboratory analysis. If composite sampling is being performed, soil should be placed in an appropriate transfer container for homogenization (see Section 8.7) prior to containerization.

The outside of sample containers is wiped free of sample residuals and placed in an iced cooler preparatory to shipping.

8.8.2 Rolloff Boxes

Rolloff boxes are typically used to store excavated soils prior to transfer and disposal. In most instances, disposal characterization will have occurred during or prior to excavation. However, if subsequent sampling of rolloff boxes is necessary, the following procedures apply.

Rolloff box soil is sampled with a hand tool (Section 8.6). An auger may be used to bore into the soil stockpile. A shovel may be used to clear away surface soil and then procure a load for sampling. A stainless steel hand tool may be used to sample from a shovel load or directly from the stockpile.

In most cases, the analyzed sample is intended to be a representative composite (Section 8.7) from many locations within the stockpile. Surface soil is cleared away so that a fresh sample can be obtained and placed in a transfer container for homogenization.

An alternative method to compositing soil from within a rolloff box is to field screen the soil and obtain a sample from an area with elevated headspace. This approach may be applied when volatile compounds are of concern.

Rolloff boxes are not entered when sampling. The physical distribution of unconsolidated soil in the rolloff box and the indeterminate contaminant nature of the soil represent health and safety considerations. Sampling is performed from a ladder or other means of viewing the soil from above or laterally. The rolloff cover is replaced when sampling is complete.

The outside of sample containers is wiped free of sample residuals and placed in an iced cooler preparatory to shipping.

8.8.3 Surface Stockpiles

Surface stockpiles are sampled similar to the method described for rolloff boxes. A stockpile may be stepped on to a limited extent in order to obtain a representative sample. The stockpile covering is replaced when sampling is complete.

8.9 Surface Sediment Sampling

Surface sediment sampling is typically performed to evaluate the environmental effects of a process or activity on surface soils. In many instances, water is either present at the sampling location or commonly flows across the target area. The effects of water on the target sampling area must be evaluated and accounted for prior to sampling. In other instances, a surface area may require qualitative and quantitative evaluation. The effects of size and pavement must be evaluated to arrive at an appropriate

sampling strategy. Individual or composite samples may be collected for analysis. The number of samples will be determined by project needs, budgetary constraints, access considerations and regulatory requirements.

Sediment sampling should be performed with a hand tool (Section 8.6) or specially-selected tool with extension capabilities into water or sediment traps.

8.9.1 Spatial Considerations

The surface area and geometry of the sampling target affects how many samples will be analyzed and the procedures employed to determine specific sampling locations.

A large equidimensional surface area can be covered with a grid. Depending on the type of analysis to be performed, field screening or compositing can be done. For instance, if volatile organic compounds are of interest, headspace organic vapors SOP 5-3 can be analyzed to select a location or locations for subsequent sampling. Metals can be composited at a grid spacing.

Grid spacings will vary with the needs of the project.

An elongate or linear surface area can be apportioned into sequential sections and treated as an equidimensional surface area.

8.9.2 Pavement Considerations

Pavement represents two primary considerations for sediment sampling. Sediment may collect on pavement in low areas or runoff may result in sediment wash to the edges of pavement. Sampling strategy should reflect the potential for accumulation of sediment on and at the edges of pavement.

8.9.3 Water Considerations

Water transports and deposits sediments and chemicals. Special consideration must be given to sampling areas where water is known to flow (e.g., streams, conduits, ditches, gullies, rivulets, other drainage areas).

If sampling sediments under water is required, consideration must also be given to whether the water is stagnant or flowing. If the water is flowing, sampling should be performed with the understanding that this is the case or that a nearby slackwater sample was procured if appropriate.

Sampling sediments under water may necessitate obtaining upstream and downstream samples.

8.9.4 Sediment Traps

A relatively-common sampling environment is a sediment trap associated with a catch basin, trench drain, grease trap or other process flow mechanism. The sediment trap may or may not contain fluids, but is likely to be beneath the surface. In general, a sediment trap should not be entered due to confined space considerations. However, if necessary, the confined space entry (SOP 1-6) procedure should be performed. When possible, sampling should be performed from the ground surface without penetrating the confined space. Hand tool extensions should be used when applicable.

8.10 Documentation

The method(s) employed to sample soil should conform to the project work plan and scope of work. Pertinent aspects of each sampling method should be documented in the Field Logbook for the project and/or on a field report form as necessary.

8.11 Related Procedures

- SOP 1-1 Use of Field Logbooks
- SOP 1-3 Labeling and Custody of Samples
- SOP 1-4 Packaging and Shipping of Samples
- SOP 3-2 Observation of Hollow Stem Auger Drilling Activities
- SOP 3-3 Observation of Cable Tool Drilling Activities
- SOP 3-4 Hand Auger Boring Installation
- SOP 3-5 Borehole Logging
- SOP 5-1 Decontamination of Soil Sampling Equipment
- SOP 5-3 Headspace Organic Vapor Screening

9.0 ATTACHMENTS

9.1 Field Report

9.2 Log of Boring

THE PAYNE FIRM, INC.
STANDARD OPERATING PROCEDURE

SUBJECT: Soil Headspace Organic (HSO) Field Screening

PROCEDURE NO.: SOP 5-3

EFFECTIVE ISSUE DATE: November 19, 1993

REVISION NO.: 0

PRIOR EFFECTIVE DATE: New

SITE-SPECIFIC AMENDMENT: None

1.0 PURPOSE

The purpose of this procedure is to describe the method for obtaining headspace organic (HSO) vapor measurements for soil samples. HSO measurements are a field screening method for determining relative volatile organic compound (VOC) concentrations emitted into the headspace of a soil sample container.

2.0 SCOPE

This procedure applies to HSO measurement for soil samples collected by split-spoon samplers, hand auger borings or other soil sampling techniques.

3.0 REQUIREMENTS

HSO measurement must be performed and documented according to the project work plan and procedures described herein. A properly calibrated vapor analyzing instrument (OVA or HNu) that is capable of detecting the expected analyte(s) must be used in accordance with manufacturer's specifications and appropriate SOPs.

4.0 REFERENCES

United States Environmental Protection Agency, December 1987. *A Compendium of Superfund Field Operations Methods*, Methods, EPA/540/P-87/001.

5.0 DEFINITIONS

Breakthrough - The situation at which complex non-methane volatile organic molecules are no longer adsorbed to the activated carbon filter, pass through the detection chamber of the organic vapor analyzer and register an elevated reading on the instrument.

Calibration - Checking, adjusting or systematically standardizing the graduations of a quantitative measuring instrument in accordance with the manufacturer's instructions and specifications.
Equilibration Period - The period of time between containerizing and performing an HSO measurement on a soil sample.
Headspace - The air volume represented by the unused portion of a partially filled sampling container such as a sealed jar or a plastic bag with a locking seal.
Headspace Organic (HSO) - Organic compound of sufficient volatility present in soil to result in an accumulation of measurable vapors in the headspace of the soil sample container.
Ionization Potential - The energy, measured in electron volts (eV), at which gaseous compounds can be ionized and detected by an organic vapor analyzer. Ionization potentials vary for the wide array of regulated and unregulated VOCs and are available in scientific literature.
Organic Vapor Analyzer - Generic term for field instruments designed to detect vapors emitted by VOCs. Two common varieties include flame-ionization detectors (FID) and photo-ionization detectors (PID).

6.0 RESPONSIBILITIES

6.1 Field Operations Leader

The Field Operations Leader is responsible for ensuring that all field personnel have been trained in the use of this procedure and for verifying that HSO measurements are performed and documented in accordance with this procedure and the project work plan.

6.2 Field Geologist/Field Technician

Field personnel are responsible for understanding this procedure and for performing and documenting HSO measurements in accordance with this procedure and the project work plan.

7.0 EQUIPMENT

- Sample Container (plastic bag with locking seal)
- Field Logbook
- Log of Boring Forms (Attachment 9.1)
- Organic Vapor Analyzer (PID or FID)

8.0 PROCEDURE

8.1 Planning

The Field Operations Leader assesses the HSO requirements for the project and selects an organic vapor analyzer capable of detecting the analytes of interest. The response of organic vapor analyzing instruments depends on the ionization potential of the chemicals of interest; therefore, the manufacturer's specifications and ionization potential charts must be consulted prior to selecting an instrument for a project. Any special calibration requirements shall be specified and addressed prior to sample collection.

8.2 Calibration

Prior to the beginning of a project and/or the day's use of the organic vapor analyzer the instrument is calibrated according to the manufacturer's specifications and the appropriate SOP.

8.3 Set Up

HSO measurements are implemented after soil sampling has been performed. Sampling has included filling one-quart plastic bags with locking seals approximately one-half full leaving the remainder of the bag as an air pocket. The samples are marked corresponding to their borehole position or spatial designation. The samples are then set aside for at least one-half hour to allow the organic vapors in the soil and headspace to reach equilibrium.

The HSO sample containers should be placed in numerical sequence on a work surface adjacent to the organic vapor analyzer. The setup should allow for the probe of the analyzer to reach the top of the bag without excessive handling of the bag. Boring logs and the Field Logbook should be easily accessible in the measurement area.

8.4 Measurement of Total HSO

The HSOs are directly measured from the plastic sample bags by inserting the probe of the organic vapor analyzer through a small breach in the bag seal. The headspace vapors enter the analyzer at the flow rate specified by the instrument's pump, and must not be forced into the vapor analyzer by applying pressure to the bag. Since transient readings tend to occur, the recorded measurement should be the highest consistent reading within the first five seconds of measurement.

8.5 Filtering the Non-Methane Fraction

If the selected organic vapor analyzer detects methane (i.e., an FID OVA), then repeat the measurement process with an activated carbon filter placed on the probe of the instrument to filter out the non-methane component of the HSO. The activated carbon filter adsorbs large complex VOCs on the surface area of the carbon granules and allows the small methane molecules to pass through. Record the remaining HSO concentration (assumed to be primarily methane) beside the total organic vapor reading previously measured. If consistently high readings or an off-scale reading is obtained with the activated carbon filter, breakthrough may have occurred. The activated carbon should be changed prior to subsequent measurements (see SOP 2-1).

8.6 Quality Assurance

Quality assurance in measuring HSO is mainly a function of the consistency of the technique. All sample bags must be filled to similar capacities, have similar headspaces and be left to equilibrate for similar periods under similar conditions. Instrument calibration is also critical and the instrument must be allowed to return to its background reading prior to obtaining a measurement. Effort must be made to measure HSO for samples that have been consistently maintained. When possible, the HSO bags should be stored at approximately 70° F, out of direct sunlight. Activated carbon should be replaced prior to separate measuring events and after breakthrough.

8.7 Documentation

Measurement sand pertinent steps of this procedure shall be documented in the Field Logbook and/or on the Log of Boring for the borehole.

8.8 Related Procedure

- SOP 2-1 Use of Flame-Ionization Detectors (Foxboro Models OVA 108 and 128)
- SOP 2-2 Use of Photo-Ionization Detectors (HNu Model PI-101)
- SOP 3-5 Borehole Logging
- SOP 3-4 Hand Auger boring Installation
- SOP 5-2 Soil Sampling

9.0 ATTACHMENTS

9.1 Log of Boring

THE PAYNE FIRM, INC.
STANDARD OPERATING PROCEDURE

SUBJECT: Decontamination of Water Sampling Equipment **PROCEDURE NO.:** SOP 6-1

EFFECTIVE ISSUE DATE: November 19, 1993 **REVISION NO.:** 1

PRIOR EFFECTIVE DATE: July 15, 1993

SITE-SPECIFIC AMENDMENT: None

1.0 PURPOSE

The purpose of this procedure is to describe methods for decontaminating water sampling equipment. Proper decontamination of water sampling equipment is essential to preventing cross-contamination of water samples. One or more methods may be applicable to a work site depending on the objectives of the project and the types of analytical data that may be required.

2.0 SCOPE

This procedure applies to the decontamination of reusable bailers, pumps and line reels that come into contact with target waters. Pumps or bailers may be dedicated to a well and are not decontaminated if kept with the well and do not come in contact with another surface. Water sampling equipment, such as nylon line, particulate filters and filter tubing, is disposed.

3.0 REQUIREMENTS

Water sampling is an integral part of a field investigation and proper decontamination of water sampling equipment must be achieved when reusing equipment to prevent potential cross-contamination of water samples. Decontamination must be planned and incorporated into the project work plan or scope of work. The necessary decontamination equipment and solutions must be identified and made available. Disposition of decontamination wastes must be arranged. Proper decontamination must be performed in accordance with this SOP and the requirements of the project. Decontamination methods, solutions and disposition of wastes must be recorded in the Field Logbook.

4.0 REFERENCES

American Society for Testing and Materials, June 1990. *Standard Practice for Decontamination of Field Equipment Used at Non-Radioactive Waste Sites,* D5088-90.

United States Environmental Protection Agency, December 1987. *A Compendium of Superfund Field Operations Methods*, EPA/540/P-87/001.

5.0 DEFINITIONS

Acid Rinse - A solution of reagent grade nitric or hydrochloric acid and deionized water used as an inorganic desorbing agent.
Cross-Contamination - The introduction of contamination from one sample, location or vertical interval to another sample, location or vertical interval.
Deionized Water - Ion-free, organic-free reagent grade water.
Detergent - A non-phosphate, laboratory-grade detergent, such as Alconox or Liquinox.
Potable Water - Water from a municipal drinking water system.
Solvent Rinse – Pesticide-grade isopropanol, acetone, hexane or methanol used as an organic desorbing agent.

6.0 RESPONSIBILITIES

6.1 Project Manager

The Project Manager is responsible for determining the proper decontamination procedures for a project and incorporating those procedures into the project work plan or scope of work. Planning includes the disposition of decontamination wastes.

6.2 Field Operations Leader

The Field Operations Leader is responsible for formulating the field scope of work and communicating the scope of work to field personnel and the drilling subcontractor, if applicable. The Field Operations Leader ensures that field personnel are trained in the use of this procedure and that the disposition of decontamination wastes has been arranged according to the project work plan.

6.3 Field Geologist/Field Technician

Field personnel are responsible for understanding this procedure and implementing decontamination. Decontamination methods and materials are recorded in the Field Logbook.

7.0 EQUIPMENT

- Non-phosphate Detergent (Alconox or Liquinox)
- Potable Water
- Acid Rinse (Nitric or Hydrochloric Acid ten percent by Volume for Teflon; one percent by Volume for Stainless Steel)
- Solvent Rinse Pesticide Grade (Methanol or Hexane)
- Deionized Water
- Distilled Water
- Scrub Brushes
- Bottle Brushes
- Plastic Buckets
- Latex Gloves

8.0 PROCEDURE

8.1 Planning

The appropriate decontamination method for reusable water sampling equipment is determined during project planning. The choice of methods is dependent on the objectives of the investigation, the types of analysis that may be performed and input from the client and regulatory agencies, if applicable.

Three general categories may be addressed when decontaminating water sampling equipment. Equipment is washed in a detergent solution to remove residues. Potential inorganic cross-contamination may be addressed with an acid rinse. Potential organic cross-contamination may be addressed with a solvent rinse.

The following considerations affect the choice of decontamination method:

- Will the potential for inorganic cross-contamination require an acid rinse to meet the objectives of the project?
- Will the potential for organic cross-contamination require a solvent rinse to meet the objectives of the project?
- How will the results of sampling be used?

- Determine presence or absence of contaminants
- Determine Remediation Goals
- Verify closure
- Qualitative Assessment
- Verify Compliance

The disposition of decontamination fluids is included in project planning.

8.2 Scope of Work

The Field Operations Leader formulates a scope of work based on project planning. The scope of work includes decontamination methods and the disposition of decontamination wastes and is communicated to field personnel and the drilling subcontractor, as applicable, prior to arrival at the work site. The scope of work communicated to the drilling subcontractor may be verbal or written. If verbal, details are noted and placed in the project file, and the scope of work is confirmed with the subcontractor prior to arrival at the work site.

8.3 Decontamination Methods

Decontamination methods remove contaminant residues and mitigate the potential for inorganic and organic cross-contamination, if warranted. At a minimum, residues are removed by a detergent wash. If required, an acid rinse and/or a solvent rinse may be applied. The acid rinse, if required, always is performed before the solvent rinse, if required.

8.3.1 Detergent Wash

A solution of laboratory-grade Alconox or Liquinox and potable water is used to wash the sampling equipment. A scrub brush and/or bottle brush is applied to the sampling equipment until residues are removed. Sampling equipment may require flushing with the detergent solution to ensure washing of internal part. The sampling equipment is then thoroughly rinsed with potable water followed by a distilled water rinse. The equipment is subsequently allowed to air dry and protected with plastic prior to its next use.

8.3.2 Acid Rinse

If it has been determined that the potential for inorganic cross-contamination must be mitigated, then an acid rinse is performed. The acid rinse consists of ten percent nitric acid (for plastic and Teflon-coated equipment) or one percent hydrochloric acid (for stainless steel equipment) in deionized water. The acid rinse immediately follows the potable water rinse after detergent washing. The acid rinse is followed by a deionized water rinse and air drying if a solvent rinse is not performed.

8.3.3 Solvent Rinse

If it has been determined that the potential for organic cross-contamination must be mitigated, then a solvent rinse is performed. The solvent rinse consists of a rinse with one or more pesticide-grade organic desorbing agents, such as methanol, hexane, isopropanol and acetone. The solvent rinse follows the acid rinse-deionized water rinse if performed or the potable water rinse after detergent washing. The solvent rinse is followed by a deionized water rinse and air drying. The equipment is enclosed in plastic prior to its next use.

8.3.3.1 Solvents

The following sequential solvent rinse steps may be used:

- Methanol Only (for organic excluding PCBs)
- Methanol to Methanol to Methanol (for organics including PCBs)
- Hexane to Hexane to Hexane (for PCBs only)

8.3.3.2 Rinse

Solvent is expensive to use and dispose. The manner of rinsing may depend on the volume of sampling to be performed. Rinsing is performed in one of the following ways:

- Immersing the sampling equipment in a volume of solvent;
- Pouring solvent on the sampling equipment in a contained area; and
- Spraying solvent onto the sampling equipment and drain into a contained area.

8.4 Decontamination Procedures

Water Sampling equipment is decontaminated by one of the following methods.

8.4.1 Detergent Wash - Distilled Water Rinse

The following decontamination procedure is used for sampling equipment when an acid rinse and/or solvent rinse is not required:

- Wash and scrub with non-phosphate detergent.
- Rinse thoroughly with potable water.
- Rinse with distilled water.
- Allow to air dry.
- Wrap in aluminum foil or plastic as necessary for later use.

8.4.2 Detergent Wash - Acid Rinse

The following decontamination procedure is used for sampling equipment when an acid rinse is required during inorganic (metals) sampling.

- Wash and scrub with non-phosphate detergent.
- Rinse thoroughly with potable water.
- Rinse plastic or Teflon-coated equipment with ten percent nitric acid solution; rinse stainless steel equipment with one percent hydrochloric acid solution.
- Rinse with deionized water.
- Allow to air dry.
- Wrap in aluminum foil or plastic as necessary for later use.

8.4.3 Detergent Wash - Solvent Rinse

The following decontamination procedure is used for sampling equipment when a solvent rinse is required during organic sampling, but PCBs are not analyzed for:

- Wash and scrub with non-phosphate detergent.
- Rinse thoroughly with potable water.
- Rinse with methanol.
- Allow to air dry.
- Rinse with deionized water.

- Allow to air dry.
- Wrap in aluminum foil or plastic as necessary for later use.

8.4.4 Detergent Wash - Triple Solvent Rinse

The following decontamination procedures is used for sampling equipment when a solvent rinse is required during organic sampling and PCB are being analyzed for:

- Wash and scrub with non-phosphate detergent.
- Rinse thoroughly with potable water.
- Rinse with methanol.
- Rinse with methanol.
- Rinse with methanol.
- Allow to air dry.
- Rinse with deionized water.
- Allow to air dry.
- Wrap in aluminum foil or plastic as necessary for later use.

8.4.5 Detergent Wash - Acid Rinse - Solvent Rinse

The following decontamination procedure is used for sampling equipment when inorganic (metals) and organic (excluding PCBs) sampling requires acid and solvent rinses:

- Wash and scrub with non-phosphate detergent.
- Rinse thoroughly with potable water.
- Rinse plastic or Teflon-coated equipment with ten percent nitric acid solution; rinse stainless steel equipment with one percent hydrochloric acid solution.
- Rinse with deionized water.
- Allow to air dry.
- Rinse with methanol.
- Allow to air dry.
- Rinse with deionized water.
- Allow to air dry.
- Wrap in aluminum foil or plastic as necessary for later use.

8.4.6 Detergent Wash - Acid Rinse - Triple Solvent Rinse

The following decontamination procedure is for sampling equipment when inorganic (metals) and organic (including PCBs) sampling requires acid and solvent rinses:

- Wash and scrub with non-phosphate detergent.
- Rinse thoroughly with potable water.
- Rinse plastic or Teflon-coated equipment with ten percent nitric acid; rinse stainless steel equipment with one percent hydrochloric acid.
- Rinse with deionized water.
- Rinse with methanol.
- Rinse with methanol.
- Rinse with methanol.
- Allow to air dry.
- Rinse with deionized water.
- Allow to air dry.
- Wrap in aluminum foil or plastic as necessary for later use.

8.5 Disposition of Decontamination Wastes

Decontamination wastewaters are properly disposed as determined in the project work plan and/or scope of work. Decontamination fluids may be managed in the following ways depending on site considerations and characterization:

- Containerized for subsequent characterization and disposal;
- Approved to an on-site treatment system;
- Permitted to an off-site sanitary sewer system; and
- Routed to the on-site sanitary sewer system.

Spent acid and solvent rinses are disposed as previously determined by the project requirements.

Nylon line, disposable filters, parameter containers and latex gloves are allowed to air dry and placed in trash bags for disposal in a site solid waste dumpster unless otherwise specified by the project requirements.

8.6 Documentation

Proper decontamination is recorded in the Field Logbook. The method is identified along with particular acid, solvent and water rinses. Disposition of decontamination wastes is identified as applicable.

8.7 Related Procedures

- SOP 1-1 Use of Field Logbooks
- SOP 6-2 Well Development
- SOP 6-3 Well Purging
- SOP 6-4 Ground Water Sampling
- SOP 6-5 Surface Water Sampling
- SOP 6-6 Field Filtration of Water Samples

9.0 ATTACHMENTS

None.

THE PAYNE FIRM, INC.
STANDARD OPERATING PROCEDURE

SUBJECT: Well Development

PROCEDURE NO.: SOP 6-2

EFFECTIVE ISSUE DATE: November 19, 1993

REVISION NO.: 1

PRIOR EFFECTIVE DATE: July 15, 1993

SITE-SPECIFIC AMENDMENT: None

1.0 PURPOSE

The purpose of this procedure is to describe the steps necessary to develop a monitoring well. Wells require development to increase the likelihood that a representative sample of ground water can be obtained from the aquifer for analytical testing.

2.0 SCOPE

This procedure applies to development of monitoring wells by hand bailing, pumping or surge blocking with the aid of a drilling rig.

3.0 REQUIREMENTS

Monitoring well development must be incorporated into the project work plan and/or scope of work. If the method of development includes use of a drill rig, this must be included in the drilling scope of work.

The borehole water volume must be calculated prior to or during development to evaluate achievement of development goals.

Water withdrawn from the well during development must be properly disposed as determined by the project requirements. Equipment used to develop a well must be properly decontaminated. Development must be documented in the field log book or on the Well Development Log.

4.0 REFERENCES

Aller, Linda, et.al., *Handbook of Suggested Practices for the Design and Installation of Ground-Water Monitoring Wells*, National Water Well Association, p. 228-245.

Barcelona, M.T., J.P. Gibb and R.A. Miller, August, 1983, *A Guide to the Selection of Materials for Monitoring Well Construction and Ground-Water Sampling*, United States Environmental Protection Agency, EPA, 600/52-84-024.

Driscoll, F.G., 1986, *Groundwater and Wells*, Johnson Division, St. Paul, Minnesota, p. 1108.

United State Environmental Protection Agency, September 1986. Resource Conservation and Recovery Act (RCRA), R*CRA Ground Water Monitoring Technical Enforcement Guidance Document*, OSWER-9950.1.

5.0 DEFINITIONS

Bailer - A cylindrical-like container, usually made of Polyvinyl Chloride (PVC) or Teflon, consisting of a ball check-valve at the bottom, creating a seal and allowing retrieval of a quantity of trapped water. (Attachment 9.2).

Bridging - The tendency for particles moving toward the monitoring well to form blockages or "bridge" together and restrict subsequent particulate and water movement.

Surge Block - A plunger-like device attached to and powered by a drill rig that is used to agitate the water column in a monitoring well (Attachment 9.3). A second type of surge block is a weighted tube that is surged manually.

Surging - A process in which a plunger-type device is moved up and down within the well screen to force ground water to alternately flow in and out through the sand pack. This back and forth movement of water facilitates the removal of fine particles from the formation immediately adjacent to the well while preventing bridging of sand grains.

Well Volume - The volume of water in the casing and filter pack of a well.

6.0 RESPONSIBILITIES

6.1 Project Manager

The Project Manager is responsible for incorporating well development into the project work plan and identifying the disposition of development water.

6.2 Field Operations Leader

The Field Operations Leader is responsible for ensuring that field personnel are trained in the use of this procedure and that the necessary equipment is available.

6.3 Field Geologist/Field Technician

Field personnel are responsible for understanding this procedure, implementing the appropriate development method and recording pertinent development information in the Field Logbook or on the Well Development Log (Attachment 9.1).

7.0 EQUIPMENT

- Bailer
- Pump
  - Pump tubing
  - Hose clamps
  - Pump frequency control box
  - Generator
  - Grounding Rod
- Nylon Line
- Water Level Meter
- Turbidity Meter
- Drums or other sufficient containers to collect the development water
- Field Logbook/Well Development Log
- Decontamination Tub
- Reel to Retrieve Bailer or surge.
- Distilled Water
- Alconox Detergent
- Scrub Brush
- Latex Gloves
- Duct Tape
- Hammer
- Flathead Screwdriver

8.0 PROCEDURE

8.1 Planning

When monitoring well are included in a project, well development is a necessary part of the project planning. Factors to be considered when planning for well development include:

- Diameter of monitoring well.
- Total depth of well.
- Presence of free product in well.
- Physical and chemical nature of the formation/aquifer, if known.
- Logistics of development method.
- Disposition of development water.

The objectives of monitoring well development are:

- To rectify damage caused by drilling to the aquifer formation where the monitoring well was installed. Clogging, smearing or compaction of formation materials at the borehole wall and localized reductions in formation hydraulic conductivity can occur due to the drilling process.
- The removal of clay, silt and fine sand from the formation adjacent to the borehole. The removal of fine particles from the formation near the borehole can increase formation and hydraulic conductivity, minimize turbidity in future samples and minimize potential for clogging and damaging pumping equipment.
- Stabilize the filter pack material adjacent to the well screen.
- To optimize well efficiency and hydraulic communication between the monitoring well and adjacent formation. This communication will maximize value of formation test data and the representativeness of ground water samples extracted from the well.

8.2 Scope of Work

A scope of work is formulated by the Field Operations Leader based on the project requirements and communicated to the drilling subcontractor and/or field personnel as appropriate. Communication of the drilling scope of work may be written or verbal. If verbal, details must be noted and placed in the project file, and the scope of work must be confirmed with the driller prior to arrival at the work site.

The scope of work includes disposition of development water and development goals.

Development will be considered complete when one of the following conditions is obtained.

- Three consecutive turbidity measurements, each separated by five minutes, show a turbidity reading less than 25 NTUs;
- Ten well volumes are removed; or
- The well has purged dry three separate times with at least one hour of separation between purgings.

8.3 Set Up

The following steps are performed prior to commencing well development.

- Open and check the monitoring well head. Visually inspect the integrity of the well casing cap, cover and lock. Replace well head parts as necessary.
- Measure the water level in the well.
- Measure the total depth of the well. If a Solinst electric tape is used, 0.3 feet must be added to the tape reading to compensate for the length of the water level probe below the sensor.
- Prepare the equipment for developing the monitoring well.
- Ensure that disposition of development water can be accomplished.

8.4 Well Volume Calculations

The well volume calculation takes well construction details and the column of standing water in the well converts the parameters to a volume of water. A multiple of the well volume may be used as a development goal or an assessment of the viability of attaining a representative sample from the formation.

The well volume calculation consists of three major elements:

1. A calculation of the volume of water in the casing;
2. A calculation of the volume of water in the filter pack outside of the casing; and
3. A conversion of the volumes from feet to gallons.

Simple alternative equations are presented following the detailed calculation. The following equations are used to calculate the well volume (refer to Attachment 9.4).

1. $V_c = (d_i/2)^2$ (TD-H)

2. $V_f = [(d_H/2)^2 - (d_o/2)^2]$ (TD- S or H) (P)

3. $V_t = (V_c + V_f)$ (7.48 gallons/ft^3)

V_c = Volume of water in casing (ft^3)
V_f = Volume of water in filter pack outside of the casing (ft^3)
V_t = Total volume of water in well (gallons)
d_i = Inside diameter of casing (ft)
d_o = Outside diameter of casing (ft)
d_H = Diameter of borehole (ft)
TD = Total depth of well (ft)
H = Depth of water from ground surface (ft)
S = Depth to base of seal from ground surface (ft)
P = Estimated porosity of filter pack (~35%)

The relative contribution to total volume from the casing and the filter pack varies with the diameter of the well, the diameter of the borehole and the height of the water column in the well. A larger diameter borehole will result a greater proportional total volume contribution from the filter pack. A water column above the top of the filter pack will result in a proportional increase from the casing volume. Different combinations of parameters vary the relative contributions from the casing and filter pack.

The relative contribution from the casing and filter pack is an important consideration, when rough field estimates are calculated. The following set of field equations are simple and conservative. The pertinent calculation assumes that the relative contribution to total volume from the filter pack and casing is constant and that the measured height of the water column corresponds to an equivalent saturated filter pack. The calculation is conservative since the filter pack may be less than the height of the water column. The following simple equations may be used most advantageously when the water column is not significantly above the filter pack:

CASING DIAMETER	HEIGHT WATER COLUMN		CONVERSION FACTOR		WELL VOLUME
2-inch	TD-H	*	0.163	=	
3-inch	TD-H	*	0.367	=	

4-inch	TD-H	*	0.653	=	
5-inch	TD-H	*	1.020	=	
6-inch	TD-H	*	1.469	=	
8-inch	TD-H	*	2.611	=	
10-inch	TD-H	*	4.080	=	
12-inch	TD-H	*	5.875	=	

8.5 Development

The basic principle of well development includes creating alternately high and low velocities of water flow in the monitoring well to loosen fine particles adjacent to the well screen or filter pack, followed by the removal of these fines from the well. Development is performed with the aid of a drilling rig, hand bailing, or by means of a pumping system.

8.5.1 Drill Rig - Surge Block Method

A surge block method is used alternately with either a bailer or pump so that materials that have been agitated and loosened by the surging action are removed. The cycle of surging-pumping/bailing is repeated until satisfactory development is achieved.

The surge block, usually attached and operated by a drill rig, is lowered to the top of the well screen and then operated in a surging action with a typical stroke of about three feet. The surging action is usually initiated at the top of the well screen and gradually worked downward through the screened interval so that sand or silt loosed by the surging action cannot cascade down on top of the surge block and prevent removal from the well. The surge block is removed at regular intervals and the fine material that has been loosened is removed by a bailer or pump.

Surging is initially gentle, and the energy of the action is gradually increased during the development process. By controlling the speed and length and stroke of the surge block, the surging activity can range from very rigorous to very gentle.

Advantages:

- Greater surge forces providing a two direction flow may be achieved.

Disadvantages:

- Too much force can easily damage well screen and/or casing.

8.5.2 Hand Bailing

Hand bailing develops a well by creating a surging action with the bailer as a result of rapid rising and descending of the bailer within the water column. Enhanced surging may be accomplished following the same procedures as hand bailing with a surge block. Suspended sediments are removed with the bailer until development goals are achieved.

The impact of the bailer, as it strikes the surface of the water produces an outward surge of water through the well construction and into the formation. This action tends to break bridges that may have formed during well installation. Movement of water back into the well suspends fine sediments into the water column which are removed with the bailer.

If the water column is relatively small, care must be taken not to let the bailer or surge block free fall in the well and damage the casing.

Advantages:

- Uses simple, highly portable equipment.
- Cost-effective for shallow wells.

Disadvantages:

- Difficult to hand bail deep wells greater than two inches in diameter.

8.5.3 Pumping

Pumping develops a well by creating a surging action as a result of variable flow rates. An electric pump (Grundfos Rediflo 2) is installed into the monitoring well. The rate of flow is varied at levels adjacent to

the well screen. The following steps are performed to properly install and operate the pump:

- New or dedicated discharge tubing is connected to the pump with a hose clamp to reinforce the connection. The length of discharge tubing must be greater than the total depth of the well.
- The electric lead from the pump is connected to the frequency control box.
- The pump is inserted into the well. The pump should not be placed at the bottom of the well since accumulated sediment may clog the pump but moved up and down the length of the screen. Therefore, it is necessary to tape the discharge tubing to the well cover restricting the pump from touching the bottom of the well casing.
- Connect the frequency control box plug and grounding rod to the portable generator. The grounding rod must be forced into the ground approximately ten feet away. Start up the generator. Turn on the pump at the frequency control box and record the amount of water flow and frequency rate from the pump.
- The level of the pump in the well should be adjusted periodically to develop different intervals of the well.
- When development is complete, shut the pump off and withdraw the pump from the well. Decontamination of the pump and discharge tubing should be performed when the pump is removed.

Advantages:

- Primarily used in high yield, low turbidity wells.
- Well suited to all types of well construction.
- Generally no potential for damaging well screen.
- Can withdraw a great amount of ground water from the formation.

Disadvantages:

- Generally requires bulky equipment and accessories, and two field personnel to set up and operate pumping equipment.
- May not sufficiently agitate filter pack or formation material to break bridges or stabilize material.

8.6 Documentation

Information from the development event should be documented in the Field Logbook or on the Well Development Log (Attachment 9.1). Information such as total depth of well, depth to water level, height

of water column in well, method of well development, and field parameters should be included in documentation of well development.

8.7 Related Procedures

- SOP 6-1 Decontamination of Water Sampling Equipment
- SOP 6-3 Well Purging
- SOP 6-4 Ground Water Sampling

9.0 ATTACHMENTS

9.1 Well Development Form

9.2 Bailer

9.3 Drill Rig Surge Block

9.4 Well Volume Calculation Definition Sketch

THE PAYNE FIRM, INC.
STANDARD OPERATING PROCEDURE

SUBJECT: Well Purging

PROCEDURE NO.: SOP 6-3

EFFECTIVE ISSUE DATE: February 7, 2003

REVISION NO.: 2

PRIOR EFFECTIVE DATE: November 19, 1993

SITE-SPECIFIC AMENDMENT: None

1.0 PURPOSE

The purpose of this procedure is to describe the steps necessary to purge stagnant water from a monitoring well such that a sample representative of formation-quality water can be obtained. Purging activities are conducted prior to sampling a monitoring well in order to minimize the bias associated with stagnant water in the well, which generally does not accurately reflect the formation ground water chemistry.

2.0 SCOPE

This procedure applies to purging ground water from a monitoring well. Methods include: 1) purging a calculated volume subject to indicator parameter stabilization; and 2) low flow/low stress purging.

3.0 REQUIREMENTS

Well purging must be planned as part of well development and sampling and incorporated into the project work plan and/or scope of work. Appropriate purging equipment must be determined for each well and the selected method. Purge water must be disposed as determined by the project requirements. Equipment used to purge a well must be properly decontaminated. Well purging procedures and ground water parameters must be documented in the Field Logbook and/or Ground Water Sampling Form.

4.0 REFERENCES

American Society for Testing and Materials, January 1998. *Standard Guide for Documenting a Ground Water Sampling Event*, D 6089-97.

American Society for Testing and Materials, October 1999. *Standard Guide for Purging Methods for Wells Used for Ground Water Quality Investigations*, D 6452-99.

American Society for Testing and Materials, March 2001. *Standard Guide for Planning and Preparing for a Ground Water Sampling Event*, D 5903-96 (Re-approved 2001).

American Society for Testing and Materials, March 2001. *Standard Guide for the Selection of Purging and Sampling Devices for Ground Water Monitoring Wells*, D 6634-01.

American Society for Testing and Materials, November 2001. *Standard Guide for Sampling Ground Water Monitoring Wells*, D 4448-01.

American Society for Testing and Materials, March 2002. *Standard Practice for Low-Flow Purging and Sampling for Wells and Devices Used for Ground Water Quality Investigations*, D 6771-02.

Ohio Environmental Protection Agency, February 1995, *Technical Guidance Manual for Hydrogeologic Investigations and Ground Water Monitoring.*

United States Environmental Protection Agency, September 1986. Resource Conservation and Recovery Act (RCRA), *RCRA Ground Water Monitoring Technical Enforcement Guidance Document*, OSWER-9950.1.

United States Environmental Protection Agency, May 2002, *Ground Water Sampling Guidelines for Superfund and RCRA Project Managers*, EPA 542-S-02-001.

5.0 DEFINITIONS

Ambient Ground Water Conditions - Natural ground water conditions in an aquifer formation surrounding the monitoring well.

Bailer - A cylindrical container, usually made of Polyvinyl Chloride (PVC) or Teflon, consisting of a ball check-valve at the bottom. When the bailer is raised, the ball settles on the bottom, creating a seal and allowing retrieval of a quantity of trapped water.

Casing Volume - The quantity of water contained in the casing above the well screen or open borehole.

Purge - The process of removing stagnant water from a well prior to sampling, which induces formation-quality water into the well representative of ambient ground water conditions.

Stabilization - A decrease in the change between measured values to a specified range or percentage of the measured value over a selected number of consecutive readings.

Stagnant Water - Water in the casing, screen, and filter pack of a well prior to purging activities. Stagnant water is usually not representative of ambient ground water conditions depending on site-specific hydrogeology.
Water Quality Indicator Parameters - Physical and/or chemical measurements used to determine when water to be sampled reflects ambient ground water conditions.
Well Volume - The volume of water in the casing, the screen, and filter pack of a well.

6.0 RESPONSIBILITIES

6.1 Project Manager

The Project Manager is responsible for selecting the appropriate purging method and determining the disposition of purge water.

6.2 Field Operations Leader

The Field Operations Leader is responsible for ensuring that field personnel are trained in the use of this procedure and that the necessary equipment is available to properly purge a monitoring well. The Field Operations Leader communicates the scope of work to field personnel prior to arrival at the work site and arranges the disposition of purge water.

6.3 Field Geologist/Field Technician

Field personnel are responsible for understanding and implementing this procedure and documenting the purge method and ground water parameters in the Field Logbook or on the ground Water Sampling Form.

7.0 EQUIPMENT

- Bailer
- Pump
- Pump tubing
- Hose clamps
- Pump frequency control box
- Generator
- Grounding Rod

- Nylon String or Rope for Bailer Line
- Water Level Indicator
- pH/Conductivity Meter
- Turbidity Meter
- Thermometer
- Graduated Container(s)
- Decontamination Tub
- Reel to Retrieve Bailer
- Distilled Water
- Alconox Detergent
- Scrub Brush
- Latex/Nitrile Gloves
- Duct Tape
- Flathead Screwdriver
- Plastic Sheeting
- Calculator
- Cellular Phone
- Well Keys
- Container for Parameter Measurements
- Health and Safety Plan

8.0 PROCEDURE

8.1 Planning

Planning for well purging includes consideration of the following factors:

- Well construction (diameter, depth, screen length)
- Purging method - calculated volume purging subject to indicator parameter stabilization or low flow/low stress purging
- Presence of non-aqueous phase liquids
- Disposition of purge water
- Historical purging method utilized
- Regulations or other guidance
- Hydrogeologic setting and hydraulic performance of the well

- Physical condition of the well
- Ground water geochemistry

The objectives of purging a monitoring well are to:

- remove stagnant water from the well prior to sampling;
- induce formation-quality water into the well; and
- create minimal disturbance to the natural flow regime of the aquifer. Achieving these objectives will increase the likelihood of obtaining a sample representative of ambient ground water conditions from the formation or aquifer.

8.2 Scope of Work

A scope of work is formulated by the Field Operations Leader based on the project requirements and communicated to the field personnel prior to arrival at the work site. The scope of work should include the purging method, disposition of purge water, and the minimum goals for completing well purging.

8.3 Set Up

The following steps are performed prior to purging a well.

- Assemble purging equipment at the well location.
- Open and check the monitoring well protective casing (stick-up or flush mount). Visually inspect the integrity of the well casing cap, cover, and lock. Replace parts as necessary.
- Measure the water level and total depth in the well.

8.4 Purging Based on Calculated Volume Subject to Indicator Parameter Stabilization

8.4.1 General Description of Method

This purge method uses measurements of indicator parameters in addition to purging calculated well volumes to determine when a well is sufficiently purged of stagnant water. A minimum number of well volumes must be removed regardless of indicator parameter values unless the well is low yielding (Sections 8.4.7 and 8.4.9). If indicator parameter stabilization does not occur after the pre-determined volume has been removed, purging continues until stabilization is achieved. Indicator parameters to be

measured, frequency of measurements, the acceptable variation of parameter value to define stabilization, and the minimum number of consecutive stable readings within the parameter variation for each indicator parameter should be specified in the scope of work. Indicator parameters that are commonly used in this purging method may include, but are not limited to, pH, specific conductance, turbidity, temperature, dissolved oxygen, and oxidation-reduction potential.

8.4.2 Purge Volume

A target minimum purge volume is determined as a goal to complete purging. The target purge volume consists of three well volumes and is evaluated by measuring ground water indicator parameters.

8.4.3 Well Volume Calculations

The well volume calculation takes well construction details and the column of standing water in the well and converts the parameters to a volume of water. A multiple of the well volume may be used as a development goal or an assessment of the viability of attaining a representative sample from the formation.

The well volume calculation consists of three major elements:

1. A calculation of the volume of water in the casing.
2. A calculation of the volume of water in the filter pack outside of the casing.
3. A conversion of the volumes from feet to gallons.

Simple alternative equations are presented following the detailed calculation. The following equations are used to calculate the well volume (refer to Attachment 9.2).

$V_c = (d_i/2)^2 * (TD-H)$
$V_f = [(d_H/2)^2 - (d_o/2)^2] * (TD- S \text{ or } H) * (P)$
$V_t = (V_c + V_f)\ (7.48 \text{ gallons/ft}^3)$
V_c = Volume of water in casing (ft^3)
V_f = Volume of water in filter pack outside of the casing (ft^3)
V_t = Total volume of water in well (gallons)
d_i = Inside diameter of casing (ft)
d_o = Outside diameter of casing (ft)

d_H = Diameter of borehole (ft)
TD = Total depth of well (ft)
H = Depth of water from ground surface (ft)
S = Depth to base of seal from ground surface (ft)
P = Estimated porosity of filter pack (~35%)

The relative contribution to total volume from the casing and the filter pack varies with the diameter of the well, the diameter of the borehole, and the height of the water column in the well. A larger diameter borehole will result in a greater proportional total volume contribution from the filter pack. A standing water column above the top of the filter pack will result in a proportional contribution increase from the casing volume. Different combinations of parameters vary the relative contributions from the casing and filter pack.

The relative contribution from the casing and filter pack is an important consideration when rough field estimates are calculated. The following set of field equations are a simple and conservative alternative to the above-detailed equations. The pertinent calculation assumes that the relative contribution to total volume from the filter pack and casing is constant and that the measured height of the water column corresponds to an equivalent saturated filter pack. The calculation is conservative since the filter pack may be less than the height of the water column. The following simple equations may be used most advantageously when the water column is not significantly above the filter pack.

CASING DIAMETER	HEIGHT WATER COLUMN		CONVERSION FACTOR		WELL VOLUME
2-inch	TD-H	*	0.163	=	
3-inch	TD-H	*	0.367	=	
4-inch	TD-H	*	0.653	=	
5-inch	TD-H	*	1.020	=	
6-inch	TD-H	*	1.469	=	
8-inch	TD-H	*	2.611	=	
10-inch	TD-H	*	4.080	=	
12-inch	TD-H	*	5.875	=	

A final alternative equation for calculating three well volumes may be used for two-inch and four-inch internal diameter wells.

two-inch well: (TH-D)/2 = 3 well volumes

or

four-inch well: (TH-D) * 2 = 3 well volumes

8.4.4 Well Purging

Well purging by this method is performed by means of a bailer or a pump.

8.4.5 Purging by Bailer

A bailer can be used to purge a well. The choice of materials used in the construction of the bailer that is used for purging should be based upon knowledge of what compounds may be present in the sampling environment and how the bailer materials may interact via leaching, adsorption, or catalysis. Typically, bailers constructed of PVC, polyethylene, polypropylene, or TFE-fluorocarbons can be used for purging activities. The following steps are performed when purging a well with a bailer.

- Fasten nylon line to the bailer (and reel if used).
- Slowly insert the bailer into the well. The bailer should not free-fall into the well.
- Remove stagnant water from the well. The bailer should be lowered into the well to a point just below the water level.
- Withdraw purge water to a bucket to determine volume.
- At the completion of each well volume, or more often, if required, partially fill a container with water to measure ground water indicator parameters.
- Measure and record the appropriate ground water indicator parameters.
- Rinse the measuring instruments with distilled water after each measurement.
- Repeat until purging is determined to be complete based on purge volume and parameter stabilization.

- If dissolved-phase contaminants of interest are known to concentrate near the top or bottom of the screened zone, it may be desirable to position the bailer to target this zone.

8.4.6 Purging by an Electric Submersible Pump

A submersible electric pump can be used to purge a well. The submersible pump should be constructed of relatively inert material, such as stainless steel, TFE-fluorocarbons, and Viton. The following steps are performed when purging a well with a pump utilizing this purging method.

- New or dedicated discharge tubing is connected to the pump with a hose clamp. The length of discharge tubing should be long enough to position the pump within the screened interval of the well. Excess tubing should be avoided.
- The pump is slowly inserted into the well. The pump should be positioned just below the water level in the well. The pump should not be positioned within the well screen if the water level is above the well screen. If the distance from the water level to the top of the well screen is long, the sample pump can be lowered gradually while purging, so that at the completion of purging the pump intake is just above the well screen. This practice will minimize the contact time between the purged ground water and the well construction materials, as well as ensure the evacuation of the stagnant water above the screen. For water columns within the well screen, the pump should be set at a sufficient depth below the water level such that drawdown during pumping does not allow air to enter the pump. If the well is screened across layers of contrasting hydraulic conductivity, the pump intake should be positioned adjacent to the zone of highest hydraulic conductivity. If dissolved-phase contaminants of interest are known to concentrate near the top or bottom of the screened zone, it may be desirable to position the pump intake to target this zone.
- Secure the discharge tubing when the desired pump position is achieved in the well.
- The electric lead from the pump is connected to its frequency control box.
- Start up the generator and turn on the pump at the frequency control box. Make sure that the initial flow rate is low. Increase the rate slowly to the desired level. The withdraw rate that minimizes drawdown while satisfying time constraints should be considered. The well-purging flow rate should not be great enough to produce excessive turbulence in the well.
- Withdraw purge water to buckets or other containers to determine volume.
- At the completion of each well volume, or more often if required, partially fill a container with purge water to measure ground water parameters.

- Measure and record the appropriate ground water indicator parameters.
- Rinse the measuring instruments with distilled water after each measurement.
- Repeat until purging is complete.

8.4.7 Purging in Low-Permeable Formations

Different purging procedures may need to be followed when purging wells that are installed into low hydraulic conductivity aquifers or formations that are not able to yield at least three well volumes during purging. If the water level in the well is above the top of the well screen, purging activities (whether using a bailer or pump) should continue until the water level is just above the top of the well screen. The purge withdraw rate should be as low as possible to minimize the drawdown in the well.

If a well has an open interval across the water table in a low permeability zone, there may be no way to avoid pumping and/or bailing the well dry. In this case, the well should be sampled at some appropriate time period such that a sufficient volume of water is in the well for sampling purposes.

8.4.8 Stabilization of Ground Water Indicator Parameters

Indicator parameters to be measured, frequency of measurements, the acceptable variation of parameter value to define stabilization, and the minimum number of consecutive stable readings within the parameter variation for each indicator parameter should be specified in the scope of work. Indicator parameters that are commonly used in this purging method may include, but are not limited to, pH, specific conductance, turbidity, temperature, dissolved oxygen, and oxidation-reduction potential. Typically, stabilization is considered achieved when measurements are within approximately ten percent over two consecutive measurements. Other more conservative stabilization criteria may be applicable under specific federal, state, or local regulatory programs.

8.4.9 Determining Completion of Well Purging

Well purging is considered complete when one of the following situations is obtained.

- For high yielding wells, purge at least three casing volumes and ground water indicator parameters have stabilized.

- For low yielding wells (well incapable of yielding three casing volumes) whose water level is above the top of the well screen, purge the well until the water level is just above the top of the well screen. One sample should be taken for measurement of ground water indicator parameters prior to sampling the well. The well should not be purged dry.
- For low yielding wells (wells incapable of yielding three casing volumes) whose water level is located below the top of the well screen, purge the well to dryness once. As soon as the well recovers sufficiently, one sample should be taken for the measurement of ground water indicator parameters prior to sampling the well.
- If ground water indicator parameters do not stabilize, additional purging should be conducted until the parameters are stable.

8.5 Low Flow/Low Stress Purging

8.5.1 Description of Method

Low flow purging involves removing water from a well directly from the screened interval without disturbing any stagnant water above the well screen. This is done by pumping the well at a low enough flow rate to maintain minimal drawdown of the water column within the well as determined through water level measurements during pumping. A variable speed, low flow pump must be used in this purging method. Pumping at low flow rates hydraulically isolates the column of stagnant water in the well and negates the need for its removal prior to sample collection. Typical flow rates used in this purging method are based on site-specific and well-specific criteria, but are typically on the order of 0.1 to 0.5 liters/minute (L/min). Pumping waters levels in the well and ground water quality indicator parameters are monitored during purging, with stabilization indicating that purging is completed and sampling can commence.

8.5.2 Description of Procedure

The following procedure describes the low flow/low stress purging method.

- Slowly insert the pump into well. If the well is screened across a single zone of interest, the pump intake should be positioned in the middle portion of the well screen. If the well is screened across layers of contrasting hydraulic conductivity, the pump intake should be positioned adjacent to the

zone of highest hydraulic conductivity. If dissolved-phase contaminants of interest are known to concentrate near the top or bottom of the screened zone, it may be desirable to position the pump intake to target this zone.

- Measure the water level in the well after the pump has been installed to the desired depth.
- Begin to pump the well at a low flow rate to minimize mobilization and entrainment of particulate matter that is not naturally mobile under ambient, non-pumping conditions. The purging flow rate for this method should be determined on a well-specific basis. In general, the initial flow rate should be 100 mL/min or less. The flow rate should be measured periodically during purging (approximately every three to five minutes).
- From the time the pump is started, the water level in the well should be measured to determine the amount of drawdown caused by pumping. The flow rate can be increased if drawdown is very slow or imperceiveable. If drawdown is rapid and continuous, the pumping rate should be reduced until drawdown decreases and stabilized. Drawdown should not be greater than 0.1 meters (0.33 feet, or approximately 4 inches). At the beginning of purging, water level measurements should be initially measured every one to two minutes to the point at which the water level has been stabilized. After the water level has stabilized, water level measurements should be measured periodically during purging (approximately every three to five minutes).
- Ground water quality indicator parameters should be measured to determine when purging is complete and sampling can commence. Water quality indicator parameters are monitored at specific intervals and should be recorded after a minimum of one tubing volume has been purged from the well (typically every three to five minutes).
- Once the indicator parameters have stabilized, purging is completed and the well may be sampled. The indicator parameters are considered stable when three successive readings fall within appropriate ranges shown below:

    - pH +/- 0.2 pH units
    - specific conductivity: +/- 3% S/cm
    - Dissolved Oxygen +/- 10% or +/- 0.2 mg/l
    - Eh or ORP +/- 20 mV
    - Turbidity +/-10% (when turbidity is greater than 10 NTUs)

- Other more conservative stabilization criteria may be applicable under specific federal, state, or local regulatory programs.

8.6 Disposition of Purge Water

Purge water is managed as determined by the project requirements. Purge water may be:

- containerized for subsequent characterization and disposal;
- approved to an on-site treatment system;
- permitted to an off-site sanitary sewer system;
- routed to an on-site sanitary sewer system;
- routed to an on-site storm sewer system; and
- directed to surface soils.

8.7 Decontamination of Purging Equipment

Well purging equipment is decontaminated in accordance with SOP 6-1 (*Decontamination of Water Sampling Equipment*) and the project requirements.

8.8 Documentation

Information from the purging event should be documented in the Field Logbook and/or Ground Water Sampling Form (Attachment 9.1). Key information includes:

- Purging method
- Pump placement in the well
- Purge volume
- Ground water indicator parameters
- Disposition of purge water

8.9 Related Procedures

- SOP 6-1 *Decontamination of Water Sampling Equipment*
- SOP 6-2 *Well Development*
- SOP 6-4 *Ground Water Sampling*
- SOP 6-6 *Field Filtration of Water Samples*

9.0 ATTACHMENTS

9.1 Ground Water Sampling Form

9.2 Well Volume Calculation Definition Sketch

9.3 Ground Water Well Purging Method Considerations

THE PAYNE FIRM, INC.
STANDARD OPERATING PROCEDURE

SUBJECT: Ground Water Sampling

PROCEDURE NO.: SOP 6-4

EFFECTIVE ISSUE DATE: February 7, 2003

REVISION NO.: 2

PRIOR EFFECTIVE DATE: November 19, 1993

SITE-SPECIFIC AMENDMENT: None

1.0 PURPOSE

The purpose of this procedure is to describe methods for sampling ground water from monitoring wells and seeps.

2.0 SCOPE

This procedure applies to methods for collecting a ground water sample from a monitoring well with a bailer, submersible pump, or peristaltic pump after proper purging has been accomplished or from a water seep with a scoop. This procedure may also be used to sample other types of wells or subsurface conduits (i.e. open boreholes, small diameter (less than two inches) wells, Geoprobe borings).

3.0 REQUIREMENTS

The appropriate sampling method must be determined for each monitoring well and incorporated into the project work plan and/or scope of work. Well development (SOP 6-2), if necessary, and well purging (SOP 6-3) must be performed prior to sampling.

If non-dedicated ground water sampling equipment is used, then it must be properly decontaminated and/or disposed after sampling. The ground water sampling method and intended analysis methods must be documented in the Field Logbook and/or Ground Water Sampling Form.

4.0 REFERENCES

American Society for Testing and Materials, May 1996 (Re-approved 2001). *Standard Guide for Planning and Preparing for a Ground Water Sampling Event*, D 5903-96.

American Society for Testing and Materials, January 1998. *Standard Guide for Documenting a Ground Water Sampling Event*, D 6089-97.

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American Society for Testing and Materials, April 2000. *Standard Guide for Field Preservation of Ground Water Samples*, D 6517-00.

American Society for Testing and Materials, August 2000. *Standard Guide for Field Filtration of Ground Water Samples*, D 6564-00.

American Society for Testing and Materials, March 2001. *Standard Guide for the Selection of Purging and Sampling Devices for Ground Water Monitoring Wells*, D 6634-01.

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American Society for Testing and Materials, March 2002. *Standard Practice for Low-Flow Purging and Sampling for Wells and Devices Used for Ground Water Quality Investigations*, D 6771-02.

Ohio Environmental Protection Agency, February 1995. *Technical Guidance Manual for Hydrogeologic Investigations and Ground Water Monitoring*.

United States Environmental Protection Agency, September 1986. Resource Conservation and Recovery Act (RCRA). *RCRA Ground Water Monitoring Technical Enforcement Guidance Document (TEGD)*, OSWER-9950.1.

United States Environmental Protection Agency, May 2002, *Ground Water Sampling Guidelines for Superfund and RCRA Project Managers*, EPA 542-S-02-001.

5.0 DEFINITIONS

Bailer - A hollow tubular receptacle, usually made of polyvinyl chloride (PVC) or Teflon, with a ball check-valve at the bottom. When the bailer is raised through the water column, the ball settles on the bottom, creating a seal and allowing retrieval of a quantity of trapped water.
Composite Sample - A non-discrete sample taken at one or more locations and/or over one or more time intervals.
Discrete (Grab) Sample - A sample collected at a particular time from a single location.
Low Flow Sampling - A ground water sampling technique where the purge and sampling rates do not result in significant changes in formation seepage velocity.
Peristaltic Pump - A low volume suction pump which causes fluid to flow through flexible tubing by sequential compression of the tubing. Flexible tubing is inserted around revolving roller heads and is sequentially compressed. A reduced pressure is created in one part of the tubing thereby drawing in fluid. Flexible tubing may be inserted to the sampling depth or connected to other tubing inserted to sampling depth.
Submersible Pump - A sealed electric motor that powers an impeller at a variable rpm.
Water Quality Indicator Parameters - Those physical or chemical properties, or both, used as a correlative measure to determine when water to be sampled reflects ambient ground water chemistry.

6.0 RESPONSIBILITIES

6.1 Project Manager

The Project Manager is responsible for selecting the appropriate sampling method, determining disposition of development and/or purge water prior to sampling and incorporating the requirements into the project work plan or scope of work.

6.2 Field Operations Leader

The Field Operations Leader is responsible for ensuring that field personnel are trained in the use of this procedure and that the necessary equipment is available to properly sample a monitoring well. The Field Operations Leader communicates the scope of work to field personnel prior to arrival at the work site and arranges the disposition of purged water.

6.3 Field Geologist/Field Technician

Field personnel are responsible for understanding and implementing this procedure and documenting sampling information in the Field Logbook and/or Ground Water Sampling Form.

7.0 EQUIPMENT

- Bailer
- Nylon Line
- Reel to Retrieve Bailer
- Water Level Meter
- Turbidity Meter
- pH/Conductivity Meter
- Thermometer
- Appropriate Chemical-Resistant Gloves
- Appropriate Sample Containers
- Sample Preservative (if needed)
- Sample Filter (if needed)
- Sample Cooler
- Sample Labels
- Chain-of-Custody Form
- Ice
- Field Logbook
- Ground Water Sampling Form
- Submersible Pump
  - Pump Tubing
  - Hose Clamps
  - Pump Frequency Control Box
  - Generator
  - Grounding Rod
  - Electrical Cord
- Masterflex Peristaltic Pump
  - Silicone Tubing
  - Electric Supply Connections
  - 12-volt Battery

- Hammer
- Flathead Screwdriver
- Plastic Sheeting
- Container for Parameter Measurements
- Utility Knife/Tubing Cutters
- Cellular Phone
- Well Keys
- Health and Safety Plan
- Decontamination Supplies (i.e. scrub brush, distilled water, alconox detergent)

Equipment that comes in contact with ground water samples should be constructed of material that is inert relative to the target analyte list.

8.0 PROCEDURE

8.1 Planning

Appropriate ground water sampling methods are evaluated for the work site and incorporated into the project scope of work. Sampling follows proper purging of monitoring wells or is directly obtained from seeps. Therefore, most planning for sampling is included in procedures for planning well development (SOP 6-2) and purging (SOP 6-3). The following factors may need consideration when planning for ground water sampling.

- Work plan or sampling and analysis plan.
- Well construction information.
- Sampling frequency.
- Sampling methods.
- Intended analyses.
- Coordination with an analytical laboratory.
- Purge water management practice.
- Whether sampling equipment should be dedicated, reusable, or disposable.
- Determination of the need for sample preservatives or filtration.
- Decontamination methods, if applicable.
- Whether special sampling requirements or equipment are necessary.

- The need for field quality assurance/quality control (QA/QC) samples (i.e. field duplicates, trip blanks, equipment/field blanks).
- Access to wells or seeps.
- Coordination with site personnel.
- Order of well sampling.
- Arranging laboratory sample bottles and supplies.
- Health and safety considerations.

Wells should be sampled in order from upgradient to downgradient and/or least contaminated to most contaminated.

8.2 Scope of Work

A scope of work is formulated by the Field Operations Leader based on the project requirements and is communicated to the field personnel prior to arrival at the work site. The scope of work will include the methods, goals, intended analyses, and disposition of excess water used in sampling a well.

8.3 Set Up

The following steps are performed prior to sampling the well.

- Assemble the necessary sample bottles and preservatives at the well location.
- Ensure that labels and a chain-of-custody record are available for proper labeling and custody of samples (SOP 1-3).
- Ensure that an iced cooler is nearby for temporary storage of samples prior to packaging and shipping (SOP 1-4).
- Properly purge the well (SOP 6-3).

8.4 Ground Water Sampling Methods

Ground water is sampled immediately after purging has been completed. Ground water can be sampled with a bailer, a submersible pump, or by means of a peristaltic pump. The sampling equipment may be dedicated to the well, reusable, or disposable. The same equipment that is used to purge the well is also used to sample the well unless otherwise specified by the project requirements or if field conditions

suggest that a representative sample may not be obtained with the same equipment (e.g. evidence of non-aqueous phase liquids (NAPL), turbidity residues, biofouling residues, extreme parameter changes).

8.4.1 Sampling with a Bailer

The following steps are performed to sample a well by means of a dedicated, reusable or disposable bailer after purging has been completed.

- Slowly insert the bailer into the well. The bailer should not freefall into the well. Freefall may induce volatilization of organic constituents, thus altering the chemistry of the sampled ground water.
- The depth at which the bailer is stopped to collect ground water is dependent on the sampling objectives and well construction. In general, the bailer should collect water from within the screened interval of the monitoring well. If light NAPL are suspected, the well should have been designed to screen the top of the water-bearing formation and samples should be collected from immediately below the water level. If dense NAPLs are suspected, the well should have been designed to screen the bottom of the water-bearing formation and the samples should be collected from immediately above the bottom of the well. Otherwise, samples should be collected from near the center portion of the screened interval.
- Slowly retrieve the bailer from the well.
- All sample bottles are carefully filled at the well head.
- Sample bottles are filled in order depending on the intended laboratory analyses. Laboratory results may be affected by sampling activities and are rated by analysis in order from most sensitive to least sensitive (Attachment 9.3).
- Transfer the contents in the bailer to a sample bottle in a way that will minimize agitation and aeration. The sample bottle(s) for one intended analysis should be filled from a single bailer, if possible.
- Preserve and/or filter samples as necessary.
- Mark each sample bottle with the appropriate sample identification label(s). Be sure to wipe residues from the outside of the bottles prior to labeling.
- Place the sample bottles in the iced cooler for temporary storage.
- Record sampling information in the Field Logbook and/or on the Ground Water Sampling Form (Attachment 9.2).

8.4.2 Sampling with a Submersible Pump

A submersible pump (e.g. Grundfos Rediflo II, piston pump, et.al.) may be used to sample a well. The following steps are performed to sample a well by means of an electric pump after purging (SOP 6-3) has been completed (with the same pump).

- When purging and sampling with a submersible pump, the pump is inserted into the well at the desired depth and secured in place. The depth at which the pump is stopped to collect ground water is dependent on the sampling objectives and well construction. In general, the pump should collect water from the same location within the well as it was positioned for purging the well. If light NAPLs are suspected, the well should have been designed to screen the top of the water-bearing formation and samples should be collected from immediately below the water level. If dense NAPLs are suspected, the well should have been designed to screen the bottom of the water-bearing formation and the samples should be collected from immediately above the bottom of the well.
- For sample collection with a submersible pump, the pump discharge is kept low to mitigate the potential for agitation and volatilization of the water. The flow rate of the pump should be maintained at less than 100 mL/min if the sample is to be analyzed for volatile organic compounds (VOCs). For most other parameters, an appropriate sampling flow rate should be approximately 300 mL/min to 500 mL/min.
- If the monitoring well was purged using the low-flow purging method, the pumping rate used for sample collection may remain at the established purging rate or it may be adjusted downward to minimize aeration, bubble formation, or turbulent filling of sample bottles.
- All sample bottles are filled from the discharge hose at the well head.
- Sample bottles are filled in order depending on the intended laboratory analyses. Laboratory results may be affected by sampling activities and are rated by analysis in order from most sensitive to least sensitive (Attachment 9.3).
- Pump the water into a sample bottle in a way that will minimize agitation and aeration.
- Preserve samples as necessary.
- Mark each sample container with the appropriate sample identification label(s). Be sure to wipe residues from the outside of the bottles prior to labeling.
- Place the sample bottles in the iced cooler for temporary storage.
- Shut pump and generator off.
- If the pump is non-dedicated, carefully withdraw the pump from the well casing.

- Record sampling information in the Field Logbook and/or on the Ground Water Sampling Form (Attachment 9.2).

8.4.3 Sampling with a Peristaltic Pump

A peristaltic pump may be used to sample the well. Typically, the peristaltic pump is used when a well is known to yield very little water, the static water level is shallower than 20 feet deep, and the analytes of concern are not affected by changes in the sample that can be caused by application of reduced pressure when used under low flow rates and low lift conditions. Depths greater than 15 feet present mechanical difficulties due to the nature of the pumping mechanism. The low well yield may necessitate a minimal amount of purging, which can be performed with the peristaltic pump prior to sampling. The following steps are performed when sampling with a peristaltic pump (e.g. Masterflex).

- Sufficient flexible tubing is attached to the peristaltic pump to properly operate the pump and reach or connect to other tubing to reach the target sampling interval of the well.
- The lower end of the tubing is kept off the bottom of the well to prevent sediment uptake and creating a vacuum lock between the tubing and the bottom of the well screen.
- Connect electric supply cord to pump. Plug in the pump to a sufficient power source (e.g. car lighter or battery).
- Turn on the pump. Check to make sure the discharge flow is in the proper direction (inform, not to the well).
- Properly purge the well according to SOP 6-3.
- If the monitoring well was purged using the low-flow purging method, the pumping rate used for sample collection may remain at the established purging rate or it may be adjusted downward to minimize aeration, bubble formation, or turbulent filling of sample bottles.
- Sample bottles are filled in order depending on the intended laboratory analyses. Laboratory results may be affected by sampling activities and are rated by analysis in order from most sensitive to least sensitive (Attachment 9.3).
- Pump the water into a sample bottle in a way that will minimize agitation and aeration.
- Preserve samples as necessary.
- Seal the sample bottle(s) and mark with the appropriate sample identification label(s). Be sure to wipe residues from the outside of the bottles prior to labeling.
- Place the sample bottles in the iced cooler for temporary storage.
- Reverse the direction of the pump to drain the water from the hose.
- Shut pump off and dispose of silicone tubing.

- Record sampling information in the Field Logbook and/or on the Ground Water Sampling Form (Attachment 9.2).

8.5 Sampling Water from a Seep

The following steps are performed to sample a water seep by means of dedicated, reusable, or disposable scoop (e.g. stainless steel, Teflon, glass, etc.).

- Press the leading edge of the scoop into the water seepage flow path with the remaining portion of the scoop tipped lower to allow for the collection of the water sample.
- When the water level in the scoop begins to overflow the retention capacity of the scoop, remove the scoop and slowly pour the ground water into the sample bottles.
- Repeat the above procedure as many times as may be required to fill all sample bottles.
- Sample bottles are filled in order in order depending on the intended laboratory analyses. Laboratory results may be affected by sampling activities and are rated by analysis in order from most sensitive to least sensitive (Attachment 9.3).
- Preserve sample as necessary.
- Seal the sample bottle(s) and mark with the appropriate sample identification label(s). Be sure to wipe residues from the outside of the bottles prior to labeling.
- Place the sample bottles in the iced cooler for temporary storage.
- Record sampling information in the Field Logbook and/or on the Ground Water Sampling Form (Attachment 9.2).

8.6 Decontamination

Decontamination of reusable sampling equipment is performed as per SOP 6-1.

8.7 Documentation

Information from the sampling event is documented in the Field Logbook and/or the Ground Water Sampling Form (Attachment 9.2). This may include, but is not limited to, the following information:

- General information (such as site name, well identification, weather conditions, sampling team members, instrument calibration information, wellhead observations, decontamination procedures, and deviations from the sampling and analysis plan or work plan).

- Static water level and total depth measurements.
- Monitoring well purging information.
- Monitoring well sampling information.
- Ground water sample preparation information. Sample labels and the chain-of-custody record are filled out as per SOP 1-3.

8.8 Related Procedures

- SOP 1-1 *Use of Field Logbooks*
- SOP 1-3 *Labeling and Custody of Samples*
- SOP 1-4 *Packaging and Shipping of Samples*
- SOP 6-1 *Decontamination of Water Sampling Equipment*
- SOP 6-2 *Well Development*
- SOP 6-3 *Well Purging*
- SOP 6-6 *Field Filtration and Preservation of Water Samples*

9.0 ATTACHMENTS

9.1 Ground Water Sampling Form

9.2 Order of Ground Water Sample Collection

THE PAYNE FIRM, INC.
STANDARD OPERATING PROCEDURE

SUBJECT: Field Filtration of Water Samples

PROCEDURE NO.: SOP 6-6

EFFECTIVE ISSUE DATE: November 19, 1993

REVISION NO.: 1

PRIOR EFFECTIVE DATE: July 15, 1993

SITE-SPECIFIC AMENDMENT: None

1.0 PURPOSE

The purpose of this procedure is to describe steps for filtering water samples in the field in order for analytical testing of dissolved constituents.

2.0 SCOPE

This procedure applies to the field filtration of water samples to remove suspended particulate matter prior to analysis.

3.0 REQUIREMENTS

The filtration of water samples collected in the field may be required for several inorganic analytical parameters including dissolved metals.

Samples for organic analyses shall never be filtered.

4.0 REFERENCES

United States Environmental Protection Agency, September 1986. *Resource Conservation and Recovery Act (RCRA) Ground Water Monitoring Technical Enforcement Guidance Document*, OSWER-9950.1.

5.0 DEFINITIONS

Peristaltic Pump - A mechanical pump that causes fluid to flow through flexible tubing by sequentially compressing parts of the tubing creating internal pressure differences.

6.0 RESPONSIBILITIES

6.1 Field Operations Leader

The Field Operations Leader is responsible for ensuring that field personnel have been trained in the use of this procedure and that the necessary filtering equipment is available for filtering.

6.2 Field Geologist

The Field Geologist/Field Technician is responsible for performing field filtration and documenting the activity in the Field Logbook and on the chain-of-custody record.

7.0 EQUIPMENT

- Peristaltic Pump
- Prepackaged Disposal In-Line Filters in Holders (0.45 micron filter for metals analyses and 0.30 micron for radionuclide analyses)
- Silicone Tubing
- Sample Bottles
- Preservative
- Utility Knife

8.0 PROCEDURE

8.1 The Situation

A ground water sample has been collected into a temporary sample container with the recognition that it will need to be filtered upon transfer to a final container.

8.2 Filtration Set-Up

The peristaltic pump tubing and appropriate filter should be assembled. A length of new silicone tubing sufficient to thread through the pump to the two sample containers (~3 feet) should be cut. The unused tubing should be secured in a clean Ziploc package. A new filter should be attached to one end of the tubing and the tubing threaded through the pulse end of the pump. The pump head should be tightened and the pump cord connected to a power supply (car cigarette lighter receptacle).

8.3 Filtration

The section end of the tubing should be submerged in the temporary sample container. Turn on the pump and draw the sample through the filter. Monitor the water movement through the filter to avoid a pressure buildup due to clogging. Change the filter as necessary.

When the sample container is almost full, stop the pump and add preservative, if required, then cap the sample bottle. Dispose of excess sample water with the purge water.

Disassemble the peristaltic pump system and properly dispose of the filter and silicone tubing.

8.4 Documentation

Identify that the samples has been filed-filtered in the Field Logbook and on the chain-of-custody record.

8.5 Related Procedures

- SOP 1-3 Labeling and Custody of Samples
- SOP 1-4 Shipping and Packaging of Samples
- SOP 6-5 Ground Water Sampling

9.0 ATTACHMENTS

None.

THE PAYNE FIRM, INC.
STANDARD OPERATING PROCEDURE

SUBJECT: Project Management

PROCEDURE NO.: SOP 8-1

EFFECTIVE ISSUE DATE: October 5, 2000

REVISION NO.: 0

PRIOR EFFECTIVE DATE: None

SITE-SPECIFIC AMMENDMENT: None

1.0 PURPOSE

The purpose of this procedure is to set forth the role and requirements for managing a technical project at the Payne Firm. Any technical person may manage a project at the discretion of the Operations Manager. This Project Management Procedure focuses on communication and documentation with the project team and client, and project finances.

2.0 SCOPE

This procedure provides protocols for documentation, communication and management of technical projects at the Payne Firm. It emphasizes client interface and financial accountability for projects. This procedure offers a methodology to perform the project management function in an efficient, documented and successful way.

The Payne Firm recognizes that each project is different and may require emphasis on specific portions of this procedure. It is within the scope of this procedure for the Project Manager to use professional judgment when implementing this procedure.

3.0 REQUIREMENTS

All technical employees must review this procedure and be trained in its application by senior management. Successful implementation of project management components shall be tracked as part of the training documentation as indicated in Attachment 10.1. A Project Manager must be familiar with the details of the job initiation process, budget development, project scope, project status and invoicing procedures. Successful implementation of project management components shall be tracked as part of training as indicated on Attachment 10.1. Variances from the procedure and reasons for the deviation must be documented immediately.

4.0 REFERENCES

Preparation of this SOP is based in part on input from the Payne Firm staff during multiple "brown bags" on project management and reference material provided by Mr. Gary Bates and the International Institute for Learning, Inc. The PRELIMINARY DRAFT Project Management Standard Operating Procedure was peer reviewed by Mr. Michael L. Woodruff, C.P.G. and Dr. Jerry Lisiecki, Ph.D. Many of the their comments are incorporated in the SOP.

5.0 DEFINITIONS

Budget – The projected amount of money available for, required for or assigned to a specific project including a plan for resources and expenditures. The budget should allow the Payne Firm to make a fair profit at a reasonable cost to the client.
Client – The client is the lifeblood of our existence. The client engages the Payne Firm for professional services and expertise. A project may have two or more client contacts - one at the corporate level, one at the local level, and/or outside counsel. The Project Manager must determine who is the primary contact.
Client Management – The art of:

- Managing a client is to complete the project as win-win for both the client and the Payne Firm; and
- Maintaining contact with a client on a frequency and in sufficient detail do that the client is satisfied with both.

The result of effective client management is a satisfied client and reasonable profit for the Payne Firm.

Communication – The process by which information is transferred between individuals. Communication may be verbal, written, electronic, pictorial or non-verbal (i.e., gesture or body language).
Contract – A binding agreement between two or more persons or parties that is legally enforceable. If at all possible, the Payne Firm standard contract should be used. If the client wants to use their contract, the Principal or Operations Manager must approve the client's contract. The project manager should review the client's contract to advise the Principal or Operations Manager of potential Payne Firm liability. To have a binding agreement for the client to acquire our services, a signed contract or, in some cases, a signed proposal is needed. Some clients choose to issue purchase orders (PO) for services performed. This is acceptable to the Payne Firm.
Critical Path – The minimum length of time in which the project can be completed and helps identify which activities should be prioritized.

Harper Shuman – Financial software used by the Payne Firm to track time, project expenses, prepare invoices and various project specific financial reports and Payne Firm financial reports. Harper Shuman is available to all members of the Project Team through their computer terminal to assess the project financial status (*Advantage*) and tracking time (*Timekeeper*).

Invoice – A billing statement for services performed as related to a proposal and the project objective. The Payne Firm can generate ***detailed invoices*** and ***condensed invoices***. The invoice preferred by the Payne Firm is a ***condensed invoice***. If the client requires a specialized invoice, review the special need with the Business Office

Out-of-Scope Issues – Any potential work that is not identified in the Contracted Scope of Work, which is often synonymous with that of the proposal. The out-of-scope work must be specific, measurable, verifiable and authorized for implementation.

Project Life Cycle – The project has a life cycle that may be divided into four sections. These are conception, development, implementation and closure. Attachment 10.2 depicts the Project Life Cycle and the typical activities involved with each step of the life cycle.

Project Management – The activity of directing and coordinating human and material resources throughout a project life cycle by using management techniques to achieve predetermined or new objectives. Objectives are defined in a contract (proposal) or verbally conveyed by the client and documented by the Project Manager relative to:

- Client Needs
- Scope
- Quality
- Time
- Cost
- Client Satisfaction
- Team Satisfaction

Project Manager – Provides total management of the project to which he/she is assigned. The Project Manager implements the project by using his/her project management skills.

Project Number Requisition and Project Plan *(Job Sheet)* – The means for completing/establishing/ initiating the administrative functions of a project, such as obtaining a project number, accounting information, project plan, project description, schedule and preliminary identification of resources needed. The Job Sheet is completed by the Project Manager and reviewed by a Senior Person or a designee. The Job Sheet facilitates project management by summarizing the Project Plan including key

components, such as scope of work, project budget, resources (project team), schedule and success criteria of the project.

Project Objectives - Simply said, it is the desired results for a project. The desired results must be specific - not general, not overly complex, measurable, tangible and verifiable, realistic and attainable, and may be task specific for larger projects. It is important to note that both the client and Project Manager may have both primary and secondary or unclear agendas or goals. These secondary agendas must be understood to the extent possible in developing and addressing the project scope.

Project Team – Members include Payne Firm personnel, client personnel and external resources (e.g., laboratory, drillers, etc.). The Project Manager serves as the primary contact with the client and provides information to the project team as a whole.

Caution: The team members must <u>not</u> discuss the project with facility personnel or other individuals unless authorized by the Project Manager. For some projects, confidentiality is critical.

Proposal – Statement of the client's objectives proposed scope of work, budget, schedule, applicable standards (if known and warranted) and contract document. The proposal is also be useable as a marketing tool to demonstrate why the Payne Firm should be used for the client's project and what value the Payne Firm will bring to the project. Remember to have a binding agreement with a client, a signed contract or in some cases, a signed proposal is needed.

Proposal Log – A spreadsheet, in the **PFI-MGT** folder that summarizes the status of proposals.

Resource Planning – Identification and assigning of resources needed for a project from its inception during budget development and throughout the project. Coordination with the Operations Manager for resource requirements is typically needed.

Schedule – The timeframe for implementing a project scope of work. The schedule may incorporate the needs of the client, Payne Firm resource availability and/or contractor availability. The size and complexity of the project will dictate the size and complexity of the schedule.

Scope or Statement of Work – A statement (written or verbal) setting forth tasks or components of a project, which are designed to fulfill project objectives. The scope of the work includes a description of work, funding constraints, project specifications and milestone schedule. A verbal Scope of Work must be put in memorandum form to the project files and a copy sent to the client. Before the verbal scope of work is undertaken, when practical, the memorandum should be submitted to the client.

6.0 RESPONSIBILITIES

6.1 Project Manager

The Payne Firm member assigned to the role of Project Manager by the Operations Manager can be a person from any level of the organization. In any project, there may be several Project Managers (e.g., one preparing the proposal, related scope of work and budget [Conceptual Manager] and one implementing the scope of work and project close out [Project Manager]). When feasible, the Operations Manager will assign one person both roles. Some parts of Project Management will require efforts of both the Conceptual Manager and the Project Manager.

6.1.1 Project's Conceptual Manager

The role of the Conceptual Manager is to establish the goals and objectives for the project; develop the proposal including scope of work, potential team, schedule, and budget. The Conceptual Manager is to convey the information to the Project Manager prior to initiation of the project.

6.1.2 Project Manager

The Project Manager is responsible for implementing and completing the project. The Project Manager is to review the scope of work, schedule, assigned resources, and budget with the Conceptual Manager. Once resource needs are identified, coordination with the Operations Manager is recommended so that the project runs smoothly. It is also the responsibility of the Project Manager to implement this SOP and to ensure the Project Team has been trained in the use of this procedure and other SOPs applicable to the project.

6.1.3 Both the Conceptual and Project Manager

Caution: Both the Conceptual Manger and the Project Manager should attempt to determine if the Client has a secondary agenda that is not conveyed. To minimize the likelihood of a "surprise," communicate with the client to identify if the work will proceed or just need budgetary estimates, review the project objective as currently planned, in one year, in two years, periodically review the objective with the client. When dealing with a client that has a law firm that we work with, you can discuss secondary agendas with the attorney. You may ask the attorney, "What does Giovanni really want on this project?" Sometimes the client does not know a secondary agenda is present, but that will surface with constant communication.

Comment: Some clients talk about a low-priced project, but want high-priced effort. When they get what they asked for, they often will complain about the cost. We will then give them the high-price work at a loss for the Payne Firm. This is one reason why discovering a "secondary agenda" before contract finalization is very important to the Payne Firm.

6.2 Project Team

Under the direction of the Project Manager, the Project Team is responsible for implementing the scope of work. Team member should offer suggestions to the Project Manager that may allow the project scope to be completed in a more efficient manner.

Unless approval is received from the Project Manager, members of the Project Team shall not discuss any aspects of the project with facility personnel or other individuals. It is the Team Member's responsibility to perform fieldwork according to the Payne Firm's SOPs.

6.3 Operations Manager

The Operations Manager can assign any Payne Firm member to the role of Project Manager. The Operations Manager will consider the Project Manager's skills, experience and ability to manage projects, client management and efficiency to assign a Project Manager. The Operations Manager assists the Project Manager in obtaining resources for a project.

The Operations Manager is responsible for assigning members to the Project Team. When doing so, the Operations Manager shall consider their skills, availability, timeframe, effort required, budget constraints, and knowledge of the project scope and client expectations.

6.4 Senior Persons

Senior Persons may be Project Managers, Conceptual Managers or Project Team Members. As a Team Member, the Senior Person serves as resource for both technical and non-technical issues. Non-technical issues include coaching, client interaction, agency assistance and other topics for which the Team needs assistance. The Senior Person should serve the role of QA/QC for the project. (The QA/QC role may also be delegated to other competent staff members.)

6.5 Staff Members

The Staff Members are any members of the technical or support staff, or the principal who assists the Project Manager with the project. Staff Members should consult with the Project Manager on all aspects of the project including, but not limited to, charging time, scope of work, schedule, procedures, budget, client communication and reporting.

6.6 Support Staff

Support Staff includes Word Processors, Drafting, 2D/3D, File Clerk and Business Office. The role of the Support Staff is as follows:

- Prepare document text and figures, as directed by the Project Manager or his/her designee;
- File documents related to the project in the appropriate file. The Project Manager shall designate the file folder list, which is part of the Job Sheet; and
- The business office role is to supply the Project Manager with project-related financial information and to advise the Project Manager of non-compliance with office procedures or client invoicing.

It is the Project Manager's responsibility to communicate and coordinate the activities of the Support Staff regarding schedule, other needs and correct project numbers on all documents.

6.7 Principal

The role of the Principal is to serve as a Project Manager and a resource. The Principal will only serve as a Project Manager and a resource for a limited number of projects when specifically requested by a client. The Principal, at his discretion, or at the request of a Project Manager, can serve as a limited resource for other Payne Firm projects. The Principal should assist, at his and the Project Manager's discretion, in Client Relations and/or critical meetings.

6.8 Business Manager

The role of the Business Manager is to assist the Project Manager in developing the project records, such as, Job Sheets, Project Numbers and evaluation of the Project Financials including preparing DRAFT and final invoices for approval by the Project Manager.

7.0 EQUIPMENT

No specific equipment is needed for this SOP. However, a Project Manager should be equipped with common sense, communication, technical and telephone skills, dependability, computer knowledge and a positive team attitude.

8.0 PROCEDURE

The procedures for implementing components of project management are detailed below. Attachment 10.3 shows a Project Management Flow Diagram.

The purpose and values of Payne Firm project management are:

- Team Building and a Common Agenda;
- The identification of time limits and formulation of schedules;
- Measurements of accomplishment against the plan;
- Quick identification of out-of-scope issues;
- Risks of overruns and delays are minimized;
- Knowing when objectives cannot be met or exceeded;
- Optimization of time and cost to complete;
- Optimization of resources;
- Enhancement of decision making; and
- Improved estimating capability for future planning.

8.1 Proposal Preparation

Project management begins with the initial communication with a potential client and the preparation of the proposal by the Conceptual Project Manager. Important elements in proposal preparation include understanding the project goals and objectives, the perceived preliminary scope of work and the desired schedule. These elements must be clearly identified prior to preparing a budget and may require follow up and clarification during proposal writing.

8.1.1 Initial Communication

Typically, but not always, "new clients" will be directed to the Operations Manager or in his absence the Principal or a Senior Person. An "old client" may contact the project manager that he/she has previously worked with on another project.

To initiate the process, the Operations Manager may assign the proposal development to a Payne Firm technical staff member. This person becomes the Conceptual Project Manager and initiates the proposal process by obtaining a Proposal Number by filling out information on the Proposal Log.

The following information (if not already known) must be obtained:

- The prospective client's name, company, address, telephone, fax and e-mail address;
- The location and address of the project;
- The purpose and objectives objective of the project;
- The work scope that the potential client envisions;
- Are there any special concerns (e.g. drilling in the vicinity of power lines);
- The desired schedule for the work to be performed and/or completed;
- When is a DRAFT Report due? and
- When is a FINAL Report due?

It is required that the initial project objectives and preliminary scope of work be repeated back to the prospective client to confirm that your understanding of this work scope and objectives is the same as that of the prospective client. For large and/or complex project additional communication may be anticipated to formulate the appropriate scope for multiple objectives.

Unless the client is well known to you, do not assume that the client is "normal." Instead assume that the client is unsophisticated and will need "hand holding" with many potential "what if" situations. For the unsophisticated client, the project goals and objectives need to be clearly defined.

8.1.2 Developing the Scope of Work

Data gathered during the initial conversation with the client is used to develop the scope of work (project definition) for the proposal. On all complex projects, (multi-tasks and high-dollar value) the scope of work must be prepared and reviewed with a Senior Person prior to preparing a proposal. For "normal" work, the Conceptual Project Manager can develop the scope of work and include it in the written proposal. The review of the scope of work will be part of the proposal review process.

It is suggested that most projects be divided into tasks to ease of cost estimating and scope development. In the written proposal, it is the Conceptual Project Manager's option if the detailed breakdown will be included in either the scope of work or the budget sections of the proposal. However, Payne Firm experience suggests that a very detailed scope or budget is preferable to those that are generic or standard.

See Caution in Section 8.1.5.

The Conceptual Project Manager is encouraged to use previous similar proposals to develop the scope of work. The Payne Firm has templates for a wide variety of projects available. If you are unsure if a template exists, consult with a Senior Person.

8.1.3 Resource Needs

After the initial communication with the prospective client is complete, the Conceptual Project Manager must determine likely resource needs based upon the identified scope of work. Once these potential needs are identified, confirm with the Operations Manager (or a Senior Person, if the Operations Manager is absent) regarding what resources may be available to meet the proposed project schedule. This is particularly critical for time sensitive or resource intensive projects.

8.1.4 Preparation of Opinion of Probable Cost (Cost Estimate or Budget)

With the scope of work developed in conjunction with the potential client and resource allocation agreed to with the Operations Manager, a project budget can now be prepared (Attachment 10.4). The budget-estimating template is in the file folder labeled **PFI-MGT**. The budget-estimating template is updated on a periodic basis and all staff is advised of the update by electronic mail.

When developing a cost estimate for clients that are considered high maintenance (i.e., demanding and unsophisticated and in need of "hand holding"), additional time for communication must be included in the budget.

Items to consider when preparing an opinion of probable cost are:

- Has a similar project been completed in the past? If so, use the actual hours spent on that project as guidance;

- Individual time allocation (share this information with your Team when the project kicks off);
- For large projects, the best estimated budgets are prepared by breaking the big picture into smaller pieces, and then, developing estimated budgets for the smaller pieces. The total the individual pieces is summarized to come up with the total project estimated budget;
- Perceived Client needs (do we think they want a Rolls Royce or a bicycle). Typically, the client is looking for a quality project that is good enough to satisfy a regulator or auditor. Listening and repeating this back to the client will clarify their true objectives for both the client contact and the project manager; and
- Project location. Must be sure to recover travel time and expenses.

The budget-estimate template should be used on all projects that are not conducted on an unlimited time and materials (T&M) basis. If the Conceptual Project Manager is uncertain as to how to prepare an estimate, using the template, then the Conceptual Project Manager should consult with the Operations Manager or Senior Personnel. A senior level person, or designee, must approve the budget estimate sheet, once prepared. While there are some other exceptions, as a general rule, budget estimates should be prepared for any project that is not an unlimited T&M. Unlimited T&M projects do not require a budget sheet. However, a budget may help the project manager assure a successful project and also to hone the budgeting skills of the project manager.

8.1.5 Preparing the Written Proposal

Once the budget estimate and scope of work are established, the written proposal is completed. The proposal includes:

- An introductory paragraph that acknowledges that the Payne Firm is pleased to offer the proposal and the location where the work will be performed;
- A paragraph or section identifying the value that the Payne Firm brings to the client's project in attaining the project objectives;
- As an optional section to discuss and describe the Project Team;
- A section discussing the scope of work. The scope of work should be in sufficient detail to clearly define the planned work. ***(Caution: We need to balance the sufficient detail with providing a road map to clients to either do the work themselves or use our proposal to obtain other bids. Consult with the Operations Manager or Senior Persons, when in doubt.)*** Consequently, any deviation from the detailed scope of work may be considered as an out-of-scope issue. When the scope of work is written in general terms, depending on the client, any cost overruns may not be recoverable,

depending on the client. The Scope of Work can be written to include only major tasks or both major tasks and subtasks;

- A tentative schedule should be included with the proposal. The schedule can be descriptive or visual (CADD illustration, Timeline, table, graphic or an Excel spreadsheet). For completing this section, items to consider are the Client schedule, resource, equipment and subcontractor availability and coordination with client site personnel and activities. When discussing the schedule with a client, try to ascertain if there is a "real schedule" that differs from what has been offered. This can be best accomplished by simply asking the client.
- A section discussing how the results of implementing the scope of work will be presented. Care must be taken to specify what will be reported and how reporting will be provided such as verbally or in a bullet summary, a written DRAFT report in text or tabular form or both and/or the number of client reviews of the DRAFT report and the number of FINAL reports must be stated;
- A section dealing with cost issues related to the project. The cost section should be entitled "**OPINION OF PROBABLE COST**" and not budget or cost estimate. The reason for this labeling deals with our Errors and Omissions (E&O) insurance potential claims in as much as we are offering an "Opinion" and not a "Budget";
- In the OPINION OF PROBABLE COST section, we reference contractual terms and conditions. Unless the client objects, the Payne Firm's standard contract is to be used. If the client wants to deviate from the standard contract, review the deviation with the Operations Manager or Principal; and
- Finally, the proposal should be ended with a closing section that again thanks the client for the opportunity to submit a proposal and to further clarify the value and/or benefits of retaining the Payne Firm for the client's project.

For small projects (under $5,000) much of the detail described above may not be necessary. The Conceptual Project Manager should use good judgment as to what to include in the proposal.

8.1.6 Proposal Review

Once the proposal is completed, the scope of work, budget estimate and schedule are to be reviewed with the Operations Manager or a Senior Person. The Proposal submitted to the client must be signed by a minimum of two persons, one of which should be a Senior Person.

8.1.7 Proposal Follow-Up

Once the proposal is submitted, following-up on the proposal is critical for successful client communication and marketing. As the Conceptual Project Manager (proposal writer), you should inquire if:

- The proposal was received;
- Whether there are there any questions; and
- Can you clarify anything in the scope of work?

Proposal follow-up should be done within one to three days of the submitting the proposal. Depending on the project's anticipated start date, the proposal should be followed up every one to two weeks (sometimes monthly) until the project is awarded.

Comment: Proposal follow-up is often not done because it often is considered unimportant. This SOP debunks that myth. What better way is there to initiate client communication? ***It is always best to start the project communication, before the project officially kicks-off.***

8.2 Project/Job Initiation

Once the proposal is accepted, the project/job is initiated. Initiating the project includes: reviewing the proposal, confirming the availability of any required resources with the Operations Manager, and preparing a "Project Number Requisition and Project Plan Requisition Form" (Job Sheet) – Attachment 10.5.

The Job Sheet has two purposes:

- One purpose is for accounting needs to establish a project number and to provide information regarding the client for invoicing; and
- The second allows the Project Manager to develop a detailed project plan by reviewing, identifying, developing or obtaining the proposal, scope of work, project budget, resource needs (project team), schedule and success criteria of the project.

For large projects, a kickoff meeting with the Project Team is recommended. For small projects or one-person projects, a scoping meeting with the Operations Manager or Senior Person is recommended.

Preparation of the Job Requisition Form is not within the scope of this SOP. However, any Project Manager not familiar with the Job Requisition Form should become familiar with it by seeking assistance from the Operations Manager or Senior Personnel.

During the job initiation phase, the Project Manager should focus on the beginning tasks of the project, project milestones, and the critical path for the project. Some of the factors affecting the critical path are available personnel, outside contractors and delays caused by the client or other unforeseen issues. These are included in the Project Plan, a document whose primary purpose is to assure the project scope is completed on time.

The Project Plan should include the project objectives, schedule, tasks, subcontractors, cost, resources and billing information. Our Job Sheet will contain these issues when properly completed. If additional tasks are later added to the Project, the Project Manager must communicate this information with the Business Manager and Operations Manager by e-mail or a new Job Sheet.

8.3 Contract Documents

Once the proposal is accepted, the Project Manager must verify that a current contract for the work is available and on file with the Business Manager. If a contract is not in place, then the Project Manager should obtain a signed contract or confirm with the Operations Manager that initiation of the project without one is acceptable.

The Operations Manager or Principal must approve of any contract language changes requested by the client.

8.4 Ongoing Project Communication

It is the Project Manager's responsibility to initiate and maintain communication with the client, project team and Operations Manager.

8.4.1 Acceptable Means for Communication

To better communicate with clients, the Project Team and Operations Manager, Payne Firm personnel use the following methods of communication:

- E-mail with a **COPY of the e-mail to the project file.** Do not assume the client received the e-mail. Confirm receipt of the e-mail verbally or through a reply from the client
- Telephone with either a note to your personal logbook (e.g., spiral notebook) or by a Phone Memo. Copies of Phone Memos must be placed in the project file;
- Voice-mail with either a note to your personal logbook or by a Phone Memo. Copies of Phone Memos must be placed in the project file;
- Logbook with a copy of the notes related to the project communication to the file;
- Tape Recording with the tape being either transcribed or placed in the project file:
- Facsimile; or
- Documents (memos, letters, etc.).

8.4.2 Client Communication

When the project is awarded, the Project Manager must contact the client to confirm the scope of work, confirm the schedule and ask how and when the client wants to be advised of project status. Both a verbal and written "thank you" to the client after project award are strongly recommended. Unless instructed otherwise by the client, at a minimum, client contact should be at least weekly while the project is active and every three to four weeks when the project is inactive. As indicated in Section 8.4.1, communication with the client can be by telephone, voice mail, memos or e-mail. At least monthly verbal communication with the client is recommended.

The Project Manager may also communicate with the client at meetings. Be sure that meeting minutes are taken and copies submitted to clients and to the project file. During the meeting, confirm the project objectives and any business/strategic changes that may impact them.

The client must be informed when a schedule or budget is likely to exceed the agreed limits. No client ever objects to getting a project completed sooner than expected or under budget, but many object to delay or cost overrun even with justification. The client must be immediately be informed of unforeseen external delays (e.g., driller's rig broke down) and how that may impact the project cost or schedule.

8.4.3 Team Communication

Keeping your Project Team informed is critical to a successful project. You should keep the Project Team abreast of the scope of work, budget and overall project progress. As part of project initiation and your communication with the Project Team, appropriate SOPs should be reviewed or, at the very least,

the team made aware of the SOPs. The Project Manager's communication with the Project Team may be on a need to know basis. The Project Manager is cautioned that the Support Staff (CADD and Word Processing) is generally part of the Team and must be involved in the communication process. Communication with all members of the Team must be timely so that no Payne Firm projects are sidetracked or deadlines are missed

8.4.4 Communication with the Operations Manager

It is the responsibility of the Operations Manager to assign resources to the Project Manager. It is imperative that the Project Manager communicates with the Operations Manager as to resource and equipment needs, including any special needs. At the discretion of the Operations Manager, he may delegate the assignment of resources to a Senior Person.

The Project Manager must periodically advise the Operations Manager of the project status. Project updates to the Operations Manager may be verbal or by e-mail and should be performed at least biweekly.

8.5 Project Implementation

8.5.1 Project Progress

Once the project is underway, the Project Manager must ensure that the project is progressing as planned. If additional specialized resources are needed, the Project Manager should obtain those resources from the Operations Manager

Periodically, the Project Manager must assess the project status relative to schedule, scope and budget. If there is any deviation, either positive or negative, the Project Manager must communicate the deviation to the client within one week of its discovery. Periodically is a relative term and the Project Manager must use personal discretion as to the frequency the project progress is evaluated. Generally, the greater the labor hours, the more frequent the project progress should be evaluated. For all projects, project progress must be assessed at least monthly.

WHEN PROJECTS ARE FIXED BIDS, POSITIVE DEVIATIONS RELATIVE TO BUDGET MUST NOT BE CONVEYED TO THE CLIENT.

In assessing the project progress, a midcourse correction may be needed. If so, review the correction with the Operations Manager and/or Senior Persons. Advise the client verbally or by a memorandum of the project course correction. If the communication is verbal (preferred for its flexibility), prepare a **PHONE MEMO** to be placed in the project file.

8.5.2 Team Management

During the course of the project, the Project Manager must manage the Project Team. Team Management includes project schedule, due dates, milestones and project-related instructions. The Project Manager needs to be certain that the Team members understand the project goals and objectives and schedule.

8.5.3 Senior Persons

Even when not assigned, Senior Persons are ex-officio members of all teams. They are to serve as a resource and provide, on an as-needed basis, assistance to the Project Manager. It is the responsibility of the Project Manager to seek input from the Senior Persons.

8.6 Budget Review

The Project Manager should review the initial budget at project inception and periodically during the course of the project. The Project Manager and team members can review the project financial status, budget versus actual, and profitability using Harper Shuman Advantage. The budget information should be shared with the Project Team focusing on high and low profit tasks. As the Project Manager, you should not assume that the Team would gather the information from Harper Shuman. Once the project is complete, the Project Manager should review the project profitability with the Project Team.

If the initial budget was low for the work performed, this information should be shared with the Operations Manager and Senior Persons so that future budgets can reflect this experience and over-budget tasks can be more critically considered in the future.

8.7 Scope Changes

The Project Manager should be aware of any out-of-scope issues, as they arise, not after the fact.

In the event the actual costs are expected to or have exceeded the original budget, the Project Manager must identify any out-of-scope work that was performed by reviewing the proposal for the project. It is the responsibility of the Project Manager to manage the scope of the project. If out-of-scope work is identified, the Project Manager must notify the client immediately. During the course of the project, the Project Manager should be aware that the client might request certain work be performed. This work is often not within, or even related to, the scope outlined in the proposal. The Project Manager must advise the client that his/her request is out-of-scope and will be billed on a T&M basis or provide a scope of work and an add-on to the opinion of probable cost for the additional work.

In the event the client disagrees that an out-of-scope is appropriate, the Project Manager should consult with the Operations Manager or a Senior Person. The Project Manager should alert the Business Manager and the Operations Manager of any scope and budget change in either case.

8.8 Client Management

The best way to manage a client is to communicate with the client (Section 8.4.1) so that the project is progressing in the eyes of the client.

If the Project Manager has a difficult client or the client expresses concern, the Project Manager should consult with the Operations Manager or a Senior Person.

In managing a client it is important to understand their needs. The "TOP TEN" Client needs identified in this SOP are as follows:

- Adhere to an Agreed Upon Project Plan
- Consistent Communication
- Quality Control
- Dependability
- Internal Teamwork
- Continued Focus on the Desired Result/End Point
- Positive Attitude
- Immediate Notification of Out-of-Scope Issues
- Anticipation of Project Needs and Action Items
- Innovative Solutions/Presentation of Findings

Remember that a satisfied client yields additional profit, enhanced reputation and additional opportunities for the Payne Firm.

8.9 Invoicing

Invoicing typically occurs on a four-week billing period. At times, clients request billing on a calendar month basis. In either case, it is the Project Manager's responsibility to review the invoice for accuracy and compare it to the budget estimate and to determine if any out-of-the-ordinary action is to be taken with the invoice. Invoices are to be returned to the Business Office ASAP (typically within 24 hours). Out-of-the-ordinary action includes transferring time from one task to another within the total project, or designating as work-in-progress (WIP), or writing off a portion of the invoice.

WIPs should not occur for more than three consecutive months. After the three month WIP, the remaining money should be written off, unless the Project Manager is absolutely certain that it will be recovered within a 12-month period and has received written sign off by the Operations Manager or in his absence, a Senior Person.

When there is a write-off of more than $200 or one percent of total billing, whichever is greater, the Operations Manager must be made aware of the write off. The Project Manager should know the underlying and fundamental reason for the write off.

All invoices should be returned to the Business Manager who will issue the invoice within 24 hours. If the Project Manager chooses to attach a note to the invoice, the Business Manager should be made aware of this.

8.10 Collection Calls

From time to time, the Business Manager may request that the Project Manager call the client about a past due invoice. While typically this is an unpleasant assignment, the Project Manager must make collection calls to collect past due invoices. The Payne Firm's profits depend upon collecting invoices for services performed.

If the Project Manager cannot successfully collect a past due invoice, both the Business Manager and Operations Manager should be advised. At this time, the Project Manager should contact the client with

the Operations Manager present. The Operations Manager will support the Project Manager and possibly influence the client to pay the invoice because of the nature of his position.

Should all of the above fail, the Operations Manager will determine if the collection process will continue or the invoice is to be considered non-collectable.

8.11 Project Profitability/Close Out

Once the project is complete, the Project Manager should review the project profitability with the Project Team to ascertain if the team made a profit, broke even or lost money on the project. The Project Profitability statement can be found in Harper Shuman. The Project Manager should ask the following:

- Did we make money? Why? Why not?
- What could we have done differently to improve profits?
- Did the project allow for professional development of the team (this is an issue to future profitability)?
- Were the client's expectations/needs met?
- Was the project appropriately staffed?
- Was the project managed efficiently?
- What did we learn about the project from a profit standpoint that we want the rest of the staff to be aware of?

For project that runs for several years, the Project Manager should review the financials with the team at a minimum on a semi-annual basis.

9.0 SPECIAL ISSUES OF CONCERN

In order to avoid or mitigate potential project difficulties, the following recommendations are made:

- Know your Client to understand their primary and secondary objectives and constraints in addition to their tolerances;
- Communicate early and often;
- Let the Client know of a likely change, but do not quote a probable cost until it is checked with the Operation Manager or Senior Person;
- Use the comment feature of Timekeeper to document critical events and specific time spent on them;

- Keep the Operations Manager and Business Office abreast of changes in the original scope of work for the project;
- Don't be afraid to discuss cost overruns and when necessary **ask** for additional money, whether in or out-of scope. We typically offer an "opinion of probable cost range" not a detailed, not-to-exceed cost. Our opinion of probable cost can be underestimated; after all it only was an opinion.

10.0 ATTACHMENTS

10.1 Training Records

10.2 Project Life Cycle

10.3 Project Management Flow Diagram

10.4 Budget Sheet

10.4 Job Sheet

THE PAYNE FIRM, INC.
STANDARD OPERATING PROCEDURE

SUBJECT: Data Validation

PROCEDURE NO.: 8-2

EFFECTIVE ISSUE DATE: January 2004

REVISION NO.: N/A

PRIOR EFFECTIVE DATE: N/A

SITE-SPECIFIC AMENDMENTS: N/A

1.0 PURPOSE

The purpose of this procedure is to outline the Payne Firm's data validation process. The components and methods associated with that facilitate a technical review of analytical data generated by an environmental laboratory. The result of the technical review is the validation of analytical data, which enables it to be used for all intended purposes within a specific environmental investigation. The results of the technical review/validation are to be recorded in a project-specific Data Validation Memorandum addressed to the Project Manager.

2.0 SCOPE

This procedure applies to large analytical data sets as determined by the Project Manager that are collected during environmental investigations. The generation of a Data Validation Memorandum is an internal process used to summarize and document the technical review of contracted laboratory analytical data reports to determine the analytical quality of a specific data set beyond method, procedural, or contractual compliance provided by the environmental laboratory.

3.0 REQUIREMENTS

Generation of a Data Validation Memorandum generally requires the following documents of the laboratory analytical report:

- Case Narrative and/or Laboratory Review Checklist
- Chain-of-Custody
- Sample Identification Cross Reference
- Test reports to include results, dilution factors, and prep methods
- Surrogate Recovery Data
- Blank Sample Reports

- Matrix Spike/Matrix Spike Duplicate Reports
- Laboratory Control Sample Reports

4.0 REFERENCES

Office of Emergency and Remedial Response, United States Environmental Protection Agency, 2002. *US EPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review,* EPA 540/R-01/008.

Office of Emergency and Remedial Response, United States Environmental Protection Agency, 1999. *US EPA Contract Laboratory Program National Functional Guidelines for Organic Data Review,* EPA 540/R-99/008.

Office of Environmental Information, United States Environmental Protection Agency, 2002. *Guidance on Environmental Data Verification and Data Validation*, EPA QA/6-8.

Division of Hazardous Waste Management, Ohio Environmental Protection Agency, 2003, *Tier I Data Validation Manual.*

5.0 DEFINITIONS

Analytical Report – Report generated by a contracted laboratory that qualifies and quantifies the potential contamination in a collected sampled medium. Includes QA/QC reports and chain-of-custody.

Chain-of-Custody – A form that accompanies a sample or group of samples that documents custody as it is transferred from one custodian to another.

Evaluator – Personnel conducting the data review.

QC Batch – A QC batch contains a number of individual samples of a similar media that are processed using the same reagents and standards. The QC batch typically consists of twenty environmental samples to include internal QC samples.

Qualifier – Codes assigned to individual data results by either the laboratory or a data validator. Qualifiers indicate QA/QC problems associated with individual samples or sample batches and raises questions concerning reported chemical identity and/or chemical concentrations.

Target Analyte List/Target Compound List (TAL/TCL) – US EPA list of common inorganic and organic chemicals commonly found at Superfund sites.

6.0 RESPONSIBILITIES

6.1 Project Manager

The Project Manager shall ensure that the Data Validation Memoranda are ultimately included in the project file.

6.2 Field Geologist/Field Engineer/Field Technician

The Field Geologist/Field Engineer/Field Technician is responsible for reviewing the completed Data Validation Memorandum and ensuring that the sampling data discussed within the memorandum corresponds to their field sampling documentation.

6.3 Evaluator

Review contracted laboratory analytical reports and generate Data Validation Memorandum.

The Evaluator is typically independent of the activity which is being validated.

7.0 PROCEDURE

The goals of data validation are:

- Evaluate whether data quality goals established during the planning phase have been met.
- Ensure all project requirements are met.
- Determine impact on data quality on those that were not met.
- Document the results of the data validation.

Through achievement of these goals, data validation provides information on analytical limitations of data as determined by specific QA/QC criteria established by the contracted laboratory. During the data validation process, the evaluator will review the laboratory analytical reports and document in the form of a Data Validation Memorandum any QA/QC criteria that were outside the laboratory-established limits and identify the associated environmental samples to determine potential impact and qualification.

QA/QC criteria are documented within the laboratory reports. If the QA/QC data is not presented in the final laboratory report, a request will have to be made to the contracted laboratory for its delivery to the evaluator. Any sampling results failing the established QA/QC criteria are generally summarized in the laboratory cover sheet accompanying the analytical report. **Sampling data results that fail established QA/QC criteria are typically qualified by the laboratory in order that they may still be used to facilitate the progress of the project**. The intent of the qualification is to justify analytical results that may be suspicious or suspect.

The following definitions provide brief explanations of general national qualifiers as stated in the National Functional Guidelines for inorganic and organic review that may be assigned during the data validation process completed by the Payne Firm.

u	The analyte was analyzed for, but was not detected above the level of the reported sample quantitation limit.
j	The result is an estimated quantity. The associated numerical value is the approximate concentration of the analyte in the sample.
j+	The result is an estimated quantity, but the result may be biased high.
j-	The result is an estimated quantity, but the result may be biased low.
n	The analysis indicates the presence of an analyte for which there is presumptive evidence to make a "tentative identification."
nj	The analysis indicates the presence of an analyte that has been "tentatively identified" and the associated numerical value represents its approximate concentration.
uj	The analyte was not detected above the reporting sample quantitation limit. However, the reported quantitation limit is approximate and may or may not represent the actual limit of quantitation necessary to accurately and precisely measure the analyte in the sample.
r	The sample results are rejected due to serious deficiencies in the ability to analyze the sample and meet quality control criteria. The presence or absence of the analyte cannot be verified.

Additional laboratory-specific or regional qualifiers may be listed within the analytical report. A complete explanation of additional qualifiers should accompany the laboratory report.

7.1 Analytical Data Report Components

The following components of an analytical data report require review during the data validation process.

Supporting Documents

- Chain-of-Custody
- Case narrative
- Statement of quality assurance
- Sample receipt form

Analytical Results

- Sample results package
- Detection limits

QA/QC Sample Results

- Method blanks
- Matrix spike / matrix spike duplicates
- Laboratory control samples
- Surrogate recoveries

7.1.1 Supporting Documents

Chain-of-Custody – Record of all persons who handled the samples prior to relinquishing them to the laboratory. The chain-of-custody should contain the following information:

- Sample field ID numbers
- Date and time for each sample collected
- List of requested parameters
- Preservatives used, if any
- Sampler name(s)
- Special handling instruction

- Signatures of people with control of the samples to include lab personnel who receive the samples
- Date and time that samples were relinquished to the laboratory

This information should be cross-checked to confirm proper handling, holding times, and laboratory request associated with the data set.

Case Narrative – Generated by the laboratory and summarizes any problems encountered between sample receipt and analysis. Must be signed by the Laboratory Manager and include certification that all analysis were performed according to approved methods.

Statement of Quality of Assurance – Serves as legal documentation that all acceptable and uniform laboratory methods and QA/QC practices were followed by the laboratory.

Sample Receipt Form – Documents the condition of the samples as they are received by the laboratory. Cooler temperature is typically the most important measurement recorded on sample receipt form.

7.1.2 Analytical Results

Sample Results Package – Should contain a complete set of analytical results that were requested in the chain-of-custody. Confirm that all requested analysis were performed.

Detection Limits – Reports must contain detection limits or acceptable reporting limits as defined in the QAPP or pertinent regulatory standards.

7.1.3 QA/QC Sample Results

The purpose of the laboratory QA/QC program is to provide scientifically valid and legally defensible data. Elements of a QA/QC program generally include:

Laboratory Control Sample (LCS) – A blank QC sample of similar media that is spiked with known concentrations of target analytes and is used to monitor the performance of the analytical instrument. If the LCS does not perform within established limits, the ability of the analytical instrument to accurately analyze non-QC samples is questionable.

Method Blank – A QC sample consisting of all the reagents used in preparing the environmental sample for analysis. The method blanks are used to determine whether laboratory contamination is present and if it can significantly bias the analytical results.

Matrix Spike/Matrix Spike Duplicate (MS/MSD) – Aliquots of an environmental sample that are spiked with known concentration of target analytes. Matrix spikes are used to evaluate the effects from a samples matrix on the analytical results. Matrix duplicates are compared to the matrix spikes using relative percent difference (RPD) to give an indication of the instruments precision. RPDs within 20 percent are generally indicate acceptance with the QAPP.

Surrogate Compounds – Each environmental sample and QC sample are spiked with surrogate compounds or system monitoring compounds to measure individual performance of a sample in the analytical system. The surrogates have similar characteristics to target analytes, but are not commonly found outside the laboratory environment. The recovery of the surrogates is used to determine accuracy and to judge the effect of the sample matrix on the recovery of target analytes.

8.0 DOCUMENTATION

Documentation of the data validation process is to be summarized in the form of a Data Validation Memorandum addressed to the Project Manager. The memorandum should qualitatively discuss each aforementioned component of the analytical data report (Section 7.1). If data is determined to be suspect based on the evaluators review, the data is flagged to indicate the suspicion of reported results. It is then the Project Managers initiative to assess the data with regards to its overall intended use.

In addition to the Data Validation Memorandum, two checklists are provided to assist in the documentation of the validation process. The Ohio Environmental Protection Agency (Ohio EPA) Division of Hazardous Waste Management, Tier I Data Validation Checklist is provided for projects that are likely to require agency or third party oversight. The Ohio EPA checklist is a step-by-step outline that guides the evaluator through all components of the validation process. The second validation checklist is an internal Payne Firm checklist highlighting basic validation components. As validation components are reviewed, a box is checked to show completion.

All completed Data Validation Memorandum will have an accompanying checklist documenting the review of the data validation components.

9.0 ATTACHMENTS

Examples:

1) Data Validation Memorandum
2) Ohio EPA Data Validation Checklist
3) Internal Payne Firm Checklist

QUANTERRA® STANDARD OPERATING PROCEDURE

TITLE: SHIPPING DEPARTMENT

(SUPERSEDES: REVISION 1)

Prepared by: _____ 4-28-99
Date

Reviewed by: _____ 4/28/99
Technology Specialist Date

Approved by: _____ 4-27-99
Quality Assurance Manager Date

Approved by: _____ for Steve Jackson 4/28/99
Environmental Health and Safety Coordinator Date

Approved by: Stacey Campbell for Christopher Overmeyer 4/28/99
Laboratory Director Date

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1. PURPOSE

1.1. The procedures listed in this document will describe the responsibilities of shipping department personnel in ensuring that all bottle orders are sent correctly and on time.

1.2. This document accurately reflects current standard operating procedures (SOP) as of the date above. All facility SOPs are maintained and updated as necessary by the laboratory QA department.

2. RESPONSIBILITIES

2.1. It is the responsibility of the employee to perform the procedure described herein in full compliance with this SOP.

2.2. It is the responsibility of the Laboratory Director, QA Manager, and departmental Supervisor of this facility to ensure that the procedures described are performed in full compliance with this SOP. It is also their responsibility to supply adequate training, materials, and equipment to enable the employee to perform this SOP correctly.

3. SAFETY

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

3.2. Eye protection that satisfies ANSI Z87.1 (as per the Chemical Hygiene Plan), laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

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

3.3.1. Chemicals that have been classified as **carcinogens,** or **potential carcinogens,** under OSHA include: **none**

3.3.2. Chemicals known to be **flammable** are: **hexane, methanol**

3.3.3. The following materials are known to be **corrosive: nitric, sulfuric and hydrochloric acids, sodium hydroxide**

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

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

4. PROCEDURES

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

4.2. Creation of Supply Request (SAR)

4.2.1. The project manager will make out the Quote/SAR. The SAR should include the following: quote number, client code, matrix, number of sets, parameters, correct address, date the shipper is needed, and shipping or supply charges, if any. After everything has been completed, the project manager will e-mail the shipping department. (See Appendix I, example of SAR)

4.3. Receiving SAR from Project Management

4.3.1. Throughout the day, shipping department personnel will go through emails and prioritize the SARs by the date needed. The SARs will then be reviewed to ensure that the information is clear and understood. If there are any discrepancies or questions, the project manager is contacted.

4.4. Making Instructions

4.4.1. When preparing an order, shipping department personnel will consult a worksheet, highlighting parameters to determine the size and type of bottles to use and to determine if there are any preservatives. Shipping department personnel will then make out the bottle chain-of-custody, which includes the size of bottles, lot number, preservative, etc. After the order is set-up, another person in the shipping department, who will then sign and date it, ensuring that no errors were made, will review the bottle chain. (See Appendix II, example of bottle chain).

4.4.2. Only 40 mL vials are pre-preserved. Preservatives are shipped in a separate container.

4.5. Beginning to Set Order Up

4.5.1. After the bottle chain is complete, shipping department personnel will then begin to set the order up by placing all the bottles and containers on the counter and packing any preservatives in correct absorbent pads. After all the bottles are set up, another person in the shipping department will review what has been done and sign the bottle chain described in Section 4.4.1.

4.6. Packing the Order

4.6.1. Shipping department personnel will determine the size of container needed to pack the bottles in and whether the bottles need to be wrapped in bubble pack (glass will always be wrapped). Before packing the bottles and preservatives, shipping department personnel will line the container with bubble wrap to deter breakage. The container will also include the bottle chain, Chains-of-Custody, examples, labels, return address labels, temperature bottle and, if any preservatives, applicable MSDS(s). Shipping department personnel will tape or strap the shipping container closed. The quote number is written on a label and taped to the lid of the cooler.

4.6.2. All containers are placed inside a plastic inner liner. Double bagging is required for DuPont clients.

NOTE: When using preservatives, refer to "Procedures for the Commercial Shipment of Dangerous Goods by Air" reference for proper shipping procedures.

4.6.3. One trip blank filled with laboratory contaminant-free purged water is shipped with each cooler containing volatile analysis. Trip blanks can be supplied for other test methods if client requested.

4.6.4. Equipment blanks are also supplied if requested. The equipment blank is supplied by QEC.

4.7. Labeling Container

4.7.1. After the container is strapped or taped closed, shipping department personnel will place security seals and an address label on the shipping container. If there are any preservatives, the container will also have hazardous labels on it. (See Appendix III, example Hazardous Labels).

NOTE: Security seals will be used on samples shipped to other subcontracted laboratories.

4.8. Shipping Package

4.8.1. The package will either be shipped RPS, Federal Express, or Airborne. If the shipment contains preservatives, it will always go Airborne, in accepted quantities. If the shipment is going RPS or Federal Express, it will be weighed and logged into a notebook. If going Airborne, it will be entered into the appropriate Airborne computer.

4.9. Documentation

4.9.1. After the order is completed, any charges will be written on the SAR. Copies will be made and filed in the department.

4.9.2. Bottle and preservative lot numbers are recorded on the SAR.

4.10. Return of Coolers

4.10.1. After coolers are unpacked in sample receiving, they are brought to shipping. Cooler receipt is documented on logsheets and entered in the computer system as received.

4.10.2. The inner plastic liner is disposed and the cooler is stored for additional usage.

5. DEFINITIONS

5.1. Refer to the glossary in the Quality Assurance Management Plan (QAMP)

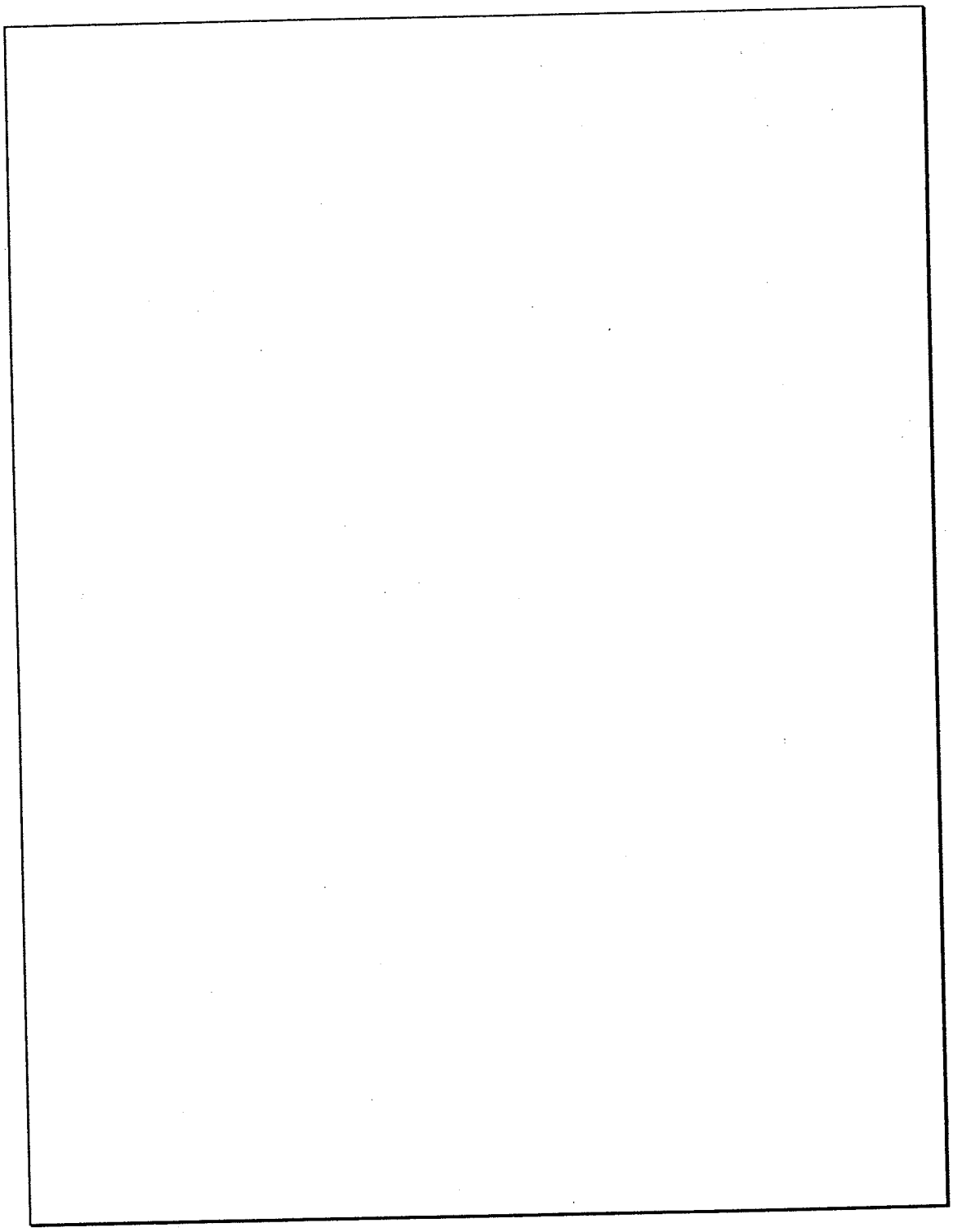
6. APPENDICES

6.1. Appendix I: Supply Request (SAR)

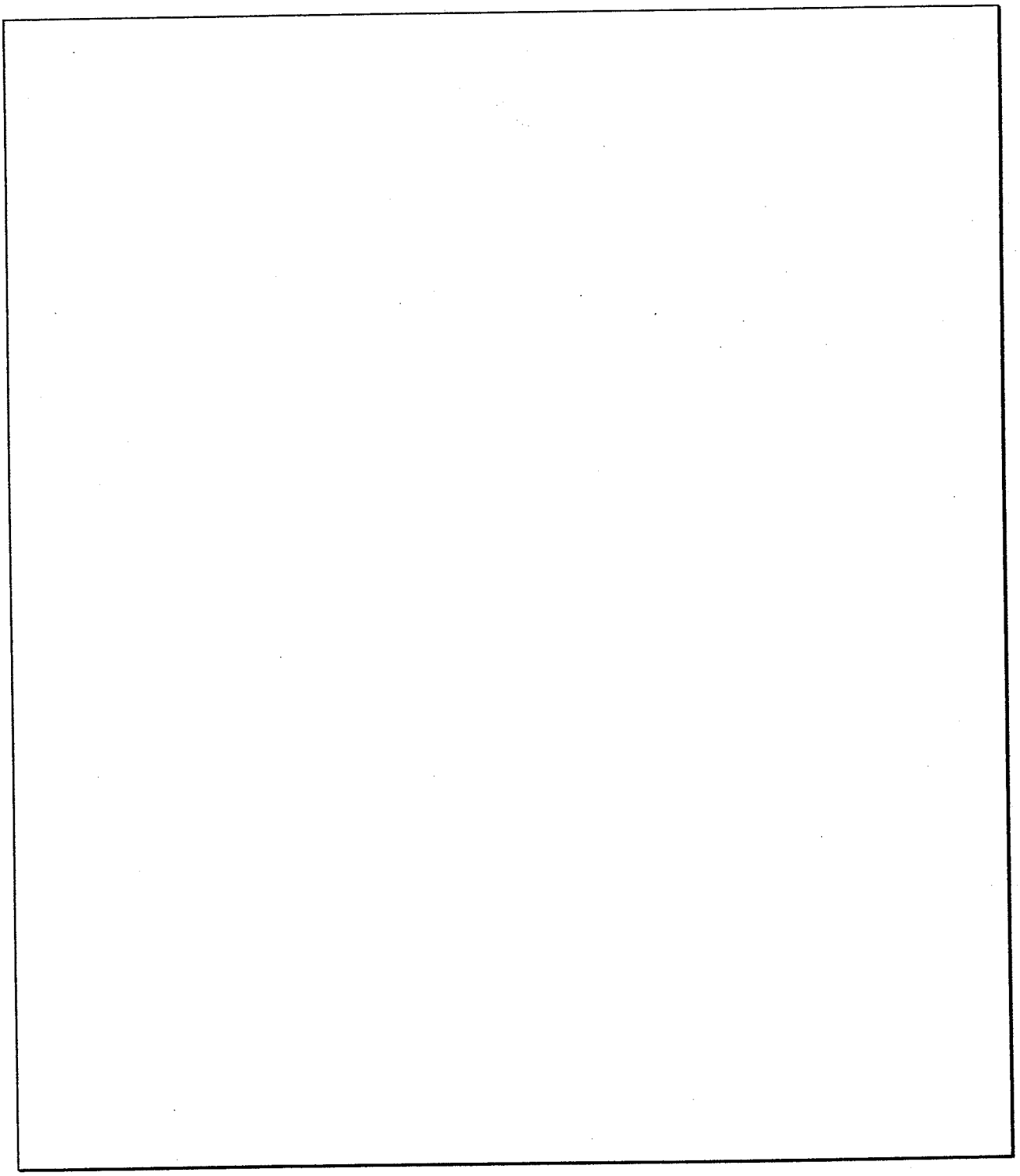
6.2. Appendix II: Bottle Chain

6.3. Appendix III: Hazardous Label

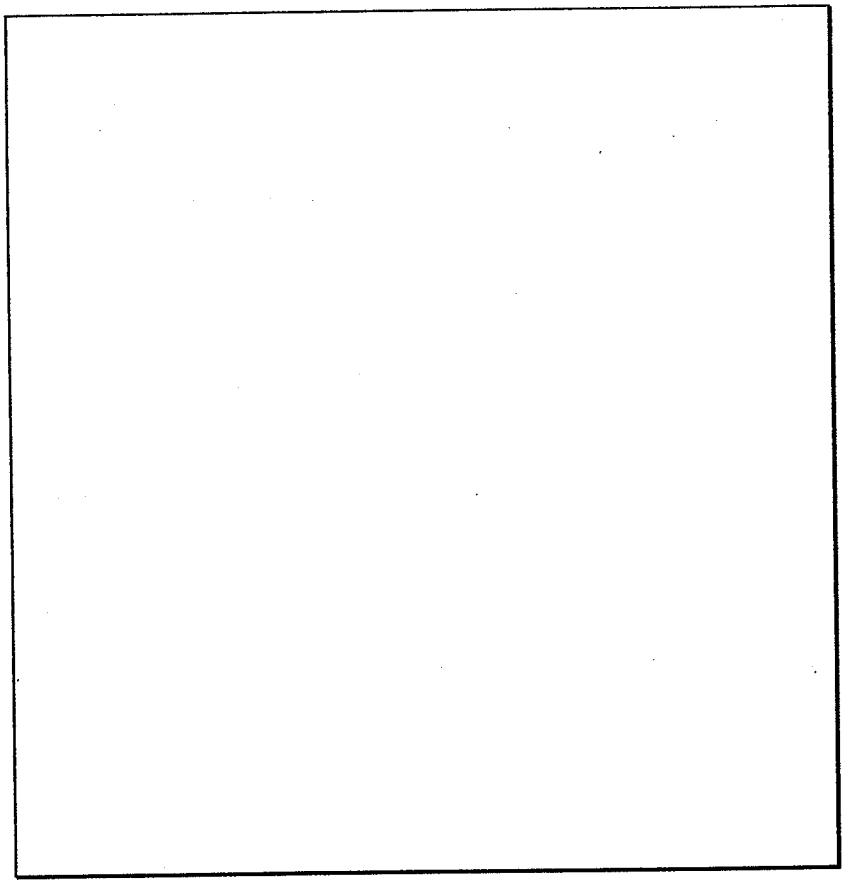
Appendix I: Supply Request (SAR)



Appendix II: Bottle Chain



Appendix III: Hazardous Label



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SOP No. CORP-MS-0002NC
Revision No. 2.3
Revision Date: 05/23/01

STL STANDARD OPERATING PROCEDURE

TITLE: DETERMINATION OF VOLATILE ORGANICS BY GC/MS BASED ON METHOD 8260B, 8260A, AND 624

(SUPERSEDES: REVISION 2.2, DATED 11/28/00)

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ANALYSIS OF VOLATILE ORGANICS BY METHOD 624 55

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Table 13	Characteristic Ions
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Table A-2	Method 624 QC Acceptance Criteria

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. Appendix A presents modifications to the procedures in the main SOP that are necessary for analysis of wastewater by method 624. The associated LIMS method codes are QK (8260B), DN (624), and MZ (8260A). Ohio VAP projects are distinguished by Program Code 2J. The following Prep Codes are used: 15 (5 mL purge), 25 (25 mL 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 25,000 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. Generally, soils are preserved by extracting the volatile analytes into methanol. If especially low detection limits are required, soil samples may be preserved with sodium bisulfate and purged directly.

2.3. In the purge and trap process, an inert gas is bubbled through the solution at ambient temperature or at 40°C (40°C required for low level soils) and the volatile components are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbant

column where the volatile components are trapped. After purging is completed, the sorbant column (trap) is heated and backflushed with inert gas to desorb the components onto a gas chromatographic column. The gas chromatographic column is then heated to elute the components which are detected with a mass spectrometer.

2.4. Qualitative identifications are confirmed by analyzing standards under the same conditions used for samples and comparing the resultant mass spectra and GC retention times. Each identified component is quantified by relating the MS response for an appropriate selected ion produced by that compound to the MS response for another ion produced by an internal standard.

3. DEFINITIONS

3.1. Batch

The batch is a set of up to 20 samples of the same matrix processed using the same procedures and reagents within the same time period. Using this method, each BFB analysis will normally start a new batch. Batches for medium level soils are defined at the sample preparation stage and may be analyzed on multiple instruments over multiple days, although reasonable effort should be made to keep the samples together.

3.1.1. The Quality Control batch must contain a matrix spike/spike duplicate (MS/MSD), a Laboratory Control Sample (LCS), and a method blank. In some cases, at client request, the MS/MSD may be replaced with a matrix spike and sample duplicate. Refer to the STL QC Program document (QA-003) for further details of the batch definition.

3.2. Method Blank

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)

SPCCs are compounds which are sensitive to system performance problems and are used to evaluate system performance and sensitivity. A response factor from the continuing calibration is calculated for the SPCC compounds and compared to the specified method criteria.

4. INTERFERENCES

4.1. Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus that lead to discrete artifacts. All of these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. The use of ultra high purity gases, pre-purged purified reagent water, and approved lots of purge and trap grade methanol will greatly reduce introduction of contaminants. In extreme cases the purging vessels may be pre-purged to isolate the instrument from laboratory air contaminated by solvents used in other parts of the laboratory.

4.2. Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride and fluorocarbons) into the sample through the septum seal during shipment and storage. A field blank prepared from reagent water and carried through the sampling and handling protocol can serve as a check on such contamination.

4.3. Matrix interferences may be caused by non-target contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from source to source depending upon the nature and diversity of the site being sampled.

4.4. Cross-contamination can occur whenever high-level and low-level samples are analyzed sequentially or in the same purge position on an autosampler. Whenever an unusually concentrated sample is analyzed, it should be followed by one or more blanks to check for cross-contamination. The purge and trap system may require extensive bake-out and cleaning after a high-level sample.

4.5. Some samples may foam when purged due to surfactants present in the sample. When this kind of sample is encountered an antifoaming agent (e.g., J.T. Baker's Antifoam B silicone emulsion) can be used. A blank spiked with this agent must be analyzed with the sample because of the non-target interferences associated with the agent.

5. SAFETY

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

5.2. The Chemical Hygiene Plan (CHP) gives details about the specific health and safety practices which are to be followed in the laboratory area. Personnel must receive training in the CHP, including the written Hazard Communication plan, prior to working in the laboratory. Consult the CHP, the STL Health and Safety Policies and Procedures Manual, and available Material Safety Data Sheets (MSDS) prior to using the chemicals in the method.

5.3. Consult the STL Health and Safety Policies and Procedures Manual for information on Personal Protective Equipment. Eye protection that protects against splash and a laboratory coat must be worn in the lab. Appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately. Disposable gloves shall not be reused.

5.4. The health and safety hazards of many of the chemicals used in this procedure have not been fully defined, therefore each chemical compound should be treated as a potential health hazard. Additional health and safety information can be obtained from the MSDS files maintained in the laboratory. The following specific hazards are known:

5.4.1. Chemicals that have been classified as carcinogens, or potential carcinogens, under OSHA include: Acrylonitrile, benzene, carbon tetrachloride, chloroform, 1,2-dibromo-3-chloropropane, 1,4-dichlorobenzene, and vinyl chloride.

5.4.2. Chemicals known to be flammable are: **Methanol.**

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

5.6. The preparation of standards and reagents will be conducted in a fume hood with the sash closed as far as the operations will permit.

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

5.8. Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices outlined in the STL Health and Safety Manual. These employees must have training on the hazardous waste disposal practices initially upon assignment of these tasks, followed by an annual refresher training.

6. EQUIPMENT AND SUPPLIES

6.1. Microsyringes: 10 µL and larger, 0.006 inch ID needle.

6.2. Syringe: 5 or 25 mL glass with luerlok tip, if applicable to the purging device.

6.3. Balance: Analytical, capable of accurately weighing 0.0001 g, and a top-loading balance capable of weighing 0.1 g

6.4. Glassware:

6.4.1. Vials: 20 mL with screw caps and Teflon liners.

6.4.2. Volumetric flasks: 10 mL and 100 mL, class A with ground-glass stoppers.

6.5. Spatula: Stainless steel.

6.6. Disposable pipets: Pasteur.

6.7. pH paper: Wide range.

6.8. Gases:

6.8.1. Helium: Ultra high purity, gr. 5, 99.999%.

6.8.2. Nitrogen: Ultra high purity, from cylinders of gas generators, may be used as an alternative to helium for purge gas.

6.8.3. Compressed air: Used for instrument pneumatics.

6.8.4. Liquid nitrogen: Used for cryogenic cooling if necessary.

6.9. Purge and Trap Device: The purge and trap device consists of the sample purger, the trap, and the desorber.

6.9.1. Sample Purger: The recommended purging chamber is designed to accept 5 mL samples with a water column at least 3 cm deep. The purge gas must pass through the water column as finely divided bubbles, each with a diameter of less than 3 mm at the origin. The purge gas must be introduced no more than 5 mm from the base of the water column. Alternative sample purge devices may be used provided equivalent performance is demonstrated. Low level soils are purged directly from a VOA vial.

6.9.2. Trap: A variety of traps may be used, depending on the target analytes required. For most purposes the Vocarb 3000 trap is suitable. Other traps, such as Vocarb 4000, or Tenax / Silica gel / Charcoal may be used if the Quality Control criteria are met.

6.9.3. Desorber: The desorber should be capable of rapidly heating the trap to 180°C. Many such devices are commercially available.

6.9.4. Sample Heater: A heater capable of maintaining the purge device at 40°C is necessary for low level soil analysis.

6.10. Gas Chromatograph/Mass Spectrometer System:

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: 105m x 0.53 ID Rtx-624 with 3 µm film thickness.

6.10.2.2. Column 2: 75 m x 0.53 ID DB-624 widebore with 3 µm film thickness.

6.10.2.3. Mass Spectrometer: The mass spectrometer must be capable of scanning 35-300 AMU every two seconds or less, using 70 volts electron energy in the electron impact mode and capable of producing a mass spectrum that meets the required criteria when 50 ng of 4-Bromofluorobenzene (BFB) are injected onto the gas chromatograph column inlet.

6.10.3. GC/MS interface: In general glass jet separators are used but any interface (including direct introduction to the mass spectrometer) that achieves all acceptance criteria may be used.

6.10.4. Data System: A computer system that allows the continuous acquisition and storage on machine readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that allows searching any GC/MS data file for ions of a specified mass and plotting such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundances in any EICP between the specified time or scan-number limits. Also, for the non-target compounds, software must be available that allows for the comparison of sample spectra against reference library spectra. The most recent release of the NIST/EPA mass spectral library should be used as

the reference library. The computer system must also be capable of backing up data for long-term off-line storage.

6.10.5. Cryogenic Cooling: Some columns require the use of liquid nitrogen to achieve the subambient temperature required for the proper separation of the gases.

7. REAGENTS AND STANDARDS

7.1. Reagents

7.1.1. Methanol: Purge and Trap Grade, High Purity

7.1.2. Reagent Water: High purity water that meets the requirements for a method blank when analyzed. (See section 9.4) Reagent water may be purchased as commercial distilled water and prepared by purging with an inert gas overnight. Other methods of preparing reagent water are acceptable.

7.2. Standards

7.2.1. Calibration Standard

7.2.1.1. Stock Solutions: Stock solutions may be purchased as certified solutions from commercial sources or prepared from pure standard materials as appropriate. These standards are prepared in methanol and stored in Teflon-sealed screw-cap bottles with minimal headspace at -10° to -20°C.

7.2.1.2. Working standards: A working solution containing the compounds of interest prepared from the stock solution(s) in methanol. These standards are stored in the freezer or as recommended by the manufacturer. Working standards are monitored by comparison to the initial calibration curve. If any of the calibration check compounds drift in response from the initial calibration by more than 20% then corrective action is necessary. This may include steps such as instrument maintenance, preparing a new calibration verification standard or tuning the instrument. If the corrective actions do not correct the problem then a new initial calibration must be performed.

7.2.1.3. Aqueous Calibration Standards are prepared in reagent water using the secondary dilution standards. These aqueous standards must be prepared daily.

7.2.1.4. If stock or secondary dilution standards are purchased in sealed ampoules they may be used up to the manufacturers expiration date.

7.2.2. Internal Standards: Internal standards are added to all samples, standards, and blank analyses. Refer to Table 7 for internal standard components.

7.2.3. Surrogate Standards: Refer to Table 8 for surrogate standard components and spiking levels.

7.2.4. Laboratory Control Sample Spiking Solutions: Refer to Table 9 for LCS components and spiking levels.

7.2.5. Matrix Spiking Solutions: The matrix spike contains the same components as the LCS. Refer to Table 9.

7.2.6. Tuning Standard: A standard is made up that will deliver 50 ng on column upon injection. A recommended concentration of 25 ng/µL of 4-Bromofluorobenzene in methanol is prepared as described in Sections 7.2.1.1 and 7.2.1.2.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Holding times for all volatile analysis are 14 days from sample collection.

8.2. Water samples are normally preserved at pH $\leq$ 2 with 1:1 hydrochloric acid. If residual chlorine is present, 2 drops of 10% sodium thiosulfate are added.

8.3. Solid samples are field preserved with sodium bisulfate solution for low level analysis, or with methanol for medium level analysis. Soil samples can also be taken using the EnCore™ sampler and preserved in the lab within 48 hours of sampling. At specific client request, unpreserved soil samples may be accepted.

8.4. There are several methods of sampling soil. The recommended method, which provides the minimum of field difficulties, is to take an EnCore™ sample. (The 5 g or 25 g sampler can be used, depending on client preference). Following shipment back to the lab the soil is preserved in methanol. This is the medium level procedure. If very low detection limits are needed (< 50 µg/kg for most analytes) then it will be necessary to use two additional 5 g EnCore™ samplers or to use field preservation.

8.5. Sample collection for medium level analysis using EnCore™ samplers.

8.5.1. Ship one 5 g (or 25 g) EnCore™ sampler per field sample position.

8.5.2. An additional bottle must be shipped for percent moisture determination.

8.5.3. When the samples are returned to the lab, extrude the (nominal) 5g (or 25 g) sample into a tared VOA vial containing 5 mL methanol (25 mL methanol for the 25 g sampler). Obtain the weight of the soil added to the vial and note on the label.

8.5.4. Add the correct amount of surrogate spiking mixture. (Add 25 µL of 2500 µg/mL solution for a nominal 25 g sample, 5 µL for a nominal 5 g sample.) Refer to Section 17.8 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 17.8 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. (50 µL of spike to 25 mL methanol or 10 µL spike to 5 mL methanol). Refer to Section 17.8 for Michigan project criteria.

8.5.7. Shake the samples for two minutes to distribute the methanol throughout the soil.

8.5.8. Allow to settle, then remove a portion of methanol and store in a clean Teflon capped vial at 4 ±2°C until analysis.

8.6. Sample collection for medium level analysis using field methanol preservation

8.6.1. Prepare a 2 oz sample container by adding 25 mL purge and trap grade methanol. (If a 5 g sample is to be used, add 5 mL methanol to a 2 oz container or VOA vial).

8.6.2. Seal the bottle and attach a label.

8.6.3. Weigh the bottle to the nearest 0.01g and note the weight on the label.

8.6.4. Ship with appropriate sampling instructions.

8.6.5. Each sample will require an additional bottle with no preservative for percent moisture determination.

8.6.6. At client request, the methanol addition and weighing may also be performed in the field.

8.6.7. When the samples are returned to the lab, obtain the weight of the soil added to the vial and note on the label.

8.6.8. Add the correct amount of surrogate spiking mixture. (Add 25 µL of 2500 µg/mL solution for a nominal 25 g sample, 5 µL for a nominal 5 g sample.) Refer to Section 17.8 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 25 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 17.8 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 µL of spike to 25 mL methanol or 100 µL spike to 5 mL methanol). Refer to Section 17.8 for Michigan project criteria.

8.6.11. Shake the samples for two minutes to distribute the methanol throughout the soil.

8.6.12. Allow to settle, then remove a portion of methanol and store in a clean Teflon capped vial at 4+2°C until analysis.

8.7. Low level procedure

8.7.1. If low detection limits are required (typically < 50 µg/kg) sodium bisulfate preservation must be used. However, it is also necessary to take a sample for the medium level (field methanol preserved or using the EnCore™ sampler) procedure, in case the concentration of analytes in the soil is above the calibration range of the low level procedure.

8.7.2. A purge and trap autosampler capable of sampling from a sealed vial is required for analysis of samples collected using this method. (Varian Archon or O.I. 4552).

8.7.3. The soil sample is taken using a 5g EnCore™ sampling device and returned to the lab. It is recommended that two EnCore™ samplers be used for each field sample position, to allow for any reruns than may be necessary. A separate sample for % moisture determination is also necessary.

8.7.4. Prepare VOA vials by adding a magnetic stir bar, approximately 1 g of sodium bisulfate and 5 mL of reagent water.

8.7.5. Seal and label the vial. It is strongly recommended that the vial is labeled with an indelible marker rather than a paper label, since paper labels may cause the autosampler to bind and malfunction. The label absolutely must not cover the neck of the vial or the autosampler will malfunction.

8.7.6. Weigh the vial to the nearest 0.1g and note the weight on the label.

8.7.7. Extrude the soil sample from the EnCore™ sampler into the prepared VOA vial. Reweigh the vial to obtain the weight of soil and note on the label.

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, analyzed within 12 days after preserving with water, and stored at a 45 degree angle in the freezer.

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

8.7.9. Alternatively the sodium bisulfate preservation may be performed in the field. This is not recommended because of the many problems that can occur in the field setting. Ship at least two vials per sample. The field samplers must determine the weight of soil sampled. Each sample will require an additional bottle with no preservative for percent moisture determination, and an additional bottle preserved with methanol for the medium level procedure. Depending on the type of soil it may also be necessary to ship vials with no or extra preservative.

8.8. Unpreserved soils

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

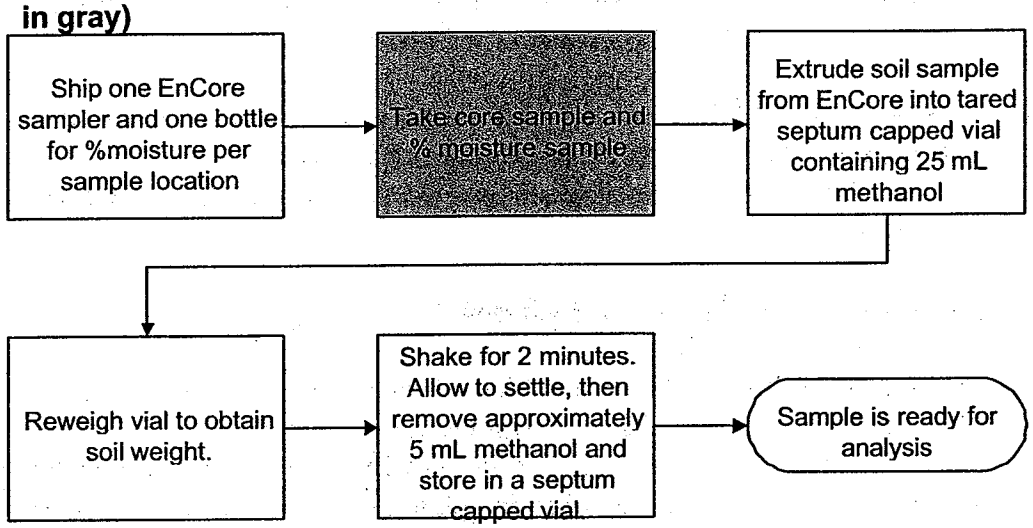
8.9. Aqueous samples are stored in glass containers with Teflon lined septa at 4°C +/- 2°C, with minimum headspace.

8.10. Medium level solid extracts are aliquoted into 2 - 5 mL glass vials with Teflon lined caps and stored at 4°C +/- 2°C. The extracts are stored with minimum headspace.

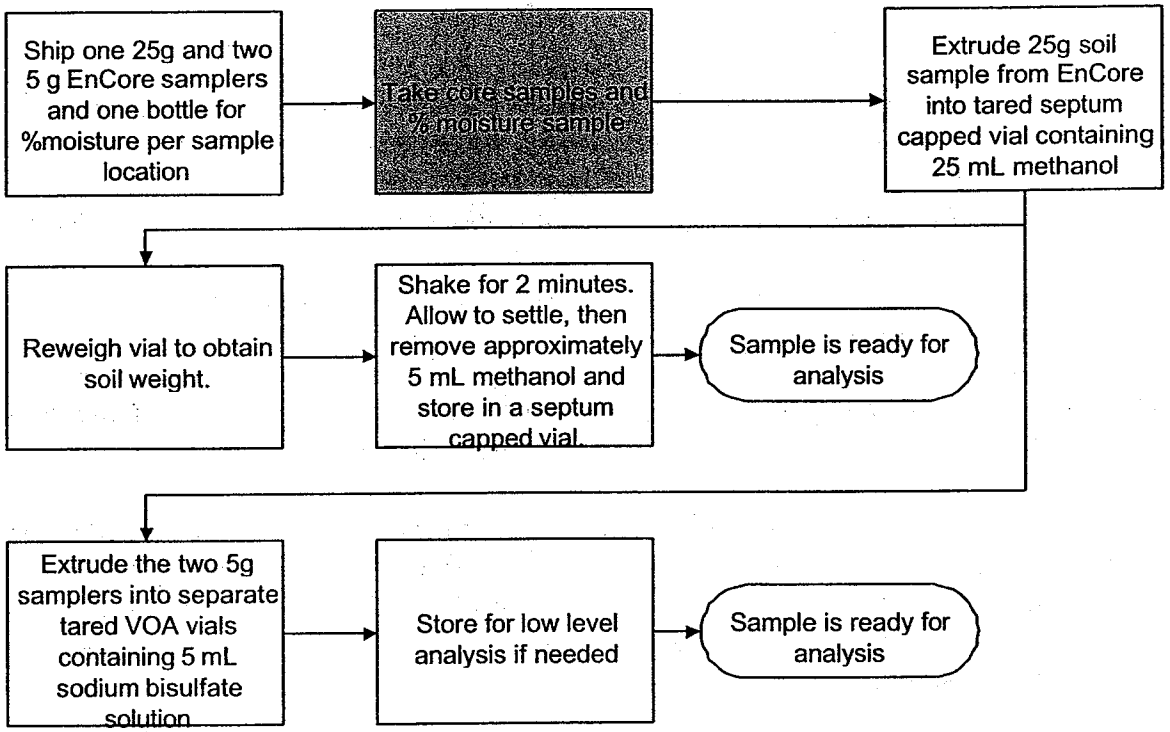
8.11. The maximum holding time is 14 days from sampling until the sample is analyzed. (Samples that are found to be unpreserved still have a 14 day holding time. However they should be analyzed as soon as possible. The lack of preservation should be addressed in the case narrative). Maximum holding time for the EnCore™ sampler (before the sample is added to methanol or sodium bisulfate) is 48 hours.

8.12. A holding blank is stored with the samples. This is analyzed and replaced if any of the trip blanks show any contamination. Otherwise it is replaced every 14 days.

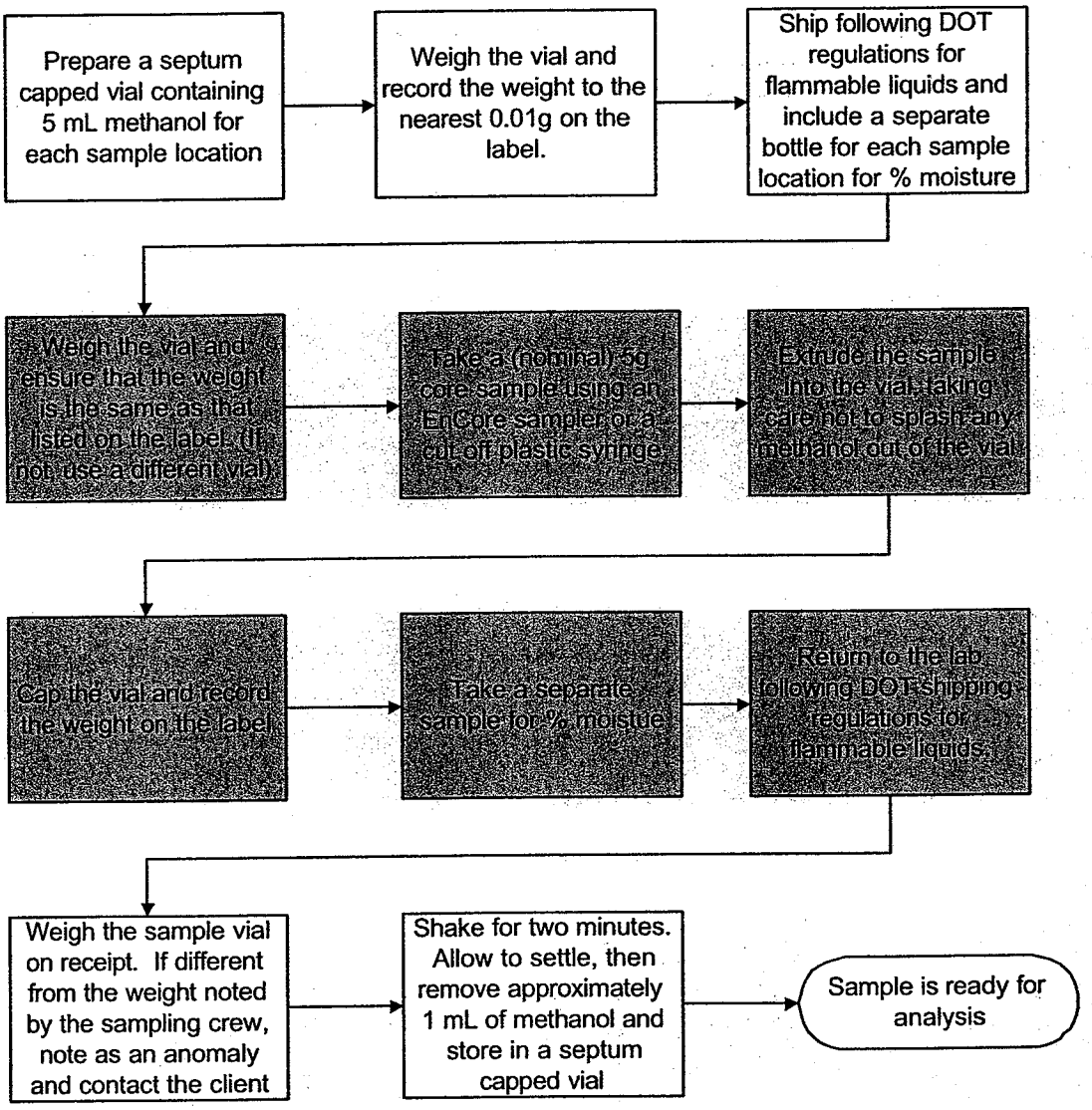
EnCore procedure when low level is not required (field steps in gray)



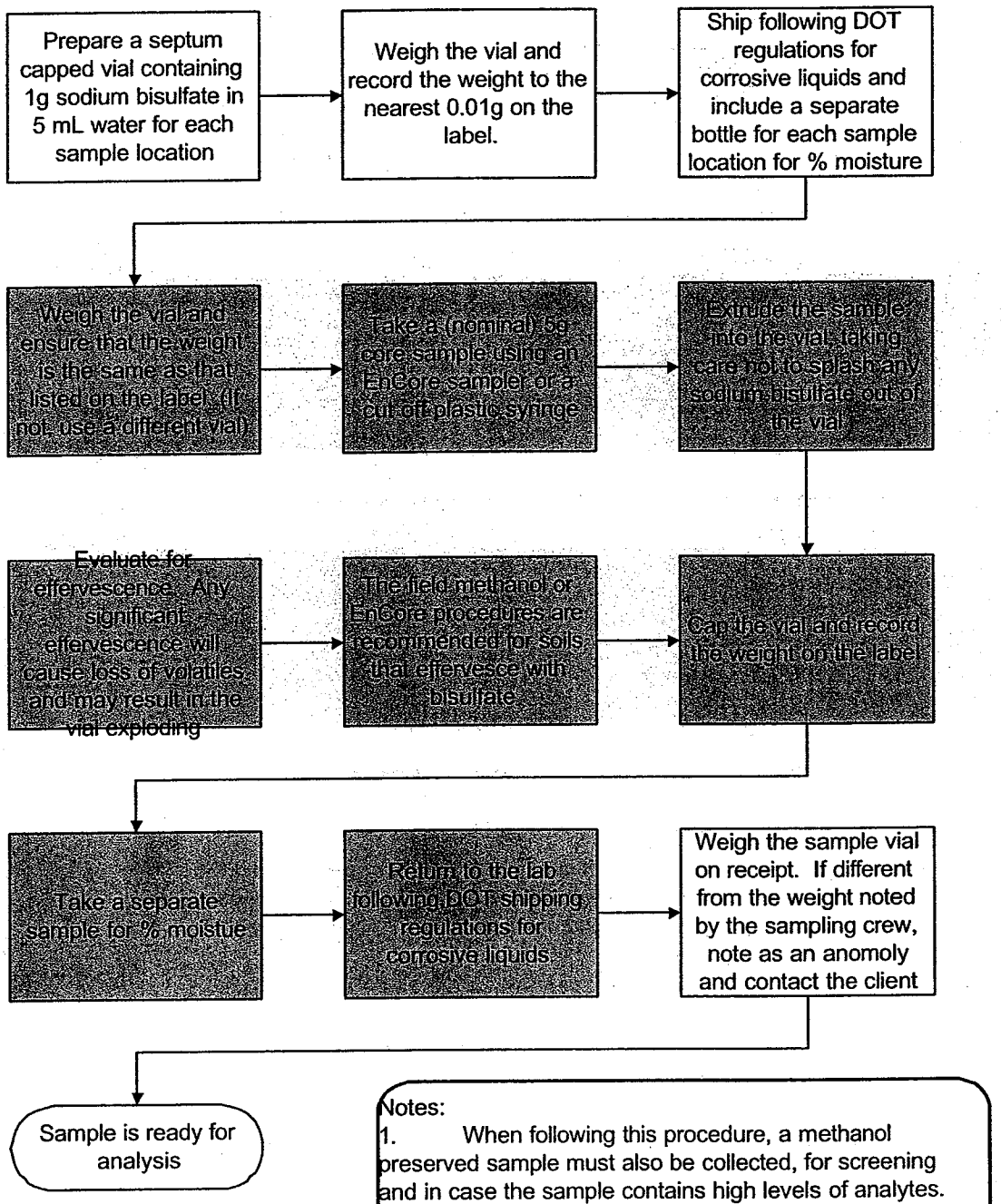
EnCore procedure when low level is required



Field methanol extraction procedure (field steps in gray)



Field bisulfate preservation procedure (field steps in gray)



9. QUALITY CONTROL

9.1. Initial Demonstration of Capability

9.1.1. For the standard analyte list, the initial demonstration described in Section 13 and method detection limit (MDL) studies must be acceptable before analysis of samples may begin. MDLs should be analyzed for low and medium soils and aqueous samples.

9.1.2. For non-standard analytes, a MDL study must be performed and calibration curve generated before analyzing any samples, unless lesser requirements are previously agreed to with the client. In any event, the minimum initial demonstration required is analysis of a standard at the reporting limit and a single point calibration.

9.2. Control Limits

In-house historical control limits must be determined for surrogates, matrix spikes, and laboratory control samples (LCS). These limits must be determined at least annually. The recovery limits are mean recovery +/- 3 standard deviations for surrogates, matrix spikes and LCS. Precision limits for matrix spikes / matrix spike duplicates are 0 to mean relative percent difference + 3 standard deviations.

9.2.1. All surrogate, LCS, and MS recoveries (except for dilutions) must be entered into QuantIMS (when available) or other database so that accurate historical control limits can be generated. For tests without a separate extraction, surrogates and matrix spikes will be reported for all dilutions.

9.2.2. Refer to the QC Program document (QA-003) for further details of control limits.

9.3. Surrogates

Every sample, blank, and QC sample is spiked with surrogates. Surrogate recoveries in samples, blanks, and QC samples must be assessed to ensure that recoveries are within established limits. The compounds included in the surrogate spiking solutions are listed in 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 or flag the data as "Estimated Concentration" if neither of the above resolves the problem.

The decision to reanalyze or flag the data should be made in consultation with the client. It is only necessary to reprepare/reanalyze a sample once to demonstrate that poor surrogate recovery is due to matrix effect, unless the analyst believes that the repeated out of control results are not due to matrix effect.

9.3.1. If the surrogates are out of control for the sample, matrix spike, and matrix spike duplicate, then matrix effect has been demonstrated for that sample and repreparation is not necessary. If the sample is out of control and the MS and/or MSD is in control, then reanalysis or flagging of the data is required.

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

9.4. Method Blanks

9.4.1. 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 25.0 mL of methanol. Surrogates are added and the method blank is carried through the entire analytical procedure. The method blank must not contain any analyte of interest at or above the reporting limit (except common laboratory contaminants, see below) or at or above 5% of the measured concentration of that analyte in the associated samples, whichever is higher.

- If the analyte is a common laboratory contaminant (methylene chloride, acetone, 2-butanone) the data may be reported with qualifiers if the concentration of the analyte is less than five times the reporting limit. Such action must be taken in consultation with the client.
- Reanalysis of samples associated with an unacceptable method blank is required when reportable concentrations are determined in the samples.
- If there is no target analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. Such action should be done in consultation with the client.

9.4.2. 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.

9.4.3. 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.

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

9.5. Laboratory Control Samples (LCS)

9.5.1. 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.

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

9.5.3. 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 17.5 for Ohio VAP specific analytes.

9.6. Matrix Spikes

9.6.1. 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 17.5 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.

9.7. 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.

9.8. Quality Assurance Summaries

Certain clients may require specific project or program QC which may supersede these method requirements. Quality Assurance Summaries should be developed to address these requirements.

9.9. STL QC Program

Further details of QC and corrective action guidelines are presented in the STL QC Program document (QA-003). Refer to this document if in doubt regarding corrective actions.

10. CALIBRATION AND STANDARDIZATION

10.1. Summary

10.1.1. Prior to the analysis of samples and blanks, each GC/MS system must be tuned and calibrated. Hardware tuning is checked through the analysis of the 4-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.

10.2.1. General

Electron Energy:	70 volts (nominal)
Mass Range:	35–300 AMU
Scan Time:	to give at least 5 scans/peak, but not to exceed 2 second/scan
Injector Temperature:	200–250°C
Source Temperature:	According to manufacturer's specifications
Transfer Line	Temperature: 250–300°C
Purge Flow:	40 mL/minute
Carrier Gas	Flow: 15 mL/minute
Make-up Gas Flow:	25–30 mL/minute

10.2.2. Gas chromatograph suggested temperature program

10.2.2.1. BFB Analysis

Isothermal:	170°C

10.2.2.2. Sample Analysis

Initial Temperature:	40°C
Initial Hold Time:	4 minutes
Temperature Program:	8°C/minute
Final Temperature:	184°C
Second Temperature	Program: 40°C/minute
Final Temperature:	240°C
Final Hold Time:	2.6 minutes

10.3. Instrument Tuning

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 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 25 mL 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. If the average of all the %RSDs in the calibration is $\leq$ 15%, then all analytes may use average response factor for calibration.

10.4.6.1. If the software in use is capable of routinely reporting curve coefficients for data validation purposes, and the necessary calibration reports can be generated, then the analyst should evaluate analytes with %RSD > 15% for calibration on a curve. If it appears that substantially better accuracy would be obtained using quantitation from a curve then the appropriate curve should be used for quantitation. If Relative Standard Error (RSE) is used to evaluate the curve it must be better than 15%. Otherwise the correlation coefficient (coefficient of determination for non-linear curves) must be ≥ 0.990.

10.4.6.2. If the average of all the %RSDs in the calibration is > 15% then calibration on a curve must be used for all analytes with %RSD > 15%. Linear or quadratic curve fits may be used. The analyst should consider instrument maintenance to improve the linearity of response. If Relative Standard Error (RSE) is used to evaluate the curve it must be better than 15%. 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 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.

10.4.6.3. Refer to Section 17.5 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. $1/Concentration^2$ 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. Medium soil extracts should be analyzed using the water (unheated or optionally heated) calibration curve as long as all calibration standards, samples, and QC samples are purged at the same temperature.

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 is 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. The level 3 calibration standard is used as the continuing calibration.

10.5.2. The RF data from the standards are compared with the average RF from the initial five-point calibration to determine the percent drift of the CCC compounds. The calculation is given in equation 4, Section 12.3.4.

10.5.3. The % drift of the CCCs must be $\leq$ 20% for the continuing calibration to be valid. The SPCCs are also monitored. The SPCCs must meet the criteria described in Table 11. In addition, the % drift of all analytes must be $\leq$ 50% with allowance for up to six target analytes to have % drift > 50%.

10.5.3.1. If none of the CCCs are required analytes, project specific calibration specifications must be agreed with the client.

10.5.3.2. Cyclohexanone, one of the components of the Appendix IX standard, is unstable in the calibration solution, forming 1,1-dimethoxycyclohexane. No calibration criteria are applied to cyclohexanone and quantitation is tentative. Cyclohexanone is included on the Universal Treatment Standard and FO-39 regulatory lists (but not on Appendix IX).

10.5.3.3. 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 µL of sample then serial dilutions must be made in volumetric flasks.

11.2.2.1. The diluted concentration is to be estimated to be in the upper half of the calibration range.

11.3. Sample Analysis Procedure

11.3.1. All analysis conditions for samples must be the same as for the continuing calibration standards (including purge time and flow, desorb time and temperature, column temperatures, multiplier setting etc.).

11.3.2. All samples must be analyzed as part of a batch. The batch is a set of up to 20 samples of the same matrix processed using the same procedures and reagents within the same time period. The batch also must contain a MS/MSD, a LCS, and a method blank.

11.3.2.1. If there is insufficient time in the 12-hour tune period to analyze 20 samples, the batch may be continued into the next tune period. However, if any re-tuning of the instrument is necessary, or if a period of greater than 24 hours from the preceding BFB tune has passed, a new batch must be started. For medium level soils the batch is defined at the sample preparation stage.

11.3.2.2. Laboratory generated QC samples (Blank, LCS, MS/MSD) do not count towards the maximum 20 samples in a batch. Field QC samples are included in the batch count.

11.3.2.3. It is not necessary to reanalyze batch QC with reanalyses of samples. However, any reruns must be as part of a valid batch.

11.4. Water Samples

11.4.1. All samples and standard solutions must be at ambient temperature before analysis.

11.4.2. Fill a syringe with the sample. If a dilution is necessary it may be made in the syringe if the sample aliquot is $\geq$ 5 µL. Check and document the pH of the remaining sample.

11.4.3. Add 250 ng of each internal and surrogate standard (10 µL of a 25 µg/mL solution, refer to Tables 7, 8 and 16). The internal standards and the surrogate standards may be mixed and added as one spiking solution (this results in a 50 µg/L solution for a 5 mL sample, and a 10 µg/L solution for a 25 mL sample). Inject the sample into the purging chamber.

11.4.3.1. For TCLP samples use 0.5 mL of TCLP leachate with 4.5 mL reagent water and spike with 10 µL of the 25 µg/mL TCLP spiking solution. (Note that TCLP reporting limits will be 10 times higher than the corresponding aqueous limits).

11.4.4. Purge the sample for eleven minutes (the trap must be below 35°C).

11.4.5. After purging is complete, desorb the sample, start the GC temperature program, and begin data acquisition. After desorption, bake the trap for 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 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. Refer to Section 17.8 for Michigan project requirements.

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

11.6.1. Pipet 2 mL of the sample into a tared vial. Use a top-loading balance. Record the weight to the nearest 0.1 gram.

11.6.2. Quickly add 7 mL of methanol, then add 1 mL of surrogate spiking solution to bring the final volume to 10 mL. Cap the vial and shake for 2 minutes to mix thoroughly. For a MS/MSD or LCS, 6 mL of methanol, 1 mL of surrogate solution, and 1 mL of matrix spike solution is used.

11.6.3. Rinse a gas-tight syringe with organic free water. Fill the syringe with the same volume of organic free water as used in the calibrations. Add no more than 2% (v/v) (100 µL for a 5 mL purge) methanolic extract (from Section 8.5 or 8.6) to the syringe. Add internal standard (if used). Load the sample onto the purge and trap device and analyze as for aqueous samples. If less than 5µL of methanolic extract is to be added to the water, dilute the methanolic extract such that a volume greater than 5µL will be added to the water in the syringe.

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

11.7.1. Units which sample from the VOA vial should be equipped with a module which automatically adds surrogate and internal standard solution to the sample prior to purging the sample.

11.7.2. If the autosampler uses automatic IS/SS injection, no further preparation of the VOA vial is needed. Otherwise the internal and surrogate standards must be added to the vial. *Note:* Aqueous samples with high amounts of sediment present in the vial may not be suitable for analysis on this instrumentation, or they may need to analyzed as soils.

11.7.3. Soil samples must be quantitated against a curve prepared with standards containing about the same amount of sodium bisulfate as the samples (1 g in 5 mL).

11.7.4. Sample remaining in the vial after sampling with one of these mechanisms is no longer valid for further analysis. A fresh VOA vial must be used for further sample analysis.

11.7.5. For aqueous samples, check the pH of the sample remaining in the VOA vial after analysis is completed.

11.8. Low-Level Solids Analysis using discrete autosamplers, 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 1.0 g. If the sample is contaminated with analytes such that a purge amount less than 1.0 g is appropriate, use the medium level method. For the medium level method, add 4g soil to 10 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 11.5.2.

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

11.8.6. Add the heater jacket or other heating device and start the purge and trap unit.

11.8.7. Soil samples that have low IS recovery when analyzed (<50%) should be reanalyzed once to confirm matrix effect.

11.9. Medium-Level Soil/Sediment and Waste Samples

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

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

11.9.5.1.1. Gently mix the contents of the sample container with a narrow metal or wood spatula. Weigh 4 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.

11.9.5.1.2. Quickly add 9 mL of methanol, and 1 mL of surrogate spiking solution to bring the final volume of methanol to 10 mL. For an LCS or MS/MSD sample add 8 mL of methanol, 1 mL of surrogate spike solution, and 1 mL of matrix spike solution. Cap the vial and vortex to mix thoroughly.

NOTE: Sections 11.9.5.1.1 and 11.9.5.1.2 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 confined to an individual sample reanalysis is not necessary. If the change in sensitivity is

due to instrumental problems all affected samples must be reanalyzed after the problem is corrected.

11.10.3. 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 to demonstrate matrix effect, but reanalysis at a dilution should be considered.

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.
- All ions present in the standard mass spectra at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100%) should be present in the sample spectrum.
- The relative intensities of ions should agree to within ±30% between the standard and sample spectra. (Example: For an ion with an abundance of 50% in the standard spectra, the corresponding sample abundance must be between 20 and 80 percent.)

12.1.1. If a compound cannot be verified by all the above criteria, but in the technical judgment of the analyst, the identification is correct, then the analyst shall report that identification and proceed with quantitation.

12.2. Tentatively Identified Compounds (TICs)

12.2.1. If the client requests components not associated with the calibration standards, a search of the NIST library may be made for the purpose of tentative identification. Guidelines are:

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

12.2.1.2. The relative intensities of the major ions should agree to within 20%. (Example: If an ion shows an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30% and 70%).

12.2.1.3. Molecular ions present in the reference spectrum should be present in the sample spectrum.

12.2.1.4. Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.

12.2.1.5. Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the spectrum because of background contamination or coeluting peaks. (Data system reduction programs can sometimes create these discrepancies.)

12.2.1.6. Computer-generated library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other. Only after visual inspection of the sample with the nearest library searches should the analyst assign a tentative identification.

12.3. Calculations.

12.3.1. Response factor (RF):

Equation 1

$$RF = \frac{A_x C_{is}}{A_{is} C_x}$$

Where:

A_x = Area of the characteristic ion for the compound to be measured

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

C_{is} = Concentration of the specific internal standard, ng

C_x = Concentration of the compound being measured, ng

12.3.2. Standard deviation (SD):

Equation 2

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

X_i = Value of X at i through N

N = Number of points

X = Average value of X_i

12.3.3. Percent relative standard deviation (%RSD):

Equation 3

$$\%RSD = \frac{\text{Standard Deviation}}{\overline{RFi}} \times 100$$

$\overline{RFi}$ = Mean of RF values in the curve

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

Equation 4

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

Where

$C_{expected}$ = Known concentration in standard

C_{found} = Measured concentration using selected quantitation method

12.3.5. Target compound and surrogate concentrations:

Concentrations in the sample may be determined from linear or second order (quadratic) curve fitted to the initial calibration points, or from the average response factor of the initial calibration points. Average response factor may only be used when the % RSD of the response factors in the initial calibration is $\leq$ 15%.

12.3.5.1. Calculation of concentration using Average Response Factors

Equation 5

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

12.3.5.2. Calculation of concentration using Linear fit

Equation 6

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

12.3.5.3. Calculation of concentration using Quadratic fit

Equation 7

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

x is defined in equations 8, 9 and 10

A is a constant defined by the intercept

B is the slope of the curve

C is the curvature

12.3.5.4. Calculation of x for Water and water-miscible waste:

Equation 8

$$x = \frac{(A_x)(I_s)(D_f)}{(A_{is})(V_o)}$$

Where:

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

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

SSR = Spike sample result

SR = Sample result

SA = Spike added

12.3.7. Relative % Difference calculation for the MS/MSD

Equation 12

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

Where:

RPD = Relative percent difference

MSR = Matrix spike result

MSDR = Matrix spike duplicate result

13. METHOD PERFORMANCE

13.1. Method Detection Limit

13.2. Generally, each laboratory must generate a valid method detection limit for each analyte of interest. The MDL must be below the reporting limit for each analyte. The procedure for determination of the method detection limit is given in 40 CFR Part 136, Appendix B, and further defined in QA Policy #: QA-005. When non-standard compounds are analyzed at client request, lesser requirements are possible with client agreement. At a minimum, a standard at the reporting limit must be analyzed to demonstrate the capability of the method.

13.3. Initial Demonstration

13.4. 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.)

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

13.4.2. 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%.

13.4.3. If any analyte does not meet the acceptance criteria, check the acceptance limits in the reference methods (Table 6 of method 8240B, paragraph 8.3.5 of method 8260A). If the recovery or precision is outside the limits in the reference methods, the test must be repeated. Only those analytes that did not meet criteria in the first test need to be evaluated. Repeated failure for any analyte indicates the need for the laboratory to evaluate the analytical procedure and take corrective action.

13.4.4. Training Qualification

13.4.4.1. 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. Waste generated in the procedure must be segregated and disposed according to the facility hazardous waste procedures. The Health and Safety Director should be contacted if additional information is required.

16. REFERENCES

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

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

17. MISCELLANEOUS

17.1. Modifications from the reference method

17.1.1. Ion 119 is used as the quantitation ion for chlorobenzene-d5 for 25 mL purge tests.

17.1.2. A retention time window of 0.2 minutes is used for all components, since some data systems do not have the capability of using the relative retention time units specified in the reference method.

17.1.3. The quantitation and qualifier ions for some compounds have been changed from those recommended in SW-846 in order to improve the reliability of qualitative identification.

17.1.4. Method 8260A recommends that the purge vessel is run through an additional purge cycle after 25 mL sample analysis to remove carryover. Instead, purge vessels are oven baked between analyses or disposable vessels are used one time only.

17.1.5. SW-846 recommends that a curve be used for any analytes with %RSD of the response factors > 15%. However, some industry standard data systems and forms generation software cannot report this data with the necessary information for data validation. In

addition most software available does not allow weighting of the curve. Unweighted curves may exhibit serious errors in quantitation at the low end, resulting in possible false positives or false negatives. Therefore, this SOP allows used of average response factors if the average %RSD for all compounds is $\leq$ 15%.

17.2. Modifications from previous revision

This SOP has been substantially revised to reflect the changes included in Update III to SW-846. Directions for method 524.2 and method 624 have also been added.

17.3. Facility specific SOPs

Each facility shall attach a list of facility-specific SOPs or approved attachments (if applicable) which are required to implement this SOP or which are used in conjunction with this SOP. If no facility specific SOPs or amendments are to be attached, a statement must be attached specifying that there are none.

17.4. Flow diagrams

17.4.1. Initial Demonstration and MDL

17.5. The following are protocols that must be followed when analyzing OhioVAP samples:

- Sections 9.5 and 9.6: 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 11.9.2: For OhioVAP projects, the laboratory will reanalyze any sample where the internal standard fails and there is no evidence of matrix interference.

17.6. 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 8.5.8 For the purpose of this project, the soil/methanol mixture may be stored for two days prior to analysis.

- Modify Section 8.6.12 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 10.4.6.2 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.

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

- **Delete** from Section 10.4.7 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 12.3.5.1

- Calculation of concentration using Quadratic fit

Equation 13

Concentration $\mu g / L = A + Bx + Cx^2$

x is defined in equations 8, 9 and 10

A is a constant defined by the intercept

B is the slope of the curve

C is the curvature

- **Change** Section 9.3 The compounds included in the surrogate spiking solutions are listed in Tables 8 *and 9*.

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

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

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

17.8.3. Modify Section 8.5.6 and 8.6.10 (add 100 uL of 50 ug/mL spike solution for a nominal 25g sample).

17.8.4. 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 1 ug/L, 2 ug/L (if a quadratic calibration is to be used), 5 ug/L, 10 ug/L, 20 ug/L and 40 ug/L. Some analytes are prepared at higher concentrations.

17.8.5. 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.

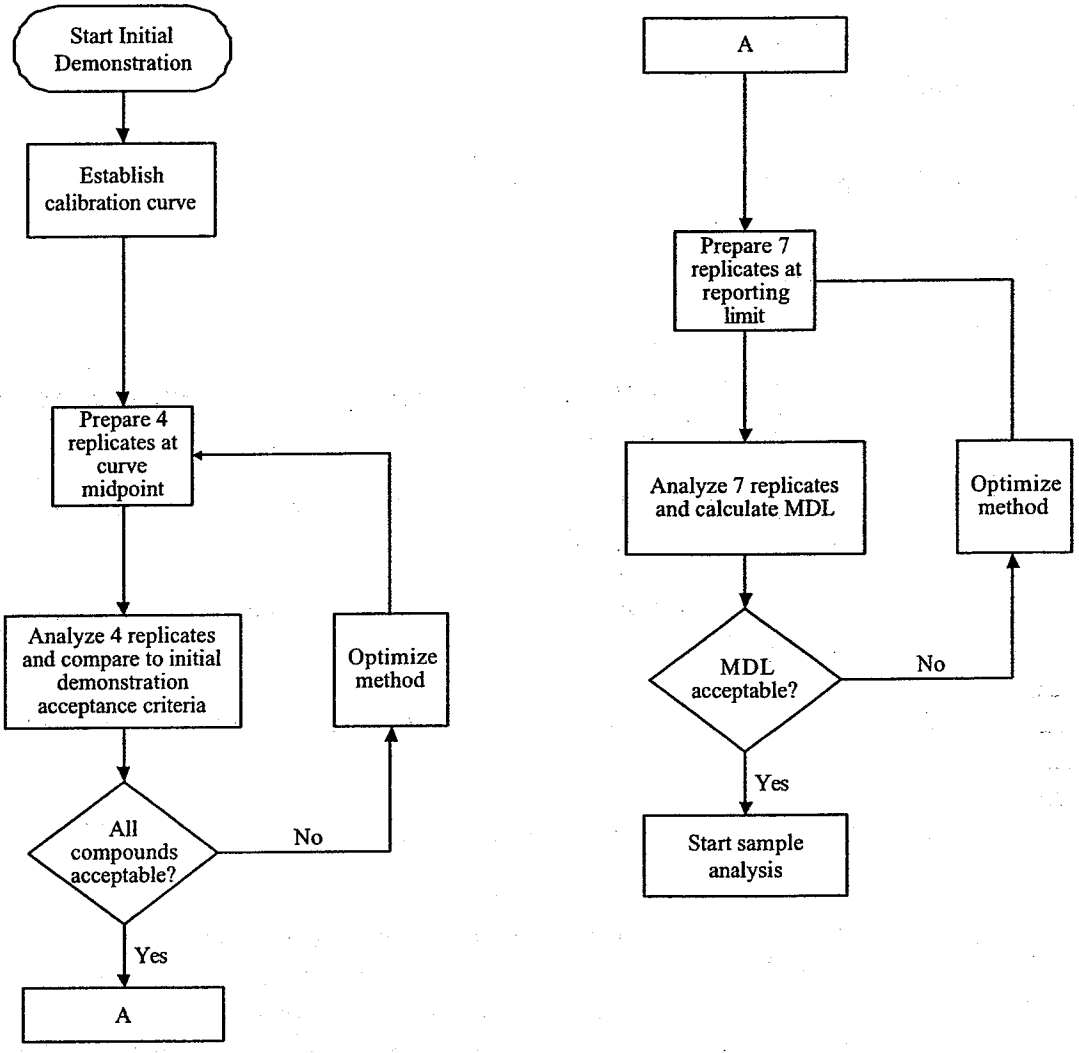

Start Initial Demonstration
Establish calibration curve
Prepare 4 replicates at curve midpoint
Analyze 4 replicates and compare to initial demonstration acceptance criteria
Optimize method
All compounds acceptable?
No
Yes
A
A
Prepare 7 replicates at reporting limit
Analyze 7 replicates and calculate MDL
Optimize method
MDL acceptable?
No
Yes
Start sample analysis

Table 1

STL Primary Standard and Reporting Limits

Compound	CAS Number	Reporting Limits[1]				
		5 mL Water µg/L	25 mL[3] water µg/L	Low soil µg/kg	8260B/ 5035 Soil ug/kg	8260A 5030A Med Level Soil µg/kg
Dichlorodifluoromethane	75-71-8	10	2	10	250	1200
Chloromethane	74-87-3	10	2	10	250	1200
Bromomethane	74-83-9	10	2	10	250	1200
Vinyl chloride	75-01-4	10	2	10	250	1200
Chloroethane	75-00-3	10	2	10	250	1200
Trichlorofluoromethane	75-69-4	10	2	10	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	5.0	1.0	5.0	250	310
1,2-Dichloroethene (Total)	540-59-0	5	1	5	250	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	25 mL[3] 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		5.0	0.5	2.5	125	310
o-xylene	95-47-6	5.0	0.5	2.5	125	310
Total xylenes	1330-20-7	5	1	5	250	620
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	25 mL[3] 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	

[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

[3] Optionally, 5 mL purge volume if adequate sensitivity is obtained.

Table 2

STL Primary Standard Calibration Levels, 5 mL purge[1]

Compound	Calibration Level ug/L				
	Level 1	Level 2	Level 3	Level 4	Level 5
1,2-Dichloroethane-d4 (Surrogate)	5	20	50	100	200
Toluene-d8 (Surrogate)	5	20	50	100	200
4-Bromofluorobenzene (Surrogate)	5	20	50	100	200
Dichlorodifluoromethane	5	20	50	100	200
Chloromethane	5	20	50	100	200
Bromomethane	5	20	50	100	200
Vinyl chloride	5	20	50	100	200
Chloroethane	5	20	50	100	200
Trichlorofluoromethane	5	20	50	100	200
Acrolein	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 purge[1]

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 purge[1]

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 Level [1]

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
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

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
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
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

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
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	25mL[2] 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	N/A[1]	N/A[1]	N/A[1]	N/A[1]
Isopropylbenzene	98-82-8	5	1	5	250
2-Methylnaphthalene (Michigan only)	91-57-6	NA	5	NA	330

[1] Cyclohexanone decomposes to 1,1-dimethoxycyclohexane in methanolic solution. Reporting limits cannot be accurately determined.

[2] Optionally, 5 mL purge volume if adequate sensitivity is obtained.

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
Chloromethane	74-87-3	X		X	X	X
Bromomethane	74-83-9	X		X	X	X
Vinyl chloride	75-01-4	X	X	X	X	X
Chloroethane	75-00-3	X		X	X	X
Trichlorofluoromethane	75-69-4				X	X
Acrolein	107-02-8				X	X
Acetone	67-64-1	X		X	X	X
Trichlorotrifluoroethane	76-13-1					X
Ethanol	64-17-5					
Iodomethane	74-88-4				X	X
Carbon disulfide	75-15-0	X		X	X	X
Methylene chloride	75-09-2	X		X	X	X
tert-Butly alcohol	75-65-0					
1,1-Dichloroethene	75-35-4	X	X	X	X	X
1,1-Dichloroethane	75-34-3	X		X	X	X
trans-1,2-Dichloroethene	156-60-5	X		X	X	X
Total dichloroethene		X		X	X	X
Acrylonitrile	107-13-1				X	X
Methyl *tert*-butyl ether (MTBE)	1634-04-4					
Hexane	110-54-3					
cis-1,2-Dichloroethene	156-59-2	X		X		
Tetrahydrofuran	109-99-9					
Chloroform	67-66-3	X	X	X	X	X
1,2-Dichloroethane	107-06-2	X	X	X	X	X
Dibromomethane	74-95-3				X	X
2-Butanone	78-93-3	X	X	X	X	X
1,4-Dioxane	123-91-1				X	X
1,1,1-Trichloroethane	71-55-6	X		X	X	X
Carbon tetrachloride	56-23-5	X	X	X	X	X
Bromodichloromethane	75-27-4	X		X	X	X
1,2-Dichloropropane	78-87-5	X		X	X	X
cis-1,3-Dichloropropene	10061-01-5	X		X	X	X
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
1,2,3-Trichloropropane	96-18-4				X	X
1,1,2-Trichloroethane	79-00-5	X		X	X	X
Benzene	71-43-2	X	X	X	X	X
Ethylmethacrylate	97-63-2				X	X
trans-1,3-Dichloropropene	10061-02-6	X		X	X	X
Bromoform	75-25-2	X		X	X	X
4-Methyl-2-pentanone	108-10-1	X		X	X	X
2-Hexanone	591-78-6	X		X	X	
Tetrachloroethene	127-18-4	X	X	X	X	X
Toluene	108-88-3	X		X	X	X
1,1,2,2-Tetrachloroethane	79-34-5	X		X	X	X
2-Chloroethyl vinyl ether	110-75-8					
Vinyl acetate	108-05-4				X	
Chlorobenzene	108-90-7	X	X	X	X	X
Ethylbenzene	100-41-4	X		X	X	X
Styrene	100-42-5	X		X	X	
t-1,4-Dichloro-2-butene	110-57-6				X	
m and p Xylenes		X		X	X	X
o-xylene	95-47-6	X		X	X	X
Total xylenes	1330-20-7	X		X	X	X
1,3-Dichlorobenzene	541-73-1					
1,4-Dichlorobenzene	106-46-7					
1,2-Dichlorobenzene	95-50-1					

Table 6

Reportable Analytes for STL Standard Tests, Appendix IX standard

Compound	Number	STL Standard List	TCLP	TCL	Appendix IX	UTS
Allyl Chloride	107-05-1				X	
Acetonitrile	75-05-8				X	X
Dichlorofluoromethane	75-43-4					
Isopropyl ether	108-20-3					
Chloroprene	126-99-8				X	
n-Butanol	71-36-3					
Propionitrile	107-12-0				X	
Methacrylonitrile	126-98-7				X	X
Isobutanol	78-83-1				X	X
Methyl methacrylate	80-62-6				X	X
1,1,1,2-Tetrachloroethane	630-20-6				X	X
1,2-Dibromo-3-chloropropane	96-12-8				X	X
Ethyl ether	60-29-7					X
Ethyl Acetate	141-78-6					X
2-Nitropropane	79-46-9					
Cyclohexanone	108-94-1					X
Isopropylbenzene	98-82-8					

Table 7

Internal Standards

	Standard Concentration µg/mL	Quantitation ion (5 mL purge)	Quantitation ion (25 mL purge)
Fluorobenzene	50	96	96
Chlorobenzene-d5	50	117	119
1,4-Dichlorobenzene-d4	50	152	152

Notes:

1) 5 µL of the internal standard is added to the sample. This results in a concentration of each internal in the sample of 50µg/L for a 5 mL purge or 10 µg/L for a 25 mL purge.

2) Except for medium level soils, the surrogate and internal standards may be combined in one solution.

Table 8

Surrogate Standards

Surrogate Compounds	Standard Concentration µg/mL
1,2-Dichloroethane-d_4	50
Dibromofluoromethane	50
Toluene-d_8	50
4-Bromofluorobenzene	50

Notes:

1) 5 µL of the surrogate standard is added to the sample. This results in a concentration of each surrogate in the sample of 50µg/L for a 5 mL purge or 10 µg/L for a 25 mL purge.

2) Except for medium level soils, the surrogate and internal standards may be combined in one solution.

3) Recovery limits for surrogates are generated from historical data and are maintained by the QA department.

Table 9

Matrix Spike / LCS 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 fromhistorical data and are maintained by the QA dedartment.

3) Full analyte spikes may also be used at the laboratories option or at client request.

Table 10

BFB Key Ion Abundance Criteria

Mass	Ion Abundance Criteria
50	15% to 40% of Mass 95
75	30% to 60% of Mass 95
95	Base Peak, 100% Relative Abundance
96	5% to 9% of Mass 95
173	Less Than 2% of Mass 174
174	Greater Than 50% of Mass 95
175	5% to 9% of Mass 174
176	Greater Than 95%, But Less Than 101% of Mass 174
177	5% to 9% of Mass 176

Table 11

SPCC Compounds and Minimum Response Factors

Compound	8260B, 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	

* 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.

1. REQUIREMENTS FOR EPA 624

1.1. Method 624 is required for demonstration of compliance with NPDES wastewater discharge permits. This method can be applied only to aqueous matrices. The standard analyte list and reporting limits are listed in Table B-1.

1.2. The tune period for this method is defined as 24 hours.

1.3. The initial calibration curve for this method requires at least three points.

1.4. Sample concentrations are calculated using the average RRF from the initial calibration curve.

1.5. Each target analyte is assigned to the closest eluting internal standard.

1.6. Initial demonstration of Proficiency

1.6.1. The spiking level for the four replicate initial demonstration of proficiency is 20 µg/L. The acceptance criteria are listed in Table B-2

1.7. Initial calibration curve requirements:

1.7.1. Target compounds must have RSD ≤ 35%.

1.7.2. If this requirement can not be met, a regression curve must be constructed for the non-compliant compounds. There is no correlation coefficient requirement for the regression curve.

1.8. Continuing calibration verification requirements:

1.8.1. The continuing calibration standard is from a different source than the initial calibration standard. The acceptance criteria are listed in Table B-2.

1.9. Matrix Spike and LCS requirements

1.9.1. The matrix spike and LCS are spiked at 20 µg/L. A matrix spike duplicate is not necessary for this method. The recovery limits for matrix spike and LCS recovery are listed in Table C-2.

1.10. Method clarifications, modifications and additions

1.10.1. Section 5.2.2 of the source method describes the trap packing materials as Tenax GC, Methyl silicone, silica gel and coconut charcoal. STL routinely employs the Supelco VOCARB 3000, which consists of Carbopack B and Carboxen 1000 and 1001.

1.10.2. Section 5.3.2 of the source method describes a packed analytical column. STL routinely employs capillary columns when performing this method.

1.10.3. The source method provides a suggested list of compounds for internal and surrogate standards. STL uses the following two compounds which are not on the table: Chlorobenzene-d_5 (internal standard) and 1,2-Difluorobenzene-d_4 (surrogate).

Table A-1.

Method 624 Analytes and Reporting Limits

Analytes	µg/L
Benzene	5
Bromodichloromethane	5
Bromoform	5
Bromomethane	5
Carbon tetrachloride	5
Chlorobenzene	5
Chloroethane	5
2-Chloroethyl vinyl ether	5
Chloroform	5
Chloromethane	5
Dibromochloromethane	5
1,2-Dichlorobenzene	5
1,3-Dichlorobenzene	5
1,4-Dichlorobenzene	5
1,1-Dichloroethane	5
1,2-Dichloroethane	5
1,1-Dichloroethene	5
trans-1,2-Dichloroethene	5
1,2-Dichloropropane	5
cis-1,3-Dichloropropene	5
trans-1,3-Dichloropropene	5
Ethylbenzene	5
Methylene chloride	5
1,1,2,2-Tetrachloroethane	5
Tetrachloroethene	5
Toluene	5
1,1,1-Trichloroethane	5
1,1,2-Trichloroethane	5
Trichloroethene	5
Trichlorofluoromethane	5
Vinyl chloride	5

Table A-2.

Method 624 QC Acceptance Criteria

Analytes	Daily QC check acceptance criteria (20µg/L spike)	Mean recovery, 4 replicate initial demonstration acceptance criteria (20µg/L spike)	Standard deviation, 4 replicate initial demonstration acceptance criteria (20µg/L spike)	Matrix spike and LCS acceptance criteria (% recovery)
Benzene	12.8-27.2	15.2-26.0	6.9	37-151
Bromodichloromethane	13.1-26.9	10.1-28.0	6.4	35-155
Bromoform	14.2-25.8	11.4-31.1	5.4	45-169
Bromomethane	2.8-37.2	D-41.2	17.9	D-242
Carbon tetrachloride	14.6-25.4	17.2-23.5	5.2	70-140
Chlorobenzene	13.2-26.8	16.4-27.4	6.3	37-160
Chloroethane	7.6-32.4	8.4-40.4	11.4	14-230
2-Chloroethyl vinyl ether	D-44.8	D-50.4	25.9	D-305
Chloroform	13.5-26.5	13.7-24.2	6.1	51-138
Chloromethane	D-40.8	D-45.9	19.8	D-273
Dibromochloromethane	13.5-26.5	13.8-26.6	6.1	53-149
1,2-Dichlorobenzene	12.6-27.4	11.8-34.7	7.1	18-190
1,3-Dichlorobenzene	14.6-25.4	17.0-28.8	5.5	59-156
1,4-Dichlorobenzene	12.6-27.4	11.8-34.7	7.1	18-190
1,1-Dichloroethane	14.5-25.5	14.2-28.5	5.1	59-155
1,2-Dichloroethane	13.6-26.4	14.3-27.4	6.0	49-155
1,1-Dichloroethene	10.1-29.9	3.7-42.3	9.1	D-234
trans-1,2-Dichloroethene	13.9-26.1	13.6-28.5	5.7	54-156
1,2-Dichloropropane	6.8-33.2	3.8-36.2	13.8	D-210
cis-1,3-Dichloropropene	4.8-35.2	1.0-39.0	15.8	D-227
trans-1,3-Dichloropropene	10.0-30.0	7.6-32.4	10.4	17-183
Ethylbenzene	11.8-28.2	17.4-26.7	7.5	37-162
Methylene chloride	12.1-27.9	D-41.0	7.4	D-221
1,1,2,2-Tetrachloroethane	12.1-27.9	13.5-27.2	7.4	46-157
Tetrachloroethene	14.7-25.3	17.0-26.6	5.0	64-148
Toluene	14.9-25.1	16.6-26.7	4.8	47-150
1,1,1-Trichloroethane	15.0-25.0	13.7-30.1	4.6	52-162
1,1,2-Trichloroethane	14.2-25.8	14.3-27.1	5.5	52-150
Trichloroethene	13.3-26.7	18.6-27.6	6.6	71-157
Trichlorofluoromethane	9.6-30.4	8.9-31.5	10.0	17-181
Vinyl chloride	0.8-39.2	D-43.5	20.0	D-251

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STL NORTH CANTON STANDARD OPERATING PROCEDURE

TITLE: EXTRACTION AND CLEANUP OF ORGANIC COMPOUNDS FROM WATERS AND SOILS, BASED ON SW-846 3500 SERIES, 3600 SERIES, 8150, 8151 AND 600 SERIES METHODS.

(SUPERSEDES: CORP-OP-0001 (Revision 2.4, Dated 10/16/98))

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1. SCOPE AND APPLICATION

This SOP describes procedures for preparation (extraction and cleanup) of semivolatile organic analytes in aqueous, TCLP leachate, and soil matrices for analysis by Gas Chromatography (GC) and Gas Chromatography / Mass Spectrometry (GC/MS). The procedures are based on SW-846 and 600 series methodology and are applicable for measurements made to comply with the Resource Conservation and Recovery Act (RCRA) and for wastewater testing.

1.1. Extraction procedures for the following determinative methods are covered:

8080A, 8100, 8140, 8141A, 8150B, 8151A, 8270B, 8310
608, 610, and 625

1.2. The extraction procedures here may be appropriate for other determinative methods when appropriate spiking mixtures are used.

2. SUMMARY OF METHOD

2.1. Separatory Funnel Extraction

A measured volume of sample, typically 1 liter, is adjusted, if necessary, to a specified pH and serially extracted with methylene chloride using a separatory funnel.

2.2. Continuous Liquid/Liquid Extraction

A measured volume of sample, typically 1 liter, is placed into a continuous liquid/liquid extractor, adjusted, if necessary, to a specific pH and extracted with methylene chloride for 18-24 hours.

2.3. Sonication Extraction

A measured weight of sample, typically 30 g, is mixed with anhydrous sodium sulfate to form a free flowing powder. This is solvent extracted three times using an ultrasonic horn.

2.4. Soxhlet Extraction

A 30 g sample is mixed with anhydrous sodium sulfate to form a free flowing powder. This is extracted with refluxing solvent.

2.5. Cleanup and Concentration

Procedures are presented for removing interferents from sample extracts, and for drying and concentration of the extract to final volume for analysis.

2.6. Phenoxy acid herbicide extractions

Procedures for the extraction and cleanup of phenoxy acid herbicides are presented in Appendix A.

3. DEFINITIONS

Definitions of terms used in this SOP may be found in the glossary of the 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 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. Visual interferences or anomalies (such as foaming, emulsions, odor, etc.) must be documented.

5. SAFETY

5.1. Procedures shall be carried out in a manner that protects the health and safety of all STL North Canton associates. The following requirements must be met:

5.2. Eye protection that satisfies ANSI Z87.1 (as per the Chemical Hygiene Plan), laboratory coat and appropriate gloves must be worn while samples, standards, solvents and reagents are being handled. Disposable gloves that have become contaminated will be removed and discarded, other gloves will be cleaned immediately. Viton gloves may be worn when halogenated solvents are used for extractions or sample preparation. Nitrile gloves may be used when other solvents are handled. [Note: VITON is readily degraded by acetone]. When good manual dexterity is needed, for example, when handling small quantities/containers, disposable gloves (such as latex or N-DEX®) shall be used. While these gloves protect against splashes, they give little or no protection against contact with large quantities of solvent, and no protection against spills or immersion.

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

Chemicals that have been classified as **carcinogens** or **potential carcinogens** under OSHA include: Methylene chloride, PCBs, certain pesticides.

The following materials are known to be **corrosive**: Concentrated sulfuric acid, sodium hydroxide, 1N nitric acid.

Sulfuric acid cleanup must not be performed on any matrix that may have water present as a violent reaction between the acid and water may result in acid exploding out of the vessel.

Chemicals known to be **flammable** are: Diethyl ether, acetone, hexane, 2-propanol.
Mercury is a highly toxic compound that must be handled with care. The analyst must be aware of the handling and clean-up techniques before handling this material.

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

5.5. The preparation of standards and reagents 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 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 North Canton associate. The situation must be reported **immediately** to a laboratory supervisor.

6. EQUIPMENT AND SUPPLIES

6.1. Glassware should be cleaned with soap and water, rinsed with water and dried in an oven at 400°C for at least 2 hours. Alternatively the glassware can be solvent rinsed with acetone or methanol followed by methylene chloride after the water rinse.

6.2. Equipment and supplies for extraction procedures

EQUIPMENT AND SUPPLIES	Sep fun.	CLLE	Soni	Sox	Conc
Separatory Funnel: 2 L	√				
Separatory Funnel Rack	√				
Balance: >1400 g capacity, accurate ±1 g	√	√			
pH indicator paper, wide-range: covers extraction pH	√	√			
Graduated cylinder: 1 liter. (other sizes may be used)	√	√			
Erlenmeyer Flask or Fleaker: 125 & 300 mL (other sizes optional)	√		√		
Solvent Dispenser Pump or 100 mL Graduated Cylinder	√		√		
Continuous Liquid/Liquid Extractor		√			

EQUIPMENT AND SUPPLIES	Sep fun.	CLLE	Soni	Sox	Conc
Round or flat Bottom: 250, 500 mL or 1 L		√			
Boiling Chips: Contaminant free, approximately 10/40 mesh (Teflon® PTFE, carbide or equivalent).		√		√	√
Cooling Condensers		√		√	
Heating Mantle: Rheostat controlled		√		√	
Auto-timer for heating mantle		√		√	
Beakers: 250 & 400 mL, graduated			√		
Balance: >100 g capacity, accurate ±0.1 g			√	√	
Soxhlet Extractor				√	
Sonicator (at least 300 watts)			√		
Sonicator horn, 3/4 inch			√		
Kuderna-Danish (K-D) Apparatus: 500 mL					√
Concentrator Tube: 10 mL, attached to K-D with clips					√
Jacketed Concentrator Tube					√
Snyder Column: Three-ball macro					√
Water Bath: Heated, with concentric ring cover, capable of temperature control (± 5°C) up to 95°C. The bath must be used in a hood or with a solvent recovery system.					√
Vials: Glass, 2 mL, 4 mL, and 10 mL capacity with Teflon®-lined screw-cap					√
Nitrogen Blowdown Apparatus					√
Nitrogen: reagent grade.					√
Culture tubes: 10 mL, 16 mmx100 mm					√
Syringe: 1 mL	√	√	√	√	
Phase Separation Paper	√	√	√	√	
Glass Wool	√	√	√	√	
Glass Funnel: 75 X 75 mm	√	√	√	√	√
Disposable Pipets	√	√	√	√	√
Aluminum foil	√	√	√	√	√
Paper Towels	√	√	√	√	√

6.3. Equipment and Supplies for Cleanup Procedures

EQUIPMENT AND SUPPLIES	GPC	Florisil	Sulfur	Acid	A/B
Gel permeation chromatography system (GPC Autoprep Model 1002A or 1002B Analytical Biochemical Laboratories, Inc. or Zymark Benchmate or equivalent).	√				
Bio Beads: (S-X3) -200-400 mesh, 70 gm (Bio-Rad Laboratories, Richmond, CA, Catalog 152-2750 or equivalent).	√				

EQUIPMENT AND SUPPLIES	GPC	Florisil	Sulfur	Acid	A/B
Chromatographic column: 700 mm x 25 mm ID glass column. Flow is upward.	√				
Ultraviolet detector: Fixed wavelength (254 nm) and a semi-prep flow-through cell.	√				
Strip chart recorder, recording integrator, or laboratory data system.	√				
Syringe: 10 mL with Luerlok fitting.	√				
Syringe filter assembly, with disposable 5 um filter discs, Millipore No. LSWP 01300 or equivalent.	√				
Chromatographic column: 250 mm long x 10 mm ID; with Pyrex glass wool at the bottom and a Teflon stopcock (for silica gel cleanup).	√				
Vacuum system for eluting multiple cleanup cartridges. Vac Elute Manifold - Analytichem International, J.T. Baker, or Supelco (or equivalent). The manifold design must ensure that there is no contact between plastics containing phthalates and sample extracts.		√			
Vacuum trap made from a 500 mL sidearm flask fitted with a one-hole stopper and glass tubing.		√			
Vacuum pressure gauge.		√			
Rack for holding 10 mL volumetric flasks in the manifold.		√			
Mechanical shaker or mixer: Vortex Genie or equivalent.			√	√	
Separatory Funnels with Ground-Glass Stoppers: 250 mL					√
Erlenmeyer Flasks: 125 mL					√
Disposable Pipets		√	√	√	√
Culture tubes: 10 mL, 16 mmx100 mm	√	√	√	√	√

7. REAGENTS AND STANDARDS

7.1. Reagents for Extraction Procedures

All reagents must be ACS reagent grade or better unless otherwise specified.

REAGENTS	Sep fun.	CLLE	Soni	Sox	Conc
Sodium hydroxide (NaOH), Pellets: Reagent Grade	√	√			
Sodium hydroxide solution, 10 N: Dissolve 40 g of NaOH in reagent water and dilute to 100 mL.	√	√			
Sulfuric acid (H_2SO_4), Concentrated: Reagent Grade	√	√			
Sulfuric acid (1:1): Carefully add 500 mL of H_2SO_4 to 500 mL of reagent water. Mix well.	√	√			
Organic free reagent water.	√	√			
Sodium sulfate (Na_2SO_4), Granular, Anhydrous: Purify by	√	√	√	√	

REAGENTS	Sep fun.	CLLE	Soni	Sox	Conc
heating at 400°C a minimum of two hours.					
Extraction/Exchange Solvents: Methylene chloride, hexane, acetonitrile, acetone, pesticide quality or equivalent	√	√	√	√	√
Acetone: Used for cleaning	√	√	√	√	√

7.2. Reagents for Cleanup Procedures

REAGENTS	GPC	Florisil	Sulfur	Acid	A/B
Florisil: 500 mg or 1 g cartridges with stainless steel or Teflon frits (calalog 694-313, Analytichem, 24201 Frampton Ave., Harbor City, CA, or equivalent.)		√			
Mercury: triple distilled			√		
Tetrabutylammonium hydrogen sulfate			√		
Sodium sulfite			√		
Tetrabutylammonium (TBA) sulfite reagent: Prepare reagent by dissolving 3.39 g of Tetrabutylammonium hydrogen sulfate in 100 mL organic-free reagent water. Extract this solution 3 times with 20 mL portions of hexane. Discard the hexane extracts. Add 25 g sodium sulfite to the water solution.			√		
2-Propanol			√		
Nitric acid: 1N			√		
Copper powder: remove oxides (if powder is dark) by treating with 1N nitric acid, rinse with organic-free reagent water to remove all traces of acid, rinse with acetone, and dry under a stream of nitrogen.			√		
Sulfuric acid, Concentrated				√	
Sodium hydroxide, Pellets					√
Sodium hydroxide, 10N: Dissolve 40 g of NaOH in 100 mL of reagent water					√
Sulfuric acid (H_2SO_4), Concentrated: Reagent Grade					√
Sulfuric acid (1:1): Carefully add 500 mL of H_2SO_4 to 500 mL of reagent water. Mix well.					√

7.3. Standards

7.3.1. Stock Standards

Stock standards are purchased as certified solutions or prepared from neats. Semivolatile stock standards are stored at ≤ 6°C. All stock standards must be protected from light. Stock standard solutions must be replaced after six months

(from the time of preparation, if prepared in house, or from the time the ampoule is opened if purchased.) Standards must be allowed to come to room temperature before use.

7.3.2. Surrogate Spiking Standards

Prepare or purchase surrogate spiking standards at the concentrations listed in Table 5. Surrogate spiking standards are prepared as dilutions of the stock standards. Surrogate spiking solutions must be refrigerated and protected from light. The standards must be replaced at least every six months or sooner if there is reason to believe that the standard has degraded or concentrated.

7.3.3. Matrix Spiking and Laboratory Control Spiking Standards.

The same spiking solution is used for the matrix spike and the Laboratory Control Sample. Prepare MS/LCS spiking standards at the concentrations listed in Table 6. Spiking standards are purchased or prepared as dilutions of the stock standards. Surrogate spiking solutions must be refrigerated and protected from light. The standards must be replaced at least every six months or sooner if there is reason to believe that the standard has degraded or concentrated.

7.3.4. GPC calibration solution - prepare or purchase a solution in methylene chloride that contains the following analytes in the concentrations listed below:

Analyte	mg/mL
Corn Oil	25.0
Bis (2-ethylhexyl) phthalate	1.0
Methoxychlor	0.2
Perylene	0.02
Sulfur	0.08

NOTE: Sulfur is not very soluble in methylene chloride, however, it is soluble in warm corn oil. Therefore, one approach is to weigh out the corn oil, warm it, and transfer the weighed amount of sulfur into the warm corn oil. Mix it and then transfer into a volumetric flask with methylene chloride, along with the other calibration compounds. This standard has a lifetime of 6 months.

8. SAMPLE COLLECTION PRESERVATION AND STORAGE

8.1. Samples are not chemically preserved.

8.2. Samples are stored at 4°C ± 2°C in glass containers with Teflon®-lined caps.

8.3. Holding Times

8.3.1. Extraction is initiated within 7 days of the sampling date for aqueous samples, 14 days for solid and waste samples.

8.3.2. For TCLP leachates, extraction is initiated within seven days from when the leaching procedure is completed.

8.3.3. Analysis of the extracts is completed within forty days of extraction.

9. QUALITY CONTROL

9.1. Quality Control Batch

The batch is a set of up to 20 samples that are of the same matrix and are processed together using the same procedures and reagents. The batch must contain a method blank, an 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.

9.2. Definition of matrix

The possible matrix types are aqueous, soil, waste and TCLP leachate.

9.3. Insufficient Sample

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. Use of a LCS pair in place of a MS/MSD must be documented as a nonconformance.

9.4. Sample count

Laboratory generated QC samples (method blanks, LCS, MS/MSD) are not included in the sample count. Field QC samples and multiple dilutions of samples are included.

9.5. Method Blank

A method blank consisting of all reagents added to the samples must be prepared and analyzed with each batch of samples. Surrogates are spiked into the method blank at the same level as the 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.

9.5.1. Aqueous Method Blanks use 1000 mL of reagent water spiked with the surrogates. The method blank goes through the entire analytical procedure, including any cleanup steps.

9.5.2. Solid method blanks use *approximately* 90 g of sodium sulfate spiked with the surrogates. The method blank goes through the entire analytical procedure, including any cleanup steps.

9.5.3. TCLP method blanks use 200 mL of leachate fluid (100 mL for pesticides or herbicides) spiked with the surrogates. The leachate may optionally be diluted to 1000 mL with reagent water. The method blank goes through the entire analytical procedure, including any cleanup steps.

9.6. Laboratory Control Sample (LCS)

Laboratory Control Samples are well-characterized, laboratory generated samples used to monitor the laboratory's day to day performance of routine analytical methods. The LCS, spiked with a group of target compounds representative of the method analytes, is used to monitor the accuracy of the analytical process, independent of matrix effects. On-going monitoring of the LCS results provides evidence that the laboratory is performing the method within accepted QC guidelines for accuracy and precision. The LCS goes through the entire analytical procedure, including any cleanup steps.

9.6.1. The LCS is made up in the same way as the method blank but spiked with the LCS standard and the surrogates (See sections 9.5.1 - 9.5.3).

9.7. Surrogates

9.7.1. 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.

9.7.2. Each applicable 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.

9.8. Matrix Spike/Matrix Spike Duplicate (MS/MSD)

A matrix spike is an environmental sample to which known concentrations of target analytes have been added. A matrix spike duplicate is a second spiked aliquot of the same sample which is prepared and analyzed along with the sample and matrix spike.

9.9. Initial Demonstration of Capability

The initial demonstration and method detection limit studies described in section 13 must be acceptable before analysis of samples may begin.

9.10. Quality Assurance Summaries

Certain clients may require specific project or program QC which may supersede these method requirements. Quality Assurance Summaries (QAS) should be developed to address these requirements.

9.11. STL North Canton QC Program

Further details of QC and corrective action guidelines are presented in the STL North Canton QC Program document (QA-003). Refer to this document if in doubt regarding corrective actions.

10. CALIBRATION AND STANDARDIZATION

Refer to section 11.8.1.2 for calibration of the GPC. Otherwise this section is not applicable.

11. PROCEDURE

Procedures for separatory funnel liquid/liquid extraction (11.2), continuous liquid/liquid extraction (11.3), sonication extraction (11.4), soxhlet extraction (11.5), waste dilution (11.6), extract concentration (11.7), and extract cleanup (11.8) are presented in this section.

11.1. Procedural Variations

Procedural variations are allowed only if deemed necessary in the professional judgment of the supervisor to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance memo and approved by a supervisor and QA/QC manager. If contractually required, the client will be notified. The Nonconformance memo will be filed in the project file.

Any deviations from this procedure identified after the work has been completed must be documented as a nonconformance, with a cause and corrective action described. A Nonconformance memo shall be used for this documentation.

11.2. Separatory Funnel Liquid/Liquid Extraction of Water Samples.

A flow chart for this procedure is included in Section 17. There are slight differences in the initial steps for SW-846 and 600 series methods, as defined below.

11.2.1. Sample preparation for SW-846 methods

11.2.1.1. For pesticides and TCLP leachates, measure the initial sample pH with wide-range pH paper and record on the extraction benchsheet. If sample is a leachate (e.g. TCLP), compare the current pH against leachate log, note on the benchsheet if there is any discrepancy.

11.2.1.2. Add 60 mL of methylene chloride directly to the separatory funnel. Transfer the sample to the separatory funnel.The sample volume is determined by marking the meniscus level on the sample container. Mark the meniscus and transfer the sample to the separatory funnel. Fill the sample container with water up to the marked level. Transfer the measured amount of water to a graduated cylinder and record the volume on the benchsheet to the nearest 5 mL. Less than one liter of sample may be used. If necessary, dilute the sample to about 1 liter with reagent water.

11.2.1.3. Prepare a method blank, LCS and MS/MSD for each batch as specified in section 9 of this SOP. Use 1 L of reagent water for method blanks and LCS.

11.2.1.4. Use 100 mL of leachate for TCLP pesticides, and 200 mL of leachate for TCLP semivolatiles, measured in a graduated cylinder. The leachate should be made up to 1 L in volume with reagent water.

11.2.1.5. For a TCLP method blank, measure 100 mL (200 mL for semivolatiles) of the buffer solution used in the leaching procedure and transfer to the separatory funnel. Dilute to about 1 liter with reagent water. Add 60 mL of methylene chloride to the separatory funnel.

11.2.1.6.Proceed to section 11.2.3 (SW-846 and 600 series).

11.2.2. 600 Series methods

11.2.2.1. Mix the sample well by shaking the container.

11.2.2.2. Measure the initial sample pH with wide-range pH paper and record on the extraction benchsheet.

11.2.2.3. Add 60 mL of methylene chloride directly to the separatory funnel. Transfer the sample to the separatory funnel. Empty the container completely. Add *approximately 10-20* mL of methylene chloride to the sample container, seal and shake to rinse the inner surface and remove residual analytes adhering to the glass walls. Transfer this solvent to the separatory funnel.

- **Warning:** Dichloromethane creates excessive pressure very rapidly! Therefore, initial venting should be done immediately after the sample container has been sealed and inverted. Vent into hood away from analysts and other samples. The sample volume may also be determined by marking the meniscus level on the sample container. Transfer the sample to the extractor (see 11.1.3). Fill the sample container with water up to the marked level. Transfer the measured amount of water to a graduated cylinder and record the volume on the benchsheet to the nearest 5 mL.
- Less than one liter of sample may be used. Dilute the sample to about 1 liter with reagent water.

11.2.2.4. Prepare a method blank, LCS and MS/MSD for each batch as specified in section 9 of this SOP. Use 1 L of reagent water for method blanks and LCS.

11.2.2.5. Proceed to section 11.2.3 (SW-846 and 600 series)

11.2.3. Add 1 mL of the surrogate spiking solution (Table 3) to each sample, method blank, Laboratory Control Sample (LCS), and Matrix Spike/Matrix Spike Duplicate (MS/MSD). Add 1 mL of the matrix spiking solution (Table 4) to each LCS and MS/MSD. Note that different matrix spiking solutions are used for 600 series, 8000 series and TCLP batches. Swirl liquid in separatory funnel gently to homogenize sample and surrogate/spiking compounds. Note that the surrogate and matrix spiking solutions should be brought to room temperature before spiking the samples.

11.2.4. Adjust sample pH as indicated in Table 1 for the initial extraction. Use the minimum amount of 1:1 H_2SO_4 or 10 N NaOH necessary. Recheck the sample with pH paper by dipping a disposable pipette into the sample and wetting the pH paper. Record adjusted pH, spiking volumes and standard numbers on the benchsheet. Return spiking solutions to the refrigerator as soon as possible.

11.2.5. Seal and shake the separatory funnel vigorously for *1*-2 minutes with periodic venting to release excess pressure.

Warning: Dichloromethane creates excessive pressure very rapidly! Therefore, initial venting should be done immediately after the separatory funnel has been sealed and inverted. Vent into hood away from analysts and other samples.

11.2.6. Allow the organic layer to separate from the water phase until complete visible separation has been achieved (approximately 10 minutes). If the emulsion interface between layers is more than one-third the size of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample and may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods. If the emulsion cannot be broken (recovery of <80% of the methylene chloride*), transfer the sample, solvent, and emulsion into the extraction chamber of a continuous extractor and proceed as described in continuous liquid-liquid extraction (Section 11.2.). If this is done, the sample must be extracted as part of a valid CLLE batch.

*Note: 15 - 20 mL of methylene chloride is expected to dissolve in 1 L of water. Thus, solvent recovery could be as low as 35 mL from the first shake and still be acceptable. Subsequent shakes should recover at least 50 mL of solvent.

11.2.7. Fill a funnel with 10-20 g of anhydrous sodium sulfate. The funnel can be plugged with glass wool or filter paper may be used to hold the sodium sulfate. *Add a small amount of methylene chloride to wet the sodium sulfate.* Drain the solvent extract from the separatory funnel through the prepared filtration funnel into a clean glass container. The extract may be drained directly into the KD flask. Close the stopcock just before the water level begins draining out of the separatory funnel. If the sodium sulfate becomes saturated with water add more to the funnel or replace the existing sodium sulfate with fresh drying agent.

11.2.8. Repeat the extraction process two more times using fresh 60 mL portions of solvent, combining the three solvent extracts in the collection container.

11.2.9. If extraction at a secondary pH is required, adjust the pH of the sample in the separatory funnel to the pH indicated in Table 1 with a minimum amount of 10 N NaOH or 1:1 H_2SO_4. Measure with pH paper and record the adjusted pH on the benchsheet. Serially extract with three 60 mL portions of methylene chloride, as outlined in Steps 11.1.7 to 11.1.9. Collect these three extracts in the same container used for the acid fraction.

Note: Alternatively, the acid and base fractions may be kept separate. This may be required for method 625. Separate analysis of the acid and base fractions may also be required for method 625. Individual client requirements must be checked before starting the extraction.

11.2.10. Rinse the extract residue from the sodium sulfate by pouring 20-30 mL of clean methylene chloride through the funnel and into the collection container.

11.2.11. Dispose of solvent and water remaining in the extractor into the appropriate waste container.

11.2.12. Cover with aluminum foil if the extract is not concentrated immediately. Refer to Section 11.7 for concentration and Section 11.8 for cleanup.

11.3. Continuous Liquid/Liquid Extraction from Water Samples.

A flow chart for this procedure is included in Section 17. There are slight differences in the initial steps for SW-846 and 600 series methods, as defined below.

11.3.1. Sample preparation for SW-846 methods.

11.3.1.1. Add 3 to 5 boiling chips to the round bottom distilling flask. Assemble *to* the *liquid/liquid body*. Add *200-300* mL of methylene chloride to the extractor body.

Note: *Other liquid/liquid designs may require the addition of different amounts of methylene chloride.*

11.3.1.2. Measure the initial sample pH with wide-range pH paper and record on the extraction benchsheet. If sample is a leachate (e.g. TCLP), compare the current pH against leachate log, note on the benchsheet if there is any discrepancy.

11.3.1.3. The sample volume *is* determined by marking the meniscus level on the sample container. Transfer the sample to the extractor (see 11.1.3). Fill the sample container with water up to the marked level. Transfer the measured amount of water to a graduated cylinder and record the volume on the benchsheet to the nearest 5 mL.

11.3.1.4. Prepare a method blank, LCS and MS/MSD for each batch as specified in section 9 of this SOP. Use 1 L of reagent water for method blanks and LCS.

11.3.1.5. Use 100 mL of leachate for TCLP *herbicides*, and *250* mL of leachate for TCLP *pesticides and* semivolatiles, measured in a graduated cylinder. The leachate may be made up to 1 L in volume with reagent water.

11.3.1.6. For a TCLP method blank, measure 100 mL *(for herbicides) or 250 mL (for pesticides and semivolatiles)* of the buffer solution used in the leaching procedure and transfer to the separatory funnel. Dilute to about 1 liter with reagent water.

11.3.1.7. Less than one liter of sample may be used, for highly contaminated samples. or if the reporting limit can be achieved with less than one liter of sample. In this event dilute the sample to about 1 liter with reagent water.

11.3.1.8. Proceed to section 11.3.3 (SW-846 and 600 series methods).

11.3.2. Sample preparation for 600 series methods.

11.3.2.1. Add 3 to 5 boiling chips to the round bottom distilling flask. Assemble *to* the *liquid/liquid body*. Add *200* mL of methylene chloride to the extractor body.

11.3.2.2. Mix the sample well by shaking the container.

11.3.2.3. Measure the initial sample pH with wide-range pH paper and record on the extraction benchsheet.

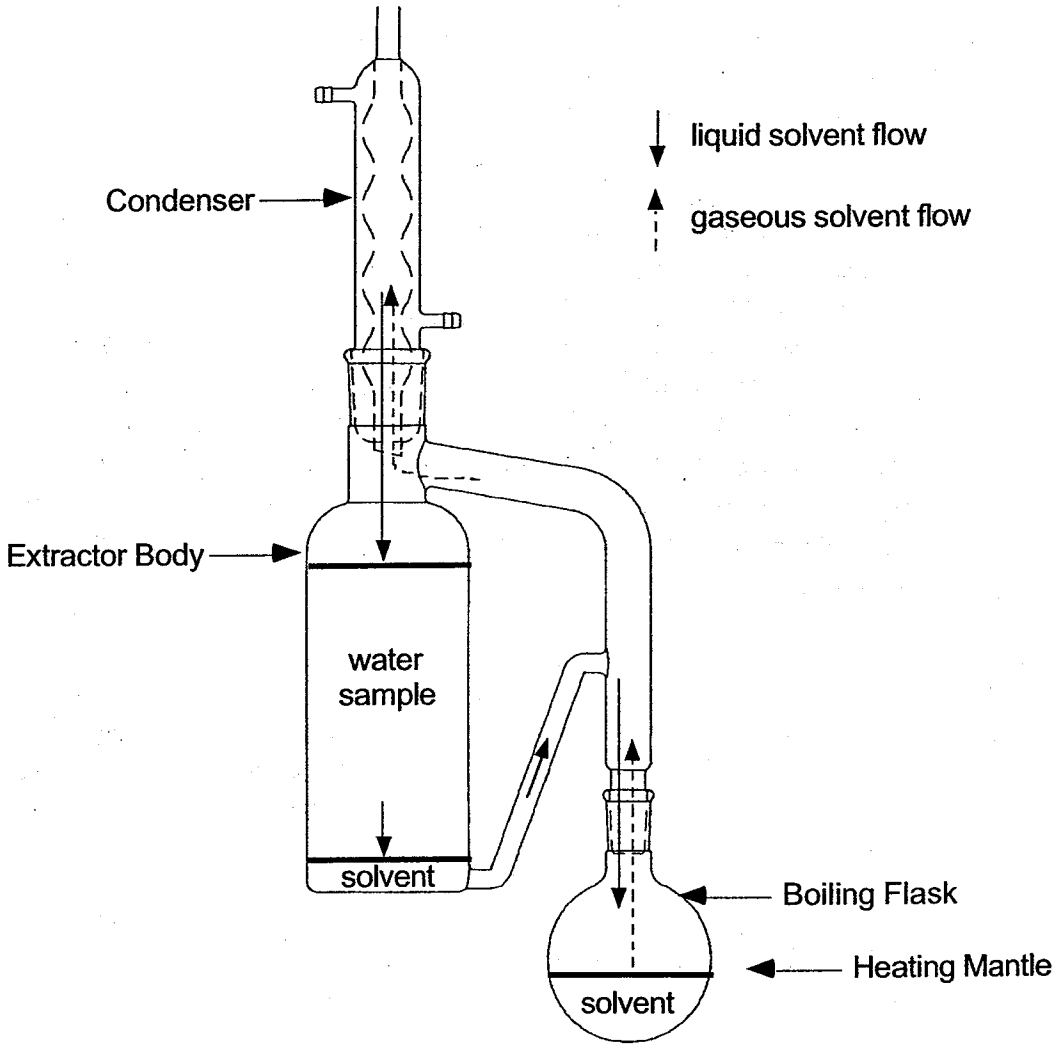
11.3.2.4. The sample volume *is* determined by marking the meniscus level on the sample container. Transfer the sample to the extractor (see 11.1.3). Fill the sample container with water up to the marked level. Transfer the measured amount of water to a graduated cylinder and record the volume on the benchsheet to the nearest 5 mL. Add *approximately 20* mL of methylene chloride to the sample container, seal and shake to rinse the inner surface and remove residual analytes adhering to the glass walls. Transfer this solvent to the continuous extractor body. If the entire sample is not used the sample volume is measured using a graduated cylinder.

Warning: Dichloromethane creates excessive pressure very rapidly! Therefore, initial venting should be done immediately after the sample container has been sealed and inverted. Vent into hood away from analysts and other samples.

11.3.2.5. Prepare a method blank, LCS and MS/MSD for each batch as specified in section 9 of this SOP. Use 1 L of reagent water for method blanks and LCS.

11.3.2.6. Less than one liter of sample may be used, for highly contaminated samples, or if the reporting limit can be achieved with less than one liter of sample. In this event dilute the sample to about 1 liter with reagent water.

11.3.2.7. Proceed to section 11.3.4 (SW-846 and 600 series methods).



11.3.3. Add 1 mL of the surrogate spiking solution (Table 3) to each sample, method blank, Laboratory Control Sample (LCS), and Matrix Spike/Matrix Spike Duplicate (MS/MSD). Add 1 mL of the matrix spiking solution (Table 4) to each LCS and MS/MSD.

- **Different matrix spiking solutions are used for 600 series, 8000 series and TCLP batches.**
- Surrogate and matrix spiking solutions should be brought to room temperature before spiking the samples.

11.3.4. Adjust sample pH as indicated in Table 1 for the initial extraction. Use the minimum amount of 1:1 H_2SO_4 or 10 N NaOH necessary. Recheck the sample with pH paper. Record adjusted pH, spiking volumes and standard numbers on the benchsheet. Return spiking solutions to the refrigerator as soon as possible.

11.3.5. Attach cold condenser (about 10°C) *to the extractor body*. Turn on heating mantle. Inspect joints for leaks once solvent has begun cycling. Extract for 18-24 hours. (24 hours required for 600 series)

11.3.6. If extraction at a secondary pH is required, (see Table 1) turn off the heating mantle and allow the extractor to cool. Detach the condenser and adjust the pH of the sample in the extractor body to the pH indicated in Table 1 with a minimum amount of 10 N NaOH or 1:1 H_2SO_4. Measure with pH paper and record the adjusted pH on the benchsheet. If desired, the acid and base fractions may be kept separate by replacing the boiling flask with a clean flask and fresh solvent. Reattach the condenser and turn on heating mantle. Extract for 18-24 hours.

Note: Alternatively, the acid and base fractions may be kept separate. This may be required for method 625. Separate analysis of the acid and base fractions may also be required for method 625. Individual client requirements must be checked before starting the extraction.

11.3.7. Turn off the heating mantle and allow the extractor to cool.

11.3.8. Place a funnel containing 10-20 g of anhydrous sodium sulfate on the Kuderna-Danish (K-D) apparatus or other glass container. The funnel can be plugged with glass wool enabling it to hold the granular anhydrous sodium sulfate or phase separation filter paper may be used.

11.3.9. Dry the extract in the round bottom flask by filtering it through the sodium sulfate filled funnel. Note that it is not necessary nor advisable to attempt to add the solvent remaining in the continuous extractor body to the extract.

11.3.10. Collect the dried extract in a K-D or other glass container . Rinse the flask which contained the solvent extract with 20-30 mL of methylene chloride and add it to the funnel to complete the quantitative transfer. Dispose of solvent and water remaining in the extractor in the appropriate waste container.

Note: Some types of CLLE apparatus have built in drying columns. If this type of apparatus is used then a drying step subsequent to the extraction may not be necessary.

11.3.11. Cover with aluminum foil if the extract is not concentrated immediately. Refer to Section 11.7 for concentration and Section 11.8 for cleanup.

11.4. Sonication

11.4.1. A flow chart for this procedure is included in Section 17.

11.4.2. Determination of percent moisture (Optional - if a different group performs this test, refer to the facility SOP.)

In some cases, sample results are needed on a dry weight basis. If this is the case, weigh 5-10 g of sample into a suitable tared container (typically an aluminum weigh pan. Determine the % moisture by drying overnight (at least 12 hours) at 105°C. Allow to cool in a desiccator before weighing.

$$\% \text{ Moisture} = \frac{(\text{weight of wet sample} - \text{weight of dry sample})}{\text{weight of wet sample}} \times 100$$

11.4.3. Determination of pH (Optional - if a different group performs this test, refer to the facility SOP.)

If pH determination is required, transfer 10 g of soil to a beaker. Add 10 mL of water. Stir for 1 hour. Determine the pH of the sample with a glass electrode and pH meter.

11.4.4. Sonication Procedure

11.4.4.1. Decant and discard any water layer on a sediment/soil sample. Homogenize the sample by mixing thoroughly. Discard any foreign objects such as sticks, leaves and rocks, unless extraction of this material is required by the client. If the sample consists primarily of foreign materials consult with the client (via the Project Manager or Administrator). Document if a water layer was discarded.

11.4.4.2. Remove surrogate and matrix spiking solutions from refrigerator and allow to warm to room temperature.

11.4.4.3. Weigh 30 g of sample ± *0.2* g into a 250 or 400 mL beaker. Record the weight to the nearest 0.1 g in the appropriate column on the benchsheet. Use *approximately* 90 g of sodium sulfate for the method blank and LCS.

11.4.4.4. Mix weighed sample with a spatula adding enough anhydrous sodium sulfate (approximately 60 g) to be free flowing. (If the sample is not free flowing extraction efficiency may be reduced)

11.4.4.5. Prepare a method blank, LCS and MS/MSD for each batch as specified in section 9 of this SOP.

11.4.4.6. Add 1 mL of the surrogate spiking solution to each sample, method blank, Laboratory Control Sample (LCS), and matrix spikes. Add 1 mL of the appropriate matrix spiking solution to each Matrix Spike/Matrix Spike Duplicate (MS/MSD) and LCS. Refer to Table 3 and 5 for details of the spiking solutions. Record spiking volumes and standard numbers on the benchsheet. Return spiking solutions promptly to refrigerator.

Note: The same volume of surrogate and matrix spiking solution is used if GPC is indicated since the final volume would be reduced to compensate for loss of extract during the GPC procedure.

11.4.4.7. Immediately add a minimum of 100 mL of 1:1 methylene chloride:acetone to the beaker.

Note: Use methylene chloride only if the extract is for Diesel Range Organics or similar tests that require determination of the total area of the chromatogram by GC-FID. If acetone is used the aldol condensation product will interfere with these tests.

Note: Steps 11.4.4.2 - 11.4.4.6 should be performed rapidly to avoid loss of the more volatile extractables.

11.4.4.8. Place the bottom surface of the appropriate disrupter horn tip approximately ½ inch below the surface of the solvent, but above the sediment layer.

11.4.4.9. Sonicate for 3 minutes, making sure the entire sample is agitated. If the W-380 or W-385 sonicator is used the output should be set at 6 for the 3/4 inch high gain (Q) horn or 10 for the 3/4 inch standard horn. with mode switch on pulse, and percent-duty cycle knob set at 50%.

Note: Do ***not*** use ***Microtip*** probe.

11.4.4.10. Loosely plug the stem of a 75 mm x 75 mm glass funnel with glass wool and/or line the funnel with filter paper. Add 10-20 g of anhydrous sodium sulfate to the funnel cup.

11.4.4.11. Place the prepared funnel on a collection apparatus (beaker or K-D Apparatus.

11.4.4.12. Decant and filter extracts through the prepared funnel into a clean beaker or K-D Apparatus.

11.4.4.13. Repeat the extraction two more times with additional 100 mL minimum portions of methylene chloride / acetone each time. Decant off extraction solvent after each sonication. On the final sonication pour the entire sample (sediment and solvent) into the funnel and rinse with an additional 10 mL-20 mL of the methylene chloride/acetone.

Note: Alternatively, the three extracts may be collected together and then filtered through the sodium sulfate.

11.4.4.14. Cover with aluminum foil if the extract is not concentrated immediately. Refer to Section 11.7 for concentration and Section 11.8 for cleanup.

11.4.5. Sonicator Tuning.

11.4.5.1. Tune the sonicator according to manufacturer's instructions. The sonicator must be tuned at least every time a new horn is installed.

11.5. Soxhlet

11.5.1. Determination of % moisture

In some cases, sample results are needed on a dry weight basis. If this is the case, weigh 5-10 g of sample into a suitable tared container (typically an aluminum weigh pan. Determine the % moisture by drying overnight at 105°C. Allow to cool in a desiccator before weighing.

$$\% \text{ Moisture} = \frac{(\text{weight of wet sample} - \text{weight of dry sample})}{\text{weight of wet sample}} \times 100$$

11.5.2. Determination of pH

If pH determination is required, transfer 10 g of soil to a beaker. Add 10 mL of water. Stir for 1 hour. Determine the pH of the sample with a glass electrode and pH meter.

11.5.3. Decant and discard any water layer on a sediment/soil sample. Homogenize the sample by mixing thoroughly. Discard any foreign objects such as sticks, leaves and rocks, unless extraction of this material is required by the client. If the sample consists primarily of foreign materials consult with the client. Document on benchsheet if a water layer was discarded.

11.5.4. Remove surrogate and matrix spiking solutions from refrigerator and allow to warm to room temperature.

11.5.5. Weigh 30 g of sample ± *0.2* g into a beaker, recording the weight to the nearest 0.1 g on the benchsheet.. Use *approximately* 30 g of sodium sulfate for the method blank and LCS. Add 30 g of anhydrous sodium sulfate and mix well. The mixture should have a free flowing texture. If not, add more sodium sulfate. Add the sample/sodium sulfate mixture to a soxhlet thimble, but do not pack the thimble tightly. The extraction thimble must drain freely for the duration of the extraction period. A glass wool plug above and below the sample in the soxhlet extractor is an acceptable alternative for the thimble.

Note: *If the sample is visibly dry, weigh directly into a thimble and mix with approximately 30 g of sodium sulfate.*

11.5.5.1. Sample weights less than 30 g but over 5 g may be used if the appropriate reporting limits can be met.

11.5.6. Prepare a method blank, LCS and MS/MSD for each batch as specified in section 9 of this SOP, using sodium sulfate as the matrix. The weight of sodium sulfate used should be approximately the weight of soil used in each sample.

11.5.7. Add 1 mL of the surrogate spiking solution to each sample, method blank, Laboratory Control Sample (LCS), and matrix spikes. Add 1 mL of the appropriate matrix spiking solution to each Matrix Spike/Matrix Spike Duplicate (MS/MSD) and LCS. Refer to Tables 3 - 6 for details of the spiking solutions. Record spiking volumes and standard numbers on the benchsheet. Return spiking solutions promptly to refrigerator.

Note: The same volume of surrogates and matrix spiking compounds is used if GPC is indicated since the final volume would be reduced to compensate for loss of extract during the GPC procedure.

11.5.8. Place *200* mL of 1:1 methylene chloride:acetone into a *250* mL *round* bottom flask containing one or two clean boiling chips. Attach the flask to the extractor and extract the sample for 16-24 hours at 4-6 cycles per hour. Check the system for leaks at the ground glass joints after it has warmed up.

Note: Use methylene chloride only if the extract is for Diesel Range Organics or similar tests that require determination of the total area of the chromatogram by GC-FID. If acetone is used the aldol condensation product will interfere with these tests.

11.5.9. Allow the extract to cool after the extraction is complete, then disassemble by gently twisting the soxhlet from the flask. Dry the extract in the flask by filtering it through a sodium sulfate filled funnel.

11.5.10. Collect the dried extract in a K-D or other glass container . Rinse the flask which contained the solvent extract with 20-30 mL of methylene chloride and add it to the funnel to complete the quantitative transfer.

11.5.11. Cover with aluminum foil if the extract is not concentrated immediately. Refer to Section 11.7 for concentration and Section 11.8 for cleanup.

11.6. Waste Dilution

11.6.1. This method is used for materials that are soluble in an organic solvent.

11.6.2. Transfer 10 mL of the solvent to be used for dilution into a Teflon capped vial. Mark the meniscus on the vial, then discard the solvent.

11.6.3. Tare the vial, then transfer 1.0 g $\pm$ 0.1 g of sample to the vial. Record the weight to the nearest 0.1 g.

11.6.4. Add 1 mL of surrogate solution (Table 3).

11.6.5. Dilute to 10 mL (make up to the meniscus mark) with the appropriate solvent. (Methylene Chloride for GC/MS analysis, hexane for pesticides analysis.)

11.6.6. Add 2 g + 0.1 g sodium sulfate to the sample. Cap and *vortex* for 2 minutes.

11.6.7. *Optional:* Add 4-5 g sodium sulfate to a small funnel. The funnel can be plugged with glass wool filter paper may be used to hold the sodium sulfate.

11.6.8. Pour the sample through the funnel, collecting as much as possible in a clean vial. Do NOT rinse the funnel with additional solvent, and do NOT concentrate the sample. The final volume is defined as 10 mL.

Note: *Concentrate extracts for GC/MS analysis to 2 mL.*

11.6.9. Label the sample, which is now ready for cleanup or analysis.

11.7. Concentration

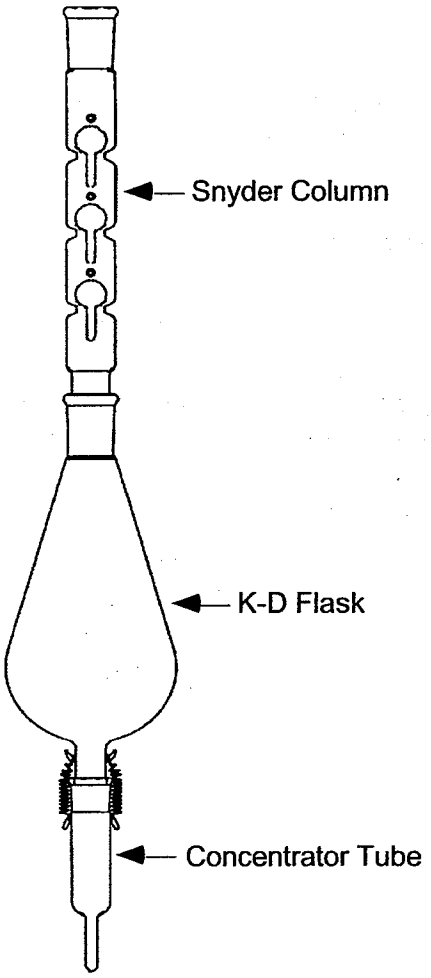
According to the type of sample and any cleanup procedures needed, different final solvents and volumes will be required. Refer to Table 2 for the appropriate final volumes and concentrations.

11.7.1. Kuderna-Danish (KD) Methods:

11.7.1.1. *Water Bath-Based Concentration Method:*

11.7.1.1.1. Assemble a Kuderna-Danish concentrator by attaching a 10 mL concentrator tube to the 500 mL KD flask. Transfer the sample to the K-D flask.

11.7.1.1.2. Add one or two clean boiling chips and the extract to be concentrated to the KD flask and attach a three ball Snyder Column. Add approximately 1 mL of clean methylene chloride to the top of the Snyder column (this is important to ensure that the balls are not stuck and that the column will work properly).



11.7.1.1.3. Place the KD apparatus on a water bath (80-90°C) so that the tip of the concentrator tube is submerged. The water level should not reach the joint between the concentrator and the KD flask. At the proper rate of distillation, the balls will actively chatter but the chambers should not flood.

11.7.1.1.4. Concentrate to 5-15 mL. If the determinative method requires a solvent exchange add the appropriate exchange solvent (50 mL hexane, 50 mL cyclohexane, 2 mL acetonitrile or 10 mL toluene) to the top of the Snyder Column, and then continue the water bath concentration back down to 1-4 mL. Refer to Table 2 for details of exchange solvents and final volumes. The Snyder column may be insulated if necessary to maintain the correct rate of distillation.

11.7.1.1.5. An alternative technique for solvent exchange is to replace the macro Snyder column and KD flask with a micro Snyder column, concentrate to

approximately 1 mL, add 10 mL of hexane, and concentrate back down to 1 mL. The extract must be cool before the macro Snyder assembly is removed.

11.7.1.1.6. ***Note:*** It is very important not to concentrate to dryness as analytes will be lost.

11.7.1.1.7. Remove the KD apparatus from the water bath and allow to cool for a minimum of 10 minutes. If the level of the extract is above the level of the concentrator tube joint, continue to distill the solvent as necessary. Again, allow the KD flask to cool for a minimum of 10 minutes.

11.7.1.1.8. If the final volume is 5 or 10 mL the extract may be made up to volume in the graduated KD tube or transferred to a 12 mL vial previously marked at the appropriate volume level. Document the final volume. Otherwise proceed to section 11.7.2

11.7.1.2. Alternative QES Concentration Method:

This concentration method uses a hot water jacketed concentrator tube (jCT) instead of the hot water bath and concentrator tube used in Section 11.7.1.1. The construction of the jacketed concentrator tube reduces the tendency of the extract to evaporate to dryness. Thus, low boiling analytes are retained in the extract better with less analyst monitoring of the concentration process.

11.7.1.2.1. Assemble the jacketed concentrator tube, KD body and hot water hoses. Add 1 mL of exchange solvent (if needed) and one large, clean boiling chip.

***NOTE**: The boiling chips used in the jacketed concentrator tube must be large enough to prevent them falling down into the tip of the jCT. If the boiling chip is not in the proper position, the extract may superheat and bump vigorously if the extract solvent warms up slowly.*

11.7.1.2.2. Pour the extract to be concentrated into the KD flask, and attach a three-ball Snyder column.

11.7.1.2.3. Turn on the hot (90°C) water flow to the jacketed concentrator tube.

11.7.1.2.4. Concentrate to 1 mL. If the determinative method requires a solvent exchange, add the appropriate exchange solvent (5-10 mL hexane, 1 mL acetonitrile, 4 mL acetone/hexane) to the top of the Snyder column. Continue to concentrate until the Snyder column balls stop chattering.

11.7.1.2.5. Cool the jacketed concentrator tube until it is cold to the touch.

11.7.1.2.6. *Quantitatively transfer the extract and dilute to final volume, or continue concentration with nitrogen evaporation (section 11.7.2).*

11.7.2. Nitrogen Evaporation to Final Concentration

11.7.2.1. Place the *concentrator* tube in a warm water bath that is at least 5°C below the boiling temperature of the solvent being evaporated and evaporate the solvent using a gentle stream of nitrogen. The nitrogen flow will form a slight depression on the surface of the solvent, but should not create splattering of the extract.

Boiling points of commonly used solvents are:

Methylene chloride	40°C
Acetone	56°C
Hexane	69°C
Acetonitrile	82°C
Toluene	111°C

11.7.2.2. *Evaporate the extract to below the final volume line, using the concentrator tube calibration line as a guide; and remove the CT from the water bath. Rinse the sides of the concentrator tube with the extract, using a pipet, and transfer the extract to the appropriate storage vial. Add a small amount of the appropriate solvent to the concentrator tube and rinse again. Bring the extract to final volume with the solvent rinse, using a measured vial for side-by-side comparison.*

Note: It is very important not to concentrate to dryness as analytes will be lost.

11.7.2.3. An alternative technique is to follow the previous steps concentrating the solvent to slightly below the required final volume and then drawing the extract into a syringe. Rinse the evaporation tube with a small amount of solvent and draw additional solvent into the syringe to make up the accurate final volume.

11.7.2.4. ***Note:*** The final concentration and volume measurement steps are critical. Use care when concentrating and make certain that the final volume measurement is accurate.

11.7.3. Turbovap Method

11.7.3.1. Turn on the Turbovap and adjust the water temperature to 5-10°C less than the boiling point of the solvent to be evaporated.

11.7.3.2. Switch all endpoint sensors to the "NO" position.

11.7.3.3. Adjust the water bath level

11.7.3.4. Adjust the nitrogen gas pressure to approximately 12 psi.

11.7.3.5. Transfer the extract into the Turbovap tube and load into the Turbovap. Do not fill the Turbovap tubes over approximately 3/4 full.

11.7.3.6. Reset the sensor and close the lid.

11.7.3.7. ***Note:*** If the extract splashes when the nitrogen flow starts, reduce the nitrogen flow or transfer a portion of the extract back into the original extract container.

11.7.3.8. As the extract concentrates, transfer the remainder of the extract into the appropriate Turbovap tube. After all of the extract has been transferred, rinse the flask with a few mL of methylene chloride and add to the Turbovap tube.

11.7.3.9. During the concentration rinse the Turbovap tube walls with a few mL of solvent 1 or 2 times.

11.7.3.10. Concentrate the extract to slightly less than the required final volume.

11.7.3.11. If solvent exchange is required, concentrate to 1-4 mL and add 50 mL of the exchange solvent. Concentrate back down to the appropriate volume. Refer to table 2 for details of exchange solvents and final volumes.

11.7.3.12. Transfer the concentrated extract to volumetric glassware for adjustment of final volume, using a small amount of solvent to rinse the tube and complete the transfer.

Note: Water contamination from condensation during concentration is not acceptable. If water is present, remove the Turbovap tube and filter the extract

through sodium sulfate. Transfer to a clean Turbovap tube and continue the concentration.

Note 2: Dark, opaque or turbid samples may not concentrate. If this occurs, set the concentrator sensor to dryness and supervise the entire concentration procedure.

11.8. Cleanup Techniques

The following techniques may be used to remove interfering peaks, and /or to remove materials that may cause column deterioration and/ or loss of detector sensitivity. *Gel Permeation Chromatography* (Section 11.8.1) is a generally applicable technique which can be used to prepare extracts for Semivolatiles (8270), PAH (8100) and pesticides (8080) analysis. It is capable of separating high molecular weight material from the sample analytes, and so is particularly useful if tissue or vegetable matter is part of the sample, and for many soil samples.

Florisil column cleanup (Section 11.8.2) is particularly useful for cleanup of pesticides for analysis by method 8080 and should normally be applied to these samples unless the matrix is clean. It separates compounds with a different polarity from the target analytes.

Gel Permeation Chromatography and Florisil column cleanup may both be applied to samples for analysis by method 8080. In this case the GPC should be performed first.

Sulfur cleanup (Section 11.8.3) is generally applied to samples for analysis by method 8080, since the Electron Capture Detector responds strongly to sulfur. It is performed after GPC and Florisil cleanup.

Sulfuric acid cleanup (Section 11.8.4) is applied to samples requiring analysis for Polychlorinated Biphenyls (PCBs) only. Most organic matter is destroyed by the sulfuric acid.

Acid Base Partition Cleanup (Section 11.8.5) is useful for separating organic acids and phenols from basic and neutral organics.

Silica gel cleanup (Section 11.8.6) may be used to separate polynuclear aromatic hydrocarbons from interfering aliphatic hydrocarbons prior to analysis by GC/FID.

11.8.1. Gel Permeation Chromatography (GPC)

Note: GPC systems include the GPC Autoprep Model 1002A or 1002B Analytical Biochemical Laboratories, Inc., Zymark Benchmate, or equivalent.

11.8.1.1. GPC Column Preparation

11.8.1.1.1. Weigh out 70 g of Bio Beads (SX-3) into a 400-mL beaker.

11.8.1.1.2. Add approximately 300 mL of methylene chloride and stir gently.

11.8.1.1.3. Cover with aluminum foil and allow the beads to swell for a minimum of two hours. Maintain enough solvent to sufficiently cover the beads at all times.

11.8.1.1.4. Position and tighten the outlet bed support (top) plunger assembly in the tube by inserting the plunger and turning it clockwise until snug. Install the plunger near the column end but no closer than 5 cm (measured from the gel packing to the collar).

11.8.1.1.5. Turn the column upside down from its normal position with the open end up. Place the tubing from the top plunger assembly into a waste beaker below the column.

11.8.1.1.6. Swirl the bead/solvent slurry to get a homogeneous mixture and pour the mixture into the open end of the column. Transfer as much as possible with one continuous pour trying to minimize bubble formation. Pour enough to fill the column. Wait for the excess solvent to drain out before pouring in the rest. Add additional methylene chloride to transfer the remaining beads and to rinse the beaker and the sides of the column. If the top of the gel begins to look dry, add more methylene chloride to rewet the beads.

11.8.1.1.7. Wipe any remaining beads and solvent from the inner walls of the column with a laboratory tissue. Loosen the seal slightly on the other plunger assembly (long plunger) and insert it into the column. Make the seal just tight enough so that any beads on the glass surface will be pushed forward, but loose enough so that the plunger can be pushed forward.

CAUTION: Do not tighten the seal if beads are between the seal and the glass surface because this can damage the seal and cause leakage.

11.8.1.1.8. Push the plunger until it meets the gel, then compress the column bed about 4 cm.

11.8.1.1.9. Connect the column inlet to the solvent reservoir and place the column outlet tube in a waste container. Pump methylene chloride through the column at a rate of 5 mL/min. for one hour.

11.8.1.1.10. After washing the column for at least one hour, connect the column outlet tube to the inlet side of the UV detector. Connect the system outlet to the outlet side of the UV detector. Placing a restrictor (made from a piece of capillary tubing of 1/16"OD x 10/1000"ID x 2") in the outlet tube from the UV detector will prevent bubble formation which causes a noisy UV

baseline. The restrictor will not effect the flow rate. After pumping methylene chloride through the column for an additional 1-2 hours, adjust the inlet bed support plunger until approximately 6-10 psi back-pressure is achieved. Push the plunger in to increase pressure or slowly pull outward to reduce pressure.

11.8.1.1.11. When the GPC column is not to be used for several days, connect the column inlet and outlet lines to prevent column drying and/or channeling. If channeling occurs, the gel must be removed from the column, re-swelled, and re-poured as described above. If drying occurs, pump methylene chloride through the column until the observed column pressure is constant and the column appears wet. Always recalibrate after column drying has occurred to verify that retention volumes have not changed.

11.8.1.2. Initial Calibration of the GPC Column

11.8.1.2.1. Before use, the GPC must be calibrated based on monitoring the elution of standards with a UV detector connected to the GPC column.

11.8.1.2.2. Pump solvent through the GPC column for 2 hours. Verify that the flow rate is 4.5-5.5 mL/min. Corrective action must be taken if the flow rate is outside this range. Record the column pressure (should be 6-10 psi) and room temperature (22°C is ideal).

Note: Changes in pressure, solvent flow rate, and temperature conditions can affect analyte retention times and must be monitored. If the flow rate and/or column pressure do not fall within the above ranges, a new column should be prepared.

11.8.1.2.3. Inject the calibration solution and retain a UV trace that meets the following requirements (See resolution calculation in section 11.8.1.6):

- Peaks must be observed and should be symmetrical for all compounds in the calibration solution.
- Corn oil and phthalate peaks must exhibit >85% resolution.
- Phthalate and methoxychlor peaks must exhibit >85% resolution.
- Methoxychlor and perylene peaks must exhibit >85% resolution.
- Perylene and sulfur peaks must not be saturated and must exhibit >90% baseline resolution.

11.8.1.2.4. A UV trace that does not meet the criteria in paragraph 11.8.1.2.3 indicates the need for system maintenance and/or the need for a new column.

11.8.1.2.5. Determine appropriate collect and dump cycles.

11.8.1.2.6. The calibrated GPC program for pesticides/PCB should dump >85% of the phthalate and should collect >95% of the methoxychlor and perylene. Use a wash time of 10 minutes.

11.8.1.2.7. For semivolatile extracts, initiate a column eluate collection just before the elution of bis (2-ethylhexyl) phthalate and after the elution of the corn oil. Stop eluate collection shortly after the elution of perylene. Stop collection before sulfur elutes. Use a wash time of 10 minutes after the elution of sulfur.

11.8.1.2.8. Reinject the calibration solution after appropriate dump and collect cycles have been set.

11.8.1.2.9. Measure and record the volume of collected GPC eluate in a graduated cylinder.

11.8.1.2.10. The retention times for both bis(2-ethylhexyl) phthalate and perylene must not vary more than +/- 5% between calibrations.

11.8.1.3. GPC calibration check

Check the calibration of the GPC immediately after the initial calibration and at least every 7 days thereafter, while the column is in use.

11.8.1.3.1. Inject the calibration solution, and obtain a UV trace. If the retention times of bis(2-ethylhexyl)phthalate or perylene have changed by more than $\pm$ 5% use this run as the start of a new initial calibration. Otherwise, proceed with the recovery check. Excessive retention time shifts may be caused by poor laboratory temperature control or system leaks, an unstabilized column, or high laboratory temperature causing outgassing of methylene chloride. Pump methylene chloride through the system and check the retention times each day until stabilized.

11.8.1.4. GPC Recovery Check for Pesticides/ PCBs

11.8.1.4.1. The recovery from the GPC must be verified immediately after the initial calibration and at least every 7 days, when the instrument is in use. Two recovery check solutions are used. The first mixture is prepared by diluting 1.0 mL of the pesticide matrix spiking solution (Table 6) to 10 mL in methylene chloride. The second mixture is prepared by diluting 1 mL of

the PCB only matrix spiking solution (Table 6) to 10 mL with methylene chloride.

11.8.1.4.2. Load the pesticide matrix spike mixture, the PCB mixture, and a methylene chloride blank onto the GPC using the GC dump and collect values.

Note: If the analysis is for PCBs only, then the pesticide recovery check is not necessary.

11.8.1.4.3. After collecting the GPC calibration check fraction, concentrate, solvent exchanging to hexane. Adjust the final volume to 5.0 mL, and analyze by GC/EC. Refer to concentration, section 11.7.

11.8.1.4.4. The methylene chloride blank may not exceed more than one half the reporting limit of any analyte. And if the recovery of each of the single component analytes is 80-110% and if the Aroclor pattern is the same as previously run standards, then the analyst may use the column. If the above criteria are not met, there may be a need for system maintenance.

11.8.1.5. GPC Recovery Check for Semivolatiles

11.8.1.5.1. The recovery from the GPC must be verified immediately after the initial calibration and at least every 7 days, when the instrument is in use. Dilute 1.0 mL of the semivolatiles matrix spiking solution (Table 6) to 10 mL in methylene chloride.

11.8.1.5.2. Load the matrix spike mixture and a methylene chloride blank onto the GPC using the semivolatiles dump and collect values.

11.8.1.5.3. After collecting the GPC recovery check fraction, concentrate to 0.5 mL, and analyze by GC/MS. Refer to the concentration section 11.7.

11.8.1.5.4. Recovery of the matrix spike analytes should be at least 85%. The blank should not contain any analytes at or above the reporting limit. If these conditions are met the column may be used for sample analysis. Otherwise correct the contamination problem, or extend the collect time to improve recovery of target analytes.

11.8.1.6. Sample Extract Cleanup

11.8.1.6.1. Reduce the sample extract volume to 1-2 mL, then adjust to 10 mL with methylene chloride prior to cleanup. This reduces the amount of acetone in the extract. Refer to section 11.7.

11.8.1.6.2. Start the pump and let the flow stabilize for 2 hours. The solvent flow rate should be 4.5-5.5 mL/min. The ideal laboratory temperature to prevent outgassing of the methylene chloride is 22°C. The normal backpressure is 6-10 psi.

11.8.1.6.3. In order to prevent overloading of the GPC column, highly viscous sample extracts must be diluted prior to cleanup. Any sample extract with a viscosity greater than that of a 1:1 glycerol:water solution (by visual comparison) must be diluted and loaded into several loops.

11.8.1.6.4. Samples being loaded onto the GPC should be filtered with a 5 micron (or less) filter disk. Attach a filter to a 10 mL Luerlok syringe and filter the 10 mL sample extract into the sample tube.

Note: The Zymark Benchmate automatically filters the sample extracts, but manual prefiltration of very dirty extracts may be necessary.

11.8.1.6.5. Load the filtered (or unfiltered if using the Benchmate) samples into the proper sample tubes and place on the GPC.

Note: For the GPC Autoprep Model 1002A, wash the loading port with methylene chloride after loading each sample loop in order to minimize cross contamination. This step is automated on the GPC Autoprep 1002B and on the Benchmate.

11.8.1.6.6. Set the collect, dump, and wash times determined by the calibration procedure.

11.8.1.6.7. Switch to the run mode and start the automated sequence. Process each sample using the collect and dump cycle times established by the calibration procedure.

11.8.1.6.8. Collect each sample in a suitable glass container. Monitor sample volumes collected.

11.8.1.6.9. Any samples that were loaded into 2 or more positions must be recombined.

11.8.1.6.10. Concentrate semivolatile sample extracts to 0.5 mL in methylene chloride. Refer to the concentration section 11.7.

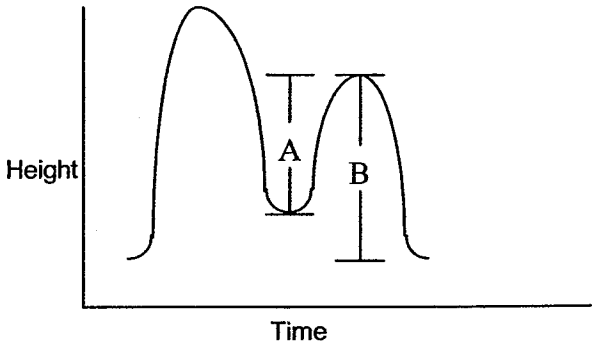
11.8.1.6.11. Solvent exchange pesticide/PCB sample extracts into hexane and concentrate to 5.0 mL. Refer to the concentration section 11.7.

11.8.1.7. Calculations

11.8.1.7.1. Resolution

To calculate the resolution between two peaks on a chromatograph, divide the depth of the valley between the peaks by the peak height of the smaller peak being resolved and multiply by 100.

Resolution Calculation



$$\% \text{ Resolution } = \frac{A}{B} \times 100$$

Where: A = depth of valley to height of smaller peak
B = peak height of smaller peak

11.8.1.7.2. Dump Time

Mark on the chromatograph the point where collection is to begin. Measure the distance from the injection point. Divide the distance by the chart speed. Alternatively the collect and dump times may be measured by means of an integrator or data system.

$$\text{Dump time (min)} = \frac{\text{Distance (cm) from injection to collection start}}{\text{Chart speed (cm / min)}}$$

11.8.1.7.3. Collection Time

$$\text{Collection time (min)} = \frac{\text{Distance (cm) between collection start and stop}}{\text{Chart speed (cm / min)}}$$

11.8.2. Florisil Cartridge Cleanup

Note 1: Systems for eluting multiple cleanup cartridges include the Supelco, Inc. Solid Phase Extraction (SPE) assembly, Zymark Benchmate, or equivalent.

Note 2: Follow the lab specific procedure when using the Zymark benchmate.

11.8.2.1. Before Florisil cleanup sample volume must be reduced to 10 mL (5 mL if GPC cleanup was used) and the solvent must be hexane. Refer to Section 11.7 for details of concentration.

11.8.2.2. Attach a vacuum manifold to a vacuum pump or water aspirator with a trap installed between the manifold and the vacuum. Adjust the vacuum in the manifold to 5-10 psi.

11.8.2.3. Place one Florisil cartridge into the vacuum manifold for each sample extract. Prior to cleanup of samples, pre-elute each cartridge with 5 mL of hexane/acetone (9:1). Adjust the vacuum applied to each cartridge so that the flow through each cartridge is approximately 2 mL/min. Do not allow the cartridges to go dry.

11.8.2.4. Just before the cartridges go dry, release the vacuum to the manifold and remove the manifold top.

11.8.2.5. Place a rack of clean labeled 12 mL concentrator tubes into the manifold and replace the manifold top. Make sure that the solvent line from each cartridge is placed inside the appropriate tube.

11.8.2.6. After the clean tubes are in place, vacuum to the manifold is restored and 2.0 mL of the extract is added to the appropriate Florisil cartridge.

11.8.2.7. The pesticides/aroclors in the extract concentrates are then eluted through the column with 8 mL of hexane/acetone (90:10) and are collected into the 10 mL culture tube or concentrator tube held in the rack inside the vacuum manifold.

11.8.2.8. Transfer the extract to a graduated concentrator tube and concentrate the extract to 2 mL. Refer to the concentration section. (11.7)

Note 1: A cartridge performance standard must be run with each lot of Florisil cartridges.

Note 2: Florisil cartridge performance check--every lot number of Florisil must be tested before use. Add 0.5 ug/mL of 2,4,5-trichlorophenol solution and 0.5 mL of GC Standard Mix A (midpoint concentration) to 4 mL hexane. Reduce volume to 0.5 mL. Add the concentrate to a pre-washed Florisil cartridge and elute with 9 mL hexane/acetone [(90:10)(v/v)]. Rinse cartridge with 1.0 mL hexane two additional times. Concentrate eluate to 1.0 mL final volume and transfer to vial. Analyze the solution by GC/EC. The test sample must show 80 to 120% recovery of all pesticide analytes with <5% trichlorophenol recovery, and no peaks interfering with target compounds can be detected. This standard has a lifetime of six months. Alternatively, this standard may be purchased as a stock solution.

11.8.3. **Sulfur Removal**

11.8.3.1. Sulfur can be removed by one of three methods: mercury, copper, or tetrabutylammonium sulfite (TBA) according to laboratory preference. If the sulfur concentration is such that crystallization occurs in the concentrated extract, centrifuge the extract to settle the crystals, and carefully draw off the sample extract with a disposable pipet, leaving the excess sulfur in the centrifuge tube. Transfer the extract to a clean concentrator tube before proceeding with further sulfur cleanup.

11.8.3.2. Sulfur Removal with Elemental Mercury

Note: Use Mercury sparingly in order to minimize exposure and disposal costs.

11.8.3.2.1. Transfer 2 mL of sample extract into a clean concentrator tube or Teflon sealed vial.

11.8.3.2.2. Add one to three drops of mercury to the extract vial and seal.

11.8.3.2.3. Shake well for 15-30 seconds. If prolonged shaking is required, use a mechanical shaker.

11.8.3.2.4. Remove the extract from the mercury using a disposable pipet and transfer to a clean vial.

11.8.3.2.5. If black precipitate forms, sulfur was present. Shake again, then centrifuge. After centrifugation, transfer the supernate to a clean test tube and repeat. Do this until relatively little precipitate remains, or the screens indicate that cleanup is complete.

11.8.3.2.6. Properly dispose of the mercury waste.

11.8.3.3. Sulfur Removal with Copper

11.8.3.3.1. Transfer 1.0 mL of sample extract into a centrifuge or concentrator tube.

11.8.3.3.2. Add approximately 2 g of cleaned copper powder (see 7.1.15.4 for copper cleaning procedure) to the sample extract tube.

11.8.3.3.3. Mix for one minute on a mechanical shaker.

11.8.3.3.4. If the copper changes color, sulfur was present. Repeat the sulfur removal procedure until the copper remains shiny.

11.8.3.3.5. Transfer the supernate to a clean vial.

11.8.3.4. Sulfur Removal with Tetrabutylammonium (TBA) Sulfite Reagent

11.8.3.4.1. Transfer 1.0 mL of sample extract into a culture tube.

11.8.3.4.2. Add 1.0 mL TBA sulfite reagent and 2 mL 2-propanol to the sample extract. Cap and shake for 1 minute. If clear crystals (precipitated sodium sulfite) form, sufficient sodium sulfite is present.

11.8.3.4.3. If a precipitate does not form, add sodium sulfite in approximately 0.1 g portions until a solid residue remains after repeated shaking.

11.8.3.4.4. Add 5 mL organic free reagent water and shake for 1 minute. Allow sample to stand for 5-10 minutes. (Centrifuge if necessary to separate the layers). Transfer the sample extract (top layer) to a vial. The final volume is defined as 1.0 mL in section 11.8.3.4.1.

11.8.4. Sulfuric Acid Cleanup

11.8.4.1. Add approximately 2-5 mL of concentrated sulfuric acid to 2 mL of sample extract in a Teflon capped vial.

Caution: There must be no water present in the extract or the reaction may shatter the sample container.

11.8.4.2. *Vortex until sample and acid are thoroughly mixed* and allow to settle. (Centrifuge if necessary)

11.8.4.3. Remove the sample extract (top layer) from the acid using a Pasteur pipet and transfer to a clean vial. ***CAUTION:*** It is not necessary to remove all the extract since the final volume is already determined. Transfer of small amounts of sulfuric acid along with the extract will result in extremely rapid degradation of the chromatographic column.

11.8.4.4. If the sulfuric acid layer becomes highly colored after shaking with the sample extract, transfer the hexane extract to a clean vial and repeat the cleanup procedure until color is no longer being removed by the acid, or a maximum of 5 acid cleanups.

11.8.4.5. Properly dispose of the acid waste.

11.8.5. **Acid/Base Partition Cleanup**

11.8.5.1. Place 10 mL of the solvent extract from a prior extraction procedure into a 125 mL separatory funnel.

11.8.5.2. Add 20 mL of methylene chloride to the separatory funnel.

11.8.5.3. Slowly add 20 mL of DI water which has been previously adjusted to a pH of 12 to 13 with 10 N sodium hydroxide.

11.8.5.4. Seal and shake the separatory funnel for at least two minutes with periodic venting to release excess pressure.

CAUTION: Methylene chloride creates excessive pressure very rapidly. Initial venting should be done immediately after the separatory funnel has been sealed.

11.8.5.5. Allow the organic layer to separate from the aqueous phase for a minimum of ten minutes.

11.8.5.6. If an emulsion interface between layers is more than one-third the size of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, and may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods.

11.8.5.7. Separate the aqueous phase and transfer it to a 125 mL Erlenmeyer flask. Repeat the extraction two more times using fresh 20 mL aliquots of dilute sodium hydroxide (pH 12-13) . Combine the aqueous extracts.

11.8.5.8. Water soluble organic acids and phenols will be primarily in the aqueous phase. Base/neutral analytes will be in the methylene chloride. If the analytes of interest are only in the aqueous phase discard the methylene chloride and proceed to Section 11.8.5.9. If the analytes of interest are only in the methylene chloride, discard the aqueous phase and proceed to Section 11.8.5.11.

11.8.5.9. Adjust the aqueous phase to a pH of 1-2 with sulfuric acid (1:1). Allow to cool and transfer the cool aqueous phase to a clean 125 mL separatory funnel.

11.8.5.10. Add 20 mL of methylene chloride to the separatory funnel and shake for at least two minutes. Allow the methyene chloride to separate from the aqueous phase and collect the methylene chloride in an Erlenmeyer flask. Repeat the extraction

two more times using fresh methylene chloride and extracting at pH 1-2. Combine the three extracts.

11.8.5.11. Dry the extract by passing through a funnel containing 10-20 g anhydrous sodium sulfate. Rinse the funnel with an additional 20-30 mL of clean methylene chloride

11.8.5.12. Cover with aluminum foil if the extract is not concentrated immediately. Refer to section 11.7 for concentration.

11.8.5.13. Dispose of solvent and water remaining in the separatory funnel into the appropriate waste container.

11.8.6. Silica Gel Cleanup

This procedure is appropriate for cleanup of extracts prior to determination of polynuclear aromatic hydrocarbons by GC/FID.

11.8.6.1. Exchange the extract solvent to cyclohexane and reduce the volume to 2 mL prior to cleanup.

11.8.6.2. Prepare a slurry of approximately 10 g of activated silica gel in about 15 mL of methylene chloride. Place this into a 10 mm ID chromatographic column. Tap the column to settle the silica gel. Add 1-2 cm of anhydrous sodium sulfate to the top of the silica gel.

11.8.6.3. Preelute the column with 40 mL of pentane. Elution rate should be approximately 2 mL/min. Discard the eluate and just prior to exposure of the sodium sulfate to air, transfer the 2 mL cyclohexane sample extract onto the column using an additional 2 mL of cyclohexane to complete the transfer. Just prior to exposure of the sodium sulfate layer to the air, add 25 mL of pentane and continue the elution of the column. Discard this pentane elute.

11.8.6.4. Elute the column with 25 mL of methylene chloride/pentane (2:3 v/v). Since the polynuclear aromatic hydrocarbons elute in this fraction, collect the eluate and concentrate to the required volume.

12. DATA ANALYSIS AND CALCULATIONS

Not applicable

13. METHOD PERFORMANCE

13.1. Method detection limit

Each laboratory must generate a valid method detection limit for each analyte of interest. The procedure for the determination of the method detection limit is given in STL North Canton QA Policy #: QA-005

13.2. Initial demonstration

Each laboratory must make an initial demonstration of capability for each individual method. This requires 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 spiking level should be equivalent to a mid level calibration. (For certain tests more than one set of QC check samples may be necessary in order to demonstrate capability for the full analyte list.)

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

13.2.2. Calculations and acceptance criteria for the QC check samples are given in the determinative SOPs. (CORP-GC-0001, CORP-MS-0001, 0002)

13.3. Training Qualification

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

14. POLLUTION PREVENTION

Within the constraints of following the methodology in this SOP, use of organic solvents should be minimized.

15. WASTE MANAGEMENT

Waste generated in this procedure will be segregated, and disposed according to the facility hazardous waste procedures. The Health and Safety Director should be contacted if additional information is required.

15.1. Solvent waste must be disposed of in the clearly labeled waste cans.

15.2. Acid waste must be collected in the clearly labeled acid waste containers.

15.3. Solid materials (soil, gloves, soiled paper products) are placed in the solid debris container. Do not put liquids in the solid waste container.

15.4. Methylene chloride saturated water and remaining sample after the extraction is dumped into Methylene chloride waste cans.

16. REFERENCES

Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW846, 3rd Edition, Final Update II (September 1994). Sections 3500A, 3510B, 3520B, 3540B, 3550A, 3600B, 3610A, 3620A, 3640A, 3650A, and 3660A.

17. MISCELLANEOUS

17.1. Modifications from Reference method

17.1.1. Some surrogate spiking concentrations are modified from those recommended in SW-846, in order to make the concentrations more consistent with the calibration levels in the determinative methods.

17.1.2. In the CLLE procedure the same solvent is used for the acid and base neutral extractions.

17.1.3. Spiking levels for method 608 have been reduced by a factor of ten to bring the levels within the normal calibration range of the instrument.

17.1.4. 10 g of soil is used for pH determination, rather than the 50 g suggested in the reference method. The volume of water is also adjusted to maintain the sample / water ratio specified in the method.

17.2. Modifications from previous revision

17.2.1. Sonicator tuning directions have been changed

17.2.2. Use of phase separation filter paper is not recommended, since organic solvents may leach siloxanes from the filter paper.

17.2.3. The quantity of sulfuric acid used in sulfuric acid cleanup has been reduced.

17.2.4. Allowance for different final solvents for organophosphorous pesticides has been added.

17.2.5. Some typographical errors have been corrected.

17.3. Facility Specific SOPs

17.3.1. Each facility shall attach a list of facility specific SOPs or approved attachments (if applicable) which are required to implement this SOP or which are used in conjunction with this SOP. If no facility specific SOPs or amendments are to be attached, a statement must be attached specifying that there are none.

17.3.2. Refer to the SOP change form on file in the North Canton Quality Assurance Department.

17.3.3. Deviation from Revision 2: Section 11.7.2.2

The extract is not concentrated to its final volume in the concentrator tube. It is transferred to the appropriate storage vial, brought up to volume with solvent rinse from the concentrator tube, and visually checked against the measured volume in another vial. A comparison study of measured samples versus samples bottled by visual comparison to a measured vial indicates no significant difference between the analyte recoveries of the alternative procedures. Data related to this study is available upon request in the Quality Assurance department.

17.3.4. Modification from previous revision 2.2, dated 04/18/94

Addition of Methylene chloride first to the extraction apparatus is due to a limitation of almost all CLLE glassware. If the sample is added first, then sample water will fill the transfer tube which connects the bottom of the continuous extractor body to the boiling flask. If Methylene chloride is now added, all the sample water in the trasnfer tube will be pushed intot he boiling flask. This can cause nonextractable sample components to end up in the extract. It can also interfere with the recovery of polar analytes (e.g. phenols, amines) since these analytes may "extract" out of the solvent in the boiling flask and back into this "misplaced" sample water.

17.4. Tables

Table 1
Liquid /Liquid Extraction Conditions

Determinative Method	Initial Ext. pH	Secondary Ext. pH
BNA: 8270	11-12	1-2
625	11-12	1-2
Pest/PCB: 8080 & 608	5-9	None
OPP: 8140	6-8	None
OPP: 8141	as received	None
Hydrocarbons: 8015	as received	None
PAH: 8310, 8100 & 610	as received	None

NOTE: ***For traditional TCL 8270 list, an acid only extraction is performed.***

Table 2
Exchange Solvents and Final Volumes

Final Volumes and Exchange Solvents if no cleanup is used		
Type	Exchange Solvent for Analysis	Final Volume for Analysis
Semivolatiles	N/A	1.0
Pesticides	Hexane	10.0
PAH by HPLC	Acetonitrile	Refer to facility SOP for HPLC
PAH by GC	N/A	1.0
TPH	N/A	1.0
OPP	Toluene, hexane or isooctane	10.0

Final Volumes and exchange solvents if GPC cleanup is used			
Type	Exchange Solvent for GPC	Final Volume for GPC	Final Volume and solvent for Analysis
Semivolatiles	CH_2Cl_2	10 mL[1]	0.5 mL CH_2Cl_2
Pesticides	CH_2Cl_2	10 mL[1]	5 mL, hexane
OPP	CH_2Cl_2	10 mL	5 mL

[1] Final volume for GPC may be 4 mL if a 2 mL sample loop is used

Final volumes and exchange solvents if Florisil cleanup is used			
Type	Exchange Solvent for Florisil	Final Volume for Florisil	Final Volume and solvent for Analysis
Pesticides	Hexane	10 mL (2 mL aliquot used)	2 mL, hexane

Final volumes and exchange solvents if both GPC and Florisil cleanup are used					
Type	Exchange Solvent for GPC	Final Volume for GPC	Exchange Solvent for Florisil	Final Volume for Florisil	Final volume for analysis
Pesticides	Methylene Chloride	10 mL	Hexane	5 mL (2 mL aliquot used)	2 mL, hexane

Note: Different final volumes may be necessary to meet special client reporting limit requirements.

Note: If silica gel cleanup is performed, exchange solvent to cyclohexane prior to cleanup.

Table 3

Surrogate Spiking Solutions

Analyte Group	Surrogate Spike Solution ID	Volume (mL)
BNA	100/150 ppm BNA	0.5
Pest	0.2 ppm DCB/TCX	1.0
Pest/PCB	0.2 ppm DCB/TCX	1.0
PCB	0.2 ppm DCB/TCX	1.0

Table 4

Matrix Spike and LCS Solutions

Analyte Group	Matrix Spike Solution ID	Volume (mL)
BNA	100/150 ppm BNA	0.5
BNA TCLP	BNA TCLP Spike	1.0
BNA NPDES	BNA NPDES Spike	1.0
Pest	0.2/0.5 ppm Pest	1.0
Pest TCLP	Pest TCLP Spike	1.0
Pest NPDES	Pest NPDES Spike	1.0
Pest/PCB	0.5 ppm pest spike	1.0
PCB	10 ppm PCB Spike	1.0

Table 5
Surrogate Spike Components

Type	Compounds	Solvent	Conc. (µg/mL)
BNA	2-Fluorobiphenyl	Methanol	50
	Nitrobenzene-d5		50
	p-Terphenyl-d14		50
	2-Fluorophenol		75
	Phenol-d6		75
	2,4,6-Tribromophenol		75
	1,2-Dichlorobenzene-d4		50
	2-Chlorophenol-d4		75
Pest/PCB	Decachlorobiphenyl	Acetone	0.2
	Tetrachloro-m-xylene		0.2

Table 6
Matrix Spike Components

Type	Compounds	Solvent	Conc. (µg/mL)
TCL BNA	Acenaphthene	Methanol	50
	4-Chloro-3-Methylphenol		75
	2-Chlorophenol		75
	1,4-Dichlorobenzene		50
	2,4-Dinitrotoluene		50
	4-Nitrophenol		75

Table 6

Matrix Spike Components

Type	Compounds	Solvent	Conc. (µg/mL)
	N-Nitroso-Di-n-Propylamine		50
	Pentachlorophenol		75
	Phenol		75
	Pyrene		50
	1,2,4-Trichlorobenzene		50
BNA TCLP	1,4-Dichlorobenzene	Methanol	50
	2,4-Dinitrotoluene		50
	Hexachlorobenzene		50
	Hexachlorobutadiene		50
	Hexachloroethane		50
	2-Methylphenol		50
	3-Methylphenol		50
	4-Methylphenol		50
	Nitrobenzene		50
	Pentachlorophenol		50
	Pyridine		50
	2,4,5-Trichlorophenol		50
	2,4,6-Trichlorophenol		50
BNA NPDES		Methanol	
	Acenaphthene		50
	Acenaphthylene		50
	Anthracene		50

Table 6

Matrix Spike Components

Type	Compounds	Solvent	Conc. (µg/mL)
	Benzo(a)anthracene		50
	Benzo(b)fluoranthene		50
	Benzo(k)fluoranthene		50
	Benzo(a)pyrene		50
	Benzo(ghi)perylene		50
	Benzyl butyl phthalate		50
	Bis(2-chloroethyl)ether		50
	Bis(2-chloroethoxy)methane		50
	Bis(2-ethylhexyl)phthalate		50
	Bis(2-chloroisopropyl)ether		50
	4-Bromophenyl phenyl ether		50
	2-Chloronaphthalene		50
	4-Chlorophenyl phenyl ether		50
	Chrysene		50
	Dibenzo(a,h)anthracene		50
	Di-n-butylphthalate		50
	1,3-Dichlorobenzene		50
	1,2-Dichlorobenzene		50
	1,4-Dichlorobenzene		50
	3,3'-Dichlorobenzidine		50
	Diethyl phthalate		50
	Dimethyl phthalate		50
	2,4-Dinitrotoluene		50

Table 6

Matrix Spike Components

Type	Compounds	Solvent	Conc. (µg/mL)
	2,6-Dinitrotoluene		50
	Di-n-octylphthalate		50
	Fluoranthene		50
	Fluorene		50
	Hexachlorobenzene		50
	Hexachlorobutadiene		50
	Hexachloroethane		50
	Indeno(1,2,3-cd)pyrene		50
	Isophorone		50
	Naphthalene		50
	Nitrobenzene		50
	N-Nitrosodi-n-propylamine		50
	Phenanthrene		50
	Pyrene		50
	1,2,4-Trichlorobenzene		50
	4-Chloro-3-methylphenol		50
	2-Chlorophenol		50
	2,4-Dichlorophenol		50
	2,4-Dimethylphenol		50
	2,4-Dinitrophenol		50
	2-Methyl-4,6-dinitrophenol		50
	2-Nitrophenol		50
	4-Nitrophenol		50

Table 6

Matrix Spike Components

Type	Compounds	Solvent	Conc. (µg/mL)
	Pentachlorophenol		50
	Phenol		50
	2,4,6-Trichlorophenol		50
Pest	Aldrin	Acetone	0.2
	gamma-BHC (Lindane)		0.2
	4,4'-DDT		0.5
	Dieldrin		0.5
	Endrin		0.5
	Heptachlor		0.2
Pest TCLP	Heptachlor	Acetone	0.5
	Heptachlor epoxide		0.5
	Lindane		0.5
	Endrin		0.5
	Methoxychlor		1.0
Pest NPDES	Aldrin	Acetone	0.2
	alpha-BHC		0.2
	beta-BHC		0.2
	delta-BHC		0.2
	gamma-BHC (Lindane)		0.2
	4,4'-DDD		1.0
	4,4'-DDE		0.2
	4,4'-DDT		1.0

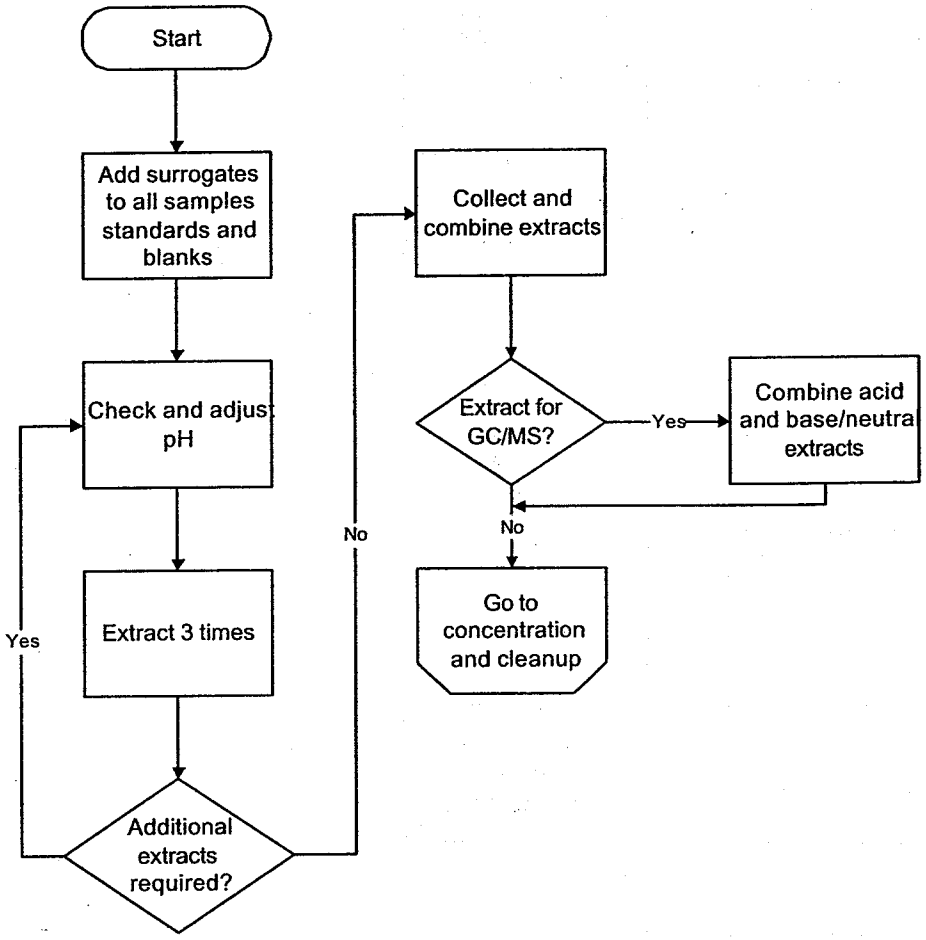
Table 6

Matrix Spike Components

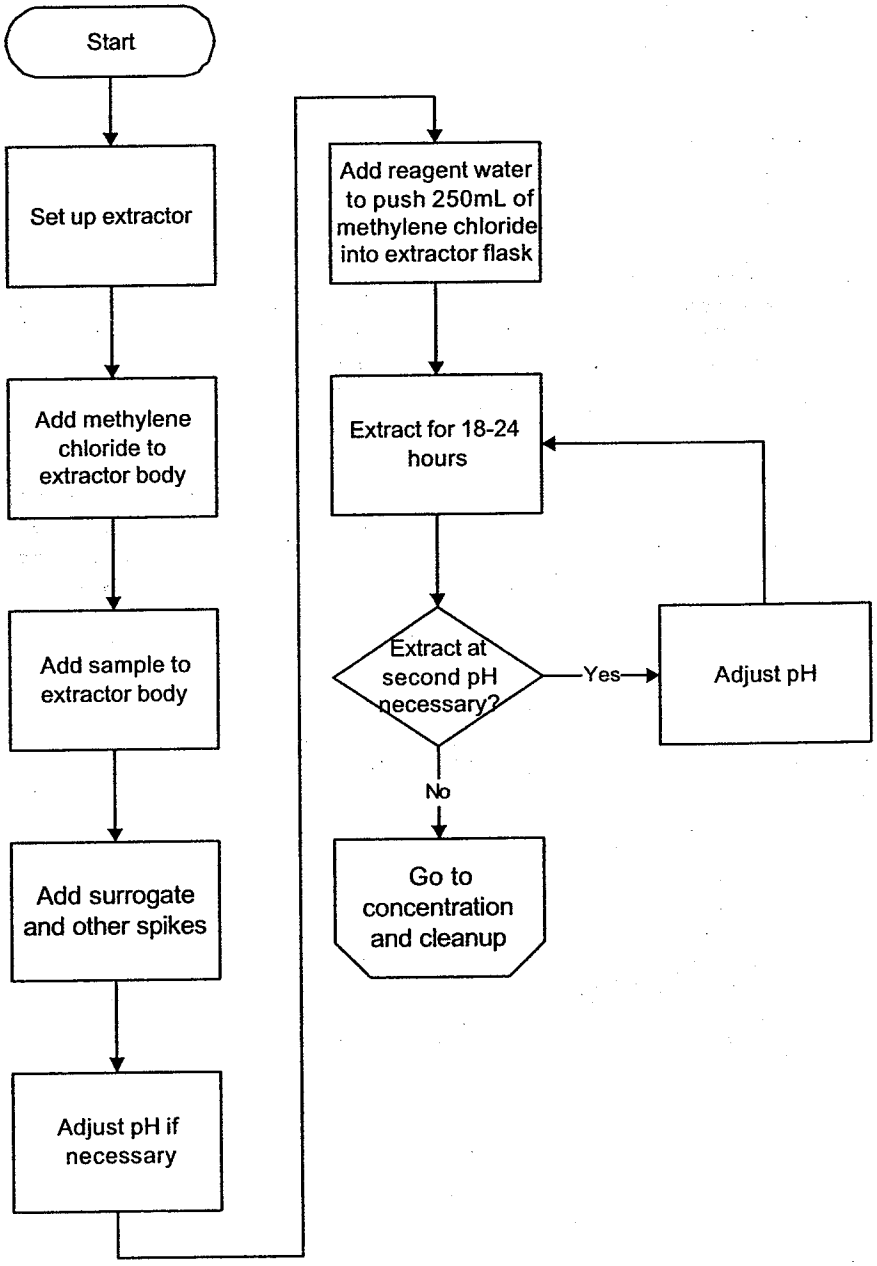
Type	Compounds	Solvent	Conc. (µg/mL)
	Dieldrin		0.2
	alpha-Endosulfan		0.2
	beta-Endosulfan		1.0
	Endosulfan Sulfate		1.0
	Endrin		1.0
	Heptachlor		0.2
	Heptachlor Epoxide		0.2
PCB only	PCB 1016/1260	Acetone	10

17.5 Flow diagrams

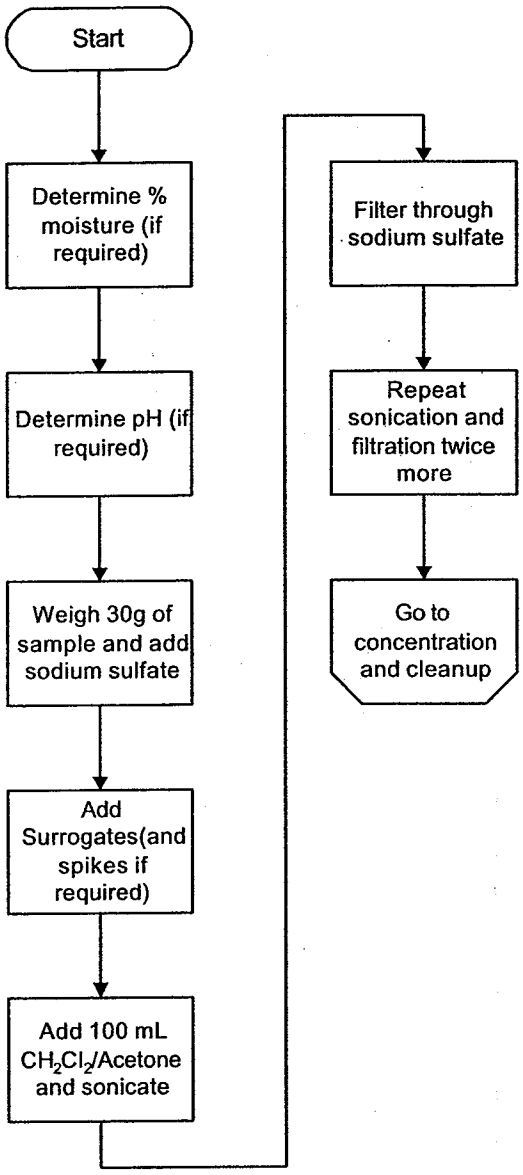
17.4.1. Separatory funnel extraction



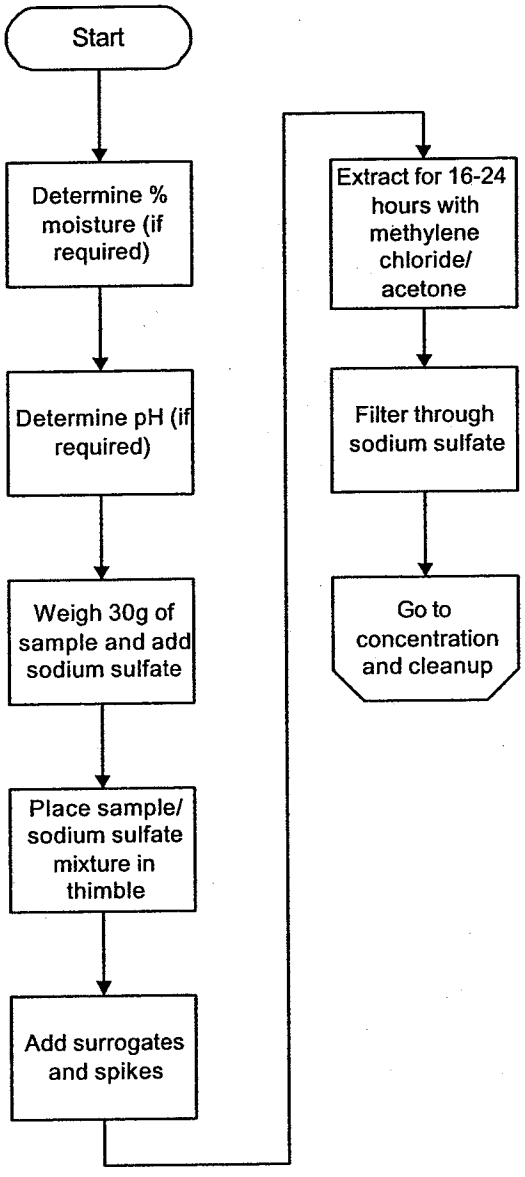
17.4.2. Continuous liquid/liquid extraction



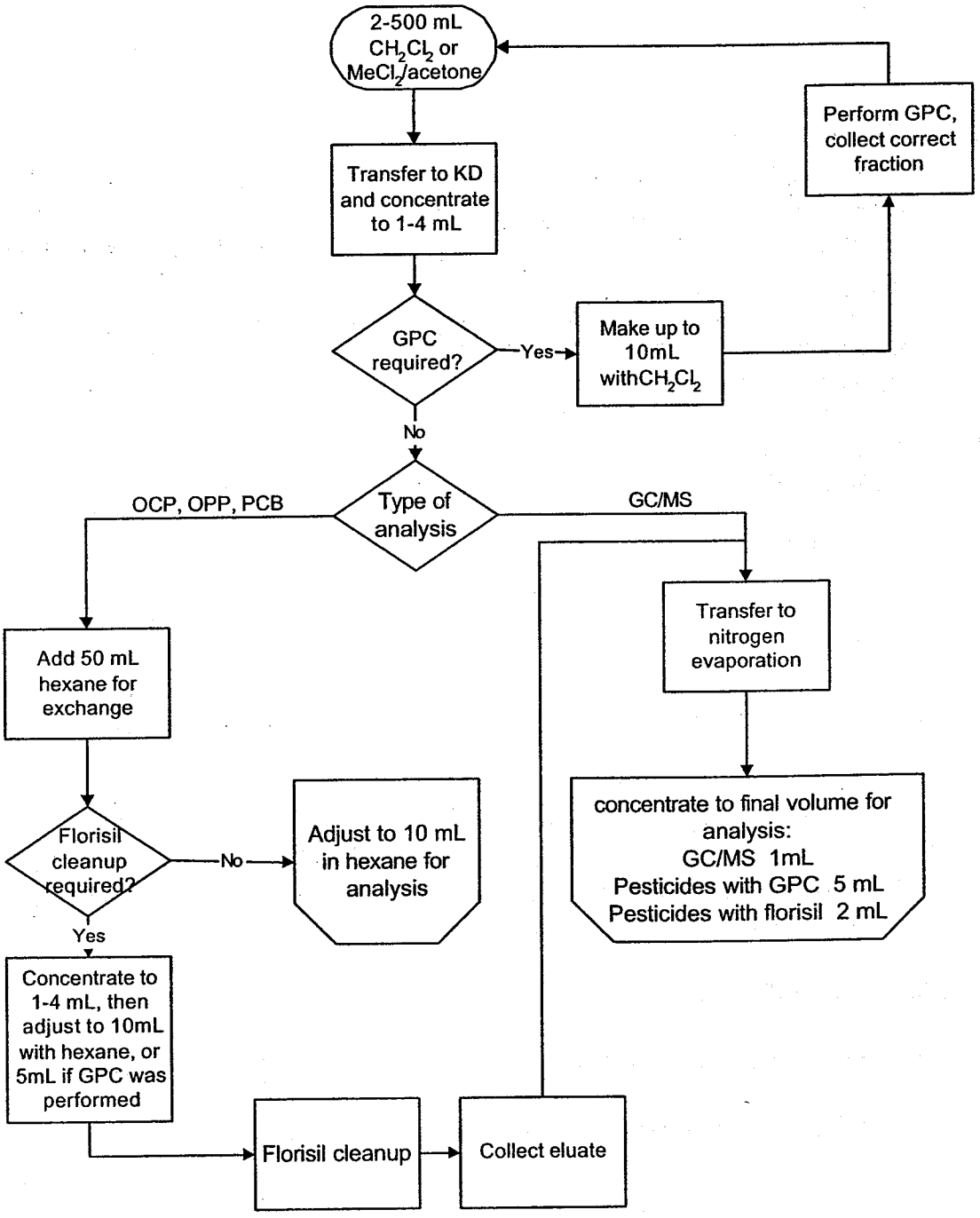
17.4.3. Sonication Extraction



17.4.4. Soxhlet extraction



17.4.5. Concentration and cleanup



1. SCOPE AND APPLICATION

This method is applicable to the extraction of chlorinated herbicides in waters, solids, oils, and TCLP extracts. Appropriate compounds for extraction by this method are listed in CORP-GC-0001, Appendix D, Gas Chromatography of Phenoxy Acid Herbicides based on Method 8150*B*.

2. SUMMARY OF METHOD

This method is based on SW846 method 8150*B*. Aqueous samples are extracted into diethyl ether by a separatory funnel extraction. Solids are extracted into diethyl ether by shaking. Phenoxy acid herbicides in the extract are hydrolyzed with potassium hydroxide and the aqueous solution is washed with diethyl ether to remove interferences. The aqueous solution is then acidified and the herbicides are extracted with diethyl ether. The ether solution is dried and the herbicides are esterified using diazomethane. The final volume is adjusted to prepare the extract for gas chromatography.

3. DEFINITIONS

Refer to section 3 of the main body of this SOP.

4. INTERFERENCES

Refer to section 4 of the main body of this SOP.

5. SAFETY

5.1. Refer to section 5 of the main body this SOP for basic safety information.

5.2. DIAZOMETHANE is an extremely toxic gas with an explosion potential. Since the explosion potential is catalyzed by imperfections in glass, generation of diazomethane must be carried out in glassware free of scratches, cracks, chips and which does not have ground glass joints. Solutions of diazomethane will be kept at temperatures below 90°C. Diazomethane must be generated and handled in a fume hood.

5.3. Diethyl ether is extremely flammable

5.4. Diethyl ether must be free of peroxides as demonstrated by EM Quant test strips.

5.5. Concentrated potassium hydroxide solution is highly caustic.

6. EQUIPMENT AND SUPPLIES

6.1. Refer to Section 6 of the main body of this SOP for basic extraction equipment and supplies. Additional equipment and supplies needed for this procedure are listed below.

6.2. Diazomethane generation apparatus

6.3. EM Peroxide test strips

7. REAGENTS AND STANDARDS

7.1. Reagents are listed in Section 7 of the main body of this SOP. Additional Reagents and standards needed for this procedure are listed below.

7.2. Reagents

7.2.1. Potassium hydroxide solution, 37% aqueous solution, (w/v): Dissolve 37 g of potassium hydroxide pellets in reagent water and dilute to 100 mL. CAUTION: Considerable heat will be generated.

7.2.2. Diazald, 99% purity

7.2.3. Sodium sulfate, Na_2SO_4, Anhydrous, granular, acidified: Heat sodium sulfate in a shallow tray at 400°C for a minimum of 4 hours to remove phthalates and other interfering organic substances. In a large beaker, acidify by slurrying 1000 g sodium sulfate with just enough diethyl ether to cover. Add 2-5 mL of concentrated sulfuric acid and mix thoroughly. Place the mixture on a steam bath in a hood to evaporate the ether, or allow the ether to evaporate overnight. Larger or smaller batches of acidified sodium sulfate may be prepared using the reagents in the same proportions.

7.2.4. Acidified 5% sodium sulfate solution

Add 50 g of sodium sulfate to one liter of reagent water. Add 10 mL of concentrated H_2SO_4. (This reagent may be prepared in different quantities if the proportions are kept the same).

7.2.5. Diethyl ether, reagent grade.

7.2.6. Methanol, reagent grade.

7.2.7. Silicic acid

7.3. Standards

7.3.1. Surrogate Standard
See Table A3.

7.3.2. Matrix Spike and LCS standard
See Table A4.

8. SAMPLE COLLECTION PRESERVATION AND STORAGE

8.1. Sample collection and storage is described in Section 8 of the main body of this SOP.

9. QUALITY CONTROL

9.1. Refer to Section 9 of the main body of this SOP for Quality control procedures.

10. CALIBRATION AND STANDARDIZATION

Not applicable

11. PROCEDURE

11.1. Preparation of soil, sediment and other solid samples

11.1.1. Weigh 50.0 g of moist solid sample into an 8 oz. glass jar. Use 50 g of sodium sulfate for the Method Blank and LCS. Acidify the sample with 5 mL of concentrated HCl.

11.1.2. There should be a small amount of liquid phase. If not, add reagent water until there is. Stir well with a spatula. (Note: This is not necessary for the method blank or LCS)

11.1.3. After 15 minutes, stir with a spatula and check the pH of the liquid phase. Add more acid if necessary to bring the pH to <2, repeating the stirring and standing time after each acid addition. (Note: The pH of the method blank and LCS is not determined.)

11.1.4. Add 60 g of acidified sodium sulfate and mix well. The sample should be free flowing. If not, add more sodium sulfate.

11.1.5. Spike with 1.0 mL of DCAA surrogate solution. Spike matrix spikes and LCS with 1 mL of herbicide matrix spiking solution. (Refer to tables A1 and A2)

11.1.6. Add 100 mL 20% acetone in ethyl ether.

Note: If dinoseb is a target, acetone should not be used. Instead, use 100 mL of ethyl ether.

11.1.7. Mix contents on orbital shaker for 20 minutes. Decant extract through glass wool plugged funnel.

11.1.8. Extract sample twice more, using 100 mL 20% acetone in ether (or 100% ether if dinoseb is a target). After each addition shake for 10 minutes and decant the extract.

11.1.9. Combine the extracts in a 1 or 2 liter separatory funnel containing 250 mL of acidified 5% sodium sulfate solution.

11.1.10. Check the pH of the extract. If it is not at or below pH 2, add more concentrated HCl until stabilized at the desired pH. Gently mix the contents of the separatory funnel for one minute to extract interferences into the aqueous layer. Allow the layers to separate. Collect the aqueous phase in a clean beaker and the extract phase in a 500 mL ground glass Erlenmeyer flask. Place the aqueous phase back in the separatory funnel and re-extract using 25 mL of diethyl ether. Allow the layers to separate and discard the aqueous layer. Combine the ether extracts in the 500 mL Erlenmeyer flask containing 5 mL of 37% potassium hydroxide. Proceed to step 11.3, Hydrolysis.

11.2. Preparation of Aqueous Samples

11.2.1. Weigh the sample bottle and pour approximately 1 liter (100 mL for TCLP leachates) into a 2 liter separatory funnel. The sample should be decanted off any sediment. Reweigh the bottle and record the sample volume on the benchsheet, assuming a density of 1.0. Alternatively, measure 1 liter in a graduated cylinder. If less than 1 liter was used, add reagent water to make the volume up to 1 liter.

11.2.2. Adjust pH to 2 with 1:1 sulfuric acid. Spike with 1 mL of surrogate solution. Spike MS/MSD and LCS samples with 1 mL of matrix spiking solution. (Refer to Tables A1 and A2). Add 150 mL diethyl ether and shake funnel for 2 minutes with frequent venting to release excess pressure. ***Caution:*** Diethyl ether will generate pressure rapidly. Vent the funnel immediately after it is first sealed and inverted, and vent frequently thereafter.

11.2.3. Allow layers to separate for at least 10 minutes and drain the aqueous phase into a clean beaker. If an emulsion forms break by centrifuge or mechanically. Collect the solvent extract (upper layer) in a 500 mL Erlenmeyer containing 2 mL of 37% potassium hydroxide. Use 5 mL of potassium hydroxide for TCLP samples.

11.2.4. Repeat the extraction two more times using 50 mL of diethyl ether each time. Combine the extracts in the Erlenmeyer flask. Rinse the beaker with each additional aliquot of extraction solvent. Proceed to section 11.3, Hydrolysis.

11.3. Hydrolysis

11.3.1. Add one or two clean boiling chips, the sample extract, and 15 mL of water for water samples (30 mL for soil samples) to the 500 mL flask. Attach a three-ball Snyder column.

11.3.2. Place the apparatus on a hot water bath (approx 60°C) so that the bottom of the flask is bathed with hot water vapor. Although the diethyl ether will evaporate in about 15 minutes, continue heating for a total of 60 minutes), beginning from the time the flask is placed in the water bath. Remove the apparatus and let stand at room temperature for at least 10 minutes. Check the pH of the solution. If not at or above 11, add additional KOH to bring the pH above 11 and hydrolyze for an additional 60 minutes.

11.4. Solvent Clean-up

11.4.1. Transfer the solution to an acid-rinsed 125 or 250 mL separatory funnel using 5-10 mL of reagent water to rinse out the flask. Wash the basic solution by shaking for 1 minute with a 20 mL portion of diethyl ether. Drain the aqueous (bottom) layer back into the flask and discard the ether layer. Pour the aqueous layer back into the separatory funnel and repeat the wash with a second 20 mL of ether. Pour the aqueous phase back into the separatory funnel. The herbicides remain in the aqueous phase. Additional washes may be used if the sample appears dirty.

11.5. Solvent Extraction

11.5.1. Acidify the contents of the separatory funnel to pH 2 by adding 1:1 sulfuric acid (2 mL for aqueous, 5 mL for soils). Test with pH indicator paper. Add 40 mL ether and shake vigorously for 1 minute. Drain and collect the aqueous phase and pour the ether phase into a flask or bottle containing 5-7 g of acidified sodium sulfate.

11.5.2. Pour the aqueous phase back into the separatory funnel and repeat the extraction twice more with 20 mL aliquots of ether, combining all solvent in the flask or bottle. Allow the extract to remain in contact with the sodium sulfate for at least 2 hours.

NOTE: The drying step is very critical to ensure complete esterfication. Any moisture remaining in the ether will result in low herbicide recoveries. The amount of sodium sulfate is adequate if some free flowing crystals are visible when swirling the flask. If all the sodium sulfate solidifies in a cake, add a few additional grams of sodium sulfate

and again test by swirling. The 2 hour drying time is a minimum, however, the extracts may be held in contact with the sodium sulfate overnight.

11.6. Concentration

11.6.1. Transfer the ether extract by decanting, or through a funnel plugged with acid washed glass wool, into a Turbovap concentrator tube or a 500 mL K-D flask equipped with a 10 mL concentrator tube. Use a stirring rod to crush the caked sodium sulfate during transfer. Rinse the Erlenmeyer with 20-30 mL ether to complete transfer.

11.6.2. Attach a three ball Snyder column to the K-D apparatus, prewet the column with a few mL of ether from the top, and place the apparatus on a water bath at approximately 60°C. At the proper rate of distillation, the balls of the column will chatter, but the chambers will not flood. When the apparent volume reaches 2-5 mL, remove from the water bath and allow to completely cool.

11.6.3. Carefully disassemble the concentrator tube and rinse the lower glass joint with a small amount of diethyl ether.

11.6.4. Add 0.1 mL of methanol.

11.6.5. The extract is now ready for esterification by either the diazomethane solution method (11.7) or the bubbler method (11.8)

11.7. Esterification (diazomethane solution method)

11.7.1. Preparation of Diazomethane solution

- **CAUTION: Diazomethane is potentially explosive.**
- **A temporary shield or the sash of the hood must protect the face and body of the analyst.**
- **Never heat solutions of diazomethane above 90°C, due to the explosive potential.**
- **Do not use glass stirring rods or any glassware with ground glass joints, as this can initiate violent reaction or explosion.**
- **All glassware must be scrupulously cleaned and free from scratches, to avoid potential initiation of violent reaction or explosion.**

11.7.1.1. Weigh out 10.0 g potassium hydroxide in a 125 mL beaker. Add 16 mL water and 20 mL ethanol. Mix well until the potassium hydroxide is dissolved and pour into the reaction vessel.

11.7.1.2. Attach a 100 mL receiving flask to the condenser and cool the receiver in an ice bath.

11.7.1.3. Fill the condenser with dry ice, then add acetone slowly until the cold finger is about one third full.

11.7.1.4. Mix 10.0 g diazald and 90 mL ether. Place in a separatory funnel over the reaction vessel.

11.7.1.5. Warm the reaction vessel on the water bath to 50-60°C or until the ether begins to reflux. CAUTION: Do not allow the temperature to exceed 70°C. Add diazald solution over a period of 40 minutes. The rate of distillation should approximate the rate of addition. Replenish the cold finger with dry ice as necessary.

11.7.1.6. When the diazald solution has been used up, slowly add 10 mL of ether and continue distillation until the distillate is colorless.

11.7.1.7. The diazomethane solution is documented with a lot number. It is stored in a freezer at -10 to -20°C and has an expiration date of six months.

11.7.2. Disposal of outdated diazomethane solutions

11.7.2.1. Add 20 mL of ether to 2 mL of glacial acetic acid in a large beaker in the hood.

11.7.2.2. Add the diazomethane solution slowly to the acetic acid. The yellow color of the diazomethane disappears as it reacts with the acetic acid. If the yellow color persists at any time during the addition, and does not disappear with gentle swirling of the beaker, add additional acetic acid in ether before continuing the diazomethane addition.

11.7.2.3. Dispose of the ether solution in the non-chlorinated wastes bottle.

11.8. Esterification (Diazomethane solution method)

11.8.1. Add approximately 2 mL of diazomethane solution and let sit for 10-15 minutes.

11.8.2. Add approximately 0.2 g of silicic acid to the extract. Allow to spontaneously evaporate to about 1.0 mL, then make up to 10 mL with hexane.

11.8.3. Extract is ready for analysis by gas chromatography.

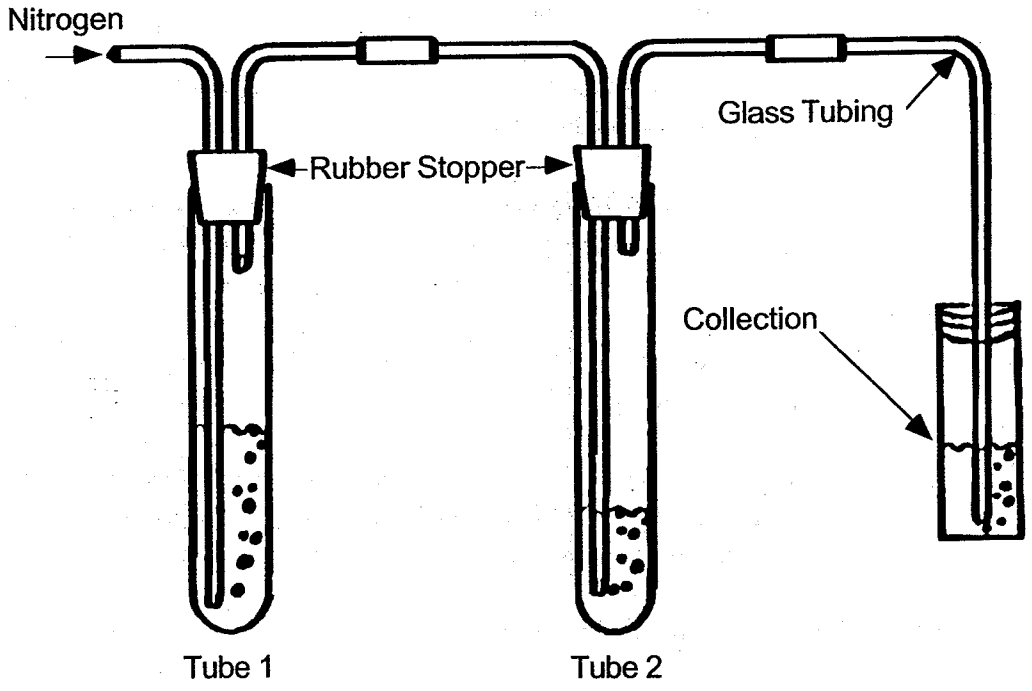
11.9. Esterification (Bubbler Method)

11.9.1. Assemble the diazomethane apparatus (Figure A1) in a hood. Add 10 mL of diethyl ether to tube 1. Add 5 mL of 2% methanolic KOH, 3 mL of ether and 0.5-1 g of diazald to tube 2.

11.9.2. Place the tip of the disposable pipet into the vial containing the first sample extract. Apply nitrogen flow (approx. 10 mL/min) to bubble diazomethane through the sample extract for about 1 minute, or until the yellow color persists. Replace the disposable pipet and place the tip into the vial containing the second extract. Continue until the diazald is consumed. (An additional 0.1-0.5 g diazald may be added to extend the generation of diazomethane).

11.9.3. Allow the extracts to stand for 20 minutes, then add approximately 0.2 g of silicic acid to each extract. Allow to stand for an additional 20 minutes.

11.9.4. Adjust the volume to 10 mL with hexane. The sample is now ready for gas chromatography.



12. DATA ANALYSIS AND CALCULATIONS

Not applicable

13. METHOD PERFORMANCE

Refer to CORP-GC-0001 for details of method performance.

14. POLLUTION PREVENTION

Refer to section 14 of the main body of this SOP.

15. WASTE MANAGEMENT

Refer to section 15 of the main body of this SOP.

16. REFERENCES

16.1. SW846, Test Methods for Evaluating Solid Waste, Third Edition, Update II, September 1994, Chlorinated Herbicides, Method 8150B.

17. MISCELLANEOUS

17.1. Modifications from Reference Method

17.1.1. Directions to add sufficient reagent water to the soil sample so that the pH can be measured have been added (Section 11.1.2)

17.1.2. Directions to add sodium sulfate to the soil sample until a free flowing texture is achieved have been added. In common with other SW-846 extraction procedures, this improves the extraction efficiency. (Section 11.1.4)

17.1.3. For the soil extraction, the acetone and ether are added together rather than separately. (Section 11.1.6)

17.1.4. The requirement for the sulfuric acid added in the solvent extraction to be cold has been removed. Since a small quantity of acid is added to a large quantity of extract, nothing is gained by having the acid cold. (Section 11.5.1)

17.1.5. Silicic acid is stored at room temperature.

17.1.6. The bubbler esterification method uses methanolic KOH in place of the aqueous KOH / carbitol mixture recommended in method 8150B. This has been found to provide a more effective and reliable esterification.

17.2. Modifications from previous revisions

In the hydrolysis procedure, the extract is added to the potassium hydroxide solution rather than visa versa.

17.3. Tables

Table A1 Herbicide Surrogate Spiking Solutions		
Analyte Group	Surrogate Spike Solution ID	Volume (mL)
Herbicides	Herbicides SS	1.0

Table A2 Herbicide Matrix Spike and LCS Solutions		
Analyte Group	Matrix Spike Solution ID	Volume (mL)
Herbicides	Herbicides MS	1.0

Table A3 Herbicide Surrogate Spike Components			
Type	Compounds[1]	Solvent	Conc. (ug/mL)
Herbicides SS	2,4-DCAA	Methanol	16

[1]The surrogate is spiked as the free acid

Table A4			
Herbicide Matrix Spike Components			
Type	Compounds[1]	Solvent	Conc. (ug/mL)
Herbicides MS	2,4-D	Methanol	16
	2,4-DB		16
	2,4,5-TP (Silvex)		4
	Dalapon		8
	2,4,5-T		4

[1]The herbicide spiking solution contains the herbicides as the free acids.

1. SCOPE AND APPLICATION

This method is applicable to the extraction of chlorinated herbicides in waters, solids, oils, and TCLP extracts. Appropriate compounds for extraction by this method are listed in CORP-GC-0001, Appendix D, Gas Chromatography of Phenoxy Acid Herbicides based on Method 8151.

2. SUMMARY OF METHOD

This method is based on SW846 method 8151. Aqueous samples are hydrolyzed if esters and acids are to be determined, then washed with methylene chloride by a separatory funnel extraction. After acidifying the sample the free acids are extracted into diethyl ether. Solids are extracted into methylene chloride/ acetone by sonication. If esters and acids are to be determined, the extract is hydrolyzed and extracted into diethyl ether. For both soils and aqueous samples, the free acid herbicides in the ether extract are esterified. The final volume is adjusted to prepare the extract for gas chromatography.

3. DEFINITIONS

Refer to section 3 of the main body of this SOP.

4. INTERFERENCES

Refer to section 4 of the main body of this SOP.

5. SAFETY

5.1. Refer to section 5 of the main body this SOP for basic safety information.

5.2. DIAZOMETHANE is an extremely toxic gas with an explosion potential. Since the explosion potential is catalyzed by imperfections in glass, generation of diazomethane must be carried out in glassware free of scratches, cracks, chips and which does not have ground glass joints. Solutions of diazomethane will be kept at temperatures below 90°C. Diazomethane must be generated and handled in a fume hood.

5.3. Diethyl ether is extremely flammable

5.4. Diethyl ether must be free of peroxides as demonstrated by EM Quant test strips.

5.5. Concentrated potassium hydroxide solution is highly caustic.

6. EQUIPMENT AND SUPPLIES

6.1. Refer to Section 6 of the main body of this SOP for basic extraction equipment and supplies. Additional equipment and supplies needed for this procedure are listed below.

6.2. Diazomethane generation apparatus

6.3. EM Peroxide test strips

7. REAGENTS AND STANDARDS

7.1. Reagents are listed in Section 7 of the main body of this SOP. Additional Reagents and standards needed for this procedure are listed below.

7.2. Reagents

7.2.1. Potassium hydroxide solution, 37% aqueous solution, (w/v): Dissolve 37 g of potassium hydroxide pellets in reagent water and dilute to 100 mL. **Caution:** Considerable heat will be generated. Other volumes of solution may be made up as convenient.

7.2.2. Sodium hydroxide solution, 6N. Dissolve 400 g NaOH in reagent water and dilute to 1.0L. **Caution:** Considerable heat will be generated. Other volumes of solution may be made up as convenient.

7.2.3. Sodium hydroxide solution, 0.1N. Dissolve 4g NaOH in reagent water and dilute to 1.0L. Other volumes of solution may be made up as convenient.

7.2.4. Sulfuric acid, 1:1 Slowly add 500 mL concentrated sulfuric acid to 500 mL water. **Caution:** Considerable heat will be generated. The acid must be added to the water. Wear protective clothing and safety glasses. Other volumes of solution may be made up as convenient.

7.2.5. Diazald, 99% purity

7.2.6. 2,3,4,5,6-Pentafluorobenzyl bromide (PFBBr)$C_6H_5CH_2Br$

7.2.7. Sodium sulfate, Na_2SO_4, Anhydrous, granular, acidified: Heat sodium sulfate in a shallow tray at 400°C for a minimum of 4 hours to remove phthalates and other interfering organic substances. In a large beaker, acidify by slurrying 1000 g sodium sulfate with just enough diethyl ether to cover. Add 2-5 mL

of concentrated sulfuric acid and mix thoroughly. Place the mixture on a steam bath in a hood to evaporate the ether, or allow the ether to evaporate overnight. Larger or smaller batches of acidified sodium sulfate may be prepared using the reagents in the same proportions.

7.2.8. Sodium Chloride, NaCl

7.2.9. Acidified 5% sodium sulfate solution

Add 50 g of sodium sulfate to one liter of reagent water. Add 10 mL of concentrated H_2SO_4. (This reagent may be prepared in different quantities if the proportions are kept the same).

7.2.10. Diethyl ether, reagent grade.

7.2.11. Methanol, reagent grade.

7.2.12. Silicic acid

7.3. Standards

7.3.1. Surrogate Standard

See Table A3.

7.3.2. Matrix Spike and LCS standard

See Table A4.

8. SAMPLE COLLECTION PRESERVATION AND STORAGE

8.1. Sample collection and storage is described in Section 8 of the main body of this SOP.

9. QUALITY CONTROL

9.1. Refer to Section 9 of the main body of this SOP for Quality control procedures.

10. CALIBRATION AND STANDARDIZATION

Not applicable

11. PROCEDURE

11.1. Preparation of Aqueous Samples

11.1.1. Weigh the sample bottle and pour approximately 1 liter (100 mL for TCLP leachates) into a 2 liter separatory funnel. Reweigh the bottle and record the sample volume on the benchsheet, assuming a density of 1.0. Alternatively, measure 1 liter in a graduated cylinder. If less than 1 liter was used, add reagent water to make the volume up to 1 liter.

11.1.2. Spike each sample blank, LCS and MS with 1.0 mL of DCAA surrogate solution. Spike matrix spikes and LCS with 1 mL of herbicide matrix spiking solution. (Refer to tables B1 and B2)

11.1.3. Add 250 g of NaCl to the sample and shake to dissolve the salt.

11.1.4. Hydrolysis

Use this step only if herbicide esters in addition to herbicide esters are to be determined. This is normally the case. If the herbicide esters are not to be determined, omit this step and go to 11.1.4.

Add 17 mL of 6N NaOH to the sample, seal and shake. Check the pH of the sample with pH paper. If the pH of the sample is not $\geq$12 adjust to $\geq$12 by adding more NaOH. Let the sample sit at room temperature for 2 hours to complete the hydrolysis.

11.1.5. If the sample was originally in a 1 liter bottle, and the whole sample was used, add 60 mL of methylene chloride to the sample bottle. Rinse the bottle (and graduated cylinder, if used) and add the methylene chloride to the separatory funnel.

11.1.6. If the whole contents of the sample bottle were not used, add 60 mL of methylene chloride to the separatory funnel.

11.1.7. Extract the sample by shaking vigorously for 2 minutes. (An automatic shaker may be used). Allow the organic layer to separate from the aqueous layer. If an emulsion layer greater than one third of the solvent layer forms, use mechanical techniques to complete the phase separation. Suggested techniques are stirring, filtration through glass wool and centrifugation.

11.1.8. Discard the **methylene chloride** phase.

11.1.9. Add a second 60 mL of methylene chloride and repeat the extraction a second time, discarding the methylene chloride. Repeat the extraction a third time.

11.1.10. Add 17 mL of cold (4°C) 1:1 sulfuric acid to the sample. Seal, and shake to mix. Check the pH of the sample with pH paper. If the pH is not ≤ 2, and more acid to adjust the pH to ≤ 2.

11.1.11. Add 120 mL diethyl ether to the sample and extract by shaking vigorously for 2 minutes. (An automatic shaker may be used). Allow the organic layer to separate from the aqueous layer. If a emulsion layer greater than one third of the solvent layer forms, use mechanical techniques to complete the phase separation. Suggested techniques are stirring, filtration through glass wool and centrifugation.

11.1.12. Drain the aqueous layer into a clean flask or beaker. Collect the ether phase in a clean flask or bottle containing approximately 10g of acidified anhydrous sodium sulfate.

11.1.13. Return the aqueous phase to the separatory funnel, add 60 mL diethyl ether and repeat the extraction procedure a second time., combining the ether extracts. Repeat the extraction a third time with 60 mL diethyl ether. Discard the aqueous phase after the third extraction.

11.1.14. Allow the extract to remain in contact with the sodium sulfate for at least 2 hours, shaking periodically. (May be left overnight). The drying step is critical: if the sodium sulfate solidifies in a cake, add a few additional grams of acidified sodium sulfate. The amount of sodium sulfate is sufficient if some free flowing crystals are visible when the flask or bottle is swirled or shaken.

11.1.15. Proceed to section 11.5, concentration.

11.2. Extraction of soil and sediment samples

11.2.1. Decant and discard any water layer on a sediment/soil sample. Homogenize the sample by mixing thoroughly. Discard any foreign objects such as sticks, leaves and rocks, unless extraction of this material is required by the client. If the sample consists primarily of foreign materials consult with the client (via the Project Manager or Administrator). Document if a water layer was discarded.

11.2.2. Weigh 50.0 g of moist solid sample into an clean glass jar. Use 50 g of sodium sulfate for the Method Blank and 50g Ottawa sand for the LCS. Acidify the sample with 5 mL of concentrated HCl.

11.2.3. There should be a small amount of liquid phase. If not, add reagent water until there is. Stir well with a spatula. (Note: This is not necessary for the method blank or LCS)

11.2.4. After 15 minutes, stir with a spatula and check the pH of the liquid phase. Add more acid if necessary to bring the pH to <2, repeating the stirring and standing time after each acid addition. (Note: The pH of the method blank and LCS are not determined.)

11.2.5. Add 60 g of acidified sodium sulfate and mix well. The sample should be free flowing. If not, add more sodium sulfate.

11.2.6. Spike each sample blank, LCS and MS with 1.0 mL of DCAA surrogate solution. Spike matrix spikes and LCS with 1 mL of herbicide matrix spiking solution. (Refer to tables B1 and B2)

11.2.7. Add a minimum of 100 mL of 1:1 methylene chloride:acetone to the beaker.

11.2.8. Place the bottom surface of the appropriate disrupter horn tip approximately ½ inch below the surface of the solvent, but above the sediment layer.

11.2.9. Sonicate for 3 minutes, making sure the entire sample is agitated. If the W-380 or W-385 sonicator is used the output should be set at 6 for the 3/4 inch high gain (Q) horn or 10 for the 3/4 inch standard horn with mode switch on pulse, and percent-duty cycle knob set at 50%.

11.2.10. Loosely plug the stem of a 75 mm x 75 mm glass funnel with glass wool and/or line the funnel with filter paper. Add 10-20 g of anhydrous sodium sulfate to the funnel cup.

11.2.11. Place the prepared funnel on a collection apparatus. If the herbicide esters are *not* to be determined, the collection apparatus is a bottle or flask containing approximately 10g of anhydrous acidified sodium sulfate. If the herbicide esters *are* to be determined, (normally the case) the collection apparatus is glassware suitable for the hydrolysis step, typically a KD flask or Turbovap tube.

11.2.12. Decant and filter extracts through the prepared funnel into the collection apparatus.

11.2.13. Repeat the extraction two more times with additional 100 mL minimum portions of methylene chloride / acetone each time. Decant off extraction

solvent after each sonication. On the final sonication pour the entire sample (sediment and solvent) into the funnel and rinse with an additional 10 mL-20 mL of the methylene chloride/acetone.

Note: Alternatively, the three extracts may be collected together and then filtered through the sodium sulfate.

11.2.14. If the herbicide esters are not to be determined, dry the extract as described in 11.4.2 or go to cleanup, section 11.3. If the herbicide esters are to be determined (normally the case) proceed to section 11.2.15

11.2.15. Add 5 mL of 37% aqueous potassium hydroxide and 30 mL of water to the extract. Check the pH with pH paper. If the pH is not $\geq$12, adjust with additional KOH.

11.2.16. Heat on a water bath at 60-60°C for 2 hours. Allow to cool.

11.2.17. Transfer the solution to a separatory funnel and extract three times with 100 mL portions of methylene chloride. **Discard the methylene chloride phase.** The aqueous solution contains the herbicides.

11.2.18. Adjust the pH of the solution to $\leq$2 with 1:1 sulfuric acid.

11.2.19. Extract once with 40 mL diethyl ether and twice with 20 mL diethyl ether.

11.2.20. Proceed to section 11.3, Cleanup, if required, or Section 11.4, Extract drying.

11.3. Cleanup

This cleanup step may be necessary if the procedure for determining the herbicide acids only is being followed. (See section 11.2.14) It is not normally required if the acids and esters are being determined. (The usual case.) If cleanup is not required, proceed to section 11.4, Extract drying.

11.3.1. Prepare 45 mL of basic extraction fluid by mixing 30 mL of reagent water with 15 mL of 37% KOH. Use three 15 mL portions of this fluid to partition the extract from section 11.2.12 or 11.2.20, using a small separatory funnel. **Discard the organic phase.**

11.3.2. Adjust the pH of the solution to $\leq$2 with cold (4°C) sulfuric acid. (1:1). Extract once with 40 mL diethyl ether and twice with 20 mL diethyl ether.

11.4. Extract drying

11.4.1. Combine the extracts and pour through a funnel containing acidified sodium sulfate into a flask or bottle containing approximately 10 g acidified sodium sulfate. Rinse the funnel with a little extra diethyl ether.

11.4.2. Allow the extract to remain in contact with the sodium sulfate for at least 2 hours, shaking periodically. (May be left overnight). The drying step is critical: if the sodium sulfate solidifies in a cake, add a few additional grams of acidified sodium sulfate. The amount of sodium sulfate is sufficient if some free flowing crystals are visible when the flask or bottle is swirled or shaken. Proceed to section 11.5, concentration.

11.5. Concentration

11.5.1. Transfer the ether extract by decanting, or through a funnel plugged with acid washed glass wool, into a Turbovap concentrator tube or a 500 mL K-D flask equipped with a 10 mL concentrator tube. Use a stirring rod to crush the caked sodium sulfate during transfer. Rinse the flask or bottle with 20-30 mL ether to complete transfer.

11.5.2. Attach a three ball Snyder column to the K-D apparatus, prewet the column with a few mL of ether from the top, and place the apparatus on a water bath at approximately 60°C. At the proper rate of distillation, the balls of the column will chatter, but the chambers will not flood. When the apparent volume reaches 2 mL, remove from the water bath and allow to completely cool.

11.5.3. Carefully disassemble the concentrator tube and rinse the lower glass joint with a small amount of diethyl ether.

11.5.4. Add 0.1 mL of methanol.

11.5.5. The extract is now ready for esterification by either the diazomethane solution method (11.6) or the bubbler method (11.7)

11.6. Esterification (diazomethane solution method)

11.6.1. Preparation of Diazomethane solution

- **CAUTION: Diazomethane is potentially explosive.**
- **A temporary shield or the sash of the hood must protect the face and body of the analyst.**

- **Never heat solutions of diazomethane above 90°C, due to the explosive potential.**
- **Do not use glass stirring rods or any glassware with ground glass joints, as this can initiate violent reaction or explosion.**
- **All glassware must be scrupulously cleaned and free from scratches, to avoid potential initiation of violent reaction or explosion.**

11.6.1.1. Weigh out 10.0 g potassium hydroxide in a 125 mL beaker. Add 16 mL water and 20 mL ethanol. Mix well until the potassium hydroxide is dissolved and pour into the reaction vessel.

11.6.1.2. Attach a 100 mL receiving flask to the condenser and cool the receiver in an ice bath.

11.6.1.3. Fill the condenser with dry ice, then add acetone slowly until the cold finger is about one third full.

11.6.1.4. Mix 10.0 g diazald and 90 mL ether. Place in a separatory funnel over the reaction vessel.

11.6.1.5. Warm the reaction vessel on the water bath to 50-60°C or until the ether begins to reflux. CAUTION: Do not allow the temperature to exceed 70°C. Add diazald solution over a period of 40 minutes. The rate of distillation should approximate the rate of addition. Replenish the cold finger with dry ice as necessary.

11.6.1.6. When the diazald solution has been used up, slowly add 10 mL of ether and continue distillation until the distillate is colorless.

11.6.1.7. The diazomethane solution is documented with a lot number. It is stored in a freezer at -10 to -20°C and has an expiration date of six months.

11.6.2. Disposal of outdated diazomethane solutions

11.6.2.1. Add 20 mL of ether to 2 mL of glacial acetic acid in a large beaker in the hood.

11.6.2.2. Add the diazomethane solution slowly to the acetic acid. The yellow color of the diazomethane disappears as it reacts with the acetic acid. If the yellow color persists at any time during the addition, and does not

disappear with gentle swirling of the beaker, add additional acetic acid in ether before continuing the diazomethane addition.

11.6.2.3. Dispose of the ether solution in the non-chlorinated wastes bottle.

11.6.3. Esterification (Diazomethane solution method)

11.6.3.1. Add approximately 2 mL of diazomethane solution and let sit for 10-15 minutes.

11.6.3.2. Add approximately 0.2 g of silicic acid to the extract. Allow to spontaneously evaporate to about 1.0 mL, then make up to 10 mL with hexane.

11.6.3.3. Extract is ready for analysis by gas chromatography.

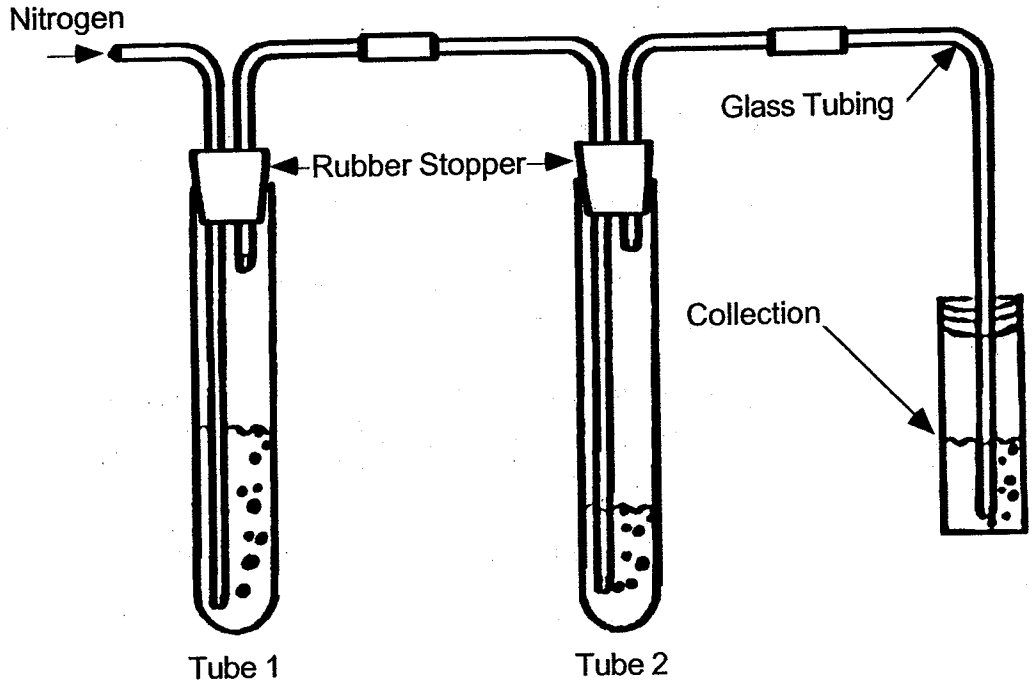
11.7. Esterification (Bubbler Method)

11.7.1. Assemble the diazomethane apparatus (Figure A1) in a hood. Add 10 mL of diethyl ether to tube 1. Add 5 mL of 2% methanolic KOH, 3 mL of ether and 0.5-1 g of diazald to tube 2.

11.7.2. Place the tip of the disposable pipet into the vial containing the first sample extract. Apply nitrogen flow (approx. 10 mL/min) to bubble diazomethane through the sample extract for about 1 minute, or until the yellow color persists. Replace the disposable pipet and place the tip into the vial containing the second extract. Continue until the diazald is consumed. (An additional 0.1-0.5 g diazald may be added to extend the generation of diazomethane).

11.7.3. Allow the extracts to stand for 20 minutes, then add approximately 0.2 g of silicic acid to each extract. Allow to stand for an additional 20 minutes.

11.7.4. Adjust the volume to 10 mL with hexane. The sample is now ready for gas chromatography.



12. DATA ANALYSIS AND CALCULATIONS

Not applicable

13. METHOD PERFORMANCE

Refer to CORP-GC-0001 for details of method performance.

14. POLLUTION PREVENTION

Refer to section 14 of the main body of this SOP.

15. WASTE MANAGEMENT

Refer to section 15 of the main body of this SOP.

16. REFERENCES

16.1. SW846, Test Methods for Evaluating Solid Waste, Third Edition, Update II, September 1994, Chlorinated Herbicides, Method 8151.

17. MISCELLANEOUS

17.1. Modifications from Reference Method

17.1.1. Directions to add sufficient reagent water to the soil sample so that the pH can be measured have been added (Section 11.1.2)

17.1.2. The bubbler esterification method uses methanolic KOH in place of the aqueous KOH / carbitol mixture recommended in method 8150B. This has been found to provide a more effective and reliable esterification.

17.2. Modifications from previous revisions

None

17.3. Tables

Table B1
Herbicide Surrogate Spiking Solutions

Analyte Group	Surrogate Spike Solution ID	Volume (mL)
Herbicides	Herbicides SS	1.0

Table B2
Herbicide Matrix Spike and LCS Solutions

Analyte Group	Matrix Spike Solution ID	Volume (mL)
Herbicides	Herbicides MS	1

Table B3
Herbicide Surrogate Spike Components

Type	Compounds[1]	Solvent	Conc. (ug/mL)
Herbicides SS	2,4-DCAA	Methanol	16

[1]The surrogate is spiked as the free acid

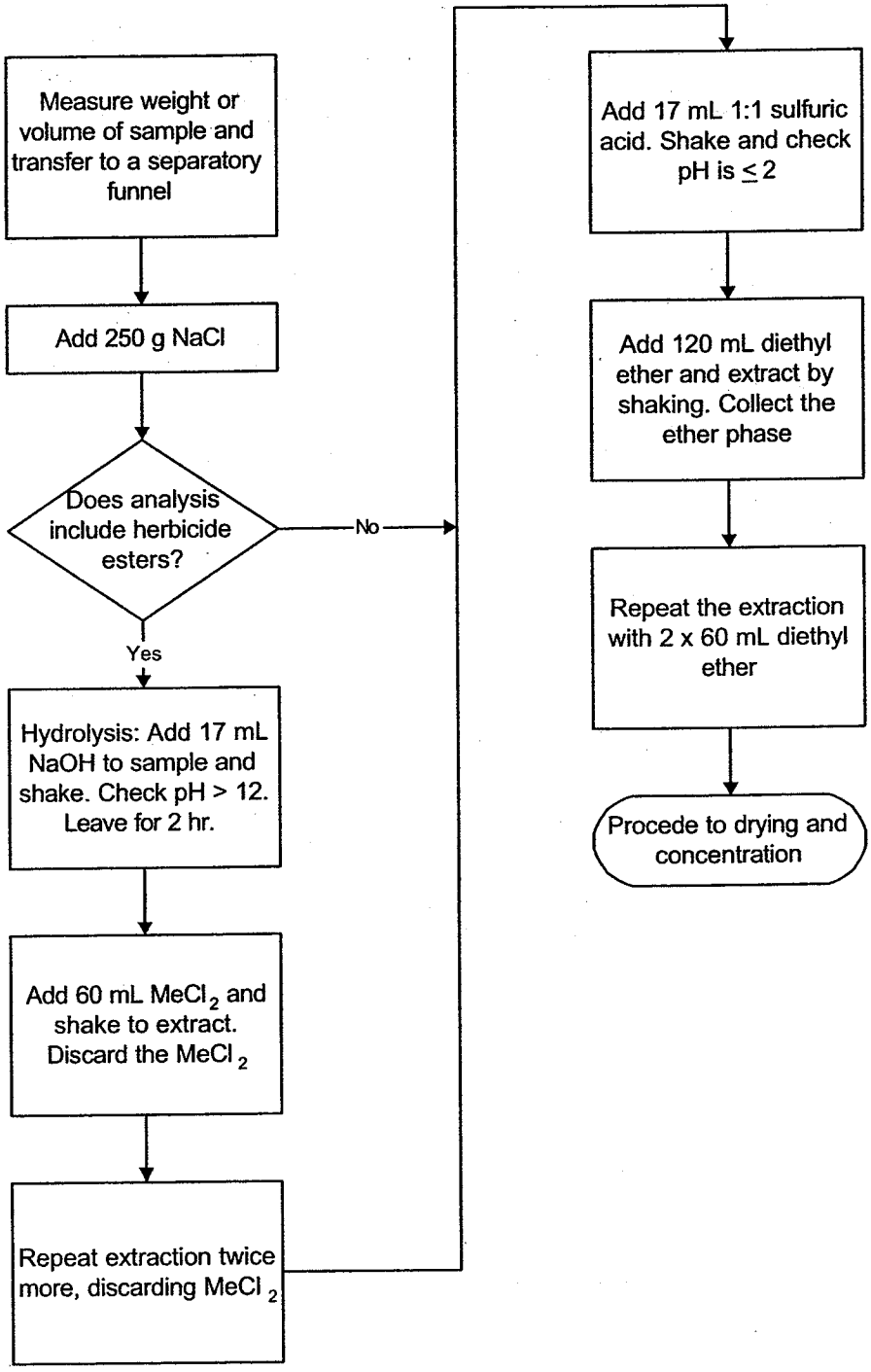
Table B4

Herbicide Matrix Spike Components

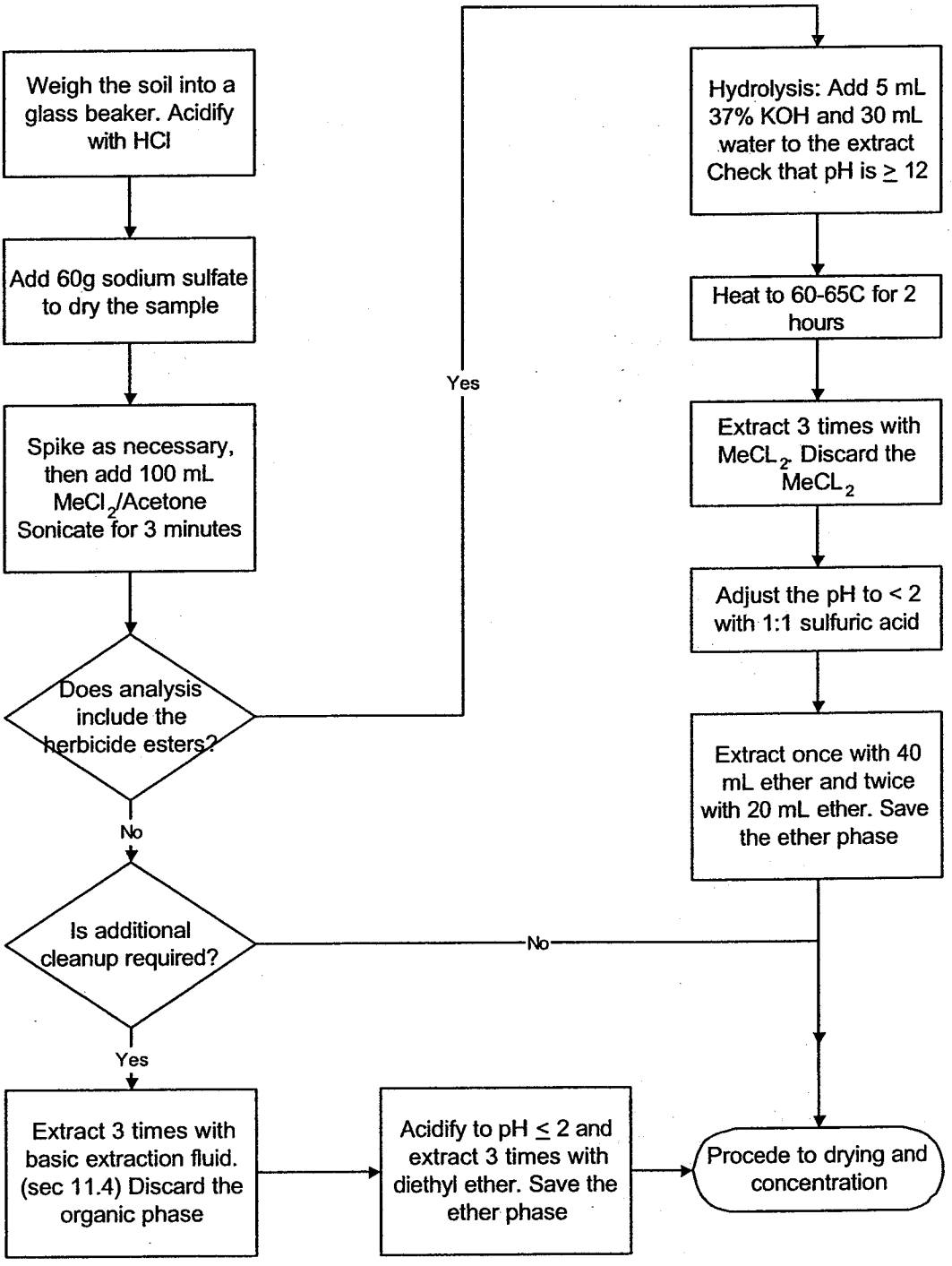
Type	Compounds[1]	Solvent	Conc. (ug/mL)
Herbicides MS	2,4-D	Methanol	16
	2,4-DB		16
	2,4,5-TP (Silvex)		4
	Dalapon		8
	2,4,5-T		4

[1]The herbicide spiking solution contains the herbicides as the free acids.

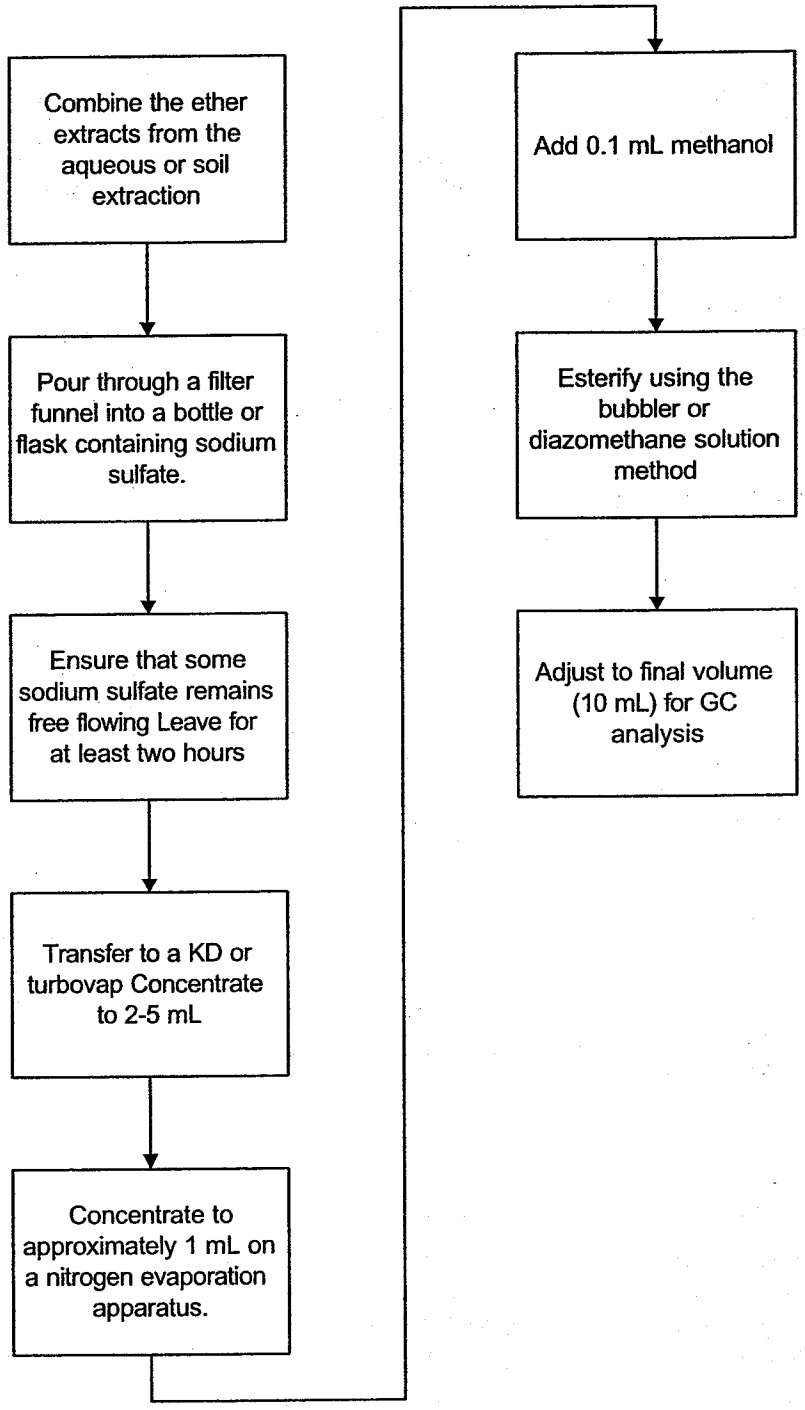
Extraction of Aqueous Samples



Extraction of Soils and Sediments



Drying, Concentration and Esterification



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SOP No: CORP-GC-0001NC
Revision No: 5.6
Revision Date: 05/25/01
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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, 608, 610 and Wisconsin DNR Modified DRO Method

(SUPERSEDES: Revision 5.5 Dated 03/16/01)

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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. Appendices B, C, and E include criteria for the analysis of wastewater by Methods 608 and 610. Appendix G describes procedures for the analysis of petroleum hydrocarbons by SW-846 methodology and the Wisconsin DNR Modified DRO method. Appendix H includes criteria for the analysis of non-halogenated organic compounds by Method 8015B, Direct Injection. Appendix I describes the analysis of Phillips 66 analytes by Method 8015B.

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-0001NCNC) Solid samples are prepared using sonication, Soxhlet or pressurized fluid extraction (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. In addition, some purge and trap autosamplers are susceptible to port specific contamination. Co-elution of target analytes with non-targets can occur, resulting in false positives or biased high results. In particular, this is a problem with non-selective detectors such as the Flame Ionization Detector (FID). See the appendices for interferences specific to individual tests and suggested corrective actions.

5. SAFETY

5.1. Procedures shall be carried out in a manner that protects the health and safety of all STL North Canton associates. The following requirements must be met:

Eye protection that prevents spalsh, 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.

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

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

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

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

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

6. EQUIPMENT AND SUPPLIES

An analytical system complete with a gas chromatograph is required. A data system capable of measuring peak area and/or height is required. Recommended equipment and supplies for individual methods are listed in each method appendix.

7. REAGENTS AND STANDARDS

7.1. Stock Standards

Stock standards are purchased as certified solutions or prepared from pure solutions. Stock standards for method 8021B are stored at -10 to -20°C. Other stock standard solutions are stored 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°C and protected from light. The standards must be replaced at least every six months or sooner if comparison with check standards indicates a problem.

7.3. Gases for carrier and make-up: Hydrogen, Helium, Nitrogen, Argon/Methane.

7.4. Quality control (QC) Standards

QC standards (matrix spiking and LCS standards) are prepared and stored in the same way as calibration standards. They must be made from a stock independent from the calibration standards.

8. SAMPLE PRESERVATION AND STORAGE

Semivolatile extracts must be refrigerated at $\leq$6°C and analyzed within 40 days of the end of the extraction. Volatile sample storage conditions and holding times are given in Appendix A.

9. QUALITY CONTROL

9.1. Initial Demonstration of Capability

9.1.1. For the standard analyte list, the initial demonstration and method detection limit (MDL) studies described in Section 13 must be acceptable before analysis of samples may begin.

9.1.2. For non-standard analytes, a MDL study must be performed and calibration curve generated before analyzing any samples, unless lesser requirements are previously agreed to with the client. In any event the minimum initial demonstration required is analysis of an extracted standard at the reporting limit and a single point calibration.

9.2. Batch Definition

Batches are defined at the sample preparation stage. Batches should be kept together through the whole analytical process as far as possible, but it is not mandatory to analyze prepared extracts on the same instrument or in the same sequence. Refer to the STL 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 must be determined for surrogates, matrix spikes, and laboratory control samples (LCS). These limits must be determined at least annually. The recovery limits are mean recovery +/- 3 standard deviations, unless that limit is tighter than the calibration criteria, in which case limits may be widened. Refer to policy QA-003 for more details.

9.3.1. These limits do not apply to dilutions (except for tests without a separate extraction), but surrogate and matrix spike recoveries will be reported unless the dilution is more than 5X.

9.3.2. All surrogate, LCS, and MS recoveries (except for dilutions) must be entered into QuantIMS (when available) or other database so that accurate historical control limits can be generated. For tests without a separate extraction, surrogates and matrix spikes will be reported for all dilutions.

9.3.3. Refer to the QC Program document (QA-003) for further details of control limits.

9.4. Surrogates

All methods must use surrogates to the extent possible. Surrogate recoveries in samples and QC samples must be assessed to ensure that recoveries are within established limits. If any surrogates are outside limits, the following corrective actions must take place (except for dilutions):

- Check all calculations for error.
- Ensure that instrument performance is acceptable.
- Recalculate the data and/or reanalyze the extract if either of the above checks reveal a problem.

- Reprepare and reanalyze the sample or flag the data as "Estimated Concentration" if neither of the above resolves the problem. Repreparation is not necessary is there is obvious chromatographic interference.
- The decision to reanalyze or flag the data should be made in consultation with the client. It is only necessary to reprepare / reanalyze a sample once to demonstrate that poor surrogate recovery is due to matrix effect, unless the analyst believes that the repeated out of control results are not due to matrix effect.

9.4.1. If dual column analysis is used the choice of which result to report is made in the same way as for samples (Section 12.1.2) unless one column is out of control, in which case the in-control result is reported.

9.4.2. If the surrogates are out of control for the sample, matrix spike, and matrix spike duplicate, then matrix effect has been demonstrated for that sample and repreparation is not necessary. If the sample is out of control and the MS and/or MSD is in control, then repreparation or flagging of the data is required.

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

9.5. Method Blanks

For each batch of samples, analyze a method blank. The method blank consists of reagent water for aqueous 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. Instrument Blanks

9.6.1. An instrument blank must be analyzed during any 12-hour period of analysis that does not contain a method blank.

9.6.2. An instrument blank consists of the appropriate solvent with internal standards added. If internal standards are not used the surrogates should be added.

9.6.3. Control criteria are the same as for the method blank, except that only reanalysis of affected samples would be required, not re-extraction.

9.7. Laboratory Control Samples (LCS)

For each batch of samples, analyze a LCS. The LCS contains a representative subset of the analytes of interest, and must contain the same analytes as the matrix spike. The LCS may also contain the full set of analytes 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 repreparation and reanalysis of the batch; however, if the matrix spike and matrix spike duplicate are within limits; the batch may be acceptable.

9.7.1. Refer to the STL North Canton QC Program document (QA-003) for further details of the corrective action.

9.7.2. If dual column analysis is used the choice of which result to report is made in the same way as for samples (Section 12.1.2) unless one column is out of control, in which case the in control result is reported.

9.7.3. LCS compound lists are included in the appendices.

9.8. Matrix Spikes

For each QC batch, analyze a matrix spike and matrix spike duplicate. Spiking compounds and levels are given in the appendices. Compare the percent recovery and relative percent difference (RPD) to those in the laboratory specific historically generated limits.

- If any individual recovery or RPD falls outside the acceptable range, corrective action must occur. The initial corrective action will be to check the recovery of that analyte in the Laboratory Control Sample (LCS). Generally, if the recovery of the analyte in the LCS is within limits, then the laboratory operation is in control and analysis may proceed.
- If the recovery for any component is outside QC limits for both the Matrix spike / spike duplicate and the LCS, the laboratory is out of control and corrective action must be taken. Corrective action will normally include repreparation and reanalysis of the batch.
- If a MS/MSD is not possible due to limited sample, then a LCS duplicate should be analyzed.
- The matrix spike / duplicate must be analyzed at the same dilution as the unspiked sample, unless the matrix spike components would then be above the calibration range.

9.8.1. If dual column analysis is used the choice of which result to report is made in the same way as for samples (Section 12.1.2) unless one column is out of control, in which case the in control result is reported.

9.9. Quality Assurance Summaries

Certain clients may require specific project or program QC that may supersede these method requirements. Quality Assurance Summaries should be developed to address these requirements.

9.10. STL North Canton QC Program

Further details of QC and corrective action guidelines are presented in the STL QC Program document (QA-003). Refer to this document if in doubt regarding corrective actions.

10. CALIBRATION AND STANDARDIZATION

Internal or external calibration may be used. Internal calibration is recommended unless the sample matrix is likely to interfere with the quantitation of the internal standard. In either event prepare standards containing each analyte of interest at a minimum of five concentration levels. The low level standard should be at or

below the reporting limit. The other standards define the working range of the detector. Recommended calibration levels are given in the appendices.

10.1. A new calibration curve must be generated after major changes to the system or when the continuing calibration criteria cannot be met. Major changes include new columns, changing PID lamps or FID jets or replacing the ECD detector. A new calibration is not required after clipping the column, replacing the septum or syringe, or other minor maintenance.

10.2. With the exception of 10.3 below, it is NOT acceptable to remove points from a calibration curve for the purpose of meeting criteria, unless the points are the highest or lowest on the curve AND the reporting limit and/or linear range is adjusted accordingly. In any event, at least 5 points must be included in the calibration curve. Quadratic (second order) calibrations require at least six points. Third order calibrations require at least seven points.

10.3. A level may be removed from the calibration if the reason can be clearly documented, for example a broken vial or no purge run. A minimum of five levels must remain in the calibration. The documentation must be retained with the initial calibration. Alternatively, if the analyst believes that a point on the curve is inaccurate, the point may be reanalyzed and the reanalysis used for the calibration. All initial calibration points must be analyzed without any changes to instrument conditions, and all points must be analyzed within 24 hours.

10.4. External standard calibration

Quantitation by the external standard method assumes a proportional relationship between the calibration run and the analyte in the sample. To use this approach, introduce each calibration standard into the GC using the technique that will be used for samples. The ratio of the peak height or area response to the mass or concentration injected may be used to prepare a calibration curve.

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

Some data systems may use the inverse of this formula. This is acceptable so long as the same formula is used for standards and samples. It is also possible to use the concentration of the standard rather than the mass injected. (This would require changes in the equations used to calculate the sample concentrations). Use of peak area or height must be consistent. However, if matrix interferences would make quantitation using peak area inaccurate for a particular sample, then peak height may be used as a substitute.

10.5. Internal standard calibration

10.5.1. The internal standard approach assumes that variations in instrument sensitivity, amount injected etc. can be corrected by determining the ratio of the response of the analyte to the response of an internal standard that has been added to the extract. To use this approach, select one or more internal standard(s) that are similar in analytical behavior to the compounds of interest. Recommended internal standards are given in the appendices. The analyst must demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. If the sample matrix interferes with quantitation of the internal standard, then the external standard approach must be used instead. In this event use the response factors from the previous continuing calibration to quantitate the analytes in the sample with the interference (applies only to the sample with the interference).

10.5.2. Introduce each calibration standard into the GC using the technique that will be used for samples. Response factors (RF) for each compound are calculated as follows:

$$RF = \frac{A_s \times C_{is}}{A_{is} \times C_s}$$

Where:

A_s = Response for the analyte to be measured
A_{is} = Response for the internal standard
C_{is} = Concentration of internal standard
C_s = Concentration of the analyte to be determined in the standard

10.6. Calibration curve fits

Average response factor, linear regression, or quadratic curves may be used to fit the data. Average response factor may be used if the average % RSD of the response factors or calibration factors of all the analytes in the calibration standard taken together is ≤ 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 ≤ 20%.

The equation for average response factor is:

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

Where: n = Number of calibration levels

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

10.6.3. Linear regression

The linear fit uses the following functions:

10.6.3.1. External Standard

$$y = ax + b$$

or

$$x = \frac{(y - b)}{a}$$

Where: y = Instrument response
x = Concentration
a = Slope
b = Intercept

10.6.3.2. Internal Standard

$$C_s = \frac{\left[\frac{A_s C_{is}}{A_{is}} - b\right]}{a}$$

Where: C_s = Concentration in the sample
A_s = Area of target peak in the sample
A_{is} = Area of internal standard in the sample
C_{is} = Concentration of the internal standard

10.6.4. Quadratic curve

The quadratic curve uses the following functions:

10.6.4.1. External standard

$$y = ax + cx^2 + b$$

Where c is the curvature

10.6.4.2. Internal Standard

$$y = a\left(\frac{A_s \times C_{is}}{A_{is}}\right) + c\left(\frac{A_s \times C_{is}}{A_{is}}\right)^2 + b$$

10.7. Evaluation of calibration curves

10.7.1. The percent relative standard error (%RSE) from the calibration curve is used to evaluate the initial calibration. This provides a measure of how much error is associated with using the calibration curve for quantitation.

10.7.2. The least squares regression line is calculated and used to calculate the predicted concentration for each level. The percent relative standard error is calculated as follows:

$$\%\ RSE = 100\% \times \sqrt{\frac{\sum_{i=1}^{N}\left[\frac{C_i - PC_i}{C_i}\right]^2}{(N-P)}}$$

Where:
N = Number of points in the curve
P = Number of parameters in the curve (= 1 for average response factor, 2 for linear, 3 for quadratic)
C_i = True concentration for level i
PC_i = Predicted concentration for level i

Note that when average response factors are used, %RSE is equivalent to %RSD.

10.8. The following requirements must be met for any calibration to be used:

- Response must increase with increasing concentration.
- If a curve is used, the intercept of the curve at zero response must be less than ± the reporting limit for the analyte.
- The average Relative Standard Error (RSD for average response factors) of the calibration points from the curve used must be ≤ 20%.
- Some data systems will not measure the %RSE from a linear or quadratic fit. For the linear case, the correlation coefficient may be used as an alternative to the %RSE, and must be greater than or equal to 0.990. For the quadratic case the Coefficient of Determination may be used, and must be greater or equal to 0.990.

Note: The Relative Standard Error (RSE) is superior to the Correlation Coefficient (r) and Coefficient of Determination (r^2) for testing the fit of a set of calibration points to a line. The lower points on a curve have little effect on r. As a result a curve may have a very good correlation coefficient (>0.995), while also having > 100% error at the low point.

10.9. Weighting of data points

10.9.1. In linear and quadratic calibration fits, the points at the lower end of the calibration curve have less absolute variance than points at the high concentration end of the curve. This can cause severe errors in quantitation at the low end of the calibration. However, in environmental analysis, accuracy at the low end of the curve is very important. For this reason it is preferable to increase the weighting of the lower concentration points. $1/Concentration^2$ weighting (often called $1/X^2$ weighting) will improve accuracy at the low end of the curve and should be used if the data system has this capability.

10.10. Non-standard analytes are sometimes requested. For these analytes, it may be acceptable to analyze a single standard at the reporting limit with each continuing calibration rather than a five point initial calibration. This action must be with client approval. If the analyte is detected in any of the samples, a five point initial calibration must be generated and the sample(s) reanalyzed for quantitation.

10.11. Calibration Verification

10.11.1. 12 hour Calibration

The working calibration curve or RF must be verified by the analysis of a mid point calibration standard at the beginning, after every 12 hours, and at the end of the analysis sequence. The center of each retention time window is updated with each 12-hour calibration or calibration verification.

10.11.2. Calibration Verification

It may be appropriate to analyze a mid point standard more frequently than every 12 hours. If these calibration verification standards are analyzed, requirements are the same as the 12-hour calibration with the exception that retention times are not updated.

10.11.3. Any individual compounds with %D < 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

% Difference for internal and external methods is calculated as follows

Internal Standard:

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

External standard:

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

Where RF_c and CF_c are the response and calibration factors from the continuing calibration

$\overline{RF}$ and $\overline{CF}$ are the average response and calibration factors from the initial calibration

10.11.10. % Drift calculation

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

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

10.11.11. Corrective Actions for Continuing Calibration

If the overall average %D of all analytes is greater than $\pm$ 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

For internal standard methods, any samples injected after a standard not meeting the calibration criteria must be re-injected.

For external standard methods, any samples injected after the last good continuing calibration standard must be re-injected.

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

Extraction procedures are referenced in the appendices.

11.2. Cleanup

Cleanup procedures are referenced in the appendices.

11.3. Gas Chromatography

Chromatographic conditions for individual methods are presented in the appendices.

11.4. Sample Introduction

In general, volatiles analytes are introduced using purge and trap as described in Appendix A. Semivolatile analytes are introduced by direct injection of the extract. Samples, standards, and QC must be introduced using the same procedure.

11.5. Analytical Sequence

An analytical sequence starts with an initial calibration or a daily calibration. Refer to the individual method appendices for method specific details of daily calibrations and analytical sequences.

11.5.1. The daily calibration includes analysis of standards containing all single response analytes and updating the retention time windows.

11.5.2. If there is a break in the analytical sequence of greater than 12 hours, a new analytical sequence must be started with a daily calibration.

11.6. Retention Time Windows

11.6.1. Retention time windows must be 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 +/- 0.05 minutes as the retention time window. 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

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:

The retention time of that compound in the standard must be within a retention time range equal to twice the original window.

No peak that would be reportable may be present on the sample chromatogram within an elution time range equal to three times the original retention time window.

11.7. Daily Retention Time Windows

The center of the retention time windows determined in Section 11.6 are adjusted to the retention time of each analyte as determined in the 12 hour calibration standards 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. Percent Moisture

Analytical results may be reported as dry or wet weight, as required by the client. Percent moisture must be determined if results will be reported as dry weight. Refer to SOP CORP-OP-0001NC for determination of percent moisture.

11.9. Procedural Variations

Procedural variations are allowed only if deemed necessary in the professional judgment of the supervisor to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo and approved by a supervisor and QA/QC manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file. The nonconformance is also addressed in the case narrative. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Qualitative Identification

12.1.1. Tentative identification occurs when a peak is found within the retention time window for an analyte, at a concentration above the reporting limit, or above the MDL if J flags are required. Normally confirmation is required on a second column, but if the detector is sufficiently specific or if the sample matrix is well enough defined, single column analysis may be adequate. In some cases GC/MS confirmation may be required. Client specific requirements may also define the need for second column confirmation and / or GC/MS confirmation. Refer to the appendices for test specific requirements for confirmation. Identification is confirmed if a peak is also present in the retention time window for that analyte on the confirmatory column, at a concentration greater than the reporting limit (MDL if J flag confirmation required).

12.1.2. Dual column quantitation

For confirmed results, two approaches are available to the analyst.
A) The primary column approach
Or
B) The better result approach
Both are acceptable to avoid the reporting of erroneous or unconfirmed data.

12.1.2.1. Primary column approach:

The result from the primary column is normally reported. The result from the secondary column is reported if any of the following three bulleted possibilities are true.

- There is obvious chromatographic interference on the primary column
- The result on the primary column is > 40% greater than the result on the secondary column
- Continuing or bracketing standard fails on the primary column but is acceptable on the secondary column. (If the primary column result is > 40% higher than the secondary and the primary column calibration fails, then the sample must be evaluated for reanalysis.)

12.1.2.2. Better result approach

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

- There is obvious chromatographic interference on the column with the lower result
- The continuing or bracketing calibration on the column with the lower result fails. (If the higher result is > 40% higher and the calibration on the column with the lower result fails, then the sample must be evaluated for reanalysis.)

12.1.3. If the Relative percent difference (RPD) between the response on the two columns is greater than 40%, or if the opinion of an experienced analyst is that the complexity of the matrix is resulting in false positives, the confirmation is suspect and the results are qualified. RPD is calculated using the following formula:

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

Where R=Result

12.1.4. Multi-response Analytes

For multi-response analytes, the analyst should use the retention time window, but should rely primarily on pattern recognition. The pattern of peaks will normally serve as confirmation.

12.1.5. The experience of the analyst should weigh heavily in the interpretation of the chromatogram. For example, sample matrix or laboratory temperature fluctuation may result in variation of retention times.

12.2. Calibration Range

If concentrations of any analytes exceed the working range as defined by the calibration standards, then the sample must be diluted and reanalyzed. Dilutions should target the most concentrated analyte in the upper half (over 50% of the high level standard) of the calibration range. It may be necessary to dilute samples due to matrix.

12.3. Dilutions

Samples may be screened to determine the appropriate dilution for the initial run. If the initial diluted run has no hits or hits below 20% of the calibration range and the matrix allows for analysis at a lesser dilution, then the sample must be reanalyzed at a dilution targeted to bring the largest hit above 50% of the calibration range.

12.3.1. Guidance for Dilutions Due to Matrix

If the sample is initially run at a dilution and only minor matrix peaks are, then the sample should be reanalyzed at a more concentrated dilution. Analyst judgement is required to determine the most concentrated dilution that will not result in instrument contamination.

12.3.2. Reporting Dilutions

The most concentrated dilution with no target compounds above the calibration range will be reported. Other dilutions 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

If peak detection is prevented by interferences, further cleanup should be attempted. If no further cleanup is reasonable, then elevation of reporting levels and/or lack of positive identification must be addressed in the case narrative.

12.5. Internal Standard Criteria for Continuing Calibration

If internal standard calibration is used, then the internal standard response in a continuing calibration standard must be within 50 to 150% of the response in the mid level of the initial calibration.

12.6. Calculations

Capabilities of individual data systems may require the use of different formulas than those presented here. When this is the case, the calculations used must be shown to be equivalent and must be documented in an appendix attached to this document.

12.6.1. External Standard Calculations

12.6.1.1. Aqueous samples

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

Where:

A_x = Response for the analyte in the sample
V_i = Volume of extract injected, µL
D_f = Dilution factor
V_t = Volume of total extract, µL
V_s = Volume of sample extracted or purged, mL
CF = Calibration factor, area or height/ng, Section 10.1

12.6.1.2. Non-aqueous Samples

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

Where:

W = Weight of sample extracted or purged, g

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

12.6.2. Internal Standard Calculations

12.6.2.1. Aqueous Samples

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

Where:

C_{is} = Amount of internal standard added, ng
A_{is} = Response of the internal standard
RF = Response factor for analyte

12.6.2.2. Non-aqueous Samples

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

12.6.3. Surrogate Recovery

Concentrations of surrogate compounds are calculated using the same equations as for the target compounds. The response factor from the initial calibration is used. Surrogate recovery is calculated using the following equation:

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

13. METHOD PERFORMANCE

13.1. Method Detection Limit

Each laboratory must generate a valid method detection limit for each analyte of interest. The MDL must be below the reporting limit for each analyte. The procedure for determination of the method detection limit is given in 40 CFR Part 136, Appendix B, and further defined in QA Policy #: QA-005.

13.2. Initial Demonstration

Each laboratory must make a one time initial demonstration of capability for each individual method. Demonstration of capability for both soils and water matrices is required. This requires analysis of QC check samples containing all of the standard analytes for the method. For some tests it may be necessary to use more than one QC check mix to cover all analytes of interest.

13.2.1. Four aliquots of the QC check sample are analyzed using the same procedures used to analyze samples, including sample preparation. The concentration of the QC check sample should be equivalent to a mid-level calibration.

13.2.2. Calculate the average recovery and standard deviation of the recovery for each analyte of interest. Compare these results with the acceptance criteria given in each appendix.

13.2.3. If any analyte does not meet the acceptance criteria, the test must be repeated. Only those analytes that did not meet criteria in the first test need to be evaluated. Repeated failure for any analyte indicates the need for the laboratory to evaluate the analytical procedure and take corrective action.

13.3. Training Qualification

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

14. POLLUTION PREVENTION

This method does not contain any specific modifications that serve to minimize or prevent pollution.

15. WASTE MANAGEMENT

Waste generated in this procedure will be segregated and disposed according to the facility hazardous waste procedures. The Environmental Health and Safety Director should be contacted if additional information is required.

16. REFERENCES

Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW846, 3rd Edition, Final Update III, December 1996, 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. Modifications from Previous Revision

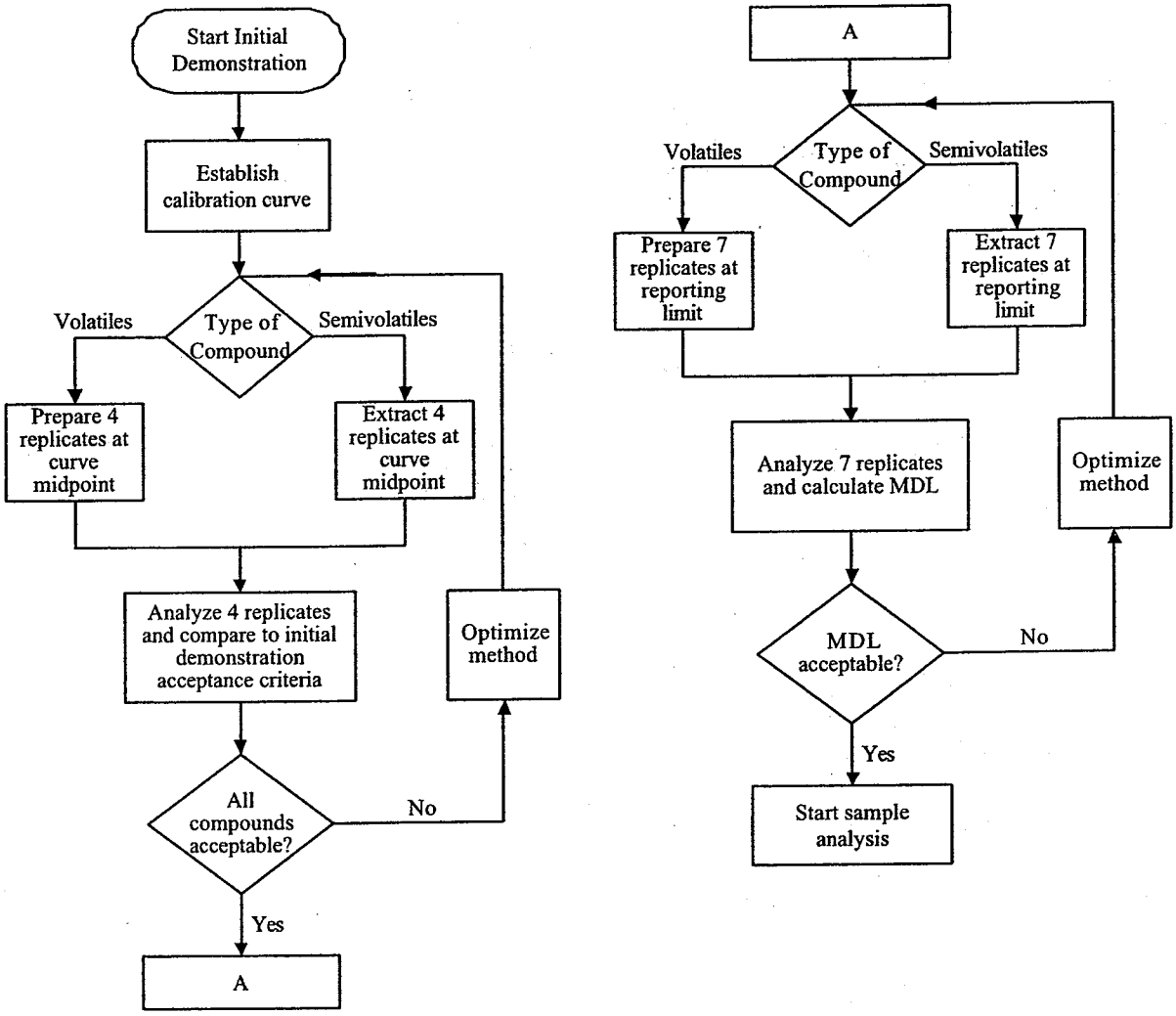
The calibration criteria in section 10.11 have been rewritten to improve consistency with SW-846 and to improve clarity.

17.3. Facility Specific SOPs

Each facility shall attach a list of facility specific SOPs or approved attachments (if applicable) which are required to implement this SOP or which are used in conjunction with this SOP. If no facility specific SOPs or amendments are to be attached, a statement must be attached specifying that there are none.

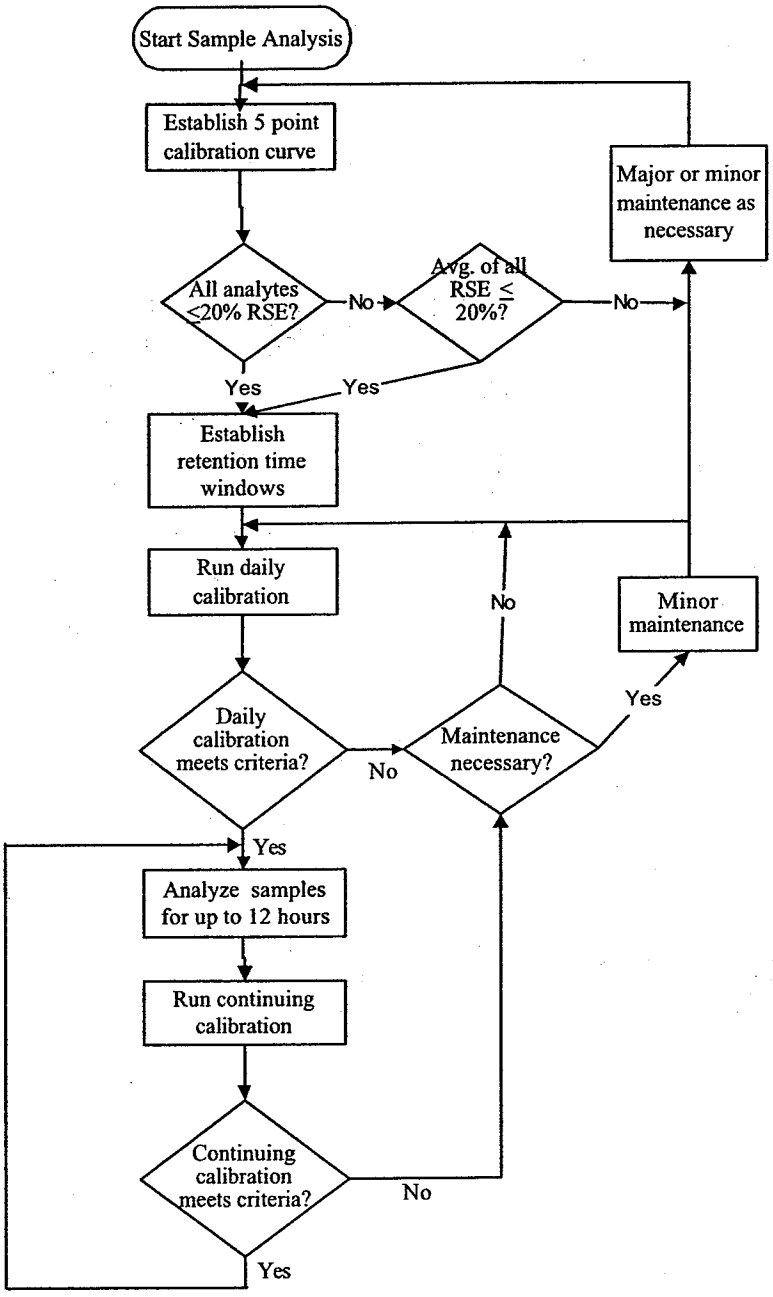
17.4. Flow Diagrams

17.4.1. Initial demonstration and MDL[1]



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

17.4.2. Sample Analysis [1]



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

1. SCOPE AND APPLICATION

1.1. This method describes sample preparation and extraction for the analysis of volatile organics by a purge and trap procedure, following method 8021B. However, where required by a client QAPP this section may also be used to analyze aromatic volatiles by discontinued methods 8020A and 8010B. All requirements of the 8000B section of this SOP must be met except when superseded by this Appendix. Refer to Table A-1 for the individual analytes normally determined by these procedures.

1.2. Compounds within the scope of this method have boiling points below 200°C and are soluble or slightly soluble in water. Classes of compounds best suited to purge-and-trap analysis include low molecular weight halogenated hydrocarbons, aromatics, ketones, nitriles, acetates, acrylates, ethers, and sulfides.

1.3. Water samples and soils samples with low levels of contamination may be analyzed directly by purge-and-trap extraction and gas chromatography. Higher concentrations of these analytes in soil may be determined by the medium level methanol extraction procedure.

1.4. This method also describes the preparation of water-miscible liquids, non-water-miscible liquids, solids, wastes, and soils/sediments for analysis by the purge-and-trap procedure.

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

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. When utilizing an autosampler system, which has multiple ports for sample analysis, it is likely that only a single stage or port may be contaminated by a highly concentrated sample. If a port is suspect, a water blank should be analyzed to verify lack of contamination. If the water blank and subsequent blanks on that port show contamination consistent with the concentrated sample, further maintenance is required. This may include replacing or cleaning the multi-port valve, transfer lines, etc.

4.6. A holding blank is kept in the sample refrigerator. This is analyzed and replaced every 14 days. If the holding blank does not meet the method blank criteria, the source of contamination must be found and corrected. Evaluation of all samples analyzed in the 14-day period prior to the analysis of the contaminated holding blank is required.

4.7. Acidification of samples may result in hydrolysis of 2-chloroethyl-vinyl ether.

5. SAFETY

5.1. Refer to section 5 of the Method 8000B section of this SOP for general safety requirements.

5.2. Often, purge vessels on purge-and-trap instrumentation are pressurized by the time analysis is completed. Therefore, vent the pressure prior to removal of these vessels to prevent the contents from spraying out.

5.3. The toxicity or carcinogenicity of each chemical used in this procedure has not been fully defined. Additional health and safety information can be obtained from the MSDS files maintained in the laboratory. The following specific hazards are known:

Methanol -- Flammable and toxic

5.4. 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.

5.5. Methanol shall not be used in a CaptAir hood.

6. EQUIPMENT AND SUPPLIES

6.1. Microsyringes -- 10µL, 25µL, 100µL, 250µL, 500µL, and 1000µL. These should be equipped with a 20 gauge (0.006" ID) needle. These will be used to measure and dispense methanolic solutions and aqueous samples.

6.2. Gas tight syringes -- 5 mL and 25 mL. Used for measuring sample volumes.

6.3. Purge and Trap Apparatus -- A device capable of extracting volatile compounds, trapping on a sorbent trap, and introducing onto a gas chromatograph.

6.4. Purge and Trap Autosampler -- In order to maintain high sample throughput, an autosampler is highly recommended.

6.5. Trap -- The trap used is dependent on the class of compound to be analyzed. Refer to Table A-2 for suggested traps for specific tests.

6.6. Purge Vessels -- These are dependent on the purge and trap unit/autosampler used. Both disposable culture tubes (needle sparge units) and specially designed vessels with fritted bottoms may be used. Follow the manufacturer's suggestions for configuration.

6.7. Columns - Refer to Table A-2 for details of columns.

6.8. Volumetric flasks, Class A: 5 mL to 250 mL

6.9. pH paper

6.10. Balance capable of weighing to 0.01g for samples.

7. REAGENTS AND SUPPLIES

7.1. Refer to the method 8000B section of this SOP for general requirements for reagents and supplies.

7.2. Organic Free Water

Organic free water is defined as water in which an interferent is not observed at the reporting limit of the compounds of interest. Suggested methods for generating organic free water include:

- Filtration through a carbon bed.
- Continuously sparging water with helium or nitrogen.
- Use of commercial water purification systems.

Other methods may be used, so long as the requirement that the water show no interference is met. The procedure used should be documented in a lab specific attachment.

7.3. Sodium Bisulfate

7.4. Methanol -- Purge and Trap Grade

7.5. Standards

Refer to tables A-5 and A-6 for details of surrogate, matrix spiking and internal standards. Calibration standard levels are not specified, since they may depend on the sensitivity and linear range of specific detectors. However, the low level standard must be equivalent to the reporting limits specified in Table A-1.

7.5.1. Volatile standards are prepared by injecting a measured volume of the stock standard into a syringe containing the appropriate volume of organic free water. The calibration standard is then loaded into the purge device.

8. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1. Holding times for all volatile analysis are 14 days from sample collection.

8.2. Water samples are normally preserved at pH < 2 with 1:1 hydrochloric acid. If residual chlorine is present, 2 drops of 10% sodium thiosulfate are added.

8.3. Solid samples are field preserved with sodium bisulfate solution for low level analysis, or with methanol for medium level analysis. Soil samples can also be taken using the EnCore™ sampler and preserved in the lab within 48 hours of sampling. At specific client request, unpreserved soil samples may be accepted.

8.4. There are several methods of sampling soil. The recommended method, which provides the minimum of field difficulties, is to take an EnCore sample. (The 5 g or 25 g sampler can be used, depending on client preference). Following shipment back to the lab the soil is preserved in methanol. This is the medium level procedure. If very low detection limits are needed (< 50 µg/kg for most analytes) then it will be necessary to use two additional 5 g EnCore samplers or to use field preservation.

8.5. Sample collection for medium level analysis using EnCore samplers.

8.5.1. Ship one 5 g (or 25 g) EnCore sampler per field sample position.

8.5.2. An additional bottle must be shipped for percent moisture determination.

8.5.3. When the samples are returned to the lab, extrude the (nominal) 5g (or 25 g) sample into a tared VOA vial containing 5 mL methanol (25 mL methanol for the 25 g sampler). Obtain the weight of the soil added to the vial and note on the label.

8.5.4. Add the correct amount of surrogate spiking mixture. (Add 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 ≥ -10°C until analysis.

8.7.9. Alternatively the sodium bisulfate preservation may be performed in the field. Ship at least two vials per sample. The field samplers must determine the weight of soil sampled. Each sample will require an additional bottle with no preservative for percent moisture determination, and an additional bottle preserved with methanol for the medium level procedure.

8.8. Aqueous samples are stored in glass containers with Teflon lined septa at 4°C +/- 2°C, with minimum headspace.

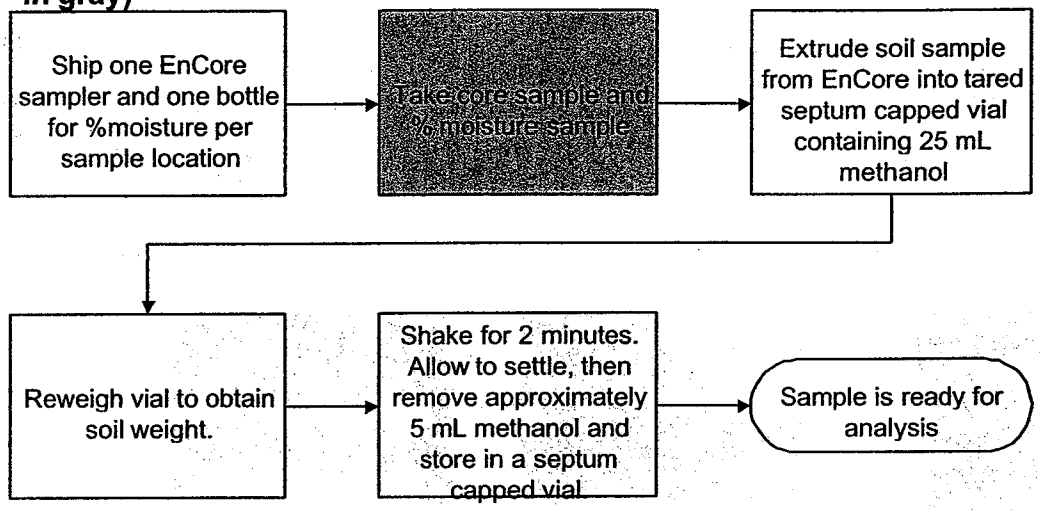
8.9. Medium level solid extracts are aliquoted into 2 - 5 mL glass vials with Teflon lined caps and stored at 4°C +/- 2°C. The extracts are stored with minimum headspace.

8.10. The maximum holding time is 14 days from sampling until the sample is analyzed. (Samples that are found to be unpreserved still have a 14 day holding time. However they should be analyzed as soon as possible. The lack of preservation should be addressed in the case narrative). Maximum holding time for the EnCore sampler (before the sample is added to methanol or sodium bisulfate) is 48 hours.

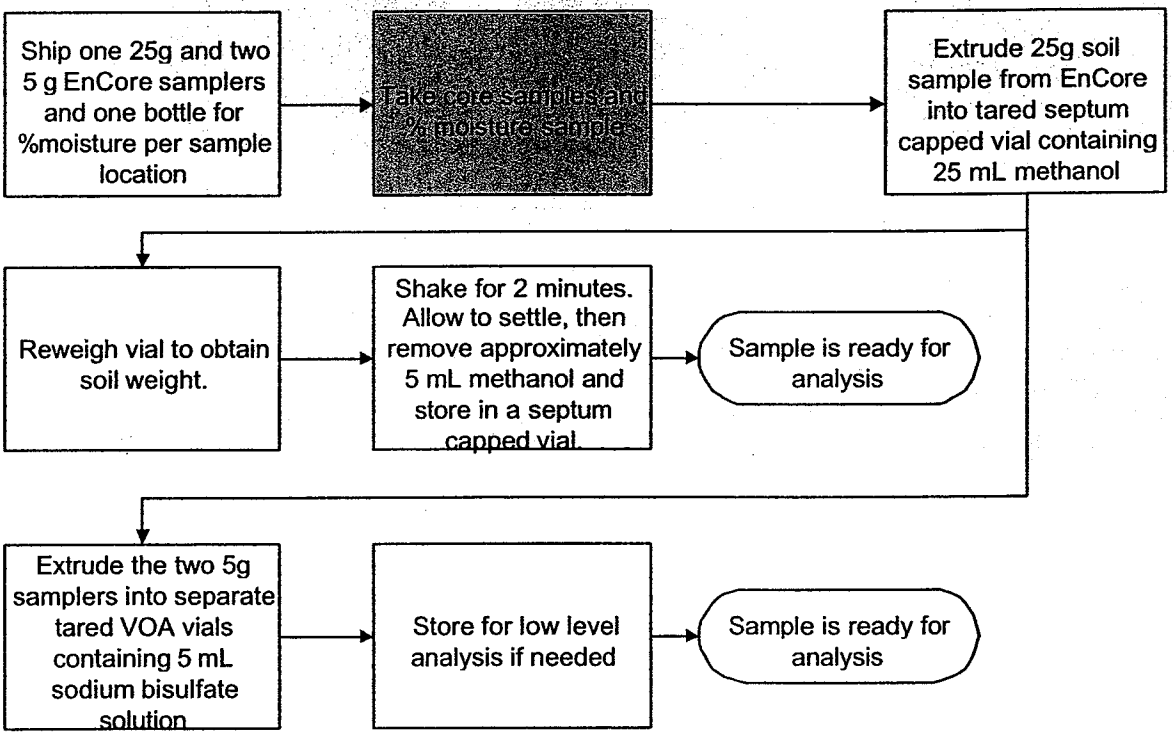
8.11. A holding blank is stored with the samples. This is analyzed and replaced if any of the trip blanks show any contamination. Otherwise it is replaced every 14 days.

Note: Freezing is not allowed for Ohio VAP solids.

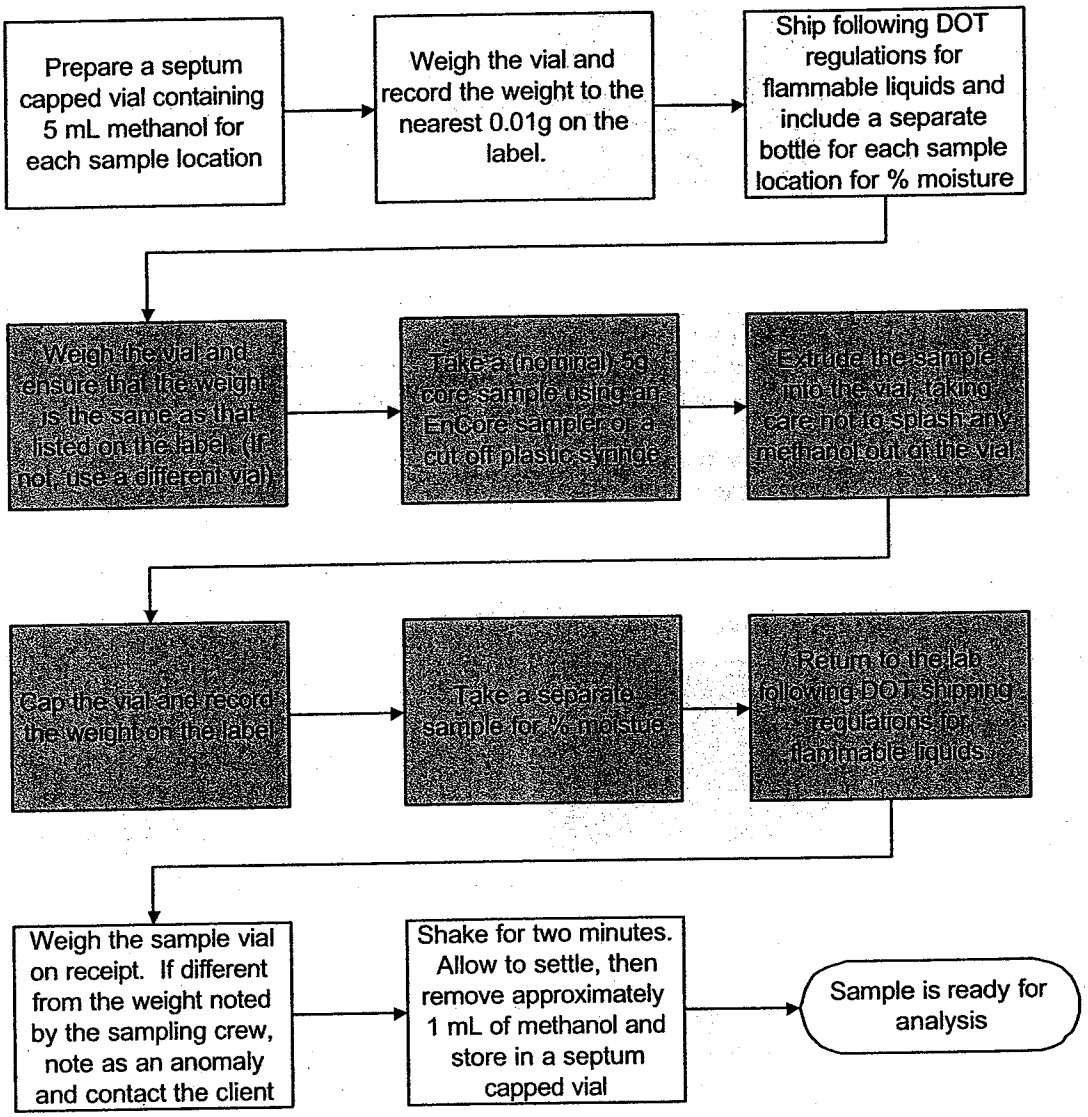
EnCore procedure when low level is not required (field steps in gray)



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. In addition, the low level soil calibration solutions should contain approximately the same amount of sodium bisulfate as the samples.

10.3.3. The low level calibration must be at the reporting limit or below. The remaining standards encompass the working range of the detector.

10.3.4. Calibrate the instrument using the same volume that will be used during sample analysis.

10.4. Calibration Verification

10.4.1. A mid level calibration standard is used for the calibration verification. The gases have 20 % D criteria rather than the 15% used for other analytes.

10.4.2. A calibration verification run is performed after every 10 samples for this method.

10.4.3. Bracketing of samples with calibration verification runs is only necessary for external standard analysis.

11. PROCEDURE

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

11.2. Analytical Sequence

The analytical sequence starts with an initial calibration of at least five points, or a 12 hour calibration that meets % difference criteria from an existing initial calibration.

11.3. Confirmation

The PID and ELCD detectors are sufficiently selective that second column confirmation is not always necessary. Requirements for second column confirmation should be decided in consultation with the

client. If the PID and ELCD are used in series confirmatory information for many analytes can be gained by comparing the relative response from the two detectors.

11.4. Aqueous Sample Analysis (Purge and Trap units using sparge vessels)

11.4.1. Depending on the sensitivity of the instrument and capabilities of the purge and trap device, 5, 10, 20, or 25 mL sample volumes may be analyzed. A 5 mL sample volume is recommended.

11.4.2. Rinse a 5 mL (or 25 mL for larger sample volumes) gas-tight syringe with organic free water. Fill the syringe with the sample to be analyzed, and compress to volume.

11.4.3. Check and document the pH of the sample remaining in the VOA vial after loading the syringe.

11.4.4. This procedure invalidates the contents of the VOA vial for further analysis, unless an aliquot is transferred to a smaller VOA vial with no headspace (e.g., 20 mL) at the same time the analysis aliquot is removed.

11.4.5. Spike with the appropriate volume of surrogate/internal standard solution and spike solution (if required) through the barrel of the syringe. The method blank is spiked with surrogates only, the LCS and matrix spikes with the surrogate and matrix spiking solutions. Refer to Tables A-5 and A-6 for volumes and concentrations of spiking solutions.

11.4.6. Load onto the purge and trap device and start the run.

11.4.7. If the initial analysis of a sample or a dilution of the sample has a concentration of analytes that exceeds the initial calibration range, the sample must be reanalyzed at a higher dilution. When a sample has a high response for a compound, an organic free water blank should follow analysis. It is recognized that during automated unattended analysis, this may not occur. If any potential carryover hits are present in samples following highly contaminated samples, the sample must be reanalyzed to determine if any of these hits are a result of carryover or are actually present in the sample.

11.4.8. Dilutions may be made in gas tight syringes unless the volume of sample used is less than 5 µL, in which case dilution in volumetric flasks will be necessary.

11.4.8.1. Spike with the same volume of surrogate/internal standard solution as used for undiluted samples prior to loading onto the purge and trap device.

11.4.8.2. For Matrix spike / matrix spike duplicates where the sample requires dilution, the sample is spiked after the dilution is performed.

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

11.5.1. Units, which sample from the VOA vial, should be equipped with a module, which automatically adds surrogate and internal standard solution to the sample prior to purging the sample.

11.5.2. If the autosampler uses automatic IS/SS injection, no further preparation of the VOA vial is needed. Otherwise the internal and surrogate standards must be added to the vial. *Note:* Aqueous samples with high amounts of sediment present in the vial may not be suitable for analysis on this instrumentation, or they may need to analyzed as soils.

11.5.3. Sample remaining in the vial after sampling with one of these mechanisms is no longer valid for further analysis. A fresh VOA vial must be used for further sample analysis.

11.5.4. Check the pH of the sample remaining in the VOA vial after analysis is completed.

11.6. Low-Level Solids Analysis using discrete autosamplers

Note: This technique may seriously underestimate analyte concentration and must not be used except at specific client request for the purpose of comparability with previous data. It is no longer part of SW-846.

This method is based on purging a heated sediment/soil sample mixed with reagent water containing the surrogate and, if applicable, internal and matrix spiking standards. Analyze all reagent blanks and standards under the same conditions as the samples (e.g., heated). The calibration curve is also heated during analysis. Purge temperature is 40°C.

11.6.1. Do not discard any supernatant liquids. Mix the contents of the container with a narrow metal spatula.

11.6.2. Weigh out 5 g (or other appropriate aliquot) of sample into a disposable culture tube or other purge vessel. Record the weight to the nearest 0.1 g. If method sensitivity is demonstrated, a smaller aliquot may be used. Do not use aliquots less than 1.0 g. If the sample is contaminated with analytes such that a purge amount less than 1.0 g is appropriate, use the medium level method described in section 11.7.

11.6.3. Connect the purge vessel to the purge and trap device.

11.6.4. Rinse a 5 mL gas-tight syringe with organic free water, and fill. Compress to 5 mL. Add surrogate/internal standard (and matrix spike solutions if required.) (See Tables A-5, A-6, A-7 and A-8.) Add directly to the sample from 11.6.2.

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

11.6.6. Add the heater jacket or other heating device and start the purge and trap unit.

11.6.7. Soil samples that have low IS recovery when analyzed (<50%) should be reanalyzed once to confirm matrix effect. If external standard calibration is used, samples with surrogate recovery below the control limit should be reanalyzed once to confirm matrix effect.

11.7. Methanol Extract Soils

11.7.1. Rinse a gas-tight syringe with organic free water. Fill the syringe with the same volume of organic free water as used in the calibrations. Add no more than 2% (v/v) (100 µL for a 5 mL purge) methanolic extract (from Section 8.5 or 8.6) to the syringe. Add internal standard (if used). Load the sample onto the purge and trap device and analyze as for aqueous samples. If less than 5µL of methanolic extract is to be added to the water, dilute the methanolic extract such that a volume greater than 5µL will be added to the water in the syringe.

12. DATA ANALYSIS AND CALCULATIONS

Refer to section 12 of the 8000B section of this SOP.

13. METHOD PERFORMANCE

13.1. Performance limits for the four replicate initial demonstration of capability required under Section 13.1 of the 8000B section of this SOP.

14. POLLUTION PREVENTION

This method does not contain any specific modifications that serve to minimize or prevent pollution.

15. WASTE MANAGEMENT

15.1. Waste generated in this procedure will be segregated and disposed according to the facility hazardous waste procedures. The Environmental Health and Safety Director should be contacted if additional information is required.

16. REFERENCES

16.1. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW846, 3rd Edition, Final Update III, December 1996, Sections 5000, 5030B, 5035 and 8021B

17. MISCELLANEOUS

17.1. Modifications from Reference Method

17.2. Modifications from previous revision

17.2.1. No revisions were made to this appendix.

17.3. Facility Specific SOPs

Each facility shall attach a list of facility specific SOPs or approved attachments (if applicable) which are required to implement this SOP or which are used in conjunction with this SOP. If no facility specific SOPs or amendments are to be attached, a statement must be attached specifying that there are none.

17.4. Tables

Table A-1

Standard Analyte List

Test	Compound	CAS number	Reporting Limit, µg/L or µg/kg		
			Aqueous	Low Soil	Medium Soil
Halogenated volatiles by 8021B	Bromodichloromethane	75-27-4	1.0	1.0	50
	Bromoform	75-25-2	1.0	1.0	50
	Bromomethane	74-83-9	1.0	1.0	50
	Carbon Tetrachloride	56-23-5	1.0	1.0	50
	Chlorobenzene	108-90-7	1.0	1.0	50
	Chloroethane	70-00-3	1.0	1.0	50
	2-Chloroethyl vinyl ether	110-75-8	5.0	5.0	250
	Chloroform	67-66-3	1.0	1.0	50
	Chloromethane	74-87-3	1.0	1.0	50
	Dibromochloromethane	124-48-1	1.0	1.0	50
	1,2-Dichlorobenzene	95-50-1	1.0	1.0	50
	1,3-Dichlorobenzene	541-73-1	1.0	1.0	50
	1,4-Dichlorobenzene	106-46-7	1.0	1.0	50
	Dichlorodifluoromethane	75-71-8	1.0	1.0	50
	1,1-Dichloroethane	75-34-3	1.0	1.0	50
	1,2-Dichloroethane	107-06-2	1.0	1.0	50
	1,1-Dichloroethene	75-45-4	1.0	1.0	50
	cis-1,2 Dichloroethene	156-59-4	1.0	1.0	50
	trans-1,2-Dichloroethene	156-60-5	1.0	1.0	50
	Dichloromethane(DCM)	75-09-2	5.0	5.0	250
	1,2-Dichloropropane	78-87-5	1.0	1.0	50
	cis-1,3-Dichloropropene	10061-01-5	1.0	1.0	50
	trans-1,3-Dichloropropene	10061-02-6	1.0	1.0	50
	1,1,2,2-Tetrachloroethane	79-34-5	1.0	1.0	50
	Tetrachloroethene	127-18-4	1.0	1.0	50
	1,1,1-Trichloroethane	71-55-6	1.0	1.0	50
	1,1,2-Trichloroethane	79-00-5	1.0	1.0	50
	Trichloroethene	79-01-6	1.0	1.0	50
	Trichlorofluoromethane	75-69-4	1.0	1.0	50
	Vinyl Chloride	75-01-4	1.0	1.0	50
Additional halogenated volatiles	Benzyl Chloride	100-44-7	5.0	5.0	250
	Bromobenzene	108-86-1	1.0	1.0	50
	Dibromomethane	74-95-3	1.0	1.0	50
	1,1,1,2-Tetrachloroethane	630-20-6	1.0	1.0	50
	Freon 113	76-13-1	1.0	1.0	50
	1,2,3-Trichloropropane	96-18-4	1.0	1.0	50
BTEX by 8021B	Benzene	71-43-2	1.0	1.0	50
	Ethyl Benzene	100-41-4	1.0	1.0	50
	Toluene	108-88-3	1.0	1.0	50
	Xylenes (total)	1330-20-7	1.0	1.0	50
Aromatic	Benzene	71-43-2	1.0	1.0	50

Table A-1

Standard Analyte List

Test	Compound	CAS number	Reporting Limit, µg/L or µg/kg		
			Aqueous	Low Soil	Medium Soil
volatiles by 8021B					
	Chlorobenzene	108-90-7	1.0	1.0	50
	1,2-Dichlorobenzene	75-34-3	1.0	1.0	50
	1,3-Dichlorobenzene	107-06-2	1.0	1.0	50
	1,4-Dichlorobenzene	75-45-4	1.0	1.0	50
	Ethyl Benzene	100-41-4	1.0	1.0	50
	Toluene	108-88-3	1.0	1.0	50
	Xylenes (total)	1330-20-7	1.0	1.0	50
Additional aromatic and unsaturated volatiles	1,2,4 Trimethylbenzene	95-63-6	1.0	1.0	50
	1,3,5 Trimethylbenzene	108-67-8	1.0	1.0	50
	Acetone	67-64-1	10	10	500
	MEK (2-butanone)	78-93-3	5.0	5.0	250
	MIBK (4-methyl-2-pentanone)	108-10-1	5.0	5.0	250
	Naphthalene	91-20-3	2.0	2.0	250
	Styrene	100-42-5	1.0	1.0	50
	Methyl tert-butyl ether (MTBE)	1634-04-4	1.0	1.0	50
Combined halogenated and aromatic volatiles by 8021B	Benzene	71-43-2	1.0	1.0	50
	Bromobenzene	108-86-1	1.0	1.0	50
	Bromochloromethane	74-97-5	1.0	1.0	50
	Bromodichloromethane	75-27-4	1.0	1.0	50
	Bromoform	75-25-2	1.0	1.0	50
	Bromomethane	74-83-9	1.0	1.0	50
	n-butylbenzene	104-51-8	1.0	1.0	50
	sec-Butylbenzene	135-98-8	1.0	1.0	50
	tert-Butylbenzene	98-06-6	1.0	1.0	50
	Carbon Tetrachloride	56-23-5	1.0	1.0	50
	Chlorobenzene	108-90-7	1.0	1.0	50
	Chlorodibromomethane	124-48-1	1.0	1.0	50
	Chloroethane	75-00-3	1.0	1.0	50
	Chloroform	67-66-3	1.0	1.0	50
	Chloromethane	74-87-3	1.0	1.0	50
	2-Chlorotoluene	95-49-8	1.0	1.0	50
	4-Chlorotoluene	106-43-4	1.0	1.0	50
	1,2-Dibromo-3-Chloropropane(DBCP)	96-12-8	1.0	1.0	50
	1,2-Dibromoethane(EDB)	106-93-4	1.0	1.0	50
	Dibromomethane	74-95-3	1.0	1.0	50
	1,2-Dichlorobenzene	95-50-1	1.0	1.0	50
	1,3-Dichlorobenzene	541-73-1	1.0	1.0	50
	1,4-Dichlorobenzene	106-46-7	1.0	1.0	50
	Dichlorodifluoromethane	75-71-8	1.0	1.0	50
	1,1-Dichloroethane	75-34-3	1.0	1.0	50
	1,2-Dichloroethane	107-06-2	1.0	1.0	50
	1,1-Dichloroethene	75-35-4	1.0	1.0	50

Table A-1
Standard Analyte List

Test	Compound	CAS number	Reporting Limit, µg/L or µg/kg		
			Aqueous	Low Soil	Medium Soil
	cis-1,2-Dichloroethene	156-59-4	1.0	1.0	50
	trans-1,2-Dichloroethene	156-60-5	1.0	1.0	50
	1,2-Dichloropropane	78-87-5	1.0	1.0	50
	1,3-Dichloropropane	142-28-9	1.0	1.0	50
	2,2-Dichloropropane	590-20-7	1.0	1.0	50
	1,1-Dichloropropene	563-58-6	1.0	1.0	50
	cis-1,3-Dichloropropene	10061-01-5	1.0	1.0	50
	trans-1,3-Dichloropropene	10061-02-6	1.0	1.0	50
	Ethylbenzene	100-41-4	1.0	1.0	50
	Hexachlorobutadiene	87-68-3	1.0	1.0	50
	Isopropylbenzene	98-82-8	1.0	1.0	50
	p-Isopropyltoluene	99-87-6	1.0	1.0	50
	Methylene Chloride	75-09-2	5.0	5.0	250
	Naphthalene	91-20-3	2.0	2.0	250
	n-Propylbenzene	10306501	1.0	1.0	50
	Styrene	100-42-5	1.0	1.0	50
	1,1,1,2-Tetrachloroethane	630-20-6	1.0	1.0	50
	1,1,2,2-Tetrachloroethane	79-34-5	1.0	1.0	50
	Tetrachloroethene	127-18-4	1.0	1.0	50
	Toluene	108-88-3	1.0	1.0	50
	1,2,3-Trichlorobenzene	87-61-6	1.0	1.0	50
	1,2,4-Trichlorobenzene	120-82-1	1.0	1.0	50
	1,1,1-Trichloroethane	71-55-6	1.0	1.0	50
	1,1,2-Trichloroethane	79-00-5	1.0	1.0	50
	Trichloroethene	79-01-6	1.0	1.0	50
	Trichlorofluoromethane	75-69-4	1.0	1.0	50
	1,2,3-Trichloropropane	96-18-4	1.0	1.0	50
	1,2,4-Trimethylbenzene	95-63-6	1.0	1.0	50
	1,3,5-Trimethylbenzene	108-67-8	1.0	1.0	50
	Vinyl Chloride	75-01-4	1.0	1.0	50
	Xylenes (total)	1330-20-7	1.0	1.0	50

Table A-2
Recommended Conditions for Aromatic Volatiles

Parameter	Recommended Conditions
Temperature program	50°C, 1min, 10°C/min to 200°C,1min
Column 1	Rtx-502.2 or DB-502.2 60m x 0.53mm 3.0um
Column 2	Rtx-1 or DB-1 60m x 0.53mm 3.0 um
Carrier gas	Helium or hydrogen
Purge Flow / time	40 mL/min, 11 minutes
Desorb Temp / time	180°C, 2 minutes (220°C for Vocarb 3000)
Bake Time / temp	200°C, 12 minutes (230°C for Vocarb 3000)
Transfer line / valve temp	115°C

Table A-3 Recommended Conditions for Method Halogenated Volatiles	
Parameter	Recommended Conditions
Temperature program	35°C, 12 min, then 4°C/min to 200°C, hold for 5 min
Column 1	DB-VRX or RTX-502.2 105m x 0.53 mm id df = 3.0um
Column 2	DB-1 or RTX-1 105m x 0.53 mm ID df = 3.0um
Column 3	Rtx - Volatiles 120m x 0.53mm ID df=2.0um
Carrier gas	Helium
Purge Flow / time	40 mL/min, 11 minutes
Desorb Temp / time	180°C, 2 minutes (220°C for Vocarb 3000)
Bake Time / temp	200°C, 12 minutes (230°C for Vocarb 3000)
Transfer line / valve temp	115°C

Table A-4 Recommended Conditions for Method Combined Aromatic and Halogenated Volatiles	
Parameter	Recommended Conditions
Temperature program	35°C, 12 min, then 4°C/min to 200°C, hold for 5 min
Column 1	DB-VRX or RTX-502.2 105m x 0.53 mm id df = 3.0um
Column 2	DB-1 or RTX-1 105m x 0.53 mm ID df = 3.0um
Column 3	Rtx - Volatiles 120m x 0.53mm ID df=2.0um
Carrier gas	Helium
Purge Flow / time	40 mL/min, 11 minutes
Desorb Temp / time	180°C, 2 minutes (220°C for Vocarb 3000)
Bake Time / temp	200°C, 12 minutes (230°C for Vocarb 3000)
Transfer line / valve temp	115°C

Table A-5
Surrogate and Internal Standard Concentrations

Standard	Components	Working Solution µg/mL	Spike amount µL (for 5 mL purge)	Final concentration µg/L (µg/kg)
Aromatic volatiles IS/SS	4-Chlorotoluene (SS) 1-Chloro-4-fluorobenzene (IS)	20 40	5	20 40
Halogenated volatiles IS/SS	4-chlorotoluene (SS) 1-Chloro-4-fluorobenzene (IS)	20 40	5	20 40
Combined Aromatic and halogenated volatiles IS/SS	Fluorobenzene (SS)	20	5	20
	1,4-Dichlorobutane (SS)	20	5	20
	1-Chloro-4-fluorobenzene (IS)	40	10	40

It may be necessary to select different surrogates in order to minimize sample interferences. 1-chloro-4-fluorobenzene and 4-chlorotoluene are fairly well resolved from analytes listed in this SOP. However 4-chlorotoluene may sometimes be requested as a target analyte. Other surrogates that may be considered, and issues associated with their use are:

Bromochloromethane: Elutes very close to chloroform and cis-1, 2-dichloroethene on the 502.2 column. May be a target analyte.

1,2-Bromochloroethane:

1-Chloro-2-fluorobenzene: Elutes close to ethylbenzene on DB-1 or Rtx-1 and close to m,p-xylene on 502.2

a,a,a-Trifluorotoluene: Good for aromatic volatiles, coelutes or very close to trichloroethene

Bromofluorobenzene: Close to 1,1,2,2-trichloroethane and 1,2,3-trichloropropane on the 502.2 column. Good on DB-1 or Rtx-1.

2-Bromo-1-chloropropane: May coelute with 1,1,2-trichloroethane

Table A-6
Concentrations for LCS and MS/MSD compounds

Standard	Components	Working Solution µg/mL	Spike amount µL (5 mL purge)	Final concentration µg/L (µg/kg)
Aromatic	Benzene	20	5	20
	Toluene	20		20
	Chlorobenzene	20		20
Halogenated	Chlorobenzene	20	5	20
	1,1-Dichloroethene	20		20
	Trichloroethene	20		20
Combination aromatic / halogenated	Benzene	20	5	20
	Toluene	20		20
	Chlorobenzene	20		20
	1,1-Dichloroethene	20		20
	Trichloroethene	20		20

1. SCOPE AND APPLICATION

This SOP Appendix describes procedures to be used when SW-846 Method 8081A is applied to the analysis of organochlorine pesticides by GC/ECD. This Appendix may also to be applied when discontinued SW-846 Method 8080A is requested, and is applicable to extracts derived from any matrix which are prepared according to the appropriate STL North Canton sample extraction SOPs. (CORP-OP-0001NC) Criteria for the analysis of wastewater by Method 608 is also included in this appendix.

Table B-1 lists compounds, which are routinely determined by this method, and gives the Reporting Limits (RL) for each matrix. RLs given are based on the low level standard and the sample preparation concentration factors. Matrix interferences may result in higher RLs than those listed.

At client request, this method may also be used for the analysis of PCBs (Arochlors) in combination with pesticides, although these are normally analyzed following method 8082, as described in Appendix C of this SOP. In any event, if samples for PCB analysis do not need the acid clean up procedure, then the same injection may be used for method 8081B and 8082, assuming all calibration and QC requirements for both methods are met. Extracts that have been acid cleaned may not be analyzed for pesticides, since several of the pesticides will be degraded.

1.1. The associated LIMS method codes are QJ (8081A) and DM (608).

2. SUMMARY OF METHOD

This method presents conditions for the analysis of prepared extracts of organochlorine pesticides. The pesticides are injected onto the column and separated and detected by electron capture detection. Quantitation may be by internal or external standard methods.

3. DEFINITIONS

Refer to the 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 CORP-OP-0001NC.

4.4. Interferences co-extracted from samples will vary considerably from source to source. The presence of interferences may raise quantitation limits for individual samples. Specific cleanups may be performed on the sample extracts, including florisil cleanup (Method 3620), Gel Permeation Chromatography (Method 3640), and Sulfur cleanup (Method 3660). These cleanup procedures are included in SOP # CORP-OP-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.

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

Tetrachloro-m-xylene and decachlorobiphenyl are the surrogate standards. Refer to tables B-5 and B-6 for details of surrogate standards.

7.4. Column Degradation Evaluation Mix

A mid-level standard containing 4,4'-DDT and Endrin and not containing any of their breakdown products must be prepared for evaluation of degradation of these compounds by the GC column and injection port. This mix must be replaced after one year, or whenever corrective action to columns fails to eliminate the breakdown of the compounds, whichever is shorter. This solution also contains the surrogates. Refer to Table B-4 for details of the column degradation evaluation mix.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

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

9. QUALITY CONTROL

Refer to Section 9 of the 8000B section of this SOP.

10. CALIBRATION AND STANDARDIZATION

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

10.2. Refer to Table B-2 for details of GC operating conditions. The conditions listed should result in resolution of all analytes listed in Table B-1 on both columns. Closely eluting pairs are DDE and Dieldrin on the Rtx-5 or DB-5 column and Endosulfan II and DDD on the 1701 column.

Note: Method 608 requires a minimum of three concentration levels for initial calibrations. The relative standard deviation, RSD must be less than 10%.

10.3. Column Degradation Evaluation

Before any calibration runs, either initial or 12 hour, The column evaluation mix must be injected before each initial or daily calibration. The degradation of DDT and endrin must be calculated (see equations 9 and 10) and each shown to be less than 15% before calibration can proceed. This is only necessary if the target compound list includes DDT, Endrin, or any of their degradation products.

If the breakdown of DDT and/or endrin exceeds the limits given above, corrective action must be taken. This action may include:

- Replacement of the injection port liner or the glass wool.
- Cutting off a portion of the injection end of a capillary column.
- Replacing the GC column.

10.4. Initial Calibration

Refer to Section 10 of the 8000B section of this SOP for details of calibration procedures.

10.4.1. Refer to Table B-7 for the initial calibration analytical sequence.

10.4.2. The response for each single-peak analyte will be calculated by the procedures described in the general method for GC analysis.

10.4.3. The surrogate calibration curve is calculated from the Individual AB mix. Surrogates in the other calibration standards are used only as retention time markers. If there are resolution problems, then the A and B mixes may be analyzed separately.

10.4.4. For multi-component pesticides:

Single point calibration is used for 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.

10.4.5. For multi-component analytes, the mid level standard must be analyzed as part of the initial calibration. This single point calibration is used to quantitate multi-component analytes.

10.4.6. The analyst may include a full 5 point calibration for any of the multi-component analytes with the initial calibration.

10.5. 12 hour Calibration Verification

The 12 hour calibration verification sequence must be analyzed within 12 hours of the start of the initial calibration and at least once every 12 hours thereafter if samples are being analyzed. If more than 12 hours have elapsed since the injection of the last sample in the analytical sequence, a new analytical sequence must be started with a 12 hour calibration. A mid level calibration standard is used for the 12 hour calibration. Refer to the 8000B section of this SOP for acceptance criteria.

Note : Method 608 requires that the working calibration curve must be verified on each working day by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than ± 15%, the test must be repeated using a fresh calibration standard.

10.5.1. At a minimum, the 12 hour calibration includes analysis of the breakdown mix followed by mid level standards of any single and multi-component analytes.

10.5.2. The retention time windows for any analytes included in the 12 hour calibration are updated.

10.6. Continuing Calibration

The AB calibration mix is analyzed as the continuing calibration standard. At a minimum, this is analyzed after every 20 samples, including matrix spikes, LCS, and method blanks. If 12 hours elapse analyze the 12 hour standard sequence instead. The continuing calibration standard need not include 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.

10.6.1. A mid level calibration standard is used for the continuing calibration.

11. PROCEDURE

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

11.2. Extraction

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

11.3. Cleanup

Cleanup procedures are described in SOP No. CORP-OP-0001NC.

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

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

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

12.3.1. 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.

12.3.1.1. Multiple peak option

This option is particularly valuable if toxaphene is identified but interferences make quantitation based on total area difficult. Select 3-10 major peaks in the analyte pattern. Calculate the response using the total area or total height of these peaks. Alternatively, find the response of each of the 3-10 peaks per multi-peak pesticide, and use these responses independently, averaging the resultant concentrations found in samples for a final concentration result. When using this option, it is appropriate to remove peaks that appear to be coeluting with contaminant peaks from the quantitation. (i.e. peaks which are significantly larger than would be expected from the rest of the pattern.)

Chlordane may be quantitated either using the multiple peak option (12.3.1.1) total area option (12.3.1.2.) or by quantitation of the major components, α-chlordane, γ-chlordane and heptachlor.

12.3.1.2. Total area option

The total area of the standards and samples may be used for quantitation of 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.

12.4. Second column confirmation multi-component analytes will only be performed when requested by the client, because the appearance of the multiple peaks in the sample usually serves as a confirmation of analyte presence.

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

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

Equation 9

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

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

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

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. Example performance limits are listed in Table B-8. The spiking level should be equivalent to a mid level calibration.

14. POLLUTION PREVENTION

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

15. WASTE MANAGEMENT

15.1. Waste generated in this procedure will be segregated and disposed according to the facility hazardous waste procedures. The Environmental Health and Safety Director should be contacted if additional information is required.

16. REFERENCES

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

16.2. CFR136A, Method 608 – Organochlorine Pesticides and PCBs

17. MISCELLANEOUS

17.1. Modifications from Reference Method

None

17.2. Modifications from Previous Revisions

17.2.1. No revisions were made to this appendix.

17.3. Tables

Table B-1
Standard Analyte list and Reporting Limits

Compound	Reporting Limit, µg/L or µg/kg		
	water	soil	waste
Aldrin	0.05	1.7	50
α-BHC	0.05	1.7	50
β-BHC	0.05	1.7	50
δ-BHC	0.05	1.7	50
γ-BHC (Lindane)	0.05	1.7	50
α-Chlordane	0.05	1.7	50
γ-Chlordane	0.05	1.7	50
Chlordane (technical)	0.5	17	500
4,4'-DDD	0.05	1.7	50
4,4'-DDE	0.05	1.7	50
4,4'-DDT	0.05	1.7	50
Dieldrin	0.05	1.7	50
Endosulfan I	0.05	1.7	50
Endosulfan II	0.05	1.7	50
Endosulfan Sulfate	0.05	1.7	50
Endrin	0.05	1.7	50
Endrin Aldehyde	0.05	1.7	50
Heptachlor	0.05	1.7	50
Heptachlor Epoxide	0.05	1.7	50
Methoxychlor	0.1	3.3	100
Toxaphene	2.0	67	2000
APPENDIX IX ADD ONs			
Diallate	1.0	33	1000
Isodrin	0.1	3.3	100
Chlorobenzilate	0.1	3.3	100
Kepone[1]	1.0	33	1000

[1] Kepone is sometimes requested for analysis by method 8081A. However kepone may produce peaks with broad tails that elute later than the standard by up to a minute (presumably due to hemi-acetal formation). As a result kepone analysis by 8081A is unreliable and not recommended. Analysis by method 8270C is a possible alternative. Note: alpha chlordane, gamma chlordane, and endrin ketone are not required for some projects.

The following concentration factors are assumed in calculating the Reporting Limits:

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

Table B-2	
Parameter	**Recommended Conditions**
Injection port temp	220°C
Detector temp	325°C
Temperature program	120°C for 1 min, 8.5°C/min to 285°C, , 6 min hold
Column 1	Rtx-CLPesticides 30m x 0.32mm id, 0.5µm
Column 2	Rtx-35 30m x 0.32 mm id, 0.5µm
Column 3	DB-608, 30m X 0.32 mm, 0.25µm
Injection	2µL
Carrier gas	Helium or Hydrogen
Make up gas	Nitrogen
Y splitter	Restek or J&W or Supelco glass tee

Table B-3						
Calibration Levels ng/mL						
	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6[2]
Individual Mix AB[1]						
Aldrin	5	10	25	50	100	200
g-BHC (Lindane)	5	10	25	50	100	200
Heptachlor	5	10	25	50	100	200
Methoxychlor	10	20	50	100	200	400
Dieldrin	5	10	25	50	100	200
Endosulfan I	5	10	25	50	100	200
Endosulfan II	5	10	25	50	100	200
4,4'-DDT	5	10	25	50	100	200
Endrin Aldehyde	5	10	25	50	100	200
Endrin Ketone	5	10	25	50	100	200
β-BHC	5	10	25	50	100	200
δ-BHC	5	10	25	50	100	200
α-BHC	5	10	25	50	100	200
4,4'-DDD	5	10	25	50	100	200
4,4'-DDE	5	10	25	50	100	200
Endosulfan Sulfate	5	10	25	50	100	200
Endrin	5	10	25	50	100	200
α-Chlordane[3]	5	10	25	50	100	200
γ-Chlordane[3]	5	10	25	50	100	200
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	
Component	Concentration
4,4'-DDT	25
Endrin	25
Tetrachloro-m-xylene (Surrogate)	20
Decachlorobiphenyl (Surrogate)	20

Table B-5			
LCS/Matrix Spike and Surrogate Spike levels µg/L or µg/kg			
	Aqueous	Soil	Waste
gamma BHC (Lindane)	0.20	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 µg/L or µg/kg		
	Aqueous	Waste
Heptachlor	5	500
Heptachlor epoxide	5	500
Lindane	5	500
Endrin	5	500
Methoxychlor	10	1000

Table B-7
Suggested Analytical Sequence

Initial Calibration

Solvent blank (optional)	
Breakdown Mix	
Individual mix AB	All levels
Technical Chlordane	Level 3[1]
Toxaphene	Level 3[1]
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 Arochlors are included, a 5 point calibration for Arochlor 1016/1260 should be included with the initial calibration and a single point for the other Arochlors. The mid point 1016/1260 mix is included with the daily calibration (every 12 hours).

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.

Table B-8

Example Performance limits, four replicate initial demonstration of capability

Compound	Initial demonstration, mean recovery limits	Initial demonstration, RSD limits
Aldrin	46-112	21
alpha-BHC	51-122	24
beta-BHC	61-120	32
delta-BHC	49.5-118.5	36
gamma-BHC	57-116	23
Chlordane	44.8-108.6	20
4,4'-DDD	52-126	28
4,4'-DDE	46-120	27.5
4,4'-DDT	54-137	36
Dieldrin	42.5-124.5	38
Endosulfan I	43-141	24.5
Endosulfan II	78-171	61
Endosulfan Sulfate	62-132	27
Endrin	49-126	37
Heptachlor	57-100	20
Heptachlor Epoxide	43.5-131.5	25.4
Toxaphene	44.4-111.2	20

1. SCOPE AND APPLICATION

1.1. This SOP Appendix describes procedures to be used when SW-846 Method 8000B is applied to the analysis of polychlorinated biphenyls (PCB) by GC/ECD. This Appendix is to be applied when SW-846 Method 8082 is requested, and is applicable to extracts derived from any matrix which are prepared according to the appropriate STL sample extraction SOPs. (CORP-OP-0001NC). The PCBs are determined and quantitated as Arochlor mixes. Criteria for the analysis of wastewater by Method 608 is also included in this appendix.

Table C-1 lists compounds, which are routinely determined by this method, and gives the Reporting Limits (RL) for each matrix. RLs given are based on the low level standard and the sample preparation concentration factors. Matrix interferences may result in higher RLs than those listed.

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

1.2. The associated LIMS method codes are QH (8082) and DM (608).

2. SUMMARY OF METHOD

This method presents conditions for the analysis of prepared extracts of PCBs. The PCBs are injected onto the column and separated and detected by electron capture detection. Quantitation is by the external standard method.

3. DEFINITIONS

Refer to the 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 CORP-OP-0001NC.

4.4. Interferences co-extracted from samples will vary considerably from source to source. The presence of interferences may raise quantitation limits for individual samples. Specific cleanups may be performed on the sample extracts, including florisil cleanup (Method 3620), Gel Permeation Chromatography (Method 3640), and Sulfur cleanup (Method 3660). These cleanup procedures are included in SOP # CORP-OP-0001NC.

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

Tetrachloro-m-xylene and decachlorobiphenyl are the surrogate standards. Other surrogates may be used at client request. Refer to Table C-4 for details of surrogate standards.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

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

9. QUALITY CONTROL

Refer to Section 9 of the 8000B section of this SOP.

10. CALIBRATION AND STANDARDIZATION

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

10.2. Initial Calibration

10.2.1. Refer to Table C-5 for the initial calibration analytical sequence.

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

10.2.3. A five point calibration of the Arochlor 1016/1260 mix is generated with at least mid level single points for the other Aroclor mixes. The average response factor is used to quantitate Arochlors 1260 and 1016, other Arochlors are quantitated from the mid level single point.

Note: Method 608 requires a minimum of three concentration levels for initial calibrations. The relative standard deviation, RSD must be less than 10%.

10.2.4. The analyst may include a full 5 point calibration for any of the Arochlors with the initial calibration.

10.2.5. The high and low standards for the initial 5 point calibration of 1016 / 1260 define the acceptable quantitation range for the other Arochlors. If any Arochlor is determined above this concentration the extract must be diluted and reanalyzed.

10.2.6. If the analyst knows that a specific Arochlor is of interest for a particular project, that Arochlor may be used for the five point calibration rather than the 1016 / 1260 mix.

10.2.7. The surrogate calibration curve is calculated from the Aroclor 1016/1260 mix. Surrogates in the other calibration standards are used only as retention time markers.

10.2.8. Two options are possible for quantitation of Aroclors. The same quantitation option must be used for standards and samples.

10.2.8.1. Multiple peak option

Select 3-10 major peaks in the analyte pattern. Calculate the response using the total area or total height of these peaks. Alternatively, find the response of each of the 3-10 peaks per Aroclor, and use these responses independently, averaging the resultant concentrations found in samples for a final concentration result. When using this option, it is appropriate to remove peaks that appear to be coeluting with contaminant peaks from the quantitation. (i.e. peaks which are significantly larger than would be expected from the rest of the pattern.)

10.2.8.2. Total area option

The total area of the standards and samples may be used for quantitation of 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.

10.3. 12 hour Calibration

The 12 hour calibration verification must be analyzed within 12 hours of the start of the initial calibration and at least once every 12 hours thereafter if samples are being analyzed. If there is a break in the analytical sequence of greater than 12 hours, then a new continuing calibration run must be analyzed before proceeding with the sequence. If more than 12 hours have elapsed since the injection of the last sample in the analytical sequence, a new analytical sequence must be started with a 12 hour calibration.

10.3.1. At a minimum, the 12 hour calibration includes analysis of the Arochlor 1260 / 1016 mix.

10.3.2. It is adequate to verify calibration with a mixture of Aroclors 1016 and 1260. If a specific Aroclor is expected, it may be included in the daily calibration check.

10.3.3. The retention time windows for any analytes included in the daily calibration and CCVs are updated.

10.3.4. For this method samples must be bracketed with successful calibration verification runs.

10.4. Calibration verification

The Arochlor 1260/1016 calibration mix is analyzed as the calibration verification standard. This is analyzed after every 20 samples, including matrix spikes, LCS, and method blanks. (Depending on the type of samples, it may be advisable to analyze verifications more frequently in order to minimize reruns.).

10.4.1. A mid level standard is used for the calibration verification.

Note : Method 608 requires that the working calibration curve must be verified on each working day by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than ± 15%, the test must be repeated using a fresh calibration standard.

11. PROCEDURE

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

11.2. Extraction

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

11.3. Cleanup

Cleanup procedures are described in SOP No. CORP-OP-0001NC.

11.4. Suggested gas chromatographic conditions are given in Table C-2.

11.5. Allow extracts to warm to ambient temperature before injection.

11.6. The suggested analytical sequence is given in Table C-5.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Identification of Arochlors

Retention time windows are used for identification of Arochlors, but the "fingerprint" produced by major peaks of those analytes in the standard is used in tandem with the retention times for identification. The ratios of the areas of the major peaks are also taken into consideration. Identification may be made even if the retention times of the peaks in the sample fall outside of the retention time windows of the standard, if in the analyst's judgment the fingerprint (retention time and peak ratios) resembles the standard chromatogram.

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

12.2. Quantitation of Arochlors

Use 3-10 major peaks or total area for quantitation

If the analyst believes that a combination of Aroclor 1254 and 1260, or a combination of 1242, 1248 and 1232 is present, then only the predominant Arochlor is quantitated and reported, but the suspicion of multiple Aroclors is discussed in the narrative. If well separated Aroclor patterns are present, and then both Aroclors are quantitated and reported.

12.3. If there are no interfering peaks within the envelope of the Arochlor, the total area of the standards and samples may be used for quantitation. Any surrogate or extraneous peaks within the envelope must be subtracted from the total area.

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

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

13. METHOD PERFORMANCE

13.1. Performance limits for the four replicate initial demonstration of capability 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 Arochlors.

14. POLLUTION PREVENTION

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

15. WASTE MANAGEMENT

15.1. Waste generated in this procedure will be segregated and disposed according to the facility hazardous waste procedures. The Environmental Health and Safety Director should be contacted if additional information is required.

16. REFERENCES

16.1. SW846, Update III, December 1996, Method 8082

16.2. CFR136A, Method 608, Organochlorine Pesticides and PCBs.

17. MISCELLANEOUS

17.1. Modifications from Reference Method

17.1.1. Method 8082 includes limited direction for congener specific quantitation. This is outside the scope of this SOP.

17.2. Modifications from Previous Revisions

No changes were made to this Appendix

17.3. Tables

Table C-1
Standard Analyte list and Reporting Limits

Compound	Reporting Limit, µg/L or µg/kg		
	water	soil	waste
Aroclor-1016	1.0	33	1000
Aroclor-1221	1.0	33	1000
Aroclor-1232	1.0	33	1000
Aroclor 1242	1.0	33	1000
Aroclor-1248	1.0	33	1000
Aroclor-1254	1.0	33	1000
Aroclor-1260	1.0	33	1000

The following concentration factors are assumed in calculating the Reporting Limits:

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

Table C-2

Parameter	Recommended Conditions
Injection port temp	220°C
Detector temp	325°C
Temperature program	70°C for 0.5min, 30°C/min to 190°C, 2.5°C/min to 225, 18°C/min to 280°C, 3 min hold
Column 1	DB-5 or Rtx-5 30m x 0.32mm id, 0.5µm
Column 2	DB-1701 or Rtx 1701 30m x 0.32 mm id, 0.25µm
Column 3	DB-608, 30m X 0.32 mm, 0.25µm
Injection	1-2µL
Carrier gas	Helium or Hydrogen
Make up gas	Nitrogen
Y splitter	Restek or J&W or Supelco glass tee

Table C-3						
Calibration Levels ng/mL						
	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6[1]
Aroclor 1016/1260	100	200	500	1000	2000	4000
Aroclor 1242[2]			500			
Aroclor 1221 +1254[2]			500			
Aroclor 1232[2]			500			
Aroclor 1248[2]			500			
Surrogates are included with all the calibration mixes at the following levels:						
Tetrachloro-m-xylene	5	10	25	50	100	200
Decachlorobiphenyl	5	10	25	50	100	200

[1] Level 6 is optional and should only be used if linearity can be maintained on the instrument to this level.
[2] Aroclors may be quantitated within the range 100 to 2000 ng/mL (4000ng/mL if the level 6 1016/1260 standard is included). If the Aroclor is more concentrated, it must be reanalyzed at a dilution.

Table C-4			
LCS/Matrix Spike and Surrogate Spike levels for Aroclor analysis with Acid Cleanup µg/L or µg/kg			
	Aqueous	Soil	Waste
Aroclor 1016/1260	10	333	10,000
Tetrachloro-m-xylene (Surrogate)	0.20	6.67	200
Decachlorobiphenyl (Surrogate)	0.20	6.67	200

Table C-5 Michigan Analyte List and Reporting Limits[1]		
	Reporting Limit	
Compound	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-5
Suggested Analytical Sequence

Initial Calibration

Injection #		
1	Solvent blank (optional)	
2	Aroclor 1016/1260	Level 1
3	Aroclor 1016/1260	Level 2
4	Aroclor 1016/1260	Level 3
5	Aroclor 1016/1260	Level 4
6	Aroclor 1016/1260	Level 5
7	Aroclor 1232	Level 3
8	Aroclor 1242	Level 3
9	Aroclor 1248	Level 3
10	Aroclor 1221/1254	Level 3
11-30	Sample 1-20 (or as many samples as can be analyzed in 12 hours	
	Solvent blank (optional)	
32	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

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.

1.1. The associated LIMS method code is QS.

2. SUMMARY OF METHOD

This method presents conditions for the analysis of prepared extracts of phenoxy acid herbicides by gas chromatography. The herbicides, as their methyl esters, are injected onto the column, separated, and detected by electron capture detectors. Quantitation is by the external standard method.

3. DEFINITIONS

Refer to the 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#CORP-OP-0001NC.

5. SAFETY

5.1. Refer to section 5 of the Method 8000B SOP for general safety requirements.

6. EQUIPMENT AND SUPPLIES

6.1. Refer to Section 6 of the 8000B section of this SOP. A Ni_{63} electron capture detector is required.

6.2. Refer to Table D2 for analytical columns.

6.3. Microsyringes, various sizes, for standards preparation, sample injection, and extract dilution.

7. REAGENTS AND STANDARDS

7.1. Refer to section 7 of the 8000B section of this SOP for general information on reagents and standards.

8. SAMPLE PREPARATION, PRESERVATION AND STORAGE

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

9. QUALITY CONTROL

9.1. Refer to Section 9 of the 8000B section of this SOP for quality control requirements, including the initial demonstration of capability, definition of a batch, surrogate limits, method blanks, laboratory control samples (LCS), and matrix spikes (MS).

9.2. Refer to Table D-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

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

11.3. Cleanup

The alkaline hydrolysis and subsequent extraction of the basic solution described in the extraction procedure provides an effective cleanup.

11.4. Analytical Sequence

The analytical sequence starts with an initial calibration of at least five points, or a daily calibration that meets % difference criteria from an existing initial calibration.

11.4.1. The daily calibration must be analyzed at least once every 24 hours when samples are being analyzed. If there is a break in the analytical sequence of greater than 12 hours, then a new continuing calibration run must be analyzed before proceeding with the sequence. If more than 24 hours have elapsed since the injection of the last sample in the analytical sequence, a new analytical sequence must be started with a daily calibration.

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

11.4.3. After every 12 hours a continuing calibration is analyzed. The continuing calibration consists of mid level standards of all analytes of interest. Retention time windows are updated with continuing calibrations.

11.5. Gas Chromatography

Chromatographic conditions are listed in Table D-2.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Refer to the 8000B section of this SOP for identification and quantitation of single component analytes.

12.2. The herbicides are analyzed as their methyl esters, but reported as the free acid. For this reason it is necessary to correct the results for the molecular weight of the ester versus the free acid. This is achieved through the concentrations of the calibration standards. For example the 20µg/L calibration standard for 2,4-D contains 21.3 µg/L of the methyl ester. No further correction is necessary.

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

This method does not contain any specific modifications that serve to minimize or prevent pollution.

15. WASTE MANAGEMENT

Waste generated in this procedure will be segregated and disposed according to the facility hazardous waste procedures. The Environmental Health and Safety Director should be contacted if additional information is required.

16. REFERENCES

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

17. MISCELLANEOUS

17.1. Modifications from Reference Method

Refer to the method 8000B section of this SOP for modifications from the reference method.

17.2. Modifications from Previous Revision

The calibration procedure has been changed to require esterification of the calibration standards

17.3. Tables

Table D-1
Standard Analyte list

Compound	CAS Number	Reporting Limit, µg/L or µg/kg		
		Aqueous	Soil	Waste
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
MCPP	93-65-2	400	8000	400,000

The following concentration factors are assumed in calculating the Reporting Limits:

	Extraction Vol.	Final Vol.	Dilution Factor
Ground water	1000 mL 10 mL	20	
Low-level Soil without GPC	50 g	10 mL	20
High-level soil / waste	1 g	10 mL	20

Specific reporting limits are highly matrix dependent. The reporting limits listed above are provided for guidance only and may not always be achievable. For special projects, the extracts may be analyzed without any dilution, resulting in reporting limits 20 times lower than those in Table D-1.

Table D-2
Instrumental Conditions

PARAMETER	Recommended conditions
Injection port temp	220°C
Detector temp	325°C
Temperature program	80,2/30/170,0/1/180,1
Column 1	DB-5MS or RTX 5 30x0.32, 0.5um
Column 2	DB-1701 or Rtx-1701
Injection	1-2µL
Carrier gas	Helium / Hydrogen
Make up gas	Nitrogen

Recommended conditions should result in resolution of all analytes listed in Table D-1.

The reporting limits listed in Table D-1 will be achieved with these calibration levels and a 20 fold dilution of the sample extract. Lower reporting limits can be achieved with lesser dilutions of the sample extract.

Table D-3			
LCS/Matrix Spike and Surrogate Spike levels µg/L or µg/kg[1]			
	Aqueous	Soil	Waste
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 SOP Appendix describes procedures to be used when SW-846 Method 8000B is applied to the analysis of polynuclear aromatic hydrocarbons (PAH) by High Performance Liquid Chromatography. This Appendix is to be applied when SW-846 Method 8310 or EPA Method 610 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).

Table E-1 lists compounds, which are routinely determined by this method, and gives the Reporting Limits (RL) for each matrix. RLs given are based on the low level standard and the sample preparation concentration factors. Matrix interferences may result in higher RLs than those listed. Note: Reporting limits are subject to change due to compound sensitivity, calibration levels, MDLs, and other factors.

1.2. The associated LIMS method codes are SG (8310) and VT (610).

2. SUMMARY OF METHOD

This method presents conditions for the analysis of prepared extracts of polynuclear aromatic hydrocarbons by high performance liquid chromatography. The compounds are injected onto a column, separated, and detected by ultraviolet and fluorescence detectors. Quantitation is by the external standard method.

3. DEFINITIONS

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.

5. SAFETY

5.1. Refer to section 5 of the Method 8000B SOP for general safety requirements.

5.2. The following parameters covered by this method have been tentatively classified as known or suspected, human or mammalian carcinogens: Benzo(a)anthracene, Benzo(a)pyrene, and Dibenzo(a,h)anthracene. Primary standards of these toxic compounds should be prepared in a hood.

6. EQUIPMENT AND SUPPLIES

6.1. Refer to Section 6 of the 8000B section of this SOP. An Ultraviolet detector and Fluorescence detector is required.

6.2. Refer to Table E2 for analytical columns.

6.3. Microsyringes, various sizes, for standards preparation, sample injection, and extract dilution.

7. REAGENTS AND STANDARDS

7.1. Refer to section 7 of the 8000B section of this SOP for general information on reagents and standards.

7.2. Refer to Table E-3 and E-4 for details of calibration and other standards.

7.3. Surrogate Standards

Terphenyl-d14 and Benzo(e)pyrene are the surrogate standards. Refer to table E-3 for details of surrogate standards.

8. SAMPLE PREPARATION, PRESERVATION AND STORAGE

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

9. QUALITY CONTROL

9.1. Refer to Section 9 of the 8000B section of this SOP for quality control requirements, including the initial demonstration of capability, definition of a batch, surrogate limits, method blanks, laboratory control samples (LCS), and matrix spikes (MS).

9.2. Refer to Table E-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.

Note: The Initial Calibration requirement for Method 610 is as follows: If the ratio of response to amount injected (calibration factor) is a constant over the working range (<10% relative standard deviation, RSD), linearity through the origin can be assumed and the average ratio or calibration factor can be used in place of a calibration curve.

10.2. Calibration standards are prepared from purchased solutions. Table E-4 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.

10.4. Refer to Table E-2, for details of LC operating conditions.

11. PROCEDURE

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

11.2. Extraction

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

11.3. Cleanup

11.4. Analytical Sequence

The analytical sequence starts with an initial calibration of at least five points, or a daily calibration that meets % difference criteria from an existing initial calibration.

Note: Method 610 requires that continuing calibration verifications may not vary from the predicted response for any parameter by more than ± 15%. The average response may not be used for Method 610.

11.4.1. The daily calibration must be analyzed at least once every 24 hours when samples are being analyzed. If there is a break in the analytical sequence of greater than 12 hours, then a new continuing calibration run must be analyzed before proceeding with the sequence. If more than 24 hours have elapsed since the injection of the last sample in the analytical sequence, a new analytical sequence must be started with a daily calibration.

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

11.4.3. After every 12 hours a continuing calibration is analyzed. The continuing calibration consists of mid level standards of all analytes of interest. Retention time windows are updated with continuing calibrations.

11.5. High Performance Liquid Chromatography

Chromatographic conditions are listed in Table E-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. Surrogate recovery results are calculated and reported for Terphenyl-d14 and Benzo(e)pyrene unless it is determined that sample interference has adversely affected the quantitation of one of the surrogates. One surrogate must be within QC criteria. Corrective action is only necessary if Terphenyl-d14 and Benzo(e)pyrene are both outside of acceptance limits.

13. METHOD PERFORMANCE

13.1. Performance limits for the four replicate initial demonstration of capability required as referenced under Section 13.1

14. POLLUTION PREVENTION

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

15. WASTE MANAGEMENT

15.1. Waste generated in this procedure will be segregated and disposed according to the facility hazardous waste procedures. The Environmental Health and Safety Director should be contacted if additional information is required.

16. REFERENCES

16.1. SW846, Update III, December 1996, Method 8310.

16.2. CFR136 Appendix A Method 610-Polynuclear Aromatic Hydrocarbons.

17. MISCELLANEOUS

17.1. Reporting limits

17.1.1. The lower standard reporting limits are listed in Table

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

17.2. Elution time

17.2.1. 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.

17.3. Analyte detection

17.3.1. Some compounds are detected only on the ultraviolet detector. For other compounds, the lower of the concentrations calculated from both detectors is reported, the second detector serving as confirmation of the analytes presence.

17.3.2. For any compound that is detected only on the ultraviolet detector, confirmation analysis is not possible. These detected compounds must be narrated that the quantitation is not confirmed by a second detector (Fluorescence).

17.3.3. Some compounds, due to calibration levels and detector limitations, can only be confirmed using the Fluorescence detector. The result will always be reported from the UV detector. These compounds will be narrated, when applicable. Table E-5 lists the compounds and respective detectors.

17.4. Troubleshooting guide

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

17.5. Tables

Table E-1
Standard Analyte list

Compound	CAS Number	Reporting Limit, µg/L or µg/kg	
		Aqueous	Soil
Acenaphthene	83-32-9	1	100
Acenaphthylene	208-96-8	1	100
Anthracene	120-12-7	2	100
Benzo(a)anthracene	56-55-3	0.1	5
Benzo(a)pyrene	50-32-8	0.1	5
Benzo(b)fluoranthene	205-99-2	0.1	5
Benzo(g,h,i)perylene	191-24-2	0.1	10
Benzo(k)fluoranthene	207-08-9	0.1	1.7
Chrysene	218-01-9	0.1	5
Dibenzo(a,h)anthracene	53-70-3	0.1	5
Fluoranthene	206-44-0	0.1	10
Fluorene	86-73-7	1	100
Indeno(1,2,3-cd)pyrene	193-39-5	0.1	5
Naphthalene	91-20-3	2	100
Phenanthrene	85-01-8	1	100
Pyrene	129-00-0	0.1	5
1-Methylnaphthalene*	90-12-0	2	100
2-Methylnaphthalene*	91-57-6	2	100

Table E-2
Instrumental Conditions

PARAMETER	Recommended conditions			
Injection volume	20 uL			
Detector	HP Series 1100 Fluorescence Detector			
Detector	HP Series 1100 Variable Wavelength Detector (UV)			
Solvent Program	Time	% Water	% Acetonitrile	Flow
	0 min.	50	50	1.5 mL/m
	5 min.	45	55	1.5 mL/m
	10 min.	35	65	2.0 mL/m
	15 min.	25	75	2.0 mL/m

	20 min. 25 min. 30 min.	15 5 45	85 95 55	2.0 mL/m 2.0 mL/m 2.0 mL/m
Column 1	PAH Hypersil 5 micron			
Injection	20 uL			
Solvent	Acetonitrile, HPLC grade			
Solvent	Reagent Water, HPLC grade			

Table E-3 LCS/Matrix Spike and Surrogate Spike Compounds

Compound	Concentration	Compound	Concentration
Acenaphthene	10 ug/mL	Dibenzo(a,h)anthracene	2 ug/mL
Acenaphthylene	10 ug/mL	**Fluoranthene**	2 ug/mL
Anthracene	10 ug/mL	Fluorene	2 ug/mL
Benzo(a)anthracene	2 ug/mL	**Indeno(1,2,3-cd)pyrene**	2 ug/mL
Benzo(a)pyrene	2 ug/mL	**Naphthalene**	10 ug/mL
Benzo(b)fluoranthene	2 ug/mL	**Phenanthrene**	2 ug/mL
Benzo(g,h,i)perylene	2 ug/mL	Pyrene	2 ug/mL
Benzo(k)fluoranthene	2 ug/mL	Terphenyl-d14*	1 ug/mL
Chrysene	2 ug/mL	Benzo(e)pyrene*	5 ug/mL

Bold print denotes control compounds in the LCS/LCSD and MS/MSD.
* Denotes surrogate compounds

Table E-4 Calibration Standards

Component	ST	1:2	1:5	1:10	1:20	1:50	1:100
Naphthalene	50	25	10	5	2.5	1	0.5
Acenaphthylene	50	25	10	5	2.5	1	0.5
Terphenyl d14 (surrogate)	50	25	10	5	2.5	1	0.5
Acenaphthene	10	5	2	1	0.5	0.2	0.1
Fluorene	10	5	2	1	0.5	0.2	0.1
Phenanthrene	10	5	2	1	0.5	0.2	0.1
Anthracene	10	5	2	1	0.5	0.2	0.1
Chrysene	10	5	2	1	0.5	0.2	0.1
1-Methylnaphthalene	50	25	10	5	2.5	1	0.5
Fluoranthene	10	5	2	1	0.5	0.2	0.1
Pyrene	10	5	2	1	0.5	0.2	0.1
Benzo(a)anthracene	10	5	2	1	0.5	0.2	0.1
Benzo(e)pyrene (surrogate)	50	25	10	5	2.5	1	0.5
Benzo(b)fluoranthene	10	5	2	1	0.5	0.2	0.1
Benzo(k)fluoranthene	10	5	2	1	0.5	0.2	0.1

Table E-4 Calibration Standards							
Component	ST	1:2	1:5	1:10	1:20	1:50	1:100
Benzo(a)pyrene	10	5	2	1	0.5	0.2	0.1
Dibenzo(a,h)anthracene	10	5	2	1	0.5	0.2	0.1
Benzo(g,h,i)perylene	10	5	2	1	0.5	0.2	0.1
Indeno(1,2,3-cd)pyrene	10	5	2	1	0.5	0.2	0.1
2-Methylnaphthalene	50	25	10	5	2.5	1	0.5

Table E-5 Compound/Detector		
Compound	Ultraviolet 254 nm	Fluorescence 280 nm
Acenaphthene	X	X
Acenaphthylene	X	
Anthracene	X	Retention Time confirmation only
Benzo(a)anthracene	X	X
Benzo(a)pyrene	X	X
Benzo(b)fluoranthene	X	X
Benzo(g,h,i)perylene	X	X
Benzo(k)fluoranthene	X	X
Chrysene	X	X
Dibenzo(a,h)anthracene	X	X
Fluoranthene	X	X
Fluorene	X	X
Indeno(1,2,3-cd)pyrene	X	X
Naphthalene	X	X
Phenanthrene	X	X
Pyrene	X	X
1-Methylnaphthalene	X	X
2-Methylnaphthalene	X	X

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 F1 shows reporting limits for compounds routinely analyzed by this method. The compounds include, but are not limited to, those shown in Table F1.

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

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. Trichlorfon 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 Trichlorfon, 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 F2 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 F-3 for details of calibration and other standards.

7.3. Surrogate Standards

Triphenyl phosphate is the surrogate standard. Refer to table F-4 for details of the surrogate standard.

8. SAMPLE PREPARATION, PRESERVATION AND STORAGE

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

9. QUALITY CONTROL

9.1. Refer to Section 9 of the 8000B section of this SOP for quality control requirements, including the initial demonstration of capability, definition of a batch, surrogate limits, method blanks, laboratory control samples (LCS), and matrix spikes (MS).

9.2. Refer to Table F-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 F-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

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

11.3. Cleanup

11.4. Analytical Sequence

The analytical sequence starts with an initial calibration of at least five points, or a daily calibration that meets % difference criteria from an existing initial calibration.

11.4.1. The daily calibration must be analyzed at least once every 24 hours when samples are being analyzed. If there is a break in the analytical sequence of greater than 12 hours, then a new continuing calibration run must be analyzed before proceeding with the sequence. If more than 24 hours have elapsed since the injection of the last sample in the analytical sequence, a new analytical sequence must be started with a daily calibration.

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

11.4.3. After every 12 hours a continuing calibration is analyzed. The continuing calibration consists of mid level standards of all analytes of interest. Retention time windows are updated with continuing calibrations.

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

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

15. WASTE MANAGEMENT

15.1. Waste generated in this procedure will be segregated and disposed according to the facility hazardous waste procedures. The Environmental Health and Safety Director should be contacted if additional information is required.

16. REFERENCES

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

17. MISCELLANEOUS

17.1. Reporting limits

17.1.1. The lower standard reporting limits are listed in Table F-1

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

17.1.2.1. 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.

17.2. Elution time

17.2.1. 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.

17.3. Troubleshooting guide

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

Table F1: Organophosphorus Pesticides Routinely Analyzed and Reporting Limits

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 F2: Instrumental Conditions	
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 F3 Initial Calibration Concentrations (ng/uL)

COMPOUND	LEVEL1	LEVEL2	LEVEL3	LEVEL4	LEVEL5	LEVEL6	LEVEL7
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 F4: LCS/Matrix Spike and Surrogate Spike Compounds – 20 ug/mL

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 and Wisconsin DNR Modified DRO method.

1.3. The associated LIMS method codes are HS (8015 MOD), KI (8015B), and C6 (Wisconsin DRO).

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. Wisconsin DRO Method is designed to measure the concentration of diesel range organics in water and soil. This corresponds to a hydrocarbon range of C_{10}-C_{28} and a boiling point range between approximately 170 °C and 430 °C.

2.3. 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).

3. Definitions

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

3.2. Wisconsin DNR DRO Method Definition - Diesel Range Organics (DRO) – All the chromatographic response falling between the onset of the n-decane (n-C_{10}) peak and the conclusion of the n-octacosane (n-C_{28}) peak. Quantitation is based on a direct comparison of the total area within this range to the total area of the Diesel Component Standard.

3.3. Wisconsin DNR DRO Method Definition –Diesel Component Standard: A ten component blend of typical diesel compounds. This standard serves as a quantitation standard and is used to establish a retention time window for diesel range organics.

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 Diesel Component Stock Standard for the Wisconsin DRO method may be commercially prepared standards if the standards are certified by the manufacturer or by an independent source.

8. SAMPLE PREPARATION, PRESERVATION AND STORAGE

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

8.2. Wisconsin DNR DRO aqueous samples must be preserved with HCL such that the pH is < 2.

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. LCS recoveries are calculated from a Diesel Calibration. The Wisconsin DNR DRO method specifies the recovery of the LCS-water spike must be between 75%-115% and the RPD <20%. LCS Soil recoveries must fall between 70%-120% of the known concentration and the RSD must be <20%.

9.2.1. The Wisconsin DNR DRO Method requires a Duplicate Laboratory Control Spike with each batch. MS/MSD samples are not required for this method. One LCS must be run at the beginning of the batch of samples and the other at the end.

9.3. MS/MSD recoveries are calculated from a Diesel calibration.

9.4. Surrogates

9.4.1. 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.

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 Appendix

10.1.4. Injection volume - 1 µL

10.2. Initial Calibration

10.2.1. Analyze a five point Diesel calibration standard and a five point DRO 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. The Wisconsin DNR DRO method requires the retention time window be defined as beginning 0.1 minutes before the onset of the n-decane peak and ending 0.1 minutes after the conclusion of the n-octacosane peak in the calibration run.

10.2.3. Wisconsin DNR DRO quantitation is based on a direct comparison of the total area within the retention time window to the total area of the Diesel Component Standard.

10.2.4. Wisconsin DNR DRO integration must be "baseline to baseline" as opposed to a "valley to valley". Baseline to baseline is defined here as a flat baseline drawn parallel to the x-axis of chromatographic graph that includes all responses within the retention time window.

10.2.5. A linear regression calibration curve must be prepared for Wisconsin DNR DRO analysis. The curve must have a correlation coefficient of at least 99%.

10.3. Continuing Calibration

10.3.1. The calibration verification must bracket the LCS, MS, MSD extracts and must meet passing criteria. The Wisconsin DNR DRO method requires the calibration verification must not vary from the calibration curve by more than 20%.

10.4. 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

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

11.3. Cleanup

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

11.5. Petroleum Hydrocarbon Identification and/or Fingerprinting

11.5.1. 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.

11.5.2. 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.

11.6. Sample Quantification

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

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

11.6.3. 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) 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 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

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. Method for Determining Diesel Range Organics, Modified DRO, Wisconsin DNR, Public Hearing Draft, September 1995.

16.3. Related SOP

16.3.1. 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 G1: 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 G2: Reporting Limits for TPH Analysis

Analyte	Reporting Limits		
	Water (µg/L)	Solids (mg/kg)	Waste Dilution (mg/kg)
TPH (as Diesel) or DRO	100	3.3	200
C10-C32 (Ohio VAP only)	100	3.3	200
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.

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 Stabilwax, fused silica, 60 m x 0.53, 0.5 µm film thickness, or equivalent column.

6.2.2. Stabilwax-DA, fused silica, 60 m x 0.32, 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 H2.

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- 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.

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

1.1.1. 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.

14. POLLUTION PREVENTION

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

15. WASTE MANAGEMENT

15.1. Waste generated in this procedure will be segregated and disposed according to the facility hazardous waste procedures. The Environmental Health and Safety Director should be contacted if additional information is required.

16. REFERENCES

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 H1 Non-halogenated Organic Compounds, Reporting Limits[1]

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

Compound	CAS Number	Reporting Limits	
		Water, mg/L	Solid, mg/kg
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.

Table H2 Non-halogenated Organic Compounds Working Standards

COMPOUND	LEVEL1	LEVEL2	LEVEL3	LEVEL4	LEVEL5	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

1. Scope and Application

1.1. This method is applicable to the determination of the concentration of Sulfolane and N-Methyl-2-pyrrolidone in water and solid samples. It is based on SW846 Method 8015B. The working linear range is 50 to 1000 µg/L. Table I1 lists the reporting limits associated with this method.

1.2. The applicable LIMS method code is KU.

2. Summary of Method

2.1. This method provides gas chromatographic conditions for the detection of mg/L levels of Phillips 66 compounds in water. Prior to use of this method, appropriate sample extraction techniques must be used.

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.

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

5.2.1. Chemicals that have been classified as **carcinogens,** or **potential carcinogens,** under OSHA include: **Methylene Chloride.**

6. EQUIPMENT AND SUPPLIES

6.1. Refer to Section 6 of the 8000B section of this SOP.

6.2. Gas Chromatograph

6.2.1. Gas Chromatograph: Modified to accept capillary columns

6.2.2. Data System: Capable of peak integration

6.2.3. Gas Chromatographic Column: 30 m x 0.32 mm ID RTX-5 fused silica capillary column

6.2.4. Autosampler: Capable of reproducible injections

6.2.5. Carrier Gas: Hydrogen

6.2.6. Detector: Flame ionization (FID)

6.3. Volumetric Flasks: 10, 50, and 100 mL

6.4. Microsyringe: 10 µL

6.5. Pipettes: Disposable µL, Pasteur

6.6. Autosampler Vials: 1 mL with 11 mm crimp cap, Teflon®/silicone septum liner.

7. REAGENTS AND STANDARDS

7.1. Refer to Section 7 of the 8000B section of this SOP.

7.2. Reagents

7.2.1. Methylene Chloride: Pesticide grade or equivalent

7.3. Standards

7.3.1. Refer to Section 7 of the 8000B section of this SOP.

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. Surrogates are not used for this analysis.

10. CALIBRATION AND STANDARDIZATION

10.1. Initial Calibration

10.1.1. 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. Sample Analysis

11.2.1. Summary

11.2.1.1. The sample extract is injected onto the GC column. The compounds are then identified and quantitated.

11.2.2. Recommended Instrument Conditions

11.2.2.1. GC Conditions

Initial Temperature:	45°C
Initial Hold Time:	4 minutes
Temperature Program:	15°C/minute
Final Temperature:	300°C, hold 2 minutes
Final Time:	23 minutes
Carrier Gas:	Hydrogen
Injection Volume:	1 µL

11.2.3. Sample Analysis Procedure

11.2.3.1. Preliminary Evaluation

The sample extracts may be screened to determine the level of analyte present. If the level of analyte exceeds the working range of the calibration curve, an appropriate dilution is performed to bring the level within the calibration range.

11.2.4. Inject 1 µL of the sample extract or diluted sample into the GC using the same conditions as those used in calibration.

11.2.5. Identification

11.2.5.1. Analytes of interest are identified by comparing retention times with known standards.

11.2.5.2. A single column is used for identification.

11.2.6. Sample Quantification

11.2.6.1. Refer to Section 11 in the 8000B Section of this SOP

11.3. Analytical Documentation

11.3.1. Record all analytical information in the analytical logbook/logsheet, including the analytical data from standards, blanks, LCSs, MS/MSDs, and any corrective actions or modifications to the method.

11.3.2. 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.

11.3.3. Documentation such as all associated instrument printouts (final runs, screens, reruns, QC samples, etc.) and daily calibration data corresponding to all final runs is available for each data file.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Refer to the 8000B section of this SOP for identification and quantitation of single component analytes.

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

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

17.1. Reporting limits

17.1.1. The lower reporting limits are shown in Table I1

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

TABLE I1
PHILLIPS 66 REPORTING LIMITS

Compound	Reporting Limits, µg/L
Tetramethylene sulfone (Sulfolane)	50
N-Methyl-2-pyrrolidone	50

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Implementation Date: 1/30/03

STL NORTH CANTON STANDARD OPERATING PROCEDURE

TITLE: GC/MS ANALYSIS BASED ON METHODS 8270C AND 625

(SUPERSEDES: Revision 2.7, Dated 11/12/02)

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1. SCOPE AND APPLICATION

1.1 This method is based upon SW846 8270C, and is applicable to the determination of the concentration of semivolatile organic compounds in extracts prepared from solid and aqueous matrices. The modifications presented in Attachment A may be followed for analysis of wastewater following method 625. Direct injection of a sample may be used in limited applications. Refer to Tables 1, 2, 3 and 4 for the list of compounds applicable for this method. Note that the compounds are listed in approximate retention time order. Additional compounds may be amenable to this method. If non-standard analytes are required, they must be validated by the procedures described in section 13 before sample analysis.

1.2 The following compounds may require special treatment when being determined by this method:

- Benzidine can be subject to oxidative losses during solvent concentration and exhibits poor chromatography. Neutral extraction should be performed if this compound is expected.
- Hexachlorocyclopentadiene is subject to thermal decomposition in the inlet of the gas chromatograph, chemical reaction in acetone solution, and photochemical decomposition.
- N-Nitrosodiphenylamine decomposes in the gas chromatographic inlet and cannot be distinguished from diphenylamine.
- Pentachlorophenol, 2,4-dinitrophenol, 4-nitrophenol, 4,6-dinitro-2-methylphenol, 4-chloro-3-methylphenol, benzoic acid, 2-nitroaniline, 3-nitroaniline, 4-chloroaniline, and benzyl alcohol are subject to erratic chromatographic behavior, especially if the GC system is contaminated with high boiling material.
- Hexachlorophene is not amenable to analysis by this method.
- 3-Methylphenol cannot be separated from 4-methylphenol by the conditions specified in this method.

1.3 The standard reporting limit (SRL) of this method for determining an individual compound is approximately 0.33 mg/kg (wet weight) for soil/sediment samples, 1 - 200 mg/kg for wastes (dependent on matrix and method of preparation), and 10 µg/L for groundwater samples. Some compounds have higher reporting limits. Refer to Tables 1 and 2 for specific SRLs. Reporting limits will be proportionately higher for sample extracts that require dilution.

1.4 The associated LIMS codes are QL (8270C) and DP (625).

2 SUMMARY OF METHOD

2.1 Aqueous samples are extracted with methylene chloride using a separatory funnel, and a continuous extractor. Solid samples are extracted with methylene chloride / acetone using

sonication, soxhlet, accelerated soxhlet or pressurized fluid extraction. The extract is dried, concentrated to a final volume of 2 mL for waters and 5 mL for soils, and analyzed by GC/MS. Extraction procedures are detailed in SOP# CORP-OP-0001NC. Qualitative identification of the parameters in the extract is performed using the retention time and the relative abundance of characteristic ions. Quantitative analysis is performed using the internal standard technique with a single characteristic ion.

3 DEFINITIONS

3.1 CCC (Calibration Check Compounds) - A subset of target compounds used to evaluate the calibration stability of the GC/MS system. A maximum percent deviation of the CCC's is specified for calibration acceptance.

3.2 SPCC (System Performance Check Compounds) - Target compounds designated to monitor chromatographic performance, sensitivity, and compound instability or degradation on active sites. Minimum response factors are specified for acceptable performance.

3.3 Batch - The batch is a set of up to 20 samples of the same matrix processed using the same procedures and reagents within the same time period. The Quality Control batch must contain a matrix spike / spike duplicate (MS/MSD), a Laboratory Control Sample (LCS), and a method blank. In some cases, at client request, the MS/MSD may be replaced with a matrix spike and sample duplicate. Batches are defined at the sample preparation stage. Batches should be kept together through the whole analytical process to the extent possible, but it is not mandatory to analyze prepared extracts on the same instrument or in the same sequence. Refer to the STL North Canton QC Program document (QA-003) for further details of the batch definition.

3.4 Method Blank - An analytical control consisting of all reagents, internal standards and surrogate standards, that is carried through the entire analytical procedure. The method blank is used to define the level of laboratory background and reagent contamination.

3.5 LCS (Laboratory Control Sample) - A blank spiked with the parameters of interest that is carried through the entire analytical procedure. Analysis of this sample with acceptable recoveries of the spiked materials demonstrates that the laboratory techniques for this method are acceptable.

3.6 MS (Matrix Spike)- aliquot of a matrix (water or soil) fortified (spiked) with known quantities of specific compounds and subjected to the entire analytical procedure in order to indicate the appropriateness of the method for the matrix by measuring recovery.

3.7 MSD (Matrix Spike Duplicate)- a second aliquot of the same sample as the matrix spike (above) that is spiked in order to determine the precision of the method.

4 INTERFERENCES

4.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus that lead to discrete artifacts. All of these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. Raw GC/MS data from all blanks, samples, and spikes must be evaluated for interferences. If an interference is detected it is necessary to determine if the source of interference is in the preparation and/or cleanup of the samples; then take corrective action to eliminate the problem.

4.2 The use of high purity reagents, solvents, and gases helps to minimize interference problems.

4.3 Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature of the sample.

4.4 Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed with solvent between samples. Whenever an unusually concentrated sample is encountered, it should be followed by the analysis of solvent to check for cross contamination.

4.5 Phthalate contamination is commonly observed in this analysis and its occurrence should be carefully evaluated as an indicator of a contamination problem in the sample preparation step of the analysis.

5 SAFETY PRECAUTIONS

5.1 Procedures shall be carried out in a manner that protects the health and safety of all STL North Canton associates. The following requirements must be met:

5.1.1 Eye protection that satisfies ANSI Z87.1 (as per the Chemical Hygiene Plan), laboratory coat, and appropriate gloves must be worn while samples, standards, solvents and reagents are being handled. Disposable gloves that have become contaminated will be removed and discarded; other gloves will be cleaned immediately.

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

5.1.3 Methylene Chloride has been classified as a carcinogen and can cause severe respiratory tract irritation. Exposure to this chemical should be limited. Always use proper PPE and handle in a hood when possible.

5.1.4 Chemicals that have been classified as carcinogens, or potential carcinogens, under OSHA

include: Benzo(a)anthracene, benzidine, 3,3'-dichlorobenzidine, benzo(a)pyrene, dibenzo(a,h)anthracene, and n-nitrosodimethylamine. Primary standards should be purchased in solution. If neat materials must be obtained, they shall be handled in a hood.

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

5.1.6 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 a laboratory supervisor.

5.1.7 Chemicals known to be **flammable** are: Acetone

5.1.8 The following materials are known to be corrosive: Sulfuric Acid (H_2SO_4)

6 EQUIPMENT AND SUPPLIES

6.1 Gas Chromatograph/Mass Spectrometer System: An analytical system complete with a temperature-programmable gas chromatograph suitable for split/splitless injection and all required accessories, including syringes, analytical columns, and gases. The capillary column should be directly coupled to the source.

6.2 Column: 30 m x 0.32 mm I.D. (or 0.25 mm I.D.) 0.5-µm film thickness silicon-coated fused-silica capillary column (J & W Scientific DB-5.625 or equivalent). Alternate columns are acceptable if they provide acceptable performance.

6.3 Mass Spectrometer: Capable of scanning from 35 to 500 AMU every one second or less, using 70 volts (nominal) electron energy in the electron impact ionization mode. The mass spectrometer must be capable of producing a mass spectrum for decafluorotriphenylphosphine (DFTPP) which meets all of the criteria in Table 6 when the GC/MS tuning standard is injected through the GC.

6.4 GC/MS Interface: Any GC-to-MS interface that gives acceptable calibration points and achieves acceptable tuning performance criteria may be used.

6.5 Data System: A computer system must be interfaced to the mass spectrometer. The system must allow the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that can search any GC/MS data file for ions of a specific mass and that can plot

such ion abundances versus time or scan number. This type of plot is defined as the Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundances in any EICP between specified time or scan-number limits. The most recent version of the EPA/NIH Mass Spectral Library is recommended.

6.6 Syringe: 10 µL Hamilton Laboratory grade syringes or equivalent.

6.7 Carrier gas: Ultra high purity helium.

7 REAGENTS AND STANDARDS

7.1 A minimum five point calibration curve is prepared. If a quadratic regression is used, six points must be analyzed for the calibration curve. The low point should be at or below the reporting limit. Refer to Tables 12 and 13 for typical calibration levels for all analytes. Other calibration levels may be used, depending on instrument capability, but the low standard must support the reporting limit and the high standard defines the range of the calibration.

7.2 An Internal Standard solution is prepared. Compounds in the I.S. Mix are: acenaphthene-d10, chrysene-d12, 1,4-dichlorobenzene-d4, naphthalene-d8, perylene-d12, and phenanthrene-d10.

7.3 Surrogate Standard Spiking Solution: Prepare as indicated in the preparative methods. See appropriate preparation SOP. Surrogate compounds and levels are listed in Table 11.

7.4 GC/MS Tuning Standard: A methylene chloride solution containing decafluorotriphenylphosphine (DFTPP) is prepared. Pentachlorophenol, benzidine, and DDT, should also be included in the Tuning Standard. All components are at 25 ug/mL.

7.5 Laboratory Control Spiking Solution: Prepare as indicated in the preparative methods. See appropriate preparation SOP. LCS compounds and levels are listed in Tables 9 and 10.

7.6 Matrix Spike Solution: Prepare as indicated in the preparative methods. See preparation SOP. The matrix spike compounds and levels are the same as the LCS compounds.

7.7 The standards listed in 7.1 to 7.6 should be refrigerated at $\leq$ 6°C when not in use. Refrigeration at -10°C to -20°C may be used if it can be demonstrated that analytes do not fall out of solution at this temperature. The standards must be replaced at least once a year. The continuing calibration standard must be replaced every week and is stored at $\leq$ 6°C.

8 SAMPLE PRESERVATION AND STORAGE

8.1 Reference appropriate facility SOP for sample bottle preservation and storage.

8.2 Samples are stored at 4 ± 2°C. Samples and extracts should be stored in suitable glass containers with Teflon lined caps. (Extracts will normally be stored for 30 days after invoicing.)

8.3 Water samples are extracted within seven days of sampling and the extracts are analyzed within forty days of extraction. Solids, sludges, and organic liquids are extracted within fourteen days of sampling and the extracts are analyzed within forty days of extraction.

9 QUALITY CONTROL

9.1 Initial Demonstration of Capability

9.1.1 For the standard analyte list, the initial demonstration and method detection limit (MDL) studies described in section 13 must be acceptable before analysis of samples may begin.

9.1.2 For non-standard analytes an MDL study should be performed and calibration curve generated before analyzing any samples, unless lesser requirements are previously agreed to with the client. In any event, the minimum initial demonstration required is analysis of an extracted standard at the reporting limit and a single point calibration.

9.2 Control Limits

In-house historical control limits must be determined for surrogates, matrix spikes, and laboratory control samples (LCS). These limits must be determined at least annually. The recovery limits are mean recovery +/- 3 standard deviations for surrogates, MS and LCS. Precision limits for matrix spikes / matrix spike duplicates are mean relative percent difference +/- 3 standard deviations.

9.2.1 These limits do not apply to dilutions (except for tests without a separate extraction), but surrogate and matrix spike recoveries will be reported.

9.2.2 All surrogate, LCS, and MS recoveries (except for dilutions) must be entered into QuantIMS (when available) or other database so that accurate historical control limits can be generated. For tests without a separate extraction, surrogates and matrix spikes will be reported for all dilutions.

9.2.3 Refer to the QC program document (QA-003) for further details of control limits.

9.3 Method Blank

A method blank is prepared and analyzed with each batch of samples. The method blank consists of reagent water for aqueous samples, and sodium sulfate for soil samples (Refer to SOP No. CORP-OP-0001NC for details). Surrogates are added and the method blank is

carried through the entire analytical procedure. The method blank must not contain any analyte of interest at or above the reporting limit (except common laboratory contaminants, see below) or at or above 5% of the measured concentration of that analyte in the associated samples, whichever is higher.

- If the analyte is a common laboratory contaminant (phthalate esters), the data may be reported with qualifiers if the concentration of the analyte is less than five times the RL. Such action must be taken in consultation with the client.

- Reanalysis of any samples with reportable concentrations of analytes found in the method blank is required unless other actions are agreed with the client.

- If there is no target analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. Such action should be taken in consultation with the client.

9.3.1 The method blank must have acceptable surrogate recoveries. If surrogate recoveries are not acceptable, the data must be evaluated to determine if the method blank has served the purpose of demonstrating that the analysis is free of contamination. If surrogate recoveries are low and there are reportable analytes in the associated samples, re-extraction of the blank and affected samples will normally be required. Consultation with the client should take place.

9.3.2 If reanalysis of the batch is not possible due to limited sample volume or other constraints, the method blank is reported, all associated samples are flagged with a "B", and appropriate comments may be made in a narrative to provide further documentation.

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

9.3.4 Sample results are NOT blank subtracted unless specific requests and arrangements have been made with a client or agency.

9.4 Instrument Blank

9.4.1 Instruments must be evaluated for contamination during each 12 hour analytical run. This may be accomplished by analysis of a method blank. If a method blank is not available, an instrument blank must be analyzed. An instrument blank consists of methylene chloride with the internal standards added. It is evaluated in the same way as the method blank.

9.5 Laboratory Control Sample (LCS)

9.5.1 A laboratory control sample (LCS) is prepared and analyzed with every batch of samples. All control analytes must be within established control limits. The LCS is spiked with the compounds listed in Tables 9 and 10 unless specified by a client or agency.

9.5.2 If any analyte in the LCS is outside the laboratory established historical control limits, corrective action must occur. Corrective action may include re-extraction and reanalysis of the batch.

- If the batch is not re-extracted and reanalyzed, the reasons for accepting the batch must be clearly presented in the project records and the report. (An example of acceptable reasons for not reanalyzing might be that the matrix spike and matrix spike duplicate are acceptable, and sample surrogate recoveries are good, demonstrating that the problem was confined to the LCS).

- If re-extraction and reanalysis of the batch is not possible due to limited sample volume or other constraints, the LCS is reported, all associated samples are flagged, and appropriate comments are made in a narrative to provide further documentation.

9.5.3 Ongoing monitoring of the LCS provides evidence that the laboratory is performing the method within accepted QC guidelines for accuracy and precision.

9.5.4 Additionally, if an all-analyte check sample is used, all non-controlling compounds must attain a recovery of 5% or greater if the compound is on the client's list.

9.6 Matrix Spike/Matrix Spike Duplicate (MS/MSD)

A matrix spike/matrix spike duplicate (MS/MSD) is prepared and analyzed with every batch of samples. The MS/MSD is spiked with the same subset of analytes as the LCS (See Tables 9 and 10). Compare the percent recovery and relative percent difference (RPD) to that in the laboratory specific historically generated limits.

- If any individual recovery or RPD falls outside the acceptable range, corrective action must occur. The initial corrective action will be to check the recovery of that analyte in the Laboratory Control Sample (LCS). Generally, if the recovery of the analyte in the LCS is within limits, then the laboratory operation is in control and analysis may proceed. The reasons for accepting the batch must be documented.

- If the recovery for any component is outside QC limits for both the Matrix spike / spike duplicate and the LCS, the laboratory is out of control and corrective action must be taken. Corrective action will normally include repreparation and reanalysis of the batch.

- If a MS/MSD is not possible due to limited sample, then a LCS duplicate should be analyzed. RPD of the LCS and LCSD are compared to the matrix spike limits.

- The matrix spike / duplicate must be analyzed at the same dilution as the unspiked sample, even if the matrix spike compounds will be diluted out.

9.7 Surrogates

9.7.1 Every sample, blank, and QC sample is spiked with surrogate standards. Surrogate spike recoveries must be evaluated by determining whether the concentration (measured as percent recovery) falls within the required recovery limits. The compounds routinely included in the surrogate spiking solution, along with recommended standard concentrations, are listed in Table 11.

9.7.2 If any surrogates are outside limits the following corrective actions must take place (except for dilutions):

- Check all calculations for error.

- Ensure that instrument performance is acceptable.

- Recalculate the data and/or reanalyze the extract if either of the above checks reveal a problem.

- Re-extract and reanalyze the sample or flag the data as "Estimated Concentration" if neither of the above resolves the problem.

The decision to reanalyze or flag the data should be made in consultation with the client. It is only necessary to reprepare / reanalyze a sample once to demonstrate that poor surrogate recovery is due to matrix effect, unless the analyst believes that the repeated out of control results are not due to matrix effect.

Note: If all associated QC meets criteria (blank, LCS/LCSD), up to one surrogate per fraction may be outside of acceptance criteria , as long as the recovery is greater than 10%.

9.7.3 If the sample with surrogate recoveries outside the recovery limits was a sample used for an MS/MSD and the surrogate recoveries in the MS/MSD are also outside of the control limits, then the sample, the MS, and the MSD do not require reanalysis as this phenomenon would indicate a possible matrix problem.

9.7.4 If the sample is reanalyzed and the surrogate recoveries in the reanalysis are acceptable,

then the problem was within the analyst's control and only the reanalyzed data should be reported. (Unless the reanalysis was outside holding times, in which case reporting both sets of results may be appropriate.)

9.7.5 If the reanalysis does confirm the original results, the original analysis is reported and the data flagged as estimated due to matrix effect.

9.8 Nonconformance and Corrective Action

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

9.9 Quality Assurance Summaries

Certain clients may require specific project or program QC which may supersede these method requirements. Quality Assurance Summaries should be developed to address these requirements.

9.10 STL North Canton QC Program

Further details of QC and corrective action guidelines are presented in the STL North Canton QC Program document (QA-003). Refer to this document if in doubt regarding corrective actions.

10 CALIBRATION AND STANDARDIZATION

10.1 Summary

10.1.1 The instrument is tuned for DFTPP, calibrated initially with a five-point calibration curve, and verified each 12-hour shift with one or more continuing calibration standard(s). Recommended instrument conditions are listed in Table 5.

10.2 All standards and extracts are allowed to warm to room temperature before injecting.

10.3 Instrument Tuning

At the beginning of every twelve hour shift when analyses are to be performed, the GC/MS system must be checked to see if acceptable performance criteria (Table 6) is achieved for DFTPP (decafluorotriphenylphosphine).

10.3.1 Inject the GC/MS tuning standard (Section 7.4) into the GC/MS system. Obtain a background-corrected mass spectra of DFTPP and confirm that all the key m/z criteria in Table 6 are achieved. If all the criteria are not achieved, the analyst must retune the mass

spectrometer and repeat the test until all criteria are achieved. The performance criteria must be achieved before any samples, blanks, or standards are analyzed.

10.3.2 The GC/MS tuning standard should also be used to evaluate the inertness of the chromatographic system. Benzidine and pentachlorophenol should not exhibit excessive tailing. If DDT is an analyte of interest, it must be included in the tuning standard, and its breakdown must be < 20%. Refer to section 12 for the appropriate calculations.

10.4 Initial Calibration

10.4.1 Internal Standard Calibration Procedure: Internal standards are listed in Table 7. Use the base peak m/z as the primary m/z for quantitation of the standards. If interferences are noted, use one of the next two most intense masses for quantitation.

10.4.2 Compounds should be assigned to the IS with the closest retention time.

10.4.3 Prepare calibration standards at a minimum of five concentration levels for each parameter of interest. Six standards must be used for a quadratic least squares calibration. Quadratic fit may NOT be used for samples analyzed under South Carolina Certification. It may also be useful to analyze six calibration levels and use the lower five for most analytes and the upper five for analytes that have poor response. Add the internal standard mixture to result in 8 ng on column. The concentrations of all analytes are listed in tables 12 and 13.

10.4.4 Analyze each calibration standard and tabulate the area of the primary characteristic m/z against concentration for each compound and internal standard. Calculate response factors (RF), average response factors, and the percent RSD of the response factors for each compound using the equations in section 12 and verify that the CCC and SPCC criteria in section 10.4.5 and 10.4.6 are met. **No sample analysis may be performed unless these criteria are met.**

10.4.5 System Performance Check Compounds (SPCCs): The minimum average RF for semivolatile SPCCs is 0.050. If the minimum response factors are not met, the system must be evaluated and corrective action must be taken before sample analysis begins. Some possible problems are standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, and active sites in the column or chromatographic system. This check must be met before analysis begins.

SPCC Compounds:

N-nitroso-di-n-propylamine
Hexachlorocyclopentadiene
2,4-Dinitrophenol

4-Nitrophenol

10.4.6 Calibration Check Compounds (CCCs): The %RSD of the response factors for each CCC in the initial calibration must be less than 30% for the initial calibration to be considered valid. This criterion must be met before sample analysis begins. Problems similar to those listed under SPCCs could affect this criterion.

10.4.6.1 If none of the CCCs are required analytes, project specific calibration specifications must be agreed with the client.

10.4.6.2 CCC Compounds:

Phenol
Acenaphthene
1,4-Dichlorobenzene
N-nitrosodiphenylamine
2-Nitrophenol
Pentachlorophenol
2,4-Dichlorophenol
Fluoranthene
Hexachlorobutadiene
Di-n-octylphthalate
4-Chloro-3-methylphenol
Benzo(a)pyrene
2,4,6-Trichlorophenol

10.4.7 If the average of all %RSDs in the initial calibration is $\leq$ 15%, then all analytes may use average response factor for calibration.

10.4.7.1 If the software in use is capable of routinely reporting curve coefficients for data validation purposes, and the necessary calibration reports can be generated, then the analyst should evaluate analytes with %RSD > 15% for calibration on a curve. If it appears that substantially better accuracy would be obtained using quantitation from a curve then the appropriate curve should be used for quantitation.

10.4.7.2 If the average of all the %RSDs in the initial calibration is > 15%, then calibration on a curve must be used for those analytes with %RSD > 15%. Linear or quadratic curve fits may be used. Linear curve fits only may be used for South Carolina Certification. The analyst should consider instrument maintenance to improve the linearity of response. Use of 1/Concentration^2 weighting is recommended to improve the accuracy of quantitation at the low end of the curve. If Relative

Standard Error (RSE) is used to evaluate the curve it must be better than 15%. If the % RSD is >15%, the analyst may drop the low or high points in the ICAL, as long as a minimum of 5 points are maintained and the quantitation range is adjusted accordingly. If the % RSD is still >15%, a quadratic or linear curve may be used. The correlation coefficient (r) must be ≥ 0.990. If the correlation coefficient is < 0.990, then any hits for these compounds must be flagged as estimated.

10.4.7.3 Note: Several components do not respond well by this method (poor linearity). These compounds are famphur, benzenethiol, kepone, and 2,4-toluenediamine. If these compounds are requested by a client and hits are found, alternate standards or methods will be needed for more accurate quantitation. Sensitivity as demonstrated by the low standard is sufficient to substantiate a non-detect.

10.4.8 Weighting of data points

In a linear or quadratic calibration fit, the points at the lower end of the calibration curve have less weight in determining the curve generated than points at the high concentration end of the curve. For South Carolina Certification, only a linear calibration fit, the points at the lower end of the calibration curve have less weight in determining the curve generated than points at the high concentration end of the curve. However, in environmental analysis, accuracy at the low end of the curve is very important. For this reason it is preferable to increase the weighting of the lower concentration points. 1/Concentration^2 weighting (often called 1/X^2 weighting) will improve accuracy at the low end of the curve and should be used if the data system has this capability.

10.4.9 If time remains in the 12 hour period initiated by the DFTPP injection before the initial calibration, samples may be analyzed. Otherwise, proceed to continuing calibration.

10.4.10 Quantitation is performed using the calibration curve or average response factor from the initial curve, not the continuing calibration.

10.5 Continuing Calibration

10.5.1 At the start of each 12-hour period, the GC/MS tuning standard must be analyzed. The injection of DFTPP must result in a mass spectrum for DFTPP which meets the criteria given in Table 6.

10.5.2 Following a successful DFTPP analysis the continuing calibration standard(s) are analyzed. The standards must contain all semivolatile analytes, including all required surrogates. A mid level calibration standard is used for the continuing calibration.

10.5.3 The following criteria must be met for the continuing calibration to be acceptable:

- The SPCC compounds must have a response factor of ≥ 0.05.
- The percent difference or drift of the CCC compounds from the initial calibration must be $\leq 20\%$. (see section 12 for calculations) In addition, the percent difference or drift of all analytes must be $\leq 50\%$, with allowance for up to (4) compounds to be greater than 50%.
- The internal standard response must be within 50-200% of the response in the mid level of the initial calibration.
- The internal standard retention times must be within 30 seconds of the retention times in the mid-level of the initial calibration.
- NOTE: There is no internal standard criteria for samples. Criteria is only for continuing and initial calibrations.
- NOTE: Ohio VAP rules require that any sample with internal standard outliers be reanalyzed. The criteria for acceptance is between 50% and 200% of same internal standard in continuing calibration.

10.5.3.1 If none of the CCCs are required analytes, project specific calibration specifications must be agreed with the client.

10.5.4 Once the above criteria have been met, sample analysis may begin. Initial calibration average RFs (or the calibration curve) will be used for sample quantitation, not the continuing calibration RFs. Analysis may proceed until 12 hours from the injection of the DFTPP have passed. (A sample *injected* less than 12 hours after the DFTPP is acceptable.)

11 PROCEDURE

11.1 Sample Preparation

Samples are prepared following SOP CORP-OP-0001NC.

11.2 Sample Analysis Procedure

11.2.1 Calibrate the instrument as described in section 10. Depending on the target compounds required by the client, it may be necessary to use more than one calibration standard.

11.2.2 All samples must be analyzed using the same instrument conditions as the preceding

continuing calibration standard.

11.2.3 Add internal standard to the extract to result in 8 ng injected on column. Mix thoroughly before injection into the instrument.

11.2.4 Inject the sample extract into the GC/MS system using the same injection technique as used for the standards.

11.2.5 The data system will determine the concentration of each analyte in the extract using calculations equivalent to those in section 12. Quantitation is based on the initial calibration, not the continuing calibration.

11.2.6 Identified compounds are reviewed for proper integration. Manual integrations are performed if necessary and are documented by the analyst or automatically by the data system.

11.2.7 Target compounds identified by the data system are evaluated using the criteria listed in section 12.1.

11.2.8 Library searches of peaks present in the chromatogram that are not target compounds (Tentatively Identified Compounds, TIC) may be performed if required by the client. They are evaluated using the criteria in section 12.3.

11.3 Dilutions

If the response for any compound exceeds the working range of the GC/MS system, a dilution of the extract is prepared and analyzed. An appropriate dilution should be in the

upper half of the calibration range. Samples may be screened to determine the appropriate dilution for the initial run. If the initial diluted run has no hits or hits below 20% of the calibration range and the matrix allows for analysis at a lesser dilution, the sample must be reanalyzed at a dilution targeted to bring the largest hit above 50% of the calibration range.

11.3.1 Guidance for Dilutions Due to Matrix

If the sample is initially run at a dilution and the baseline rise is less than the height of the internal standards, or if individual non-target peaks are less than two times the height of the internal standards, the sample should be reanalyzed at a more concentrated dilution. This requirement is approximate and subject to analyst judgement. For example, samples containing organic acids may need to be analyzed at a higher dilution to avoid destroying the column.

11.3.2 Reporting Dilutions

The most concentrated dilution with target compounds within the calibration range will be reported. Other dilutions will only be reported at client request.

11.4 Perform all qualitative and quantitative measurements. When the extracts are not being used for analyses, refrigerate them at 4 ± 2°C, protected from light in screw cap vials equipped with unpierced Teflon lined septa.

11.5 Retention time criteria for samples

If the retention time for any internal standard changes by more than 0.5 minutes from the last continuing calibration standard, the chromatographic system must be inspected for malfunctions and corrected. Reanalysis of samples analyzed while the system was malfunctioning is required.

11.5.1 If the retention time of any internal standard in any sample varies by more than 0.1 minute from the preceding continuing calibration standard, the data must be carefully evaluated to ensure that no analytes have shifted outside their retention time windows.

11.6 Percent Moisture

Analytical results may be reported as dry or wet weight, as required by the client. Percent moisture must be determined if results will be reported as dry weight. Refer to the facility specific SOP for determination of percent moisture.

11.7 Procedural Variations

11.7.1 One-time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo and approved by a Technical Specialist and QA Manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file. Any unauthorized deviations from this procedure must also be documented as a non-conformance, with a cause and corrective action described.

11.8 Troubleshooting Guide

11.8.1 Daily Instrument Maintenance

In addition to the checks listed in the instrument maintenance schedule in the STL North Canton Quality Assurance Manual (LQM), current version, the following daily maintenance should be performed.

- Clip Column as necessary.
- Install new or cleaned injection port liner as necessary.
- Install new septum as necessary.
- Perform mass calibration as necessary.

11.8.2 Major Maintenance

A new initial calibration is necessary following major maintenance. Major maintenance includes changing the column, cleaning the ion volume or repeller, cleaning the source, and replacing the multiplier. Refer to the manufacturer's manual for specific guidance.

12 DATA ANALYSIS AND CALCULATIONS

12.1 Qualitative identification

An analyte is identified by retention time and by comparison of the sample mass spectrum with the mass spectrum of a standard of the suspected compound (standard reference spectrum). Mass spectra for standard reference may be obtained on the user's GC/MS by analysis of the calibration standards or from the NBS library. Two criteria must be satisfied to verify identification: (1) elution of sample component at the same GC retention time as the standard component; and (2) correspondence of the sample component and the standard component characteristic ions. (Note: Care must be taken to ensure that spectral distortion due to co-elution is evaluated.)

- The sample component retention time must compare to within ± 0.2 min. of the retention time of the standard component. For reference, the standard must be run within the same twelve hours as the sample.
- All ions present in the standard mass spectra at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100%) should be present in the sample spectrum.
- The characteristic ions of a compound must maximize in the same scan or within one scan of each other.
- The relative intensities of ions should agree to within ±30% between the standard and sample spectra. (Example: For an ion with an abundance of 50% in the standard spectra, the corresponding sample abundance must be between 20% and 80%.)

12.1.1 If a compound cannot be verified by all the above criteria, but in the technical judgment of the analyst the identification is correct, the analyst shall report that identification and proceed with quantitation.

12.2 Mass chromatogram searches.

Certain compounds are unstable in the calibration standard and cannot be calibrated in the normal way. In particular, the compound hexachlorophene (CAS 70-30-4) falls into this category, and is required for Appendix IX analysis. For this analyte a mass chromatogram search is made.

12.2.1 Hexachlorophene

Display the mass chromatograms for mass 196 and mass 198 for the region of the chromatogram from at least 2 minutes before chrysene-d12 to at least 4 minutes after chrysene-d12. If peaks for both ions coincide then the analyst evaluates the spectrum for the presence of hexachlorophene. No quantitation is possible.

12.3 For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The necessity to perform this type of identification will be determined by the type of analyses being conducted. Computer generated library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other. Only after visual comparison of sample spectra with the nearest library searches shall the mass spectral interpretation specialist assign a tentative identification. Guidelines for making tentative identification are:

- Relative intensities of major ions in the reference spectrum (ions >10% of the most abundant ion) should be present in the sample spectrum.
- The relative intensities of the major ions should agree within ±20%. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance should be between 30%and 70%.)
- Molecular ions present in the reference spectrum should be present in the sample spectrum.
- Ions present in the sample spectrum, but not in the reference spectrum, should be reviewed for possible background contamination or presence of coeluting compounds.
- Ions present in the reference spectrum, but not in the sample spectrum, should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting peaks. Data system library reduction programs can sometimes create these discrepancies.

- Automatic background subtraction can severely distort spectra from samples with unresolved hydrocarbons.

12.4 Anyone evaluating data is trained to know how to handle isomers with identical mass spectra and close elution times. These include:

Dichlorobenzenes
Methylphenols
Trichlorophenols
Phenanthrene, anthracene
Fluoranthene, pyrene
Benzo(b) and (k)fluoranthene
Chrysene, benzo(a)anthracene

Extra precautions concerning these compounds are to more closely scrutinize retention time vs. the calibration standard and also to check that all isomers have distinct retention times.

A second category of problem compounds would be the poor responders or compounds that chromatograph poorly. Included in this category would be:

Benzoic acid
Chloroanilines
Nitroanilines
2,4-Dinitrophenol
4-Nitrophenol
Pentachlorophenol
3,3'-Dichlorobenzidine
Benzyl alcohol
4,6-Dinitro-2-methylphenol

Manually checking the integrations would be appropriate for these compounds.

12.5 Calculations

12.5.1 Percent Relative Standard Deviation for Initial Calibration

$$\%RSD = \frac{SD}{\overline{RF}} \times 100$$

$\overline{RF}$ = Mean of RFs from intial caibration for a compound

SD = Standard deviation of RFs from initial calibration for a compound,

$$= \sqrt{\sum_{i=1}^{N} \frac{\left(RFi - \overline{RF}\right)^2}{N-1}}$$

RFi = RF for each of the calibration levels

N = Number of RF values

12.5.2 Continuing calibration percent drift

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

C_{actual} = Known concentration in standard

C_{found} = Measured concentration using selected quantitation method

12.5.3 Concentration in the extract

The concentration of each identified analyte and surrogate in the extract is calculated from the linear or quadratic curve fitted to the initial calibration points, or from the average RF of the initial calibration. For South Carolina Certification the concentration of each identified analyte and surrogate in the extract is calculated from the linear curve only fitted to the initial calibration points, or from the average RF of the initial calibration.

12.5.3.1 Average response factor

If the average of all the %RSDs of the response factors in the initial calibration is ≤ 15%, the average response factor from the initial calibration may be used for quantitation.

$$C_{ex} = \frac{R_x C_{is}}{R_{is} \overline{RF}}$$

12.5.3.2 Linear fit (Use only Linear fit for South Carolina Certification)

$$C_{ex} = A + B\frac{(R_x C_{is})}{R_{is}}$$

C_{ex} = Concentration in extract, µg/mL

R_x = Response for analyte

C_{is} = Concentration of internal standard

A = Intercept

B = Slope

12.5.3.3 Quadratic fit

$$C_{ex} = A + B\left(\frac{R_x C_{is}}{R_{is}}\right) + C\left(\frac{R_x C_{is}{}^2}{R_{is}}\right)$$

C = Curvature

12.5.4 The concentration in the sample is then calculated.

12.5.4.1 Aqueous Calculation

$$\text{Concentration, } \mu g / L = \frac{C_{ex} V_t}{V_o}$$

Where:

V_t = Volume of total extract, µL, taking into account dilutions (i.e., a 1-to-10 dilution of a 1 mL extract will mean V_t = 10,000 µL. If half of the

base/neutral extract and half of the acid extract are combined, V_t = 2,000.)

V_o = Volume of water extracted (mL)

12.5.5 Sediment/Soil, Sludge (on a dry-weight basis) and Waste (normally on a wet-weight basis:

$$\text{Concentration, } \mu g / kg = \frac{C_{ex} V_t}{W_s D}$$

W_s = Weight of sample extracted or diluted in grams

D = (100 - % moisture in sample)/100, for a dry weight basis or 1 for a wet weight basis

12.6 MS/MSD percent recovery calculation.

$$\text{Matrix Spike Recovery} = \frac{S_{SR} - S_R}{S_A} \times 100\%$$

S_{SR} = Spike sample result

S_R = Sample result

S_A = Spike added

12.7 Relative % Difference calculation for the MS/MSD

$$RPD = \frac{MS_R - MSD_R}{1/2(MS_R + MSD_R)} \times 100$$

RPD = Relative percent difference

MS_R = Matrix spike result

MSD_R = Matrix spike duplicate result

12.8 Relative response factor calculation.

$$RF = \frac{A_x C_{is}}{A_{is} C_x}$$

A_x=Area of the characteristic ion for the compound being measured

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

C_x=Concentration of the compound being measured (µg/L)

C_{is} =Concentration of the specific internal standard (µg/L)

12.9 Calculation of TICs: The calculation of TICs (tentatively identified compounds) is identical to the above calculations with the following exceptions:

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

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

RF = 1

12.10 Percent DDT breakdown

$$\% \text{ DDT breakdown} = \frac{\text{DDEarea} + \text{DDDarea}}{\text{DDTarea} + \text{DDEarea} + \text{DDarea}}$$

The total ion current areas are used for this calculation

13 METHOD PERFORMANCE

13.1 Method Detection Limit

Each laboratory must generate a valid method detection limit for each analyte of interest. The MDL must be below the reporting limit for each analyte. The procedure for determination of the method detection limit is given in 40 CFR Part 136, Appendix B, and further defined in QA Policy #: QA-005.

13.2 Initial Demonstration

Each laboratory must make an initial demonstration of capability for each individual method. Demonstration of capability for both soil and water matrices is required. This requires analysis

of QC check samples containing all of the standard analytes for the method. For some tests it may be necessary to use more than one QC check mix to cover all analytes of interest.

13.2.1 Four aliquots of the QC check sample are analyzed using the same procedures used to analyze samples, including sample preparation. The concentration of the QC check sample should be equivalent to the level 4 calibration standard.

13.2.2 Calculate the average recovery and standard deviation of the recovery for each analyte of interest. Compare these results with the acceptance criteria given in table 14.

13.2.3 If any analyte does not meet the acceptance criteria the test must be repeated. Only those analytes that did not meet criteria in the first test need to be evaluated. Repeated failure for any analyte indicates the need for the laboratory to evaluate the analytical procedure and take corrective action.

13.3 Non-standard analytes

For non-standard analytes, an MDL study must be performed and calibration curve generated before analyzing any samples, unless lesser requirements are previously agreed to with the client. In any event, the minimum initial demonstration required is analysis of an extracted standard at the reporting limit and a single point calibration.

13.4 Training Qualification

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

13.5 Data Quality Objectives (DQO). Refer to project-specific Quality Assurance plans for DQO information.

14 POLLUTION PREVENTION

14.1 This section is not applicable to this procedure.

15 WASTE MANAGEMENT

15.1 Waste generated during aliquotting and from used vials must be disposed of in accordance with the facility hazardous waste procedures. The Health and Safety Director should be contacted if additional information is required.

16 REFERENCES

16.1 SW846, Test Methods for Evaluating Solid Waste, Third Edition, Update II, October 1994,

Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS): Capillary Column Technique, Method 8270C.

16.2 J. W. Eichelberger, L. E. Harris, and W. L. Budde, "Reference Compound to Calibrate Ion Abundance Measurement in Gas Chromatography/Mass Spectrometry," Analytical Chemistry, 47, 995 (1975)

16.3 Method 625

17 MISCELLANEOUS

17.1 Modifications from Reference Method

17.1.1 A retention time window of 0.2 minutes is used for all components, since some data systems do not have the capability of using the relative retention time units specified in the reference method.

17.1.2 The quantitation and qualifier ions for some compounds have been changed from those recommended in SW-846 in order to improve the reliability of qualitative identification.

17.2 Modifications from Previous Revision

17.2.1 This SOP has been substantially revised to meet the requirements of method 8270C.

17.2.2 Directions for analysis be method 625 have been added as an attachment.

17.2.3 SOP has been revised to include a 5 mL final volume for soils and 2 mL final volume for waters.

17.3 Facility Specific SOPs

Each facility shall attach a list of facility specific SOPs or approved attachments (if applicable) which are required to implement this SOP or which are used in conjunction with this SOP. If no facility specific SOPs or amendments are to be attached, a statement must be attached specifying that there are none.

17.4 Tables

Table 1

STL North Canton Primary Standard[1] and Standard Reporting Limits

Analytes	CAS Number	Standard Reporting Limits	
		Aqueous µg/L	Low Soil/Sediment µg/kg
Pyridine	110-86-1	20	660
N-nitrosodimethylamine	62-75-9	10	330
Aniline	62-53-3	10	330
Phenol	108-95-2	10	330
Bis(2-chloroethyl)ether	111-44-4	10	330
2-Chlorophenol	95-57-8	10	330
1,3-Dichlorobenzene	541-73-1	10	330
1,4-Dichlorobenzene	106-46-7	10	330
Benzyl alcohol	100-51-6	10	330
1,2-Dichlorobenzene	95-50-1	10	330
2-Methylphenol	95-48-7	10	330
2,2'-oxybis(1-chloropropane)[2]	108-60-1	10	330
4-Methylphenol	106-44-5	10	330
N-Nitroso-di-n-propylamine	621-64-7	10	330
Hexachloroethane	67-72-1	10	330
Nitrobenzene	98-95-3	10	330
Isophorone	78-59-1	10	330
2-Nitrophenol	88-75-5	10	330
2,4-Dimethylphenol	105-67-9	10	330
Benzoic acid	65-85-0	50	1600
Bis(2-chloroethoxy)methane	111-91-1	10	330
2,4-Dichlorophenol	120-83-2	10	330
1,2,4-Trichlorobenzene	120-82-1	10	330
Naphthalene	91-20-3	10	330
4-Chloroaniline	106-47-8	10	330
Hexachlorobutadiene	87-68-3	10	330
4-Chloro-3-methylphenol	59-50-7	10	330
2-Methylnaphthalene	91-57-6	10	330
Hexachlorocyclopentadiene	77-47-4	50	1600
2,4,6-Trichlorophenol	88-06-2	10	330
2,4,5-Trichlorophenol	95-95-4	10	330
2-Chloronaphthalene	91-58-7	10	330
2-Nitroaniline	88-74-4	50	1600
Dimethyl phthalate	131-11-3	10	330
Acenaphthylene	208-96-8	10	330
3-Nitroaniline	99-09-2	50	1600
Acenaphthene	83-32-9	10	330
2,4-Dinitrophenol	51-28-5	50	1600
4-Nitrophenol	100-02-7	50	1600
Dibenzofuran	132-64-9	10	330

Table 1

STL North Canton Primary Standard[1] and Standard Reporting Limits

Analytes	CAS Number	Standard Reporting Limits	
		Aqueous µg/L	Low Soil/Sediment µg/kg
2,4-Dinitrotoluene	121-14-2	10	330
2,6-Dinitrotoluene	606-20-2	10	330
Diethylphthalate	84-66-2	10	330
4-Chlorophenyl phenyl ether	7005-72-3	10	330
Fluorene	86-73-7	10	330
4-Nitroaniline	100-01-6	50	1600
4,6-Dinitro-2-methylphenol	534-52-1	50	1600
N-Nitrosodiphenylamine	86-30-6	10	330
Azobenzene	103-33-3	10	330
4-Bromophenyl phenyl ether	101-55-3	10	330
Hexachlorobenzene	118-74-1	10	330
Pentachlorophenol	87-86-5	50	1600
Phenanthrene	85-01-8	10	330
Anthracene	120-12-7	10	330
Carbazole	86-74-8	10	330
Di-n-butyl phthalate	84-74-2	10	330
Fluoranthene	206-44-0	10	330
Benzidine	92-87-5	100	3300
Pyrene	129-00-0	10	330
Butyl benzyl phthalate	85-68-7	10	330
3,3'-Dichlorobenzidine	91-94-1	50	1600
Benzo(a)anthracene	56-55-3	10	330
Bis(2-ethylhexyl)phthalate	117-81-7	10	330
Chrysene	218-01-9	10	330
Di-n-octylphthalate	117-84-0	10	330
Benzo(b)fluoranthene	205-99-2	10	330
Benzo(k)fluoranthene	207-08-9	10	330
Benzo(a)pyrene	50-32-8	10	330
Indeno(1,2,3-cd)pyrene	193-39-5	10	330
Dibenz(a,h)anthracene	53-70-3	10	330
Benzo(g,h,i)perylene	191-24-2	10	330
Benzaldehyde	100-52-7	10	330
Caprolactam	105-60-2	10	330
1,1-Biphenyl	92-52-4	10	330
Atrazine	1912-24-9	10	330

[1] The STL North Canton primary standard is the standard normally used at F. Additional standards, such as the Appendix IX standard may be necessary to include all target analytes required for some clients.

[2] 2,2'oxybis(1-chloropropane) was formerly known as bis (2-chloroisopropyl)ether

Table 2

STL North Canton Appendix IX[1] Standard Reporting Limits

Semivolatiles	CAS Number	Standard Reporting Limits	
		Aqueous µg/L	Low Soil/Sediment µg/kg
2-Picoline	109-06-8	20	660
N-Nitrosomethylethylamine	10595-95-6	10	330
Methyl methanesulfonate	66-27-3	10	330
N-Nitrosodiethylamine	55-18-5	10	330
Ethyl methanesulfonate	62-50-0	10	330
Pentachloroethane	76-01-7	50	1600
Acetophenone	98-86-2	10	330
N-Nitrosopyrrolidine	930-55-2	10	330
N-Nitrosomorpholine	59-89-2	10	330
o-Toluidine	95-53-4	20	660
3-Methylphenol	108-39-4	10	330
N-Nitrosopiperidine	100-75-4	10	330
o,o,o-Triethyl-Phosphorothioate[2]	126-68-1	50	1600
a,a-Dimethyl-phenethylamine	122-09-8	50	1600
2,6-Dichlorophenol	87-65-0	10	330
Hexachloropropene	1888-71-7	100	3300
p-Phenylenediamine	106-50-3	100	3300
n-Nitrosodi-n-butylamine	924-16-3	10	330
Safrole	94-59-7	20	660
1,2,4,5-Tetrachlorobenzene	95-94-3	10	330
Isosafrole	120-58-1	20	660
1,4-Dinitrobenzene	100-25-4	10	330
1,4-Naphthoquinone	130-15-4	50	1600
1,3-Dinitrobenzene	99-65-0	10	330
Pentachlorobenzene	608-93-5	10	330
1-Naphthylamine	134-32-7	10	330
2-Naphthylamine	91-59-8	10	330
2,3,4,6-Tetrachlorophenol	58-90-2	50	1600
5-Nitro-o-toluidine	99-55-8	20	660
Thionazin[2]	297-97-2	50	1600
1,3,5-Trinitrobenzene	99-35-4	50	1600
Sulfotepp[2]	3689-24-5	50	1600
Phorate[2]	298-02-2	50	1600
Phenacetin	62-44-2	20	660
Diallate[2]	2303-16-4	20	660
Dimethoate[2]	60-51-5	20	660
4-Aminobiphenyl	92-67-1	50	1600
Pentachloronitrobenzene	82-68-8	50	1600
Pronamide	23950-58-5	20	660

Table 2

STL North Canton Appendix IX[1] Standard Reporting Limits

Semivolatiles	CAS Number	Standard Reporting Limits	
		Aqueous µg/L	Low Soil/Sediment µg/kg
Disulfoton[2]	298-04-4	50	1600
2-secbutyl-4,6-dinitrophenol (Dinoseb[2])	88-85-7	20	660
4-Nitroquinoline-1-oxide	56-57-5	100	3300
Methapyrilene	91-80-5	50	1600
Aramite	140-57-8	20	660
Famphur[3]	52-85-7	100	3300
p-(Dimethylamino)azobenzene	60-11-7	20	660
p-Chlorobenzilate	510-15-6	10	330
3,3'-Dimethylbenzidine	119-93-7	50	1600
2-Acetylaminofluorene	53-96-3	100	3300
Dibenz(a,j)acridine	224-42-0	20	660
7,12-Dimethylbenz(a)anthracene	57-97-6	20	660
3-Methylcholanthrene	56-49-5	20	660

[1] The Appendix IX standard contains additional analytes required for the Appendix IX list. The STL North Canton primary standard must also be analyzed to include all of the Appendix IX list

[2] May also be analyzed by method 8141, which can achieve lower reporting limits.

[3] It is highly recommended that Famphur is analyzed by method 8081. It is a poor responder by 8270C.

Table 2A
STL North Canton Michigan Program[1]

Semivolatile	CAS Number	Michigan Reporting Limits	
		Aqueous µg/L	Low Soil/Sediment µg/kg
Acenaphthene	83-32-9	5	330
Acenaphthylene	208-96-8	5	330
Acetophenone	98-86-2	5	330
Anthracene	120-12-7	5	330
Atrzine	1912-24-9	5	330
Benzaldehyde	100-52-7	10	330
Benzo(a)anthracene*	56-55-3	1	330
Benzo(a)pyrene*	50-32-8	2	330
Benzo(b)fluoranthene*	205-99-2	2	330
Benzo(g,h,i)perylene	191-24-2	5	330
Benzo(k)fluoranthene	207-08-9	5	330
1,1'-Biphenyl	92-52-4	10	330
4-Bromophenylphenyl ehter	101-55-3	5	330
Butylbenzylphthalate	85-68-7	5	330
di-n-Butylphthalate	84-74-2	5	330
Caprolactam	105-60-2	10	330
Carbazole	86-74-8	10	330
4-Chloroaniline	106-47-8	20	1700
bis(2-Chloroethoxy)methane	111-91-1	5	330
bis(2-Chloroethyl)ether	111-44-4	4	330
bis(2-Chloroisopropyl)ether	108-60-1	5	330
4-Chloro-3-Methylphenol	59-50-7	5	330
2-Chloronaphthalene	91-58-7	5	330
2-Chlorophenol	95-57-8	5	330
4-Chlorophenyl phenyl ether	7005-72-3	5	330
Chrysene	218-01-9	5	330
Dibenz(a,h)anthracene*	53-70-3	2	330
Dibenzofuran	132-64-9	5	330
3,3'-Dichlorobenzidine	91-94-1	4	2000
2,4-Dichlorophenol	120-83-2	10	330
Diethylphthalate	84-66-2	5	330
2-4-Dimethylphenol	105-67-9	5	330
Dimethylphthalate	131-11-3	5	330
4,6-Dinitro-2-methylphenol	534-52-1	20	1700
2,4-Dinitrophenol	51-28-5	20	1700
2,4-Dinitrotoluene	121-14-2	5	330
2,6-Dinitrotoluene	606-20-2	5	330
bis(2-Ethylhexyl)phthalate	117-81-7	5	330
Fluoranthene	206-44-0	5	330
Fluorene	86-73-7	5	330
Hexachlorobenzene	118-74-1	5	330
Hexachlorobutadiene	87-68-3	5	330
Hexachlorocyclopentadiene	77-47-4	5	330

Table 2A
STL North Canton Michigan Program[1]

Semivolatile	CAS Number	Michigan Reporting Limits	
		Aqueous µg/L	Low Soil/Sediment µg/kg
Hexachloroethane	67-72-1	5	330
Indeno(1,2,3-cd)pyrene*	193-39-5	2	330
Isophorone	78-59-1	5	330
2-Methylnapthalene	91-57-6	5	330
2-Methylphenol	95-48-7	5	330
4-Methylphenol	106-44-5	5	330
Naphthalene	91-20-3	5	330
2-Nitroaniline	88-74-4	20	1700
3-Nitroaniline	99-09-2	20	1700
4-Nitroaniline	100-01-6	20	1700
Nitrobenzene	95-95-3	4	330
2-Nitrophenol	88-75-5	5	330
4-Nitrophenol	100-02-7	20	1700
N-Nitroso-di-n-propylamine	621-64-7	5	330
N-Nitrosodiphenylamine (diphenylamine)	62-75-9	5	330
di-n-Octylphthalate	117-84-0	5	330
Pentachlorophenol	87-86-5	20	800
Phenanthrene	85-01-8	5	330
Phenol	108-95-2	5	330
Pyrene	129-00-0	5	330
2,4,5-Trichlorophenol	95-95-4	5	330
2,4,6-Trichlorophenol	88-06-2	4	330

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

* These compounds are reported at limits that are below the low standard of the ICAL.

Table 3

Reportable Analytes for STL North Canton Standard Tests, Primary Standard

Analyte	CAS Number	STL North Canton Standard List	TCLP	TCL	Appendix IX
Pyridine	110-86-1		X		X
N-nitrosodimethylamine	62-75-9				X
Aniline	62-53-3				X
Phenol	108-95-2	X		X	X
Bis(2-chloroethyl)ether	111-44-4	X		X	X
2-Chlorophenol	95-57-8	X		X	X
1,3-Dichlorobenzene	541-73-1	X		X	X
1,4-Dichlorobenzene	106-46-7	X	X	X	X
Benzyl alcohol	100-51-6				X

Table 3

Reportable Analytes for STL North Canton Standard Tests, Primary Standard

Analyte	CAS Number	STL North Canton Standard List	TCLP	TCL	Appendix IX
1,2-Dichlorobenzene	95-50-1	X		X	X
2-Methylphenol	95-48-7	X	X	X	X
2,2'-oxybis(1-chloropropane)[1]	180-60-1	X		X	X
4-Methylphenol	106-44-5	X	X	X	X
N-Nitroso-di-n-propylamine	621-64-7	X		X	X
Hexachloroethane	67-72-1	X	X	X	X
Nitrobenzene	98-95-3	X	X	X	X
Isophorone	78-59-1	X		X	X
2-Nitrophenol	88-75-5	X		X	X
2,4-Dimethylphenol	105-67-9	X		X	X
Benzoic acid	65-85-0				
Bis(2-chloroethoxy)methane	111-91-1	X		X	X
2,4-Dichlorophenol	120-83-2	X		X	X
1,2,4-Trichlorobenzene	120-82-1	X		X	X
Naphthalene	91-20-3	X		X	X
4-Chloroaniline	106-47-8	X		X	X
Hexachlorobutadiene	87-68-3	X	X	X	X
4-Chloro-3-methylphenol	59-50-7	X		X	X
2-Methylnaphthalene	91-57-6	X		X	X
Hexachlorocyclopentadiene	77-47-4	X		X	X
2,4,6-Trichlorophenol	88-06-2	X	X	X	X
2,4,5-Trichlorophenol	95-95-4	X	X	X	X
2-Chloronaphthalene	91-58-7	X		X	X
2-Nitroaniline	88-74-4	X		X	X
Dimethyl phthalate	131-11-3	X		X	X
Acenaphthylene	208-96-8	X		X	X
3-Nitroaniline	99-09-2	X		X	X
Acenaphthene	83-32-9	X		X	X
2,4-Dinitrophenol	51-28-5	X		X	X
4-Nitrophenol	100-02-7	X		X	X
Dibenzofuran	132-64-9	X		X	X
2,4-Dinitrotoluene	121-14-2	X	X	X	X
2,6-Dinitrotoluene	606-20-2	X		X	X
Diethylphthalate	84-66-2	X		X	X
4-Chlorophenyl phenyl ether	7005-72-3	X		X	X
Fluorene	86-73-7	X		X	X
4-Nitroaniline	100-01-6	X		X	X
4,6-Dinitro-2-methylphenol	534-52-1	X		X	X
N-Nitrosodiphenylamine	86-30-6	X		X	X
Azobenzene[2]	103-33-3				
4-Bromophenyl phenyl ether	101-55-3	X		X	X
Hexachlorobenzene	118-74-1	X	X	X	X
Pentachlorophenol	87-86-5	X	X	X	X
Phenanthrene	85-01-8	X		X	X

Table 3

Reportable Analytes for STL North Canton Standard Tests, Primary Standard

Analyte	CAS Number	STL North Canton Standard List	TCLP	TCL	Appendix IX
Anthracene	120-12-7	X		X	X
Carbazole	86-74-8	X		X	
	84-74-2	X		X	X
Fluoranthene	206-44-0	X		X	X
Benzidine	92-87-5				
Pyrene	129-00-0	X		X	X
Butyl benzyl phthalate	85-68-7	X		X	X
3,3'-Dichlorobenzidine	91-94-1	X		X	X
Benzo(a)anthracene	56-55-3	X		X	X
Bis(2-ethylhexyl)phthalate	117-81-7	X		X	X
Chrysene	218-01-9	X		X	X
Di-n-octylphthalate	117-84-0	X		X	X
Benzo(b)fluoranthene	205-99-2	X		X	X
Benzo(k)fluoranthene	207-08-9	X		X	X
Benzo(a)pyrene	50-32-8	X		X	X
Indeno(1,2,3-cd)pyrene	193-39-5	X		X	X
Dibenz(a,h)anthracene	53-70-3	X		X	X
Benzo(g,h,i)perylene	191-24-2	X		X	X
Benzaldehyde	100-52-7			X	
Caprolactam	105-60-2			X	
1,1-Biphenyl	92-52-4			X	
Atrazine	1912-24-9			X	

[1] 2,2'oxybis(1-chloropropane) was formerly known as bis(2-chloroisopropyl)ether

[2] Azobenzene is formed by decomposition of 1,2-diphenyhydrazine. If 1,2-diphenylhydrazine is requested, it will be analyzed as azobenzene.

Table 4

Reportable analytes for STL North Canton Standard Tests, Appendix IX Standard

Semivolatiles	CAS Number	STL North Canton Standard List	TCLP	TCL	Appendix IX
2-Picoline	109-06-8				X
N-Nitrosomethylethylamine	10595-95-6				X
Methyl methanesulfonate	66-27-3				X
N-Nitrosodiethylamine	55-18-5				X
Ethyl methanesulfonate	62-50-0				X
Pentachloroethane	76-01-7				X
Acetophenone	98-86-2			X	X
N-Nitrosopyrrolidine	930-55-2				X
N-Nitrosomorpholine	59-89-2				X
o-Toluidine	95-53-4				X
3-Methylphenol	108-39-4				X
N-Nitrosopiperidine	100-75-4				X
o,o,o-Triethyl-Phosphorothioate[1]	126-68-1				X
a,a-Dimethyl-phenethylamine	122-09-8				X
2,6-Dichlorophenol	87-65-0				X
Hexachloropropene	1888-71-7				X
p-Phenylenediamine	106-50-3				X
n-Nitrosodi-n-butylamine	924-16-3				X
Safrole	94-59-7				X
1,2,4,5-Tetrachlorobenzene	95-94-3				X
Isosafrole	120-58-1				X
1,4-Dinitrobenzene	100-25-4				X
1,4-Naphthoquinone	130-15-4				X
1,3-Dinitrobenzene	99-65-0				X
Pentachlorobenzene	608-93-5				X
1-Naphthylamine	134-32-7				X
2-Naphthylamine	91-59-8				X
2,3,4,6-Tetrachlorophenol	58-90-2				X
5-Nitro-o-toluidine	99-55-8				X
Thionazin[1]	297-97-2				X
1,3,5-Trinitrobenzene	99-35-4				X
Sulfotepp[1]	3689-24-5				X
Phorate[1]	298-02-2				X
Phenacetin	62-44-2				X
Diallate	2303-16-4				X
Dimethoate[1]	60-51-5				X
4-Aminobiphenyl	92-67-1				X
Pentachloronitrobenzene	82-68-8				X
Pronamide	23950-58-5				X
Disulfoton[1]	298-04-4				X
2-secbutyl-4,6-dinitrophenol (Dinoseb)[1]	88-85-7				X
4-Nitroquinoline-1-oxide	56-57-5				X

Table 4

Reportable analytes for STL North Canton Standard Tests, Appendix IX Standard

Semivolatiles	CAS Number	STL North Canton Standard List	TCLP	TCL	Appendix IX
Famphur[2]	52-85-7				X
Methapyrilene	91-80-5				X
Aramite	140-57-8				X
p-(Dimethylamino)azobenzene	60-11-7				X
p-Chlorobenzilate	510-15-6				X
3,3'-Dimethylbenzidine	119-93-7				X
2-Acetylaminofluorene	53-96-3				X
Dibenz(a,j)acridine[3]	224-42-0				
7,12-Dimethylbenz(a)anthracene	57-97-6				X
3-Methylcholanthrene	56-49-5				X
Hexachlorophene[4]	70-30-4				X
Diphenylamine[5]	122-39-4				X

1 May also be analyzed by method 8141, which can achieve lower reporting limits.

2 May also be analyzed by method 8081, which can achieve lower reporting limits.

3 Skinner List Compound

4 Hexachlorophene is a required analyte for Appendix IX. This compound is not stable, and therefore not included in the calibration standard. The characteristic ions for hexachlorophene are searched for in the chromatogram. (See section 12.2.1)

5 Diphenylamine is a required compound for Appendix IX. N-nitrosodiphenylamine decomposes in the injection port to form diphenylamine. Therefore these two compounds cannot be distinguished. Diphenylamine is not included in the calibration standard.

Table 5

Suggested Instrumental Conditions

Mass Range	35-500 amu
Scan Time	≤1 second/scan
Initial Column Temperature/Hold Time	40°C for 2 minutes
Column Temperature Program	40 - 320°C at 11.5°C/min
Final Column Temperature/Hold Time	320°C (until at least one minute after benzo(g,h,i)perylene has eluted)
Injector Temperature	250 - 300°C
Transfer Line Temperature	250 - 300°C
Source Temperature	According to manufacturer's specifications
Injector	Grob-type, split / splitless
Sample Volume	1 or 2 µl
Carrier Gas	Helium at 30 cm/sec

Table 6

DFTPP Key Ions and Ion Abundance Criteria

Mass	Ion Abundance Criteria
51	30 - 60% of mass 198
68	<2% of mass 69
70	<2% of mass 69
127	40 - 60% of mass 198
197	<1% of mass 198
198	Base peak, 100% relative abundance
199	5 - 9% of mass 198
275	10 - 30% of mass 198
365	>1% of mass 198
441	Present, but less than mass 443
442	>40% of mass 198
443	17 - 23% of mass 442

Table 7

Analytes in Approximate Retention Time Order and Characteristic Ions, Primary Standard

Analyte	Primary	Secondary	Tertiary
N-nitrosodimethylamine	74	42	
Pyridine	79	52	
2-Fluorophenol (Surrogate Standard)	112	64	63
Phenol-d5 (Surrogate Standard)	99	42	71
Benzaldehyde	77	105	106
Aniline	93	66	
Phenol	94	65	66
Bis(2-chloroethyl)ether	93	63	95
2-Chlorophenol	128	64	130
1,3-Dichlorobenzene	146	148	113
1,4-Dichlorobenzene-d4 (Internal Standard)	152	150	115
1,4-Dichlorobenzene	146	148	113
Benzyl Alcohol	108	79	77
1,2-Dichlorobenzene	146	148	113
2-Methylphenol	108	107	79
2,2'-oxybis(1-chloropropane)[1]	45	77	79
4-Methylphenol	108	107	79
N-Nitroso-di-n-propylamine	70	42	101,130
Hexachloroethane	117	201	199
Nitrobenzene-d5 (Surrogate Standard)	82	128	54
Nitrobenzene	77	123	65
Isophorone	82	95	138
2-Nitrophenol	139	65	109
2,4-Dimethylphenol	107	121	122
Benzoic Acid	122	105	77
Bis(2-chloroethoxy)methane	93	95	123
2,4-Dichlorophenol	162	164	98
1,2,4-Trichlorobenzene	180	182	145
Naphthalene-d8 (Internal Standard)	136	68	54
Naphthalene	128	129	127
4-Chloroaniline	127	129	65
Hexachlorobutadiene	225	223	227
Caprolactam	113	55	56
4-Chloro-3-methylphenol	107	144	142
2-Methylnaphthalene	142	141	115
Hexachlorocyclopentadiene	237	235	272
2,4,6-Trichlorophenol	196	198	200
2,4,5-Trichlorophenol	196	198	200
1,1'-Biphenyl	154	153	76
2-Fluorobiphenyl (Surrogate Standard)	172	171	170
2-Chloronaphthalene	162	164	127
2-Nitroaniline	65	92	138
Dimethylphthalate	163	194	164

Table 7

Analytes in Approximate Retention Time Order and Characteristic Ions, Primary Standard

Analyte	Primary	Secondary	Tertiary
Acenaphthylene	152	151	153
2,6-Dinitrotoluene	165	63	89
Acenaphthene-d10 (Internal Standard)	164	162	160
3-Nitroaniline	138	108	92
Acenaphthene	153	152	154
2,4-Dinitrophenol	184	63	154
Dibenzofuran	168	139	84
4-Nitrophenol	109	139	65
2,4-Dinitrotoluene	165	63	89
Diethylphthalate	149	177	150
Fluorene	166	165	167
4-Chlorophenylphenylether	204	206	141
4-Nitroaniline	138	92	108
4,6-Dinitro-2-methylphenol	198	182	77
N-Nitrosodiphenylamine	169	168	167
2,4,6-Tribromophenol (Surrogate Standard)	330	332	141
Azobenzene	77	182	105
4-Bromophenylphenylether	248	250	141
Hexachlorobenzene	284	142	249
Atrazine	200	173	215
Pentachlorophenol	266	264	268
Phenanthrene-d10 (Internal Standard)	188	94	80
Phenanthrene	178	179	176
Anthracene	178	179	176
Carbazole	167	166	139
Di-n-butylphthalate	149	150	104
Fluoranthene	202	101	100
Benzidine	184	92	185
Pyrene	202	101	100
Terphenyl-d14 (Surrogate Standard)	244	122	212
Butylbenzylphthalate	149	91	206
Benzo(a)Anthracene	228	229	226
Chrysene-d12 (Internal Standard)	240	120	236
3,3'-Dichlorobenzidine	252	254	126
Chrysene	228	226	229
Bis(2-ethylhexyl)phthalate	149	167	279
Di-n-octylphthalate	149	167	43
Benzo(b)fluoranthene	252	253	125
Benzo(k)fluoranthene	252	253	125
Benzo(a)pyrene	252	253	125
Perylene-d12 (Internal Standard)	264	260	265
Indeno(1,2,3-cd)pyrene	276	138	277
Dibenz(a,h)anthracene	278	139	279
Benzo(g,h,i)perylene	276	138	277

Table 8

Analytes in Approximate Retention Time Order and Characteristic Ions, Appendix IX Standard

Analyte	Primary	Secondary	Tertiary
2-Picoline	93	66	92
N-Nitrosomethylethylamine	88	42	43
Methyl methanesulfonate	80	79	65
N-Nitrosodiethylamine	102	44	57
Ethyl methanesulfonate	79	109	97
Pentachloroethane	117	119	167
Acetophenone	105	77	120
N-Nitrosopyrrolidine	100	41	42
N-Nitrosomorpholine	116	56	86
o-Toluidine	106	107	
3-Methylphenol	108	107	77
N-Nitrosopiperidine	114	42	55
o,o,o-Triethyl-Phosphorothioate	198	121	93
a,a-Dimethyl-phenethylamine	58	91	
2,6-Dichlorophenol	162	164	63
Hexachloropropene	213	215	211
p-Phenylenediamine	108	80	
n-Nitrosodi-n-butylamine	84	57	41
Safrole	162	104	77
1,2,4,5-Tetrachlorobenzene	216	214	218
Isosafrole 1	162	104	131
Isosafrole 2	162	104	131
1,4-Dinitrobenzene	168	75	122
1,4-Naphthoquinone	158	104	102
1,3-Dinitrobenzene	168	75	76
Pentachlorobenzene	250	248	252
1-Naphthylamine	143	115	
2-Naphthylamine	143	115	
2,3,4,6-Tetrachlorophenol	232	230	131
5-Nitro-o-toluidine	152	77	106
Thionazin	97	96	143
1,3,5-Trinitrobenzene	213	75	120
Sulfotepp	97	322	202
Phorate	75	97	121
Phenacetin	108	179	109
Diallate	86	234	
Dimethoate	87	93	125
4-Aminobiphenyl	169		
Pentachloronitrobenzene	237	142	214
Pronamide	173	175	255
Disulfoton	88	97	89
2-secbutyl-4,6-dinitrophenol (Dinoseb)	211	163	147
Methyl parathion	109	125	263
4-Nitroquinoline-1-oxide	190	128	160

Table 8

Analytes in Approximate Retention Time Order and Characteristic Ions, Appendix IX Standard

Analyte	Primary	Secondary	Tertiary
Famphur	218	125	93
Methapyrilene	97	58	
Aramite 1	185	319	
Aramite 2	185	319	
p-(Dimethylamino)azobenzene	120	225	77
p-Chlorobenzilate	251	139	253
3,3'-Dimethylbenzidine	212	106	
2-Acetylaminofluorene	181	180	223
Dibenz(a,j)acridine	279	280	
7,12-Dimethylbenz(a)anthracene	256	241	120
3-Methylcholanthrene	268	252	253

Table 9

8270C LCS Control Compounds

LCS Compounds	Spiking Level, Conc. Added = 20 ug/L
1,2,4-Trichlorobenzene	20
Acenaphthene	20
2,4-Dinitrotoluene	20
Pyrene	20
N-Nitroso-di-n-propylamine	20
1,4-Dichlorobenzene	20
Pentachlorophenol	20
Phenol	20
2-Chlorophenol	20
4-Chloro-3-methylphenol	20
4-Nitrophenol	20

Table 9A

8270C All-Analyte Spike Mix

BNA NPDES		Methanol	
	Acenaphthene		100
	Acenaphthylene		100
	Anthracene		100
	Benzo(a)anthracene		100
	Benzo(b)fluoranthene	Methanol	100
	Benzo(k)fluoranthene		100
	Benzo(a)pyrene		100
	Benzo(ghi)perylene		100
	Benzyl butyl phthalate		100
	Bis(2-chloroethyl)ether		100
	Bis(2-chloroethoxy)methane		100
	Bis(2-ethylhexyl)phthalate		100
	Bis(2-chloroisopropyl)ether		100
	4-Bromophenyl phenyl ether		100
	2-Chloronaphthalene		100
	4-Chlorophenyl phenyl ether		100
	Chrysene		100
	Dibenzo(a,h)anthracene		100
	Di-n-butylphthalate		100
	1,3-Dichlorobenzene		100
	1,2-Dichlorobenzene		100

	1,4-Dichlorobenzene		100
	3,3'-Dichlorobenzidine		100
	Diethyl phthalate		100
	Dimethyl phthalate		100
	2,4-Dinitrotoluene		100
	2,6-Dinitrotoluene		100
	Di-n-octylphthalate		100
	Fluoranthene		100
	Fluorene		100
	Hexachlorobenzene		100
	Hexachlorobutadiene		100
	Hexachloroethane		100
	Indeno(1,2,3-cd)pyrene		100
	Isophorone		100
	Naphthalene		100
	Nitrobenzene		100
	N-Nitrosodi-n-propylamine		100
	Phenanthrene		100
	Pyrene		100
	1,2,4-Trichlorobenzene		100
	4-Chloro-3-methylphenol		100
	2-Chlorophenol		100
	2,4-Dichlorophenol		100
	2,4-Dimethylphenol		100

	2,4-Dinitrophenol		100
	2-Methyl-4,6-dinitrophenol		100
	2-Nitrophenol		100
	4-Nitrophenol		100
	Pentachlorophenol		100
	Phenol		100
	2,4,6-Trichlorophenol		100
	Acetophenone		100
	Atrazine		100
	Caprolactum		100
	Benzaldehyde		100
	1,1'-Biphenyl		100
	Safrole		100
	1,4-Dioxane		100
	Pronamide		100
	p-Chlorobenzilate		100
	Phenacetin		100
	Ethyl methanesulfonate		100
	2-Picoline		100
	Phorate		100
	Quinoline		100

Table 10

TCLP LCS Compounds

LCS Compounds	Spiking Level, mg/L in extract
1,4-Dichlorobenzene	0.08
2,4-Dinitrotoluene	0.08
Hexachlorobenzene	0.08
Hexachlorobutadiene	0.08
Hexachloroethane	0.08
2-Methylphenol	0.08
3-Methylphenol	0.08
4-Methylphenol	0.08
Nitrobenzene	0.08
Pentachlorophenol	0.08
Pyridine	0.08
2,4,5-Trichlorophenol	0.08
2,4,6-Trichlorophenol	0.08

Recovery limits for the LCS and for matrix spikes are generated from historical data and are maintained by the QA department.

Table 11

8270C Surrogate Compounds

Surrogate Compounds	Spiking Level, Conc. Added = 20 ug/L / 30 ug/L
Nitrobenzene-d5	20
2-Fluorobiphenyl	20
Terphenyl-d14	20
1,2-Dichlorobenzene-d4[1]	20
Phenol-d5	30
2-Fluorophenol	30
2,4,6-Tribromophenol	30
2-Chlorophenol-d4[1]	30

Recovery limits for surrogates are generated from historical data and are maintained by the QA department.

Table 12
Calibration Levels, Primary Standard, µg/mL

Analyte	Level 1	Level 2	Level 3	Level 4	Level 5
Pyridine	2	5	8	12	16
N-nitrosodimethylamine	2	5	8	12	16
Aniline	2	5	8	12	16
Phenol	2	5	8	12	16
Bis(2-chloroethyl)ether	2	5	8	12	16
2-Chlorophenol	2	5	8	12	16
1,3-Dichlorobenzene	2	5	8	12	16
1,4-Dichlorobenzene	2	5	8	12	16
Benzyl alcohol	2	5	8	12	16
1,2-Dichlorobenzene	2	5	8	12	16
2-Methylphenol	2	5	8	12	16
2,2'-oxybis(1-chloropropane)[1]	2	5	8	12	16
4-Methylphenol	2	5	8	12	16
N-Nitroso-di-n-propylamine	2	5	8	12	16
Hexachloroethane	2	5	8	12	16
Nitrobenzene	2	5	8	12	16
Isophorone	2	5	8	12	16
2-Nitrophenol	2	5	8	12	16
2,4-Dimethylphenol	2	5	8	12	16
Benzoic acid	2	5	8	12	16
Bis(2-chloroethoxy)methane	2	5	8	12	16
2,4-Dichlorophenol	2	5	8	12	16
1,2,4-Trichlorobenzene	2	5	8	12	16
Naphthalene	2	5	8	12	16
4-Chloroaniline	2	5	8	12	16
Hexachlorobutadiene	2	5	8	12	16
4-Chloro-3-methylphenol	2	5	8	12	16
2-Methylnaphthalene	2	5	8	12	16
Hexachlorocyclopentadiene	2	5	8	12	16
2,4,6-Trichlorophenol	2	5	8	12	16
2,4,5-Trichlorophenol	2	5	8	12	16
2-Chloronaphthalene	2	5	8	12	16
2-Nitroaniline	2	5	8	12	16
Dimethyl phthalate	2	5	8	12	16
Acenaphthylene	2	5	8	12	16
3-Nitroaniline	2	5	8	12	16
Acenaphthene	2	5	8	12	16
2,4-Dinitrophenol	2	5	8	12	16
4-Nitrophenol	2	5	8	12	16
Dibenzofuran	2	5	8	12	16
2,4-Dinitrotoluene	2	5	8	12	16
2,6-Dinitrotoluene	2	5	8	12	16
Diethylphthalate	2	5	8	12	16
4-Chlorophenyl phenyl ether	2	5	8	12	16
Fluorene	2	5	8	12	16
4-Nitroaniline	2	5	8	12	16

Table 12
Calibration Levels, Primary Standard, µg/mL

Analyte	Level 1	Level 2	Level 3	Level 4	Level 5
4,6-Dinitro-2-methylphenol	2	5	8	12	16
N-Nitrosodiphenylamine	2	5	8	12	16
Azobenzene[2]	2	5	8	12	16
4-Bromophenyl phenyl ether	2	5	8	12	16
Hexachlorobenzene	2	5	8	12	16
Pentachlorophenol	2	5	8	12	16
Phenanthrene	2	5	8	12	16
Anthracene	2	5	8	12	16
Carbazole	2	5	8	12	16
Di-n-butyl phthalate	2	5	8	12	16
Fluoranthene	2	5	8	12	16
Benzidine	2	5	8	12	16
Pyrene	2	5	8	12	16
Butyl benzyl phthalate	2	5	8	12	16
3,3'-Dichlorobenzidine	2	5	8	12	16
Benzo(a)anthracene	2	5	8	12	16
Bis(2-ethylhexyl)phthalate	2	5	8	12	16
Chrysene	2	5	8	12	16
Di-n-octylphthalate	2	5	8	12	16
Benzo(b)fluoranthene	2	5	8	12	16
Benzo(k)fluoranthene	2	5	8	12	16
Benzo(a)pyrene	2	5	8	12	16
Indeno(1,2,3-cd)pyrene	2	5	8	12	16
Dibenz(a,h)anthracene	2	5	8	12	16
Benzo(g,h,i)perylene	2	5	8	12	16
Benzaldehyde	2	5	8	12	16
Caprolactam	2	5	8	12	16
1,1'-Biphenyl	2	5	8	12	16
Atrazine	2	5	8	12	16

[1] 2,2'oxybis(1-chloropropane) was formerly known as bis(2-chloroisopropyl)ether

[2]Azobenzene is formed by decomposition of 1,2-diphenyhydrazine. If 1,2-diphenylhydrazine is requested, it will be analyzed as azobenzene.

***Note**: 2 uL injections are used resulting in on-column standard concentrations of 4, 10, 16, 24, 32, 40, etc.

Table 13[1]

Calibration Levels, Appendix IX Standard, µg/mL

Semivolatiles	Level 1	Level 2	Level 3	Level 4	Level 5
2-Picoline	2	5	8	12	16
N-Nitrosomethylethylamine	2	5	8	12	16
Methyl methanesulfonate	2	5	8	12	16
N-Nitrosodiethylamine	2	5	8	12	16
Ethyl methanesulfonate	2	5	8	12	16
Pentachloroethane	2	5	8	12	16
Acetophenone	2	5	8	12	16
N-Nitrosopyrrolidine	2	5	8	12	16
N-Nitrosomorpholine	2	5	8	12	16
o-Toluidine	2	5	8	12	16
3-Methylphenol	2	5	8	12	16
N-Nitrosopiperidine	2	5	8	12	16
o,o,o-Triethyl-Phosphorothioate	2	5	8	12	16
a,a-Dimethyl-phenethylamine	2	5	8	12	16
2,6-Dichlorophenol	2	5	8	12	16
Hexachloropropene	2	5	8	12	16
p-Phenylenediamine	2	5	8	12	16
n-Nitrosodi-n-butylamine	2	5	8	12	16
Safrole	2	5	8	12	16
1,2,4,5-Tetrachlorobenzene	2	5	8	12	16
Isosafrole 1 + 2	2	5	8	12	16
1,4-Dinitrobenzene	2	5	8	12	16
1,4-Naphthoquinone	2	5	8	12	16
1,3-Dinitrobenzene	2	5	8	12	16
Pentachlorobenzene	2	5	8	12	16
1-Naphthylamine	2	5	8	12	16
2-Naphthylamine	2	5	8	12	16
2,3,4,6-Tetrachlorophenol	2	5	8	12	16
5-Nitro-o-toluidine	2	5	8	12	16
Thionazin	2	5	8	12	16
1,3,5-Trinitrobenzene	2	5	8	12	16
Sulfotepp	2	5	8	12	16
Phorate	2	5	8	12	16
Phenacetin	2	5	8	12	16
Diallate 1 + 2	2	5	8	12	16
Dimethoate	2	5	8	12	16
4-Aminobiphenyl	2	5	8	12	16
Pentachloronitrobenzene	2	5	8	12	16
Pronamide	2	5	8	12	16
Disulfoton	2	5	8	12	16
2-secbutyl-4,6-dinitrophenol (Dinoseb)	2	5	8	12	16
*Methyl parathion	2	5	8	12	16
4-Nitroquinoline-1-oxide	2	5	8	12	16
*Parathion	2	5	8	12	16

Table 13[1]

Calibration Levels, Appendix IX Standard, µg/mL

Semivolatiles	Level 1	Level 2	Level 3	Level 4	Level 5
*Isodrin	2	5	8	12	16
*Kepone	2	5	8	12	16
Famphur	2	5	8	12	16
Methapyrilene	2	5	8	12	16
Aramite 1 and 2	2	5	8	12	16
p-(Dimethylamino)azobenzene	2	5	8	12	16
p-Chlorobenzilate	2	5	8	12	16
3,3'-Dimethylbenzidine	2	5	8	12	16
2-Acetylaminofluorene	2	5	8	12	16
Dibenz (a,j)acridine	2	5	8	12	16
7,12-Dimethylbenz(a)anthracene	2	5	8	12	16
3-Methylcholanthrene	2	5	8	12	16

* These compounds are not in the STL North Canton Standard Mix,

[2]Optional concentration levels = 1/5 of the listed concentrations for samples with a final volume of 5 mL.

Table 14
Initial demonstration recovery and precision limits

Compound	Spiking concentration µg/L	Limit for Relative Standard Deviation	Limit for average recovery, %
Acenaphthene	60	27.6	60.1-132.3
Acenaphthylene	60	40.2	53.5-126.0
Aldrin[1]	60	39.0	7.2-152.2
Anthracene	60	32.0	43.4-118.0
Benz(a)anthracene	60	27.6	41.8-133.0
Benzo(b)fluoranthene	60	38.8	42.0-140.4
Benzo(k)fluoranthene	60	32.3	25.2-145.7
Benzo(a)pyrene	60	39.0	31.7-148.0
Benzo(ghi)perylene	60	58.9	D-195.0
Benzylbutyl phthalate	60	23.4	D-139.9
B-BHC[1]	60	31.5	41.5-130.6
d-BHC[1]	60	21.6	D-100.0
Bis(2-chloroethyl) ether	60	55.0	42.9-126.0
Bis(2-chloroethoxy)methane	60	34.5	49.2-164.7
Bis(2-chloroisopropyl) ether	60	46.3	62.8-138.6
Bis(2-ethylhexyl) phthalate	60	41.1	28.9-136.8
4-Bromophenyl phenyl ether	60	23.0	64.9-114.4

Table 14
Initial demonstration recovery and precision limits

Compound	Spiking concentration µg/L	Limit for Relative Standard Deviation	Limit for average recovery, %
2-Chloronaphthalene	60	13.0	64.5-113.5
4-Chlorophenyl phenyl ether	60	33.4	38.4-144.7
Chrysene	60	48.3	44.1-139.9
4,4'-DDD[1]	60	31.0	D-134.5
4,4'-DDE[1]	60	32.0	19.2-119.7
4,4'-DDT[1]	60	61.6	D-170.6
Dibenzo(a,h)anthracene	60	70.0	D-199.7
Di-n-butyl phthalate	60	16.7	8.4-111.0
1,2-Dichlorobenzene	60	30.9	48.6-112.0
1,3-Dichlorobenzene	60	41.7	16.7-153.9
1,4-Dichlorobenzene	60	32.1	37.3-105.7
3,3'-Dichlorobenzidine	60	71.4	8.2-212.5
Dieldrin[1]	60	30.7	44.3-119.3
Diethyl phthalate	60	26.5	D-100.0
Dimethyl phthalate	60	23.2	D-100.0
2,4-Dinitrotoluene	60	21.8	47.5-126.9
2,6-Dinitrotoluene	60	29.6	68.1-136.7
Di-n-octylphthalate	60	31.4	18.6-131.8
Endosulfan sulfate[1]	60	16.7	D-103.5
Endrin aldehyde	60	32.5	D-188.8
Fluoranthene	60	32.8	42.9-121.3
Fluorene	60	20.7	71.6-108.4
Heptachlor[1]	60	37.2	D-172.2
Heptachlor epoxide[1]	60	54.7	70.9-109.4
Hexachlorobenzene	60	24.9	7.8-141.5
Hexachlorobutadiene	60	26.3	37.8-102.2
Hexachloroethane	60	24.5	55.2-100.0
Indeno(1,2,3-cd)pyrene	60	44.6	D-150.9
Isophorone	60	63.3	46.6-180.2
Naphthalene	60	30.1	35.6-119.6
Nitrobenzene	60	39.3	54.3-157.6
N-Nitrosodi-n-propylamine	60	55.4	13.6-197.9
PCB-1260[1]	60	54.2	19.3-121.0
Phenanthrene	60	20.6	65.2-108.7
Pyrene	60	25.2	69.6-100.0
1,2,4-Trichlorobenzene	60	28.1	57.3-129.2
4-Chloro-3-methylphenol	60	37.2	40.8-127.9
2-Chlorophenol	60	28.7	36.2-120.4

Table 14
Initial demonstration recovery and precision limits

Compound	Spiking concentration µg/L	Limit for Relative Standard Deviation	Limit for average recovery, %
2,4-Chlorophenol	60	26.4	52.5-121.7
2,4-Dimethylphenol	60	26.1	41.8-109.0
2,4-Dinitrophenol	60	49.8	D-172.9
2-Methyl-4,6-dinitrophenol	60	93.2	53.0-100.0
2-Nitrophenol	60	35.2	45.0-166.7
4-Nitrophenol	60	47.2	13.0-106.5
Pentachlorophenol	60	48.9	38.1-151.8
Phenol	60	22.6	16.6-100.0
2,4,6-Trichlorophenol	60	31.7	52.4-129.2

[1]Since the organochlorine pesticides and PCBs are normally determined by method 8081 at STL North Canton, they will not be included in the initial demonstration of capability for method 8270C.

ATTACHMENT A

MODIFICATIONS REQUIRED FOR ANALYSIS OF WASTEWATER FOLLOWING METHOD 625

18. REQUIREMENTS FOR METHOD 625

18.1 Method 625 is required for demonstration of compliance with NPDES wastewater discharge permits. The standard analyte list and reporting limits are listed in Table A-1.

18.2 This method can be applied only to aqueous matrices.

18.3 The tune period for this method is defined as 24 hours.

18.4 Initial calibration curve requirements:

18.4.1 The initial calibration curve for this method requires at least three points.

18.4.2 Target compounds must have RSD ≤ 35%.

18.4.3 If this requirement can not be met, a regression curve must be constructed for the non-compliant compounds.

18.5 Continuing calibration verification requirements: All target compounds must have %D ≤ 20%.

18.6 Matrix Spike and LCS requirements:

18.6.1 A full analyte spike is required for method 625. The spiking levels are given in Table A-2.

Table A-1. STL North Canton Method 625 standard reporting list and reporting limits.

Analytes	CAS Number	Aqueous µg/L
Phenol	108-95-2	10
Bis(2-chloroethyl)ether	111-44-4	10
2-Chlorophenol	95-57-8	10
1,3-Dichlorobenzene	541-73-1	10
1,4-Dichlorobenzene	106-46-7	10
1,2-Dichlorobenzene	95-50-1	10
2,2'-oxybis(1-chloropropane)	108-60-1	10
N-Nitroso-di-n-propylamine	621-64-7	10
Hexachloroethane	67-72-1	10
Nitrobenzene	98-95-3	10
Isophorone	78-59-1	10
2-Nitrophenol	88-75-5	10
2,4-Dimethylphenol	105-67-9	10
Bis(2-chloroethoxy)methane	111-91-1	10
2,4-Dichlorophenol	120-83-2	10
1,2,4-Trichlorobenzene	120-82-1	10
Naphthalene	91-20-3	10
Hexachlorobutadiene	87-68-3	10
4-Chloro-3-methylphenol	59-50-7	10
Hexachlorocyclopentadiene	77-47-4	50
2,4,6-Trichlorophenol	88-06-2	10
2-Chloronaphthalene	91-58-7	10
Dimethyl phthalate	131-11-3	10
Acenaphthylene	208-96-8	10
Acenaphthene	83-32-9	10
2,4-Dinitrophenol	51-28-5	50
4-Nitrophenol	100-02-7	50
2,4-Dinitrotoluene	121-14-2	10
2,6-Dinitrotoluene	606-20-2	10
Diethylphthalate	84-66-2	10
4-Chlorophenyl phenyl ether	7005-72-3	10
Fluorene	86-73-7	10
4,6-Dinitro-2-methylphenol	534-52-1	50
N-Nitrosodiphenylamine	86-30-6	10
4-Bromophenyl phenyl ether	101-55-3	10
Hexachlorobenzene	118-74-1	10
Pentachlorophenol	87-86-5	50
Phenanthrene	85-01-8	10
Anthracene	120-12-7	10
Di-n-butyl phthalate	84-74-2	10
Fluoranthene	206-44-0	10
Benzidine	92-87-5	100
Pyrene	129-00-0	10

Analytes	CAS Number	Aqueous µg/L
Butyl benzyl phthalate	85-68-7	10
3,3'-Dichlorobenzidine	91-94-1	50
Benzo(a)anthracene	56-55-3	10
Bis(2-ethylhexyl)phthalate	117-81-7	10
Chrysene	218-01-9	10
Di-n-octylphthalate	117-84-0	10
Benzo(b)fluoranthene	205-99-2	10
Benzo(k)fluoranthene	207-08-9	10
Benzo(a)pyrene	50-32-8	10
Indeno(1,2,3-cd)pyrene	193-39-5	10
Dibenz(a,h)anthracene	53-70-3	10
Benzo(g,h,i)perylene	191-24-2	10

Table A-2. Method 625 LCS and MS compounds and spike concentrations.

LCS Compounds	Spiking Level, ng/µL in extract[1]
Phenol	20
Bis(2-chloroethyl)ether	20
2-Chlorophenol	20
1,3-Dichlorobenzene	20
1,4-Dichlorobenzene	20
1,2-Dichlorobenzene	20
2,2'-oxybis(1-chloropropane)	20
N-Nitroso-di-n-propylamine	20
Hexachloroethane	20
Nitrobenzene	20
Isophorone	20
2-Nitrophenol	20
2,4-Dimethylphenol	20
Bis(2-chloroethoxy)methane	20
2,4-Dichlorophenol	20
1,2,4-Trichlorobenzene	20
Naphthalene	20
Hexachlorobutadiene	20
4-Chloro-3-methylphenol	20
Hexachlorocyclopentadiene	20
2,4,6-Trichlorophenol	20
2-Chloronaphthalene	20
Dimethyl phthalate	20
Acenaphthylene	20
Acenaphthene	20
2,4-Dinitrophenol	20
4-Nitrophenol	20
2,4-Dinitrotoluene	20
2,6-Dinitrotoluene	20
Diethylphthalate	20
4-Chlorophenyl phenyl ether	20
Fluorene	20
4,6-Dinitro-2-methylphenol	20
N-Nitrosodiphenylamine	20
4-Bromophenyl phenyl ether	20
Hexachlorobenzene	20
Pentachlorophenol	20
Phenanthrene	20
Anthracene	20
Di-n-butyl phthalate	20
Fluoranthene	20
Benzidine	20
Pyrene	20
Butyl benzyl phthalate	20
3,3'-Dichlorobenzidine	20

LCS Compounds	Spiking Level, ng/µL in extract[1]
Benzo(a)anthracene	20
Bis(2-ethylhexyl)phthalate	20
Chrysene	20
Di-n-octylphthalate	20
Benzo(b)fluoranthene	20
Benzo(k)fluoranthene	20
Benzo(a)pyrene	20
Indeno(1,2,3-cd)pyrene	20
Dibenz(a,h)anthracene	20
Benzo(g,h,i)perylene	20

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 2.3, DATED 05/15/01)

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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. 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 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. The problem can be eliminated by reducing the volume of original sample used.

4.6. The most common interference is laboratory contamination, which may arise from impure reagents, dirty glassware, improper sample transfers, dirty work areas, etc. Be aware of potential sources of contamination and take appropriate measures to minimize or avoid them.

5. SAFETY

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

5.2. Eye protection that satisfies ANSI Z87.1 (as per the Chemical Hygiene Plan), laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

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

5.3.1. The following materials are known to be **corrosive:**

hydrochloric acid, nitric acid and sulfuric acid.

5.3.2. The following materials are known to be **oxidizing agents**:

nitric acid, potassium permanganate, potassium persulfate and magnesium perchlorate.

5.3.3. Mercury is a highly toxic element that must be handled with care. The analyst must be aware of the handling and clean up techniques before working with mercury.

Since mercury vapor is toxic, precaution must be taken to avoid its inhalation, ingestion or absorption through skin. All lines should be checked for leakage and the mercury vapor must be vented into a hood or passed through a mercury absorbing media such as:

5.3.3.1. Equal volumes of 0.1 M $KMnO_4$ and 10% H_2SO_4, or

5.3.3.2. Iodine, 0.25%, in a 3% KI solution.

5.3.4. Magnesium sulfate is known to be a reproductive toxin (mutagen).

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

5.5. 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) or autoclave that is able to obtain conditions of 15 lbs., 120 °C for 15 minutes.

6.2. Atomic Absorption Spectrophotometer equipped with:

6.2.1. Absorption Cell with quartz end windows perpendicular to the longitudinal axis. Dimensions of the cell must result in sufficient sensitivity to meet the SOP defined reporting limit. The quartz windows must be maintained to provide accurate

measurements. Any scratches or fingerprints can alter the absorption of UV radiation.

6.2.2. Mercury specific hollow cathode lamp (HCL) or electrodeless discharge lamp (EDL).

6.2.3. Peristaltic pump, which can deliver 1 L/min, air.

6.2.4. Flowmeter capable of measuring an airflow of 1 L/min.

6.2.5. Recorder or Printer.

6.2.6. Aeration Tubing: A straight glass frit having a course porosity and Tygon tubing is used for the transfer of mercury vapor from the sample bottle to the absorption cell and return.

6.2.7. Drying device (a drying tube containing magnesium perchlorate or magnesium sulfate and/or a lamp with a 60 W bulb) to prevent condensation in cell. The lamp is positioned to shine on the absorption cell maintaining the air temperature in the cell about 10 °C above room temperature. Other drying devices that achieve the same purpose are also acceptable (i.e., Gortex filter).

NOTE: Instruments designed specifically for the measurement of mercury using the cold vapor technique may be substituted for the atomic absorption spectrophotometer.

6.3. BOD bottles or equivalent.

6.4. Nitrogen or argon gas supply, welding grade, or equivalent.

6.5. Calibrated automatic pipettes or Class A glass volumetric pipettes.

6.6. Class A volumetric flasks.

6.7. Thermometer (capable of accurate readings at 95 °C).

6.8. Disposable cups or tubes.

7. REAGENTS AND STANDARDS

7.1. Reagent water must be produced by a Millipore DI system or equivalent. Reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks.

7.2. Stock (10 ppm) mercury standards (in 10% HNO_3) 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% HNO_3. This acid (150 uL of concentrated HNO_3) must be added to the flask/bottle before the addition of the stock standard aliquot.

7.4. 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.

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. 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.

7.10. 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.

7.11. Potassium permanganate, 5% solution (w/v): Dissolve 5 g of potassium permanganate for every 100 mL of reagent water.

7.12. Potassium persulfate, 5% solution (w/v): Dissolve 5 g of potassium persulfate for every 100 mL of reagent water.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Sample holding time for mercury is 28 days from time of collection to the time of analysis.

8.2. Aqueous samples are preserved with nitric acid to a pH of <2 and may be stored in either plastic or glass. Refrigeration is not required. Preservation must be verified prior to analysis.

9. QUALITY CONTROL

Table II (Appendix A) provides a summary of quality control requirements including type, frequency, acceptance criteria and corrective action.

9.1. Initial Demonstration of Capability

Prior to the analysis of any analyte using 7470A or the 245.1, the following requirements must be met.

9.1.1. Method Detection Limit (MDL) - An MDL must be determined for each analyte/matrix prior to the analysis of any samples. The MDL is determined using seven replicates of reagent water, spiked with all the analytes of interest, that have been carried through the entire analytical procedure. MDLs must be redetermined

on an annual basis in accordance with 40 CFR Part 136 Appendix B requirements. The spike level must be between the calculated MDL and 10X the MDL to be valid. The result of the MDL determination must be below the STL 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, and MS/MSDs) are not included in the sample count for determining the size of a preparation batch.

9.4. Method Blank (MB) - One method blank must be processed with each preparation batch. The method blank consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The method blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. The method blank should not contain any analyte of interest at or above the reporting 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 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 80 - 120% recovery must be applied.

- In the instance where the LCS recovery is > 120% and the sample results are < RL, the data may be reported with qualifiers. Such action must be taken in consultation with the client and must be addressed in the case narrative.

- In the event that an MS/MSD analysis is not possible, a Laboratory Control Sample Duplicate (LCSD) must be analyzed. The RPD of the LCS and LCSD must be compared to the matrix spike RPD limits.

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

9.6. Matrix Spike/Matrix Spike Duplicate (MS/MSD) - One MS/MSD pair must be processed for each preparation batch. A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added. A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked identically as the MS) prepared and analyzed along with the sample and matrix spike. Some client specific data quality objectives (DQO's) may require the use of sample duplicates in place of or in addition to MS/MSD's. The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Due to the potential variability of the matrix of each sample, these results may have immediate bearing only on the specific sample spiked. Samples identified as field blanks cannot be used for MS/MSD analysis. Spiking levels are provided in Table I (Appendix A).

- If analyte recovery or RPD falls outside the acceptance range, the recovery of that analyte must be in control for the LCS. Until in-house control limits are established, a control limit of 75 - 125 % recovery and 20% RPD must be applied to the MS/MSD. If the LCS recovery is within limits, then the laboratory operation is in control and the results may be accepted. If the recovery of the LCS is outside limits, corrective action must be taken. Corrective action will include repreparation

and reanalysis of the batch. MS/MSD results, which fall outside the control limits, must be addressed in the narrative.

- If the native analyte concentration in the MS/MSD exceeds 4 times the spike level for that analyte, the recovery data are reported as NC (i.e., not calculated). If the reporting software does not have the ability to report NC then the actual recovery must be reported and narrated as follows: "Results outside of limits do not necessarily reflect poor method performance in the matrix due to high analyte concentrations in the sample relative to the spike level."

- If an MS/MSD is not possible due to limited sample volume, then a laboratory control sample duplicate (LCSD) should be analyzed. The RPD of the LCS and LCSD must be compared to the matrix spike RPD limits.

9.7. Initial Calibration Verification (ICV/ICB) - Calibration accuracy is verified by analyzing a second source standard (ICV). The ICV result must fall within 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 11.2.11 and Section 11.2.12 for required run sequence). If the cause of the ICV or ICB failure was not directly instrument related the corrective action will include repreparation of the 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 11.2.11 and 11.2.12 for required run sequence.) The CCB result must fall within +/- RL from zero. Each CCV and CCB analyzed must reflect the conditions of analysis of all associated samples. Sample results may only be reported when bracketed by valid ICV/CCV and ICB/CCB pairs.

9.9. Method of Standard Addition (MSA) -This technique involves adding known amounts of standard to one or more aliquots of the sample prior to preparation. This technique compensates for a sample interferent that may enhance or depress the analyte signal, thus producing a different slope from that of the calibration standards. It will not correct for additive interferences, which cause a baseline shift. Refer to Section 11.2.13 for additional information on when full 4 point MSA is required as well as Appendix C for specific MSA requirements.

10. CALIBRATION AND STANDARDIZATION

10.1. Calibration standards must be processed through the preparation procedure as described in Section 11.1.

10.2. Due to the differences in preparation protocols separate calibration and calibration verification standards must be prepared for aqueous and solid matrices.

10.3. Calibration must be performed daily (every 24 hours) and each time the instrument is set up. The instrument calibration date and time must be included in the raw data.

10.4. Set up the instrument with the operating parameters recommended by the manufacturer. Allow the instrument to become thermally stable before beginning calibration (approximately 30 minutes of warm-up is required). Refer to the facility specific instrument SOP and CVAA instrument manual for detailed setup and operation protocols.

10.5. Calibrate the instrument according to instrument manufacturer's instructions, using a minimum of five standards and a blank. One standard must be at the STL 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. 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.

NOTE: Alternatively, for RCRA analyses using 7470A, samples may be digested using an autoclave for 15 minutes at 120 °C and 15 lbs.

11.1.6. Cool samples.

11.2. Sample Analysis:

11.2.1. Refer to the Appendix G of this SOP for detailed setup and operation protocols.

11.2.2. All labs are required to detail the conditions/programs utilized for each instrument within the facility specific instrument operation SOP.

11.2.3. When ready to begin analysis, add 6 mL of sodium chloride-hydroxylamine hydrochloride solution to the samples to reduce the excess permanganate (the permanganate has been reduced when no purple color remains). Add this solution in 6-mL increments until the permanganate is completely reduced.

11.2.4. Manual determination:

11.2.4.1. Treating each sample individually, purge the headspace of the sample bottle for at least one minute.

11.2.4.2. Add 5 mL of stannous chloride solution and immediately attach the bottle to the aeration apparatus.

11.2.4.3. Allow the sample to stand quietly without manual agitation while the sample is aerated (1 L/min flow). Monitor the sample absorbance during aeration. When the absorbance reaches a maximum and the signal levels off, open the bypass valve and continue aeration until the absorbance returns to its baseline level. Close the bypass valve and remove the aeration device.

11.2.4.4. Place the aeration device into 100 mL of 1% HNO_3 and allow to bubble rinse until the next sample is analyzed.

11.2.5. Automated determination: Follow instructions provided by instrument manufacturer.

11.2.6. Perform a linear regression analysis of the calibration standards by plotting maximum response of the standards vs. concentration of mercury. Determine the mercury concentration in the samples from the linear regression fit of the calibration curve. Calibration using computer or calculation based regression curve fitting techniques on concentration/response data is acceptable.

11.2.7. All measurements must fall within the defined calibration range to be valid. Dilute and reanalyze all samples for analytes that exceed the highest calibration standard.

11.2.8. If the sample results are negative and the absolute value of the negative result is greater than the reporting limit, the sample must be diluted and reanalyzed.

11.2.9. The samples must be allowed to cool to room temperature prior to analysis or a decrease in the response signal can occur.

11.2.10. Baseline correction is acceptable as long as it is performed after every sample or after the CCV and CCB; resloping is acceptable as long as it is immediately preceded and followed by a compliant CCV and CCB.

11.2.11. The following analytical sequence must be used with 7470A and 245.1:

Instrument Calibration
ICV
ICB
Maximum 10 samples
CCV
CCB
Repeat sequence of 10 samples between CCV/CCB pairs as required to complete run
CCV
CCB

Refer to Quality Control Section 9.0 and Table II (Appendix A) for quality control criteria to apply to Methods 7470A and 245.1.

Note: Samples include the method blank, LCS, MS, MSD, duplicate, field samples and sample dilutions.

11.2.12. The following run sequence is consistent with 7470A, CLP and 245.1 and may be used as an alternate to the sequence in 11.2.11. This run sequence is

recommended if multiple method requirements must be accommodated in one analytical run:

Instrument Calibration
ICV
ICB
CRA*
CCV
CCB
10 samples
CCV
CCB
Repeat sequence of 10 samples between CCV/CCB pairs as required to complete run.
CCV
CCB

Refer to the appropriate CLP SOP (CORP-MT-0006) for quality control requirements for QC samples.

* Refer to the CLP SOP for information on the CRA.

11.2.13. For TCLP samples, full four point MSA will be required if all of the following conditions are met:

1) recovery of the analyte in the matrix spike is not at least 50%,

2) the concentration of the analyte does not exceed the regulatory level, and,

3) the concentration of the analyte is within 20% of the regulatory level.

The reporting and matrix spike levels for TCLP analyses are detailed in Table I (Appendix A). Appendix E provides guidance on performing MSA analyses. For TCLP mercury determinations, MSA spikes must be added prior to sample preparation.

11.3. To facilitate the early identification of QC failures and samples requiring rerun it is strongly recommended that sample data 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. One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo and is approved by a Technical Specialist and QA Manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file.

11.6. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

12. DATA ANALYSIS AND CALCULATIONS

12.1. ICV percent recoveries are calculated according to the equation:

$$\%R = 100\left(\frac{Found(ICV)}{True(ICV)}\right)$$

12.2. CCV percent recoveries are calculated according to the equation:

$$\%R = 100\left(\frac{Found(CCV)}{True(CCV)}\right)$$

12.3. Matrix spike recoveries are calculated according to the following equation:

$$\%R = 100\left(\frac{SSR - SR}{SA}\right)$$

Where:

SSR = Spike Sample Result
SR = Sample Result
SA = Spike Added

12.4. The relative percent difference (RPD) of matrix spike/matrix spike duplicates or sample duplicates are calculated according to the following equations:

$$RPD = 100\left[\frac{|MSD - MS|}{\left(\frac{MSD + MS}{2}\right)}\right]$$

Where:

MS = determined spiked sample concentration
MSD = determined matrix spike duplicate concentration

$$RPD = 100\left[\frac{|DU1 - DU2|}{\left(\frac{DU1 + DU2}{2}\right)}\right]$$

Where:

DU1 = Sample result
DU2 = Sample duplicate result

12.5. The final concentration for an aqueous sample is calculated as follows:

$$mg/L = \text{C x D}$$

Where:

C = Concentration (mg/L) from instrument readout
D = Instrument dilution factor

12.6. The LCS percent recovery is calculated according to the following equation:

$$\%R = 100\left(\frac{Found(LCS)}{True(LCS)}\right)$$

12.7. Appropriate factors must be applied to sample values if dilutions are performed.

12.8. Sample results should be reported with up to three significant figures in accordance with the STL 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. Waste generated in the procedure must be segregated and disposed according to the facility hazardous waste procedures. The Environmental Health and Safety Director should be contacted if additional information is required.

16. REFERENCES

16.1. 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.

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

17.1. Modifications/Interpretations from reference method.

17.1.1. Modifications from both 7470A and 245.1.

17.1.1.1. The 200 series methods and Chapter 1 of SW846 specify the use of reagent water with a purity equivalent to ASTM Type II water. This SOP specifies the use of a Millipore DI system or equivalent to produce reagent water. This SOP requires that reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks.

17.1.1.2. This SOP allows for the use of reduced sample volumes to decrease waste generation. Reagent levels are adjusted to maintain the same ratios as stated in the source methods. According to a letter from Robert Booth of EPA EMSL-Cinn to David Payne of EPA Region V, "Reduction in sample size and appropriate corresponding reduction in sample volume is not considered a significant change in the methodology."

17.1.1.3. The alternate run sequence presented in Section 11.2.12 is consistent with method requirements. An additional QC analysis (CRA) was added to accommodate the CLP protocol requirements.

17.1.2. Modifications from Method 7470A

17.1.2.1. Chapter 1 of SW-846 states that the method blank should not contain any analyte of interest at or above the MDL. This SOP states that the

method blank must not contain any analyte of interest at or above the reporting limit.

17.1.2.2. Documentation is on file from EPA's Office of Solid Waste (Olliver Fordham 11/28/95) regarding the acceptance of the autoclave as an equivalent heating device to the water bath. In his letter, Mr. Fordham cited the CLP water protocol 245.1 CLP-M and therefore the operating parameters from that method were adopted for 7470A (15 minutes at 120 °C and 15 lbs.).

17.1.3. 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.

17.2. Modifications from previous SOP

17.2.1. 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.

17.2.2. Documentation is on file from EPA's Office of Solid Waste (Olliver Fordham 11/28/95) regarding the acceptance of the autoclave as an equivalent heating device to the water bath. In his letter, Mr. Fordham cited the CLP water protocol 245.1 CLP-M and therefore the operating parameters from the method were adopted for 7470A (15 minutes at 120° C and 15 lbs.).

17.3. Facility Specific SOPs

Each facility shall attach a list of facility specific SOPs or approved attachments (if applicable) which are required to implement this SOP or which are used in conjunction with this SOP. If no facility specific SOPs or amendments are to be attached, a statement must be attached specifying that there are none. Refer to the Appendices for any facility specific information required to support this SOP.

17.4. Documentation and Record Management

The following documentation comprises a complete CVAA raw data package:

- Raw data (direct instrument printout)
- Run log printout from instrument software where this option is available or manually generated run log. (A bench sheet may be substituted for the run log as long as it contains an accurate representation of the analytical sequence).
- Data review checklist - See Appendix B
- Standards Documentation (source, lot, date).
- Copy of digestion log.
- Non-conformance summary (if applicable).

Figure 1. Aqueous Sample Preparation - Mercury

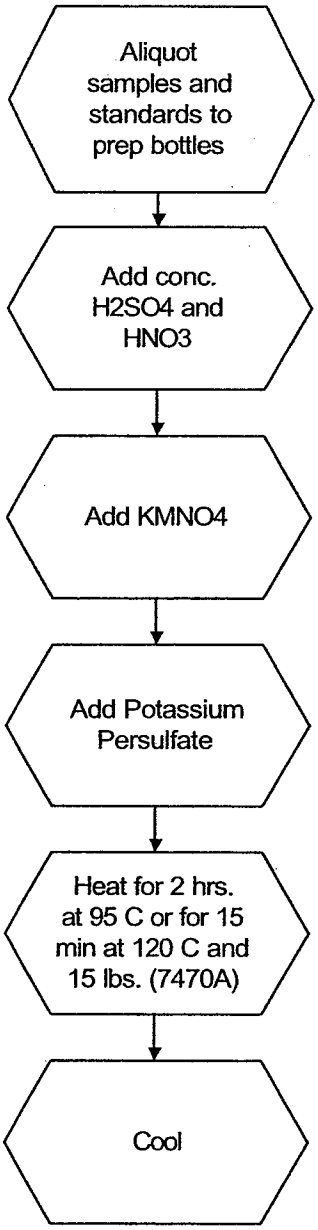
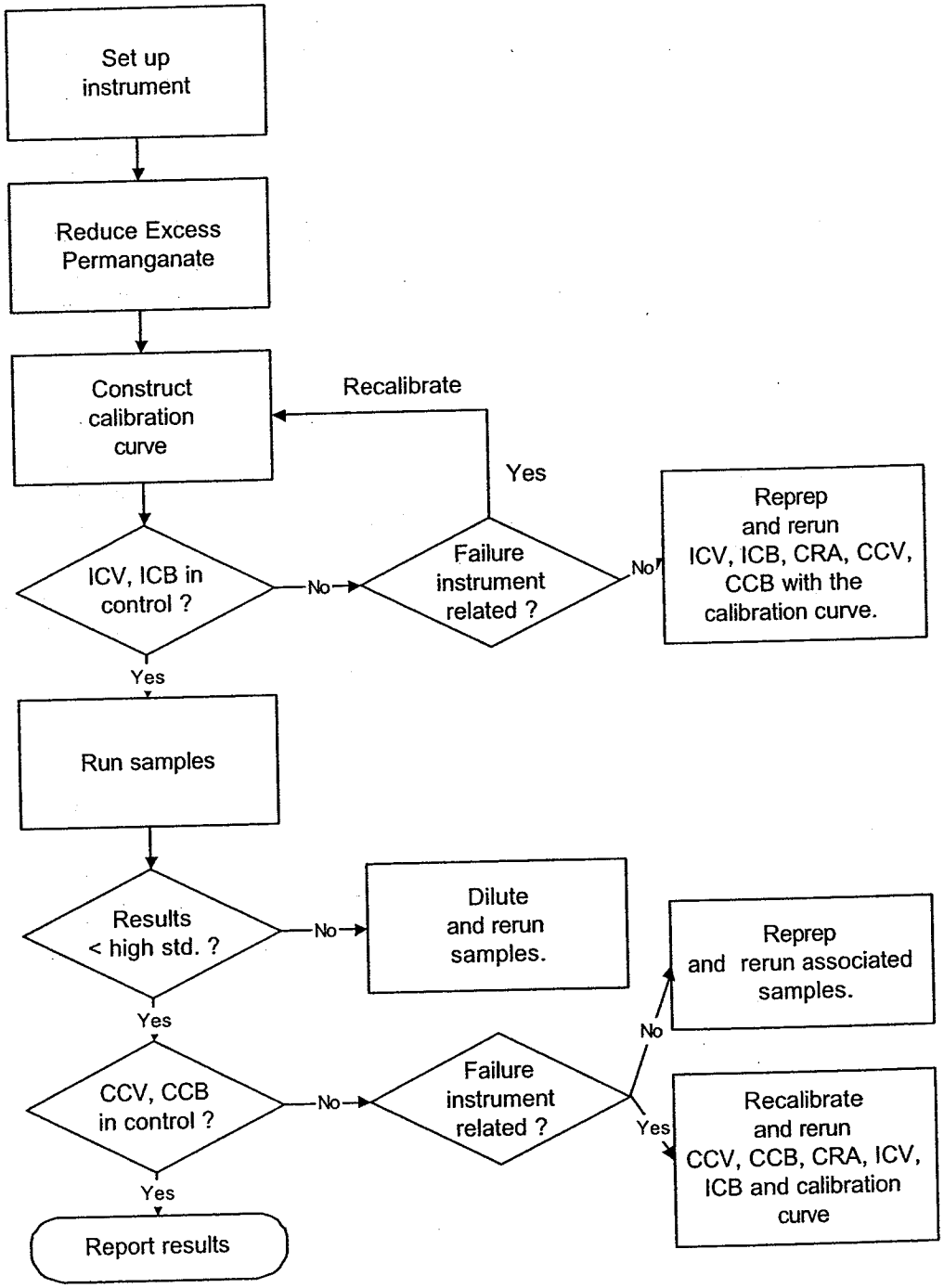


Figure 2. CVAA Mercury Analysis



APPENDIX A

TABLES

TABLE I . MERCURY REPORTING LIMITS, CALIBRATION STANDARD*, QC STANDARD AND SPIKING LEVELS (MG/L)

Standard Aqueous RL	0.0002
TCLP RL	0.002
Std 0	0
Std 1	0.0002
Std 2	0.0005
Std 3	0.001
Std 4	0.005
Std 5 **	0.010
ICV	0.001 or 0.0025 ***
LCS/CCV	0.0025 or 0.005 ***
Aqueous MS	0.001
TCLP MS	0.005

* **SOP specified calibration levels must be used unless prevented by the instrument configuration or client specific requirements. Deviations from specified calibration levels must be documented in the facility specific instrument operation SOP and must be approved by the facility technical manager and Quality Assurance Manager.**

** **Optional standard which may be used to extend the calibration range as allowed by the instrument configuration. If the instrument configuration prevents the use of 6 standards, the 2-ppb standard may be eliminated in favor of the 10 ppb standard.**

*** **Concentration level dependent on high calibration standard used. CCV must be 50% of high standard concentration and ICV must be 20-25% of high standard concentration.**

TABLE II. Summary Of Quality Control Requirements

QC PARAMETER	FREQUENCY *	ACCEPTANCE CRITERIA	CORRECTIVE ACTION
ICV	Beginning of every analytical run.	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 11.2.11 and 11.2.12 for exact run sequence to be followed.

TABLE II. Summary of Quality Control Requirements (Continued)

QC PARAMETER	FREQUENCY	ACCEPTANCE CRITERIA	CORRECTIVE ACTION
Laboratory Control Sample (LCS)	One per sample preparation batch of up to 20 samples.	Aqueous LCS must be within 80 - 120% recovery or in-house control limits.	Terminate analysis; Correct the problem; Redigest and reanalyze all samples associated with the LCS (see Section 9.5).
Matrix Spike	One per sample preparation batch of up to 20 samples.	75 - 125 % recovery or in-house control limits. If the MS/MSD is out for an analyte, it must be in control in the LCS.	In the absence of client specific requirements, flag the data; no flag required if the sample level is > 4x the spike added. (see Section 9.6) For TCLP see Section 11.2.13
Matrix Spike Duplicate	See Matrix Spike	75 - 125 % recovery or in-house control limits; RPD ≤ 20%. (See MS)	See Corrective Action for Matrix Spike.

APPENDIX B
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

	Yes	No	N/A	2ndLevel
A. Calibration/Instrument Run QC				
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

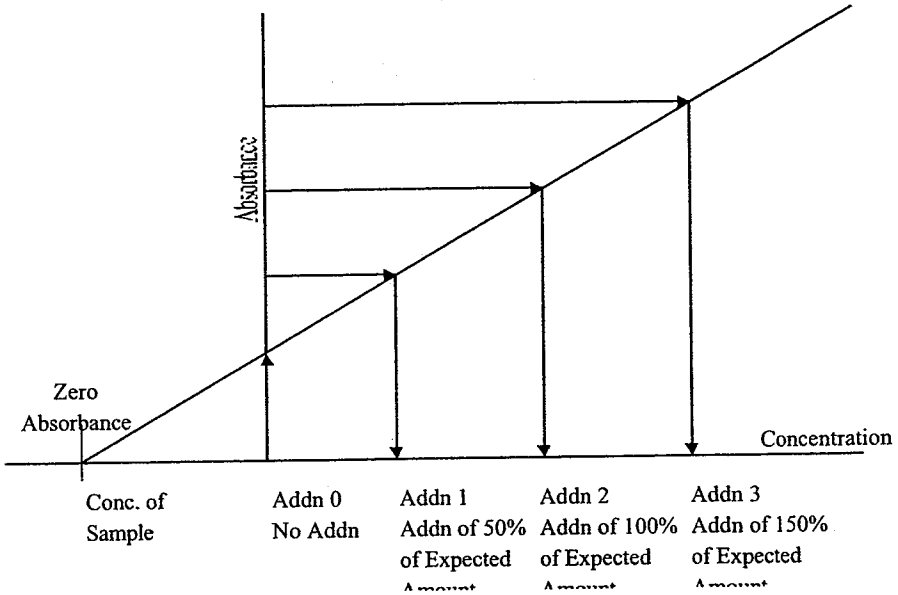
APPENDIX C. MSA GUIDANCE

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.

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.

STL NORTH CANTON STANDARD OPERATING PROCEDURE

TITLE: **EXTRACTION AND CLEANUP OF ORGANIC COMPOUNDS FROM WATERS AND SOILS, BASED ON SW-846 3500 SERIES, 3600 SERIES, 8151A AND 600 SERIES METHODS.**

(SUPERSEDES: Revision 3.8 (Dated 05/23/01)

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Corporate Technology Date

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Table A3 Herbicide surrogate spike components
Table A4 Herbicide matrix spike and LCS components

1. SCOPE AND APPLICATION

This SOP describes procedures for preparation (extraction and cleanup) of semivolatile organic analytes in aqueous, TCLP leachate, and soil matrices for analysis by Gas Chromatography (GC) and Gas Chromatography / Mass Spectrometry (GC/MS). The procedures are based on SW-846 and 600 series methodology and are applicable for measurements made to comply with the Resource Conservation and Recovery Act (RCRA) and for wastewater testing.

1.1. Extraction procedures for the following determinative methods are covered:
8081A, 8082, 8141A, 8151B, 8270C, 8310, 8015B, 8100, 608, 610, and 625

1.2. The extraction procedures here may be appropriate for other determinative methods when appropriate spiking mixtures are used.

1.3. Other extraction procedures (PFE, SPE, accelerated Soxhlet, etc.) may be used but are not currently covered in this SOP.

1.4. The applicable LIMS method codes are: P2 (8141A), QJ (8081A), QS (8151A), QL (8270C), SG (8310), DM (608), VT (610), DP (625), A1 (8100), HS (8015B)

2. SUMMARY OF METHOD

2.1. Separatory Funnel Extraction

A measured volume of sample, typically 1 liter, is adjusted, if necessary, to a specified pH and serially extracted with methylene chloride using a separatory funnel.

2.2. Continuous Liquid/Liquid Extraction

A measured volume of sample, typically 1 liter, is placed into a continuous liquid/liquid extractor, adjusted, if necessary, to a specific pH and extracted with methylene chloride for 18-24 hours.

2.3. Sonication Extraction

A measured weight of sample, typically 30 g, is mixed with anhydrous sodium sulfate to form a free flowing powder. This is solvent extracted three times using an ultrasonic horn.

2.4. Soxhlet Extraction

A 30 g sample is mixed with anhydrous sodium sulfate to form a free flowing powder. This is extracted with refluxing solvent.

2.5. Cleanup and Concentration

Procedures are presented for removing interferents from sample extracts, and for drying and concentration of the extract to final volume for analysis.

2.6. Phenoxy acid herbicide extractions

Procedures for the extraction and cleanup of phenoxy acid herbicides are presented in Appendix A.

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

4.1. Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus. All 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. Visual interferences or anomalies (such as foaming, emulsions, odor, etc.) must be documented.

5. SAFETY

5.1. Procedures shall be carried out in a manner that protects the health and safety of all STL North Canton associates. The following requirements must be met:

5.2. Eye protection that satisfies ANSI Z87.1 (as per the Chemical Hygiene Plan), laboratory coat and appropriate gloves must be worn while samples, standards, solvents and reagents are being handled. Disposable gloves that have become contaminated will be removed and discarded, other gloves will be cleaned immediately. Viton gloves may be worn when halogenated solvents are used for extractions or sample preparation. Nitrile gloves may be used when other solvents are handled. [Note: VITON is readily degraded by acetone]. When good manual dexterity is needed, for example, when handling small quantities/containers, disposable gloves (such as latex or N-DEX®) shall be used. While these gloves protect against splashes, they give little or no protection against contact with large quantities of solvent, and no protection against spills or immersion.

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

Chemicals that have been classified as **carcinogens** or **potential carcinogens** under OSHA include methylene chloride, PCBs, certain pesticides.

The following materials are known to be **corrosive**: Concentrated sulfuric acid, sodium hydroxide, 1N nitric acid.
Sulfuric acid cleanup must not be performed on any matrix that may have water present as a violent reaction between the acid and water may result in acid exploding out of the vessel.

Chemicals known to be **flammable** are: Diethyl ether, acetone, hexane, 2-propanol.
Mercury is a highly toxic compound that must be handled with care. The analyst must be aware of the appropriate handling and clean-up techniques before handling this material.

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

5.5. The preparation of standards and reagents 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 operations will permit. Use of methylene chloride for glassware cleaning should be avoided as far as possible. If more than 500 mL of Methylene chloride is spilled, evacuate the area until the area has been cleaned by a Hazardous Material Team.

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 a laboratory supervisor.

6. EQUIPMENT AND SUPPLIES

6.1. Glassware should be cleaned with soap and water, rinsed with water and dried in an oven at 400°C for at least 2 hours. Alternatively the glassware can be solvent rinsed with acetone or methanol followed by methylene chloride after the water rinse.

6.2. Equipment and supplies for extraction procedures

EQUIPMENT AND SUPPLIES	Sep fun.	CLLE	Soni	Sox	Conc
Separatory Funnel: 2 L	√				
Separatory Funnel Rack	√				
Balance: >1400 g capacity, accurate ±1 g	√	√			
pH indicator paper, wide-range: covers extraction pH	√	√			
Graduated cylinder: 1 liter. (other sizes may be used)	√	√			
Erlenmeyer Flask or Fleaker: 125 & 300 mL (other sizes optional)	√		√		
Centrifuge	√				
Auto-Shaker	√				
Methylene Chloride Collection Tank	√	√			
Solvent Dispenser Pump or 100 mL Graduated Cylinder	√		√		
Continuous Liquid/Liquid Extractor		√			
Round or flat Bottom: 250, 500 mL or 1 L		√			
Boiling Chips: Contaminant free, approximately 10/40 mesh		√		√	√

EQUIPMENT AND SUPPLIES	Sep fun.	CLLE	Soni	Sox	Conc
(Teflon® PTFE, carbide or equivalent).					
Cooling Condensers		√		√	
Heating Mantle: Rheostat controlled		√		√	
Auto-timer for heating mantle		√		√	
Beakers: 250 & 400 mL, graduated			√		
Balance: >100 g capacity, accurate ±0.1 g			√	√	
Soxhlet Extractor				√	
Sonicator (at least 300 watts)			√		
Sonicator horn, 3/4 inch			√		
Kuderna-Danish (K-D) Apparatus: 500 mL					√
Concentrator Tube: 10 mL, attached to K-D with clips					√
Supply Manifold: Heated, capable of temperature control (± 5°C) up to 95°C.					√
MegaCT: 150 ml					√
Snyder Column: Three-ball macro					√
Water Bath: Heated, with concentric ring cover, capable of temperature control (± 5°C) up to 95°C. The bath must be used in a hood or with a solvent recovery system.					√
Vials: Glass, 2 mL, 4 mL, and 10 mL capacity with Teflon®-lined screw-cap					√
Nitrogen Blowdown Apparatus					√
Nitrogen: reagent grade.					√
Culture tubes: 10 mL, 16 mmx100 mm					√
Syringe: 1 mL	√	√	√	√	
Phase Separation Paper	√	√	√	√	
Glass Wool	√	√	√	√	
Glass Funnel: 75 X 75 mm	√	√	√	√	√
Disposable Pipets	√	√	√	√	√
Aluminum foil	√	√	√	√	√
Paper Towels	√	√	√	√	√
Wrist Shaker					

6.3. Equipment and Supplies for Cleanup Procedures

EQUIPMENT AND SUPPLIES	GPC	Florisil	Sulfur	Acid	A/B	*FC*
Gel permeation chromatography system (GPC Autoprep Model 1002A or 1002B Analytical Biochemical Laboratories, Inc. or Zymark Benchmate or equivalent).	√					
Bio Beads: (S-X3) -200-400 mesh, 70 gm (Bio-Rad Laboratories, Richmond, CA, Catalog 152-2750 or equivalent).	√					
Chromatographic column: 700 mm x 25 mm ID glass column. Flow is upward.	√					
Ultraviolet detector: Fixed wavelength (254 nm) and a semi-prep	√					

EQUIPMENT AND SUPPLIES	GPC	Florisil	Sulfur	Acid	A/B	*FC*
flow-through cell.						
Strip chart recorder, recording integrator, or laboratory data system.	√					
Syringe: 10 mL with Luerlok fitting.	√					
Syringe filter assembly, with disposable 5 um filter discs, Millipore No. LSWP 01300 or equivalent.	√					
Chromatographic column: 250 mm long x 10 mm ID; with Pyrex glass wool at the bottom and a Teflon stopcock (for silica gel cleanup).	√					
Vacuum system for eluting multiple cleanup cartridges. Vac Elute Manifold - Analytichem International, J.T. Baker, or Supelco (or equivalent). The manifold design must ensure that there is no contact between plastics containing phthalates and sample extracts.		√				
Vacuum trap made from a 500 mL sidearm flask fitted with a one-hole stopper and glass tubing.		√				
Vacuum pressure gauge.		√				
Rack for holding 10 mL volumetric flasks in the manifold.		√				
Mechanical shaker or mixer: Vortex Genie or equivalent.			√	√		
Separatory Funnels with Ground-Glass Stoppers: 250 mL					√	
Erlenmeyer Flasks: 125 mL					√	
Disposable Pipets		√	√	√	√	√
Culture tubes: 10 mL, 16 mmx100 mm	√	√	√	√	√	√

7. REAGENTS AND STANDARDS

7.1. Reagents for Extraction Procedures

All reagents must be ACS reagent grade or better unless otherwise specified.

REAGENTS	Sep fun.	CLLE	Soni	Sox	Conc
Sodium hydroxide (NaOH), Pellets: Reagent Grade	√	√			
Sodium hydroxide solution, 10 N: Dissolve 40 g of NaOH in reagent water and dilute to 100 mL.	√	√			
Sulfuric acid (H_2SO_4), Concentrated: Reagent Grade	√	√			
Sulfuric acid (1:1): Carefully add 500 mL of H_2SO_4 to 500 mL of reagent water. Mix well.	√	√			
Hydrochloric Acid (HCl)					
Organic free reagent water.	√	√			
Sodium sulfate (Na_2SO_4), Granular, Anhydrous: Purify by heating at 400°C a minimum of two hours.	√	√	√	√	√
Extraction/Exchange Solvents: Methylene chloride, hexane, acetonitrile, acetone, pesticide quality or equivalent	√	√	√	√	√

REAGENTS	Sep fun.	CLLE	Soni	Sox	Conc
Acetone: Used for cleaning	√	√	√	√	√

7.2. Reagents for Cleanup Procedures

REAGENTS	GPC	Florisil	Sulfur	Acid	A/B	*FC*
Florisil: 500 mg or 1 g cartridges with stainless steel or Teflon frits (calalog 694-313, Analytichem, 24201 Frampton Ave., Harbor City, CA, or equivalent.)		√				
Mercury: triple distilled			√			
Tetrabutylammonium hydrogen sulfate			√			
Sodium sulfite			√			
Tetrabutylammonium (TBA) sulfite reagent: Prepare reagent by dissolving 3.39 g of Tetrabutylammonium hydrogen sulfate in 100 mL organic-free reagent water. Extract this solution 3 times with 20 mL portions of hexane. Discard the hexane extracts. Add 25 g sodium sulfite to the water solution.			√			
2-Propanol			√			
Nitric acid: 1N			√			
Copper powder: remove oxides (if powder is dark) by treating with 1N nitric acid, rinse with organic-free reagent water to remove all traces of acid, rinse with acetone, and dry under a stream of nitrogen.			√			
Sulfuric acid, Concentrated				√		
Sodium hydroxide, Pellets					√	
Sodium hydroxide, 10N: Dissolve 40 g of NaOH in 100 mL of reagent water					√	
Sulfuric acid (H_2SO_4), Concentrated: Reagent Grade					√	
Sulfuric acid (1:1): Carefully add 500 mL of H_2SO_4 to 500 mL of reagent water. Mix well.					√	
Fluorocarbon: PF-5080, 3M						√

7.3. Standards

7.3.1. Stock Standards

Stock standards are purchased as certified solutions or prepared from neats. Semivolatile stock standards are stored at $\leq 6^{\circ}C$. All stock standards must be protected from light. Stock standard solutions must be replaced after one year (from the time of preparation, if prepared in house, or from the time the ampoule is opened if purchased.) Standards must be allowed to come to room temperature before use.

7.3.2. Surrogate Spiking Standards

Prepare or purchase surrogate spiking standards at the concentrations listed in Table 5. Surrogate spiking standards are purchased or prepared as dilutions of the stock standards. Surrogate spiking solutions must be refrigerated and protected from light.

The standards must be replaced at least every six months or sooner if there is reason to believe that the standard has degraded or concentrated.

7.3.3. Matrix Spiking and Laboratory Control Spiking Standards.

The same spiking solution is used for the matrix spike and the Laboratory Control Sample. Prepare MS/LCS spiking standards at the concentrations listed in Table 6. Spiking standards are purchased or prepared as dilutions of the stock standards. Spiking solutions must be refrigerated and protected from light. The standards must be replaced at least every six months or sooner if there is reason to believe that the standard has degraded or concentrated.

7.3.4. GPC calibration solution - prepare or purchase a solution in methylene chloride that contains the following analytes in the concentrations listed below:

Analyte	mg/mL
Corn Oil	25.0
Bis (2-ethylhexyl) phthalate	1.0
Methoxychlor	0.2
Perylene	0.02
Sulfur	0.08

NOTE: Sulfur is not very soluble in methylene chloride, however, it is soluble in warm corn oil. Therefore, one approach is to weigh out the corn oil, warm it, and transfer the weighed amount of sulfur into the warm corn oil. Mix it and then transfer into a volumetric flask with methylene chloride, along with the other calibration compounds. This standard has a lifetime of 6 months.

8. SAMPLE COLLECTION PRESERVATION AND STORAGE

8.1. Samples are not chemically preserved.

8.2. Samples are stored at 4°C ± 2°C in glass containers with Teflon®-lined caps.

8.3. Holding Times

8.3.1 Extraction is initiated within 7 days of the sampling date for aqueous samples, 14 days for solid and waste samples.

8.3.2 For TCLP leachates, extraction is initiated within seven days from when the TCLP Leach tumbling has been completed, excluding the filtration step. If the filtration step requires extended times, this time counts as part of the seven day holding time.

8.3.3. Analysis of the extracts is completed within forty days of extraction.

9. QUALITY CONTROL

9.1. Quality Control Batch

The batch is a set of up to 20 samples that are of the same matrix and are processed together using the same procedures and reagents. The batch must contain a method blank, an 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. See policy QA-003 for further definition of the batch.

9.2. Definition of matrix

The possible matrix types are aqueous, soil, waste and TCLP leachate.

9.3. Insufficient Sample

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. Use of a LCS pair in place of a MS/MSD must be documented.

9.4. Sample count

Laboratory generated QC samples (method blanks, LCS, MS/MSD) are not included in the sample count. Field samples are included.

9.5. Method Blank

A method blank consisting of all reagents added to the samples must be prepared and analyzed with each batch of samples. Surrogates are spiked into the method blank at the same level as the 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.

9.5.1. Aqueous Method Blanks use 1000 mL of reagent water spiked with the surrogates. The method blank goes through the entire analytical procedure, including any cleanup steps.

9.5.2. Solid method blanks use 30 g of sodium sulfate spiked with the surrogates. The method blank goes through the entire analytical procedure, including any cleanup steps.

9.5.3. TCLP method blanks use 250 mL of leachate fluid (100 mL for herbicides) spiked with the surrogates. The leachate may optionally be diluted to 1000 mL with reagent water. The method blank goes through the entire analytical procedure, including any cleanup steps.

9.6. Laboratory Control Sample (LCS)

Laboratory Control Samples are well-characterized, laboratory generated samples used to monitor the laboratory's day to day performance of routine analytical methods. The LCS, spiked with a group of target compounds representative of the method analytes, is used to monitor the accuracy of the analytical process, independent of matrix effects. On-going

monitoring of the LCS results provides evidence that the laboratory is performing the method within accepted QC guidelines for accuracy and precision. The LCS goes through the entire analytical procedure, including any cleanup steps.

9.6.1. The LCS is made up in the same way as the method blank (See sections 9.5.1 - 9.5.3) but spiked with the LCS standard and the surrogates.

9.7. Surrogates

9.7.1. 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.

9.7.2. Each applicable 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.

9.8. Matrix Spike/Matrix Spike Duplicate (MS/MSD)

A matrix spike is an environmental sample to which known concentrations of target analytes have been added. A matrix spike duplicate is a second spiked aliquot of the same sample which is prepared and analyzed along with the sample and matrix spike.

9.9. Initial Demonstration of Capability

The initial demonstration and method detection limit studies described in section 13 must be acceptable before analysis of samples may begin.

9.10. Quality Assurance Summaries

Certain clients may require specific project or program QC which may supersede these method requirements. Quality Assurance Summaries (QAS) should be developed to address these requirements.

9.11. STL North Canton QC Program

Further details of QC and corrective action guidelines are presented in the STL North Canton QC Program document (QA-003). Refer to this document if in doubt regarding corrective actions.

10. CALIBRATION AND STANDARDIZATION

10.1. On a weekly basis, measure 1.0 mL of solvent into an autovial using a gastight syringe that is manufactured to a certified volume delivery tolerance of ±0.01 mL (1mL total volume). The "standard" autovial is sealed and the top and bottom of the meniscus are marked. The autovials containing the sample extracts are then compared against the "standard" vial to ensure that the final volume is consistently 1.0 ± 0.01mL. If a new box of autovials are used, then the steps are repeated to further ensure that variations due to vial size and shape are minimized. A log is kept of the lot number of the vials and the day the vials were prepared.

10.2. Refer to section 11.8.1.2. for calibration of the GPC. Otherwise this section is not applicable.

11. PROCEDURE

Procedures for separatory funnel liquid/liquid extraction (11.2), continuous liquid/liquid extraction (11.3), sonication extraction (11.4), soxhlet extraction (11.5), waste dilution (11.6), extract concentration (11.7), and extract cleanup (11.8) are presented in this section.

11.1. Procedural Variations

Procedural variations are allowed only if deemed necessary in the professional judgment of the supervisor to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance memo and approved by a supervisor and QA/QC manager. If contractually required, the client will be notified. The Nonconformance memo will be filed in the project file. Any deviations from this procedure identified after the work has been completed must be documented as a nonconformance, with a cause and corrective action described. A Nonconformance memo shall be used for this documentation.

11.2. Separatory Funnel Liquid/Liquid Extraction of Water Samples.

A flow chart for this procedure is included in Section 17.

11.2.1. Measure the initial sample pH with wide-range pH paper and record on the extraction benchsheet. If sample is a leachate (e.g. TCLP), compare the current pH against leachate log, note on the benchsheet if there is any discrepancy.

11.2.2. The normal sample volume is 1 liter. Other sample volumes may be used to obtain specific reporting limits, and reduced sample volumes, diluted to 1 liter with reagent water, may be used for very dirty samples.

11.2.3. Weigh the sample container on a balance (± 1 g), taring the sample and container. Transfer the sample to the separatory funnel. . Add the appropriate volume of surrogate spiking solution (see Table 3). Also add appropriate volume of matrix spiking solution to any matrix spike / matrix spike duplicate samples (see.Table 4) Mix well. If the sample is a 600 series analysis or BP GCLN sample rinse the sample bottle with 60 mL methylene chloride and transfer to the separatory funnel. Reweigh the container. Assume a density of 1 g/mL and record the difference as the sample volume on the benchsheet to the nearest milliliter.

Note: Aqueous samples must be determined volumetrically for Ohio VAP samples.

Warning: Dichloromethane creates excessive pressure very rapidly! Therefore, initial venting should be done immediately after the sample container has been sealed and inverted. Vent into hood away from analysts and other samples.

11.2.3.1. If the entire sample bottle will not be used, transfer the aliquot to the separatory funnel, then add the spiking solutions to the sample in the separatory funnel.

Note: Alternative methods of measurement of sample volume include a) transferring the sample to a measuring cylinder and b) marking a meniscus on the sample bottle and then measuring the volume of water required to fill the bottle to the meniscus after the sample is transferred. The former method is not recommended because of the risk of cross contamination while the latter is not recommended because of poor accuracy. However, either method may be necessary for specific client programs.

11.2.4. Prepare a method blank, LCS and MS/MSD for each batch as specified in section 9 of this SOP. Use 1 L of reagent water for method blanks and LCS. The LCS is spiked with the surrogate and matrix spike solutions, the method blank only with the surrogates.

11.2.5. Use 250 mL of leachate for TCLP pesticides and TCLP semivolatiles, measured in a graduated cylinder. An alternative method would be to tare 400ml beaker on the balance and then add 250g to the beaker. Assume a density of 1g/mL and record the volume on the benchsheet. The leachate may be made up to 1 L in volume with reagent water.

11.2.6. For a TCLP method blank,LCS and LCS Dup measure 250 mL of the buffer solution used in the leaching procedure and transfer to the separatory funnel. Add 60 mL of methylene chloride to the separatory funnel. The TCLP leachate may be diluted to approximately 1 liter before extraction if desired.

11.2.7. Adjust sample pH as indicated in Table 1 for the initial extraction. Use the minimum amount of 1:1 H_2SO_4 or 10 N NaOH necessary. Recheck the sample with pH paper by dipping a disposable pipette into the sample and wetting the pH paper. Record adjusted pH, spiking volumes and standard numbers on the benchsheet. Return spiking solutions to the refrigerator as soon as possible.

11.2.8. Seal and shake or rotate the separatory funnel vigorously for 2 minutes with periodic venting to release excess pressure. An autoshaker may be used to shake and rotate the separatory funnel.

Warning: Dichloromethane creates excessive pressure very rapidly! Therefore, initial venting should be done immediately after the separatory funnel has been sealed and inverted. Vent into hood away from analysts and other samples.

11.2.9. Allow the organic layer to separate from the water phase until complete visible separation has been achieved (approximately 10 minutes). If the emulsion interface between layers is more than one-third the size of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample and may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods. If the emulsion cannot be broken (recovery of <80% of the methylene chloride*), transfer the sample, solvent, and emulsion into the extraction chamber of a continuous extractor and proceed as

described in continuous liquid-liquid extraction (Section 11.2.). If this is done, the sample must be extracted as part of a valid CLLE batch.

*Note: 15 - 20 mL of methylene chloride is expected to dissolve in 1 L of water. Thus, solvent recovery could be as low as 35 mL from the first shake and still be acceptable. Subsequent shakes should recover at least 50 mL of solvent.

11.2.10. Fill a funnel with 10-20 g of anhydrous sodium sulfate. The funnel can be plugged with glass wool or filter paper may be used to hold the sodium sulfate. Drain the solvent extract from the separatory funnel through the prepared filtration funnel into a clean glass container. The extract may be drained directly into the KD flask. Close the stopcock just before the water level begins draining out of the separatory funnel. If the sodium sulfate becomes saturated with water add more to the funnel or replace the existing sodium sulfate with fresh drying agent.

11.2.11. Repeat the extraction process two more times using fresh 60 mL portions of solvent, combining the three solvent extracts in the collection container.

11.2.12. If extraction at a secondary pH is required, adjust the pH of the sample in the separatory funnel to the pH indicated in Table 1 with a minimum amount of 10 N NaOH or 1:1 H_2SO_4. Measure with pH paper and record the adjusted pH on the benchsheet. Serially extract with three 60 mL portions of methylene chloride, as outlined in Steps 11.1.7 to 11.1.9. Collect these three extracts in the same container used for the previous fraction.

11.2.13. Rinse the extract residue from the sodium sulfate by pouring 20-30 mL of clean methylene chloride through the funnel and into the collection container.

11.2.14. Dispose of solvent and water remaining in the extractor into the appropriate waste container.

11.2.15. Cover with aluminum foil if the extract is not concentrated immediately. Refer to Section 11.8 for concentration and Section 11.9 for cleanup.

11.3 Short-Term Continuous Liquid-Liquid Extraction

11.3.1 Extraction personnel must first determine if one liter of sample exists in the sample bottle.

11.3.2 Mark the meniscus on the side of the sample bottle for later determination of sample volume.

11.3.3 Add 225 mL methylene chloride to the extractor, turn stopcock to the open position. Connect extractor to a 250 ml boiling flask with boiling chips.

11.3.4 Check the pH of the sample and adjust, if necessary, using 1:1 H2SO4 or 10N sodium

hydroxide. Quantitatively transfer the sample from the sample bottle to the extractor. *Rinse the sample bottle with 25-ml of methylene chloride for BP samples. Pour the rinsate from the sample bottle into the continuous extractor.

11.3.5 Adjust the volume of solvent in the boiling flask by adding reagent water to the extractor, if necessary.

11.3.6 Next, fill the sample bottle to the mark with reagent water. Pour the reagent water into a graduated cylinder. Measure the reagent water to ± 10 ml and document this sample volume on the extraction benchsheet.

11.3.7 Add the appropriate volume of surrogate to each sample and spiking solutions to the MS, MSD, LCS, and/or LCSD in the extractor and mix well.

11.3.8 Extract samples for 12 hours. 8270 extractions will still be performed in two pH extraction steps. Each step will run 6 hours, however, where timing is a factor the samples may be left to extract for longer than 12 hours.

11.3.9 Turn stopcocks to the closed position.

11.3.10 Allow the extractors to run another 5 minutes, then turn off the rheostats and mantles.

11.3.11 The samples will macro concentrate in the CLLE. After the flasks have cooled, continue to concentrate the extracts by KD or QES methodology.

11.3.12 This method of extraction **cannot** be used for method 625, 610 or 608.

11.4 Continuous Liquid/Liquid Extraction from Water Samples.
A flow chart for this procedure is included in Section 17.

11.4.1. Assemble the apparatus. Add 250-400mL of methylene chloride to the extractor body. Add 3 to 5 boiling chips to the round-bottom distilling flask.

11.4.2. Measure the initial sample pH with wide-range pH paper and record on the extraction benchsheet. If sample is a leachate (e.g. TCLP), compare the current pH against leachate log, note on the benchsheet if there is any discrepancy.

11.4.3. Weigh the sample container on a balance (± 1 g), taring the sample and container. Transfer the sample to the continuous liquid/liquid extractor . Add the appropriate volume of surrogate spiking solution (see Table 3). Also add appropriate volume of matrix spiking solution to any matrix spike / matrix spike duplicate samples (see.Table 4) Mix well. If the sample is a 600 series analysis or BP GCLN sample rinse the sample bottle with 60 mL methylene chloride and transfer to the continuous liquid/liquid extractor. Reweigh the container. Assume

a density of 1 g/mL and record the difference as the sample volume on the benchsheet to the nearest milliliter.

Note: Aqueous samples must be determined volumetrically for Ohio VAP samples.

Warning: Dichloromethane creates excessive pressure very rapidly! Therefore, during the rinse for 600 series methodology venting should be done immediately after the sample container has been sealed and inverted. Vent into hood away from analysts and other samples.

11.4.3.1. If the entire sample bottle will not be used, transfer the aliquot to the extractor, then add the spiking solutions to the sample in the extractor.

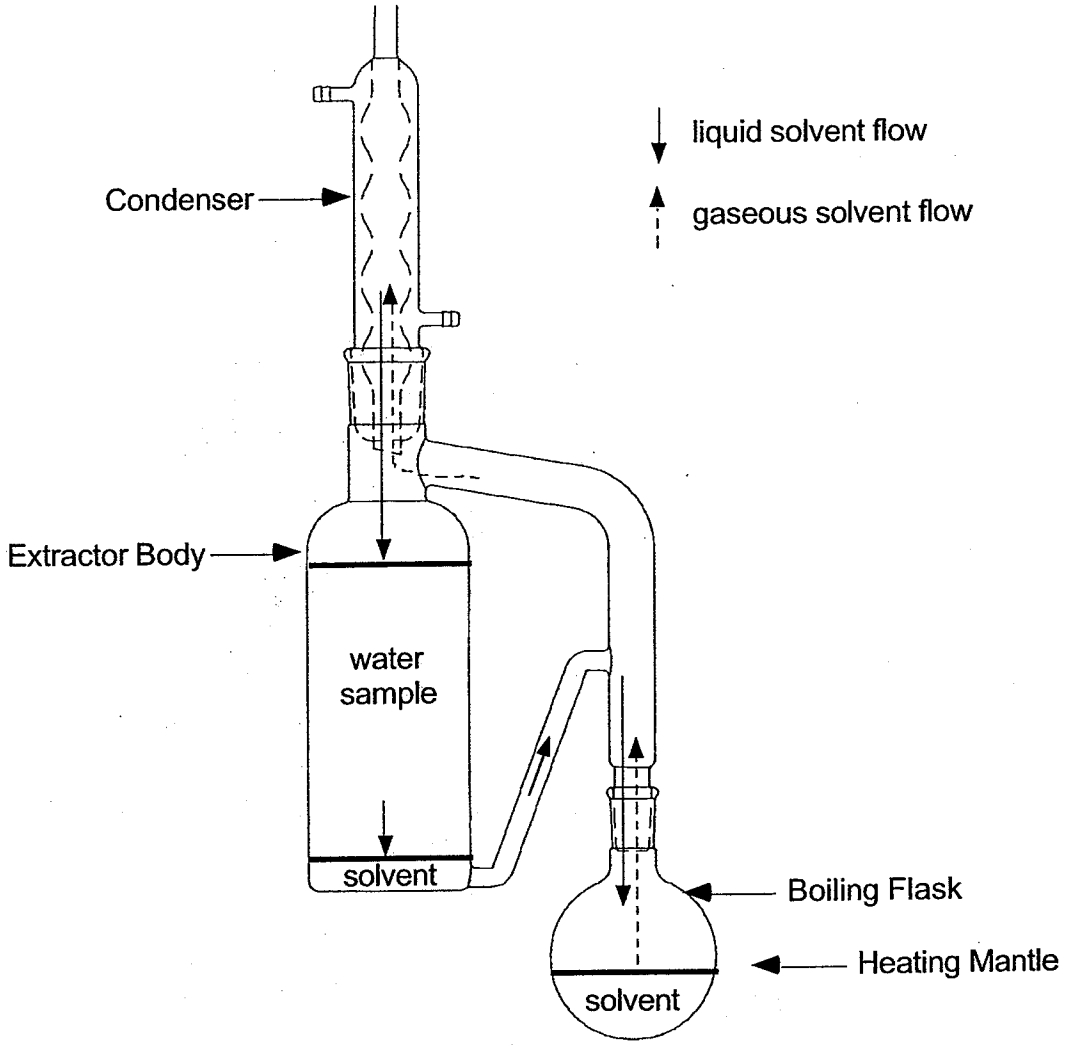
Note: Alternative methods of measurement of sample volume include: a.) transferring the sample to a measuring cylinder and b.) marking a meniscus on the sample bottle and then measuring the volume of water required to fill the bottle to the meniscus after the sample is transferred. The former method is not recommended because of the risk of cross contamination while the latter is not recommended because of poor accuracy. However, either method may be necessary for specific client programs.

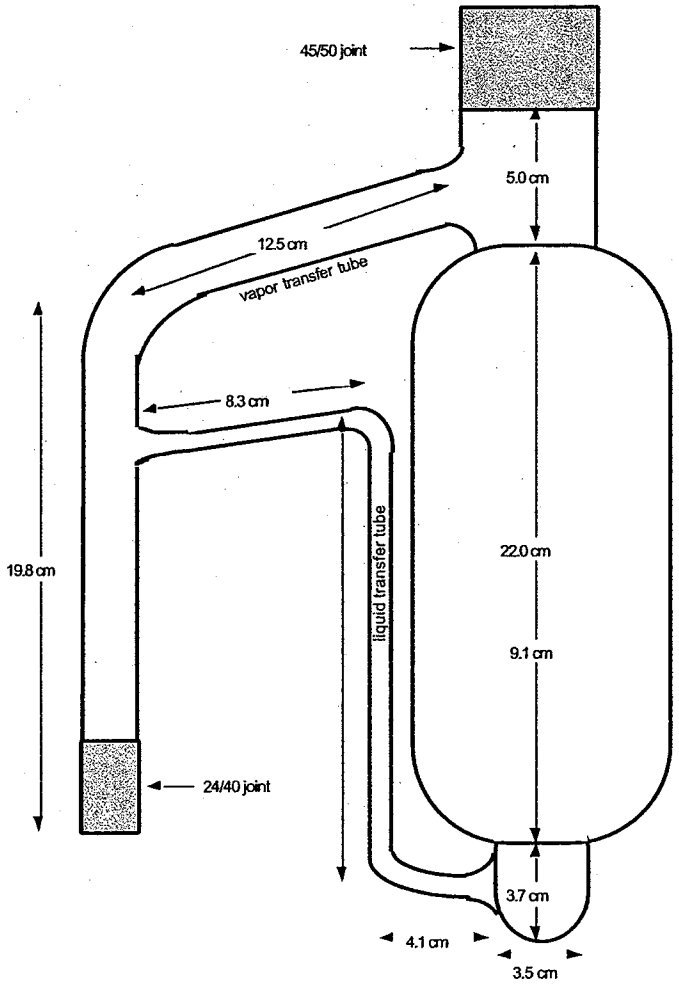
11.4.3.2. Prepare a method blank, LCS and MS/MSD for each batch as specified in section 9 of this SOP. Use 1 L of reagent water for method blanks and LCS. The method blank is spiked with the surrogates, the LCS and matrix spikes with the surrogates and matrix spiking solutions.

11.4.3.3. Use 250mL of leachate for TCLP for TCLP semivolatiles and TCLP pesticides measured in a graduated cylinder. An alternative method would be to tare 400ml beaker on the balance and then add 250g to the beaker. Assume a density of 1g/mL and record the volume on the benchsheet. Dilute to about 1 liter with reagent water.

11.4.3.4. For a TCLP method blank, LCS and LCS Dup measure 250 mL of the buffer solution used in the leaching procedure and transfer to the separatory funnel. Dilute to about 1 liter with reagent water.

11.4.3.5. Less than one liter of sample may be used, for highly contaminated samples, or if the reporting limit can be achieved with less than one liter of sample. In this event dilute the sample to about 1 liter with reagent water.


liquid solvent flow
gaseous solvent flow
Condenser
Extractor Body
water sample
solvent
Boiling Flask
Heating Mantle
solvent



11.4.4. Adjust sample pH as indicated in Table 1 for the initial extraction. Use the minimum amount of 1:1 H_2SO_4 or 10 N NaOH necessary. Recheck the sample with pH paper. Record adjusted pH, spiking volumes and standard numbers on the benchsheet. Return spiking solutions to the refrigerator as soon as possible.

11.4.5. Add reagent water to the extractor body until approximately 250 mL of methylene chloride is pushed over into the round-bottomed flask to ensure proper operation and solvent cycling. Attach cold condenser (about 10°C). Turn on heating mantle. Inspect joints for leaks once solvent has begun cycling. Extract for 18-24 hours. (24 hours required for 600 series)

11.4.6. If extraction at a secondary pH is required, (see Table 1) turn off the heating mantle and allow the extractor to cool. Detach the condenser and adjust the pH of the sample in the extractor body to the pH indicated in Table 1 with a minimum amount of 10 N NaOH or 1:1 H_2SO_4. Measure with pH paper and record the adjusted pH on the benchsheet. Reattach the condenser and turn on heating mantle. Extract for 18-24 hours.

11.4.7. Turn off the heating mantle and allow the extractor to cool.

11.4.8. Place a funnel containing 10-20 g of anhydrous sodium sulfate on the Kuderna-Danish (K-D) apparatus or other glass container. The funnel can be plugged with glass wool enabling it to hold the granular anhydrous sodium sulfate or phase separation filter paper may be used.

11.4.9. Dry the extract in the round bottom flask by filtering it through the sodium sulfate filled funnel. Note that it is not necessary or advisable to attempt to add the solvent remaining in the continuous extractor body to the extract.

11.4.10. Collect the dried extract in a K-D or other glass container. Rinse the flask which contained the solvent extract with 20-30 mL of methylene chloride and add it to the funnel to complete the quantitative transfer. Dispose of solvent and water remaining in the extractor in the appropriate waste container.

Note: Some types of CLLE apparatus have built in drying columns. If this type of apparatus is used then a drying step subsequent to the extraction may not be necessary.

11.4.11. Cover with aluminum foil if the extract is not concentrated immediately. Refer to Section 11.8 for concentration and Section 11.9 for cleanup.

11.5. Sonication

A flow chart for this procedure is included in Section 17.

11.5.1. Determination of percent moisture (Optional - if a different group performs this test, refer to the facility SOP.)

In some cases, sample results are needed on a dry weight basis. If this is the case, weigh 5-10 g of sample into a suitable tared container (typically an aluminum weigh pan. Determine the % moisture by drying overnight (at least 12 hours) at 105°C. Allow to cool in a desiccator before weighing.

$$\% \text{ Moisture} = \frac{(\text{weight of wet sample} - \text{weight of dry sample})}{\text{weight of wet sample}} \times 100$$

11.5.2. Determination of pH (Optional - if a different group performs this test, refer to the facility SOP.)

If pH determination is required, transfer 10 g of soil to a beaker. Add 10 mL of water. Stir for five minutes then let stand for 1 hour. Determine the pH of the sample with a glass electrode and pH meter.

11.5.3. Decant and discard any water layer on a sediment/soil sample. Record and document if a water layer was discarded on the benchsheet. Homogenize the sample by mixing it thoroughly in the container. If this is not possible place the sample in clean beaker and homogenize. Upon completion of homogenization in beaker return sample to original container. Discard foreign objects such as sticks, leaves and rocks, unless extraction of this material is required by client. If the sample consists primarily of foreign materials consult with the client (via the Project Manager or Administrator).

11.5.4. Remove surrogate and matrix spiking solutions from refrigerator and allow to warm to room temperature.

11.5.5. Weigh 30 g of sample ± 0.2g into a 250 or 400 mL beaker. Record the weight to the nearest 0.01 g in the appropriate column on the benchsheet. Use 30 g of sodium sulfate for the method blank and 30 g of sodium sulfate with 30 g of reagent sand for the LCS.

11.5.6. Mix weighed sample with a spatula adding enough anhydrous sodium sulfate (approximately 30 g) to be free flowing. (If the sample is not free flowing extraction efficiency may be reduced)

11.5.7. Prepare a method blank, LCS and MS/MSD for each batch as specified in section 9 of this SOP.

11.5.8. Add the appropriate volume of surrogate spiking solution (see Table 3). Also add appropriate volume of matrix spiking solution to any matrix spike / matrix spike duplicate samples (see.Table 4) Add 1 mL of the surrogate spiking solution to each sample, method blank, Laboratory Control Sample (LCS), and matrix spikes. Refer to Table 6 for details of the surrogate spiking solutions. Add 1 mL of the appropriate matrix spiking solution to each Matrix Spike/Matrix Spike Duplicate (MS/MSD) and LCS. Refer to Tables 3 and 5 for details of the spiking solutions. Record spiking volumes and standard numbers on the benchsheet. Return spiking solutions promptly to refrigerator.

Note: The same volume of surrogate and matrix spiking solution is used if GPC is indicated since the final volume would be reduced to compensate for loss of extract during the GPC procedure.

11.5.9. Immediately add a minimum of 100 mL of solvent to the beaker.

Solvents:

Semivolatile GC/MS, TPH, Organochlorine pesticides and PCBs	1:1 Methylene Chloride / Acetone

Note: Steps 11.5.5 - 11.5.9 should be performed rapidly to avoid loss of the more volatile extractables.

11.5.10. Place the bottom surface of the appropriate disrupter horn tip approximately ½ inch below the surface of the solvent, but above the sediment layer.

11.5.11. Sonicate for 3 minutes, making sure the entire sample is agitated. If the W-380 or W-385 sonicator is used the output should be set at 6 for the 3/4 inch high gain (Q) horn or 10 for the 3/4 inch standard horn. with mode switch on pulse, and percent-duty cycle knob set at 50%.

Note: Do ***not*** use ***Microtip*** probe.

11.5.12. Loosely plug the stem of a 75 mm x 75 mm glass funnel with glass wool and/or line the funnel with filter paper. Add 10-20 g of anhydrous sodium sulfate to the funnel cup.

11.5.13. Place the prepared funnel on a collection apparatus (beaker or K-D Apparatus.

11.5.14. Decant and filter extracts through the prepared funnel into a clean beaker or K-D Apparatus.

11.5.15. Repeat the extraction two more times with additional 100 mL minimum portions of solvent each time. Decant off extraction solvent after each sonication. On the final sonication pour the entire sample (sediment and solvent) into the funnel and rinse with an additional 10 mL-20 mL of the methylene chloride/acetone appropriate solvent (Refer to Table in 11.5.9).

Note: Alternatively, the three extracts may be collected together and then filtered through the sodium sulfate.

11.5.16. Cover with aluminum foil if the extract is not concentrated immediately. Refer to Section 11.8 for concentration and Section 11.9 for cleanup.

11.5.17. Sonicator Tuning.

11.5.17.1. Tune the sonicator according to manufacturer's instructions. The sonicator must be tuned at least every time a new horn is installed.

11.6. Soxhlet

11.6.1. Determination of % moisture

In some cases, sample results are needed on a dry weight basis. If this is the case, weigh 5-10 g of sample into a suitable tared container (typically an aluminum weigh pan. Determine the % moisture by drying overnight at 105°C. Allow to cool in a desiccator before weighing.

$$\% \text{ Moisture} = \frac{(\text{weight of wet sample} - \text{weight of dry sample})}{\text{weight of wet sample}} \times 100$$

11.6.2. Determination of pH

If pH determination is required, transfer 10 g of soil to a beaker. Add 10 mL of water. Stir for 1 hour. Determine the pH of the sample with a glass electrode and pH meter.

11.6.3. Decant and discard any water layer on a sediment/soil sample. Record and document if a water layer was discarded on the benchsheet. Homogenize the sample by mixing it thoroughly in the container. If this is not possible place the sample in clean beaker and homogenize. Upon completion of homogenization in beaker return sample to original container. Discard foreign objects such as sticks, leaves and rocks, unless extraction of this material is required by client. If the sample consists primarily of foreign materials consult with the client (via the Project Manager or Administrator).

11.6.4. Remove surrogate and matrix spiking solutions from refrigerator and allow to warm to room temperature.

11.6.5. Weigh 30 g of sample ± 0.2g into a beaker, recording the weight to the nearest 0.01 g on the benchsheet.. Use 30 g of sodium sulfate for the method blank and LCS. Add 30 g of anhydrous sodium sulfate and mix well. The mixture should have a free flowing texture. If not, add more sodium sulfate. Add the sample/sodium sulfate mixture to a soxhlet thimble, but do not pack the thimble tightly. The extraction thimble must drain freely for the duration of the extraction period. A glass wool plug above and below the sample in the soxhlet extractor is an acceptable alternative for the thimble.

11.6.6. Add the appropriate amount of surrogate and matrix spiking solution as indicated in Tables 3, 4, 5, and 6.

Sample weights less than 30 g but over 5 g may be used if the appropriate reporting limits can be met.

11.6.7. Prepare a method blank, LCS and MS/MSD for each batch as specified in section 9 of this SOP, using sodium sulfate as the matrix. The weight of sodium sulfate used should be approximately the weight of soil used in each sample.

11.6.8. Place approximately 200mL of solvent into a 250 mL flat bottom flask containing one or two clean boiling chips. Attach the flask to the extractor and extract the sample for 16-24 hours at 4-6 cycles per hour. Check the system for leaks at the ground glass joints after it has warmed up.

NOTE: If a reduced quantity of sample is extracted, it is usually necessary to increase the amount of sodium sulfate added or increase the solvent boiling rate to properly set the cycling rate.

Solvents:

Semivolatile GC/MS, OPP, PAH, TPH Organochlorine pesticides and PCBs	1:1 Methylene Chloride / Acetone

11.6.9. Allow the extract to cool after the extraction is complete, then disassemble by gently twisting the soxhlet from the flask. Dry the extract in the flask by filtering it through a sodium sulfate filled funnel.

11.6.10. Collect the dried extract in a K-D or other glass container. Rinse the flask which contained the solvent extract with 20-30 mL of methylene chloride and add it to the funnel to complete the quantitative transfer.

11.6.11. Cover with aluminum foil if the extract is not concentrated immediately. Refer to Section 11.8 for concentration and Section 11.9 for cleanup.

11.7. Waste Dilution

11.7.1. This method is used for materials that are soluble in an organic solvent.

11.7.2. Transfer 10 mL of the solvent to be used for dilution into a Teflon capped vial. Mark the meniscus on the vial, then discard the solvent.

11.7.3. Tare the vial, then transfer approximately 1g of sample to the vial. Record the weight to the nearest 0.01 g.

11.7.4. Add appropriate volume of surrogate and spike solutions (Table 3).

11.7.5. Dilute to 10 mL with the appropriate solvent. (Methylene Chloride for GC/MS-BNA and GCS-TPH. Add 10 mL of appropriate solvent (Hexane) for GCS-pesticide and/or PCB analysis.

11.7.6. Add 2 g + 0.1 g sodium sulfate to the sample. Cap and shake or vortex each extract for 2 minutes.

11.7.7. If H2O is still present, add 4-5 g sodium sulfate to a small pipette funnel. The funnel can be plugged with glass wool or phase separation filter paper may be used to hold the sodium sulfate.

11.7.8. Pour the sample through the funnel, collecting as much as possible in a clean vial. Do NOT rinse the funnel with additional solvent, and do NOT concentrate the sample. The final volume is defined as 10 mL.

11.7.9. Label the sample, which is now ready for cleanup or analysis.

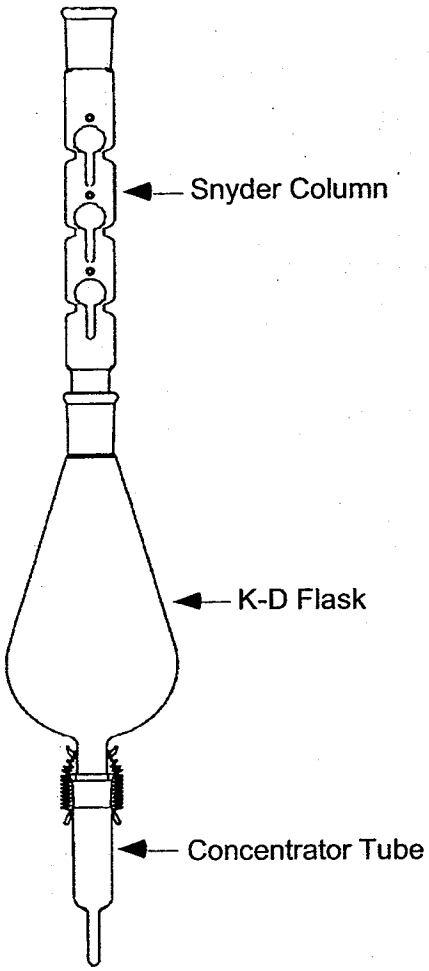
11.8. Concentration

According to the type of sample and any cleanup procedures needed, different final solvents and volumes will be required. Refer to Table 2 for the appropriate final volumes and concentrations.

11.8.1. Kuderna-Danish (KD) Method:

11.8.1.1. Assemble a Kuderna-Danish concentrator by attaching a 10 mL concentrator tube to the 500 mL KD flask. Transfer the sample to the K-D flask.

11.8.1.2. Add one or two clean boiling chips and the extract to be concentrated to the KD flask and attach a three ball Snyder Column. Add approximately 1 mL of clean methylene chloride to the top of the Snyder column (this is important to ensure that the balls are not stuck and that the column will work properly).



11.8.1.3. Place the KD apparatus on a water bath (90-98°C) so that the tip of the concentrator tube is submerged. The water level should not reach the joint between the concentrator and the KD flask. At the proper rate of distillation, the balls will actively chatter but the chambers should not flood.

11.8.1.4. Concentrate to 5-15 mL. If the determinative method requires a solvent exchange add the appropriate exchange solvent (50 mL hexane, 20 ml hexane/acetone, or 4 mL acetonitrile ,4mL toluene (Herbicide TCLP), or 10 mL toluene) to the top of the Snyder Column, and then continue the water bath concentration back down to 1-4 mL. Refer to Table 2 for details of exchange solvents and final volumes.

The Snyder column may be insulated if necessary to maintain the correct rate of distillation.

Note: Add an additional boiling chip with the addition of exchange solvent. An alternative technique for solvent exchange is to replace the macro Snyder column and KD flask with a micro Snyder column, concentrate to approximately 1 mL, add the appropriate solvent, and concentrate back down to 1 mL. The extract must be cool before the macro Snyder assembly is removed.

Note: It is very important not to concentrate to dryness as analytes will be lost.

11.8.1.5. Remove the KD apparatus from the water bath and allow to cool for a minimum of 10 minutes. If the level of the extract is above the level of the concentrator tube joint, continue to distill the solvent as necessary. Again, allow the KD flask to cool for a minimum of 10 minutes.

11.8.1.6. If the final volume is 5 or 10 mL the extract may be made up to volume in the graduated KD tube or transferred to a 12 mL vial previously marked at the appropriate volume level. Document the final volume. Otherwise proceed to section 11.8.2

11.8.2. Nitrogen Evaporation to Final Concentration

11.8.2.1. Transfer the entire extract to a calibrated evaporation tube. Rinse the concentrator tube with 1-2 mL of the appropriate solvent and transfer the solvent rinsate to the evaporation tube.

11.8.2.2. Place the tube in a warm water bath that is at least 5°C below the boiling temperature of the solvent being evaporated and evaporate the solvent using a gentle stream of nitrogen. The nitrogen flow will form a slight depression on the surface of the solvent, but should not create splattering of the extract.

Boiling points of commonly used solvents are:

Methylene chloride	40°C
Acetone	56°C
Hexane	69°C
Acetonitrile	82°C
Toluene	111°C

11.8.2.3. During the course of the evaporation rinse the sides of the evaporation tube twice with approximately 1 mL of clean solvent. The first rinse should be about half way through he process, with the second rinse when the solvent volume gets close to 1 mL. Concentrate the solvent accurately to the calibrated volume line and transfer the extract to the appropriate storage vial.

Note: It is very important not to concentrate to dryness as analytes will be lost.

An alternative technique is to follow the previous steps concentrating the solvent to slightly below the required final volume and then drawing the extract into a syringe. Rinse the evaporation tube with a small amount of solvent and draw additional solvent into the syringe to make up the accurate final volume.

Note: It is very important not to concentrate to dryness as analytes will be lost.

Note: The final concentration and volume measurement steps are critical. Use care when concentrating and make certain that the final volume measurement is accurate.

Alternative QES Concentration Method:

This concentration method uses a hot water jacketed concentrator tube (CT) instead of the hot water bath and concentrator tube used in Section 11.8.1.1. The construction of the jacketed concentrator tube reduces the tendency of the extract to evaporate to dryness. Thus, low boiling analytes are retained in the extract better with less analyst monitoring of the concentration process.

Assemble the jacketed concentrator tube, KD body and hot water hoses. Add 1mL of exchange solvent (if needed) and one large, clean boiling chip.

***NOTE**: The boiling chips used in the jacketed concentrator tube must be large enough to prevent them falling down into the tip of the CT. If the boiling chip is not in the proper position, the extract may superheat and bump vigorously if the extract solvent warms up slowly.*

Pour the extract to be concentrated into the KD flask, and attach a three-ball Snyder column.

Turn on the hot (95°C) water flow to the jacketed concentrator tube.

Concentrate to 1 mL. If the determinative method requires a solvent exchange, add the appropriate exchange solvent (5-10 mL hexane, 1 mL acetonitrile, 4 mL acetone/hexane) to the top of the Snyder column. Continue to concentrate until the Snyder column balls stop chattering.

Cool the jacketed concentrator tube until it is cold to the touch.

Quantitatively transfer the extract and dilute to final volume, or continue concentration with nitrogen evaporation (section 11.8.2).

11.8.3. Turbovap Method

11.8.3.1. Turn on the Turbovap and adjust the water temperature to 5-10°C less than the boiling point of the solvent to be evaporated.

11.8.3.2. Switch all endpoint sensors to the "NO" position.

11.8.3.3. Adjust the water bath level

11.8.3.4. Adjust the nitrogen gas pressure to approximately 12 psi.

11.8.3.5. Transfer the extract into the Turbovap tube and load into the Turbovap. Do not fill the Turbovap tubes over approximately 3/4 full.

11.8.3.6. Reset the sensor and close the lid.

Note: If the extract splashes when the nitrogen flow starts, reduce the nitrogen flow or transfer a portion of the extract back into the original extract container.

11.8.3.7. As the extract concentrates, transfer the remainder of the extract into the appropriate Turbovap tube. After all of the extract has been transferred, rinse the flask with a few mL of methylene chloride and add to the Turbovap tube.

11.8.3.8. During the concentration rinse the Turbovap tube walls with a few mL of solvent 1 or 2 times.

11.8.3.9. Concentrate the extract to slightly less than the required final volume.

11.8.3.10. If solvent exchange is required, concentrate to 1-4 mL and add 50 mL of the exchange solvent. Concentrate back down to the appropriate volume. Refer to Table 2 for details of exchange solvents and final volumes.

11.8.3.11. Transfer the concentrated extract to volumetric glassware for adjustment of final volume, using a small amount of solvent to rinse the tube and complete the transfer.

Note: Water contamination from condensation during concentration is not acceptable. If water is present, remove the Turbovap tube and filter the extract through sodium sulfate. Transfer to a clean Turbovap tube and continue the concentration.

Note 2: Dark, opaque or turbid samples may not concentrate. If this occurs, set the concentrator sensor to dryness and supervise the entire concentration procedure.

11.9. Cleanup Techniques

The following techniques may be used to remove interfering peaks, and /or to remove materials that may cause column deterioration and/ or loss of detector sensitivity.
Gel Permeation Chromatography (Section 11.9.1) is a generally applicable technique which can be used to prepare extracts for Semivolatiles (8270), and pesticides (8081) analysis. It is capable of separating high molecular weight material from the sample analytes, and so is particularly useful if tissue or vegetable matter is part of the sample, and for many soil samples.
Note: GPC used only for CLP Projects

Florisil column cleanup (Section 11.9.2) is particularly useful for cleanup of pesticides for analysis by method 8081 and should normally be applied to these samples unless the matrix is clean. It separates compounds with a different polarity from the target analytes.
Note: GPC used only for CLP Projects
Gel Permeation Chromatography and Florisil column cleanup may both be applied to samples for analysis by method 8081/8082. In this case the GPC should be performed first.

Sulfur cleanup (Section 11.9.3) is generally applied to samples for analysis by method 8081/8082, since the Electron Capture Detector responds strongly to sulfur. It is performed after GPC and Florisil cleanup.

Sulfuric acid cleanup (Section 11.9.4) is applied to samples requiring analysis for Polychlorinated Biphenyls (PCBs) only. Most organic matter is destroyed by the sulfuric acid.
WARNING: Sulfuric acid cleanup must not be performed on any matrix that may have water present as a violent reaction between the acid and water may result in acid exploding out of the vessel.

Acid Base Partition Cleanup (Section 11.9.5) is useful for separating organic acids and phenols from basic and neutral organics.

Fluorocarbon cleanup (Section 11.9.7) is used to remove hydrocarbons from water samples to be analyzed for water soluble alcohols.

11.9.1. Gel Permeation Chromatography (GPC)

Note: GPC systems include the GPC Autoprep Model 1002A or 1002B Analytical Biochemical Laboratories, Inc., Zymark Benchmate, or equivalent.

11.9.1.1. GPC Column Preparation

11.9.1.1.1. Weigh out 70 g of Bio Beads (SX-3) into a 400-mL beaker.

11.9.1.1.2. Add approximately 300 mL of methylene chloride and stir gently.

11.9.1.1.3. Cover with aluminum foil and allow the beads to swell for a minimum of two hours. Maintain enough solvent to sufficiently cover the beads at all times.

11.9.1.1.4. Position and tighten the outlet bed support (top) plunger assembly in the tube by inserting the plunger and turning it clockwise until snug. Install the plunger near the column end but no closer than 5 cm (measured from the gel packing to the collar).

11.9.1.1.5. Turn the column upside down from its normal position with the open end up. Place the tubing from the top plunger assembly into a waste beaker below the column.

11.9.1.1.6. Swirl the bead/solvent slurry to get a homogeneous mixture and pour the mixture into the open end of the column. Transfer as much as possible with one continuous pour trying to minimize bubble formation. Pour enough to fill the column. Wait for the excess solvent to drain out before pouring in the rest. Add additional methylene chloride to transfer the remaining beads and to rinse the beaker and the sides of the column. If the top of the gel begins to look dry, add more methylene chloride to rewet the beads.

11.9.1.1.7. Wipe any remaining beads and solvent from the inner walls of the column with a laboratory tissue. Loosen the seal slightly on the other plunger assembly (long plunger) and insert it into the column. Make the seal just tight enough so that any beads on the glass surface will be pushed forward, but loose enough so that the plunger can be pushed forward.

CAUTION: Do not tighten the seal if beads are between the seal and the glass surface because this can damage the seal and cause leakage.

11.9.1.1.8. Push the plunger until it meets the gel, then compress the column bed about 4 cm.

11.9.1.1.9. Connect the column inlet to the solvent reservoir and place the column outlet tube in a waste container. Pump methylene chloride through the column at a rate of 5 mL/min. for one hour.

11.9.1.1.10. After washing the column for at least one hour, connect the column outlet tube to the inlet side of the UV detector. Connect the system outlet to the outlet side of the UV detector. Placing a restrictor (made from a piece of capillary tubing of 1/16"OD x 10/1000"ID x 2") in the outlet tube from the UV detector will prevent bubble formation which causes a noisy UV baseline. The restrictor will not effect the flow rate. After pumping methylene chloride through the column for an additional 1-2 hours, adjust the inlet bed support plunger until approximately 6-10 psi back-pressure is achieved. Push the plunger in to increase pressure or slowly pull outward to reduce pressure.

11.9.1.1.11. When the GPC column is not to be used for several days, connect the column inlet and outlet lines to prevent column drying and/or channeling. If channeling occurs, the gel must be removed from the column, re-swelled, and re-poured as described above. If drying occurs, pump methylene chloride through the column until the observed column pressure is constant and the column appears wet. Always recalibrate after column drying has occurred to verify that retention volumes have not changed.

11.9.1.2. Initial Calibration of the GPC Column

11.9.1.2.1. Before use, the GPC must be calibrated based on monitoring the elution of standards with a UV detector connected to the GPC column.

11.9.1.2.2. Pump solvent through the GPC column for 2 hours. Verify that the flow rate is 4.5-5.5 mL/min. Corrective action must be taken if the flow rate is outside this range. Record the column pressure (should be 6-10 psi) and room temperature (22°C is ideal).

Note: Changes in pressure, solvent flow rate, and temperature conditions can affect analyte retention times and must be monitored. If the flow rate and/or column pressure do not fall within the above ranges, a new column should be prepared.

11.9.1.2.3. Inject the calibration solution and retain a UV trace that meets the following requirements (See resolution calculation in section 11.9.1.6):

- Peaks must be observed and should be symmetrical for all compounds in the calibration solution.
- Corn oil and phthalate peaks must exhibit >85% resolution.
- Phthalate and methoxychlor peaks must exhibit >85% resolution.
- Methoxychlor and perylene peaks must exhibit >85% resolution.
- Perylene and sulfur peaks must not be saturated and must exhibit >90% baseline resolution.

11.9.1.2.4. A UV trace that does not meet the criteria in paragraph 11.9.1.2.3 indicates the need for system maintenance and/or the need for a new column.

11.9.1.2.5. Determine appropriate collect and dump cycles.

11.9.1.2.6. The calibrated GPC program for pesticides/PCB should dump >85% of the phthalate and should collect >95% of the methoxychlor and perylene. Use a wash time of 10 minutes.

11.9.1.2.7. For semivolatile extracts, initiate a column eluate collection just before the elution of bis (2-ethylhexyl) phthalate and after the elution of the corn oil.

Stop eluate collection shortly after the elution of perylene. Stop collection before sulfur elutes. Use a wash time of 10 minutes after the elution of sulfur.

11.9.1.2.8. Reinject the calibration solution after appropriate dump and collect cycles have been set.

11.9.1.2.9. Measure and record the volume of collected GPC eluate in a graduated cylinder.

11.9.1.2.10. The retention times for both bis(2-ethylhexyl) phthalate and perylene must not vary more than +/- 5% between calibrations.

11.9.1.3. GPC calibration check

Check the calibration of the GPC immediately after the initial calibration and at least every 7 days thereafter, while the column is in use.

11.9.1.3.1. Inject the calibration solution, and obtain a UV trace. If the retention times of bis(2-ethylhexyl)phthalate or perylene have changed by more than $\pm$ 5% use this run as the start of a new initial calibration. Otherwise, proceed with the recovery check. Excessive retention time shifts may be caused by poor laboratory temperature control or system leaks, an unstabilized column, or high laboratory temperature causing outgassing of methylene chloride. Pump methylene chloride through the system and check the retention times each day until stabilized.

11.9.1.4. GPC Recovery Check for Pesticides/ PCBs

11.9.1.4.1. The recovery from the GPC must be verified immediately after the initial calibration and at least every 7 days, when the instrument is in use. Two recovery check solutions are used. The first mixture is prepared by diluting 1.0 2.0 mL of the pesticide matrix spiking solution (Table 6) to 10 mL in methylene chloride. The second mixture is prepared by diluting 12.0 mL of the PCB only matrix spiking solution (Table 6) to 10 mL with methylene chloride.

11.9.1.4.2. Load the pesticide matrix spike mixture, the PCB mixture, and a methylene chloride blank onto the GPC using the GC dump and collect values.

Note: If the analysis is for PCBs only, then the pesticide recovery check is not necessary.

11.9.1.4.3. After collecting the GPC calibration check fraction, concentrate, solvent exchanging to hexane. Adjust the final volume to 5.0 mL, and analyze by GC/EC. Refer to concentration, section 11.8.

11.9.1.4.4. The methylene chloride blank may not exceed more than one half the reporting limit of any analyte. And if the recovery of each of the single component analytes is 80-10120% and if the Aroclor pattern is the same as previously run standards, then the analyst may use the column. If the above criteria are not met, there may be a need for system maintenance.

11.9.1.5. GPC Blank for Semivolatiles

11.9.1.5.1. The recovery from the GPC must be verified immediately after the initial calibration and at least every 7 days, when the instrument is in use.

11.9.1.5.2. Load a methylene chloride blank onto the GPC using the semivolatiles dump and collect values.

11.9.1.5.3. After collecting the GPC recovery check fraction, concentrate, and analyze by GC/MS. Refer to the concentration section 11.8.

The blank should not contain any analytes at or above the reporting limit. If these conditions are met the column may be used for sample analysis. Otherwise correct the contamination problem, or extend the collect time to improve recovery of target analytes.

11.9.1.6. Sample Extract Cleanup

11.9.1.6.1. Reduce the sample extract volume to 1-2 mL, then adjust to 10 mL with methylene chloride prior to cleanup. This reduces the amount of acetone in the extract. Refer to section 11.8.

11.9.1.6.2. Start the pump and let the flow stabilize for 2 hours. The solvent flow rate should be 4.5-5.5 mL/min. The ideal laboratory temperature to prevent outgassing of the methylene chloride is 22°C. The normal backpressure is 6-10 psi.

11.9.1.6.3. In order to prevent overloading of the GPC column, highly viscous sample extracts must be diluted prior to cleanup. Any sample extract with a viscosity greater than that of a 1:1 glycerol:water solution (by visual comparison) must be diluted and loaded into several loops.

11.9.1.6.4. Samples being loaded onto the GPC should be filtered with a 5 micron (or less) filter disk. Attach a filter to a 10 mL Luerlok syringe and filter the 10 mL sample extract into the sample tube.

Note: The Zymark Benchmate automatically filters the sample extracts, but manual prefiltration of very dirty extracts may be necessary.

11.9.1.6.5. Load the filtered (or unfiltered if using the Benchmate) samples into the proper sample tubes and place on the GPC.

Note: For the GPC Autoprep Model 1002A, wash the loading port with methylene chloride after loading each sample loop in order to minimize cross contamination. This step is automated on the GPC Autoprep 1002B and on the Benchmate.

11.9.1.6.6. Set the collect, dump, and wash times determined by the calibration procedure.

11.9.1.6.7. Switch to the run mode and start the automated sequence. Process each sample using the collect and dump cycle times established by the calibration procedure.

11.9.1.6.8. Collect each sample in a suitable glass container. Monitor sample volumes collected.

11.9.1.6.9. Any samples that were loaded into 2 or more positions must be recombined.

11.9.1.6.10. Concentrate semivolatile sample extracts to 0.5 mL in methylene chloride. Refer to the concentration section 11.8.

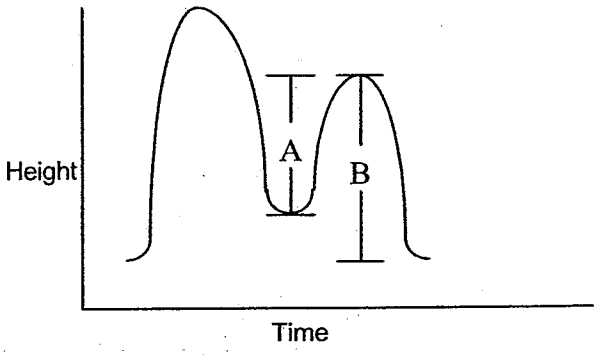
11.9.1.6.11. Solvent exchange pesticide/PCB sample extracts into hexane and concentrate to 5.0 mL. Refer to the concentration section 11.8.

11.9.1.7. Calculations

11.9.1.7.1. Resolution

To calculate the resolution between two peaks on a chromatograph, divide the depth of the valley between the peaks by the peak height of the smaller peak being resolved and multiply by 100.

Resolution Calculation



$$\% \text{ Resolution} = \frac{A}{B} \times 100$$

Where: A = depth of valley to height of smaller peak

B = peak height of smaller peak

11.9.1.7.2. Dump Time

Mark on the chromatograph the point where collection is to begin. Measure the distance from the injection point. Divide the distance by the chart speed. Alternatively the collect and dump times may be measured by means of an integrator or data system.

$$\text{Dump time (min)} = \frac{\text{Distance (cm) from injection to collection start}}{\text{Chart speed (cm / min)}}$$

11.9.1.7.3. Collection Time

$$\text{Collection time (min)} = \frac{\text{Distance (cm) between collection start and stop}}{\text{Chart speed (cm / min)}}$$

11.9.2. Florisil Cartridge Cleanup

Florisil cleanup is generally used for organochlorine pesticides, although it may be applied to other analytes. Sections 11.9.8.2.1 through 11.9.8.2.8 outline the procedure for organochlorine pesticides, while section 11.9.2.9 outlines modifications required for other analytes.

Note 1: Systems for eluting multiple cleanup cartridges include the Supelco, Inc. Solid Phase Extraction (SPE) assemblyor equivalent.

Note 2: Follow the lab specific procedure when using ABC Model 1002B.

11.9.2.1. Before Florisil cleanup sample volume must be reduced to 10 mL (5 mL if GPC cleanup was used) and the solvent must be hexane. Refer to Section 11.8 for details of concentration.

11.9.2.2. Attach a vacuum manifold to a vacuum pump or water aspirator with a trap installed between the manifold and the vacuum. Adjust the vacuum in the manifold to 5-10 psi.

11.9.2.3. Place one Florisil cartridge into the vacuum manifold for each sample extract. Prior to cleanup of samples, pre-elute each cartridge with 5 mL of hexane/acetone (9:1). Adjust the vacuum applied to each cartridge so that the flow through each cartridge is approximately 2 mL/min. Do not allow the cartridges to go dry.

11.9.2.4. Just before the cartridges go dry, release the vacuum to the manifold and remove the manifold top.

11.9.2.5. Place a rack of clean labeled 12 mL concentrator tubes into the manifold and replace the manifold top. Make sure that the solvent line from each cartridge is placed inside the appropriate tube.

11.9.2.6. After the clean tubes are in place, vacuum to the manifold is restored and 2.0 mL of the extract is added to the appropriate Florisil cartridge.

11.9.2.7. The pesticides/aroclors in the extract concentrates are then eluted through the column with 8 mL of hexane/acetone (90:10) and are collected into the 10 mL culture tube or concentrator tube held in the rack inside the vacuum manifold.

11.9.2.8. Transfer the extract to a graduated concentrator tube and concentrate the extract to 2 mL. Refer to the concentration section. (11.8)

Note 1: A cartridge performance standard must be run with each lot of Florisil cartridges.

Note 2: Florisil cartridge performance check--every lot number of Florisil must be tested before use. Add 0.5 ug/mL of 2,4,5-trichlorophenol solution and 0.5 mL of GC Standard Mix A (midpoint concentration) to 4 mL hexane. Reduce volume to 0.5 mL. Add the concentrate to a pre-washed Florisil cartridge and elute with 9 mL hexane/acetone [(90:10)(v/v)]. Rinse cartridge with 1.0 mL hexane two additional times. Concentrate eluate to 1.0 mL final volume and transfer to vial. Analyze the solution by GC/EC. The test sample must show 80 to 120% recovery of all pesticide analytes with <5% trichlorophenol recovery, and no peaks

interfering with target compounds can be detected. This standard has a lifetime of six months. Alternatively, this standard may be purchased as a stock solution.

11.9.2.9. Modifications for other analyte classes

11.9.2.9.1. PCBs

Pre-elute the cartridge with 4 mL hexane. Add 2 mL of the sample extract and elute with 3 mL hexane. The eluant will contain the PCBs together with any heptachlor, aldrin, 4,4'DDE and part of any 4,4'DDT. Any BHC isomers, heptachlor epoxide, chlordane, endosulfan I and II, endrin aldehyde and endrin sulfate and methoxychlor will be retained on the column and can be eluted in a separate fraction with 8 mL 90:10 hexane:acetone if required.

11.9.3. Sulfur Removal

11.9.3.1. Sulfur can be removed by one of three methods: mercury, copper, or tetrabutylammonium sulfite (TBA) according to laboratory preference. If the sulfur concentration is such that crystallization occurs in the concentrated extract, centrifuge the extract to settle the crystals, and carefully draw off the sample extract with a disposable pipet, leaving the excess sulfur in the centrifuge tube. Transfer the extract to a clean concentrator tube before proceeding with further sulfur cleanup.

11.9.3.2. Sulfur Removal with Elemental Mercury

Note: Use Mercury sparingly in order to minimize exposure and disposal costs.

11.9.3.2.1. Transfer 2 mL of sample extract into a clean concentrator tube or Teflon sealed vial.

11.9.3.2.2. Add one to three drops of mercury to the extract vial and seal.

11.9.3.2.3. Shake well for 15-30 seconds. If prolonged shaking is required, use a mechanical shaker.

11.9.3.2.4. Remove the extract from the mercury using a disposable pipette and transfer to a clean vial.

11.9.3.2.5. If black precipitate forms, sulfur was present. Shake again, then centrifuge. After centrifugation, transfer the supernate to a clean test tube and repeat. Do this until relatively little precipitate remains, or the screens indicate that cleanup is complete.

11.9.3.2.6. Properly dispose of the mercury waste.

11.9.3.3. Sulfur Removal with Copper

11.9.3.3.1. Transfer 1.0 mL of sample extract into a centrifuge or concentrator tube.

11.9.3.3.2. Add approximately 2 g of cleaned copper powder (see 8.2 for copper cleaning procedure) to the sample extract tube.

11.9.3.3.3. Mix for one minute on a mechanical shaker.

11.9.3.3.4. If the copper changes color, sulfur was present. Repeat the sulfur removal procedure until the copper remains shiny.

11.9.3.3.5. Transfer the supernate to a clean vial.

11.9.3.4. Sulfur Removal with Tetrabutylammonium (TBA) Sulfite Reagent

11.9.3.4.1. Transfer 1.0 mL of sample extract into a culture tube.

11.9.3.4.2. Add 1.0 mL TBA sulfite reagent and 2 mL 2-propanol to the sample extract. Cap and shake for 1 minute. If clear crystals (precipitated sodium sulfite) form, sufficient sodium sulfite is present.

11.9.3.4.3. If a precipitate does not form, add sodium sulfite in approximately 0.1 g portions until a solid residue remains after repeated shaking.

11.9.3.4.4. Add 5 mL organic free reagent water and shake for 1 minute. Allow sample to stand for 5-10 minutes. (Centrifuge if necessary to separate the layers). Transfer the sample extract (top layer) to a vial. The final volume is defined as 1.0 mL in section 11.9.3.4.1.

11.9.4. Sulfuric Acid Cleanup

11.9.4.1. Add approximately 2-5 mL of concentrated sulfuric acid to 2 mL of sample extract in a Teflon capped vial.

Caution: There must be no water present in the extract or the reaction may shatter the sample container.

11.9.4.2. Shake or vortex for about thirty seconds and allow to settle. (Centrifuge if necessary)

11.9.4.3. Remove the sample extract (top layer) from the acid using a Pasteur pipette and transfer to a clean vial. ***CAUTION:*** It is not necessary to remove all the extract since the final volume is already determined. Transfer of small amounts of sulfuric acid along with the extract will result in extremely rapid degradation of the chromatographic column.

11.9.4.4. If the sulfuric acid layer becomes highly colored after shaking with the sample extract, transfer the hexane extract to a clean vial and repeat the cleanup procedure until color is no longer being removed by the acid, or a maximum of 5 acid cleanups.

11.9.4.5. Properly dispose of the acid waste.

11.9.5. Acid/Base Partition Cleanup

11.9.5.1. Place 10 mL of the solvent extract from a prior extraction procedure into a 125 mL separatory funnel.

11.9.5.2. Add 20 mL of methylene chloride to the separatory funnel.

11.9.5.3. Slowly add 20 mL of DI water which has been previously adjusted to a pH of 12 to 13 with 10 N sodium hydroxide.

11.9.5.4. Seal and shake the separatory funnel for at least two minutes with periodic venting to release excess pressure.

CAUTION: Methylene chloride creates excessive pressure very rapidly. Initial venting should be done immediately after the separatory funnel has been sealed.

11.9.5.5. Allow the organic layer to separate from the aqueous phase for a minimum of ten minutes.

11.9.5.6. If an emulsion interface between layers is more than one-third the size of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, and may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods.

11.9.5.7. Separate the aqueous phase and transfer it to a 125 mL Erlenmeyer flask. Repeat the extraction two more times using fresh 20 mL aliquots of dilute sodium hydroxide (pH 12-13) . Combine the aqueous extracts.

11.9.5.8. Water-soluble organic acids and phenols will be primarily in the aqueous phase. Base/neutral analytes will be in the methylene chloride. If the analytes of interest are only in the aqueous phase discard the methylene chloride and proceed to Section 11.9.5.9. If the analytes of interest are only in the methylene chloride, discard the aqueous phase and proceed to Section 11.9.5.11.

11.9.5.9. Externally cool the flask with ice while adjusting the aqueous phase to a pH of 1-2 with sulfuric acid (1:1). Transfer the cool aqueous phase to a clean 125 mL separatory funnel.

11.9.5.10. Add 20 mL of methylene chloride to the separatory funnel and shake for at least two minutes. Allow the methylene chloride to separate from the aqueous phase and collect the methylene chloride in an Erlenmeyer flask. Repeat the extraction two more times using fresh methylene chloride and extracting at pH 1-2. Combine the three extracts.

11.9.5.11. Dry the extract by passing through a funnel containing 10-20 g anhydrous sodium sulfate. Rinse the funnel with an additional 20-30 mL of clean methylene chloride

11.9.5.12. Cover with aluminum foil if the extract is not concentrated immediately. Refer to section 11.9 for concentration.

11.9.5.13. Dispose of solvent and water remaining in the separatory funnel into the appropriate waste container.

11.9.6. Fluorocarbon Cleanup

This procedure is appropriate for the removal hydrocarbons from water samples prior to analysis for water soluble alcohols

11.9.6.1. Transfer 1-2 mL of water sample to a 10 mL culture tube.

11.9.6.2. Add 1-2 mL of fluorocarbon solvent (PF-5080) to the culture and cap.

11.9.6.3. Shake for 30-60 seconds.

11.9.6.4. After the two phases have separated, pipette about 1 mL of water sample (top layer) into an autosampler vial for analysis. If necessary, centrifuge to enhance the phase separation.

12. DATA ANALYSIS AND CALCULATIONS

Not applicable

13. METHOD PERFORMANCE

13.1. Method detection limit

Each laboratory must generate a valid method detection limit for each analyte of interest. The procedure for the determination of the method detection limit is given in STL North Canton QA Policy #: QA-005

13.2. Initial demonstration

Each laboratory must make an initial demonstration of capability for each individual method. This requires 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 spiking level should be equivalent to a mid-level calibration. (For certain tests more than one set of QC check samples may be necessary in order to demonstrate capability for the full analyte list.)

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

13.2.2. Calculations and acceptance criteria for the QC check samples are given in the determinative SOPs. (CORP-GC-0001, CORP-MS-0001, 0002)

13.3. Training Qualification

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

14. POLLUTION PREVENTION

Within the constraints of following the methodology in this SOP, use of organic solvents should be minimized.

15. WASTE MANAGEMENT

Waste generated in this procedure will be segregated, and disposed according to the facility hazardous waste procedures. The Laboratory Environmental, Health and Safety Coordinator should be contacted if additional information is required.

15.1. Solvent waste must be disposed of in the clearly labeled waste cans.

15.2. Acid waste must be collected in the clearly labeled acid waste containers.

15.3. Solid materials (soil, gloves, soiled paper products) are placed in the solid debris container. Do not put liquids in the solid waste container.

15.4. Methylene chloride saturated water and remaining sample after the extraction is dumped into Methylene chloride waste cans.

16. REFERENCES

Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW846, 3rd Edition, Final Update III (December 1996). Sections 3500B, 3510C, 3520C, 3540C, 3550B, 3600C, 3610B, 3620B, 3640A, 3650B, 3660B, AND 3665A.

17. MISCELLANEOUS

17.1. Modifications from Reference method

17.1.1. Some surrogate spiking concentrations are modified from those recommended in SW-846, in order to make the concentrations more consistent with the calibration levels in the determinative methods.

17.1.2. Aqueous sample volumes may be determined by weight.

17.1.3. Spiking levels for method 608 have been reduced by a factor of ten to bring the levels within the normal calibration range of the instrument.

17.1.4. 10 g of soil is used for pH determination, rather than the 50 g suggested in the reference method. The volume of water is also adjusted to maintain the sample / water ratio specified in the method.

17.2. Modifications from previous revision

17.2.1. SOP change forms are on record in the Quality Assurance Department.

17.3. Facility Specific SOPs

Each facility shall attach a list of facility specific SOPs or approved attachments (if applicable) which are required to implement this SOP or which are used in conjunction with this SOP. If no facility specific SOPs or amendments are to be attached, a statement must be attached specifying that there are none.

17.4. Tables

Table 1
Liquid /Liquid Extraction Conditions

Determinative Method	Initial Ext. pH	Secondary Ext. pH
BNA: 8270C[1]	1-2	11-12
625	11-12	1-2
Pest/PCB: 8081A, 8082 & 608	5-9	None
Wisconsin DRO	2	
OPP: 8141A	as received	None
Hydrocarbons: 8015B	as received	None
PAH: 8310, & 610	as received	None

[1] If the laboratory has validated acid only 8270 extraction for the target compound list required then the base extraction step may be omitted. The required validation consists of a 4 replicate initial demonstration of capability and a method detection limit study. (See section 13). Additionally, either of the base or acid fractions of Method 8270 can be run first.

Table 2
Exchange Solvents and Final Volumes

Final Volumes and Exchange Solvents if no cleanup is used		

Type	Exchange Solvent for Analysis	Final Volume for Analysis in mL
Semivolatiles	N/A	5.0*- Solids, 2.0 for H2O
PCB	Hexane	10.0 for solids 5.0 for H2O 2.0 for H2O**
Pesticides	Hexane	10.0 for solids 5.0 for H2O
Pesticides/TCLP	Hexane	3.0 mL
PAH by HPLC	Acetonitrile	1.0 mL
BNA – SIM	N/A	2.0 mL - Solids & H2O
TPH	N/A	1.0
OPP	Hexane/Acetone	2.0

*Requires high sensitivity mass spec tune (refer to NC-MS-0015 PAH by SIM)
** Michigan work requires a final volume of 2 mL.

Final Volumes and exchange solvents if GPC cleanup is used CLP ONLY – SOLIDS ONLY			
Type	Exchange Solvent for GPC	Final Volume for GPC	Final Volume and solvent for Analysis
Semivolatiles Semivolatiles	CH_2Cl_2 CH_2Cl_2	10 mL[1] 10 mL[1]	0.5 mL CH_2Cl_2 -OLM03.1 2.5 mL CH_2Cl_2 -OLM04.2
Pesticides	CH_2Cl_2	10 mL[1]	5 mL, Hexane

[1] Final volume for GPC may be 4 mL if a 2 mL sample loop is used

Final volumes and exchange solvents if Florisil cleanup is used CLP ONLY			
Type	Exchange Solvent for Florisil	Final Volume for Florisil	Final Volume and solvent for Analysis
Pesticides	Hexane	10 mL (2 mL aliquot used)	2 mL, hexane

Final volumes and exchange solvents if both GPC and Florisil cleanup are used CLP ONLY					
Type	Exchange Solvent for GPC	Final Volume for GPC	Exchange Solvent for Florisil	Final Volume for Florisil	Final volume for analysis
Pesticides	Methylene Chloride	10 mL	Hexane	5 mL (2 mL aliquot used)	2 mL, hexane

Note: Different final volumes may be necessary to meet special client reporting limit requirements.

Table 3		
Surrogate Spiking Solutions		
Analyte Group	Surrogate Spike Solution ID	Volume (mL)
BNA-SOLIDS	100/150 ppm BNA	0.5

BNA / SIM	100/150 ppm BNA	.2 / 0.02
BNA-H2O	100/150 ppm BNA	0.2
Pest	0.2 ppm DCB/TCX	1.0
TPH	40ng C9	1.0
PCB	0.2 ppm DCB/TCX	1.0
PAH	1.0 ug/mL p-Terphenyl-d14 5.0 ug/mL Benzo(e)pyrene	1.0
OPP	10 ug/mL Triphenyl Phosphate	1.0

Table 4

Matrix Spike and LCS Solutions

Analyte Group	Matrix Spike Solution ID	Volume (mL)
BNA-H2O, BNA-TCLP	100 ppm BNA All-Analyte Spike & Restek Spike	0.2
BNA- SOLIDS	100 ppm BNA All-Analyte Spike & Restek Spike	0.5
BNA / SIM	100 ppm BNA All-Analyte Spike & Restek Spike	0.2 / 0.02
PEST – SOLIDS & H2O	Pest NPDES Spike	1.0
PEST TCLP	Pest TCLP Spike	1.0
PCB	10 ppm PCB Spike	1.0
PAH	See Spike List – Table 6	1.0
TPH	See Spike List – Table 6	1.0
OPP	See Spike List – Table 6	1.0

Table 5
Surrogate Spike Components

Type	Compounds	Solvent	Conc. (µg/mL)
BNA	2-Fluorobiphenyl	Methanol	100
	Nitrobenzene-d5		100
	p-Terphenyl-d14		100
	2-Fluorophenol		150
	Phenol-d6		150
	2,4,6-Tribromophenol		150
	1,2-Dichlorobenzene-d4		100
	2-Chlorophenol-d4		150
Pest/PCB	Decachlorobiphenyl	MethanolAcetone	0.2
	Tetrachloro-m-xylene		0.2
TPH	Nonane (C9)	Methanol	40.0
PAH	p-Terphenyl-d-14	CH3CN	1.0
	Benzo(e)pyrene		5.0
OPP	Triphenylphosphate	Acetone	10.0

Table 6

Matrix Spike Components

Type	Compounds	Solvent	Conc. (µg/mL)
TCL BNA	Acenaphthene	Methanol	100
	4-Chloro-3-Methylphenol		150
	2-Chlorophenol		150
	1,4-Dichlorobenzene		100
	2,4-Dinitrotoluene		100
	4-Nitrophenol		150
	N-Nitroso-Di-n-Propylamine		100
	Pentachlorophenol		150
	Phenol		150
	Pyrene		100
	1,2,4-Trichlorobenzene		100
BNA TCLP	1,4-Dichlorobenzene	Methanol	100
	2,4-Dinitrotoluene		100
	Hexachlorobenzene		100
	Hexachlorobutadiene		100
	Hexachloroethane		100
	2-Methylphenol		100
	3-Methylphenol		100
	4-Methylphenol		100
	Nitrobenzene		100
	Pentachlorophenol		100
	Pyridine		100
	2,4,5-Trichlorophenol		100
	2,4,6-Trichlorophenol		100
BNA		Methanol	

Table 6

Matrix Spike Components

Type	Compounds	Solvent	Conc. (µg/mL)
NPDES			
	Acenaphthene		100
	Acenaphthylene		100
	Anthracene		100
	Benzo(a)anthracene		100
	Benzo(b)fluoranthene	Methanol	100
	Benzo(k)fluoranthene		100
	Benzo(a)pyrene		100
	Benzo(ghi)perylene		100
	Benzyl butyl phthalate		100
	Bis(2-chloroethyl)ether		100
	Bis(2-chloroethoxy)methane		100
	Bis(2-ethylhexyl)phthalate		100
	Bis(2-chloroisopropyl)ether		100
	4-Bromophenyl phenyl ether		100
	2-Chloronaphthalene		100
	4-Chlorophenyl phenyl ether		100
	Chrysene		100
	Dibenzo(a,h)anthracene		100
	Di-n-butylphthalate		100
	1,3-Dichlorobenzene		100
	1,2-Dichlorobenzene		100
	1,4-Dichlorobenzene		100
	3,3'-Dichlorobenzidine		100
	Diethyl phthalate		100

Table 6

Matrix Spike Components

Type	Compounds	Solvent	Conc. (µg/mL)
	Dimethyl phthalate		100
	2,4-Dinitrotoluene		100
	2,6-Dinitrotoluene		100
	Di-n-octylphthalate		100
	Fluoranthene		100
	Fluorene		100
	Hexachlorobenzene		100
	Hexachlorobutadiene		100
	Hexachloroethane		100
	Indeno(1,2,3-cd)pyrene		100
	Isophorone		100
	Naphthalene		100
	Nitrobenzene		100
	N-Nitrosodi-n-propylamine		100
	Phenanthrene		100
	Pyrene		100
	1,2,4-Trichlorobenzene		100
	4-Chloro-3-methylphenol		100
	2-Chlorophenol		100
	2,4-Dichlorophenol		100
	2,4-Dimethylphenol		100
	2,4-Dinitrophenol		100
	2-Methyl-4,6-dinitrophenol		100
	2-Nitrophenol		100
	4-Nitrophenol		100

Table 6

Matrix Spike Components

Type	Compounds	Solvent	Conc. (µg/mL)
	Pentachlorophenol		100
	Phenol		100
	2,4,6-Trichlorophenol		100
	Acetophenone		100
	Atrazine		100
	Caprolactum		100
	Benzaldehyde		100
	1,1′-Biphenyl		100
	Safrole		100
	1,4-Dioxane		100
	Pronamide		100
	p-Chlorobenzilate		100
	Phenacetin		100
	Ethyl methanesulfonate		100
	2-Picoline		100
	Phorate		100
	Quinoline		100
Pest TCLP	Heptachlor	Methanol Acetone	0.5
	Heptachlor epoxide		0.5
	Lindane		0.5
	Endrin		0.5
	Methoxychlor		1.0
Pest NPDES /Pest	Aldrin	MethanolAcetone	1.0

Table 6			
Matrix Spike Components			
Type	Compounds	Solvent	Conc. (µg/mL)
	alpha-BHC		1.0
	beta-BHC		1.0
	delta-BHC		1.0
	gamma-BHC (Lindane)		1.0
	4,4'-DDD		1.0
	4,4'-DDE		1.0
	4,4'-DDT		1.0
	Dieldrin		1.0
	alpha-Endosulfan		1.0
	beta-Endosulfan		1.0
	Endosulfan Sulfate		1.0
	Endrin		1.0
	Heptachlor		1.0
	Heptachlor Epoxide		1.0

Diesel Range Organics (8015B) Spike	
Compound	**Final Concentration**
n-decane	50 µg/ml
n-dodecane	50 µg/ml
n-tetradecane	50 µg/ml
n-hexadecane	50 µg/ml
n-octadecane	50 µg/ml
n-eicosane	50 µg/ml
n-docosane	50 µg/ml
n-tetracosane	50 µg/ml
n-hexacosane	50 µg/ml
n-octacosane	50 µg/ml

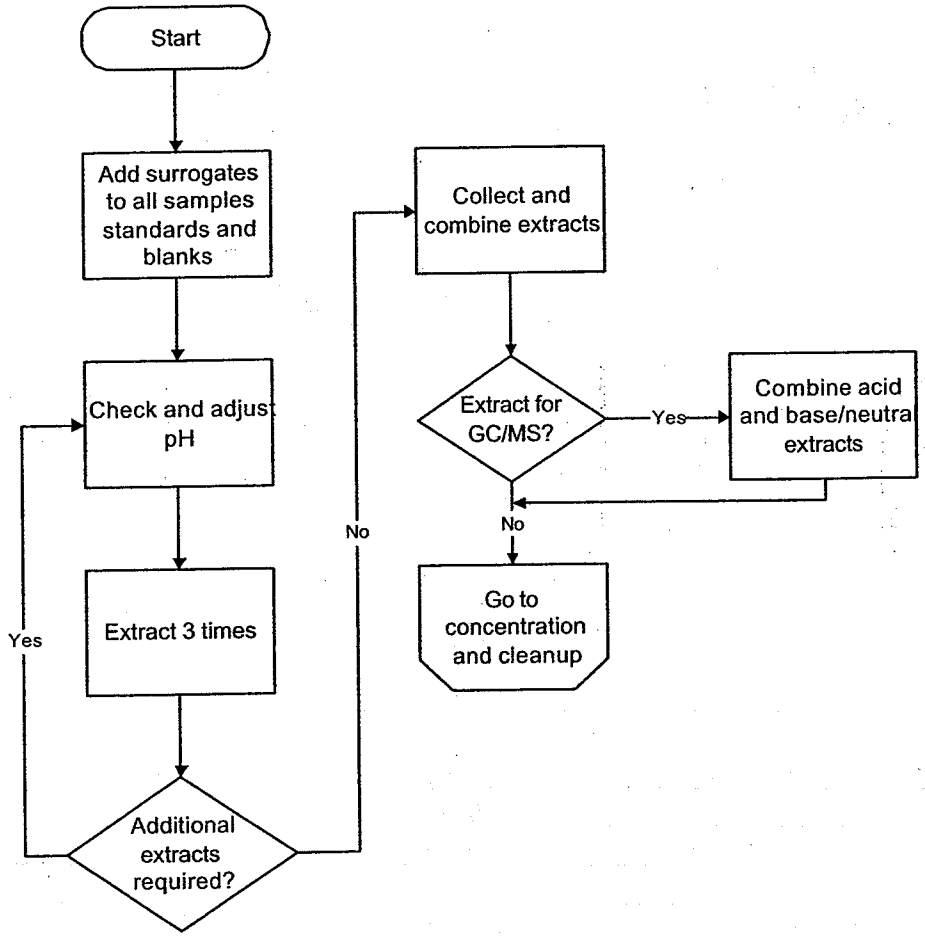
Organophorphorous Pesticides (8141A)

Compound	Final Concentration
dimethoate	20 µg/mL
disulfoton	20 µg/mL
famphur	20 µg/mL
methyl parathion	20 µg/mL
parathion (ethyl)	20 µg/mL
phorate	20 µg/mL
sulfotepp	20 µg/mL
thionazin	20 µg/mL
o,o,o-triethyl phosphorothioate	20 µg/mL
triphenylphosphate (surrogate)	20 µg/mL

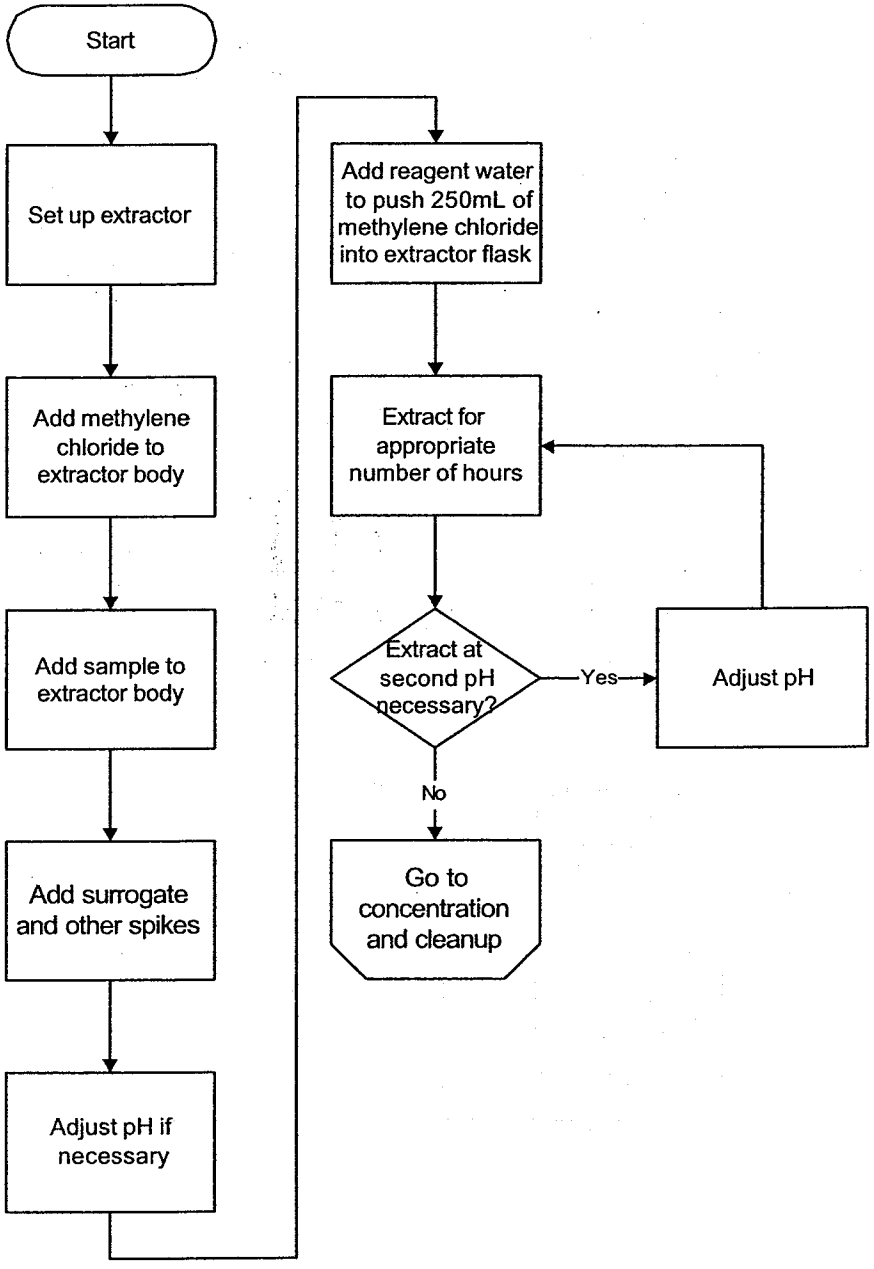
Polynuclear Aromatic Hydrocarbons (8310)	
Compound	**Final Concentration**
Acenaphthylene	10 µg/mL
Carbazole	10 µg/mL
Naphthalene	10 µg/mL
1-Methylnaphthalene	10 µg/mL
2-Methylnaphthalene	10 µg/mL
Acenaphthene	10 µg/mL
Fluorene	2 µg/mL
Phenanthrene	2 µg/mL
Anthracene	2 µg/mL
Fluoranthene	2 µg/mL
Pyrene	2 µg/mL
Benzo(a)anthracene	2 µg/mL
Chrysene	2 µg/mL
Benzo(a)pyrene	2 µg/mL
Benzo(k)fluoranthene	2 µg/mL
Benzo(a)pyrenek)fluoranthene	2 µg/mL
Dibenzo(a,h)anthracene	2 µg/mL
Benzo(g,h,I)perylene	2 µg/mL
Indeno(1,2,3-cd)pyrene	2 µg/mL

17.5. Flow diagrams

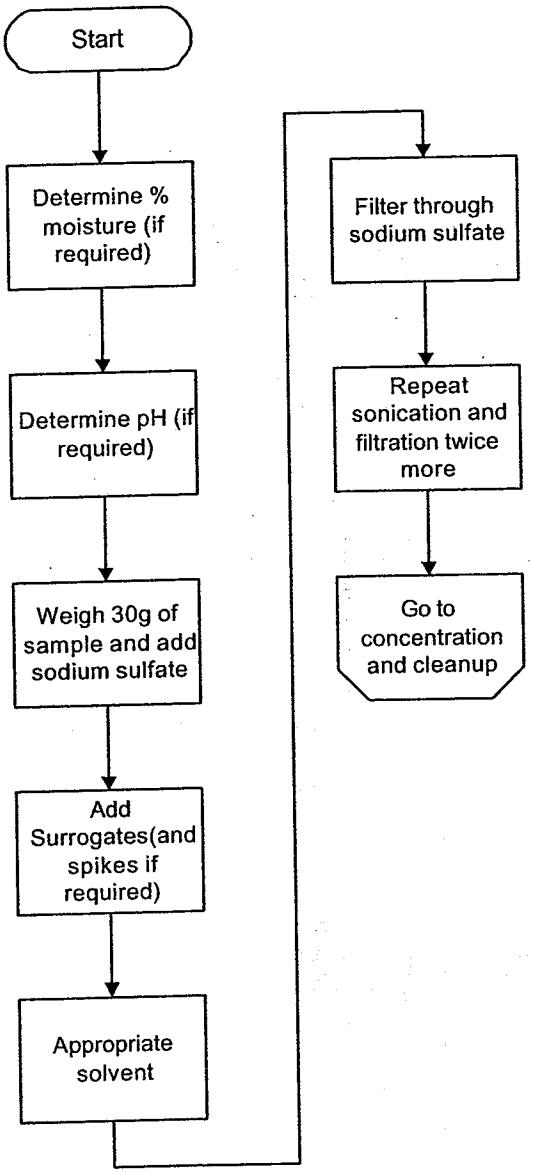
17.5.1. Separatory funnel extraction



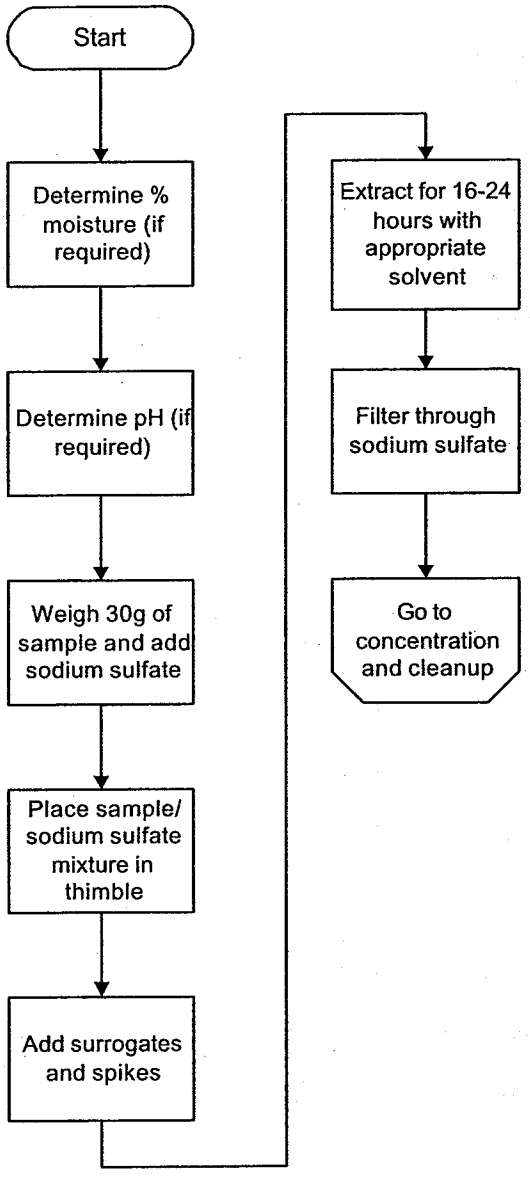
17.5.2. Continuous liquid/liquid extraction



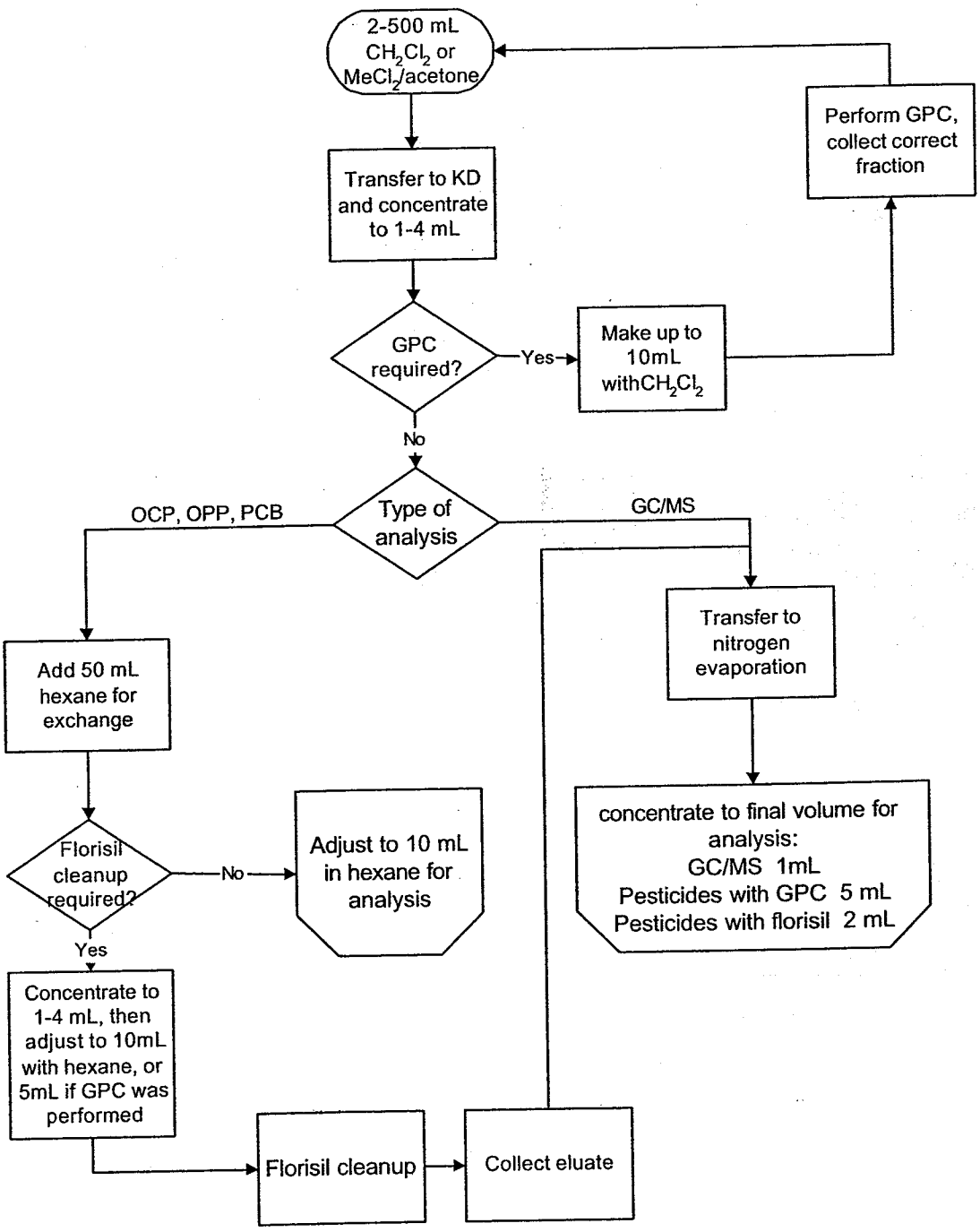
17.5.3. Sonication Extraction



17.5.4. Soxhlet extraction



17.5.5. Concentration and cleanup



18. SCOPE AND APPLICATION

This method is applicable to the extraction of chlorinated herbicides in waters, solids, oils, and TCLP extracts. Appropriate compounds for extraction by this method are listed in CORP-GC-0001, Appendix D, Gas Chromatography of Phenoxy Acid Herbicides based on Method 8151A.

19. SUMMARY OF METHOD

This method is based on SW846 method 8151A. Aqueous samples are hydrolyzed if esters and acids are to be determined, then washed with methylene chloride by a separatory funnel extraction. After acidifying the sample the free acids are extracted into diethyl ether. Solids are extracted into methylene chloride/ acetone by sonication. If esters and acids are to be determined, the extract is hydrolyzed and extracted into diethyl ether. For both soils and aqueous samples, the free acid herbicides in the ether extract are esterified. The final volume is adjusted to prepare the extract for gas chromatography.

20. DEFINITIONS

Refer to section 3 of the main body of this SOP.

21. INTERFERENCES

Refer to section 4 of the main body of this SOP.

22. SAFETY

22.1. Refer to section 5 of the main body this SOP for basic safety information.

22.2. DIAZOMETHANE is an extremely toxic gas with an explosion potential. Since the explosion potential is catalyzed by imperfections in glass, generation of diazomethane must be carried out in glassware free of scratches, cracks, chips and which does not have ground glass joints. Solutions of diazomethane will be kept at temperatures below 90°C. Diazomethane must be generated and handled in a fume hood.

22.3. Diethyl ether is extremely flammable. It also tends to form peroxides when exposed to air. The peroxides can present an explosion hazard, especially when the ether is concentrated.

22.4. Diethyl ether must be free of peroxides as demonstrated by EM (or equivalent) Quant test strips. This test can be done every time the ether is used or once per week if the bottle is marked with the test date(s).

22.5. Concentrated potassium hydroxide solution is highly caustic.

23. EQUIPMENT AND SUPPLIES

23.1. Refer to Section 6 of the main body of this SOP for basic extraction equipment and supplies. Additional equipment and supplies needed for this procedure are listed below.

23.2. Diazomethane generation apparatus

24. REAGENTS AND STANDARDS

24.1. Reagents are listed in Section 7 of the main body of this SOP. Additional reagents and standards needed for this procedure are listed below.

24.2. Reagents

24.2.1. Potassium hydroxide solution, 37% aqueous solution, (w/v): Dissolve 37 g of potassium hydroxide pellets in reagent water and dilute to 100 mL. **Caution:** Considerable heat will be generated. Other volumes of solution may be made up as convenient.

24.2.2. Toluene, reagent grade

24.2.3. 2-(2-Ethoxyethoxy)ethanol, trade name Carbitol, 98%+purity

24.2.4. Diazald, 99% purity

24.2.5. Sodium sulfate, Na_2SO_4, Anhydrous, granular, acidified: Heat sodium sulfate in a shallow tray at 400°C for a minimum of 4 hours to remove phthalates and other interfering organic substances. In a large beaker, acidify by slurrying 500 g sodium sulfate with just enough diethyl ether to cover. Add 20 mL of concentrated sulfuric acid and mix thoroughly. Place the mixture on a steam bath in a hood to evaporate the ether, or allow the ether to evaporate overnight. Larger or smaller batches of acidified sodium sulfate may be prepared using the reagents in the same proportions.

24.2.6. Sodium Chloride, NaCl

24.2.7. BF3-Methanol, Boron trifluoride-MeOH, lab use only

24.2.8. Diethyl ether, reagent grade.

24.2.9. Methanol, reagent grade.

24.2.10. Silica gel

24.2.11. 2% methanolic KOH, semi-conductor grade

24.3. Standards

24.3.1. Surrogate Standard
See Table A3.

24.3.2. Matrix Spike and LCS standard
See Table A4.

25. SAMPLE COLLECTION PRESERVATION AND STORAGE

25.1. Sample collection and storage is described in Section 8 of the main body of this SOP.

26. QUALITY CONTROL

26.1. Refer to Section 9 of the main body of this SOP for Quality control procedures.

27. CALIBRATION AND STANDARDIZATION

Not applicable

28. PROCEDURE

28.1. Preparation of Aqueous Samples

28.1.1. Weigh the sample bottle and pour approximately 500 ml (100 mL for TCLP leachates) into a 1 liter wide-mouth amber jar. Reweigh the bottle and record the sample volume on the benchsheet, assuming a density of 1.0. Alternatively, measure 500 ml in a graduated cylinder. If less than 500 mL was used, reagent water may be added to make the volume up to 500 mL.

Note: Aqueous samples must be determined volumetrically for Ohio VAP samples.

28.1.2. Spike each sample blank, LCS and MS with 1.0 mL of DCAA surrogate solution. Spike matrix spikes and LCS with 1 mL of herbicide matrix spiking solution. (Refer to tables A1 and A2)

28.1.3. Add 60-80 g of NaCl to the sample and shake to dissolve the salt.

28.1.4. Hydrolysis

Use this step only if herbicide esters in addition to herbicide acids are to be determined. This is normally the case. If the herbicide esters are not to be determined, omit this step and go to 28.1.10.

Add 3 mL of 10N NaOH to the sample, seal and shake. Check the pH of the sample with pH paper. If the pH of the sample is not $\geq$12 adjust to $\geq$12 by adding more NaOH. Let the sample sit at room temperature for 2 hours to complete the hydrolysis.

28.1.6. Add 300 mL of methylene chloride to the amber jar.

28.1.7. Prior to placing samples in tumbler, the samples should be shaken or rotated vigorously for 2 minutes, venting as necessary. Place the samples in tumbler and allow them to tumble for one (1) hour. Allow the organic layer to separate from the aqueous layer. If an emulsion layer greater than one third of the solvent layer forms, use mechanical techniques to complete the phase separation. Suggested techniques are stirring, filtration through glass wool and centrifugation.

28.1.8. Pour contents of amber jar into a pre-rinsed teflon sep funnel.

28.1.9. Discard the **methylene chloride** phase.

28.1.10. Add 6 mL of cold (4°C) 1:1 sulfuric acid to the sample. Seal, and shake to mix. Check the pH of the sample with pH paper. If the pH is not $\leq$ 2, and more acid to adjust the pH to $\leq$ 2.

Caution: Addition of acid may cause heat and / or pressure build up.

28.1.11. Add 100 mL diethyl ether to the sample and extract by shaking or rotating vigorously for 10 minutes, venting as necessary. Allow the organic layer to separate from the aqueous layer. If an emulsion layer greater than one third of the solvent layer forms, use mechanical techniques to complete the phase separation. Suggested techniques are stirring, filtration through glass wool and centrifugation.

28.1.12. Drain the aqueous layer into a clean flask or beaker. Collect the ether phase in a clean flask or bottle containing approximately 10g of acidified anhydrous sodium sulfate.

28.1.13. Return the aqueous phase to the separatory funnel, add 100 mL diethyl ether and repeat the extraction procedure a second time, combining the ether extracts. Repeat the extraction a third time with 100 mL diethyl ether. Discard the aqueous phase after the third extraction.

28.1.14. Allow the extract to remain in contact with the sodium sulfate for at least 2 hours, shaking periodically. (May be left overnight). The drying step is critical: if the sodium sulfate solidifies in a cake, add a few additional grams of acidified sodium sulfate. The amount of sodium sulfate is sufficient if some free flowing crystals are visible when the flask or bottle is swirled or shaken.

28.1.15. Proceed to section 28.5, concentration.

28.2. Extraction of soil and sediment samples

28.2.1. Decant and discard any water layer on a sediment/soil sample. Record and document if a water layer was discarded on the benchsheet. Homogenize the sample by mixing it thoroughly in the container. If this is not possible place the sample in clean beaker and homogenize. Upon completion of homogenization in beaker return sample to original container. Discard foreign objects such as sticks, leaves and rocks, unless extraction of this material is required by client. If the sample consists primarily of foreign materials consult with the client (via the Project Manager or Administrator).

28.2.2. Weigh 50.0 g of moist solid sample into a clean glass jar. Use 50 g of sodium sulfate for the Method Blank and the LCS. Acidify the sample with 5 mL of concentrated HCl.

28.2.3. There should be a small amount of liquid phase. If not, add reagent water until there is. Stir well with a spatula. (Note: This is not necessary for the method blank or LCS)

28.2.4. After 15 minutes, stir with a spatula and check the pH of the liquid phase. Add more acid if necessary to bring the pH to <2, repeating the stirring and standing time after each acid addition. (Note: The pH of the method blank and LCS are not determined.)

28.2.5. Add 60 g of acidified sodium sulfate and mix well. The sample should be free flowing. If not, add more sodium sulfate.

28.2.6. Spike each sample blank, LCS and MS with 1.0 mL of DCAA surrogate solution. Spike matrix spikes and LCS with 1 mL of herbicide matrix spiking solution. (Refer to tables A1 and A2)

28.2.7. Add a minimum of 100 mL of 1:1 methylene chloride:acetone to the beaker or 100 mL of methylene chloride for long list (dinoseb).

28.2.8. Place the bottom surface of the appropriate disrupter horn tip approximately ½ inch below the surface of the solvent, but above the sediment layer.

28.2.9. Sonicate for 3 minutes, making sure the entire sample is agitated.

28.2.10. Loosely plug the stem of a 75 mm x 75 mm glass funnel with glass wool and/or line the funnel with filter paper. Add 10-20 g of anhydrous sodium sulfate to the funnel cup.

28.2.11. Place the prepared funnel on a collection apparatus. If the herbicide esters are *not* to be determined, the collection apparatus is a bottle or flask containing approximately 10g of anhydrous acidified sodium sulfate. If the herbicide esters *are* to be determined, (normally the case) the collection apparatus is glassware suitable for the hydrolysis step, typically a KD flask or Turbovap tube.

28.2.12. Decant and filter extracts through the prepared funnel into the collection apparatus.

28.2.13. Repeat the extraction two more times with additional 100 mL minimum portions of the appropriate solvent each time. Decant off extraction solvent after each sonication. On the final sonication pour the entire sample (sediment and solvent) into the funnel and rinse with an additional 10 mL-20 mL of the methylene chloride/acetone.

Note: Alternatively, the three extracts may be collected together and then filtered through the sodium sulfate.

28.2.14. If the herbicide esters are not to be determined, dry the extract as described in 28.4 or go to cleanup, section 28.3. If the herbicide esters are to be determined (normally the case) proceed to section 28.2.15

28.2.15. Add 5 mL of 37% aqueous potassium hydroxide and 30 mL of water to the extract. Check the pH with pH paper. If the pH is not $\geq$12, adjust with additional KOH.

28.2.16. Heat on a water bath at 60-65°C for 2 hours. Allow to cool. Higher temperatures, up to 90°C, may be used if needed to remove the ether layer within 2 hours.

28.2.17. Transfer the solution to a separatory funnel and extract three times with 100 mL portions of methylene chloride. **Discard the methylene chloride phase.** The aqueous solution contains the herbicides.

28.2.18. Adjust the pH of the solution to ≤2 with 1:1 sulfuric acid.

28.2.19. Extract three times with 60 mL diethyl ether.

28.2.20. Proceed to section 28.3, Cleanup, if required, or Section 28.4, Extract drying.

28.3. Cleanup

This cleanup step may be necessary if the procedure for determining the herbicide acids only is being followed. (See section 28.2.14) It is not normally required if the acids and esters are being determined. (The usual case.) If cleanup is not required, proceed to section 28.4, Extract drying.

28.3.1. Prepare 45 mL of basic extraction fluid by mixing 30 mL of reagent water with 15 mL of 37% KOH. Use three 15 mL portions of this fluid to partition the extract from section 28.2.12 or 28.2.20, using a small separatory funnel. **Discard the organic phase.**

28.3.2. Adjust the pH of the solution to ≤2 with cold (4°C) sulfuric acid. (1:1). Extract once with 40 mL diethyl ether and twice with 20 mL diethyl ether.

Caution: Addition of acid may cause heat and / or pressure build up.

28.4. Extract drying

28.4.1. Pour the extracts through a funnel containing acidified sodium sulfate into a flask or bottle containing approximately 10 g acidified sodium sulfate. Rinse the funnel with a little extra diethyl ether.

28.4.2. Allow the extract to remain in contact with the sodium sulfate for at least 2 hours, shaking periodically. (May be left overnight). The drying step is critical: if the sodium sulfate solidifies in a cake, add a few additional grams of acidified sodium sulfate. The amount of sodium sulfate is sufficient if some free flowing crystals are visible when the flask or bottle is swirled or shaken. Proceed to section 28.5, concentration.

28.5. Concentration

28.5.1. Transfer the ether extract into a Turbovap concentrator tube or a 500 mL K-D flask equipped with a 10 mL concentrator tube. Use a stirring rod to crush the caked sodium sulfate during transfer. Rinse the flask or bottle with 20-30 mL ether to complete transfer.

28.5.2. Attach a three ball Snyder column to the K-D apparatus, prewet the column with a few mL of ether from the top, and place the apparatus on a water bath at approximately 60°C. At the proper rate of distillation, the balls of the column will chatter, but the chambers will not flood. When the apparent volume reaches 2 mL, remove from the water bath and allow to completely cool.

28.5.3. For TCLP extracts only, add 4 mL of toluene to the K-D (buffer reacts with diazald solution used in esterification).

28.5.4. Remove TCLP extracts at approximately 2 mL when boiling slows and only toluene is remaining. Cool and cap in CT.

28.5.5. Carefully disassemble the concentrator tube and rinse the lower glass joint with a small amount of diethyl ether.

28.5.6. The extract is now ready for esterification by the Diazomethane Bubbler Method (28.7) or the TCLP esterification by Boron Triflouride Method (28.8).

28.6. Esterification (Bubbler Method)

28.6.1. Assemble the diazomethane apparatus (see figure below) in a hood. Add 25-30 mL of diethyl ether to tube 1. Add 1.5 mL 37% KOH, 1 mL Carbitol, and 1 mL of ether and 3-4 g of diazald to tube 2.

28.6.2. Place the tip of the disposable pipette into the vial containing the first sample extract. Apply nitrogen flow (approx. 10 mL/min) to bubble diazomethane through the sample extract for about 4-5 minutes. Replace the disposable pipette and place the tip into the vial containing the second extract. Replace Tube 2 solution after second extract.

28.6.3. Allow the extracts to stand for 20 minutes, then add approximately 0.2 g of silica gel to each extract. Allow to stand for an additional 20 minutes.

28.6.4. Adjust the volume to 10 mL with hexane. The sample is now ready for gas chromatography.

28.6.5. 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.

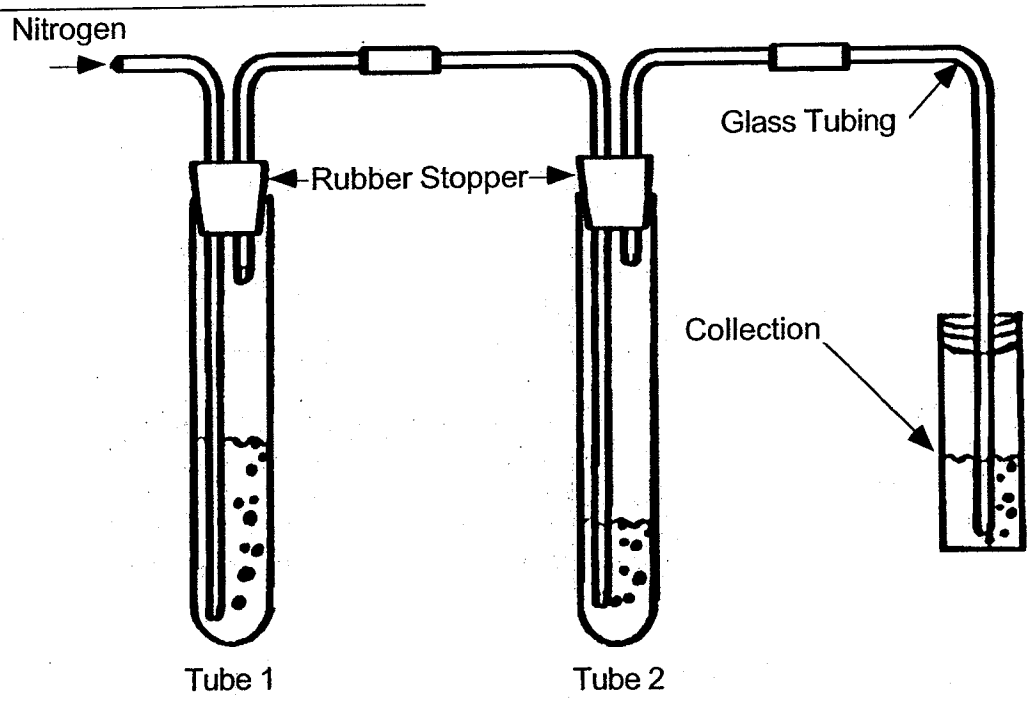
28.7. Exterification by Boron trifluoride (TCLP extracts only).

28.7.1. To the concentrator tube with the extract, add 2 mL of Boron trifluoride. Place a two-ball micro-Snyder column on the concentrator tube and place in the Hot-Blok water bath adjusted to 35-40°C for 60 minutes. Remove and let cool for approximately ten minutes.

28.7.2 With a 10 mL graduated disposable 5-3/4" pipette 4.5 mL of 5% neutral sodium sulfate and place it in the concentrator tube. Seal with a tight fitting ground glass stopper. Vortex the mixture for one minute. Let stand for ten minutes to settle. With a 5-3/4" disposable pipette, withdraw the bottom aqueous layer into a 16 x 100 culture tube for proper disposal.

28.7.3 Prepare a clean up column in a 5-3/4" disposable pipette by placing a small amount of glass wool in the narrow end of the pipette and add about ½ inch – 1 inch of florisil and sodium sulfate each. Leave about a 1 inch gap at the top. Place the extract in the clean-up column and gently force it through by using a pipette bulb into a small test tube. **Care should be taken to avoid channeling.** Rinse the concentrator tube with 1-2 mL of toluene. Transfer the column rinsate into the test tube. Rinse the column with additional toluene. There should be approximately 4 mL collected in the test tube. Bring the final volume to 10 mL with toluene by visually comparing it to a calibrated collection tube.

Note: It is critical that all toluene is retained and no water should enter the column.



29. DATA ANALYSIS AND CALCULATIONS

Not applicable

30. METHOD PERFORMANCE

Refer to CORP-GC-0001 for details of method performance.

31. POLLUTION PREVENTION

Refer to section 14 of the main body of this SOP.

32. WASTE MANAGEMENT

Refer to section 15 of the main body of this SOP.

33. REFERENCES

33.1. SW846, Test Methods for Evaluating Solid Waste, Third Edition, Update III, December 1996, Chlorinated Herbicides, Method 8151A.

34. MISCELLANEOUS

34.1. Modifications from Reference Method

34.1.1. Directions to add sufficient reagent water to the soil sample so that the pH can be measured have been added (Section 11.1.2)

34.1.2. The bubbler esterification method uses methanolic KOH in place of the aqueous KOH / carbitol mixture recommended in method 8150B. This has been found to provide a more effective and reliable esterification.

34.2. Modifications from previous revisions

References have been updated

34.3. Tables

Table A1
Herbicide Surrogate Spiking Solutions

Analyte Group	Surrogate Spike Solution ID	Volume (mL)
Herbicides	Herbicides Water	1.0
Herbicides	Herbicides Soil	1.0

Table A2
Herbicide Matrix Spike and LCS Solutions

Analyte Group	Matrix Spike Solution ID	Volume (mL)
Herbicides	Herbicides MS-Soil	1.0
Herbicides	Herbicides MS-Water	1.0

Table A3
Herbicide Surrogate Spike Components

Type	Compounds[1]	Solvent	Conc. (ug/mL)
Herbicides WS	2,4-DCAA	Acetone	2

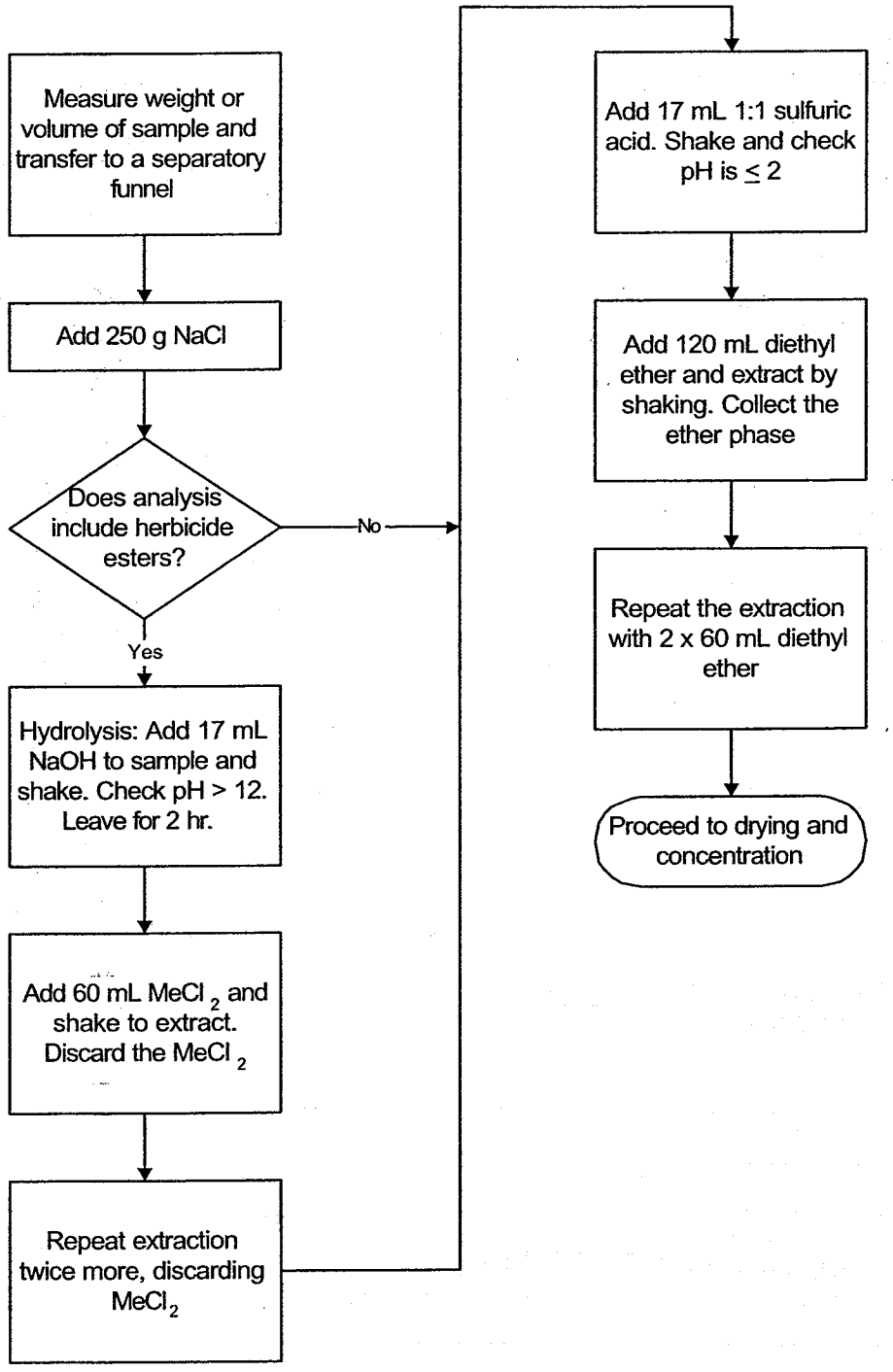
Table A3 Herbicide Surrogate Spike Components			
Type	Compounds[1]	Solvent	Conc. (ug/mL)
Herbicides SS	2,4-DCAA	Acetone Methanol	20

[1]The surrogate is spiked as the free acid

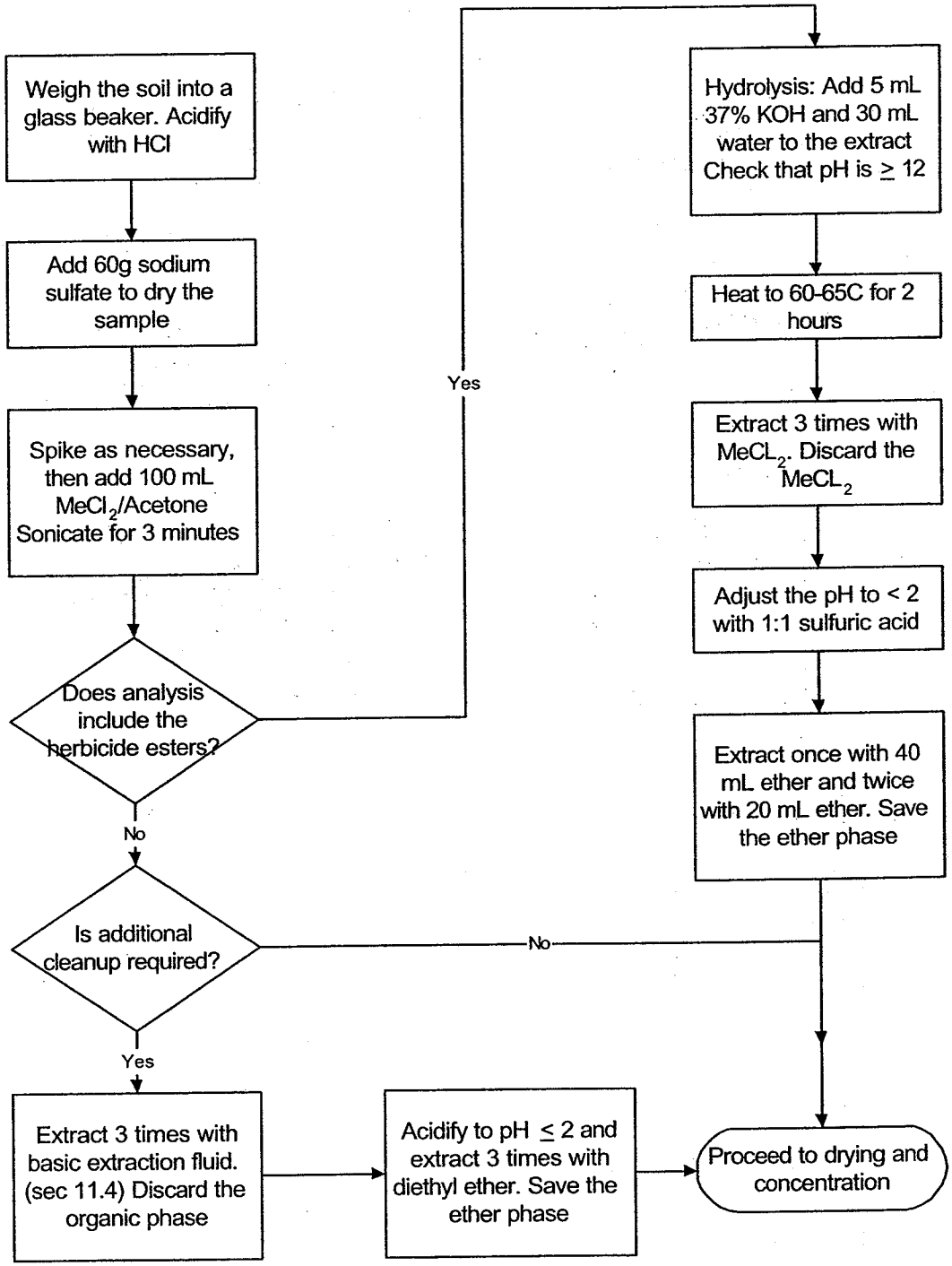
Table A4 Herbicide Matrix Spike Components				
Type	Compounds[1]	Compounds[1] Solvent	Soil Conc. (ug/mL) Solvent	Water Conc. (ug/mL)
Herbicides MS	2,4-D	Acetone	20 Methanol	2
	2,4-DB		20	2
	2,4,5-TP (Silvex)		5	0.5
	Dalapon		10	1
	Dicamba		10	1
	Dichloroprop		10	1
	Dinoseb		3	.3
	2,4,5-T		5	0.5

[1]The herbicide spiking solution contains the herbicides as the free acids.

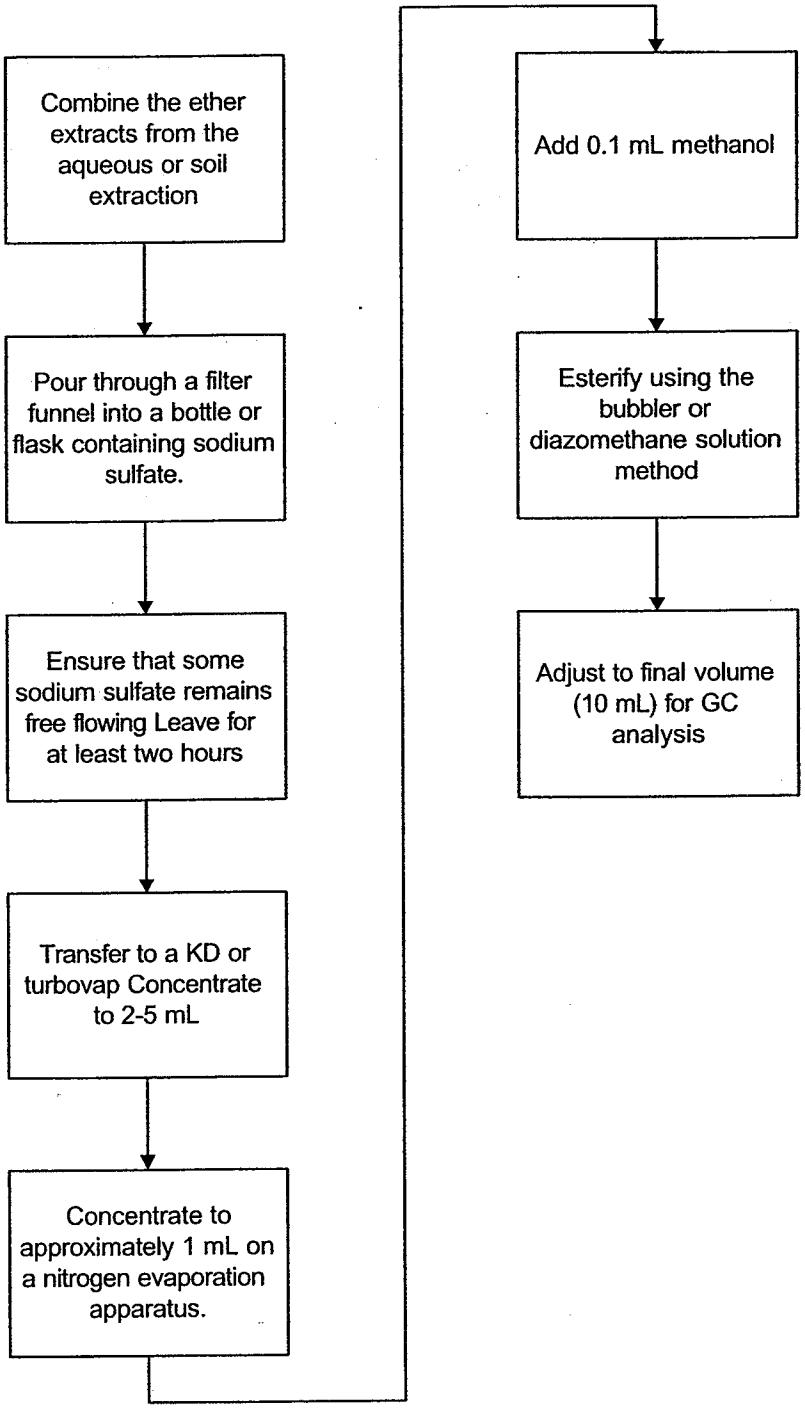
Extraction of Aqueous Samples



Extraction of Soils and Sediments



Drying, Concentration and Esterification



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Revision Date: 10/28/02
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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 2.3, DATED 05/15/01)

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

5.2. Eye protection that satisfies ANSI Z87.1 (as per the Chemical Hygiene Plan), laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

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

5.3.1. The following materials are known to be **corrosive:**

hydrochloric acid, nitric acid and sulfuric acid.

5.3.2. The following materials are known to be **oxidizing agents**:

nitric acid, potassium permanganate, potassium persulfate and magnesium perchlorate.

5.3.3. Mercury is a highly toxic element that must be handled with care. The analyst must be aware of the handling and clean-up techniques before working with mercury. Since mercury vapor is toxic, precaution must be taken to avoid its inhalation, ingestion or absorption through skin. All lines should be checked for leakage and the mercury vapor must be vented into a hood or passed through a mercury absorbing media such as:

5.3.3.1. Equal volumes of 0.1 M $KMnO_4$ and 10% H_2SO_4, or

5.3.3.2. Iodine, 0.25%, in a 3% KI solution.

5.3.4. Magnesium sulfate is known to be a reproductive toxin (mutagen).

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

5.5. 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 be 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 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 course porosity and Tygon tubing is used for the transfer of mercury vapor from the sample bottle to the absorption cell and return.

6.2.7. Drying device (a drying tube containing magnesium perchlorate or magnesium sulfate and/or a lamp with a 60 W bulb) to prevent condensation in cell. The lamp is positioned to shine on the absorption cell maintaining the air temperature in the cell about 10 °C above room temperature. Other drying devices that acheive the same purpose are also acceptable (i.e., Gortex filter).

Note: Instruments designed specifically for the measurement of mercury using the cold vapor technique may be substituted for the atomic absorption spectrophotometer.

6.3. BOD bottles or equivalent.

6.4. Nitrogen or argon gas supply, welding grade or equivalent.

6.5. Calibrated automatic pipettes or Class A glass volumetric pipettes.

6.6. Class A volumetric flasks.

6.7. Top-loading balance, capable of reading up to two decimal places.

6.8. Thermometer (capable of accurate readings at 95 °C).

6.9. Disposable cups or tubes.

7. REAGENTS AND STANDARDS

7.1. Reagent water must be produced by a Millipore DI system or equivalent. Reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks.

7.2. Stock (10 ppm) mercury standards (in 10% HNO_3) 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% HNO_3. This acid (150 uL of concentrated HNO_3) must be added to the flask/bottle before the addition of the stock standard aliquot.

7.4. 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° C ± 2° C until the time of analysis.

9. QUALITY CONTROL

Table II (Appendix A) provides a summary of quality control requirements including type, frequency, acceptance criteria and corrective action.

9.1. Initial Demonstration of Capability

Prior to the analysis of any analyte using 7471A or the 245.5, the following requirements must be met.

9.1.1. Method Detection Limit (MDL) - An MDL must be determined for each analyte/matrix prior to the analysis of any samples. The MDL is determined using seven replicates of reagent water, spiked with all the analytes of interest, that have been carried through the entire analytical procedure. MDLs must be redetermined on an annual basis in accordance with 40 CFR Part 136 Appendix B requirements. The spike level must be between the calculated MDL and 10X the MDL to be valid. The result of the MDL determination must be below the STL 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 < 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 repreparation and reanalysis of the batch. MS/MSD results which fall outside the control limits must be addressed in the narrative.
- If the native analyte concentration in the MS/MSD exceeds 4 times the spike level for that analyte, the recovery data are reported as NC (i.e., not calculated). If the reporting software does not have the ability to report NC then the actual recovery must be reported and narrated as follows: "Results outside of limits do not

necessarily reflect poor method performance in the matrix due to high analyte concentrations in the sample relative to the spike level."

- If an MS/MSD is not possible due to limited sample volume, then a laboratory control sample duplicate (LCSD) should be analyzed. The RPD of the LCS and LCSD must be compared to the matrix spike RPD limits.

9.7. Initial Calibration Verification (ICV/ICB) - Calibration accuracy is verified by analyzing a second source standard (ICV). The ICV result must fall within 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 repreparation 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 10mL 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% HNO_3 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:

$$\%R = 100\left(\frac{Found(ICV)}{True(ICV)}\right)$$

12.2. CCV percent recoveries are calculated according to the equation:

$$\%R = 100\left(\frac{Found(CCV)}{True(CCV)}\right)$$

12.3. Matrix spike recoveries are calculated according to the following equation:

$$\%\,R = 100\left(\frac{SSR - SR}{SA}\right)$$

Where:

SSR = Spike Sample Result
SR = Sample Result
SA = Spike Added

12.4. The relative percent difference (RPD) of matrix spike/matrix spike duplicates or sample duplicates are calculated according to the following equations:

$$RPD = 100\left[\frac{|MSD - MS|}{\left(\frac{MSD + MS}{2}\right)}\right]$$

Where:

MS = determined spiked sample concentration
MSD = determined matrix spike duplicate concentration

$$RPD = 100\left[\frac{|DU1 - DU2|}{\left(\frac{DU1 + DU2}{2}\right)}\right]$$

Where:

DU1 = Sample result
DU2 = Sample duplicate result

12.5. For automated determinations, the final concentration determined in solid samples when reported on a dry weight basis is calculated as follows:

$$mg/kg,\ dry\ weight = (C \times V \times D)/(W \times S)$$

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. Waste generated in the procedure must be segregated and disposed according to the facility hazardous waste procedures. The Environmental Health and Safety Director should be contacted if additional information is required.

16. REFERENCES

16.1. 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.

16.2. STL Laboratory Quality Manual (LQM), current version. 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 form 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

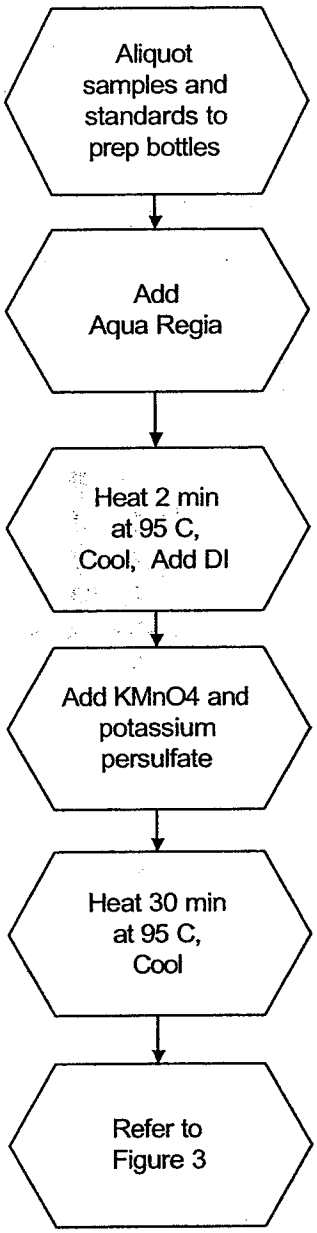
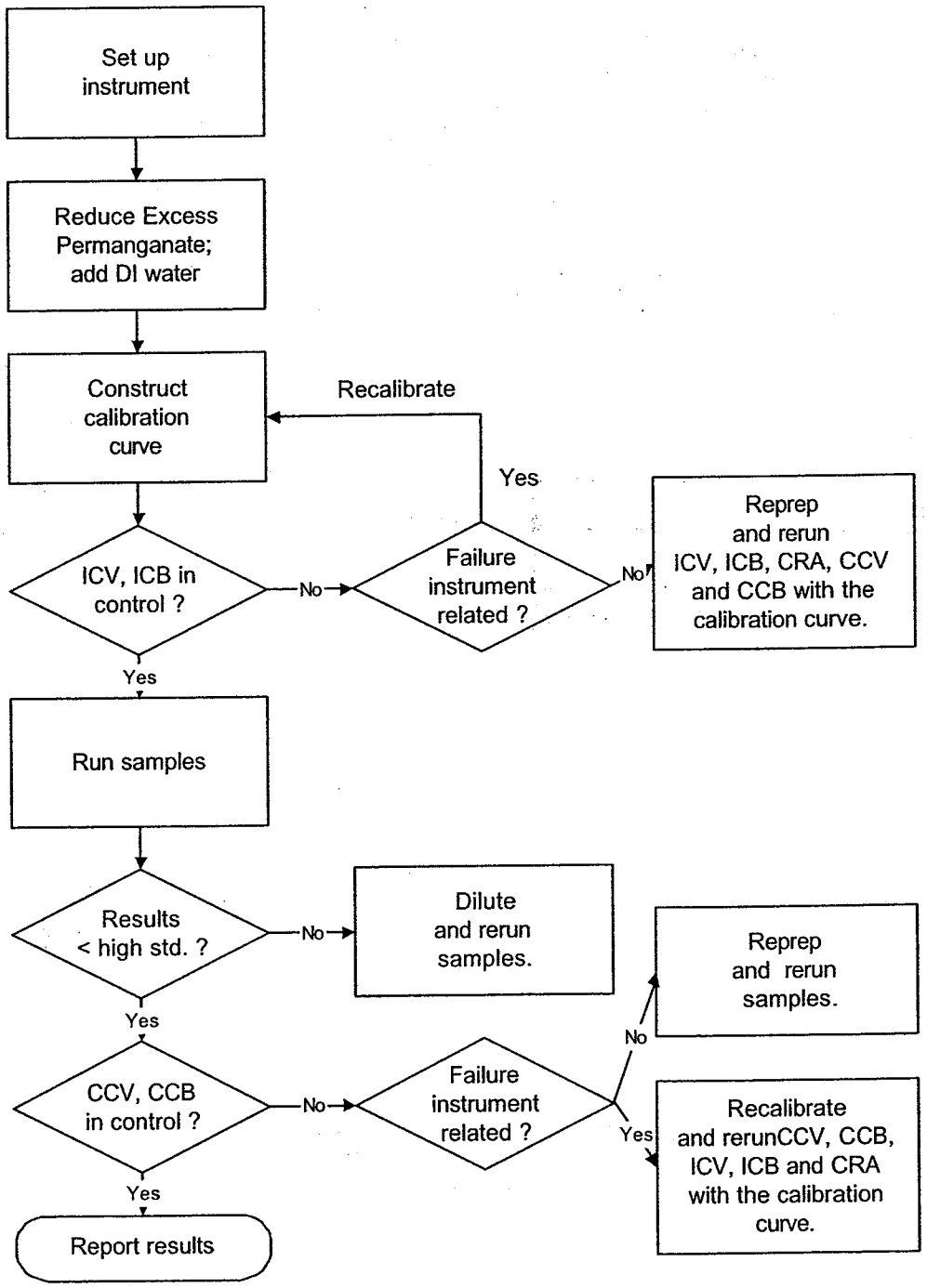


Figure 2. CVAA Mercury Analysis



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

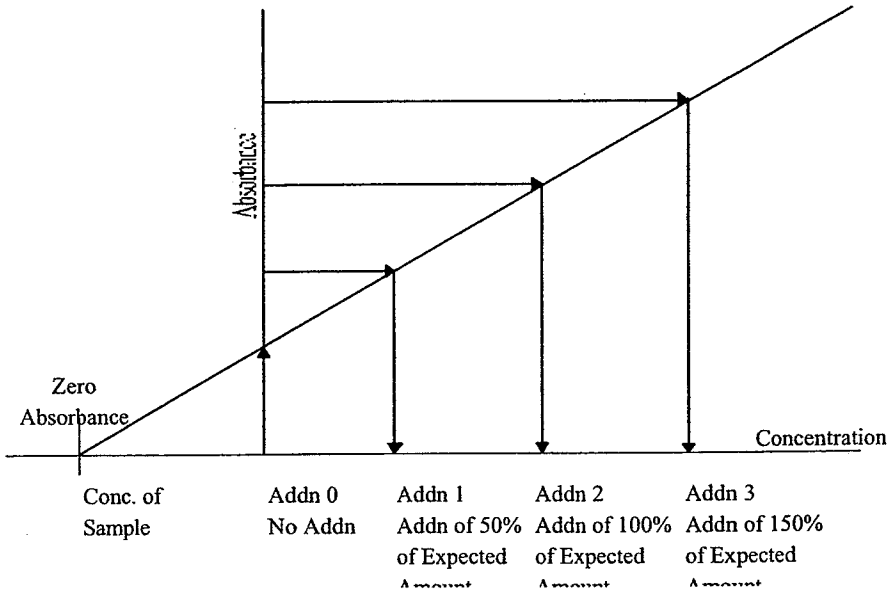
APPENDIX C. MSA GUIDANCE

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:_____

SOP No. CORP-MT-0001NC
Revision No. 3.3
Revision Date: 12/05/01

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 3.2, REVISION DATE 01/19/01)

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Date

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Approved by: _____ 12/10/01
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Approved by: _____ 12-6-01
Environmental, Health and Safety Coordinator 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. For instance, in comparison to conventional ICP technique, ICP-Trace can achieve detection levels comparable to those determined using the graphite furnace atomic absorption spectroscopy (GFAAS) technique.

1.3. Method 6010B is applicable to the determination of dissolved, suspended, total recoverable and total elements in ground water, aqueous samples, soils, sludges, wastes, sediments, and TCLP, EP and other leachates/extracts. All matrices require digestion prior to analysis with the exception of analyses for dissolved metals in filtered and acidified aqueous samples. Although digestion is not specifically required by the method, some clients and regulators may require digestion of **dissolved samples** and this must be clarified and documented before project initiation. Silver concentrations must be below 2.0 mg/L in aqueous samples and 100 mg/kg in solid matrix samples. Precipitation may occur in samples where silver concentrations exceed these levels and lead to the generation of erroneous data.

1.4. Method 200.7 is applicable to the determination of dissolved, suspended, total recoverable, and total elements in water, waste water, and solid wastes. All matrices require digestion prior to analysis with the exception of analyses for dissolved metals in filtered and acidified aqueous samples if the criteria in Section 11.1 are met. Silver concentrations must be below 0.1 mg/L in aqueous samples and 50 mg/kg in solid matrix samples.

1.5. State-specific requirements may take precedence over this SOP for drinking water sample analyses.

1.6. The applicable LIMS method codes are QO (6010B), QM (6010B Trace), AS (200.7), JI (200.7 Trace).

2. SUMMARY OF METHOD

2.1. This method describes a technique for the determination of multi elements in solution using sequential or simultaneous optical systems and axial or radial viewing of the plasma. The basis of the method is the measurement of atomic emission by an optical spectroscopic technique. Samples are nebulized and the aerosol that is produced is transported to the plasma torch where excitation occurs. Characteristic atomic-line emission spectra are produced by a radio frequency inductively coupled plasma (ICP). The spectra are dispersed by a grating spectrometer and the intensities of the emission lines are monitored by photomultiplier tubes. The photocurrents from the photomultiplier tubes are processed and controlled by a computer system. A background correction technique is required to compensate for variable background contribution to the determination of trace elements. Background must be measured adjacent to analyte lines during analysis. The position selected for the background intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used must be free of spectral interferences and reflect the same change in background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result. The possibility of additional interferences should also be recognized and appropriate actions taken. Alternatively, multivariate calibration methods may be chosen for which point selection for background correction is superfluous since whole spectral regions are processed.

2.2. Refer to the appropriate SOPs for details on sample preparation methods.

3. DEFINITIONS

3.1. Dissolved Metals: Those elements which pass through a 0.45 um membrane. (Sample is acidified 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. Procedures shall be carried out in a manner that protects the health and safety of all STL North Canton associates.

5.2. Eye protection that satisfies ANSI Z87.1 (as per the Chemical Hygiene Plan), laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.3. The health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the Material Safety Data Sheets (MSDS) maintained in the laboratory.

5.3.1. The following materials are known to be **corrosive**:

sulfuric acid, hydrochloric acid, nitric acid and hydrofluoric acid. (NOTE: sulfuric and hydrofluoric acids are used in cleaning the ICP torch and hydrofluoric acid is also commonly used in air toxics preparations.)

5.3.2. The following materials are known to be **oxidizing agents**:

nitric acid and hydrogen peroxide.

5.3.3. The plasma emits strong UV light and is harmful to vision. **NOTE: AVOID looking directly at the plasma.**

5.3.4. The RF generator produces strong radio frequency waves, most of which are unshielded. People with pacemakers should not go near the instrument while in operation.

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

5.5. 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. The use of hydrofluoric acid requires special safety precautions. Consult the facility EH&S Manager and laboratory supervisor for guidance.

6. EQUIPMENT AND SUPPLIES

6.1. Inductively Coupled Plasma Atomic Emission Spectrometer equipped with autosampler and background correction.

6.2. Radio Frequency Generator.

6.3. Argon gas supply, welding grade or equivalent.

6.4. Coolflow or appropriate water cooling device.

6.5. Peristaltic Pump.

6.6. Calibrated automatic pipettes or Class A glass volumetric pipettes.

6.7. Class A volumetric flasks.

6.8. Autosampler tubes.

7. REAGENTS AND STANDARDS

7.1. Intermediate standards are purchased as custom STL 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. An exception to this is in the event the Trace ICP is utilized without the internal standard. In this case, the standard acid matrix must be matched to the final preparation matrix as listed in Section 11.9.

7.3. Refer to Tables III, IV, IVA, V and VI (Appendix A) for details regarding the working standard concentrations for calibration, calibration verification, interference correction and spiking solutions.

7.4. Concentrated nitric acid (HNO_3), trace metal grade or better.

7.5. Concentrated hydrochloric acid (HCl), trace metal grade or better.

7.6. Reagent water must be produced by a Millipore DI system or equivalent. Reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Sample holding times for metals are six months from time of collection to the time of analysis.

8.2. Aqueous samples are preserved with nitric acid to a pH of <2 and may be stored in either plastic or glass. If boron or silica are to be determined, plastic containers are preferred. Refrigeration is not required. Preservation must be verified prior to analysis.

8.3. Soil samples do not require preservation but must be stored at 4°C ± 2° until the time of preparation .

9. QUALITY CONTROL

Table VII (Appendix A) provides a summary of quality control requirements including type, frequency, acceptance criteria and corrective action.

9.1. Initial Demonstration of Capability

Prior to analysis of any analyte using either Method 200.7 or Method 6010B, the following requirements must be met.

Instrument Detection Limit (IDL) - The IDL for each analyte must be determined for each analyte wavelength used least each instrument. The IDL must be determined annually. If the instrument is adjusted in anyway that may affect the IDL, the IDL for that instrument must be redetermined. The IDL shall be determined by multiplying by 3, the standard deviation obtained from the analysis of a standard solution (each analyte in reagent water) at a concentration 3x - 5x the previously determined IDL, with seven consecutive measurements. Each measurement must be performed as though it were a separate analytical sample (i.e., each measurement must be followed by a rinse and/or any other procedure performed between the analysis of separate samples). The result of the IDL determination must be below the STL North Canton reporting limit. The CLP IDL procedure can be used for this method.

9.1.1. 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.

9.1.2. Linear Range Verification (LR) - The linear range must be determined 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.

9.1.3. Background Correction Points - To determine the appropriate location for off-line background correction when establishing methods, the user must scan the area on either side adjacent to the wavelength and record the apparent emission intensity from all other method analytes. This spectral information must be documented and kept on file. The location selected for background correction must be either free of off-line interelement spectral interference or a computer routine must be used for automatic correction on all determinations. Tests to determine spectral interference must be done using analyte concentrations that will adequately describe the interference. Background correction points must be set prior to determining IECs. Refer to the facility-specific instrument

operation SOP and ICP instrument manual for specific procedures to be used in setting background correction points.

9.1.4. Inter-element Corrections (IECs) - ICP interelement correction factors must be determined prior to the analysis of samples and every six months thereafter. If the instrument is adjusted in any way that may affect the IECs, the IECs must be redetermined. When initially determining IECs for an instrument, wavelength scans must be performed to ensure that solutions in use are free from contaminants. If an IEC varies significantly from the previously determined IEC then the possibility of contamination should be investigated. The purity of the IEC check solution can be verified by using a standard from a second source or an alternate method (i.e., GFAA or ICP-MS). Published wavelength tables (e.g. MIT tables, Inductively Coupled Plasma-Atomic Spectroscopy: Prominent Lines) can also be consulted to evaluate the validity of the IECs. Refer to the facility specific instrument operation SOP and instrument manufacturer's recommendations for specific procedures to be used in setting IECs. An IEC must be established to compensate for any interelement interference which results in a false analyte signal greater than ± the RL as defined in Tables I, IA or II. To determine IECs, run a single element standard at the established linear range. To calculate an IEC, divide the observed concentration of the analyte by the 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.

9.1.5. 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 9.1.3) should be aspirated as a regular sample followed by the analysis of a series of rinse blanks. The length of time required to reduce the analyte signals to < RL will define the rinse time for a particular ICP system. For some analytes it may be impractical to set the rinse time based on the linear range standard result (i.e., analyte not typically detected in environmental samples at that level and an excessive rinse time would be required at the linear range level). Until the required rinse time is established, the method recommends a rinse period of at least 60 seconds between samples and standards. If a memory effect is suspected, the sample must be reanalyzed after a rinse period of sufficient length. Rinse time studies can be conducted at additional concentration levels. These additional studies must be documented and kept on file, if a concentration other than the linear range level is used to set the rinse time. The

concentration levels used to establish the rinse time must be taken into consideration when reviewing the data.

9.2. Method Blank (MB) - One method blank must be processed with each preparation batch. The method blank consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The method blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. The method blank should not contain any analyte of interest at or above the reporting limit (exception: common laboratory contaminants, see below) or at or above 5% of the measured concentration of that analyte in associated samples, whichever is higher (sample result must be a minimum of 20x higher than the blank contamination level).

- If the analyte is a common laboratory contaminant (copper, iron, lead (Trace only) or zinc) the data may be reported with qualifiers if the concentration of the analyte in the method blank is less than two times the RL. **Such action must be taken in consultation with the client and must be addressed in the project narrative.**
- Repreparation and reanalysis of all samples associated with an unacceptable method blank is required when reportable concentrations are determined in the samples (see exception noted above).
- If there is no analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. **Such action must be taken in consultation with the client and must be addressed in the project narrative.**
- If the above criteria are not met and reanalysis is not possible, then the sample data must be qualified. **This anomaly must be addressed in the project narrative and the client must be notified.**
- For dissolved metals samples which have not been digested, a CCB result is reported as the method blank. The CCB run immediately prior to the start of the dissolved sample analyses must be used for this purpose. No more than 20 samples can be associated with one CCB.

9.3. Laboratory Control Sample (LCS) - One aqueous LCS must be processed with each preparation batch. The LCS must contain all analytes of interest and must be carried through the entire analytical procedure. Aqueous LCS spike levels are provided in Table III (Appendix A). The LCS is used to monitor the accuracy of the analytical process. On-going monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines.

- If any analyte is outside established control limits the system is out of control and corrective action must occur. 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 taken in consultation with the client and must be addressed in the report narrative.**

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

- For dissolved metals samples which have not been digested, a CCV result is reported as the LCS. The CCV run immediately prior to the start of the dissolved sample analyses must be used for this purpose. No more than 20 samples can be associated with one CCV.

9.4. Matrix Spike/Matrix Spike Duplicate (MS/MSD) - One MS/MSD pair must be processed for each preparation batch. A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added. A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked identically as the MS) prepared and analyzed along with the sample and matrix spike. Some client specific data quality objectives (DQO's) may require the use of sample duplicates in place of or in addition to MS/MSDs. The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Due to the potential variability of the matrix of each sample, these results may have immediate bearing only on the specific sample spiked. Samples identified as field blanks cannot be used for MS/MSD analysis. Spiking levels are provided in Tables III and VI (Appendix A).

- If any analyte recovery or RPD falls outside the acceptance range, the recovery of that analyte must be in control for the LCS. For both methods 200.7 and 6010B, control limits of 75-125% recovery and 20% RPD or historical acceptance criteria must be applied to the MS/MSD. If the LCS recovery is within limits, then the laboratory operation is in control and the results may be accepted. If the recovery of the LCS is outside limits corrective action must be taken. Corrective action will include repreparation and reanalysis of the batch. MS/MSD results which fall outside the control limits must be addressed in the narrative.

- If the native analyte concentration in the MS/MSD exceeds 4x the spike level for that analyte, the recovery data are reported as NC, MSB (i.e., not calculated). If the reporting software does not have the ability to report NC, MSB 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." 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.

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 11.10 or 11.13 for required run sequence).

9.7. Continuing Calibration Verification (CCV/CCB) - Calibration accuracy is monitored throughout the analytical run through the analysis of a known standard after every 10 samples. The CCV is be a mid-range standard made from a dilution of the calibration standard. The CCV for both methods must fall within 10% of the true value for that

solution with relative standard deviation <5% from replicate (minimum of two) exposures. A CCB is analyzed immediately following each CCV. (See Section 11.10 or 11.13 for required run sequence.) The CCB result must fall within +/- RL from zero. If the blank is less than 1/10 the concentration of the action level of interest, and no sample is within 10% of the action limit, reanalysis and recalibration are not required before continuation of the run. Sample results may only be reported when bracketed by valid CCV/CCB pairs. If a mid-run CCV or CCB fails, the analysis for the affected element must be terminated, the problem corrected, the instrument recalibrated, the calibration verified and the affected samples reanalyzed. (Refer to Section 11.13 for an illustration of the appropriate rerun sequence).

9.8. Interference Check Analysis (ICSA/ICSAB) - The validity of the interelement correction factors is demonstrated through the successful analysis of interference check solutions. The ICSA contains only interfering elements, the ICSAB contains analytes and interferents. Refer to Table V (Appendix A) for the details of ICSA and ICSAB composition. Custom STL 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 interferents on a required analyte must be included in the ICP run when that analyte is determined. Aluminum, iron, calcium and magnesium must always be included in all ICP runs.

9.8.1. The ICSA and ICSAB solutions must be run at the beginning of the run. (See Section 11.10 or 11.13 for required run sequence.)

9.8.2. The ICSAB results for the interferents must fall within 80 - 120% of the true value. If any ICSAB interferent result fails criteria, the analysis should be terminated, the problem corrected, the instrument recalibrated and the samples rerun.

9.8.3. ICSA results for the non-interfering elements with reporting limits ≤ 10 ug/L must fall within the STL North Canton guidelines of ± 2x RL from zero. ICSA results for the non-interfering elements with RLs> 10 µg/L must fall within the STL North Canton guidelines of ± 1x RL from zero. If the ICSA results for the non-interfering elements do not fall within +/- 2x RL (RL ≤10) or ± 1xRL (RL>10) from zero the field sample data must be evaluated as follows:

- If the non-interfering element concentration in the ICSA is the result of contamination versus a spectral interference, and this reason is documented, the field sample data can be accepted.

- If the affected element was not required then the sample data can be accepted.
- If the interfering elements are not present in the field sample at a concentration which would result in a false positive or negative result greater than +/- 2x RL from zero then the field sample data can be accepted.
- If the interfering element is present in the field sample at a level which would result in a false analyte signal greater than ± 2x RL from zero, the data can be accepted only if the concentration of the affected analyte in the field sample is more than 10x the analyte signal in the ICSA.
- If the data does not meet the above conditions then the IECs must be re-evaluated and corrected if necessary and the affected samples reanalyzed or the sample results manually corrected through application of the new IEC to the raw results. If the results are recalculated manually the calculations must be clearly documented on the raw data.

9.9. 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.

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 D for specific MSA requirements.

9.11. Quality Assurance/Project Summaries - Certain clients may require project- or program-specific QC which may supersede this SOP requirements. Quality Assurance Summaries (QASs) or equivalent documents providing project-specific requirements should be developed so that project staff clearly understand the special project requirements.

10. CALIBRATION AND STANDARDIZATION

10.1. Set up the instrument with the operating parameters recommended by the manufacturer. Allow the instrument to become thermally stable before beginning calibration (approximately 30 minutes of warm-up is required).

10.2. Profile and calibrate the instrument according to the instrument manufacturer's recommended procedures. Flush the system with the calibration blank between each standard or as the manufacturer recommends. The calibration curve must consist of a minimum of a blank and a standard. Refer to the facility-specific instrument SOP or ICP instrument manual for a detailed set up and operation protocols.

10.3. Calibration must be performed daily and each time the instrument is set up. Instrument runs may be continued over periods exceeding 24 hours as long as all calibration verification (CCV) and interference check QC criteria are met. The instrument standardization date and time must be included in the raw data.

10.4. Refer to Section 9.0 for calibration verification procedures, acceptance criteria and corresponding corrective actions.

11. PROCEDURE

11.1. For 200.7 analyses, dissolved (preserved) samples must be digested unless it can be documented that the sample meets all of the following criteria:

A. Visibly transparent with a turbidity measurement of 1 NTU or less.

B. Is of one liquid phase and free of particulate or suspended matter following acidification.

C. Is NOT being analyzed for silver.

11.2. A minimum of <u>two exposures</u> for each standard, field sample and QC sample is required. The average of the exposures is reported. For Trace ICP analyses, the results of the sum channel must be used for reporting.

11.3. Prior to calibration and between each sample/standard the system is rinsed with the calibration blank solution. The minimum rinse time between analytical samples is 60 seconds unless following the protocol outlined in 9.1.6 it can be demonstrated that a shorter rinse time may be used. Triton-X can be added to the rinse solution to facilitate the rinse process.

11.4. The use of an autosampler for all runs is strongly recommended.

11.5. The use of automated QC checks through the instrument software is highly recommended for all calibration verification samples (ICV,CCV), blanks

(ICB,CCB,PB), interference checks (ICSA,ICSAB) and field samples (linear range) to improve the data review process.

11.6. To facilitate the early identification of QC failures and samples requiring rerun it is strongly recommended that sample data be reviewed periodically throughout the run.

11.7. To facilitate the data review and reporting processes it is strongly recommended that all necessary dilutions be performed before closing out the instrument run.

11.8. The use of an internal standard is recommended on the conventional, non-Trace ICPs as an alternative to using the method of standard additions. This technique is useful in overcoming matrix interferences especially in high solids matrices. However, for conventional ICP techniques, internal standards may not be necessary provided that one of the following is performed to minimize physical interferences: (1) peristaltic pump is used, (2) high solids nebulizer is used, or (3) high solids samples are diluted and reanalyzed.

11.9. 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:

11.9.1. Typically used internal standards are: yttrium or scandium. (Note: Any element can be used that is not typically found in environmental samples at a high rate of occurrence.)

11.9.2. 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.

11.9.3. 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.

11.9.4. The internal standard raw intensity counts must be printed on the raw data.

11.9.5. 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.

11.9.5.1. If the internal standard counts fall within ±30% of the counts observed in the ICB then the data is acceptable.

11.9.5.2. If the internal standard counts in the field samples are more than ±30% higher than the expected level, the field samples must then be:

(1) Diluted and reanalyzed;

(2) The IS concentrations must be raised; or

(3) A different internal standard must be used.

11.10. 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.

11.11. 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.

11.12. Full method required QC must be available for each wavelength used in determining reported analyte results.

11.13. 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 E 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.

12 DATA ANALYSIS AND CALCULATIONS

12.1 ICV percent recoveries are calculated according to the equation:

$$\%R = 100\left(\frac{Found(ICV)}{True(ICV)}\right)$$

12.2 CCV percent recoveries are calculated according to the equation:

$$\%R = 100\left(\frac{Found(CCV)}{True(CCV)}\right)$$

12.3 Matrix Spike Recoveries are calculated according to the following equation:

$$\%R = 100\left(\frac{SSR - SR}{SA}\right)$$

Where:
SSR = Spike Sample Result
SR = Sample Result
SA = Spike Added

12.4 The relative percent difference (RPD) of matrix spike/matrix spike duplicates are calculated according to the following equations:

$$RPD = 100\left[\frac{|MSD - MS|}{\left(\frac{MSD + MS}{2}\right)}\right]$$

Where:
MS = determined spiked sample concentration
MSD = determined matrix spike duplicate concentration

12.5 The final concentration for a digested aqueous sample is calculated as follows:

$$mg/L = \frac{C \times V1 \times D}{V2}$$

Where:
C = Concentration (mg/L) from instrument readout
D = Instrument dilution factor
V1 = Final volume in liters after sample preparation
V2 = Initial volume of sample digested in liters

12.6 The final concentration determined in digested solid samples when reported on a dry weight basis is calculated as follows:

$$mg/Kg, dry\,weight = \frac{C \times V \times D}{W \times S}$$

Where:
C = Concentration (mg/L) from instrument readout
D = Instrument dilution factor
V = Final volume in liters after sample preparation
W = Weight in Kg of wet sample digested
S = Percent solids/100

Note: A Percent Solids determination must be performed on a separate aliquot when dry weight concentrations are to be reported. If the results are to be reported on wet weight basis the "S" factor should be omitted from the above equation.

12.7 The LCS percent recovery is calculated according to the following equation:

$$\%R = 100\left(\frac{Found(LCS)}{True(LCS)}\right)$$

12.8 The dilution test percent difference for each component is calculated as follows:

$$\%Difference = \frac{|I - S|}{I} \times 100$$

Where:
I = Sample result (Instrument reading)
S = Dilution test result (Instrument reading × 5)

12.9 Appropriate factors must be applied to sample values if dilutions are performed.

12.10 Sample results should be reported with up to three significant figures in accordance with the STL 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 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:

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

14 POLLUTION PREVENTION

14.1 This method does not contain any specific modifications that serve to minimize or prevent pollution.

15 WASTE MANAGEMENT

15.1 Waste generated in the procedure must be segregated and disposed of according to the facility hazardous waste procedures and per the local, state, and federal regulations. The Environmental Health and Safety Director should be contacted, if additional information is required.

15.2 Standards should be purchased and prepared in volumes consistent with laboratory use to minimize the volume of expired standards to be disposed.

16 REFERENCES

16.1 40 CFR Part 136, Appendix B, 7-5-95, Determination of Method Detection Limits.

16.2 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition, Final Update III, Revision 2, December 1996. Method 6010B.

16.3 Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma-Atomic Emission Spectrometry, Revision 4.4, May 1994. Method 200.7.

16.4 CORP-MT-0002NC, Inductively Coupled Plasma-Atomic Emission Spectroscopy, Method 200.7 & CLP-M, SOW ILMO3.0 and ILMO4.0).

16.5 QA-003, STL North Canton QC Program.

16.6 QA-004, Rounding and Significant Figures.

16.7 QA-005, Method Detection Limits.

17 MISCELLANEOUS (TABLES, APPENDICES, ETC.)

17.1 Modifications/Interpretations from reference method

17.1.1 Modifications/interpretations from both Methods 6010B and 200.7.

17.1.1.1 STL 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 LABS, 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 CLP IDL definition as defined in Section 9.1.1 of this SOP.

17.1.2.2 The calibration blank is prepared in an acid matrix of 5% HNO_3/5% HCl instead of the specified 2% HNO_3/10% HCl matrix as the former matrix provides for improved performance relative to the wide variety of digestate acid matrices which result from the various EPA preparation protocols applied.

17.1.2.3 Method section 9.3.4 specifies that "Analysis of the IPC (ICSA/AB) solution immediately following calibration must verify that the instrument is within ± 5% of calibration with a relative standard deviation <3% from replicate integrations ≥ 4." STL North Canton uses a minimum of two exposures.

17.1.2.4 Section 7.12 of 200.7 indicates that the QCS (ICV) should be prepared at a concentration near 1 ppm. The ICV specified in this SOP accommodates the 1 ppm criteria for the majority of analytes. For the remaining analytes, this SOP specifies ICV concentrations which are appropriate to the range of calibration. The intent of the ICV, verification of calibration standard accuracy, is independent of the ICV concentration used.

17.1.2.5 The ICS criteria applied by this SOP differ from those stated in the method. Method 200.7 section 10.4 states that results should fall within the established control limits of 3 times the standard deviation of the calibration blank for that analyte. The control limits listed in this SOP are those applicable to the EPA designed solution.

17.1.2.6 Method 200.7 section 9.3.4 states the CCB should be less than the IDL, but > the lower 3-sigma control limit of the calibration blank. The intent of this requirement is to ensure that the calibration is not drifting at the low end. STL 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.

17.2 Modifications from previous SOP

Refer to revision 2 of this SOP.

17.3 Facility-Specific SOPs

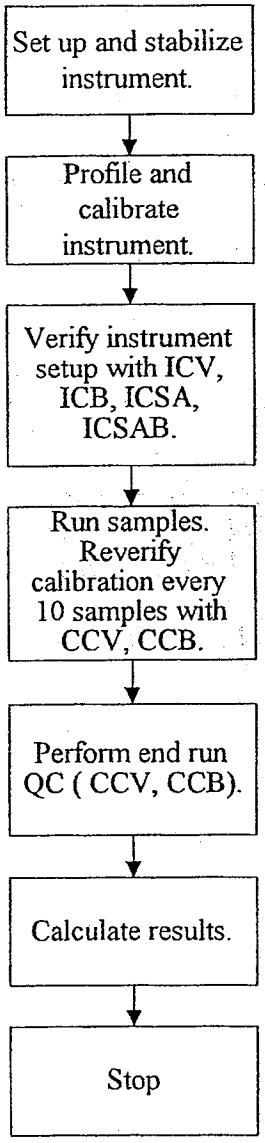
Each facility shall review and revise as appropriate this SOP to reflect any facility-specific requirements. If no facility-specific amendments are required, the SOP can be adopted as is.

17.4 Documentation and Record Management

The following documentation comprises a complete ICP raw data package:

- Raw data (direct instrument printout).
- Relevant sample preparation benchsheets.
- Run log printout from instrument software where this option is available (TJA) or manually generated run log (i.e., Ward WSL printout).
- Data review checklist - See Appendix B.
- Standards documentation (including prep and expiration dates, source, and lot #).
- Nonconformance/anomaly documentation (if applicable).

17.5 Flow Diagram



APPENDIX A

TABLES

TABLE I. Method 200.7 and 6010B Target Analyte List

ELEMENT	Symbol	CAS #	6010B analyte	200.7 analyte	Reporting Limit (ug/L) Water	Reporting Limit (mg/kg) Soil
Aluminum	Al	7429-90-5	X	X	200	20
Antimony	Sb	7440-36-0	X	X	60	6
Arsenic	As	7440-38-2	X	X	300	30
Barium	Ba	7440-39-3	X	X	200	20
Beryllium	Be	7440-41-7	X	X	5.0	0.5
Boron	B	7440-42-8		X	200	20
Cadmium	Cd	7440-43-9	X	X	5.0	0.5
Calcium	Ca	7440-70-2	X	X	5000	500
Chromium	Cr	7440-47-3	X	X	10	1
Cobalt	Co	7440-48-4	X	X	50	5
Copper	Cu	7440-50-8	X	X	25	2.5
Iron	Fe	7439-89-6	X	X	100	10
Lead	Pb	7439-92-1	X	X	100	10
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 after consultation with the client (See 9.2). Sample results greater than 10x the blank concentration are acceptable. Samples for which the contaminant is < RL may not require redigestion or reanalysis (see Section 9.2).	Redigest and reanalyze samples. Note exceptions under criteria section. See Section 9.2 for additional requirements.
Laboratory Control Sample (LCS)	One per sample preparation batch of up to 20 samples.	Aqueous LCS must be within 80 - 120% recovery or in-house control limits. 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

STL NORTH CANTON ICP DATA REVIEW CHECKLIST

(EXAMPLE)

SCAL STD_____ ICSA STD_____ SCAL2 STD_____ ICSAB STD_____

CRI STD_____ ICV STD_____ CLP CRI STD_____ CCV STD_____

(Example)

STL North Canton ICP Data Review Checklist

Run/Project Information:

Run Date: _____ **Analyst:**_____ **Instrument:**_____

Prep Batches Run:_____

Cu/MnRatio:_____

Circle Methods used: **6010B / 200.7: CORP-MT-0001 Rev 2 CLP ILM03.0: CORP-MT-0002 Rev 1**

6010A/200.7: CORP-MT-0001NC, Rev 2

Review Items

A. Calibration/Instrument Run QC	Yes	No	N/A	2nd Level
1. Instrument calibrated per manufacturer's instructions and at SOP specified levels ?				
2. ICV/CCV analyzed at appropriate frequency and within control limits ? *(ICV:* 6010B, CLP = 90 - 110%, 200.7 = 95 -105%) *(CCV: 90 - 110%)*				
3. ICB/CCB analyzed at appropriate frequency and within +/- RL or +/- CRDL (CLP) ?				
4. High Std. (HCAL) reanalyzed before samples and recovered within QC limits ? (6010A/200.7 95-105%, CLP- N/A)				
5. CRI run and recovered within QC limits ? (+/- 50% for non-CLP - 6010A only)				
6. ICSA/ICSAB run at required frequency and within SOP limits ?				
B. Sample Results				
1. Were samples with concentrations > the linear range for any parameter diluted and reanalyzed ?				
2. All reported results bracketed by in control QC ?				
3. Sample analyses done within holding time ?				
C. Preparation/Matrix QC				
1. LCS done per prep batch and within QC limits ?				
2. Method blank done per prep batch and < RL or CRDL (CLP) ?				

3. MS/MSD run at required frequency and within limits ?				
4. MSD or DU run at required frequency and RPD within SOP limits ?				
5. Serial dilution done per prep batch (or per SDG for CLP) ?				
6. Post digest spike analyzed if required (CLP only) ?				
D. Other				
1. Are all nonconformances documented appropriately ?				
2. Current IDL/LR/IEC data on file ?				
3. Calculations checked for error ?				
4. Transcriptions checked for error ?				
5. All client/project specific requirements met ?				
6. Date/time of analysis verified as correct ?				

Level I Analyst:_____ **Date:**_____ **Time:**_____

Comments:_____

Level II Reviewer:_____ **Date:**_____ **Time:**_____

APPENDIX C

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 D

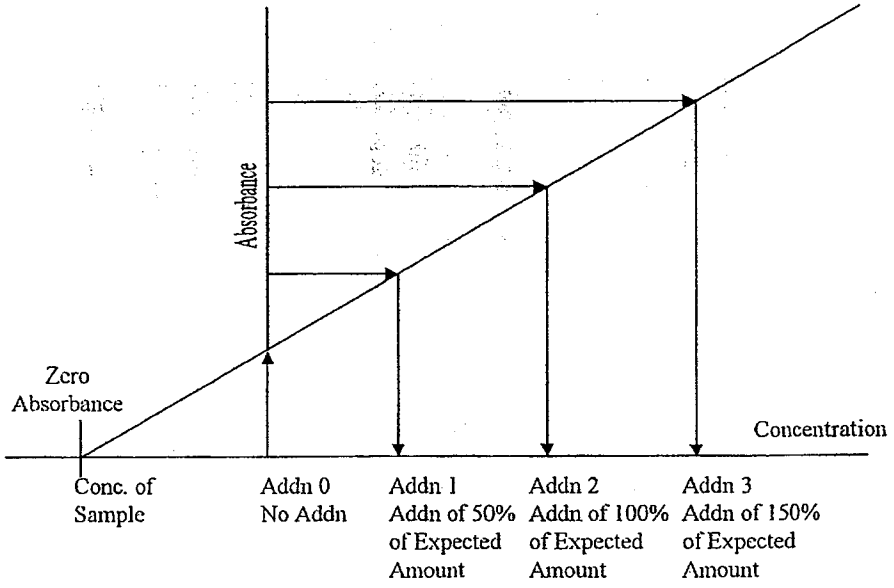
MSA GUIDANCE

Appendix D. MSA Guidance

Method of Standard Addition

Four equal volume aliquots of sample are measured and known amounts of standards are added to three aliquots. The fourth aliquot is the unknown and no standard is added to it. The concentration of standard added to the first aliquot should be 50% of the expected concentration. The concentration of standard added to the second aliquot should be 100% of the expected concentration and the concentration of standard added to the third aliquot should be 150% of the expected concentration. The volume of the unspiked and spiked standard should be the same.

In order to determine the concentration of analyte in the sample, the analytical value of each solution is determined and a plot or linear regression performed. On the vertical axis the analytical value is plotted versus the concentrations of the standards on the horizontal axis. An example plot is shown in Figure 1. When the resulting line is extrapolated back to zero absorbance, the point of interception of the horizontal axis is the concentration of the unknown.



For the method of standard additions to be correctly applied, the following limitations must be taken into consideration:

- The plot of the sample and standards must be linear over the concentration range of concern. For best results, the slope of the curve should be similar to that of a plot of the aqueous standard curve.
- The effect of the interference should not vary as the ratio of the standard added to the sample matrix changes.

APPENDIX E

TROUBLESHOOTING GUIDE

APPENDIX E. TROUBLESHOOTING GUIDE

Problem	Possible Cause/ Solution
High Blanks	Increase rinse time Clean or replace tip Clean or replace torch Clean or replace sample tubing Clean or replace nebulizer Clean or replace mixing chamber Lower Torch
Instrument Drift	RF not cooling properly Vacuum level is too low Replace torch (Crack) Clean or replace nebulizer (blockage) Check room temperature (changing) Replace pump tubing Room humidity too high Clean torch tip (salt buildup) Check for argon leaks Adjust sample carrier gas Reprofile Horizontal Mirror Replace PA tube
Erratic Readings, Flickering Torch or High RSD	Check for argon leaks Adjust sample carrier gas Replace tubing (clogged) Check drainage(back pressure changing) Increase uptake time (too short) Increase flush time (too short) Clean nebulizer, torch or spray chamber Increase sample volume introduced Check that autosampler tubes are full Sample or dilution of sample not mixed Increase integration time (too short) Realign torch Reduce amount of tubing connectors
Cu/Mn Ratio Outside Limits or Low Sensitivity	Plasma conditions changed Clean nebulizer, torch or spray chamber Replace tubing (clogged) Realign torch Check IECs
Standards reading twice normal absorbance or concentration	Incorrect standard used Incorrect dilution performed

APPENDIX F

CONTAMINATION CONTROL GUIDELINES

APPENDIX F. CONTAMINATION CONTROL GUIDELINES

The following procedures are strongly recommended to prevent contamination:

All work areas used to prepare standards and spikes should be cleaned before and after each use.

All glassware should be washed with detergent and tap water and rinsed with 1:1 nitric acid followed by deionized water.

Proper laboratory housekeeping is essential in the reduction of contamination in the metals laboratory. All work areas must be kept scrupulously clean.

Powdered or Latex Gloves must not be used in the metals laboratory since the powder contains silica and zinc as well as other metallic analytes. Only vinyl or nitrile gloves should be used in the metals laboratory.

Glassware should be periodically checked for cracks and etches and discarded if found. Etched glassware can cause cross contamination of any metallic analytes.

Autosampler trays should be covered to reduce the possibility of contamination. Trace levels of elements being analyzed in the samples can be easily contaminated by dust particles in the laboratory.

The following are helpful hints in the identification of the source of contaminants:

Yellow pipet tips and volumetric caps can sometimes contain cadmium.

Some sample cups have been found to contain lead.

The markings on glass beakers have been found to contain lead. If acid baths are in use for glassware cleaning, they should be periodically checked for contaminants since contaminant concentrations will increase over time.

New glassware especially beakers can be a source of silica and boron.

Reagents or standards can contain contaminants or be contaminated with the improper use of a pipette.

Improper cleaning of glassware can cause contamination.

Latex gloves contain over 500 ppb of zinc.

APPENDIX G

PREVENTIVE MAINTENANCE

APPENDIX G. PREVENTIVE MAINTENANCE

A maintenance log is used to record when maintenance is performed on instruments. When an instrument problem occurs indicate the date, time and instrument number, then identify the problem and corrective action in the maintenance log.

The following procedures are required to ensure that that the instrument is fully operational.

Daily	Change sample pump tubing and pump windings Check argon gas supply level Check rinse solution and fill if needed Check waste containers and empty if needed Check sample capillary tubing is clean and in good condition Check droplet size to verify nebulizer is not clogged. Check sample flow for cross flow nebulizer Check Cu/Mn ratio-should be 30% of value at date that IECs were performed Check pressure for vacuum systems
As Needed	Clean plasma torch assembly to remove accumulated deposits Clean nebulizer and drain chamber; keep free-flowing to maintain optimum performance Replace peristaltic pump tubing, sample capillary tubing and autosampler sipper probe
Weekly	Apply silicon spray on autosampler tracks Check water level in coolflow
Monthly	Clean air filters on back of power unit to remove dust Check D mirror for air instruments
Bi-yearly	Change oil for vacuum systems Replace coolant water filter (may require more or less frequently depending on quality of cooling water)

APPENDIX H

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

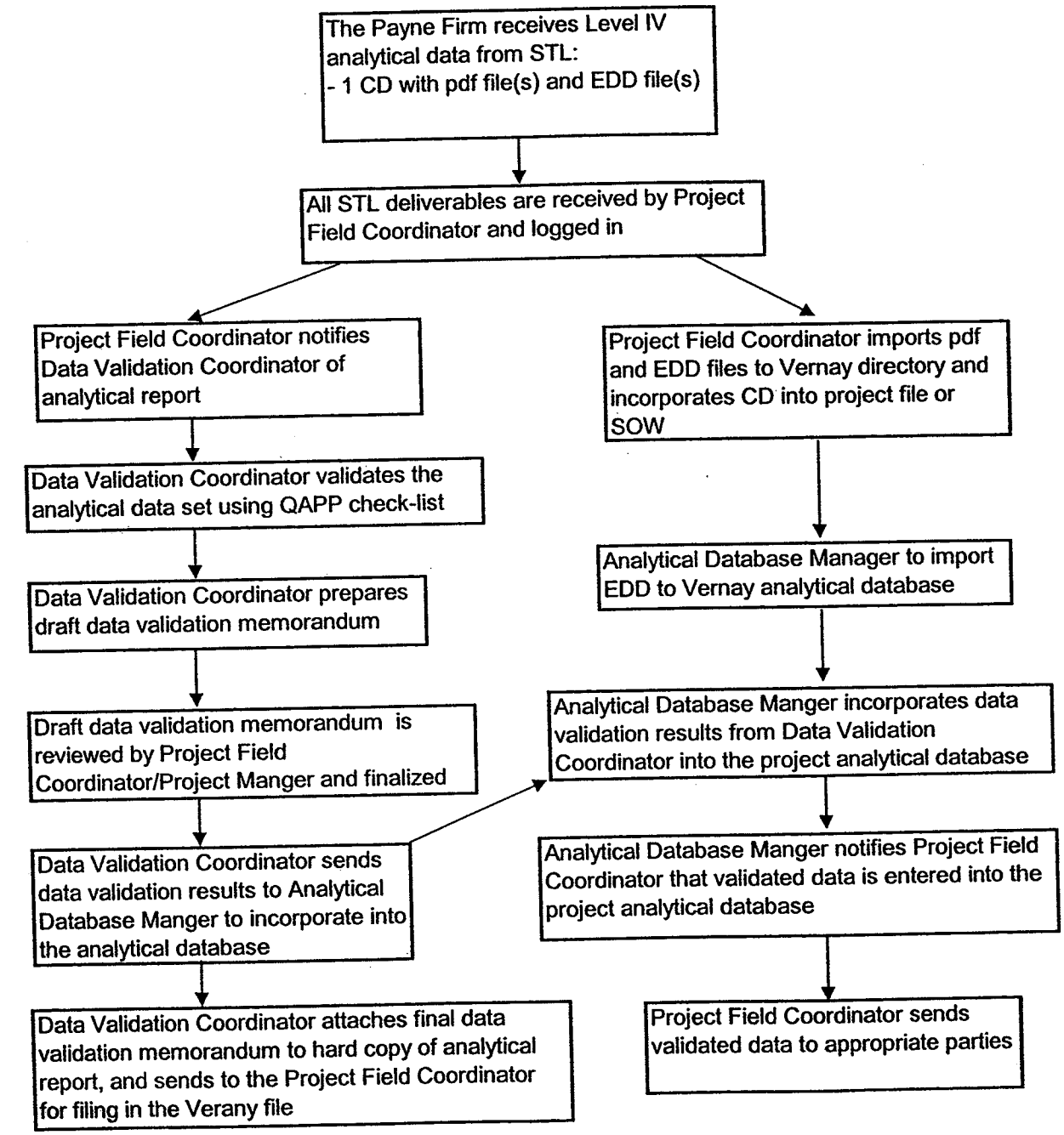
a. Analysis (enter)

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



DRAWN BY	APPROVED BY	PROJECT NO	DATE	APPENDIX
MRD	KDK	0100.58.19	07/26/04	V

CLIENT: EMD CHEMICALS INC.

The Payne Firm, Inc.
Environmental Consultants
Cincinnati, Ohio 45242

TITLE: RCRA FACILITY INVESTIGATION
ANALYTICAL DATA HANDLING FLOW CHART

The Payne Firm, Inc.
Data Validation Checklist

Project:
Sampling Event Description:
Reviewer:
Lot Numbers:
Laboratory Name:
Checklist Completion Date:

Note: "X" – Applies; "--" – Does Not Apply

1.0 Sample Report Completeness		
This Section provides a checklist of important components of data reports. If the report is incomplete, it may be necessary to halt data validation procedures until all missing information is provided.		
1.1	Review any discrepancies between the Chain-of-Custody (COC) and submitted sampling data.	
1.2	Presence of signed laboratory statement that attests to the validity of the data.	
1.3	Presence of case narrative that summarizes QA/QC discrepancies and/or other problems.	
1.4	Are COC forms present for all samples?	
1.5	Review the COC forms, Sample Receipt form, or the Case Narrative for any problems with the sample receipt, condition of samples, analytical problems or special circumstances affecting the quality of the data.	
1.6	Were Custody Seals present and intact?	
1.7	Is a Sample receipt form present?	
2.0 Holding times		
Technical holding times are an important component of assuring that data is valid and not biased from inappropriate handling procedures.		
2.1	Holding Times - Volatile Organic Compounds	
2.1.1	Are samples properly preserved? Check preservation requirements, chain-of-custody, and sample receipt form for discrepancies.	

2.1.2	If samples were improperly preserved, or unpreserved, and the technical holding times were exceeded, qualify all positive results for affected samples as "J" estimated and all non-detected results as "UJ" estimated undetected.	
2.1.3	If samples were properly preserved, but technical holding times were exceeded, qualify all positive results for affected samples as "J" estimated and all non-detected results as "UJ" estimated undetected.	
2.1.4	If technical holding times are greatly exceeded (>2x the time requirement) upon analysis or re-analysis then the reviewer may use professional judgment to qualify all non-detected compounds as "R" rejected and all positive results as "J" estimated.	
2.2	**Holding Times - Semi-Volatile Organic Compounds**	
2.2.1	If technical holding times are exceeded (Table 1), qualify all positive results for affected samples as "J" estimated and all non-detected results as "UJ" estimated undetected.	
2.2.2	If holding times are greatly exceeded (>2x the time requirement), the reviewer may use professional judgment to qualify all non-detected compounds as "R" rejected and all positive results as "J" estimated.	
2.3	**Holding Times Inorganic Compounds**	
3.1	Review whether samples were properly preserved (4 degrees Celsius for solids: acid preservation for aqueous).	
2.3.2	If samples were improperly preserved and the holding times were exceeded, qualify all positive results for affected samples as "J" estimated and all non-detected results as "UJ" estimated undetected.	
2.3.3	If samples were properly preserved, but technical holding times were exceeded, qualify all positive results for affected samples as "J" estimated and all non-detected results as "UJ" estimated undetected.	
2.3.4	If holding times are greatly exceeded (>2x requirement), the reviewer may use professional judgment to qualify all non-detect compounds as "R" rejected and all positive results as "J" estimated.	
2.4	*Holding Times – pH*	
2.4.1	If technical holding times are exceeded the reviewer may use professional judgment to qualify data as "R" rejected or "J" estimated.	

3.0	**Quality Assurance Summary Data Review**	
VOC Surrogate Compound Recovery - Surrogate compounds are spiked compounds of known composition that are added to samples and blanks. The recovery of surrogate compounds allows assessment interference. VOC surrogate recoveries are used with other QA/QC data to qualify sample results and to justify laboratory re-analysis. Specific examples are listed in the data validation guidance document.		
3.1.1	Were surrogate recoveries present for each batch?	
3.1.2	Were any outliers marked correctly (based upon the laboratory's criteria)?	
3.1.3	If any surrogate compound was out of compliance was re-analysis performed to confirm matrix interference?	
3.2	**SVOC Surrogate Compound Recovery- Surrogate compounds are spiked compounds of known composition that are added to samples and blanks. The recovery of surrogate compounds allows an assessment of matrix interference. SVOC analyses include compounds that can be divided into two classes: acid compounds and base/neutral compounds. Each class has a specific assigned set of surrogate compounds.**	
3.2.1	Are the surrogate recovery data present for each batch (method and matrix), including TCLP?	
3.2.2	Were any outliers marked correctly?	
3.2.3	If any two surrogate compounds in either the acid or base/neutral classes were out of compliance, was re-analysis performed to confirm a matrix interference? Note: Check the report narrative for an indication of re-analysis.	
3.2.4	If any one surrogate compound has a recovery of less than 10% in either the acid or base/neutral classes, check for indications that re-analysis was performed to confirm a matrix interference?	

3.2.5	Based on the findings, qualify data in either the acid or base/neutral classes with the following criteria: Note: Qualification may not be appropriate for TCLP data. Best professional judgment may be used to qualify data. Action: If two surrogates in a particular class are above the upper control limit, all positive results, for that fraction, in that class should be qualified as "J". If any two surrogates in a particular class have recoveries less than the lower criteria, but the recovery is greater than or equal to 10%, all detected compounds, for that fraction, should be qualified as "J". If any surrogate in a particular class have recoveries less than 10%, all detected compounds, for that fraction, should be qualified as "J" estimated and all non detected compounds as "R" rejected.	
Quality Assurance Summary Review - Matrix Spike/Matrix Spike Duplicates		
Matrix spike and matrix spike duplicates are performed to assess method precision for VOC and SVOC analyses. Matrix spikes and duplicates are required for every batch of samples (every 20 - 30 samples). The reviewer should be aware that MS/MSD are batch specific not sample specific.		
3.3.1	Is matrix spike/matrix spike duplicate recovery data present?	
3.3.2	Were any VOC spike recoveries are outside the QC limits?	
3.3.3	Check RPDs for matrix spike and matrix spike duplicate recoveries.	
3.4	**Matrix Spike/Matrix Spike Duplicates, SVOC**	
3.4.1	Is matrix spike/matrix spike duplicate recovery data present?	
3.4.2	Were any SVOC spike recoveries are outside the QC limits?	
3.4.3	Check RPDs for matrix spike and matrix spike duplicate recoveries.	
3.5	**Sample Specific**	
Metal Spike Recovery - Spikes are elements of known composition that are added to blanks and to samples that measure accuracy and precision of the analyses. At least one spike should be included for each batch of samples. Spike recovery criteria listed in this section are determined from US EPA's National Functional Guidelines for Inorganic Data Review. The criteria applied by an individual laboratory may vary. The laboratory should be consulted and its QA/QC criteria supplied to the reviewer.		

4.2	**Blank Summary Review – SVOC**	
4.2.1	Is the method blank summary data present for each batch (method and matrix), including TCLP?	
2.2	Check for dilution associated with that blank.	
4.2.3	Check field/trip/rinseate blanks for any positive results for semi-volatile target analytes.	
4.2.4	Check method blanks for SVOCs.	
4.3	**Blank Summary Review – Metals**	
4.3.1	Were the method blank summary data present for each batch (method and matrix), including TCLP?	
4.3.2	Check for detections in blank.	

3.5.1 matrix	Confirm that at least one spike sample was analyzed per batch and per type.	
5.2	Are all spike recoveries (except Hg and Ag) within control limits?	
3.5.3	Based on the results of 3.5.2, if the sample results were <4x the spike amount and spike recoveries were out of criteria, a post-digestion spike should be analyzed. Note: Post-digestion spikes are not required for Ag or Hg. The post digestion spike confirms a matrix interference and should not be used for qualification.	
3.5.4	Are any Aqueous spike recoveries (pre and post digestion): 1. Less than 30%? 2. Between 30% and 74%? 3. Between 126% and 150%? 4. Greater than 150%?	
3.5.5	Are any soil/solid/waste spike recoveries (pre and post digestion): 1. Less than 10%? 2. Between 10% and 74%? 3. Between 126% and 200%? 4. Greater than 200%?	
3.5.6	If the pre-digestion spike was outside the QC limits for Atomic Adsorption furnace analysis (e.g. SW-846 methods in the 7000 series), was a post-digestion spike performed?	
3.5.7	Based on the results from 3.5.6, were the post-digestion spike recoveries within the quality control range (75% to 125%)?	
4.0	**Blank Data Review**	
Blank Data - Laboratory blanks are used to assess whether contamination from the laboratory, reagents or other samples exists and whether this contamination can bias sample results. The qualification of sample results will depend upon the magnitude of blank contamination.		
4.1	**Blank Summary Review - VOC**	
4.1.1	Is the method blank summary data present for each batch (method and matrix), including TCLP?	
4.1.2	Is there an indication that the samples associated with that blank were diluted?	
4.1.3	Check field/trip/rinseate blanks for any positive results for volatile target analytes.	
.4	Check method blanks for VOCs.	