SOIL PRE-DESIGN STUDY WORK PLAN

WAUKEGAN MANUFACTURED GAS AND COKE PLANT SITE
WAUKEGAN, ILLINOIS

US EPA RECORDS CENTER REGION 5
394833

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June 17, 2002

Reference No. 019023-15

Mr. Kevin Adler
Remedial Project Manager
Mail Code SR-6J
U.S. Environmental Protection Agency – Region 5
77 W. Jackson Boulevard
Chicago, Illinois 60604-3590

Dear Mr. Adler:

Re: Soil Pre-Design Study Work Plan
Waukegan Manufactured Gas and Coke Plant Site
Waukegan, Illinois

Enclosed please find a hard copy version of the approved Soil Pre-Design Study Work Plan which was previously submitted electronically. Please note the hard copy version includes an updated Quality Assurance Project Plan.

Should you have any questions regarding the enclosed document, please contact me at your convenience.

Yours truly,

CONESTOGA-ROVERS & ASSOCIATES

Walter J. Pochron

WP/lg/8
Encl.

c.c.: E. Rednour - IEPA
J. Keiser – CH2M Hill
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SOIL PRE-DESIGN STUDY WORK PLAN

WAUKEGAN MANUFACTURED GAS AND COKE PLANT SITE
WAUKEGAN, ILLINOIS

Prepared by:
Conestoga-Rovers & Associates

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1.0 INTRODUCTION

This document presents the Soil Pre-Design Study Work Plan (Work Plan) for the Waukegan Manufactured Gas and Coke Plant site, Waukegan, Illinois (Site). The Work Plan has been prepared on behalf of the "Performing Respondents" by Conestoga-Rovers & Associates (CRA) and Barr Engineering (Barr) in accordance with the Remedial Design Work Plan, Waukegan Manufactured Gas and Coke Plant Site (RDWP). The RDWP was prepared consistent with the Remedial Design Scope of Work (RD SOW) which is Attachment II to the Administrative Order on Consent for Remedial Design (RDAOC) at the Waukegan Coke Plan Site, U.S. EPA Docket No. V-W-01-C-651. The RDWP was approved by the United States Environmental Protection Agency (U.S. EPA) in a letter dated December 11, 2001. The Work Plan is Task S1 of the RDWP.

The Work Plan outlines a scope of work for a soil pre-design study to refine the extent of soils that exceed soil cleanup levels for arsenic and polynuclear aromatic hydrocarbons (PAHs), including soil in the Designated Soil Stockpile (DSS) that may contain creosote residuals. The Work Plan also outlines the scope of work to characterize the soil for treatment and/or disposal. The delineation activities may lead to a revision of the estimated quantity of soil to be removed and/or treated.

In addition to the Work Plan, supporting additional documents were prepared to assist in the overall goal of successfully completing the Soil Pre-Design Study, including:

- Health and Safety Plan (HASP),
- Quality Assurance Project Plan (QAPP), and
- Sampling and Analysis Plan (SAP).

The Work Plan has been organized into the following sections:

Section 1.0 Introduction;
Section 2.0 Background;
Section 3.0 Soil Investigation Zones;
Section 4.0 Soil Pre-Design Studies;
Section 5.0 Health and Safety Plan;
Section 6.0 Project Data Management;
Section 7.0 Project Organization and Responsibility;
Section 8.0 Reporting; and
Section 9.0 Schedule.

2.0 BACKGROUND

2.1 SITE LOCATION

The Waukegan Manufactured Gas and Coke Plant (WCP) Site is located in Waukegan, Illinois, on the peninsula separating Waukegan Harbor from Lake Michigan (Figure 2.1). The property and its environs have been part of the industrial/commercial waterfront in Waukegan. The sand dunes and beach area east of the WCP Site are used for public recreation. Figure 2.2 provides a plan view of the WCP Site.

2.2 PREVIOUS STUDIES

2.2.1 REMEDIAL INVESTIGATION

Results from the RI conducted by Barr were submitted to the U.S. EPA in two reports. The first report was entitled "Preliminary Site Characterization Summary (PSCS) (Barr, 1994) was submitted to the U.S. EPA in April 1994 and was approved on May 5, 1994. The purpose of this report was to provide the U.S. EPA with a preliminary transmission of the data collected from the RI. The second report entitled "Remedial Investigation Report" (RI Report) (Barr, 1995) was submitted to the U.S. EPA in February 1995 and approved on February 16, 1996. The RI Report included an evaluation of the RI data previously submitted in the PSCS report. The RI Report contained information on,

- Site background and regional information, geotechnical and chemical data obtained from previous investigations conducted in the vicinity of the Site,
- a description of RI activities and methods of investigations of soil, groundwater, surface water, and surface features,
- an evaluation of site geology and hydrogeology,
- characterization of contaminant nature and extent, and
- evaluation of contaminant fate and transport.

2.2.2 RISK ASSESSMENTS

In 1995, using the information obtained during the RI and presented in the PSCS, a baseline risk assessment consisting of a Human Health Risk Assessment (HHRA) and a screening Ecological Risk Assessment (ERA) for the Site was performed by CH2M Hill for the U.S. EPA. Results from these assessments were submitted in the following documents:

- Technical Memorandum, Waukegan Manufactured Gas and Coke Plant Site, Waukegan, Illinois. Human Health Risk Assessment. (U.S. EPA 1995a), and
- Technical Memorandum, Waukegan Manufactured Gas and Coke Plant Site, Waukegan, Illinois. Ecological Risk Assessment. (U.S. EPA 1995b).

2.2.3 FEASIBILITY STUDY

Utilizing the information from the above noted studies a Feasibility Study Report (Barr, 1998) was prepared and submitted to the U.S. EPA on November 6, 1998. The FS Report provided the basis for the remedy selection by the U.S. EPA.

2.3 RECORD OF DECISION

The U.S. EPA issued a ROD for the Remedial Action at the Site and a supplement to the FS regarding the DSS in September 1999. The selected groundwater remedy is a mobile, cell-based, low-flow extraction/treatment/reinjection system. Pre-design studies related to the groundwater component of the selected remedy will be addressed in a separate submittal to the U.S. EPA.

The U.S. EPA selected remedy in the ROD for the vadose zone soil remedial component consisted of a slight modification of Alternative 3 presented in the FS Report. The selected vadose zone soil remedy consists of the following five components.

- Excavation of the PAH-contaminated soil and the temporary DSS, and either off-Site: 1) treatment by power plant co-burning, or 2) disposal at a RCRA Subtitle C or D landfill[1].
- In-situ stabilization/solidification or off-Site disposal of soils containing arsenic at concentrations above cleanup levels.
- Combination vegetative, asphalt and building cover for Marginal Zone soil and the backfilled excavation areas.
- Institutional controls.
- Development of a comprehensive Soil Management Plan (SMP).

[1] Treatment is the preferred alternative for both the PAH and arsenic contaminated soils. Placement of the PAH soils in a landfill will only be selected if it is determined during the Remedial Design that treatment is not practicable (e.g., not feasible excessive cost, etc.).

This Work Plan has been developed to collect the data needed to design and implement the soil remedy.

3.0 SOIL INVESTIGATION ZONES

3.1 CLEANUP LEVELS

Figure 13 of the ROD depicts the anticipated areas of soil remediation and is presented in Appendix A. The areas identified on the figure in Appendix A represent Soil Investigation Zones (SIZs) that will be investigated further as described in this Work Plan. The preliminary determination for these anticipated areas of soil remediation were based on an evaluation of the soil analytical data collected during the RI, using the most conservative human health exposure scenarios under the expected future use of the property and visual observations of soil made in the field during the investigative work. The intent of the soil pre-design study is to refine the extent of the soils, which are above the soil cleanup levels.

The anticipated areas of soil remediation shown in Appendix A were based on the following preliminary soil cleanup levels that were developed in the FS Report.

- Arsenic Remediation Zone - 940 mg/kg protective to a 1.0E-05 cancer risk using the representative high exposure (RHE) utility worker exposure.
- PAH Remediation Zone - the area where the concentrations of PAHs pose carcinogenic risk exceeding the commercial and industrial or the utility worker RHE of 1.0E-05 or a Hazard Index (HI) of 1.0 for non-cancer effects..

A summary of the soil cleanup levels presented in the ROD is presented in Table 3.1. The soil cleanup levels established in the ROD are compound-specific, based upon a carcinogenic risk exceeding 1.0E-05 or a HI of 1.0 for the most severe RHE scenario.

A comparison of the soil analytical data presented in the RI report to the actual soil cleanup levels presented on Table 3.1 identified five samples where PAHs were detected above the ROD soil cleanup levels and three samples where the arsenic was detected above the ROD soil cleanup level of 940 mg/kg. Table 3.2 summarizes the analytical data for soil samples where the PAH or arsenic concentrations were above the ROD soil cleanup levels. Figure 3.1 illustrates the locations where detections of arsenic and PAHs were above the ROD soil cleanup levels.

3.2 SOIL INVESTIGATION ZONE DESCRIPTIONS

Three anticipated areas of soil remediation were described in the ROD: the PAH Zone, the Arsenic Zone, and the Marginal Zone. The following summarizes the areas of soil investigation under the soil pre-design investigation.

3.2.1 PAH SOIL INVESTIGATION ZONE

The PAH Zone includes the soils in the DSS and soils where the concentrations of PAHs may pose a carcinogenic risk exceeding 1.0E-05 or an HI of 1.0 for the most severe RHE scenario. Soil Cleanup Levels for individual PAHs are presented in Table 3.1. The volume of soil in the DSS is estimated to be between 2,600 and 4,500 cubic yards and the volume of other PAH-containing soil is estimated to be between 7,100 to 14,900 in-place cubic yards.

The PAH Soil Investigation Zone (PAH SIZ) consists of seven separate areas located across the Site (identified as PAH SIZ-1 through PAH SIZ-7 in Figure 3.1) plus the DSS. Three of these areas (PAH SIZ-3, PAH SIZ-6, and PAH SIZ-7) encompass previous soil sampling locations where PAH concentrations exceeded the ROD soil cleanup levels listed in Table 3.1. These areas include the large area located at the far southern side of the Site were soil cleanup levels were exceeded at ground sample location GS-15 and at soil borings SB-50 and SB-55 (PAH SIZ-7). The small area just to the north of the previous area where soil cleanup levels were exceeded at soil boring SB-40 (PAH SIZ-6). The third area is located just to the east of the DSS were soil cleanup levels were exceeded at soil boring SB-27 (PAH SIZ-3). The remaining four areas (PAH SIZ-1, PAH SIZ-2, PAH SIZ-4, and PAH SIZ-5) represent areas of the Site where concentrations of carcinogenic PAHs in soil were above the FS preliminary soil cleanup objectives and/or locations where signs of visual contamination were observed during the RI, but there were no exceedences of the ROD soil cleanup levels in these locations.

3.2.2 ARSENIC SOIL INVESTIGATION ZONE

Arsenic Zone includes areas where the concentrations of arsenic in soil may pose a carcinogenic risk of 1.0E-05 for the most severe RHE scenario. The soil cleanup level for arsenic is presented in Table 3.1. The volume of arsenic-containing soil is estimated to be between 3,300 and 7,200 cubic yards, in place.

The Arsenic Soil Investigation Zone (Arsenic SIZ) consists of one area located just to the west of the former IT Building parking lot (Figure 3.1). Soils containing arsenic above 940 mg/kg were detected in soil samples collected from test trenches TT-07 and TT-25 during the RI and from a soil sample collected by the Illinois Environmental Protection Agency (X-105). The southern portion of PAH SIZ-4 and the Arsenic SIZ overlap west of the IT Building parking lot.

3.2.3 MARGINAL ZONE SOIL

The ROD requires that approximately two-thirds of the 36-acre Site be covered with a combination of vegetation, asphalt, and building cover. The cover is intended to minimize infiltration, manage surface water drainage and provide erosion control, enhance in-situ degradation of low-level residual soil organic parameters, and provide a barrier to direct contact exposure. The Marginal Zones are generally associated with the PAH and Arsenic concentrations between 1.0E-5 and 1.0E-6 excess carcinogenic risk, RHE, or arsenic concentrations above the 25 mg/kg protection of groundwater value. The limits of the Marginal Zone are identified on Figure 13 of the ROD (see Appendix A) and on Figures 3.1 and 4.1.

4.0 SOIL PRE-DESIGN STUDIES

4.1 SCOPE OF WORK

The objectives of the Soil Pre-Design Study are to refine the extent of soils that exceed soil cleanup levels for PAHs and arsenic and characterize the soil for treatment and/or disposal. The approximate limits anticipated areas of soil remediation are based on soil analytical data collected during the RI. The soil pre-design studies are intended to define both the lateral and vertical limits of soils exceeding the cleanup levels.

The scope of work to be completed during the Soil Pre-Design Study consists of the following tasks:

1. grid the Site and conduct a walkover inspection to identify any areas of tar at the ground surface;
2. conduct a survey to re-establish the locations soil sampling locations shown in Figure 4.1, establish the perimeter of the anticipated areas of soil remediation shown in Figure 13 of the ROD, and the establish the locations of surficial tar deposits;
3. collect waste characterization soil samples from the DSS.
4. delineate the limits of the areas of PAH and Arsenic remediation with test pits, and soil borings, with collection of soil samples for laboratory analysis;
5. obtain waste characterization samples from the PAH and Arsenic SIZs.
6. survey the test pre-design investigative locations; and
7. evaluate and report the results of the Soil Pre-Design Study.

The following sections present the actions necessary to investigate Site soils. Detailed field procedures are provided in Appendix B. The QAPP for the soil pre-design studies is presented in Appendix C.

4.2 SITE WALKOVER INSPECTION

Deposits of coal tar are present at scattered locations at the Site. Many of the surficial tar deposits are located in the identified SIZs. However, a Site walkover inspection will be conducted to identify surface deposits of tar. The Site walkover inspection will be conducted by establishing a 25-foot rectangular grid (oriented north-south, east-west) and physically walking the Site in a grid pattern. The grid will be walked and the ground inspected in the north-south and east-west directions.

Depending on the season the Site walkover inspection is conducted, the Site may need to be mowed and grubbed before performing the inspection. Mowing and grubbing will be performed as necessary, before performing the walkover inspection.

The locations of surficial tar deposits larger than two feet in diameter will be staked and flagged. The size of the tar deposits will be measured and recorded in the field logbook. The flagged locations will be uniquely identified with an alphanumeric numbering system. The flagged locations will be surveyed by a professional surveyor for future recovery of the locations. The locations of surface tar deposits outside the PAH Investigation Zones identified during the Site walkover inspection, if any, will be investigated further as described in Section 4.3.

4.3 INVESTIGATION OF SOIL INVESTIGATION ZONES

Figure 3.1 illustrates the pre-design soil investigation zones and identifies the soil sampling locations on which the limits were based. Survey coordinates from the RI will be used to relocate each of these sampling locations. The locations will be relocated and staked by an Illinois-registered surveyor. These locations will be used as the reference points to verify and delineate the limits of the Vadose Zone SIZs. Investigative activities proposed in each of the SIZs are described by the following.

4.3.1 DESIGNATED SOIL STOCKPILE

The location of the DSS is identified on Figure 3.1. The volume of soil in the DSS is estimated to be up to 4,500 cubic yards. The soil within the DSS was generated during the construction of Slip No. 4 and contains soil designated by the U.S. EPA for segregation during the construction of Slip No. 4. The DSS is lined and covered.

The objective of the pre-design studies for the DSS is to characterize the soil to allow an evaluation of disposal and/or treatment alternatives. The sampling program includes dividing the DSS into four quadrants and collecting one soil sample from each of the four quadrants for waste characterization and geotechnical analyses discussed in Sections 4.3.3 and 4.3.4. A soil boring will be advanced in the approximate center of each of the quadrants (as illustrated of Figure 4.1) using direct-push technology (DPT) or hand auger techniques. Soil samples will be obtained through the entire depth interval. A composite soil sample will be obtained of the entire depth interval at each sampling location. Soil sampling will terminate at an elevation of approximately one foot above

the estimated base of the DSS to prevent accidental penetration of the DSS underliner during soil sampling activities.

The soil samples collected from each of the four soil borings within the DSS will be submitted for waste characterization and geotechnical analyses discussed in Sections 4.3.3 and 4.3.4.

4.3.2 SOIL INVESTIGATION

The proposed soil sampling locations are illustrated on Figure 4.1. In general, the larger soil investigation zones will be gridded (i.e., PAH SIZ-4, PAH SIZ-7, and Arsenic SIZ). The remainder of the soil investigation areas are relatively small and require fewer test pits to investigate. The proposed sampling program consists of collecting soil samples from test pits and/or soil borings. Test pits are preferred over soil borings because test pits allow a better opportunity to visually inspect the subsurface conditions and more flexibility in selecting representative soil samples. Soil borings will only be used at those locations where asphalt pavement is present. Soil borings will likely be required along the east side of the Arsenic SIZ and the south end of PAH SIZ-7.

Test pits and soil borings will be excavated/advanced to the water table or a maximum depth of approximately 6 feet below ground surface. Test pits straddling the boundaries of the SIZs will be initiated approximately 10 to 15 feet inside the boundary and will continue outwards past the boundary of the SIZ until field observations indicate that the limits of the contamination have been delineated. At a minimum, soil samples will be collected from boundary test pits at the point of test pit origin and the point of test pit termination. This will provide soil samples from inside and outside the SIZ. Where soil borings are required for delineation, soil samples will be collected using DPT. A line of soil borings will be advanced perpendicular to the boundary of the SIZ beginning 10 to 15 feet inside the boundary and will proceed outwards at approximately 10-foot on center past the boundary of the SIZ until field observations indicate that the limits of the contamination have been delineated.

Test pits will also be excavated in the interior of the SIZs. The interior test pits will be between 5 and 10 feet in length and soil samples will be collected at one location within the interior test pits. In general, soil samples will be collected from the test pits and soil borings at two-foot intervals through the entire depth of the test pit or soil boring. It is anticipated that three vertical soil samples will be collected at each sampling location to provide a vertical distribution of PAH and/or arsenic concentrations at each location. Additionally, in the event a soil layer is encountered that differs in composition from the

surrounding soil and is laterally or vertically significant, a grab soil sample will be obtained for analysis. Layers of tar will also be delineated for future removal. However, samples of the tar layers will not be collected for analysis as these will be assumed to exceed the PAH cleanup levels and will be removed during future soil remediation activities.

Collected soil samples will be analyzed for PAHs and/or arsenic. At several locations, the PAH and Arsenic SIZ overlap (see Figure 4.1). Samples collected from these locations will be analyzed for arsenic and PAHs. Upon completion, each test pit will be backfilled with excavated soil. Completed test pit and soil boring locations will be staked and later surveyed by a professional surveyor.

Test pits will also be excavated near surface tar deposits identified during the Site walkover inspection. A sufficient number of test pits will be advanced in the near-surface tar deposits to determine the limits of the tar. Soil samples will be collected beyond the limits of the tar deposits for PAH analysis to determine whether soil adjacent to the tar deposits exceed the ROD cleanup objectives.

Up to five soil samples will be collected from the PAH SIZ and up to four soil samples from the Arsenic SIZ will be collected for geotechnical analysis as discussed in Section 4.3.4. Composite soil samples from the PAH SIZ (including the DSS) and the Arsenic SIZ will be developed by the project laboratory as discussed in Section 4.3.3.

Test pit/borehole logs will be recorded during investigative activities to document significant observations during test pit excavation and borehole advancement.

4.3.3 WASTE CHARACTERIZATION

A number of composite soil samples will be developed by the project laboratory from pre-design soil samples collected from the PAH SIZ and the Arsenic SIZ during the soil investigation. The project laboratory will retain the unused portions of soil samples in storage. Following receipt and evaluation of the pre-design soil analytical data, several soil samples will be composited by the project laboratory and waste characterization analyses will be conducted on these samples to evaluate soil disposal options. It is expected that the soil samples that will be composited will be samples located within the limits of the soil investigation zones as determined by pre-design soil sampling activities. Prior to conducting the waste characterization analysis, a plan will be submitted to the U.S. EPA that provides the pre-design soil analytical results, identifies the number of composite samples to be developed and analyzed, and identifies the

pre-design soil samples to be composited. In addition, four soil samples will be collected from the DSS for characterization analysis as discussed in Section 4.3.1.

Characterization analyses will include TCLP organic and inorganic analytes, polychlorinated biphenyls, reactivity, soil pH, flash point, and paint filter tests. In addition, characterization samples from the PAH SIZ and the DSS will be analyzed for sulfate and sulfide.

4.3.4 GEOTECHNICAL ANALYSES

Up to five soil samples from the PAH SIZ, four soil samples from the DSS, and up to three soil samples from the Arsenic SIZ will be analyzed for geotechnical parameters. Geotechnical analyses will include grain-size distribution, bulk density, TOC, and moisture content. In addition, soil samples from the PAH SIZ and the DSS will be analyzed for heat content.

4.3.5 ARSENIC TREATABILITY STUDIES

The scope of arsenic soil treatability evaluation involving soil solidification/stabilization will determined once the extent of arsenic-contaminated soil requiring remediation has been delineated. Once the extent of the arsenic-contaminated soil is delineated through the collection of the soil samples described herein, a volume of soil from arsenic-contaminated area may be required for the solidification/stabilization treatability evaluation. Details regarding the arsenic solidification/stabilization treatability evaluation will be forwarded to the U.S. EPA for approval prior to implementation.

4.4 CONTINGENCY PLAN

In the event a review of the analytical data collected from the Soil Pre-Design Study identifies areas of the SIZs that require additional delineation, a short Work Plan will be developed and submitted to the U.S. EPA identifying to proposed scope of work and any modifications to the schedule required to complete the work. The additional delineation studies would be conducted in accordance with the procedures outlined in this Work Plan.

5.0 HEALTH AND SAFETY PLAN

A Site-specific Health and Safety Plan has been developed to address the Soil Pre-Design Study related activities to be performed at the Site. All field activities will be conducted in accordance with the health and safety protocols outlined in the HASP. The HASP is presented in Appendix D. The HASP may be modified in the future to incorporate additional activities proposed during supplemental activities.

6.0 PROJECT DATA MANAGEMENT

Field activities will be recorded daily in the field logbooks. Upon completion of the fieldwork or during periods when fieldwork is not scheduled, the field logbooks will be maintained in CRA's Chicago office. All data originals, including field forms, chain-of-custody forms, and laboratory data deliverables will be maintained in CRA's Chicago office.

Computer-based data tables will be verified with original laboratory certificates of analyses and with the original field logbook or field-generated forms. Both hard paper copies and computer-based versions of summary tables will be saved in the files. Land survey data will be maintained in the project file as hard copy, and the electronic survey data will be stored with the project's AUTOCAD files.

7.0 PROJECT ORGANIZATION AND RESPONSIBILITY

CRA has overall responsibility for all stages of the investigation. CRA will perform the sampling activities. Barr will provide historical continuity with previous investigations and will peer review the investigation. All samples will be analyzed by STL of North Canton, Ohio.

All subcontracted firms will provide project management as appropriate to their responsibilities. CRA will maintain a file copy of all laboratory deliverables. All final project deliverables will be issued by CRA at the explicit direction of the WCP PRP Group. A summary of each of the key person's responsibilities is presented in the QAPP.

Primary responsibility for project quality rests with CRA's Project Manager. Independent quality assurance will be provided by the laboratory's Project Manager and QA Officer prior to release of all data to CRA.

During the sampling stage of the project, daily telephone contact between the field sampling personnel and the laboratory subcontractor will occur. The laboratory will provide status updates by means of preliminary data telefacsimiles and/or e-mails. Should unexpected delays or other problems with the laboratory analyses occur, these would be communicated directly to CRA's Project Coordinator for resolution. Daily meetings with subcontractors will be held to update the progress of the project activities.

Key CRA contacts during the soil pre-design investigation activities are:

Alan Van Norman - Project Manager	519-884-0510
Steven Wanner - Project Coordinator	773-380-9933
Stephen Castagneri - Quality Assurance Officer	773-380-9933
Walter Pochron – Field Coordinator and Field Quality Assurance Officer	773-380-9933
Matthew Lazaric – Health and Safety Officer	773-380-9933

8.0 REPORTING

Upon completion of the soil pre-design activities, a report of findings will be prepared and submitted to the U.S. EPA. At a minimum, the soil pre-design study report will:

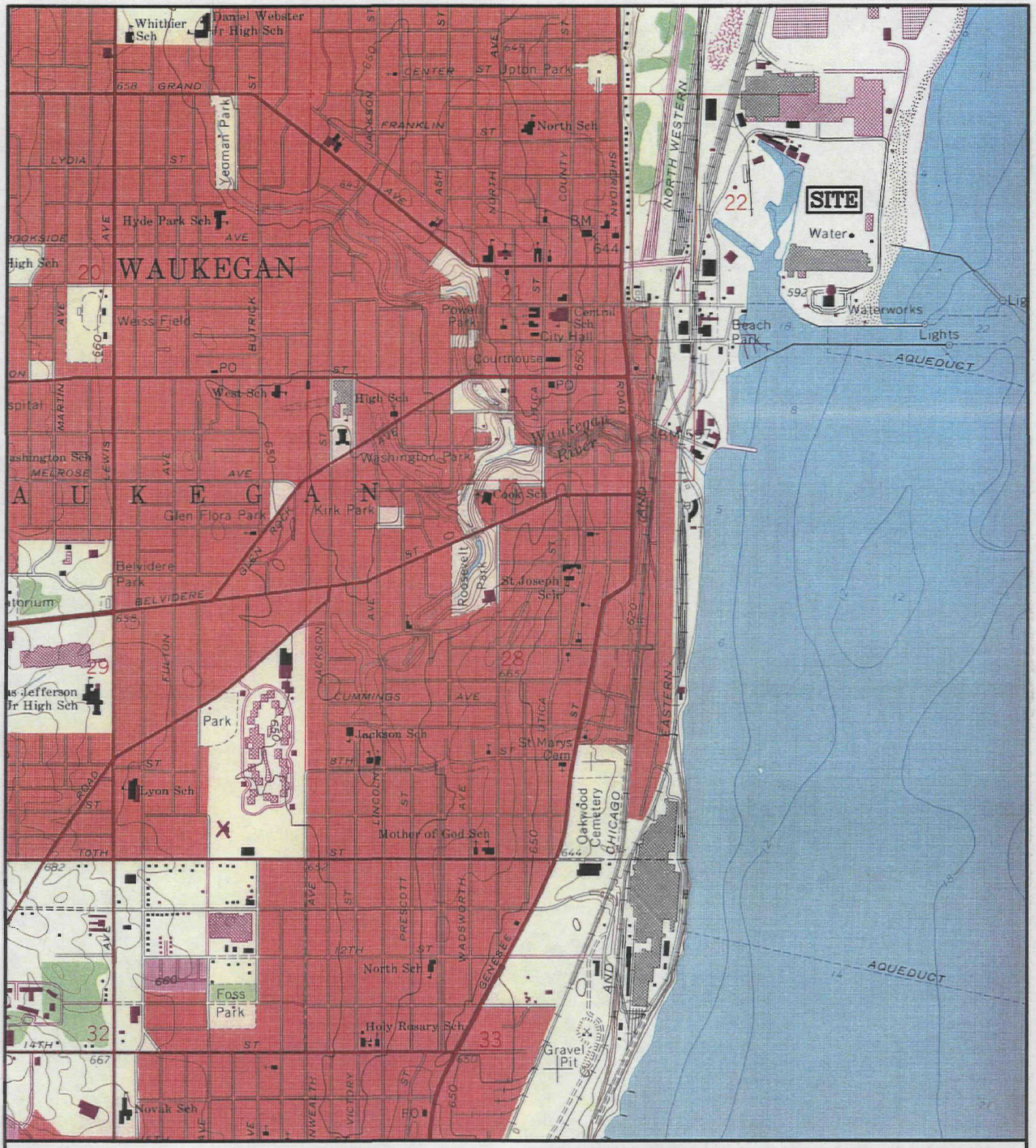
- summarize the work tasks completed, describe field protocols adhered to during field activities,
- provide all data sheets (test trench logs, soil boring logs, etc.) summarizing observations made during the investigation,
- provide survey data,
- provide laboratory analytical reports,
- provide summaries of the analytical data in tables and figures, and
- describe interpretations made based upon the results of the investigation.

Figures and cross-sections will be developed from which estimates of the volume of soil requiring remediation will be developed. The soil pre-design study report will provide the basis for the design of the soil remedy at the Site.

9.0 SCHEDULE

The schedule for the soil pre-design study work tasks is presented in Figure 9.1. The schedule for the soil pre-design work tasks is consistent with the schedule provided in the approved Remedial Design Work Plan.

FIGURES



BASE SOURCE: USGS 7.5 MINUTE TOPOGRAPHIC QUADRANGLE; WAUKEGAN, ILLINOIS 1960

figure 2.1

SITE LOCATION
WAUKEGAN MANUFACTURED GAS AND COKE PLANT
Waukegan, Illinois

CRA

19023-00(002)GN-CO001 MAY 10/2002

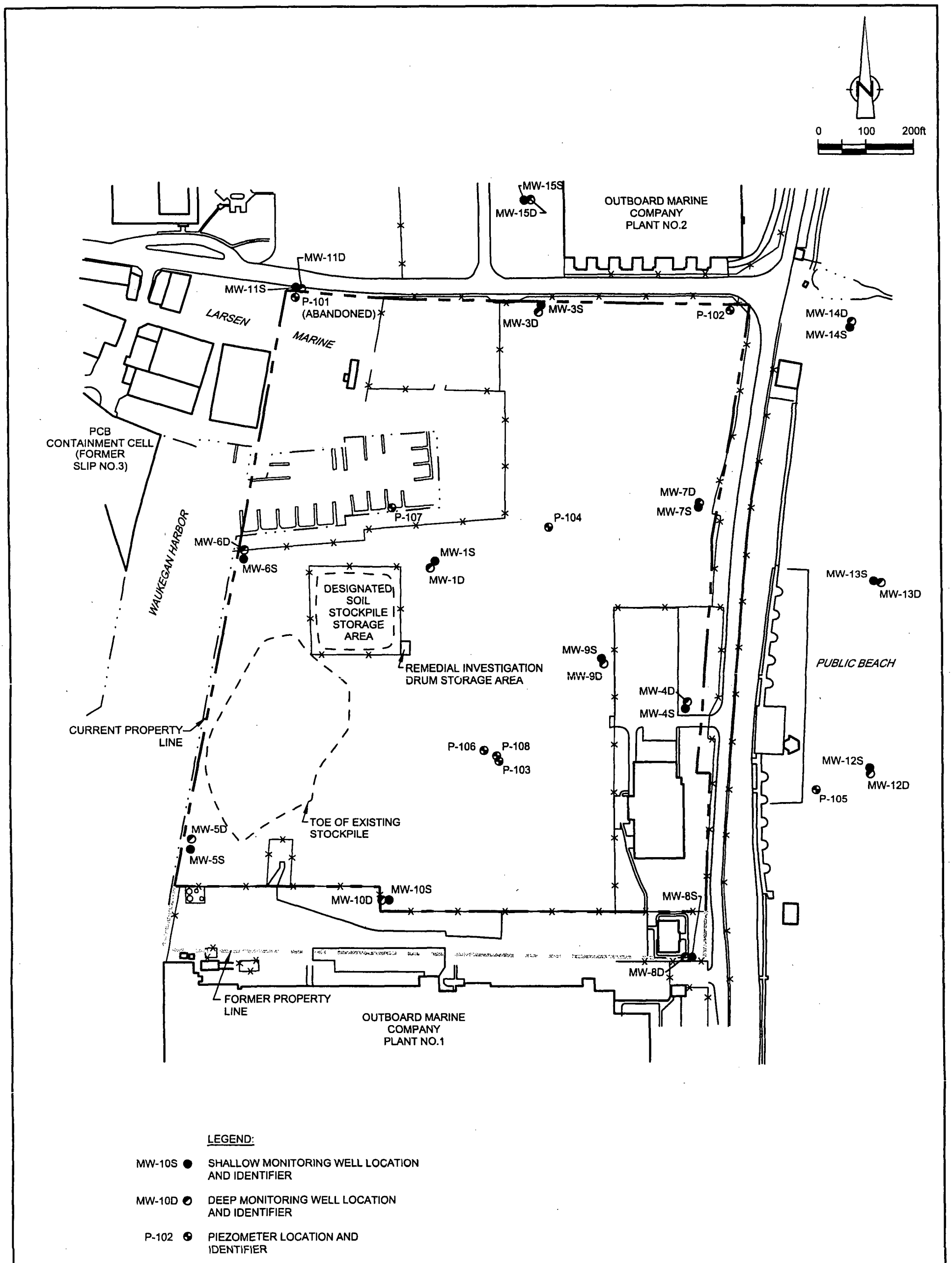
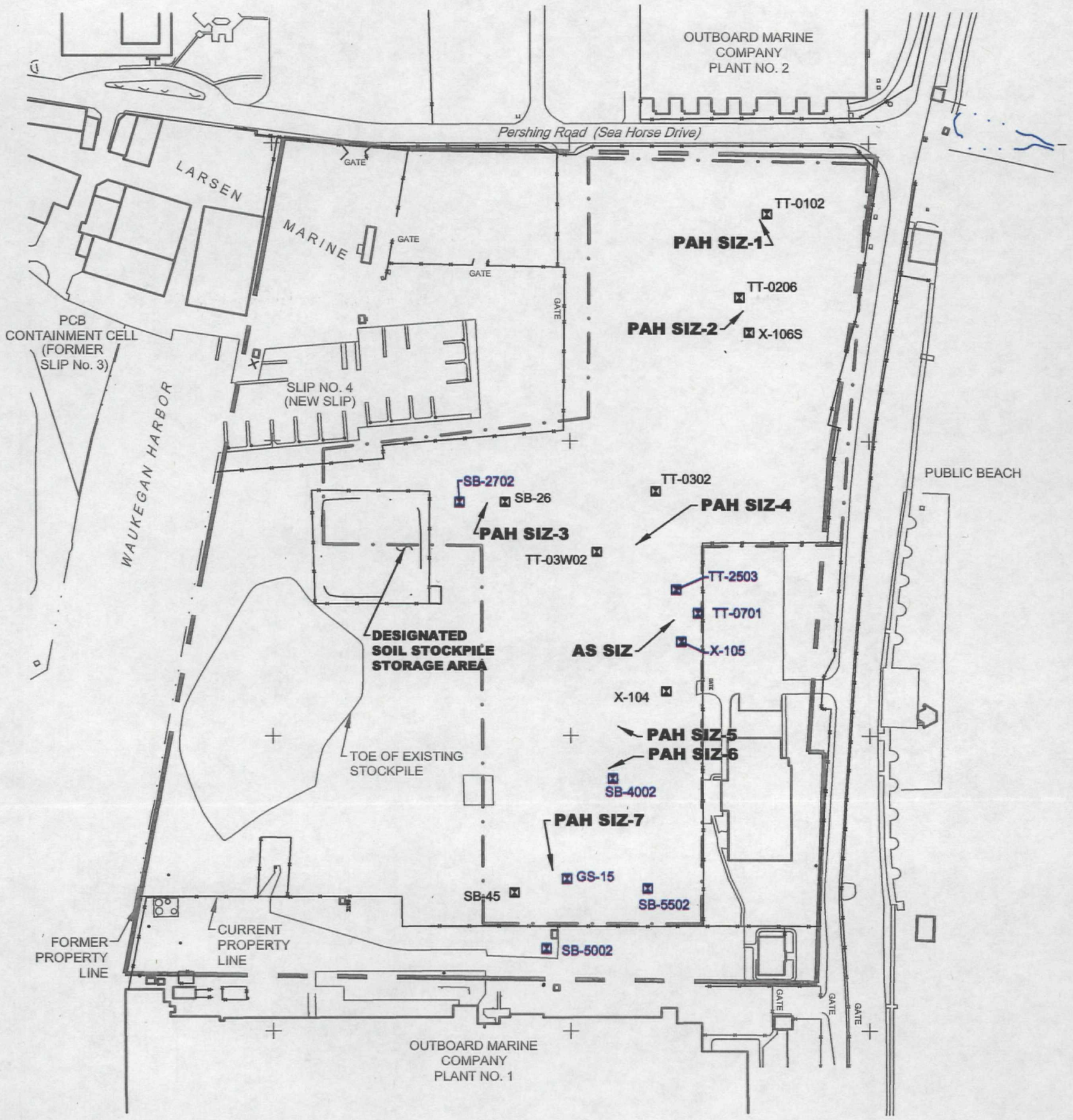


figure 2.2

SITE PLAN
WAUKEGAN MANUFACTURED GAS AND COKE PLANT SITE
Waukegan, Illinois

19023-00(002)GN-CO002 APR 22/2002



LEGEND:

— · —	MARGINAL ZONE SOIL
PAH SIZ-1	PAH SOIL INVESTIGATION ZONE IDENTIFIER
AS SIZ	ARSENIC SOIL INVESTIGATION ZONE IDENTIFIER
SB-26 ⊠	EXISTING SOIL SAMPLING LOCATION AND IDENTIFIER
GS-15	LOCATION WHERE ROD SOIL CLEANUP LEVEL WAS EXCEEDED

NOTE:

INFORMATION BASED ON TEST TRENCH LOGS AND SOIL BORING LOGS.

ACTUAL LIMITS OF THE SOIL REMEDIATION ZONES WILL BE DETERMINED FROM SOIL ANALYTICAL DATA OBTAINED DURING THE PREDESIGN STUDIES.

N

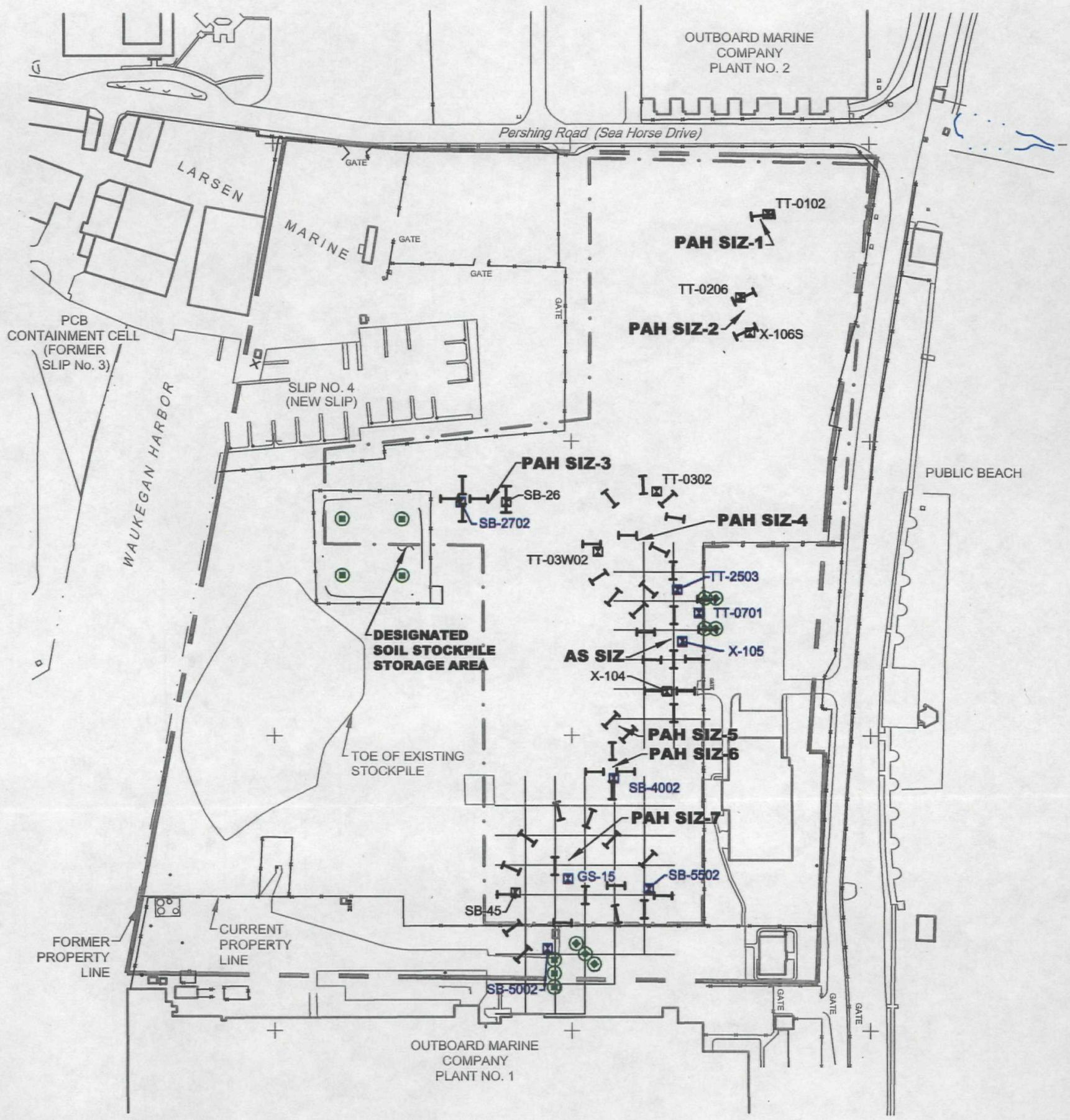
0 100 200ft

figure 3.1

PRE-DESIGN SOIL INVESTIGATION ZONES
WAUKEGAN MANUFACTURED GAS AND COKE PLANT
Waukegan, Illinois

CRA

19023-00(002)GN-CO004 MAY 10/2002



LEGEND:

— · —	MARGINAL ZONE SOIL
PAH SIZ-1	PAH SOIL INVESTIGATION ZONE IDENTIFIER
AS SIZ	ARSENIC SOIL INVESTIGATION ZONE IDENTIFIER
SB-26	EXISTING SOIL SAMPLING LOCATION AND IDENTIFIER
	PROPOSED SOIL SAMPLING LOCATION
	PROPOSED TEST PIT LOCATION
GS-15	LOCATION WHERE ROD SOIL CLEANUP LEVEL WAS EXCEEDED

NOTE:

INFORMATION BASED ON TEST TRENCH LOGS AND SOIL BORING LOGS.

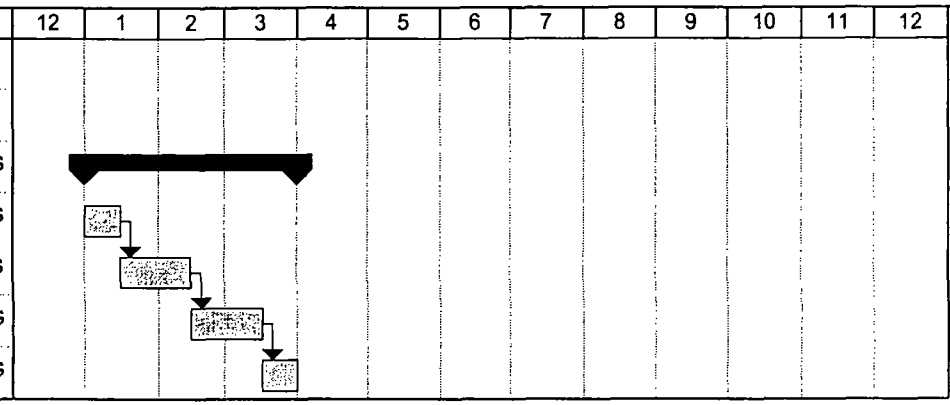
ACTUAL LIMITS OF THE SOIL REMEDIATION ZONES WILL BE DETERMINED FROM SOIL ANALYTICAL DATA OBTAINED DURING THE PREDESIGN STUDIES.

figure 4.1

PRE-DESIGN SOIL INVESTIGATIVE LOCATIONS
WAUKEGAN MANUFACTURED GAS AND COKE PLANT
Waukegan, Illinois

19023-00(002)GN-CO005 MAY 10/2002

Element	Task Name	Duration
S2	**Conduct Soil Predesign Study**	90 days
S2.1	Sample Collection	15 days
S2.2	Laboratory Analysis	30 days
S2.3	Data Analysis	30 days
S2.4	Status Meeting	15 days



Project: 19023 - Soil Predesign Sched
Date: Mon 1/21/02

Summary Task

figure 9.1
SOIL PREDESIGN SCHEDULE
WAUKEGAN MANUFACTURED GAS AND COKE PLANT, Waukegan, Illinois

TABLES

TABLE 3.1

ROD SOIL CLEANUP LEVELS
WAUKEGAN MANUFACTURED GAS AND COKE PLANT SITE
WAUKEGAN, ILLINOIS

Chemical	*Commercial/Industrial RHE*[1] *mg/kg*[2]	*Utility/Construction RHE mg/kg*
Arsenic	2,050	940
Benzo(a)anthracene	1,500	1,160
Benzo(a)pyrene	150	116
Benzo(b)fluoranthene	1,500	1,160
Dibenzo(a,h)anthracene	150	116
Indeno(1,2,3-cd)pyrene	1,500	1,160
Dibenzofuran	NA	5,390
4-Methylphenol	NA	6,738
Naphthalene	NA	48,556

[1] RHE - Representative high exposure
[2] mg/kg - milligram per kilogram

TABLE 3.2

RI SOIL SAMPLES EXCEEDING FINAL SOIL CLEANUP LEVELS
WAUKEGAN MANUFACTURED GAS AND COKE PLANT SITE
WAUKEGAN, ILLINOIS

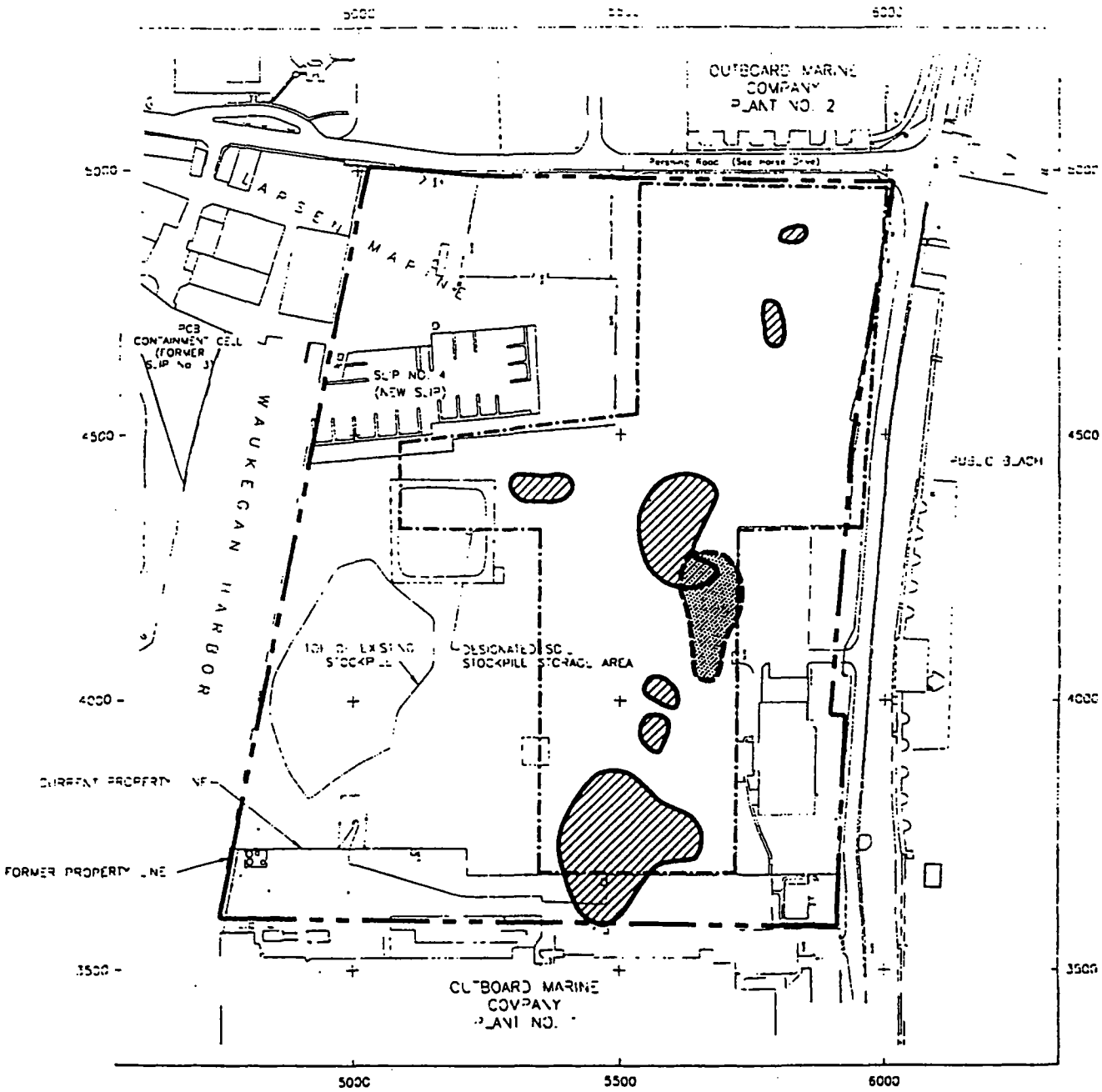
	Soil Cleanup Levels									
	Commercial Industrial	*Utility Construction*	*RI Soil Sample Concentration (mg/kg)* [1]							*IEPA* [2]
Compound	*mg/kg*	*mg/kg*	*TT-0701 4' - 5'*	*TT-2503 3'*	*GS-15*	*SB-4002 2' - 4'*	*SB-2702 2' - 4'*	*SB-5002 2' - 4'*	*SB-5502 2' - 4'*	*X-105*
Arsenic	2,050	940	1,820	1,720J[3]	--[4]	--	--	--	--	956
Benzo(a)anthracene	1,500	1,160	--	--	--	2,700J	--	2,100	1,600	--
Benzo(a)pyrene	150	116	--	--	320	1,600J	140	1,400	950	--
Benzo(b)fluoranthene	1,500	1,160	--	--		1,800J	--	1,600	1,300	--
Dibenzo(a,h)anthracene	150	116	--	--	--	--	--	290J	120J	--
Indeno(1,2,3-cd)pyrene	1,500	1,160	--	--	--	--	--	--	--	--
Dibenzofuran	NA	5,390	--	--	--	--	--	--	--	--
4-Methylphenol	NA	6,738	--	--	--	--	--	--	--	--
Naphthalene	NA	48,556	--	--	--	--	--	--	--	--

[1] mg/kg - milligram per kilogram
[2] IEPA - Illinois Environmental Protection Agency
[3] J - estimated value
[4] -- - Concentration of listed analyte was below soil cleanup level

APPENDICES

APPENDIX A

ROD FIGURE 13



Marginal Zone Soil

PAH Remediation Zone

Arsenic Remediation Zone

NOTE:
Information Based On Test Trench Logs And Soil Boring Logs.

0 300
SCALE IN FEET

Figure 13
ANTICIPATED AREA OF

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APPENDIX B

FIELD SAMPLING AND ANALYSIS PLAN

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TABLE B.4.1 SUMMARY OF ANALYTICAL METHODS

TABLE B.4.2 SUMMARY OF SAMPLING AND ANALYSIS PROGRAM

1.0 INTRODUCTION

This Sampling and Analysis Plan (SAP) has been prepared by Conestoga-Rovers and Associates (CRA) on behalf of the "Performing Respondents" for the Waukegan Manufactured Gas and Coke Plant Site, Waukegan, Illinois (Site). The SAP is Appendix B of the Soil Pre-Design Study Work Plan (Work Plan) submitted in compliance the Record of Decision (ROD) issued for the WCP Site in September 1999.). CRA has been retained by the "Performing Respondents" to implement the scope of work outlined in the Work Plan.

In addition to the Work Plan and SAP, several other documents have been prepared to assist in the overall goal of successfully completing the Soil Pre-Design Study Work Plan, including:

- Quality Assurance Project Plan (provided as Appendix C), and
- Health and Safety Plan (provided as Appendix D).

The purpose of this SAP is to outline the protocols that will be implemented to perform field activities associated with the Soil Pre-Design Study. The SAP supplements the Quality Assurance Project Plan (QAPP) and addresses all sample and field data collection activities. The SAP specifies the sample collection schedules, equipment, and personnel, and includes a Site Plan. The SAP includes a description of monitoring equipment, sampling, and laboratory testing, including:

- description of sampling tasks;
- description of required data collection and laboratory tests;
- required quality assurance and quality control;
- schedule of monitoring frequency;
- identification of monitoring equipment;
- installation of monitoring components; and
- maintenance of site equipment.

The SAP also includes recording and reporting mechanism requirements, including:

- daily operating logs, including the field log book;
- laboratory records;
- mechanisms for reporting emergencies or operational difficulties; and
- personnel and maintenance records.

2.0 GENERAL FIELD PROTOCOLS

2.1 OVERVIEW

General protocols applicable to a number of field activities to be completed under this Soil Pre-Design Study are summarized herein.

2.2 DECONTAMINATION PROCEDURES

2.2.1 DRILLING/EXCAVATION EQUIPMENT

Upon mobilization of the drill rig, direct push, or backhoe test rig to the Site and prior to subsurface explorations, the equipment will be thoroughly steam-cleaned to remove oil, grease, mud, and other foreign matter. Before explorations at each subsequent testing location, the augers, cutting bits, probes, samplers, drill steel, bucket and associated equipment will be decontaminated to prevent cross contamination from the previous drilling/excavation activities. Equipment decontamination will be accomplished by flushing and wiping the components to remove all visible sediments followed by:

i) steam-cleaning and/or high pressure washing with potable water to remove particulate matter and surface films; and

ii) rinsing thoroughly with potable water.

Equipment decontamination will be performed on the existing temporary decontamination pad constructed during the Pilot Project. The decontamination pad will facilitate capture of cleaning fluids for proper management. Collected decontamination fluids will be managed as described in Section 2.4.

2.2.2 SAMPLING EQUIPMENT

Sampling equipment will be decontaminated prior to field use and after each sample is collected to prevent cross-contamination between samples. Whenever practicable, dedicated sampling equipment will be used to minimize the potential for sample cross contamination.

Decontamination of equipment used for collection of samples for laboratory analyses will be performed as follows:

i) wash with potable water and a low-phosphate detergent (Alconox™, Liquinox™ or similar) using a brush, if necessary, to remove all visible foreign matter;

ii) rinse thoroughly with potable water;

iii) rinse thoroughly with distilled water; and

iv) allow the equipment to air dry on a clean plastic sheet as long as possible.

Following the final rinse, equipment will be visually inspected to verify that it is free of soil particulates and other solid material that could contribute to possible sample cross-contamination.

Fluids used for cleaning will not be recycled. Decontamination fluids will be managed as described in Section 2.4.

2.3 FIELD LOG DOCUMENTATION

The field logbook will be a bound document with consecutively numbered pages. The entries for each day will commence on a new page, which will be dated. All entries will be made only in indelible ink. Corrections will be made by marking through the error with a single line, to remain legible, and initialing this action followed by writing the correction. The person making the entries in the logbook will sign or initial each page of entries as they are completed.

The field logbooks generated will be numbered consecutively and maintained by one of CRA's Site representatives. Upon completion of the fieldwork or during periods when fieldwork is not scheduled, the field logbooks will be maintained in CRA's Chicago office. Ultimately, after completion of all stages of fieldwork, the logbooks will be maintained in the document file in CRA's Chicago, Illinois office.

The following information will be recorded in the field logbook for each sample collected:

i) Site location identification;

ii) unique sample identification number;

iii) date and time (in 2400-hour time format) of sample collection;

iv) weather conditions;

v) designation as to the type of sample (groundwater, soil, etc.);

vi) designation as to the means of collection (grab, bailer, etc.);

vii) name of sampler;

viii) analyses to be performed on sample;

ix) any other relevant comments such as odor, staining, texture, filtering, preservation, etc.; and

x) sample location.

Records of equipment maintenance and calibration, and observations on equipment performance will also be recorded in the field logbook. Alternatively, CRA may utilize standard forms to record information such as stratigraphy, well construction and well development.

2.4 WASTE HANDLING PROTOCOLS

Wastes generated during the investigation will include general refuse, soil cuttings from soil borings, and decontamination fluids. General refuse, including plastic sheeting, buckets, paper bags, etc. will be disposed of in the waste receptacles. Daily refuse and personal protective equipment (PPE) will be collected in plastic bags and disposed of as necessary to keep the Site area neat. Soil cuttings from soil borings will be placed into 55-gallon drums and staged near the Remedial Investigation (RI) drum storage area. Decontamination fluids will be staged in 55-gallon drums and staged near the RI drum storage area.

3.0 INVESTIGATIVE PROTOCOLS

3.1 OVERVIEW

The Work Plan outlines a scope of work for a Soil Pre-Design Study to refine the extent of soils that exceed soil cleanup levels for PAHs and arsenic and to characterize the material for treatment and/or disposal. These additional delineation activities may lead to a revision of the estimated quantity of soil to be removed and/or treated.

An intricate part of the Soil Pre-Design Study is the accurate delineation of the impacted soils. In addition, accurate delineation of the volume of clean soils overlying the impacted soils area of equal importance. A soil sampling program has been developed to meet these requirements.

3.2 TEST PIT EXCAVATIONS

3.2.1 TEST PIT LOCATIONS AND INVESTIGATIVE METHODS

Test pits will be excavated to assist in defining the limits and characterize the interiors of the Soil Investigation Zones (SIZs), and to collect soil samples. Test pits will be excavated/advanced to the water table or a maximum depth of approximately 6 feet below ground surface. Test pits excavated across the boundaries of the SIZs will be initiated approximately 10 to 15 feet inside the boundary and will continue outwards past the boundary of the SIZ until field observations indicate that the limits of the contamination have been delineated. Figure B.3.1 depicts the locations of test pits/soil borings

Test pits will also be excavated near surface tar deposits identified during Site walkover inspection. A sufficient number of test pits will be advanced in the near the surface tar deposits to determine the limits of the tar. Soil samples will be collected beyond the limits of the tar deposits for PAH analysis to determine whether soil adjacent to the tar deposits exceed the ROD cleanup objectives.

Test pits will also be excavated in the interior of the SIZs. The interior test pits will be between 5 and 10 feet in length and soil samples will be collected from locations within the interior test pits. Test pit logs will be recorded during investigative activities to document significant observations during test pit excavation and borehole advancement. An example test pit log is provided in Figure B.3.2.

3.2.2 TEST EXCAVATION SAMPLING PROTOCOLS

At a minimum, soil samples will be collected from boundary test pits at the point of test pit origin and the point of test pit termination. This will provide soil samples from inside and outside the SIZ. Soil samples will be collected from the test pits at two-foot intervals through the entire depth of the test pit. It is anticipated that three vertical soil samples will be collected at each sampling location to provide a vertical distribution of PAH and/or arsenic concentrations at each location. Additionally, in the event a soil layer is encountered that differs in composition from the surrounding soil, exhibits visual evidence of significant contamination, and is laterally or vertically significant; a grab soil sample will be obtained for analysis. Layers of tar will also be delineated for future removal. However, samples of the tar layers will not be collected for analysis as these will be assumed to exceed the PAH cleanup levels and will be removed during future soil activities.

Upon completing the test pit excavation, soil samples will be obtained from the test pits using the following protocols.

i) The supervising geologist or engineer will thoroughly inspect the test pit and record this information on test pit logs. Information to be recorded on the test pit logs will include the length and width of the excavation, soil type and composition, soil color, relative moisture content, presence and description of odors, visual evidence of contamination, unique stratigraphic horizons, presence of concrete rubble or other debris. The supervising geologist or engineer will not enter the test pit to conduct this inspection.

ii) The supervising engineer or geologist will identify the soil sample locations in the test pit based on the visual inspection noted above.

iii) At the selected soil sample locations in each test pit, soil samples will be collected in 2-foot intervals from the surface to the top of the water table, or a maximum depth of 6 feet, whichever occurs first.

iv) A new pair of disposable latex or nitrile gloves will be used for each sample. Soil samples will be obtained from each 2-foot depth interval using an appropriate pre-cleaned long-handled sampling tool such as a spade or shovel, trowel, hand shovel, etc. Sampler will measure each 2-foot sample interval down from the surface using a tape measure. The supervising geologist or engineer will not enter the test pit to collect the soil samples.

v) Use of a long-handled sampling devise will be the preferred sample collection methodology. However, if attempts to collect the soil samples with a long-handled

sampling devise are unsuccessful, the backhoe will be used to obtain soil from the desired sampling interval.

vi) Soil samples will be obtained by scraping the sidewall of the test pit through the desired sample interval until a sufficient volume of soil is obtained to fill the sample containers. The soil sample may be homogenized in a stainless steel bowl prior to placement in the laboratory supplied containers to ensure the sample is representative of the entire depth interval.

vii) These procedures will be repeated until soil samples from all the depth intervals at a sample location are obtained. In the event a soil sample is collected from a unique stratigraphic horizon, the sampling procedures noted above will be repeated for the desired sample interval to obtain a soil sample from the unique soil zone.

Collected soil samples will be analyzed for the PAHs and/or arsenic. At several locations, the PAH and Arsenic SIZ overlap (see Figure B.3.1). Samples collected from these locations will be analyzed for arsenic and PAHs.

Up to 5 soil samples from the PAH SIZ, 4 soil samples from the Designated Soil Stockpile (DSS), and up to 3 soil samples from the Arsenic SIZ will be analyzed for geotechnical parameters. Soil samples for bulk density analysis will be collected using Direct-Push technology (DPT) to obtain a minimally disturbed soil sample. Table B.3.1 summarizes soil geotechnical methods.

Upon completion, each test pit will be backfilled with excavated soil, recompacted to match previous grade, as practicable, and seeded with a standard lawn seed mixture. Completed test pit locations will be staked and surveyed by a professional surveyor.

3.3 SOIL BORINGS

3.3.1 DESIGNATED SOIL STOCKPILE

The location of the DSS is shown on Figure B.3.1. The DSS will be divided into quadrants one soil sample will be collected from each of the four quadrants for characterization. A soil boring will be advanced in each of the quadrants (as illustrated of Figure B.3.1) using DPT. Soil samples will be obtained through the entire depth interval. A composite soil sample will be obtained of the entire depth interval at each sampling location. Soil sampling will terminate at an elevation of approximately one foot above surrounding grade to prevent accidental penetration of the DSS underliner during soil sampling activities.

Soil sample collection protocols for the DSS are summarized below.

i) The DSS will be divided into quadrants and one borehole location will be spotted in each quadrant.

ii) To ensure the underliner is not accidentally punctured, the elevation of each borehole location relative to surrounding grade will be shot. The total depth of each boring will be a minimum of 1 foot less that the difference in elevation between the borehole location and the ground surface.

iii) The DPT sample tool will be advanced through the desired interval and soil samples will be collected in acetate liners.

iv) Soil samples will be extracted from the acetate liners by cutting the liner lengthwise using a clean utility knife.

v) The soil will be placed into a clean stainless steel mixing bowl and the sample will be composited and placed into laboratory-supplied containers. Composite soil samples will be collected by placing representative sample aliquots from the separate depth intervals at each soil boring location into a pre-cleaned stainless-steel bowl. The soils within the stainless-steel bowl will be homogenized by mixing the soils with a pre-cleaned stainless-steel spoon or trowel. The composite soil sample will then be placed in laboratory-supplied containers and sent to the laboratory for analyses.

vi) Soil samples for bulk density analysis will be collected from a separate borehole using DPT and will not be composited in order to obtain a minimally disturbed soil sample.

Observations made during borehole advancement will be recorded on stratigraphic log forms (Figure B.3.3). The samples collected from each of the four soil borings will be submitted for characterization analyses. Waste characterization analyses will include TCLP organic and inorganic analytes, polychlorinated biphenyls, reactivity, soil pH, flash point, sulfate, sulfide, and paint filter tests.

One soil sample from each of the quadrants will be obtained from the DSS for geotechnical analysis. The geotechnical soil samples, with the exception of bulk density, will be obtained from the homogenized sample used to collect the waste characterization samples noted above.

Geotechnical analyses to be performed on representative samples collected from each quadrant. Table B.3.1 summarizes soil geotechnical analytical methods.

3.3.3 SIZ SOIL BORINGS

As discussed in the Work Plan, soil borings will be used at those locations where asphalt pavement is present or the excavation of test pits is otherwise impractical. Soil borings will be advanced using either DPT. Each boring will be advanced to the top of the water table or a maximum depth of 6 feet below ground surface. The contents of each soil core will be classified in the field by a geologist using the Unified Soil Classification System (USCS) and recorded on stratigraphic log forms. Where soil borings are required for delineation of SIZs, soil samples will be collected using DPT. Additionally, soil samples for bulk density will be collected using DPT to obtain minimally disturbed samples. A line of soil borings will be advanced perpendicular to the boundary of the SIZ beginning 10 to 15 feet inside the boundary. Soil borings will proceed outwards, at approximately 10-foot on-center, past the boundary of the SIZ until field observations indicate that the limits of the contamination have been delineated.

In general, soil samples will be collected from the soil borings at two-foot intervals through the entire depth of the test pit or soil boring. It is anticipated that three vertical soil samples will be collected at each sampling location to provide a vertical distribution of PAH and/or arsenic concentrations at each location. Additionally, in the event a soil layer is encountered that differs in composition from the surrounding soil and is laterally or vertically significant, a grab soil sample will be obtained for analysis. Layers of tar will also be delineated for future removal. However, samples of the tar layers will not be collected for analysis as these will be assumed to exceed the PAH cleanup levels and will be removed during future soil activities.

Soil samples will be obtained from boreholes for visual classification and laboratory analysis. Soil samples slated for chemical analysis will be collected using the procedures outlined below.

i) A new pair of disposable latex or nitrile gloves will be used for each sample.

ii) Prior to use at each sampling location, all sampling equipment will be decontaminated in accordance with Section 2.0.

iii) A DPT sampler will be advanced through the designated sampling interval, and samples will be collected in acetate liners.

iv) The sample device will be opened and the soil inspected and described by the supervising geologist or engineer. Observations will be recorded on stratigraphic logs.

v) Upon selection for analysis, soil will be transferred to a laboratory supplied sample container, sealed, labeled, and sent directly to the project laboratory under Chain-of-Custody protocols.

Collected soil samples will be collected and analyzed for the PAHs and/or arsenic. At several locations, the PAH and Arsenic SIZ overlap (see Figure B.3.1). Samples collected from these locations will also be analyzed for arsenic and PAHs. The procedure described above will be repeated as necessary to obtain soil for geotechnical analysis. Geotechnical analyses will be performed on representative samples collected from the Arsenic SIZ and PAH SIZ as summarized in Table B.3.1.

Soil cuttings and cores will be containerized for future disposal. Boreholes will be backfilled to near surface with a bentonite. The remainder of the borehole will be backfilled with soil. Completed soil boring locations will be staked and later surveyed by a professional surveyor.

3.4 SURVEYING

Test pits excavated, soil borings advanced, and surficial free product locations identified during the soil pre-design study will be surveyed for horizontal and vertical control. An Illinois-registered land surveyor will perform the surveying activities. Locations will be surveyed to the nearest 0.5 foot for horizontal control and to the nearest 0.01 foot for vertical control. Vertical coordinates will be referenced to U.S. Geological Survey Average Mean Sea Level datum.

4.0 ANALYTICAL PLAN

4.1 OVERVIEW

Soil samples collected during the Soil Pre-Design Study will be analyzed for PAHs, arsenic, and the waste characterization parameters listed on Table B.4.1. Severn Trent Laboratories of North Canton, Ohio (STL) will perform analyses. The Soil Pre-Design Study sampling and analytical program is summarized in the QAPP (Appendix C of this Work Plan).

4.2 SAMPLE HANDLING AND DOCUMENTATION PROTOCOLS

4.2.1 SAMPLE LABELING

Each sample will be labeled with a unique sample number that will facilitate tracking and cross-referencing of sample information. The sample numbering system to be used is described as follows:

Example: GW-MMDDYY-XX-001

where:

S	-	designates types of sample (GW-groundwater, S-soil, SD-sediment, SW-surface water)
MMDDYY	-	designates date of collection presented as month/day/year
XX	-	designates sampler's initials
001	-	designates sequential number starting with 001 at the start of the project

Field blank and field duplicate samples also will be numbered with a unique sample number, consistent with the numbering system described above, to prevent laboratory bias of field QC samples.

4.2.2 SAMPLE CONTAINERS AND HANDLING

Required sample containers, sample preservation methods, maximum holding times, and filling instructions are provided in the QAPP. Samples will be placed in appropriate sample containers, labeled, and properly sealed. Sample labels will include

sample number, date and time of collection, and analyses to be performed. Samples will be cushioned within the shipping coolers by the use of bubble pack. Samples will be kept cool by the use of plastic bags of ice, as required.

Samples will be shipped by commercial courier or hand delivered on a regular basis to the project laboratory. The exception to this will be samples that are collected on a Saturday, Sunday or holiday. For samples collected on a Sunday or holiday, additional ice will be placed in the coolers, as required, and the coolers will be sealed and kept under surveillance by a CRA representative. Immediately prior to shipment, on the next business day, the CRA representative will check the samples to ensure that the samples have been stored appropriately and have not been tampered with.

Two seals comprised of the engineer's chain-of-custody tape will be placed over the lid on the front and back of each shipping cooler prior to shipment to secure the lid and provide evidence that the samples have not been tampered with en route to the laboratory. Clear tape will be placed over the seals to ensure that they are not accidentally broken during shipment. The on-Site CRA representative conducting the sampling will be responsible for packaging the samples and sealing and delivering the cooler to an overnight courier.

Upon receipt of the cooler at the laboratory, the cooler will be inspected by the designated sample custodian. The sample custodian will note the condition of the cooler and seal on the chain-of-custody form. The sample custodian will document the date and time of receipt of the cooler and sign the chain-of-custody forms.

The sample custodian then will check the contents of the cooler with those samples listed on the chain-of-custody form. If damage or discrepancies are noticed, they will be recorded in the remarks column of the chain-of-custody form, dated and signed. They will be reported to the laboratory supervisor who will inform the laboratory manager and QA officer.

Sample disposal will be the responsibility of the laboratory. Upon disposal, the laboratory shall sign the next open "Relinquished by" box, and the word "Disposed" shall be written in the "Received by" box.

4.2.3 CHAIN-OF-CUSTODY FORMS

Chain-of-custody records will be used to track all samples from time of sampling to the arrival of samples at the laboratory. Each shipping container being sent to the

laboratory will contain a chain-of-custody form. The chain-of-custody form consists of four copies, which are distributed to the sampler, to the shipper, to the contract laboratory, and to the office file of the engineer. The sampler and shipper will maintain their copies while the other two copies are enclosed in a waterproof enclosure within the sample container. The laboratory, upon receiving the samples, will complete the remaining copies. The laboratory will maintain one copy for its records. The executed original will be returned to the engineer with the data deliverables package.

A typical chain-of-custody form is presented in Figure B.4.1.

4.3 QUALITY CONTROL

Rinsate blanks, field duplicates, and matrix spike samples will be collected and analyzed to assess the quality of the data resulting from the field sampling program. Rinsate 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.

Rinsate blank samples are analyzed to document that decontamination procedures are not causing cross-contamination between samples. A rinsate blank sample will consist of pouring distilled/deionized water over pre-cleaned sampling equipment and into laboratory supplied sample containers. Rinsate blanks will be obtained at a rate of one per every 10 investigative samples. Field duplicates are obtained to assess the reproducibility of the analytical data. Field duplicates will be prepared by placing a sufficient volume of soil in a clean stainless steel mixing bowl and thoroughly homogenizing the sample with a stainless steel spoon. The sample and duplicate sample will be obtained from the homogenized aliquot of soil. Each sample will be assigned a unique sample identification number. Field duplicates will be obtained at a rate of one per 20 investigative samples analyzed for arsenic and PAHs

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 samples or fewer investigative samples. MS/MSD samples are investigative samples and no additional volume is required. MS/MSD samples will be identified on the chain-of-custody forms.

The general level of the QC effort will involve collection of one rinsate blank per ten or fewer investigative samples or a minimum of one per sampling event. Field duplicate

and MS/MSD samples will consist of one MS/MSD per twenty or fewer investigative samples or a minimum of one per event. The estimated number of investigative, rinsate, field duplicates, and MS/MSD samples to be collected is provided in Table B.4.2.

The level of QC effort provided for soil samples will be equivalent to the level of QC effort specified in "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods", SW-846 3rd edition, November 1986, with revisions (SW-846). The level of QC effort for geotechnical analyses will be equivalent to the level of QC effort specified in "Annual Book of ASTM Standards", American Society for Testing and Materials, 1995 (ASTM).

The Quality Assurance Project Plan (QAPP) prepared for this project provides specific details regarding protocols and checks associated with laboratory analyses and sampling procedures.

4.4 ANALYTICAL LABORATORY

Samples for chemical analysis will be delivered to the following laboratory:

Severn Trent Laboratories (STL)
4101 Shuffel Drive NW
North Canton, Ohio 44720
Telephone: (330) 497-9396
Telefax: (330) 497-0772

5.0 PROJECT ORGANIZATION AND RESPONSIBILITY

CRA, as consultant to the WCP Group, has overall responsibility for all stages of the investigation. CRA will perform the sampling activities. All samples will be analyzed by STL of North Canton, Ohio.

All subcontracted firms will provide project management as appropriate to their responsibilities. CRA will maintain a file copy of all laboratory deliverables. All final project deliverables will be issued by CRA at the explicit direction of the WCP PRP Group. A summary of each of the key person's responsibilities is presented in the QAPP.

Primary responsibility for project quality rests with CRA's Project Manager. Independent quality assurance will be provided by the laboratory's Project Manager and QA Officer prior to release of all data to CRA.

During the sampling stage of the project, daily telephone contact between the field sampling personnel and the laboratory subcontractor will occur. The laboratory will provide status updates by means of preliminary data telefacsimiles. Should unexpected delays or other problems with the laboratory analyses occur, these would be communicated directly to CRA's Project Coordinator for resolution. Daily meetings with subcontractors will be held to update the progress of the project activities.

Key CRA contacts during the soil pre-design investigation activities are:

Alan Van Norman - Project Manager	519-884-0510
Steven Wanner - Project Coordinator	773-380-9933
Stephen Castagneri - Quality Assurance Officer	773-380-9933
Walter Pochron – Field Coordinator and Field Quality Assurance Officer	773-380-9933
Matthew Lazaric – Health and Safety Officer	773-380-9933

6.0 HEALTH AND SAFETY PLAN

A Site-specific Health and Safety Plan (HASP) has been developed to address activities to be performed at the Site. The HASP is provided as Appendix D to this Work Plan. All field activities will be conducted in accordance with the health and safety protocols outlined in the HASP. The HASP may be modified in the future to incorporate additional activities proposed during supplemental activities.

7.0 PROJECT DATA MANAGEMENT

All field activities will be recorded daily in the field logbooks. Upon completion of the fieldwork or during periods when fieldwork is not scheduled, the field logbooks will be maintained in CRA's Chicago office. All data originals, including field forms, chain-of-custody forms, and laboratory data deliverables will be maintained in CRA's Chicago office.

Computer-based data tables will be verified with original laboratory certificates of analyses and with the original field logbook or field-generated forms. Both hard paper copies and computer-based versions of summary tables will be saved in the files. Land survey data will be maintained in the project file as hard copy, and the electronic survey data will be stored with the project's AUTOCAD files.

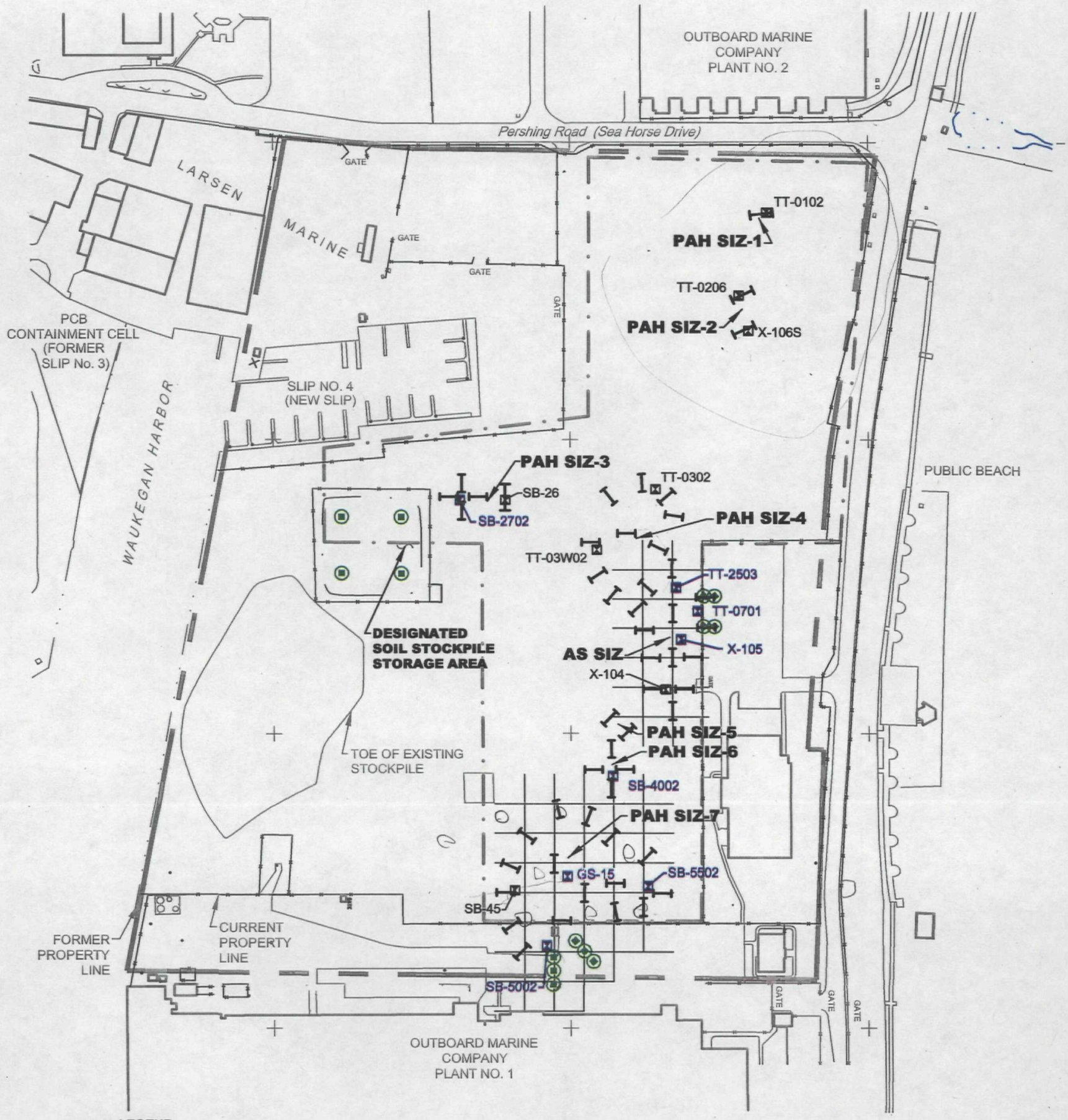

figure B.3.1

PRE-DESIGN SOIL INVESTIGATIVE LOCATIONS
WAUKEGAN MANUFACTURED GAS AND COKE PLANT
Waukegan, Illinois

19023-00(002)GN-CO010 MAY 10/2002

TEST PIT STRATIGRAPHY LOG

PAGE ____ OF ____

PROJECT NAME _____
PROJECT NUMBER _____
CLIENT _____
LOCATION _____

CONTRACTOR _____
SURFACE ELEVATION _____
WEATHER (A.M.) _____
(P.M.) _____

TEST PIT DESIGNATION _____
DATE/TIME STARTED _____
DATE/TIME COMPLETED _____
TEST PIT METHOD _____
CRA SUPERVISOR _____

STRATIGRAPHIC INTERVALS (DEPTHS IN ft/m BGS)			SAMPLE DESCRIPTION	SAMPLE DETAILS			GEOLOGIC PROFILE
FROM	AT	TO	ORDER OF DESCRIPTORS: SOIL TYPE SYMBOL(S) – MAIN COMPONENT(S), (NATURE OF DEPOSIT), SECONDARY COMPONENTS, RELATIVE DENSITY/CONSISTENCY, GRAIN SIZE/PLASTICITY, GRADATION/STRUCTURE, COLOUR, MOISTURE CONTENT, SUPPLEMENTARY DESCRIPTORS NOTE: PLASTICITY DETERMINATION REQUIRES THE ADDITION OF MOISTURE IF THE SAMPLE IS TOO DRY TO ROLL (INDICATE IF MOISTURE WAS ADDED OR NOT).	SAMPLE #	SAMPLE	INTERVAL	PID / FID (ppm)	

NOTES AND COMMENTS CRA	

figure B.3.2

TYPICAL TEST PIT LOG FORM
WAUKEGAN MANUFACTURED GAS AND COKE PLANT
Waukegan, Illinois

STRATIGRAPHY LOG (OVERBURDEN)

PAGE ____ OF ____

PROJECT NAME _____
PROJECT NUMBER _____
CLIENT _____
LOCATION _____

DRILLING CONTRACTOR _____
DRILLER _____
SURFACE ELEVATION _____
WEATHER (A.M.) _____
(P.M.) _____

HOLE DESIGNATION _____
DATE/TIME STARTED _____
DATE/TIME COMPLETED _____
DRILLING METHOD _____
CRA SUPERVISOR _____

STRATIGRAPHIC INTERVALS (DEPTHS IN ft/m BGS)			SAMPLE DESCRIPTION	SAMPLE DETAILS								PID / FID (ppm)	CHEMICAL ANALYSIS	GRAIN SIZE
FROM	AT	TO	ORDER OF DESCRIPTORS: SOIL TYPE SYMBOL(S) – MAIN COMPONENT(S), (NATURE OF DEPOSIT), SECONDARY COMPONENTS, RELATIVE DENSITY/CONSISTENCY, GRAIN SIZE/PLASTICITY, GRADATION/STRUCTURE, COLOUR, MOISTURE CONTENT, SUPPLEMENTARY DESCRIPTORS NOTE: PLASTICITY DETERMINATION REQUIRES THE ADDITION OF MOISTURE IF THE SAMPLE IS TOO DRY TO ROLL (INDICATE IF MOISTURE WAS ADDED OR NOT).	SAMPLE #	SAMPLING METHOD	PENETRATION RECORD SPLIT SPOON BLOWS (RECORD N-VALUES & RECOVERIES) 6"	6"	6"	6"	SAMPLE INTERVAL			

NOTES AND COMMENTS

CRA

DEPTH OF BOREHOLE CAVING _____ DEPTH OF FIRST GROUNDWATER ENCOUNTER _____ TOPSOIL THICKNESS _____

WATER LEVEL IN OPEN BOREHOLE ON COMPLETION _____, AFTER __HOURS __

COMPLETION DETAILS: _____

NOTE: FOR EACH SPLIT-SPOON SAMPLE, RECORD BLOW COUNTS, N-VALUE, SAMPLE RECOVERY LENGTH, AND SAMPLE INTERVAL.

figure B.3.3

TYPICAL STRATIGRAPHIC LOG FORM
WAUKEGAN MANUFACTURED GAS AND COKE PLANT
Waukegan, Illinois

CRA
CONESTOGA-ROVERS & ASSOCIATES
8615 West Bryn Mawr Avenue
Chicago, IL 60631 (773)380-9933

CHAIN OF CUSTODY RECORD

SHIPPED TO (Laboratory Name):

REFERENCE NUMBER:

PROJECT NAME:

SAMPLER'S SIGNATURE: ______________ PRINTED NAME: ______________

SEQ. No.	DATE	TIME	SAMPLE No.	SAMPLE MATRIX	No. OF CONTAINERS	PARAMETERS									REMARKS
TOTAL NUMBER OF CONTAINERS															

SAMPLE

RELINQUISHED BY: ①	DATE: TIME:	RECEIVED BY: ②	DATE: TIME:
RELINQUISHED BY: ②	DATE: TIME:	RECEIVED BY: ③	DATE: TIME:
RELINQUISHED BY: ③	DATE: TIME:	RECEIVED BY: ④	DATE: TIME:

METHOD OF SHIPMENT: AIR BILL No.

White –Fully Executed Copy Yellow –Receiving Laboratory Copy Pink –Shipper Copy Goldenrod –Sampler Copy	SAMPLE TEAM:	RECEIVED FOR LABORATORY BY: DATE: TIME:

figure B.4.1

TYPICAL CHAIN-OF-CUSTODY RECORD
WAUKEGAN MANUFACTURED GAS AND COKE PLANT
Waukegan, Illinois

CRA

19023-00(002)GN-CO006 MAY 10/2002

TABLE B.3.1

SUMMARY OF GEOTECHNICAL METHODS
WAUKEGAN MANUFACTURED GAS AND COKE PLANT SITE
WAUKEGAN, ILLINOIS

Parameter	*Analysis Method*[1]
Particle Size	ASTM D 422/D 1140
Bulk Density	ASTM D 2437
Moisture Content	ASTM D 2216
Total Organic Carbon	ASTM D 2974
Heat Content[2]	ASTM D 2015

[1] ASTM - American Society for Testing and Materials

[2] Soil samples for heat content analysis will be collected from the Designated Soil Stockpile and PAH Soil Investigation Zone. Soil samples from the Arsenic Soil Investigation Zone not be analyzed for heat content.

TABLE B.4.1

SUMMARY OF ANALYTICAL METHODS
WAUKEGAN MANUFACTURED GAS AND COKE PLANT SITE
WAUKEGAN, ILLINOIS

Parameter[1]	*Analysis Method*
PAHs	SW-846 8270C[2]
Total Arsenic	SW-846 6010B
TCLP Extraction	SW-846 1311
TCLP VOCs	SW-846 8260B
TCLP SVOCs	SW-846 8270C
TCLP Pesticides	SW-846 8081A
TCLP Herbicides	SW-846 8151A
TCLP Metals	SOPs for SW-846 6010B/7470A
Reactive Sulfide	SW-846 Section 7.3.4.2
Reactive Cyanide	SW-846 Section 7.3.3.2
Corrosivity (as pH)	SW-846 9045C
Ignitability (as flashpoint)	SW-846 1010
Paint Filter Test (free liquids)	SW-846 9095A
PCBs	SW-846 8082
Sulfate[3]	EPA 300.0 modified)
Sulfide[3]	SW-846 9030B

1 PAHs - Polynuclear Aromatic Hydrocarbons
VOCs - Volatile Organic Compounds
SVOCs - Semivolatile Organic Compounds
PCBs - Polychlorinated Biphenyls

2 SW-846 - "Test Methods for Evaluating Solid Wastes, Physical/Chemical Methods", EPA SW-846, 3rd Edition with Updates I through III, November 1986.

3 Soil samples for sulfate and sulfide analysis will be collected from the Designated Soil Stockpile (DSS) and PAH Soil Investigation Zone. Soil samples from the Arsenic Soil Investigation Zone will not be analyzed for heat content.

TABLE B.4.2

SUMMARY OF SAMPLING AND ANALYSIS PROGRAM
WAUKEGAN MANUFACTURED GAS AND COKE PLANT SITE
WAUKEGAN, ILLINOIS

				QC Samples			
Location	*Sample Matrix*	*Laboratory Parameters* [1]	*Number of Samples*	*Field Blanks*	*Field Duplicates*	*MS/MSD* [2] *MS/DUP*	*Total*
Designated Soil Stockpile (DSS)	Soil	Waste Characterization	4	0	0	0	4
	Soil	Geotechnical	4	0	0	0	4
PAH Investigation Zone (PAH SIZ)	Soil	Site-specific SVOCs	270	27	14	14	325
		Geotechnical	5	0	0	0	5
	Soil	Waste Characterization	5	0	0	0	5
Arsenic Investigation Zone (As SIZ)	Soil	Arsenic	78	8	4	4	94
	Soil	Geotechnical	3	0	0	0	3
	Soil	Waste Characterization	2	0	0	0	2

[1] Waste Characterization includes Toxic Characteristic Leaching Procedure (TCLP) VOCs, TCLP Semivolatile Organic Compounds (SVOCs), TCLP pesticides, TCLP herbicides, TCLP metals, polychlorinated biphenyls (PCBs), reactive sulfide, reactive cyanide, corrosivity, sulfate (DSS and PAH SIZ only), sulfide(DSS and PAH SIZ only), paint filter test for free liquids and ignitability.
Geotechnical analyses include grain size distribution, bulk density, heat content (DSS and PAH SIZ only), and moisture content.

[2] Matrix spike/matrix duplicate (MS/MSD) analyses will be performed for PAH analyses. MS/MSD samples will be collected at a frequency of one per group of twenty (20) or fewer investigative samples. Double the normal sample volumes will be collected for PAHs.
MS/MSD or Matrix spike/laboratory duplicate (MS/DUP) analyses will be performed for inorganics analyses. Samples designated for MS/MSD or MS/DUP analyses will be collected at a frequency of one per group of twenty (20) or fewer investigative samples.

APPENDIX C

QUALITY ASSURANCE PROJECT PLAN

QUALITY ASSURANCE PROJECT PLAN (QAPP)

PROJECT TITLE: REMEDIAL DESIGN/SOIL PRE-DESIGN STUDY
WAUKEGAN MANUFACTURED GAS AND COKE PLANT SITE
WAUKEGAN, ILLINOIS

REVISION NUMBER: 0

REVISION DATE: January 21, 2002

PREPARED BY: CONESTOGA-ROVERS & ASSOCIATES

PREPARED FOR: Performing Respondents

Approved By: _____ Date: 4/30/02
Project Manager - CRA
Alan Van Norman

Approved By: _____ Date: 4-29-02
QA Officer - CRA
Stephen Castagneri

Approved By: _____ Date: 4/24/02
Field QA Officer - CRA
Walter Pochron

Approved By: _____ Date: 5/6/02
Project Manager - STL
Amy McCormick

Approved By: _____ Date: 5/6/02
QA Officer - STL
Mary Beth Lambert

Approved By: _____ Date: 4/24/02
U.S. EPA Remedial Project Manager
Kevin Adler

Approved By: _____ Date: 4/24/02
U.S. EPA Region 5 Quality Assurance Reviewer

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QAPP DISTRIBUTION LIST

Name/Organization	*Number of Copies*
Kevin Adler - U.S. EPA	2
Alan Van Norman - CRA	1
Steve Castagneri - CRA	1
Walt Pochron - CRA	1
Mary Beth Lambert - STL	1
Amy McCormick - STL	1

LIST OF ACRONYMS AND SHORT FORMS

CERCLA	-	Comprehensive Environmental Response, Compensation and Liability Act
CLP SOW	-	Contract Laboratory Program Statement of Work
CRA	-	Conestoga-Rovers & Associates
DQOs	-	Data Quality Objectives
FSP	-	Field Sampling Plan
FSS	-	Field Support Section
GC/MS	-	Gas Chromatography/Mass Spectroscopy
IEPA	-	Illinois Environmental Protection Agency
LCS	-	Laboratory Control Sample
MS/DUP	-	Matrix Spike/Laboratory Duplicate
MS/MSD	-	Matrix Spike/Matrix Spike Duplicate
PAHs	-	Polynuclear Aromatic Hydrocarbons
PARCCS	-	Precision, Accuracy, Representativeness, Comparability, Completeness, Sensitivity
PE	-	Performance Evaluation
%R	-	Percent Recovery
%RSD	-	Percent Relative Standard Deviation
RCRA	-	Resource Conservation and Recovery Act
QA	-	Quality Assurance
QA/QC	-	Quality Assurance/Quality Control
QAPP	-	Quality Assurance Project Plan
QC	-	Quality Control
RD	-	Remedial Design
RI	-	Remedial Investigation
ROD	-	Record of Decision
RI/FS	-	Remedial Investigation/Feasibility Study
RPD	-	Relative Percent Difference
Site	-	Waukegan Manufactured Gas and Coke Plant Site
SDG	-	Sample Delivery Group
SOPs	-	Standard Operating Procedures
SOW	-	Statement of Work
SVOC	-	Semivolatile Organic Compounds
SW-846	-	"Test Methods for Evaluating Solid Waste, Physical/Chemical Methods", EPA SW-846, 3rd Edition with Updates I through III
TAL	-	Target Analyte List
TCL	-	Target Compound List
TCLP	-	Toxicity Characteristic Leaching Procedure
U.S. EPA	-	United States Environmental Protection Agency
VOCs	-	Volatile Organic Compounds
WCP	-	Waukegan Manufactured Gas and Coke Plant

1.0 INTRODUCTION

United States Environmental Protection Agency (U.S. EPA) policy requires that all work preformed by or on behalf of U.S. EPA involving the collection of environmental data be implemented in accordance with a U.S. EPA-approved Quality Assurance Project Plan (QAPP). The QAPP is a planning document that provides a "blueprint" for obtaining the type and quantity of data needed to support environmental decision making. The QAPP integrates all technical and quality aspects of a project and documents all quality assurance (QA), quality control (QC), and technical activities and procedures associated with planning, implementing, and assessing environmental data collection operations.

This QAPP has been prepared by Conestoga-Rovers & Associates (CRA) in accordance with the U.S. EPA QAPP guidance documents "EPA Requirements for Quality Assurance Project Plans", EPA QA/R-5, March 2001, "EPA Guidance for Quality Assurance Project Plans", EPA QA/G-5, February 1998, and "Region 5 Instructions on the Preparation of a Superfund Division Quality Assurance Project Plan, Revision 0", June 2000. In accordance with these documents, there are four basic groups of elements that must be included in a QAPP. These four groups and associated elements follow:

- Group A - Project Management. The elements in this group include all aspects of project management, project objectives, and project history.
- Group B - Data Generation and Acquisition. The elements in this group include descriptions of the design and implementation of all measurement systems that will be used during the project.
- Group C - Assessment/Oversight. The elements in this group encompass the procedures used to ensure proper implementation of the QAPP.
- Group D - Data Validation and Usability. The elements in this group cover the QA activities that occur after the data collection phase of the project is completed.

The elements that comprise project management, data generation and acquisition, assessment/oversight, and data validation and usability for the Remedial Design (RD) activities to be conducted at the Waukegan Manufactured Gas and Coke Plant Site (Site) in Waukegan, Illinois are documented in this QAPP. This QAPP is Appendix C of "Soil Pre-Design Study Work Plan, Waukegan Manufactured Gas and Coke Plant Site, Waukegan, Illinois" (Soil Pre-Design Study Work Plan). This QAPP will be modified as

necessary to address additional studies and other work associated with the RD at the Site. The modifications to this QAPP will be submitted with future work plans associated with the RD.

2.0 PROJECT ORGANIZATION

The responsibilities of management, QA personnel, field personnel, and laboratory personnel are provided in the following subsections. Additionally, any special training/certification requirements for the project are identified and a organization chart that identifies the lines of communication among the participants in the RD activities is presented herein.

2.1 MANAGEMENT RESPONSIBILITIES

The "Performing Respondents" have selected CRA as one of the technical consultants for the RD activities at the Site. CRA has technical responsibility for the soil pre-design data collection activities at the Site. CRA's Project Manager is ultimately responsible for ensuring that the project objectives are achieved. CRA's Project Manager has selected a project team consisting of CRA's technical personnel (engineering, chemistry, and data management), QA personnel, and the analytical laboratory. CRA's Project Manager for the RD activities and his specific responsibilities follow:

Alan Van Norman - Project Manager – CRA

- technical representation for Performing Respondents
- overview of field activities
- overview of laboratory activities
- advise on corrective actions
- preparation and review of reports
- coordinate CRA's technical group
- final evidence file custodian
- approval of the QAPP

The analytical laboratory's Project Manager is responsible for ensuring that the project objectives are achieved by the laboratory. The laboratory selected for this project is Severn Trent Laboratories, Inc. (STL) located at 4101 Shuffel Drive, NW in North Canton, Ohio (phone: 330-497-9396; fax: 330-497-0772). The laboratory's Project Manager and her specific responsibilities follow:

Amy McCormick - Project Manager - STL

- ensures all resources of the laboratory are available on an as-required basis
- review of final analytical reports
- approve final reports prior to submission to CRA

The U.S. EPA Region 5 Remedial Project Manager is responsible for overview of this project. He also is responsible for submitting this QAPP and any subsequent revisions or amendments to the appropriate U.S. EPA personnel for review and approval and for providing approval of the QAPP. Kevin Adler is the Remedial Project Manager for the RD at the Site.

The Illinois Environmental Protection Agency (IEPA) representative is responsible for reviewing and providing comments to U.S. EPA on project plans for the RD activities. Erin Rednour is IEPA's representative for this project.

2.2 QUALITY ASSURANCE RESPONSIBILITIES

Project team members with QA responsibilities include CRA's QA Officer, CRA's Field QA Officer, and the laboratory's QA Officer. These individuals and their specific responsibilities follow:

Steve Castagneri - Quality Assurance Officer - CRA

- overview and review field QA/QC
- review laboratory QA/QC
- perform data validation and assessment
- advise on laboratory corrective action procedures
- preparation and review of QA reports
- QA/QC representation of project activities
- approval of QAPP

Walter Pochron - Field Quality Assurance Officer - CRA

- management of field activities and field QA/QC
- field data assessment
- internal field technical system audits
- technical representation of field activities
- preparation of standard operating procedures (SOPs) for field activities
- implement and document field corrective actions, if necessary
- approval of QAPP

Mary Beth Lambert – QA Officer - STL

- coordinate and overview of laboratory systems audits
- overview of QA/QC documentation
- conduct detailed data review
- implement and document laboratory corrective actions, if required
- technical representation of laboratory QA procedures
- oversee preparation of laboratory SOPs
- approval of the QAPP

The U.S. EPA Region 5 Field Support Section (FSS) Quality Assurance Reviewer is responsible for reviewing and providing final approval of the QAPP.

2.3 FIELD RESPONSIBILITIES

CRA will conduct all field sampling related to the PD activities. The specific procedures for field sample collection are presented in the Field Sampling Plan (FSP), which is Appendix B of the Soil Pre-Design Study Work Plan. Surveying of soil sampling grid locations will be performed by an Illinois-licensed surveyor consistent with the requirements of the FSP.

CRA's field sampling team will consist of technical staff from CRA's Chicago, Illinois office. CRA's Field QA Officer (Walter Pochron) will be responsible for documenting

any non-conformances and subsequent corrective actions. The Field QA Officer or any field team member can identify and report non-conformances.

2.4 LABORATORY RESPONSIBILITIES

STL will perform all analyses of samples collected during the Site activities. Soil samples collected will be analyzed for a select list of semivolatile organic compounds [including certain polynuclear aromatic hydrocarbons, dibenzofuran, and 4-methylphenol (collectively referred to herein as "PAHs" or "Site-Specific SVOCs")] and arsenic. In addition, select soil samples will be analyzed for waste disposal analysis including the Resource Conservation and Recovery Act (RCRA) characteristics of reactivity, ignitability, corrosivity, and toxicity, and sulfate, sulfide, heat content (Btu/lb.), polychlorinated biphenyls (PCBs), and free liquids (using the Paint Filter Test).

A qualified geotechnical laboratory will be retained to analyze a limited number of soil samples for grain size distribution, bulk density, organic carbon content, and moisture content. Specific information regarding the sampling and analysis program is provided in Section 3.3.1 of this QAPP.

The specific responsibilities of laboratory personnel involved in the project follow:

Opal Davis-Johnson - Operations Manager - STL

- coordinate laboratory analyses
- supervise in-house chain-of-custody
- schedule sample analyses
- oversee data review
- oversee preparation of analytical reports

Lois Ezzo - Sample Custodian - STL

- receive and inspect the incoming sample containers
- record the condition of the incoming sample containers
- sign appropriate documents
- verify correctness of chain-of-custody documentation

- notify project manager of any non-conformances identified during sample receipt and inspection
- assign a unique identification number and customer number, and enter each into the sample receiving log
- initiate transfer of the samples to appropriate lab sections
- control and monitor access/storage of samples and extracts

2.5 SPECIAL TRAINING/CERTIFICATION REQUIREMENTS

CRA field sampling team members are required to have received the 40-hour Hazardous Waste Operations and Emergency Response (HAZWOPER) safety training and annual 8-hour refresher courses required by 29 CFR Parts 1910 and 1926. On-Site subcontractor personnel involved in invasive activities (e.g., drilling, excavation) are required to have received the same training. The subcontractor is responsible for compliance of their personnel with the applicable regulations.

Laboratory personnel training records are maintained at the laboratory. No special training or certification requirements are required for the laboratory for this project.

The surveyor used for the project will be an Illinois-licensed surveyor.

2.6 PROJECT ORGANIZATION

Figure 2.1 presents the organizational chart for the soil pre-design data collection activities.

3.0 PROBLEM DEFINITION/BACKGROUND INFORMATION

The purpose of the soil pre-design study and background information for the Site are presented in the following sections.

3.1 PROBLEM DEFINITION

The purpose of the soil pre-design study is to refine the extent of soils that exceed soil cleanup levels for PAHs and arsenic and to characterize the material for treatment and/or disposal. These delineation activities may lead to a revision of the estimated quantity of soil to be removed and/or treated.

3.2 BACKGROUND INFORMATION

The Site background is provided in Section 2.0 of the Soil Pre-Design Study Work Plan.

3.2.1 SITE DESCRIPTION AND HISTORY

The Site occupies 36 acres in Waukegan, Illinois on a peninsula separating Waukegan Harbor on the west from Lake Michigan on the east. Commercial and industrial land and a harbor surround the Site on the north, west, and south. To the east of the Site lies Waukegan Beach recreational area. The Site was initially purchased and developed as a creosote wood-treating plant in 1908. The creosote plant was dismantled sometime after 1917. The Site was then developed as a large manufactured gas and coke plant and operated under various owners until 1969. The coke plant structures were subsequently demolished in 1972 and the Site was filled and leveled. Between 1973 and 1989 the Site was used for various activities including fire training, public parking, and snowmobile testing. The northwest portion of the Site is currently used for seasonal boat and trailer storage.

3.2.2 PREVIOUS INVESTIGATIONS AND RESPONSE ACTIONS

Results of previous investigations and response actions are provided in Section 2.2 of the Soil Pre-Design Study Work Plan.

3.2.3 PAST DATA COLLECTION ACTIVITIES

A Remedial Investigation/Feasibility Study (RI/FS) was conducted at the Site between 1992 and 1998. Results of the RI/FS data collection activities identified coal tar compounds, arsenic, ammonia, phenols and several other compounds as chemicals of concern at the Site.

3.2.4 CURRENT STATUS

A Remedial Design Work Plan (RDWP) for the Site was prepared and submitted to U.S. EPA in August 2001 and was subsequently approved in December 2001. The RDWP was prepared consistent with the Remedial Design Scope of Work (RD SOW), which is Attachment II to the Administrative Order on Consent for Remedial Design (RDAOC) at the Waukegan Coke Plan Site, USEPA Docket No. V-W-01-C-651. The soil pre-design study is a component of the RDWP.

3.3 PROJECT/TASK DESCRIPTION

The scope of work to be completed during the soil pre-design study consists of the following tasks:

i) grid the Site and conduct a walkover inspection to identify any areas of tar at the ground surface;

ii) conduct a survey to establish the locations of the PAH and arsenic soil investigation zones (SIZs) and surficial tar deposits;

iii) collect waste characterization soil samples from the Designated Soil Stockpile (DSS).

iv) delineate the limits of the PAH and Arsenic SIZs with test pits, soil borings, and collection of soil samples for laboratory analysis;

v) collect and analyze characterization samples from the PAH and Arsenic Investigation Zones.

vi) surveying the test pre-design investigative locations; and

vii) evaluate and report the results of the Soil Pre-Design Study.

This QAPP is applicable to task iii, iv, v, and vii, above. Descriptions of these tasks are provided in the following subsections.

3.3.1 DESIGNATED SOIL STOCKPILE

The location of the DSS is identified on Figure 3.1 of the Soil Pre-Design Study Work Plan. The volume of soil in the DSS is estimated to be approximately 4,500 cubic yards. The soil within the DSS was generated during the construction of Slip No. 4. The DSS is lined and covered. The objective of the pre-design studies for the DSS is to characterize the soil to allow an evaluation of disposal and/or treatment alternatives. The sampling program includes dividing the DSS into four quadrants and collecting one soil sample from each of the four quadrants for characterization. The samples collected from each of the four soil borings will be submitted for waste characterization and geotechnical analyses.

3.3.2 PAH AND ARSENIC SOIL INVESTIGATION ZONES

The proposed soil sampling locations at the PAH and Arsenic SIZs are illustrated on Figure 4.1 of the Soil Pre-Design Work Plan. Test pits and soil borings will be excavated/advanced to the water table or a maximum depth of approximately 6 feet below ground surface. Test pits straddling the boundaries of the SIZs will be initiated approximately 10 to 15 feet inside the boundary and will continue outwards past the boundary of the SIZ until field observations indicate that the limits of the contamination have been delineated. At a minimum, soil samples will be collected from boundary test pits at the point of test pit origin and the point of test pit termination. This will provide soil samples from inside and outside the SIZ. Where soil borings are required for

delineation, a line of soil borings will be advanced perpendicular to the boundary of the SIZ beginning 10 to 15 feet inside the boundary and will proceed outwards at approximately 10-foot on center past the boundary of the SIZ until field observations indicate that the limits of the contamination have been delineated.

Test pits also will be excavated in the interior of the SIZs. The interior test pits will be between 5 and 10 feet in length and soil samples will be collected at one location within the interior test pits.

Collected soil samples will be analyzed for the PAHs and/or arsenic. At several locations, the PAH and Arsenic SIZs overlap (see Work Plan Figure 4.1). Samples collected from these locations will also be analyzed for arsenic and Site-specific SVOCs. Upon completion, each test pit will be backfilled with excavated soil. Completed test pit and soil boring locations will be staked and later surveyed by a professional surveyor.

Test pits will also be excavated near surface tar deposits identified during the Site walkover inspection. A sufficient number of test pits will be advanced in the near surface tar deposits to determine the limits of the tar. Soil samples located beyond the limits of the tar deposits will be collected and analyzed for Site-specific SVOCs to determine whether soil adjacent to the tar deposits exceed the ROD cleanup objectives.

3.3.3 SOIL CHARACTERIZATION

A number of composite soil samples will be prepared by the project laboratory from discrete soil samples collected during the SIZ investigations. Following receipt and evaluation of the pre-design soil analytical data, several soil samples will be composited by the project laboratory, and waste characterization analyses will be conducted on these samples to evaluate soil disposal options. It is anticipated that the soil samples to be composited will be samples located within the limits of the soil investigation zones as determined by pre-design soil sampling activities. Prior to conducting the waste characterization analyses, a plan will be submitted to the U.S. EPA that provides the pre-design soil analytical results, identifies the number of composite samples to be prepared and analyzed, and identifies the pre-design soil samples to be composited.

3.3.4 SOIL DATA VERIFICATION AND VALIDATION

CRA will internally verify the soil sample data by reviewing field documentation and chain-of-custody records. The laboratory will internally verify the data by reviewing and documenting sample receipt, sample preparation, sample analysis (including internal QC checks), data reduction and reporting. The data will be validated by CRA by assessing the precision, accuracy, representativeness, comparability, completeness, and sensitivity (PARCCS) data from field QC samples and internal laboratory QC checks relative to the requirements in this QAPP. Detailed data verification and validation procedures are presented in Section 7.0 of this QAPP.

3.4 PROJECT SCHEDULE

The project schedule is provided as Figure 9.1 in the Soil Pre-Design Study Work Plan.

4.0 QUALITY OBJECTIVES AND CRITERIA FOR MEASUREMENT DATA

The data quality objectives and measurement performance criteria for the PD activities are presented in the following subsections.

4.1 DATA QUALITY OBJECTIVES

Data quality objectives (DQOs) are qualitative and quantitative statements derived from the outputs of each step of the DQO process. The DQO process is a series of planning steps based on the scientific method that is designed to ensure that the type, quantity, and quality of environmental data used in decision making are appropriate for the intended application.

There are seven steps in the DQO process that include:

1. stating the problem;
2. identifying the decision;
3. identifying inputs to the decision;
4. defining the boundaries of the study;
5. developing a decision rule;
6. specifying limits on decision errors; and
7. optimizing the design for obtaining data.

The details of DQO process for the soil investigation and surface and groundwater sampling programs are provided below.

The problem as identified in Section 3.1 of this QAPP is to refine the extent of soils that exceed soil cleanup levels for PAHs and arsenic and to characterize the material for treatment and/or disposal.

The primary decision for the soil investigation is to determine whether or not PAH and arsenic concentrations in the SIZs exceed their cleanup objectives.

The inputs to the decision for the soil investigation are the cleanup objectives.

The spatial boundaries of the soil investigation are the SIZs. The temporal boundary for the soil investigation is the sampling anticipated to occur in the Spring of 2002. The only practical constraints for the soil investigation are inclement weather conditions.

The decision rules for the soil investigation are: if the arsenic and Site-specific SVOC concentrations from samples collected from the Arsenic and PAH SIZs are greater than the cleanup objectives, then the need for remediation will be based on an evaluation of the data; and if the regulatory levels for the waste characterization analyses are exceeded, then the final disposition of the material will be based on an evaluation of the data.

The limits on decision errors expressed as percent error for the RD activities should be no greater than 25 percent. The aggregate sampling and analysis error may be greater, but error resulting from sampling procedures or the nature of the sample matrix are not quantifiable.

The design of the sampling and analysis program has been developed from the RD SOW for the Site and negotiations between U.S. EPA and the Performing Respondents. The soil sampling program is presented in Section 4.3 of the Soil Pre-Design Study Work Plan.

4.2 MEASUREMENT PERFORMANCE CRITERIA

The measurement performance criteria for precision, accuracy, representativeness, completeness, and comparability are provided in the following subsections.

4.2.1 PRECISION

Precision is a measure of the degree to which two or more measurements of the same characteristic (i.e., analyte, parameter) under the same or similar conditions are in agreement.

4.2.1.1 FIELD PRECISION CRITERIA

Precision of the field sample collection procedures will be assessed by the data from analysis of field duplicate samples. Relative percent differences (RPDs) will be calculated for detected analytes from field duplicate sample sets. Field duplicate samples will be collected at a minimum frequency of 1 per 20 investigative samples. An RPD of 50 percent for soil sample field duplicates will be used as an advisory limit. Professional judgment will be used for any data qualification. Field duplicates will not be collected for waste characterization sampling.

4.2.1.2 LABORATORY PRECISION CRITERIA

Laboratory precision will be assessed through the calculation of RPDs for replicate/duplicate sample analyses. In general, these will be matrix spike/matrix spike duplicate (MS/MSD) samples. The equation to be used to determine precision is presented in Section 7.3 of this QAPP. Precision control limits for the analyses are presented in Table 4.1.

4.2.2 ACCURACY

Accuracy is the extent of agreement between an observed value (i.e., sample result) and the accepted or true value for the parameter being measured.

4.2.2.1 FIELD ACCURACY CRITERIA

The criteria for accuracy of the field sample collection procedures will be to ensure that samples are not affected by sources external to the sample, such as sample contamination by ambient conditions or inadequate equipment decontamination procedures. Field sampling accuracy will be assessed by the data from field and trip blank samples.

Field blank samples will be collected at a frequency of one per ten sampling equipment decontamination procedures or a least once per day of sampling equipment cleanings, whichever is more frequent. Field blank samples will be collected by routing laboratory-provided deionized water through decontaminated sampling equipment. Field blank samples will be analyzed to check procedural contamination and/or ambient conditions and/or sample container contamination at the Site that may cause sample contamination. Field blank samples will not be collected for waste characterization sampling and for samples collected using pre-cleaned or pre-cleaned, disposable sampling equipment.

Field blank samples should not contain target analytes. The field blank sample data will be evaluated using the procedures specified in Section 7.3 of this QAPP. Accuracy will be ensured by adhering to all sample handling procedures, sample preservation requirements, and holding time periods.

4.2.2.2 LABORATORY ACCURACY CRITERIA

Laboratory accuracy will be assessed by determining percent recoveries from the analysis of laboratory control samples (LCSs) or standard reference materials (SRMs). Accuracy relative to the sample matrix will be assessed by determining percent recoveries from the analysis of MS/MSD samples. MS/MSD samples will be collected/designated for the analyses at a minimum frequency of 1 per 20 or fewer samples. The equation to be used to determine accuracy for this project is presented in Section 7.3 of this QAPP. Accuracy control limits are presented in Table 4.1.

The accuracy of the organics analyses also will be monitored through the analysis of surrogate compounds. Surrogate compounds are added to each sample, standard, blank, and QC sample prior to sample preparation and analysis. Surrogate compounds are not expected to be found occurring naturally in the samples, but behave analytically similar to the compounds of interest. Consequently, surrogate compound percent recoveries will provide information on the effect that the sample matrix exhibits on the accuracy of the analyses. Table 4.2 provides surrogate compound percent control limits for the organic analyses.

4.2.3 REPRESENTATIVENESS

Representativeness is a qualitative term that describes the extent to which a sampling design adequately reflects the environmental condition of a site Representativeness also reflects the ability of the sample team to collect samples and laboratory personnel to analyze those samples in such a manner that the data generated accurately and precisely reflect the conditions at a site.

4.2.3.1 FIELD REPRESENTATIVENESS CRITERIA

Representativeness is dependent upon the proper design of the sampling program. The representativeness criteria for field sampling will be to ensure that the sampling grids are properly established at the site, that the correct monitoring wells are sampled, and that the sampling procedures in the FSP are followed. The sampling programs were designed to provide data representative of Site conditions. During development of these programs, consideration was given to past waste disposal practices, existing analytical data, physical setting and processes, and constraints inherent to the Superfund program. The rationale for the sampling network is provided in Section 3.3.1 of this QAPP.

4.2.3.2 LABORATORY REPRESENTATIVENESS CRITERIA

The representativeness criteria for laboratory data will be to ensure that the proper analytical procedures are used for sample preparation (e.g., homogenizing the sample prior to subsampling), sample analysis, and that sample holding times are met. Additionally, the accuracy and precision of the laboratory data affect representativeness. The laboratory representativeness criteria will include achieving the accuracy and precision criteria for the sample analyses.

4.2.4 COMPARABILITY

Comparability is an expression of the confidence with which one data set can be compared with another.

4.2.4.1 FIELD COMPARABILITY CRITERIA

The criteria for field comparability will be to ensure and document that the sampling networks designed for the RD activities are properly implemented and the sampling procedures in the FSP are followed for the duration of the sampling programs.

4.2.4.2 LABORATORY COMPARABILITY CRITERIA

The criteria for laboratory data comparability will be to ensure that the analytical methods used for the RD sampling and analysis events that are comparable to the methods used for previous sampling events. The analytical methods identified in Section 5.3 of this QAPP are comparable to the methods used to generate data for previous investigations.

4.2.5 COMPLETENESS

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.

4.2.5.1 FIELD COMPLETENESS CRITERIA

The criteria for field completeness will be that a minimum of 90 percent of the field-measured data are valid. The procedure for determining field data validity is provided in Section 7.0 of this QAPP. The equation for calculating completeness is presented in Section 7.3.4 of this QAPP.

4.2.5.2 LABORATORY COMPLETENESS CRITERIA

The criteria for laboratory completeness will be that a minimum of 90 percent of the laboratory data will be determined to be valid (usable) for the intended purpose. The procedure for determining laboratory data validity is provided in Section 7.0 of this

QAPP. The equation for calculating completeness is presented in Section 7.3.4 of this QAPP.

4.2.6 SENSITIVITY

Sensitivity is the ability of a method or instrument to detect a parameter to be measured at a level of interest.

4.2.6.1 FIELD SENSITIVITY CRITERIA

The field measurements for the project only consist of distance measurements. Sensitivity is not applicable to these measurements.

4.2.6.2 LABORATORY SENSITIVITY CRITERIA

The sensitivity requirements for the laboratory analyses are provided in Table 3.2. Where evaluation criteria for a sampling program exist, the concentration of the evaluation criteria are included in the table. The analytical methods are sufficiently sensitive for the project.

4.3 SPECIAL TRAINING/CERTIFICATION REQUIREMENTS

Special training/certification requirements for this project were provided in Section 2.5.

4.4 DOCUMENTATION AND RECORDS

The documents, records, and reports generated during the RD are identified in the following subsections.

4.4.1 FIELD AND LABORATORY RECORDS

Documents and records generated during the project include sample collection records, QC sample records, field measurement records, laboratory records, and data handling records. A brief description of these documents and records are provided below. Detailed information on these records is provided in subsequent sections of this QAPP.

Sample collection records that will be used during the sampling activities include field logbooks, stratigraphic logs, chain-of-custody records, and shipping papers.

QC sample records that will be used during the project to document the generation of QC samples include field logbooks for recording field blank samples, field duplicate samples, and MS/MSD samples. The laboratory will maintain appropriate documentation of trip blank sample preparation, quality records for deionized water sent for field blank samples, and sample integrity information. Records of sample preservation will be maintained in field logbooks and by the laboratory.

Laboratory records that will be maintained for the project include sample receipt documentation, field and laboratory chain-of-custody documentation, sample container cleanliness certifications, reagent and standard reference material certifications, sample preparation records, sample analysis records (e.g., run logs), instrument/raw data, QC data, calibration data, corrective action reports, and final reports.

Data handling records that will be maintained include verification of computer programs used to manipulate or reduce raw data into final results and data validation reports. The laboratory will maintain documentation of data verification and reduction procedures as necessary for the analyses used during the RD activities. CRA will maintain checklists, notes, and reports generated during the external data validation process.

4.4.2 DATA REPORTING FORMAT

Field data will be recorded in bound logbooks or on standard forms (e.g., stratigraphic logs). The details for recording field data are provided in Section 5.2.2.1 of this QAPP.

Field data will be primarily generated from observations. These data will be tabulated and included in project reports or submittals, as appropriate.

Laboratory reports for the RD activities will consist of the following data deliverables:

1. Case Narrative
   i) date of issuance;
   ii) any deviations from intended analytical strategy;
   iii) laboratory batch number;
   iv) number of samples and respective matrices;
   v) project name and number;
   vi) condition of samples "as received";
   vii) discussion of whether or not sample holding times were met;
   viii) discussion of technical problems or other observations which may have created analytical difficulties; and
   ix) discussion of an laboratory quality control checks which failed to meet project criteria.

2. Chemistry Data Package
   i) dates of sample collection, receipt, preparation, and analysis;
   ii) cross-reference of laboratory to project sample identification numbers;
   iii) description of data qualifiers used;
   iv) methods of sample preparation and analysis;
   v) sample results in tabular format;
   vi) MS/MSD data, LCS data, method blank data, surrogate compound percent recovery data; and
   vii) fully executed chain-of-custody document.

Raw instrument data (including calibration data and instrument performance checks), method detection limit (MDL) studies, instrument detection limit (IDL) studies, and method performance and validation studies will be maintained by the laboratory.

5.0 DATA GENERATION AND ACQUISITION

The design and implementation of the measurement systems that will be used during the RD activities, including sampling procedures, analytical procedures, and data handling and documentation are detailed in the following subsections.

5.1 SAMPLING PROCESS DESIGN

The rationale for the sampling programs is provided in Section 4.0 of the Soil Pre-Design Study Work Plan and was detailed in Section 3.3 of this QAPP. The sampling programs were developed based on the requirements of the SOW and refined through planning meetings.

5.1.1 SAMPLING METHODS

Sampling methods for the collection of soil samples are provided in the FSP.

5.1.2 FIELD EQUIPMENT AND SAMPLE CONTAINER CLEANING PROCEDURES

Equipment cleaning/decontamination procedures are provided in the FSP. Sample containers will be provided by STL. The laboratory's vendor for sample containers is QEC of Beaver, West Virginia. All containers will be precleaned in accordance with the U.S. EPA guidance document entitled "Specifications and Guidance for Contaminant-Free Sample Containers", EPA 540/R-93/051. Certificates of analysis for each lot of containers will be maintained by the laboratory.

5.1.3 FIELD EQUIPMENT MAINTENANCE, TESTING, AND INSPECTION REQUIREMENTS

Field equipment will be inspected and tested prior being shipped to the field. Maintenance logs for all field equipment are kept in CRA's field equipment files at the CRA office from which the equipment was shipped. Prior to use in the field, the

equipment is checked again, generally during field calibration, and the performance information is recorded in the field logbook. All equipment shipped back from the field is inspected and tested upon return. Any required maintenance is performed and documented prior to the equipment being returned to service.

Critical spare parts for field equipment and replacement field equipment are available at each CRA office and can be shipped for overnight delivery, picked up at the CRA office, or delivered to the field when the need is identified. Alternately, field equipment vendors (e.g., Hazco) can provide replacement equipment if needed. The replacement equipment can be shipped for overnight delivery as necessary.

5.1.4 INSPECTION AND ACCEPTANCE REQUIREMENTS FOR SUPPLIES AND SAMPLE CONTAINERS

The field supplies for the RD activities consist of detergent (Alconox) for equipment cleaning, distilled water for sample collection equipment rinsing, deionized water for final sample collection equipment rinsing and for collecting field (equipment rinsate) blank samples, and sample containers to collect the samples. Alconox, which is a standard laboratory-grade detergent, is obtained from Cole Parmer. Distilled water will be purchased as needed from a variety of vendors.

Deionized water and sample containers will be provided by STL, which will maintain documentation of the purity/cleanliness for these materials. STL's QA Officer is ultimately responsible for ensuring that these materials are acceptable for the project. The acceptability of these materials for use will be evaluated by reviewing lot analysis certificates. Water and containers that do not meet the laboratory's acceptability requirements will not be shipped to the field.

5.2 SAMPLE HANDLING AND CUSTODY REQUIREMENTS

The procedures for sample handling, labeling, shipping, and chain-of-custody documentation are provided in the subsections that follow.

5.2.1 SAMPLE HANDLING

The procedures used to collect the samples are provided in the FSP. Sample aliquots will be containerized in order of decreasing analyte volatility. The majority of the samples collected during the soil investigation will be analyzed only for PAHs and total arsenic. These analyses will be performed from a sample aliquot from the same sample container. The containers for soil samples collected for waste characterization will be filled in the following sequence: TCLP VOCs first; TCLP extractable organics (including SVOCs, pesticides, herbicides) and PCBs next; and the remaining parameters. Table 5.1 identifies the requirements for the number of containers, container volume, container type (material of construction), preservation, holding time periods, packaging, and shipping for the analyses.

The sample numbering system for the project has been designed to uniquely identify each sample from each sampling program and event. This numbering system consists of the sample matrix code, sample collection date, sampler's initials, and sequential number beginning with 01 for each sampling program and event.

An example of the sample numbering system follows:

MC-mmddyy-XX-01

where:

MC (Matrix Code)	=	S–soil, W-field blank samples
mmddyy	=	Date in month/day/year
XX	=	Sampler's first and last initials
01	=	Sequential number for event

An example of a sample identification number for a soil sample collected on April 12, 2002 by field sampler John Smith would be S-041202-JS-01.

Field duplicate samples will be numbered consistent with this system to avoid laboratory bias of field QC samples. Samples designated for MS/MSD analysis will be identified as such in the remarks column of the chain-of-custody form.

Samples will be placed in shipping coolers containing bagged, cubed ice immediately following collection. The samples will be grouped in the shipping cooler by the order in which the samples are collected, and shipped to the laboratory via an overnight courier service, generally on the day they are collected. The only exceptions to this procedure will be for samples collected after the courier service has picked up the shipment for the day (generally only at remote sites) and samples collected on a Sunday or holiday. In these instances, the samples will be shipped on the next business day. An example shipping form is provided in Attachment 2.

The laboratory will group the samples in sample delivery groups (SDGs) by sampling program. An SDG is a group of 20 or fewer field samples (including field QC samples) received by the laboratory within 14 calendar days.

5.2.2 SAMPLE CUSTODY

Chain-of-custody is the sequence of possession of an item. An item (such as a sample or final evidence file) is considered to be in custody if the item is in actual possession of a person, the item is in the view of the person after being in his/her actual possession, or the item was in a person's physical possession but was placed in a secure area by that person. Field, laboratory, and final evidence files custody procedures are described in the subsections that follow.

5.2.2.1 FIELD CUSTODY PROCEDURES

Logbooks will used to record field data collection activities. Entries into field logbooks will be described in as much detail as possible to ensure that a particular situation could be reconstructed solely from logbook entries. Field logbooks will be bound field survey books or notebooks with consecutively numbered pages. Logbooks will be assigned to field personnel and will be stored at CRA's Chicago, Illinois office when not in use. Each logbook will be identified by the project-specific document number (019023).

The title page of each logbook will contain the following information:

- person to whom the logbook is assigned;

- logbook number;
- project name;
- project start date; and
- end date.

Entries into the logbook will contain a variety of information. At the beginning of each day's logbook entry, the date, start time, weather, names of all sampling team members present, and the signature of the person making the entry will be entered. The names of individuals visiting the site or field sampling team and the purpose of their visit will also be recorded in the field logbook.

All field measurements obtained and samples collected will be recorded. All logbook entries will be made in ink, signed, and dated with no erasures. If an incorrect logbook entry is made, the incorrect information will be crossed out with a single strike mark which is initialed and dated by the person making the erroneous entry. The correct information will be entered into the logbook adjacent to the original entry.

Whenever a sample is collected or a measurement is made, a detailed description of the location will be recorded in the logbook. Photographs taken at a location, if any, will also be noted in the logbook. All equipment used to obtain field measurements will be recorded in the field logbook. In addition, the calibration data for all field measurement equipment will be recorded in the field logbook or on standard field forms.

Samples will be collected following the sampling procedures documented in the FSP. The equipment used to collect samples, time of sample collection, sample description, volume and number of containers, preservatives added (if applicable) will be recorded in the field logbook. Each sample will be uniquely identified using the sample numbering system provided in Section 5.2.1 of this QAPP.

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

1. The field sampler is personally responsible for the care and custody of the samples until they are transferred to another person or the laboratory. As few people as possible will handle the samples.

2. All sample containers will be identified by using sample labels that include the date of collection and analyses to be performed. Sample labels will be completed for each sample using waterproof ink. An example sample label is provided in Attachment 2.
3. Samples will be accompanied by a properly completed chain-of-custody form. The sample identification numbers and required analyses will be listed on the chain-of-custody form. When transferring the possession of samples, the individuals relinquishing and receiving the samples will sign and record the date and time on the form. The chain-of-custody form documents sample custody transfers from the sampler to another person, to the laboratory, or to/from a secure storage area.
4. Samples will be properly packaged for shipment (see Table 5.1) and dispatched to the laboratory for analysis with a separate signed chain-of-custody form enclosed in and secured to the inside top of each shipping cooler. Shipping coolers will be secured with custody tape for shipment to the laboratory. The custody tape is then covered with clear plastic tape to prevent accidental damage to the custody tape. An example of the custody tape to be used for this project is provided in Attachment 2.
5. If samples are collocated with a government agency or other entity, it is the responsibility of that entity to prepare its own chain-of-custody form for the samples. Information regarding the identity of the entity and the samples that are being collocated will be recorded in the field logbook.
6. All sample shipments will be accompanied by the chain-of-custody form identifying its contents. The chain-of-custody form is a four part carbonless-copy form. The form is completed by the sampling team which, after signing and relinquishing custody to the shipper, retains the bottom (goldenrod) copy. The shipper, if different than the sampling team members, retains the pink copy after relinquishing custody to the laboratory. The yellow copy is retained by the laboratory and the fully executed white copy is returned as part of the data deliverables package. An example chain-of-custody form is provided in Attachment 2.
7. If the samples are sent by common carrier, a bill of lading (e.g., FedEx airbill) will be used and copies will be retained as permanent documentation. Commercial carriers are not required to sign the chain-of-custody form as long as the form is sealed inside the sample cooler and the custody tape remains intact.

5.2.2.2 LABORATORY CUSTODY PROCEDURES

Laboratory sample custody begins when the samples are received at the laboratory. The labs sample custodian will assign a unique laboratory sample identification number to each incoming sample. The field sample identification numbers, laboratory sample identification numbers, date and time of sample collection, date and time of sample receipt, and requested analyses will be entered into the sample receiving log. The lab's sample log-in, custody, and document control procedures are detailed in the appropriate SOPs in Attachment 1.

Following log-in, all samples will be stored within an access-controlled location and will be maintained properly preserved (as defined in Table 5.1) until completion of all laboratory analyses. Unused sample aliquots and sample extracts/digestates/distillates will be maintained properly preserved for a minimum of 30 days following receipt of the final report by CRA. The lab will be responsible for the disposal of unused sample aliquots, sample containers, and sample extracts/digestates/distillates in accordance with all applicable local, state, and federal regulations.

The laboratory will be responsible for maintaining analytical log books and laboratory data. Raw laboratory data files will be inventoried and maintained by the laboratory for a period of five years, at which time CRA will advise the laboratory regarding the need for additional storage.

5.2.2.3 FINAL EVIDENCE FILES CUSTODY PROCEDURES

The final evidence file for the project will be maintained by CRA and will consist of the following:

1. project plan;
2. project log books;
3. field data records;
4. sample identification documents;
5. chain-of-custody records;
6. correspondence;

7. references, literature;
8. final data packages;
9. miscellaneous - photos, maps, drawings, etc.; and
10. final report.

The final evidence file materials will be the responsibility of the evidentiary file custodian (CRA's Project Manager) with respect to maintenance and document removal.

5.3 ANALYTICAL METHOD REQUIREMENTS

The field and laboratory analytical methods that will be used during the RD activities are detailed in the following subsections.

5.3.1 FIELD ANALYTICAL METHODS

There are no field analytical methods for the soil pre-design study.

5.3.2 LABORATORY ANALYTICAL METHODS

Soil samples will be analyzed off Site by the project laboratory. Samples from the soil investigation for total arsenic analysis will be acid digested and the digestates will be analyzed using inductively coupled plasma (ICP) emission spectrometry. Samples for Site-specific SVOC analysis will be extracted and the extracts will be analyzed using gas chromatography/mass spectrometry (GC/MS).

Samples collected from the DSS, PAH SIZ, and Arsenic SIZ also will be analyzed for the RCRA characteristics of reactivity, corrosivity, ignitability, and toxicity, and sulfate, sulfide, heat content, PCBs, and free liquids. The characteristic of reactivity, consisting of reactive cyanide and reactive sulfide, will be determined by distilling two aliquots of soil under specific conditions and analyzing the distillates for total cyanide and total sulfide. The characteristic of corrosivity will be determined electrometrically as pH on a water/soil suspension. The characteristic of ignitability will be determined as flash point

using a closed cup flash point tester. The characteristic of toxicity will be determined by leaching an aliquot of soil using an acetate buffer under specific conditions and analyzing the TCLP extract for a specific list of VOCs, semivolatile organic compounds (SVOCs), pesticides, herbicides, and metals.

TCLP VOCs will be analyzed using purge-and-trap sample concentration/introduction and gas GC/MS separation/detection techniques. TCLP SVOCs will be solvent extracted from the TCLP leachate and the extract will be analyzed using GC/MS. TCLP pesticides and herbicides will be solvent extracted from the TCLP leachate, separated by GC, and detected using an electron capture detector. TCLP metals will be determined by acid digesting the TCLP extract and analyzing the digestate using ICP and cold vapor mercury atomic absorption spectrophotometry.

Sulfate will be solvent extracted from soil samples using deionized water, and sulfate ions in the extract will separated by ion chromatography and detected by electrical conductivity. Sulfide will be analyzed by the iodometric method, which consists of back-titrating excess iodine added to oxidize sulfide in the soil samples. Heat content of the soil samples will be measured by a bomb calorimeter. PCBs will be solvent extracted from the soil, separated by GC, and detected using an electron capture detector. Free liquids will be determined by placing an aliquot of soil in a standard paint filter and observing any free liquids migrating from the sample.

Geotechnical analyses will be performed using standard methods from "Annual Book of ASTM Standards" (ASTM Methods).

The analytical methods that will be used by the laboratory for analyzing the soil samples are presented in Table 5.2. SOPs for the analytical methods are presented in Attachment 1. Method validation and detection limit study information for the analyses are included in the laboratories SOPs.

The quantities and types of QC samples for the soil investigation are included in Table 3.1.

5.4 QUALITY CONTROL REQUIREMENTS

The field and laboratory QC requirements for the RD activities are discussed in the following subsections. Specific QC checks and acceptance criteria are provided in the SOPs in Attachment 1.

5.4.1 FIELD SAMPLING QUALITY CONTROL

Field QC samples for this project include field blank samples to determine the existence and magnitude of sample contamination resulting from ambient conditions or sampling procedures and field duplicate samples to assess the overall precision of the sampling and analysis event. The frequency of collection of these field QC samples was provided in Section 4.2 of this QAPP. The evaluation of field QC data is provided in Section 7.3 of this QAPP.

5.4.2 ANALYTICAL QUALITY CONTROL

The laboratory QC requirements for the arsenic analyses to be performed for the soil investigation include analyzing preparation blanks, initial calibration blanks, continuing calibration blanks, initial calibration verification standards, continuing calibration verification standards, interference check standards, serial dilution samples, MS/MSD samples, and LCSs. The analysis frequency for these QC samples are included in the applicable laboratory SOPs in Attachment 1. The acceptance criteria for all these QC checks except MS/MSD samples and LCSs are in the laboratory's SOPs. The acceptance criteria for MS/MSD samples and LCSs are provided in Table 4.1 of this QAPP.

The laboratory QC requirements for soil samples analyzed for cyanide and sulfide reactivity include analyzing method blanks and duplicate samples. The acceptance criteria for method blank sample analyses are provided in the applicable laboratory SOPs in Attachment 1. The acceptance criteria for duplicate sample analyses are provided in Table 4.1 of this QAPP.

The laboratory QC requirements for soil samples analyzed for flash point include analyzing method blanks, a p-xylene reference standard and duplicate samples. The

acceptance criteria for these QC checks are provided in the laboratory's SOP in Attachment 1 and Table 4.1 of this QAPP.

The laboratory QC requirements for soil samples analyzed for corrosivity as pH include analyzing duplicate samples and LCSs. The acceptance criteria for these QC checks are provided in the lab's SOP in Attachment 1 and Table 4.1 of this QAPP.

The laboratory QC requirements for soil samples analyzed for sulfate include analyzing method blanks, initial calibration standards, continuing calibration standards, MS/MSDs, and LCSs. The acceptance criteria for all these QC checks except MS/MSD samples and LCSs are in the laboratory's SOPs. The acceptance criteria for MS/MSD samples and LCSs are provided in Table 4.1 of this QAPP.

The laboratory QC requirements for soil samples analyzed for sulfide include method blanks, MS/MSDs, and LCSs. The acceptance criteria for method blank sample analysis is provided in the applicable laboratory SOPs in Attachment 1. The acceptance criteria for MS/MSD samples and LCSs are provided in Table 4.1 of this QAPP.

The laboratory QC requirements for soil samples analyzed for heat content include the analysis of a benzoic acid SRM. The acceptance criteria for the SRM is in the ASTM method.

The paint filter test for free liquids is a qualitative method. There are no unique QC requirements for this method.

The laboratory QC requirements for TCLP extracts analyzed for VOCs include analyzing instrument performance check (mass tuning) standards, method blanks, initial calibration standards, continuing calibration standards, surrogate standards, internal standards, MS/MSDs, and LCSs. The acceptance criteria for all these QC checks except MS/MSD samples and LCSs are in the laboratory's SOPs. The acceptance criteria for MS/MSD samples and LCSs are provided in Table 4.1 of this QAPP.

The laboratory QC requirements for soil samples analyzed for Site-specific SVOCs and TCLP extracts analyzed for SVOCs include analyzing instrument performance check (mass tuning) standards, method blanks, initial calibration standards, continuing calibration standards, surrogate standards, internal standards, MS/MSDs, and LCSs. The

acceptance criteria for all these QC checks except MS/MSD samples and LCSs are in the laboratory's SOPs. The acceptance criteria for MS/MSD samples and LCSs are provided in Table 4.1 of this QAPP.

The laboratory QC requirements for soil samples analyzed for PCBs and TCLP extracts analyzed for pesticides include analyzing instrument performance evaluation standards, method blanks, instrument blanks, initial calibration standards, continuing calibration verification standards, surrogate standards, MS/MSDs, and LCSs. Positive pesticide detections are confirmed by the data from a second chromatography column, and the percent difference between the data from the two columns is determined. The acceptance criteria for all these QC checks except MS/MSD samples and LCSs are in the laboratory's SOPs. The acceptance criteria for MS/MSD samples and LCSs are provided in Table 4.1 of this QAPP.

The laboratory QC requirements for TCLP extracts analyzed for herbicides include analyzing method blanks, instrument blanks, initial calibration standards, continuing calibration verification standards, surrogate standards, MS/MSDs, and LCSs. Positive detections are confirmed by the data from a second chromatography column, and the percent difference between the data from the two columns is determined. The acceptance criteria for all these QC checks except MS/MSD samples and LCSs are in the laboratory's SOPs. The acceptance criteria for MS/MSD samples and LCSs are provided in Table 4.1 of this QAPP.

The laboratory QC requirements for the TCLP extracts analyzed for metals include analyzing preparation blanks, initial calibration blanks, continuing calibration blanks, initial calibration verification standards, continuing calibration verification standards, interference check standards, serial dilution samples, MS/MSD samples, and LCSs. The analysis frequency for these QC samples are included in the applicable laboratory SOPs in Attachment 1. The acceptance criteria for all these QC checks except MS/MSD samples and LCSs are in the laboratory's SOPs. The acceptance criteria for MS/MSD samples and LCSs are provided in Table 4.1 of this QAPP.

5.5 INSTRUMENT/EQUIPMENT TESTING, INSPECTION, AND MAINTENANCE REQUIREMENTS

The procedures used to verify that instruments and equipment are functional and properly maintained are described in the following subsections.

5.5.1 FIELD INSTRUMENT MAINTENANCE

There are no field instruments being used for the soil pre-design study.

5.5.2 LABORATORY INSTRUMENT MAINTENANCE

As part of their QA/QC program, the laboratory conducts routine preventive maintenance program to minimize the occurrence of instrument failure and other system malfunctions. Designated laboratory employees will regularly perform routine scheduled maintenance and repair of (or coordinate with the instrument manufacturer for the repair of) all instruments. All maintenance that is performed will be documented in the laboratory's maintenance logbooks. All laboratory instruments are maintained in accordance with manufacturer's specifications.

Table 5.3 provides examples of the frequency at which components of key analytical instruments or equipment will be serviced. The SOPs in Attachment 1 provide complete details for instrument preventive maintenance.

5.6 CALIBRATION PROCEDURES AND FREQUENCY

The procedures for maintaining the accuracy for all the instruments and measuring equipment which are used for conducting field tests and laboratory analyses are described in the following subsections. These instruments and equipment will be calibrated prior to each use or according to a periodic schedule.

5.6.1 FIELD INSTRUMENTS/EQUIPMENT

There are no field instruments being used for the soil pre-design study. Equipment to be used for field sampling will be examined to confirm that it is in operating condition.

5.6.2 LABORATORY INSTRUMENTS

Calibration of laboratory equipment will be based on approved written procedures. 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 a properly trained repair staff with in-house spare parts or will maintain service contracts with vendors.

The records of calibration will be kept as follows:

1. If possible, each instrument will have record of calibration permanently affixed with an assigned record number.
2. A logbook will be assigned to each instrument showing description, manufacturer, model numbers, date of last calibration and the signature of the person who calibrated the instrument, due date of next calibration and compensation or correction figures, as appropriate.
3. A written stepwise calibration procedure will be available for each piece of test and measurement equipment.
4. Any instrument that is not calibrated to the manufacturer's original specification will display a warning tag or will otherwise be removed from service, as appropriate.

Specific calibration procedures and frequencies are detailed in the laboratory SOPs in Attachment 1.

5.7 INSPECTION/ACCEPTANCE CRITERIA FOR SUPPLIES AND CONSUMABLES

The procedures that will be used to ensure that supplies and consumables used in the field and laboratory will be available as needed and free of contaminants are detailed in the following subsections.

5.7.1 FIELD SUPPLIES AND CONSUMABLES

Supplies and consumables for field measurements and sampling will be obtained from various vendors and include sample containers, preservatives, detergent and water for equipment decontamination, and field blank water. The vendors and inspection and acceptance criteria for these field supplies were presented in Section 5.1.4 of this QAPP. Additional field supplies and consumables include pump tubing, Geoprobe liners, and personnel protective equipment (PPE). Pump tubing will be constructed of pre-cleaned high density polyethylene and Geoprobe liners will be constructed of pre-cleaned polyvinyl chloride or cellulose acetate polymers. These materials will not introduce contaminants into the samples or interfere with the analyses. All field supplies will be consumed or replaced with sufficient frequency to prevent deterioration or degradation that may interfere with the analyses.

5.7.2 LABORATORY SUPPLIES AND CONSUMABLES

STL's vendor for general labware and reagents is Fisher Scientific. Vendors for chromatography supplies and organic standards include Ultra Scientific, Supelco, Accustandard, Restek, ChemService, and Aldrich Chemical. Vendors for metals and general chemistry parameters supplies and standards include Ultra Scientific, High Purity Standards, and Inorganic Ventures. The lot numbers of reagents and standards are recorded and dates of receipt, first use, and expiration are documented. Certificates of analysis are maintained on file to document reagent/standard purity.

The SOPs in Attachment 1 provide details on identifying contaminants in reagents and standards, determining deterioration of reagents and standards, and the corrective actions required if contaminants or deterioration are identified. The laboratory QA Officer is ultimately responsible for the ensuring the acceptability of supplies and consumables.

5.8 DATA ACQUISITION REQUIREMENTS (NON-DIRECT MEASUREMENTS)

Historical data for the Site were generated during the various studies and monitoring vents. Data generated during the RI and additional studies were validated by U.S. EPA Region 5 or its contractors.

5.9 DATA MANAGEMENT

The procedures for managing data from generation to final use and storage are detailed in subsections that follow.

5.9.1 DATA RECORDING

Field data will be recorded in field logbooks and consist of measurements from direct reading instruments or direct measurements. Field staff are responsible for recording field data and the Field QA Officer is responsible for identifying and correcting recording errors.

Laboratory data are recorded in a variety of formats. Data from instruments are recorded on magnetic media, strip charts, or bench sheets. The laboratory SOPs in Attachment 1 provide the data recording requirement for each preparation and analysis method.

5.9.2 DATA VALIDATION

Validation of field data for this project will primarily consist of checking for transcription errors and review of data recorded in field logbooks. Data transcribed from the field logbook into summary tables for reporting purposes will be verified for correctness by the Field QA Officer or his designee. Any limitations on the use of field data will be included in the RD reports.

Validation of the analytical data will be performed by CRA's QA Officer or his designee based on the relevant and applicable evaluation criteria outlined in "USEPA Contract Laboratory Program National Functional Guidelines for Organic Data Review", EPA540/R-99/008, October 1999 and "USEPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review", EPA-540/R-94-013, February 1994. The evaluation and action criteria specified in these documents (referred to hereafter as the National Functional Guidelines) will be used for validating the data. However, the acceptance limits for QC data will be the control limits determined statistically by the laboratory, not the control limits specified in the National Functional Guidelines. Qualifiers assigned to the data will be consistent with the data qualifiers specified in the National Functional Guidelines.

The following QC data deliverables will be evaluated on 100 percent of the data.

Organic Analyses

1. Technical Holding Times;
2. Blanks;
3. Surrogate Spikes;
4. MS/MSD Results;
5. LCS Results;
6. Field Duplicates; and
7. Field Blank Samples.

Inorganic Analyses

1. Technical Holding Times;
2. Blanks;
3. MS/MSD results;
4. LCS Results;
5. Field Duplicates; and
6. Field Blank Samples.

The results of the data validation process will be documented in a memorandum that specifies all limitations on the usability of the analytical data.

5.9.3 DATA TRANSFORMATION/DATA REDUCTION

Field data reduction procedures will be minimal in scope compared to those implemented for laboratory data. Only direct reading instrumentation (e.g., survey tapes) will be employed in the field. These data will be recorded into field logbooks immediately after the measurements are taken.

Laboratory data reduction procedures will be followed according to the following protocol:

1. Raw data produced and checked by the responsible analyst is turned over for independent review by another analyst.
2. The area supervisor or senior chemist 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 reviews and acceptance of the raw data by the area 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. Following review and approval of the preliminary report by the laboratory Project Manager, final reports will be generated and signed by the laboratory Project Manager.

Specific equations used for data reduction are contained in the SOPs in Attachment 1.

5.9.4 DATA TRANSMITTAL/TRANSFER

Field data from surveying and water level measurements will be entered into a standard Microsoft Excel spreadsheet format. CRA's Field QA Officer is responsible for verifying

the correctness of the field data after the data are transferred to a spreadsheet format. The geographical data are maintained in a database that is described below.

The laboratory will provide electronic data deliverables (EDDs) in the EQuIS 4-file format. EQuIS is a database product from EarthSoft that uses Microsoft Access as the database engine. The laboratory data are downloaded into the EDDs directly from the laboratory information management system (LIMS), thus eliminating the possibility of manual transcription errors. The EDDs are imported into EQuIS and the data are maintained in the database for manipulation and presentation.

CRA's QA Officer is responsible for verifying the correctness of the analytical database after the laboratory data for each event have been imported. This is accomplished by comparing the data from the database to the hardcopy analytical reports for a minimum of 10 percent of the sample results. If discrepancies between the database and hardcopy analytical reports are detected, a complete verification of the database will be performed or a new EDD will be submitted, imported, and verified as described previously.

5.9.5 DATA ANALYSIS

The data from the soil investigation will compared to the cleanup objectives to further delineate the extent of soil contamination. Waste characterization data will be compared to the regulatory criteria in 40 CFR Part 261.

5.9.6 DATA ASSESSMENT

Assessment of laboratory data by the laboratory will be performed using the procedures detailed in the laboratory's SOPs in Attachment 1. These assessments included determining the mean, standard deviation, relative standard deviation, percent difference, RPD, and percent recovery for certain QC elements.

Assessment of QC data for data validation purposes will include determining the percent recovery, RPD, and percent completeness. The statistical equations to determine these parameters are provided in Section 7.3 of this QAPP.

5.9.7 DATA TRACKING

Data generated in the field, such as sample depth measurements, will be recorded in field logbooks. Survey data will be generated by the surveying subcontractor and provided to CRA. There are no unique or special tracking requirements for these data. The data will be transcribed for analysis and reporting and the original survey data and field logbooks will be maintained in the final evidence file.

Laboratory data tracking procedures are provided in the SOPs in Attachment 1. These SOPs provide the procedures for tracking data from generation to reporting. The laboratory's LIMS also provides a means for tracking data in the laboratory. The laboratory Operations Manager is ultimately responsible for data tracking in the laboratory.

Tracking of analytical data in the EQuIS database includes recording the laboratory generating the data, the date when EDD was received and imported, the date when qualifiers were applied to the results, and the level of data validation performed. CRA's Project Manager is ultimately responsible for tracking data from entry into the database to reporting.

5.9.8 DATA STORAGE AND RETRIEVAL

Laboratory data will be stored by the laboratory in hardcopy format at their facility. Data are archived on site for a period of 5 years, after which time the data are warehoused off site. Electronic instrument data are maintained on magnetic media (i.e., magnetic tape) for this same time period. The laboratory's records manager, who is responsible for data archiving and retrieval at their facility.

CRA's Project Manager is responsible for project data storage and retrieval. Field logbooks will be maintained in CRA's Chicago, Illinois office between groundwater/surface water sampling events. At the conclusion of the soil pre-design study, field logbooks associated with this task will be archived at CRA's Waterloo, Ontario, Canada headquarters. Upon completion of the RD activities, the final evidence file will be archived at CRA's Waterloo, Ontario, Canada headquarters.

5.9.9 DATA SECURITY

Laboratory data security is the responsibility of the laboratory's records manager. Archived data cannot be accessed without authorization and the name of purpose of personnel accessing archived data are recorded. The laboratory's LIMS is password protected and access rights are restricted by job function.

CRA's data security procedures include limiting project database access to database analysts and general building security procedures.

6.0 ASSESSMENT/OVERSIGHT

The following subsections describe the procedures used to ensure proper implementation of this QAPP and the activities for assessing the effectiveness of the implementation of the project and associated QA/QC activities.

6.1 ASSESSMENTS AND RESPONSE ACTIONS

Assessments consisting of internal and external audits may be performed during the project. Internal technical system audits of both field and laboratory procedures will be conducted to verify that sampling and analysis are being performed in accordance with the procedures established in the FSP and QAPP. External field and laboratory audits may be conducted by U.S. EPA.

An internal field technical system audit of field activities, including sampling and field measurements, will be conducted by the Field QA Officer or his designee at the beginning of the field sampling activities to identify deficiencies in the field sampling and documentation procedures. The field technical system audit will include examining field sampling records, field instrument operating records (if applicable), field instrument calibration records (if applicable), and chain-of-custody documentation. In addition, sample collection, handling, and packaging in compliance with the established procedures will be reviewed during the field audit. Any deficiencies identified will be documented and corrective actions will be taken to rectify the deficiencies.

Corrective action resulting from internal field technical system audits will be implemented immediately if data may be adversely affected due to unapproved or improper use of approved methods. The Field QA Officer will identify deficiencies and recommended corrective action to the Project Manager. Implementation of corrective actions will be performed by the Field QA Officer and field team. Corrective action will be documented in the field logbook and/or the project file. Follow-up audits will be performed as necessary to verify that deficiencies have been corrected, and that the QA/QC procedures described in this QAPP and the FSP are maintained throughout the project.

An external field technical system audit may be conducted by U.S. EPA Region 5 FSS any time during the field operations. These audits may or may not be announced and are conducted at the discretion of U.S. EPA Region 5.

An internal laboratory technical system audit will be conducted by the laboratory QA Officer or her designee. The laboratory technical system audit is conducted on an annual basis and includes examining laboratory documentation regarding sample receiving, sample log-in, storage and tracking, chain-of-custody procedures, sample preparation and analysis, instrument operating records, data handling and management, data tracking and control, and data reduction and verification. The laboratory QA Officer will evaluate the results of the audit and provide a final report to section managers and the Operations Manager that includes any deficiencies and/or noteworthy observations.

Corrective action resulting from deficiencies identified during the internal laboratory technical system audit will be implemented immediately. The Operations Manager or section leaders, in consultation with the laboratory supervisor and staff, will approve the required corrective action to be implemented by the laboratory staff. The laboratory QA/QC Officer will ensure implementation and documentation of the corrective action. All problems requiring corrective action and the corrective action taken will be reported to the laboratory Project Manager. Follow-up audits will be performed as necessary to verify that deficiencies have been corrected, and that the QA/QC procedures described in the QAPP are maintained throughout the project.

An external laboratory audit may be conducted by U.S. EPA Region 5 FSS personnel. These audits may or may not be announced and are at the discretion of U.S. EPA Region 5. The external laboratory audits will include, but not be limited to, reviewing laboratory analytical procedures, laboratory on-site audits, and/or submitting performance evaluation samples to the laboratory for analysis.

An external laboratory audit may be conducted at least once prior to the initiation of the sampling and analysis activities.

6.2 REPORTS TO MANAGEMENT

Quality Assurance Management Reports will be prepared during the RD activities. These QA Management Reports will be included with the monthly progress reports that are submitted to U.S. EPA and IEPA when data gathering or assessment activities are being conducted. Minimally, these reports will include project status, results of performance evaluations and system audits, results of periodic data quality validation and assessment and data use limitations, and any significant QA problems identified and corrective actions taken.

CRA's QA Officer will be responsible within the organizational structure for preparing these reports. CRA's Project Manager will be provided with these reports for distribution with monthly status reports. The soil pre-design study report will also include a separate QA/QC section that will summarize data quality information contained in the periodic QA Management Reports and provides an overall data quality assessment compared to the data quality objectives outlined in this QAPP.

7.0 DATA VERIFICATION/VALIDATION AND USABILITY

The QA activities that will be performed to ensure that the RD data are scientifically defensible, properly documented, of known quality, and meet the project objectives are described in the following sections.

7.1 DATA REVIEW, VERIFICATION, AND VALIDATION REQUIREMENTS

All field and laboratory data will be reviewed and verified/validated. The procedures and criteria used to verify and validate field and laboratory data will consist of evaluating the data to the measurement performance criteria in Section 4.2 of this QAPP. Field data and logbooks will be reviewed to ensure that the requirements of the sampling program, including the number of samples and locations, sampling procedures, and sample handling, were fulfilled. Acceptable departures from the planned sampling program, such as collecting a sample from an adjacent location because of a subsurface obstruction, will not impact the data usability.

Sample collection procedures will be reviewed for compliance with the requirements of the FSP and QAPP. If alternate sampling procedure were used, the acceptability of the procedure will be evaluated to determine the affect on the usability of the data. Data usability will not be affected if the procedure used is determined to be an acceptable alternative that fulfills the measurement performance criteria in Section 4.2 of this QAPP. Acceptable alternate sampling procedures include collecting soil samples with a drill rig instead of a direct-push sampling device. However, data generated from sampling procedures that do not provide representative samples will be rejected.

Sample handling records will be reviewed to ensure that sample integrity remained intact from collection to laboratory receipt and that samples were properly preserved. Chain-of-custody documentation and sample condition upon laboratory receipt will be reviewed. The data from samples for which the chain-of-custody or sample identification cannot be verified will be rejected. The data for samples that were not properly preserved will be qualified or rejected depending on the severity of the deviation from the requirements of the FSP and QAPP. The criteria for rejecting improperly preserved samples will be that the sample has been rendered unsuitable for analysis. The criteria for qualifying or rejecting data for samples that are received at the laboratory without being properly

preserved, but not rendered unsuitable for analysis, will be based on the sample holding time period evaluation criteria for unpreserved samples specified in the National Functional Guidelines. Data qualification will be consistent with the action specified in the National Functional Guidelines.

Field and laboratory data will be verified to ensure that the methods used to analyze the samples were consistent with the requirements of this QAPP. Data generated from the use of unapproved methods will be rejected.

QC data will be reviewed to determine compliance with the acceptance criteria in Section 4.2 of this QAPP. QC data that do not meet the acceptance criteria will result in sample data qualification. Significant departures from the QC acceptance criteria may result in rejected data. Situations that result in data rejection include samples analyzed beyond twice the technical holding time period, internal standard recoveries less than 10 percent for non-detected analytes quantitated with that internal standard, surrogate standard recoveries less than 10 percent for non-detected analytes in that sample, inorganic LCS analyte recoveries less than 50 percent if the analyte is not detected in the associated samples, inorganic matrix spike analyte recoveries less than 30 percent if the analyte is not detected in the associated samples, organic matrix spike compound recoveries less than 10 percent if the compound is not detected in the MS/MSD sample, and organic LCS compound recoveries less than 10 percent if the compound is not detected in the associated samples.

7.2 VERIFICATION AND VALIDATION METHODS

Field data will be verified by reviewing field documentation and chain-of-custody records. The laboratory will internally verify the laboratory data by reviewing and documenting sample receipt, sample preparation, sample analysis (including internal QC checks), data reduction and reporting. Any deviations from the acceptance criteria, corrective actions taken, and data determined to be of limited usability (i.e., laboratory-qualified data) will be noted in the case narrative of the laboratory report.

Data validation will be conducted by CRA consistent with the procedure identified in Section 5.9.2 of this QAPP. The data verification/validation procedure will identify data as being acceptable, of limited usability (qualified as estimated), or rejected. The

conditions that result in data being qualified as estimated or rejected are identified in Section 7.1 of this QAPP. The results of the data verification/validation will be provided in data validation memoranda that are provided to CRA's Project Manager and are included in Quality Assurance Management Reports.

Data determined to be unusable may require that corrective action to be taken. Potential types of corrective action may include resampling by the field team or reanalysis of samples by the laboratory. The corrective actions taken are dependent upon the ability to mobilize the field team and whether the data are critical for project DQOs to be achieved. Should CRA's QA Officer identify a situation requiring corrective action during data verification/validation, CRA's Project Manager will be responsible for approving the implementation of the corrective action.

7.3 USABILITY/RECONCILIATION WITH DATA QUALITY OBJECTIVES

The overall usability of the data for the RD activities will be assessed by evaluating the PARCCS of the data set to the measurement performance criteria in Section 4.2 of this QAPP using basic statistical quantities as applicable. The procedures and statistical formulas to be used for these evaluations are presented in the following subsections.

7.3.1 PRECISION

Project precision will be evaluated by assessing the RPD data from field duplicate samples. Analytical precision will be evaluated by assessing the RPD data from either duplicate spiked sample analyses or duplicate sample analyses. The RPD between two measurements is calculated using the following simplified formula:

$$RPD = \frac{|R_1 - R_2|}{R_1 + R_2} X \ 200$$

where:

R_1 = value of first result
R_2 = value of second result

Overall precision for the sampling programs will be determined by calculating the mean RPD for all field duplicates in a given sampling program. This will provide an evaluation of the overall variability attributable to the sampling procedure, sample matrix, and laboratory procedures in each sampling program.

The overall precision requirement will be the same as the project precision. It should be noted that the RPD of two measurements can be very high when the data approach the quantitation limit of an analysis. The calculation of the mean RPD will only include the RPD values for field duplicate sample analyte data that are greater than or equal to 5 times the quantitation limit for an analysis.

7.3.2 ACCURACY/BIAS

The data from method/preparation blank samples, field blank samples, surrogate spikes, MS/MSD samples, and LCSs will be used to determine accuracy and potential bias of the sample data.

The data from method/preparation blank samples provide an indication of laboratory contamination that may result in bias of sample data. Sample data associated with method/preparation blank contamination will have been identified during the data verification/validation process. Sample data associated with method/preparation blank contamination are evaluated during data validation procedure to determine if analytes detected in the samples and the associated method/preparation blanks are "real" or are the result of laboratory contamination. The procedure for this evaluation involves comparing the concentration of the analyte in the sample to the concentration in the method/preparation blank taking into account adjustments for sample dilutions and dry-weight reporting. In general, the sample data are qualified as not detected if the sample concentration is less than 5 times (10 times for common laboratory contaminants) the method/preparation blank concentration. Typically, the quantitation limit for the affected analyte is elevated to the concentration detected in the sample.

The data from field blanks provide an indication of field conditions that may result in bias of sample data. Sample data associated with contaminated field blank samples will have been identified during the data verification/validation process. The evaluation procedure and qualification of sample data associated with field blank contamination is performed in

the same manner as the evaluation procedure for method blank sample contamination, taking into account the difference in units for aqueous field blank samples collected during soil sampling programs.

Surrogate spike recoveries provide information regarding the accuracy/bias of the organic analyses on an individual sample basis. Surrogate compounds are not expected to be found in the samples and are added to every sample prior to sample preparation/purging. The percent recovery data provide an indication of the effect that the sample matrix may have on the preparation and analysis procedure. Sample data exhibiting matrix effects will have been identified during the data verification/validation process.

Matrix spike sample data provide information regarding the accuracy/bias of the analytical methods relative to the sample matrix. Matrix spike samples are field samples that have been fortified with target analytes prior to sample preparation and analysis. The percent recovery data provide an indication of the effect that the sample matrix may have on the preparation and analysis procedure. Sample data exhibiting matrix effects will have been identified during the data verification/validation process.

Analytical accuracy/bias will be determined by evaluating the percent recovery data of LCSs. LCSs are artificial samples prepared in the laboratory using a blank matrix that is fortified with analytes from a standard reference material that is independent of the calibration standards. LCSs are prepared and analyzed in the same manner as the field samples. The data from LCS analyses will provide an indication of the accuracy and bias of the analytical method for each target analyte.

Percent recovery is calculated using the following formula:

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

where:

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

The percent recovery of LCSs samples are determined by dividing the measured value by the true value and multiplying by 100.

Overall accuracy/bias for the sampling events will be determined by calculating the percent of accuracy measurements that meet the measurement performance criteria specified in Section 4.2 of this QAPP. Overall accuracy will be considered acceptable if the surrogate percent recoveries, MS/MSD percent recoveries, and LCS percent recoveries are met for at least 75 percent of the samples.

7.3.3 SAMPLE REPRESENTATIVENESS

Representiveness of the samples will be assessed by reviewing the results of field audits and the data from field duplicate samples. Overall sample representativeness will be determined by calculating the percent of field duplicate sample data that achieved the RPD criteria specified in Section 4.2 of this QAPP. Overall sample representativeness will be considered acceptable if the results of field audits indicate that the approve sampling methods or alternate acceptable sampling methods were used to collect the samples and the field duplicate RPD data are acceptable for at least 75 percent of the samples.

7.3.4 COMPLETENESS

Completeness will be assessed by comparing the number of valid (usable) sample results to the total possible number of results within a specific sample matrix and/or analysis. Percent completeness will be calculated using the following formula:

$$\% \text{ Completeness} = \frac{\text{Number of Valid (usable) measurements}}{\text{Number of Measurements Planned}} \times 100$$

Overall completeness will be assessed by calculating the mean percent completeness for the entire set of data obtained for each sampling program. The overall completeness for the soil investigation will be calculated when all sampling and analysis is concluded. Overall completeness will be considered acceptable if at least 90 percent of the data are determined to be valid.

7.3.5 COMPARABILITY

The comparability of data sets will be evaluated by reviewing the sampling and analysis methods used to generate the data for each data set. Project comparability will be determined to be acceptable if the sampling and analysis methods specified in this QAPP and any approved QAPP revisions or amendments are used for generating the data.

Overall comparability of data from split samples (samples that are collected at the same time from the same location and split equally between two parties using sample containers from the same source or vendor) will be evaluated by determining the RPD of detected analytes in both samples following data verification/validation. Analytes that are detected in only one of the two samples will be assessed by reviewing the data verification/validation reports for both data sets and determining the cause of the discrepancy. Overall comparability of split sample data will be considered acceptable if the RPD for detected analytes with concentrations greater than or equal to 5 times their respective quantitation limits does not exceed RPD acceptance criteria for field duplicate samples.

7.3.6 SENSITIVITY AND QUANTITATION LIMITS

The quantitation limits for the sample data will be reviewed to ensure that the sensitivity of the analyses was sufficient to achieve the cleanup objectives for the soil investigation. The method/preparation blank sample data and LCSs percent recovery data will be reviewed to assess compliance with the measurement performance criteria specified in Section 4.2 of this QAPP.

Overall sensitivity will be assessed by comparing the sensitivity to the detectability requirements for the analyses. Overall sensitivity will be considered acceptable if quantitation limits for the samples are less than the applicable evaluation criteria.

It should be noted that quantitation limits may be elevated as a result of high concentrations of target compounds, non-target compounds, and matrix interferences (collectively known as sample matrix effects). In these cases, the sensitivity of the analyses will be evaluated on an individual sample basis relative to the applicable evaluation

criteria. The need to investigate the use of alternate analytical methods may be required if the sensitivity of the analytical methods identified in this QAPP cannot achieve the evaluation criteria as a result of sample matrix effects.

7.3.7 DATA LIMITATIONS AND ACTIONS

Data use limitations will be identified in data quality assessment reports. Data that do not meet the measurement performance criteria specified in this QAPP will be identified and the impact on the project quality objectives will be assessed and discussed in these reports. Specific actions for data that do not meet the measurement performance criteria depends on the use of the data, and may require that additional samples are collected or the use of the data be restricted.

Determination of the overall data quality for a specific sampling program will be conducted at the completion of the program. Data quality assessment reports will be included with the project reports identified in the Soil Pre-Design Study Work Plan.

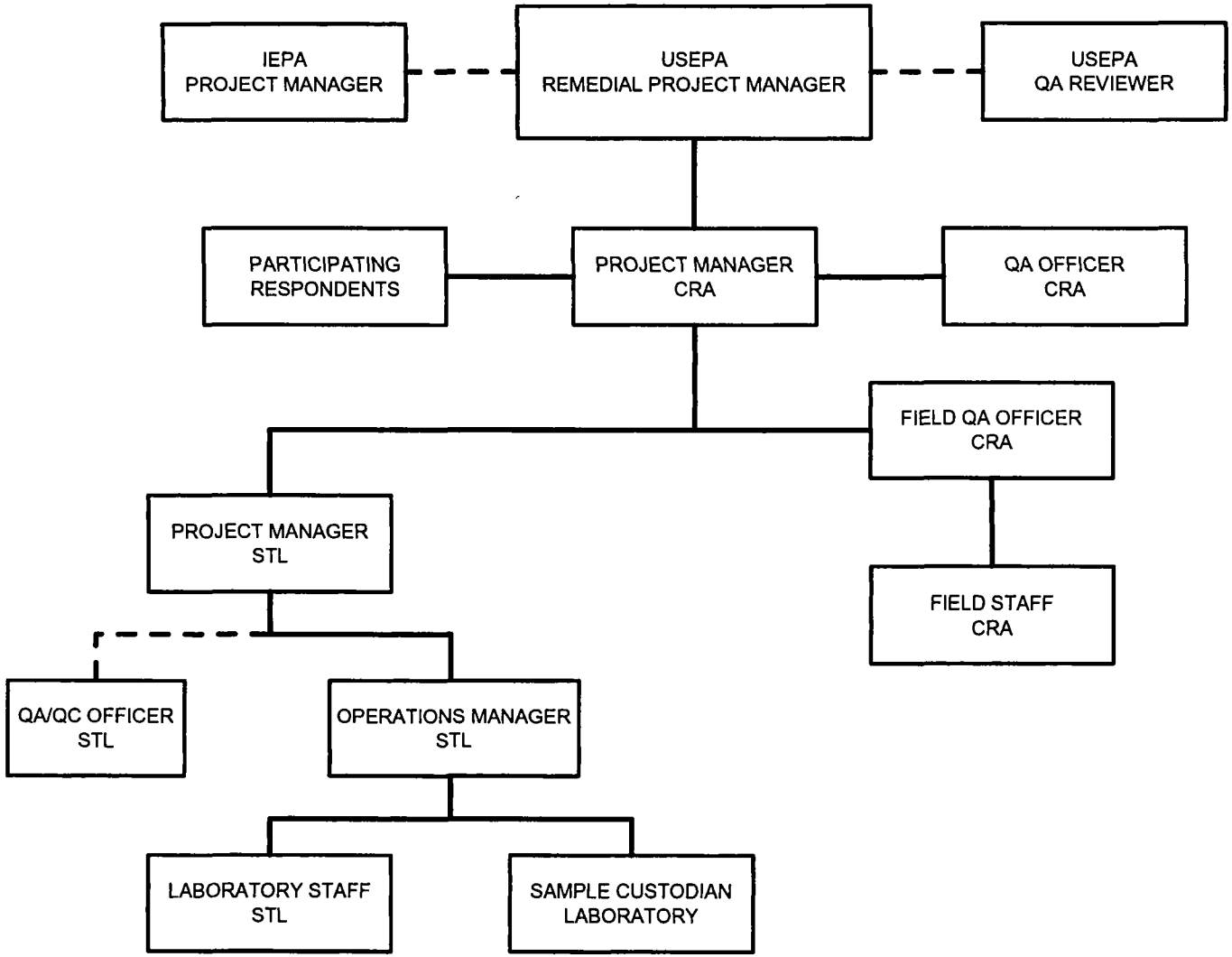

figure 2.1

PROJECT ORGANIZATION
WAUKEGAN MANUFACTURED GAS AND COKE PLANT
Waukegan, Illinois

19023-00(002)GN-CO009 JAN 22/2002

TABLE 3.1

SUMMARY OF SAMPLING AND ANALYSIS PROGRAM
SOIL PRE-DESIGN STUDY
WAUKEGAN MANUFACTURED GAS AND COKE PLANT SITE
WAUKEGAN, ILLINOIS

				QC Samples			
Location	*Sample Matrix*	*Laboratory Parameters* [1]	*Number of Samples*	*Field Blanks*	*Field Duplicates*	*MS/MSD* [2] *MS/DUP*	*Total*
Designated Soil Stockpile	Soil	Waste Characterization, Geotechnical	4	0	0	0	4
PAH Investigation Zone	Soil	Site-Specific SVOCs	270	27	14	14	325
	Soil	Waste Characterization, Geotechnical	5	0	0	0	5
Arsenic Investigation Zone	Soil	Arsenic	78	8	4	4	94
	Soil	Geotechnical	3	0	0	0	3
	Soil	Waste Characterization	2	0	0	0	2

[1] Waste Characterization includes Toxicity Characteristic Leaching Procedure (TCLP) volatile organic compounds (VOCs), TCLP semivolatile organic compounds (SVOCs), TCLP pesticides, TCLP herbicides, TCLP metals, polychlorinated biphenyls (PCBs), cyanide and sulfide reactivity, corrosivity (as pH), ignitability, sulfate, sulfide, heat content (Btu/lb.), and free liquids (paint filter test). Geotechnical analyses include grain size distribution, bulk density, organic carbon content, and moisture content.

[2] Matrix spike/matrix duplicate (MS/MSD) analyses will be performed for Site-specific SVOCs. MS/MSD samples will be collected at a frequency of 1 per 20 or fewer investigative samples. MS/MSD or MS/laboratory duplicate (MS/DUP) analyses will be performed for inorganics. Samples designated for MS/MSD or MS/DUP analyses will be collected at a frequency of 1 per 20 or fewer investigative samples.

TABLE 3.2

TARGETED QUANTITATION LIMITS
SOIL PRE-DESIGN STUDY
WAUKEGAN MANUFACTURED GAS AND COKE PLANT SITE
WAUKEGAN, ILLINOIS

	Targeted Quantitation Limit[1] *(mg/kg)*	*Cleanup Objective (mg/kg)*
Inorganics		
Arsenic	30	940
Site-specific SVOCs		
Benzo(a)anthracene	0.33	1,160
Benzo(a)pyrene	0.33	116
Benzo(b)fluoranthene	0.33	1,160
Dibenz(a,h)anthracene	0.33	116
Indeno(1,2,3-cd)pyrene	0.33	1,160
Naphthalene	0.33	48,556
Dibenzofuran	0.33	5,390
4-Methylphenol	0.33	6,738

	Targeted Quantitation Limit (mg/kg)	*Regulatory Level (mg/kg)*
PCBs		
Aroclor 1016	0.033	50
Aroclor 1221	0.033	50
Aroclor 1232	0.033	50
Aroclor 1242	0.033	50
Aroclor 1248	0.033	50
Aroclor 1254	0.033	50
Aroclor 1260	0.033	50

	Targeted Quantitation Limit (mg/L)	*Regulatory Level (mg/L)*
TCLP Volatile Organic Compounds		
Benzene	0.005	0.5
Methyl ethyl ketone (2-Butanor	0.020	200.0
Carbon Tetrachloride	0.005	0.5
Chlorobenzene	0.005	100.0
Chloroform	0.005	6.0
1,2-Dichloroethane	0.005	0.5
1,1-Dichloroethylene	0.005	0.7
Tetrachloroethylene	0.005	0.7
Trichloroethene	0.005	0.5
Vinyl chloride	0.010	0.2

TABLE 3.2

TARGETED QUANTITATION LIMITS
SOIL PRE-DESIGN STUDY
WAUKEGAN MANUFACTURED GAS AND COKE PLANT SITE
WAUKEGAN, ILLINOIS

	Targeted Quantitation Limit (mg/L)	*Regulatory Level (mg/L)*
TCLP Semivolatile Organic Compounds		
m&p-Cresol	0.010	200.0
1,4-Dichlorobenzene	0.010	7.5
2,4-Dinitrotoluene	0.010	0.13
Hexachlorobenzene	0.010	0.13
Hexachlorobutadiene	0.010	0.5
Hexachloroethane	0.010	3.0
o-Cresol	0.010	200.0
Nitrobenzene	0.010	2.0
Pentachlorophenol	0.050	100.0
Pyridine	0.020	5.0
2,4,5-Trichlorophenol	0.010	400.0
2,4,6-Trichlorophenol	0.010	2.0
TCLP Pesticides		
Lindane	0.00005	0.4
Chlordane	0.005	0.03
Endrin	0.00005	0.02
Heptachlor	0.00005	0.008
Heptachlor epoxide	0.00005	0.008
Methoxychlor	0.0001	10.0
Toxaphene	0.002	0.5
TCLP Herbicides		
2,4-D	0.004	10.0
2,4,5-TP (Silvex)	0.001	1.0
TCLP Metals		
Arsenic	0.5	5.0
Barium	10	100.0
Cadmium	0.1	1.0
Chromium	0.5	5.0
Lead	0.5	5.0
Selenium	0.25	1.0
Silver	0.5	5.0
Mercury	0.002	0.2

TABLE 3.2

TARGETED QUANTITATION LIMITS
SOIL PRE-DESIGN STUDY
WAUKEGAN MANUFACTURED GAS AND COKE PLANT SITE
WAUKEGAN, ILLINOIS

	Targeted Quantitation Limit	*Regulatory Level*
RCRA Characteristics		
Cyanide Reactivity	10 mg/kg	NA[2]
Sulfide Reactivity	200 mg/kg	NA[2]
Corrosivity (as pH)	1 SU	pH ≤ 2; pH ≥ 12.5
Ignitability (as flash point)	Ambient °C	60 °C
Other		
Sulfate	10 mg/kg	
Sulfide	50 mg/kg	
Heat Content	100 Btu/lb.[3]	
Paint Filter Test (Free Liquids)	Present/Absent	

[1] The targeted quantitation limits for soil samples are presented on a wet-weight basis. Quantitation limits reported by the laboratory on a dry-weight basis will be higher. Targeted quantitation are presented for guidance and may not be achievable for all samples because of matrix interference, sample dilutions, or elevated concentrations of target or non-target compounds.

[2] Guidance for reactive cyanide and sulfide was withdrawn by U.S. EPA.

[3] Actual minimum detectable heat content will depend on sample size and matrix composition.

TABLE 4.1

PERCENT RECOVERY AND RELATIVE PERCENT DIFFERENCE CONTROL LIMITS
SOIL PRE-DESIGN STUDY
WAUKEGAN MANUFACTURED GAS AND COKE PLANT SITE
WAUKEGAN, ILLINOIS

Analyses	*% Recovery Control Limits* [1]	
	MS/MSD	*LCS*
Inorganics		
Arsenic	75-125 (20)	80-120
SVOCs		
Benzo(a)anthracene	30-136 (63)	56-110
Benzo(a)pyrene	28-142 (86)	56-115
Benzo(b)fluoranthene	31-139 (67)	54-116
Dibenz(a,h)anthracene	31-142 (99)	50-129
Indeno(1,2,3-cd)pyrene	20-147 (73)	44-128
Naphthalene	31-138 (65)	59-110
Dibenzofuran	35-132 (58)	57-110
4-Methylphenol	36-123 (86)	56-110
PCBs		
Aroclor 1016	26-144 (39)	49-122
Aroclor 1260	37-138 (33)	51-127
TCLP Volatile Organic Compounds		
Benzene	55-138 (20)	75-129
Carbon tetrachloride	32-143 (68)	57-137
Chlorobenzene	49-139 (22)	75-127
Chloroform	59-128 (46)	73-115
1,2-Dichloroethane	56-126 (38)	78-121
Vinyl chloride	30-136 (80)	24-152
TCLP Semivolatile Organic Compounds		
m&p-Cresol	46-109 (32)	46-109
1,4-Dichlorobenzene	18-110 (36)	28-110
2,4-Dinitrotoluene	31-131 (32)	47-131
Hexachlorobenzene	36-132 (22)	57-128
Hexachlorobutadiene	18-116 (32)	36-116
Hexachloroethane	18-110 (33)	30-110
o-Cresol	49-109 (32)	46-109
Nitrobenzene	19-211 (59)	45-130
Pentachlorophenol	10-140 (56)	10-140
Pyridine	10-148 (65)	10-148
2,4,5-Trichlorophenol	24-143 (22)	41-125
2,4,6-Trichlorophenol	36-135 (27)	46-135

TABLE 4.1

PERCENT RECOVERY AND RELATIVE PERCENT DIFFERENCE CONTROL LIMITS
SOIL PRE-DESIGN STUDY
WAUKEGAN MANUFACTURED GAS AND COKE PLANT SITE
WAUKEGAN, ILLINOIS

Analyses	*% Recovery Control Limits* [1]	
	MS/MSD	*LCS*
TCLP Pesticides		
Lindane	50-150 (50)	56-110
Endrin	50-150 (50)	50-110
Heptachlor	50-150 (50)	57-110
Heptachlor epoxide	50-150 (50)	56-110
Methoxychlor	50-150 (50)	41-126
TCLP Herbicides		
2,4-D	54-114 (67)	35-136
TCLP Metals		
Arsenic	50-150 (20)	50-150
Barium	50-150 (20)	50-150
Cadmium	50-150 (20)	50-150
Chromium	50-150 (20)	50-150
Lead	50-150 (20)	50-150
Selenium	50-150 (20)	50-150
Silver	50-150 (20)	50-150
Mercury	50-150 (20)	50-150
RCRA Characteristics		
Ignitability (as flash point)	75-125 (20)	75-125
Sulfide Reactivity	NA (20)	NA
Cyanide Reactivity	NA (20)	NA
Corrosivity (as pH)	97-103 (20)	97-103
Other		
Sulfate	80-110 (20)	90-110
Sulfide	64-110 (20)	74-110
Heat Content	NA	NA
Paint Filter Test (free liquids)	NA	NA

[1] Values in parentheses are the maximum RPD values allowed for MS/MSD or MS/DUP analytes. Laboratory control limits are updated on a periodic basis, and the control limits in effect when the samples are analyzed will be used for data validation purposes.

[2] NA - Not Applicable

TABLE 4.2

SURROGATE COMPOUND PERCENT RECOVERY CONTROL LIMITS
SOIL PRE-DESIGN STUDY
WAUKEGAN MANUFACTURED GAS AND COKE PLANT SITE
WAUKEGAN, ILLINOIS

		% Recovery Control Limits [1]	
Analysis	*Surrogate Compound*	*Soil*	*TCLP Leachate*
VOCs	Toluene-d_8	NA[2]	60-143
	4-Bromofluorobenzene	NA	47-158
	1,2-Dichloroethane-d_4	NA	61-130
	Dibromofluoromethane	NA	59-138
SVOCs	Nitrobenzene-d_5	42-110	32-112
	2-Fluorobiphenyl	43-110	30-110
	Terphenyl-d_{14}	37-137	10-144
	Phenol-d_5	25-115	10-113
	2-Fluorophenol	11-116	13-110
	2,4,6-Tribromophenol	35-116	21-122
Pesticides/PCBs	Tetrachloro-m-xylene	31-127	47-110
	Decachlorobiphenyl	23-141	31-115
Herbicides	2,4-Dichlorophenylacetic acid	NA	37-116

[1] Laboratory control limits are updated on a periodic basis, and the control limits in effect when the samples are analyzed will be used for data validation purposes.
[2] NA - Not Applicable

TABLE 5.1

CONTAINER, PRESERVATION, SHIPPING, AND PACKAGING REQUIREMENTS
SOIL PRE-DESIGN STUDY
WAUKEGAN MANUFACTURED GAS AND COKE PLANT SITE
WAUKEGAN, ILLINOIS

Analysis	*Sample Containers* [1]	*Preservation* [2]	*Maximum Holding Time from Sample Collection* [3]	*Volume of Sample*	*Shipping*	*Normal Packaging*
Arsenic	One 60-mL glass or polyethylene jar	Iced	180 days for analysis	Fill to shoulder of jar	Federal Express Priority 1	Bubble Wrap or Foam Chips
Site-Specific SVOCs	One 120-mL glass jar	Iced	14 days for extraction 40 days from extraction for analysis	Fill to shoulder of jar	Federal Express Priority 1	Bubble Wrap or Foam Chips
TCLP VOCs	One 120-mL glass jar	None	14 days for TCLP extraction 14 days from TCLP extraction for analysis	Fill completely	Federal Express Priority 1	Bubble Wrap or Foam Chips
TCLP SVOCs, Pesticides, Herbicides	One 500-mL glass jar	None	14 days for TCLP extraction 7 days from TCLP extraction for preparative extraction 40 days from preparative extraction for analysis	Fill to shoulder of jar	Federal Express Priority 1	Bubble Wrap or Foam Chips
TCLP Metals	One 120-mL glass jar	None	180 days for TCLP extraction 180 days from TCLP extraction for analysis (mercury - 28 days for TCLP extraction; 28 days from TCLP extraction for analysis)	Fill to shoulder of jar	Federal Express Priority 1	Bubble Wrap or Foam Chips

TABLE 5.1

CONTAINER, PRESERVATION, SHIPPING, AND PACKAGING REQUIREMENTS
SOIL PRE-DESIGN STUDY
WAUKEGAN MANUFACTURED GAS AND COKE PLANT SITE
WAUKEGAN, ILLINOIS

Analysis	*Sample Containers*[1]	*Preservation*[2]	*Maximum Holding Time from Sample Collection*[3]	*Volume of Sample*	*Shipping*	*Normal Packaging*
Sulfate	One 120-mL glass jar	Iced	28 days for analysis	Fill to shoulder of jar	Federal Express Priority 1	Bubble Wrap or Foam Chips
Sulfide	One 120-mL glass jar	Iced	7 days for analysis	Fill to shoulder of jar	Federal Express Priority 1	Bubble Wrap or Foam Chips
PCBs	One 120-mL glass jar	Iced	14 days for extraction 40 days from extraction for analysis	Fill to shoulder of jar	Federal Express Priority 1	Bubble Wrap or Foam Chips
Reactivity, Corrosivity, Ignitability, Heat Content, Free Liquids	One 500-mL glass jar	None	None Established	Fill to shoulder of jar	Federal Express Priority 1	Bubble Wrap or Foam Chips
Geotechnical	One 500-mL glass jar	None	None Established	Fill to shoulder of jar	Federal Express Priority 1	Bubble Wrap or Foam Chips

[1] To the extent possible, analyses will be combined to minimize the sample containers required.
[2] Samples requiring refrigeration will be shipped with bagged, cubed ice, and will be stored at 4°± 2°C following laboratory receipt and log-in.
[3] The holding times presented are technical holding times that are based on the time from sample collection.

TABLE 5.2

SUMMARY OF ANALYTICAL METHODS
SOIL PRE-DESIGN STUDY
WAUKEGAN MANUFACTURED GAS AND COKE PLANT SITE
WAUKEGAN, ILLINOIS

Parameter[1]	*Preparation Method*[2]	*Analysis Method*
Site-Specific SVOCs	SOP for SW-846 3550B	SOP for SW-846 8270C
Total Arsenic	SOP for SW-846 3050B	SOP for SW-846 6010B
TCLP Extraction	SOP for SW-846 1311	NA[3]
TCLP VOCs	SOP for SW-846 5030B	SOP for SW-846 8260B
TCLP SVOCs	SOP for SW-846 3520C	SOP for SW-846 8270C
TCLP Pesticides	SOP for SW-846 3520C	SOP for SW-846 8081A
TCLP Herbicides	SOP for SW-846 8151A	SOP for SW-846 8151A
TCLP Metals	SOP for SW-846 3010A/7470A	SOPs for SW-846 6010B/7470A
PCBs	SOP for SW-846 3550B	SOP for SW-846 8082
Reactive Sulfide	SOP for SW-846 Section 7.3.4.2	SOP for SW-846 Section 7.3.4.2
Reactive Cyanide	SOP for SW-846 Section 7.3.3.2	SOP for SW-846 Section 7.3.3.2
Corrosivity (as pH)	SOP for SW-846 9045C	SOP for SW-846 9045C
Ignitability (as flashpoint)	SOP for SW-846 1010	SOP for SW-846 1010
Sulfate	SOP for EPA 300.0	SOP for EPA 300.0
Sulfide	SOP for SW-846 9030A	SOP for SW-846 9030A
Paint Filter Test	SOP for SW-846 9095A	SOP for SW-846 9095A
Heat Content (Btu/lb.)	ASTM E 711/D 2015	ASTM E 711/D 2015
Grain Size Distribution	ASTM D 421	ASTM D 422, D 1140
Bulk Density	ASTM D 2437	ASTM D 2437
Moisture Content	ASTM D 2216	ASTM D 2216
Organic Carbon Content	ASTM D 2974	ASTM D 2974

[1] SVOCs - Semivolatile Organic Compounds
TCLP - Toxicity Characteristic Leaching Procedure
VOCs - Volatile Organic Compounds
PCBs - Polychlorinated Biphenyls

[2] Laboratory Standard Operating Procedures (SOPs) are presented in Attachment 2. SOP numbers are provided on the attachment cover page.
SW-846 - "Test Methods for Evaluating Solid Wastes, Physical/Chemical Methods", EPA SW-846, 3rd Edition with Updates I through III.
EPA - "Methods for the Determination of Inorganic Substances in Environmental Samples", EPA/600/R-93-100.
ASTM - "Annual Book of ASTM Standards", American Society for Testing and Materials.

[3] NA - Not Applicable

TABLE 5.3

ROUTINE PREVENTIVE MAINTENANCE PROCEDURES AND SCHEDULES
SOIL PRE-DESIGN STUDY
WAUKEGAN MANUFACTURED GAS AND COKE PLANT SITE
WAUKEGAN, ILLINOIS

Instrument	*Maintenance Procedures/Schedule*	*Spare Parts in Stock*
Gas Chromatograph/Mass Spectrometer	1. Replace pump oil as needed. 2. Change septa weekly or as often as needed. 3. Change gas line dryers as needed. 4. Replace electron multiplier as often as needed. 5. Replace gas jet splitter as needed. 6. Replace GC injector glass liner weekly or as often as needed. 7. Replace GC column as needed. 8. Check to ensure that gas supply is sufficient for the day's activity and the delivery pressures are set as described in the SOP. 9. Check to ensure the pressure on the primary regulator never falls below 100 psi.	1. Syringes 2. Septa 3. Various electronic components 4. Glass jet splitters 5. GC columns 6. Glass liners
Gas Chromatograph	1. Change septa weekly or as often as needed. 2. Change gas line dryers as needed. 3. Replace GC injector glass liner weekly or as often as needed. 4. Replace GC column as needed. 5. Clean/replace GC detector as needed. 6. Check to ensure that gas supply is sufficient for the day's activity and the delivery pressures are set as described in the SOP. 7. Check to ensure the pressure on the primary regulator never falls below 100 psi.	1. Syringes 2. Septa 3. Detectors 4. Glass liners 5. GC columns

TABLE 5.3

ROUTINE PREVENTIVE MAINTENANCE PROCEDURES AND SCHEDULES
SOIL PRE-DESIGN STUDY
WAUKEGAN MANUFACTURED GAS AND COKE PLANT SITE
WAUKEGAN, ILLINOIS

Instrument	*Maintenance Procedures/Schedule*	*Spare Parts in Stock*
Purge and Trap Sample Concentrator	1. Replace trap as needed. 2. Decontaminate the system after running high concentration samples or as required by blank analysis. 3. Leak check system daily and as often as needed. 4. Check to ensure the gas supply is sufficient for the day's activity and the delivery pressures are set as described in the SOP. 5. Check to ensure the pressure on the primary regulator never run below 100 psi.	1. Traps 2. Spargers 3. Various electronic components/ circuits 4. Plumbing supplies - tubing, fittings
Inductively Coupled Plasma Spectrometer	1. Clean torch assembly and mixing chamber when discolored or after eight hours of running high dissolved solid samples. 2. Clean nebulizer as needed. 3. Check to ensure the gas supply is sufficient for the day's activity and the delivery pressures are set as described in the SOP.	1. Torch and mixing chamber 2. Nebulizer
Cold Vapor Mercury Analyzer	1. Clean quartz window as necessary. 2. Check to ensure the gas supply is sufficient for the day's activity and the delivery pressures are set as described in the SOP. 3. Check tubing daily and replace as necessary.	1. Mercury lamp 2. Tubing

TABLE 5.3

ROUTINE PREVENTIVE MAINTENANCE PROCEDURES AND SCHEDULES
SOIL PRE-DESIGN STUDY
WAUKEGAN MANUFACTURED GAS AND COKE PLANT SITE
WAUKEGAN, ILLINOIS

Instrument	*Maintenance Procedures/Schedule*	*Spare Parts in Stock*
Ion Chromatograph	1. Change pre-column as needed. 2. Replace injection loop monthly or as often as needed. 3. Replace column as needed. 4. Clean/replace conductivity detector as needed.	1. Syringes 2. Injection loops 3. Pre-columns 4. Detectors 5. Chromatography column
Flash Point Tester	1. Check gas supply daily. Replace as needed. 2. Check operation of flame lowering mechanism daily. Lubricate as needed. 3. Clean cup with appropriate solvent after each use. Rinse with DI water and allow cup to dry thoroughly prior to analyzing next sample. 4. Check thermometer for mercury gaps prior to use. Replace as necessary.	1. Ignition gas 2. Thermometers 3. Cups
pH Meter	1. Check battery and replace if discharged (if applicable). 2. Check electrolyte solution and replenish as needed. 3. Rinse electrode with DI water after each sample. 4. Store electrode as recommended in operation manual.	1. Standard pH buffer solutions 2. Electrolyte filling solution 3. Electrodes

ATTACHMENT 1

LABORATORY
STANDARD OPERATING PROCEDURES

Title		*SOP Number*
1)	Sample Receipt and Sample Control	NC-SC-0005
2)	Quality Control Program	QA-003
3)	Statistical Evaluation of Data and Control Charts	NC-QA-0018
4)	Metals Digestion	CORP-IP-0002NC
5)	Metals Analysis	CORP-MT-0001NC
6)	PCBs/SVOCs Extraction	CORP-OP-0001NC
7)	PCBs Analysis	CORP-GC-0001NC
8)	SVOCs Analysis	CORP-MS-0001NC
9)	TCLP Extraction	CORP-IP-0004NC
10)	VOCs Preparation and Analysis	CORP-MS-0002NC
11)	Mercury Preparation and Analysis	CORP-MT-0005NC
12)	Ignitability (flashpoint)	NC-WC-0034
13)	Soil pH	NC-WC-0010
14)	Reactive Cyanide	NC-WC-0033
15)	Reactive Sulfide	NC-WC-0061
16)	Paint Filter	NC-WC-0046
17)	Sulfate	NC-WC-0084
18)	Sulfide	NC-WC-0060

STL STANDARD OPERATING PROCEDURE

TITLE: SAMPLE RECEIVING AND SAMPLE CONTROL

(SUPERSEDES: REVISION 6, 09/02/99)

Prepared by:		6/27/01 Date
Reviewed by:	Technology Specialist	6-27-01 Date
Approved by:	Quality Assurance Manager	6/28/01 Date
Approved by:	Environmental Health and Safety Coordinator	6-28-01 Date
Approved by:	Laboratory Director	7-2-01 Date

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1 SCOPE AND APPLICATION

1.1 It is the responsibility of Sample Receiving and Control personnel to perform the procedures described herein in full compliance with this SOP.

1.2 It is the responsibility of the Laboratory Director, QA Manager, and departmental Supervisor of the facility to assure 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 personnel to perform this SOP correctly.

1.3 Analyst

1.3.1 It is the responsibility of the analyst to provide the correct request(s) for bottles to the sample custodian by using the QuantIMS program, PSR024.01 (as described in section 5.3) and to return all bottles to the custodian.

1.4 Sample Custodian

1.4.1 It is the responsibility of the sample custodian or designee to fill all bottle requests in a timely fashion and document the transfers on the request/return forms (Appendix 17.1.6).

1.4.2 It is the responsibility of the sample custodian or designee to correctly document the bottle information required (Appendix 17.1.6).

1.4.3 It is the responsibility of the sample custodian or designee to ensure that the returned bottle is the same as the one relinquished and to return it to the proper storage area.

1.4.4 This document accurately reflects current laboratory standard operating procedures (SOP) as of the date above. All facility SOPs are maintained and updated as necessary.

2 SUMMARY OF METHOD

2.1 Not applicable.

3 DEFINITIONS

3.1 Sample Custodian refers to sample control personnel or designee.

3.2 Refer to the glossary in the Laboratory Quality Manual (LQM), latest version

4 INTERFERENCES

4.1 Not applicable.

5 SAFETY

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

5.2 Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. If personnel are required to perform any portion of the procedure in laboratory areas, appropriate personal protective equipment and precautions must be utilized. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately. {VITON gloves may be worn when halogenated solvents are used for extraction or sample preparation, nitrile gloves may be used when other solvents are handled. [Note: VITON is readily degraded by acetone; all solvents will readily pass through disposable latex rubber gloves.]}

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} The following specific hazards are known:

5.3.1 The following materials are known to be corrosive: Sulfuric Acid, Nitric Acid, Hydrochloric Acid, Sodium Hydroxide.

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

5.5 The preparation of standards and reagents {and glassware cleaning procedures that involve solvents such as methylene chloride} will be conducted in a fume hood with the sash closed as far as the operation will permit.

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

5.7 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.

6 EQUIPMENT AND SUPPLIES

6.1 Thermometers

6.2 PPE such as gloves, lab coats, safety glasses, etc.

6.3 Utility knives

6.4 PH paper

6.5 Copier, printer, computer and label generator

6.6 Carts

7 REAGENTS AND STANDARDS

7.1 Not applicable.

8 SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1 Not applicable.

9 QUALITY CONTROL

9.1 Nonconformance and Corrective Action

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

10 CALIBRATION AND STANDARDIZATION

10.1 Not applicable.

11 PROCEDURE

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

11.2 The procedures listed in this document describe the responsibilities of Sample Control personnel in ensuring that data is transmitted correctly from the client samples to all personnel involved with sample analysis and review.

11.3 The intent of the sample custodian maintenance program is to show custody of individual bottles based on workorder number as well as bottle control numbers. This program acts as an internal chain of custody.

11.4 The sample control group opens each cooler and removes the enclosed sample documents. Coolers are prioritized based on rush status and expirable tests. If a COC (chain-of-custody) is marked rush, the following occurs:
24 hour TAT – flag with red folder
48 hour TAT – flag with blue folder
72 hour TAT – flag with yellow folder
1 week TAT – flag with green folder

11.5 If tests on the COC are expirable, the cooler is marked with a manila folder.

11.6 Rush and expirable coolers are to be unpacked first and logged as soon as possible. The lab groups are to be notified with any rush 72 hours or less.

11.7 The following information on the Cooler Receipt/ Narrative Form (Appendix 17.2.1).

11.7.1 Presence of the custody seals on the outside of the cooler

11.7.2 Presence of the custody papers inside the cooler

11.7.3 The custody papers were properly filled out (ink, signed, match labels)

11.7.4 The custody papers were signed in the appropriate place

11.7.5 Presence of the shipper's packing slip

11.7.6 Presence of packing material information: if yes, type of packing material

11.7.7 Conditions of samples at receipt (chilled, etc.).

11.7.7.1 If temp vial is present, it is used to take the temperature. The temperature of the temp vial is taken as soon as it is removed from the cooler. If a temp vial is not present, proceed to section 11.7.7.2.

11.7.7.2 When a temp vial is not present the temp is taken by placing the thermometer probe between the coolant and the sample(s). If a coolant is not present, proceed to section 11.7.7.3.

11.7.7.3 If no coolant is in the cooler, the thermometer probe is placed between two sample bottles and the temperature recorded.

11.7.7.4 If the temperature is outside 4°C ± 2°C, the anomaly is recorded on the cooler receipt form. The project manager is contacted when the temperature is >6°C.

11.7.8 Bottles sealed in separate plastic bags

11.7.9 Condition of bottles upon receipt (good condition, broken, etc.)

11.7.10 Complete bottle labels (date, time, client ID)

11.7.11 Information on bottle labels and tags agree with custody papers

11.7.12 Correct bottles used for the tests indicated

11.7.13 VOA bottles were checked for the presence of air bubbles. Any bubbles exceeding 6 mm in diameter are narrated and the PM is contacted.

11.7.14 Sufficient amount of sample sent in each bottle

11.7.15 Samples were received via overnight courier, client drop off, or other means

11.7.16 pH's are taken, on all preserved samples less Volatiles, TOC, and TOX by removing sample lids and using a droplet of sample from in the lid to test the pH. The pH's are then recorded on the cooler receipt form. The pH paper strips are then discarded.

11.7.16.1 In determining if the sample is preserved to the correct pH for Navy samples, the sample custodian or receiving personnel must take an aliquot of sample out of the sample container either by pouring out a small aliquot or using a disposable pasteur pipette and place a drop of the sample on a pH paper strip.

11.7.17 Purchased prepared vials of preservatives are used if samples are not at the correct pH. The pH is adjusted by adding the appropriate preservative in 5 mL increments up to a maximum of 20 mL or unless there is a reaction. Sulfides are preserved with 5 mL Sodium hydroxide and 1 mL Zinc acetate. The pH adjustment is noted on the cooler receipt form.

11.7.18 The concentrations of the preservatives used:

4N Sodium Hydroxide
1N Zn Acetate
1:1 HCL (18%)
1:4 $HN0_3$ (18%)
1:2 H_2SO_4 (33%)

11.7.18.1 If the pH of Navy samples are adjusted, the sample custodian or receiving personnel must record on the cooler receipt form the laboratory assigned reagent ID number.

11.8 The Sample Control person is to remove all sample containers. Any broken, leaking, or dirty sample containers are to be placed inside the fume hood. Dirty sample containers are to be cleaned appropriately, so as not to contaminate the sample storage area. The Sample Control person is to wear disposable latex gloves, safety glasses, and a lab coat while handling any samples.

11.9 Any volatile sample(s) suspected (e.g., odor) or known (client information or site history) to be high in volatile concentration, the volatiles department will be contacted for pick-up and segregation of sample(s).

11.10 The Sample Control person is to examine all documents and compare information from sample container labels and Chain-of-Custody Records to insure that there is no discrepancy between documents, ensuring that all documents are properly completed and signed.

11.11 If any problems or discrepancies are noted during the sample receiving process that compromise sample integrity, such as limited sample volume, sample identification cannot be determined from the COC, incorrect pH levels (or preservatives if known), or broken, leaking samples, the Project Manager is immediately notified. They in turn will contact the client in an attempt to solve discrepancies.

11.12 Expirable tests (hold time 48 hours or less) must be written on the top of the bottles from which they are to be analyzed. If more than one method exists for the analysis, the method must also be written. These bottles designated for expirable tests will be given directly to the wet chem lab group.

11.13 All solid /soil samples received are split off for the total solid analysis. Splitting these samples is the responsibility of the receiving group. A small portion (approx. 5-10 grams) from each sample is put into a small plastic snap-top container designated for the TS analysis. If the TS container is not labeled with a QuantIMS label at the time of splitting off, the TS container must be labeled with handwritten client ID. Containers designed for VOC analysis must not be opened/used for TS aliquot. When only one solid container is received for VOC analysis, receiving group must **not** split off because of possible contamination or possible lost volatiles. An empty TS container with a QuantIMS label is given to the VOC analysis group for each solid. The VOC group will aliquot for the TS when they open container for analysis. TS plastic containers are placed into baggies by lot (project) and the baggies are put into a box inside the walk-in cooler door.

11.14 If all samples recorded on the Chain-of-Custody Record were received by the laboratory and there are no problems observed with the sample shipment, the Sample Control person will sign the Chain-of-Custody Record in the "Received for Laboratory by:" box on the document. If problems are noted, sign for shipment and note the problems. All discrepancies are recorded on Cooler Receipt Form.

11.15 A quote must reflect what is on the chain-of-custody. Any discrepancies must be resolved by the project manager. Likewise, if there is not an associated quote in QuantIMs, the samples are placed on hold until a quote is completed by the project manager.

11.16 In the event that a project is on hold until the next day or longer, all associated paperwork is placed into a black folder and all samples and black folder are put into cold storage. Any project that is on hold must be recorded on the dry-erase board posted on walk-in cooler door.

11.17 The Sample Control person will enter each sample into the laboratory computer (QuantIMS), where a unique lot number is assigned to each project received, and sequential sample numbers are designated for each client identification within the lot.

11.17.1 Lot Numbers: The lot number is nine characters in length and is based on the date of receipt. Lot number A9J010121 is described as follows:

A - STL location where the samples were received.

(A = North Canton, B = Tampa, C = Pittsburgh, etc.)

9 - Last digit of the year (i.e. 1999).

J - Month (i.e. A = January, B = February, J = October, etc.)

01 - The next 2 numeric characters identify the day of the month, in this case, the first day of the month.

0121 - The next 4 numeric characters are the sequential assignment of numbers specific to each lot received. Each day the first lot logged in receives the number "0101", the second lot receives the number "0102", etc..

For example:

If four bottles were submitted under Client ID numbers AB100-AB103 and the laboratory identification number generated by the computer is A9K100101, then the assigned laboratory number recorded on the Sample Log-In Sheet would be as follows.

Client ID Sample Number	Assigned Laboratory Number
AB 100	A9K100101-001
AB 101	A9K100101-002
AB 102	A9K100101-003
AB 103	A9K100101-004

11.17.2 Sample Numbers: The samples in each lot are assigned a sample number that is attached to the lot number and are reset at each new lot. For example: the first and second samples in the lot above are labeled A9J010121-001 and A9J010121-002.

11.17.3 Sample Suffixes: Each sample also has a 1 character field (which is not a required field for all samples) called the suffix which identifies the sample as specified below.

Client Sample	no suffix
Method Blank	B
Laboratory Control Sample	C
Laboratory Control Sample Duplicate	L
Matrix Spike	S
Matrix Spike Duplicate	D
Sample Duplicate	X
Serial Dilution	P
Sample Confirmation	Y
Post Digestion Spike	Z
Re-analysis	I

Example: A9J010121-001X is a sample duplicate for sample A9J010121-001.

11.17.4 Work Order Numbers: Each test requested by the client for an individual sample receives an individual 8 digit work order number assigned by QuantIMS. Work order number A5WE1-2-1C is described as follows:

A5WE1 - In addition to the three digit sample identification described in 4.7.2 (i.e. - 001 and - 002), the first 5 characters of the work order number also identifies each unique sample. This identification is generated in QuantIMS using a sequential logic that is beyond the scope of this SOP to describe.

2 - The "modifier" indicates the type of run. In this case this is the second time the sample had to be run. If it needs reprepped and run again, the number would indicate a "3". The original analysis work order number assigns "1" to the modifier position.

1C - The "suffix" is the identification of the specific test for that sample. The suffix in this case is not always sequential, but is unique to the test to be performed on the sample.

Example: A5WE1-2-1C is the assigned 8 digit work order number for the reanalysis of the chloride test on the sample A5WE1. A5WE1-1-05 could be the 8 digit work order number for the analysis of SW846 8270 on sample A5WE1.

11.17.5 Each sample container with the same client ID has a unique number. Each container will be labeled with the same 5 digit work order number and then will contain a suffix beginning with – 001, -002, -003, etc. For example, if 5 containers are submitted from the same sample point and the LIMS-generated work order number is CREE4, LIMS will generate 5 labels: CREE4-001, CREE4-002, CREE4-003, CREE4-004, CREE4-005. The specific bottle number is the number used for sample request/removal paperwork.

11.17.6 Expirable tests must be given to the lab groups the day they are received. The expirable test/method is written on top of the bottle and the bottle must be put in the red bin designated for expirables. The work order or sample ID must be recorded on the expirable logsheet – also must record the test to be run, special method if necessary and the initials of the person relinquishing the sample. The wet chem lab group checks this bin throughout the day and is responsible for signing out the sample container when they take it.

11.17.7 Once all sample containers have been properly labeled and all the information has been recorded by the Sample Lot Summary, the Sample Control person will place the samples into the proper storage locations. These locations are as follows:

11.17.8 Organic extractable samples (Semivolatiles, Pesticides/PCBs) are to be placed into the walk-in refrigerators located in Sample Receiving.

11.17.9 Volatile samples are to be stored in the double-door refrigerator located in the Sample Custodian area.

11.17.9.1 Samples known or suspected to be of high concentration are not stored in these refrigerators. The applicable volatile group is contacted to obtain the samples for segregation.

11.17.10 Inorganic samples are to be placed into the walk-in refrigerators located in Sample Receiving.

11.18 Preserved metal samples are placed in a non-refrigerated room located in the Sample Custodian area. Metals samples that need to be lab filtered and preserved are stored in the walk-in cooler. All metals for Navy projects are stored in the walk-in cooler.

11.19 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.

11.20 Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

11.21 For clients who request a show of sample transfer from sample receipt to storage, a sample control record is completed (see Appendix 17.2.4 or Appendix 17.2.5). STL LIMS will generate this record for Expanded Deliverable and CLP designated samples. This record is also referred to as an internal chain of custody (COC). The form is completed as follows:

11.21.1 Laboratory sample number - record/list the individual five digit work order number in this column. List all pertaining samples in the project lot. Use an additional sheet if necessary. Do not record multiple lots on a sample control record.

11.21.2 Transferred by - record name of person making the transfer

11.21.3 Date - record date of sample transfer

11.21.4 Entered - "X" or "√" since samples are already logged into the LIMs.

11.21.5 Removed - leave blank since samples are not being removed

11.21.6 Reason - record "storage"

11.21.7 Date returned - leave blank

11.22 The completed sample control record is attached to the summary package. The sample control record can be manually printed using the SAM S31 command in QuantIMS. Note: The report package for the lot must be "D" (Expanded Deliverable) or "C" (CLP) for the report to print.

11.23 Samples are requested by an analyst through the QuantIMS program PSR024.01. This program is accessed from the Sample Receiving Menu (SAM) by selecting option S24 (Sample Removal Requests).

Bottles are requested based on method code, workorder number, prep code, QA batch number, lot number, or method group.

11.24 Each bottle has an associated lot number, sample workorder number, and bottle suffix number (Appendix 17.2.9).

11.25 When an analyst requests bottles and exits the request program, a requisition (Appendix 17.2.6) prints in the custodian's work area. This requisition identifies the requestor and the method/parameter requested. The sample custodian fills the requisition, recording each bottle number on the form. The bottle(s) is/are signed out to the custody of the requestor by indicating the name and the date of transfer. The request is relinquished with the custodian's initials and accepted by the requestor's initials.

11.26 When bottles are returned, the sample custodian records the return on the original requisition form and re-enters custody of the bottles to the sample control area. The custodian initials and dates the return on the form (Appendix 17.2.6).

11.27 When sample bottles are consumed in the analysis process, the empty container is returned to the custodian. The custodian marks a "C" by the appropriate sample on the request form to indicate a consumed sample (Appendix 17.2.6).

11.28 Samples returned after the custodian has left at the end of the day are placed in the walk-in cooler by a custodian designee and recorded as received by the custodian the next working day.

11.28.1 All request forms remain in the sample custodian area while samples are being analyzed. The final form is also kept in the sample custodian area after samples have been analyzed and reported.

11.28.2 When a sample custodian is not available, a designee gets the samples, and all request paperwork is completed properly.

11.29 Subcontracting of samples

11.29.1 Samples that are logged but not analyzed at the laboratory are subcontracted to different laboratories for analysis including other STL facilities.

11.29.2 The LIMs system will automatically print a Sample Analysis Requisition for these samples upon completion of the log-in process (Appendix 17.2.7).

11.29.3 This form contains information necessary for sample analysis. The original form is sent to the subcontracted laboratory and a copy is attached to the summary package. The Sample Analysis Requisition form must have a relinquished signature with a date and time. Any additional information necessary for sample analysis must be handwritten on the form (e.g. list of compounds, homogenizing of samples, limited quantity, etc.). In order to track subcontracted samples, the lab purchase order number on the Sample Analysis Requisition form must be recorded in the subcontracted sample PO book located in the receiving log-in area.

11.29.4 For samples sent to a non QuantIMS lab a chain of custody form is filled out and accompanies the samples.

11.29.5 A sample analysis request (SAR) can be printed from LIMS by entering the Lot Number. The SAR form can be found on Main Screen on receiving computer terminals.

12 DATA ANALYSIS AND CALCULATIONS

12.1 Not applicable.

13 METHOD PERFORMANCE

13.1 Training Qualifications:

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

13.1.2 The only personnel authorized to execute this SOP are the Sample Log-In persons.

14 POLLUTION PREVENTION

14.1 This method does not contain any specific modifications that serve to minimize or prevent pollution.

15 WASTE MANAGEMENT

15.1 All samples may be disposed of 30 days after the report date except for those samples associated with special client retention. Shelves are purged in chronological order. All lots on a specific shelf must be noted. If a lot can be disposed of, a disposal date must be recorded.

15.2 Disposal dates are recorded on a print-out of lots according to a storage location. When clearing samples that cannot yet be disposed of because of special client retention, samples are boxed or stored on carts. Stored samples must have a specific date listed in which samples can be disposed of, or a note that indicates "SAVE" and client name or reason.

15.3 All lots assigned to a certain shelf can be obtained from QuantIMS.

15.3.1 UTL – "Enter"

15.3.2 Type "wrk" – "Enter"

15.3.3 Type "2" by option

15.3.4 Choose one query name and "Enter"

15.3.5 SLOIS for metals shelves

15.3.6 CLOIS for cooler shelves C1 – C272

15.3.7 WLOIS for cooler shelves W1-163

15.3.8 Type "1" next to "select records"

15.3.9 Enter the shelf location 3x where prompted (appears on two different screens). Then hit "Enter".

15.3.10 Dates need to be updated every four to six months so shelf locations only print most recent lots assigned.

15.3.11 "F3" to run query and "Enter".

15.3.12 At save definition type "Y" and run option "2" and "Enter".

15.4 Solid samples that can be disposed of are boxed and labeled "SOLIDS NOW."

15.5 Liquid wastes that can be disposed of are boxed and labeled "LIQUID NOW." These boxes are taken to the facility waste building and drummed by the Health and Safety Coordinator or designee.

15.6 Water samples that can be disposed of are placed on carts and purged down the drain in one of the following areas: sample receiving, wet chemistry, or extractions.

15.7 Solvent waste must be disposed of in clearly labeled waste cans.

15.8 Acid waste must be collected in clearly labeled acid waste containers. Solid materials (gloves, soiled paper products, etc.) are placed in the solid debris container. Do not put liquids in the solid waste container.

15.9 Refer to the Laboratory Sample and Waste Disposal plan.

15.10 Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices of STL. They must have training on the hazardous waste disposal practices upon initial assignment to these tasks, followed by an annual refresher training.

16 REFERENCES

16.1 STL Quality Management Plan (QMP), current version.

16.1.1 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 Navy/Army SOP, NC-QA-0016

17 MISCELLANEOUS

17.1 Wherever "Sample Control" is mentioned in all SOPs, it is assumed to include the sample custodian or any alternate that is designated by the Sample Control Coordinator.

17.2 Appendix:

17.2.1 Cooler Receipt Form/Narrative

17.2.2 Preservative Preparation

17.2.3 Preservative Requirements

17.2.4 Internal Chain of Custody – CLP

17.2.5 Internal Chain of Custody – Regular Production Organic LIMS generated

17.2.6 Sample Custodian Removal Request

17.2.7 Sample Analysis Requisition

17.2.8 Subcontracted PO Logbook

17.2.9 Laboratory Generated Bottle Label

17.1.1

Example

Cooler Receipt/Narrative Form

STL Cooler Receipt Form/Narrative

North Canton Facility

Client:_____ Project:_____ Quote#:_____

Cooler Received on:_____ Opened on:_____ by: _____

(Signature)

Fedx ☐ Client Drop Off ☐ UPS ☐ Airborne ☐ Other:_____

Cooler ☐ Safe ☐ Foam Box ☐ Client Cooler ☐ Other:_____

STL Shipper No#:_____

1. Were custody seals on the outside of the cooler and intact? Yes ☐ No ☐

   If YES, Quantity_____ Location_____

   Were the custody seals signed and dated? Yes ☐ No ☐ NA ☐

2. Shipper's packing slip attached to this form? Yes ☐ No ☐

3. Were custody papers included inside the cooler and relinquished? Yes ☐ No ☐

4. Did you sign the custody papers in the appropriate place? Yes ☐ No ☐

5. Packing material used:

Peanuts ☐ Bubble Wrap ☐ Vermiculite ☐ Foam ☐ None ☐ Other :_____

6. Cooler temperature upon receipt _____ °C (see back of form for multiple coolers/temp)

METHOD: Temperature Vial ☐ Between Coolant & Sample Container ☐ Against Bottles ☐

COOLANT: Wet Ice ☐ Blue Ice ☐ Dry Ice ☐ Water ☐ None ☐

7. Were all the bottles sealed in separate plastic bags? Yes ☐ No ☐

8. Did all bottles arrive in good condition (Unbroken)? Yes ☐ No ☐

9. Did all bottle labels and tags agree with the custody papers? Yes ☐ No ☐

10. Were samples at the correct pH? Yes ☐ No ☐ NA ☐

11. Were correct bottles used for the tests indicated? Yes ☐ No ☐

12. Were air bubbles >6 mm in any VOA vials? Yes ☐ No ☐ NA ☐

13. Was a sufficient amount of sample sent in each bottle? Yes ☐ No ☐

Contacted PM _____ Date:_____ by:_____ via Voice Mail ☐ Verbal ☐ Other ☐

Concerning:_____

√	MACRO	MACRO
1. CHAIN OF CUSTODY		
	SR1A	Samples were received under proper custody procedures and without discrepancies.
	SR1B	The chain of custody and sample bottles did not agree. The following discrepancies occurred_____
2. SAMPLE CONDITION		
	SR2A	Sample(s)_____ were received or requested after the recommended holding time had expired.
	SR2B	Sample(s) _____ were received with insufficient volume
	SR2C	Sample(s)_____ were received in a broken container.
3. SAMPLE PRESERVATION		
	SR3A	Sample(s) _____ were further preserved in sample receiving to meet recommended pH level(s).
	SR3B	Sample(s)_____were received with bubble > 6 mm in diameter (cc: PM)
4. NCM		
	SR4A	NCM has been generated. Refer to Clouseau for details
5. Other Anomalies (see below or back)		

STL Cooler Receipt Form/Narrative

North Canton Facility

Client ID	pH	Date	Initials

Discrepancies Cont.

Macro Name:

Macro Name:

Macro Name:

Macro Name:

Other Anomalies:

17.1.2

Preservative Preparation

Preservative Preparation

(If purchased preservative solution vials are not used)

1:1 Hydrochloric Acid (18%): Slowly add 1000 mL concentrated HCl to 1000 mL reagent water and mix. Store in a well labeled plastic coated acid bottle.

1:2 Sulfuric Acid (33%): In a 2000 mL beaker, SLOWLY and CAREFULLY add 500 mL concentrated H_2SO_4 to 1000 mL reagent water and mix. A cool water bath may be needed to cool the solution and beaker. Store in a well labeled plastic acid bottle.

NOTE: *All preparations must be performed in a hood and proper personal protective equipment must be worn. All reagents and final preservative solution must be documented in applicable reagent logbooks.*

17.1.3

Preservative Requirements

PRESERVATIVES, CONTAINERS, AND VOLUMES

Parameter	Container	Preservative[1,2]	Volume	Parameter	Container	Preservative [1,2]	Volume
Asbestos	P	None	250 mL	Radiological	P	HNO_3	4 L
				Alpha, Beta, Radium			
Acidity	P	None	250 mL	Hardness	P	HNO_3	250 mL
Alkalinity (Sep)	P	None	250 mL	Metals	P	HNO_3	1 L
BOD	P	None	250 mL	Dissolved Metals*	P	HNO_3	1 L
Carbonaceous BOD	P	None	250 mL	Total Organic Carbon (TOC)	G	HCl	2 x40 mL
Bromide (Br)	P	None	250 mL	Chemical Oxygen Demand	P	H_2SO_4	250 mL
Chloride (Cl)	P	None	250 mL	Total Organic Halogens	G	H_2SO_4	250 mL
Chromium, $^{6+}$	P	None	250 mL	COD	P	H_2SO_4	250 mL
R. Chlorine	P	None	100 mL	Ammonia Nitrogen (NH_3)	P	H_2SO_4	500 mL
Color	P	None	50 mL	TKN	P	H_2SO_4	1L
Conductivity	P	None	250 mL	Nitrate/Nitrite	P	H_2SO_4	250 mL
Corrosivity	P	None	250 mL	Oil & Grease	G	H_2SO_4	1 L
Dissolved Oxygen	G	None	300 mL	Phenols	G	H_2SO_4	1 L
Fecal Coliform	P	None	125 mL	Total Phosphorus	P	H_2SO_4	250 mL
Flashpoint	G	None	100 mL	TON	P	H_2SO_4	1 L
Fluoride	P	None	250 mL				
Nitrate	P	None	250 mL	TRPH - IR 418.1	G	HCl	2 L
Nitrite	P	None	250 mL	VOC 601	G	HCl	3x40 mL
pH	P	None	50 mL	VOC 8010	G	HCl	3x40 mL

PRESERVATIVES, CONTAINERS, AND VOLUMES

Parameter	Container	Preservative[1,2]	Volume	Parameter	Container	Preservative [1,2]	Volume
Elemental PO_4	G	None	250 mL	VOC 624	G	HCl	8x40 mL
Orthophosphate	P	None	250 mL	BTEX 8020	G	HCl	3x40 mL
TDS	P	None	250 mL	VOC 8240	G	HCl	3x40 mL
TSS	P	None	250 mL	THM/502.2	G	HCl	2x40 mL
Total Solids	P	None	250 mL	502.2	G	HCl & Asc. Acid	2x40 mL
TVS	P	None	250 mL	VOC 624	G	HCl	3x40 mL
T. Coliform	P	None	125 mL	VOC 602	G	HCl	3x40 mL
Settleable Solids	P	None	1L	465 C & D	G	HCl	4x40 mL
Silica	P	None	250 mL	BTEX 8021	G	HCl	3x40 mL
Sulfate	P	None	250 mL	VOC	G	HCl	3x40 mL
Sulfite	P	None	250 mL	VOC 8260	G	HCl	3x40 mL
Surfactants (MBAS)	P	None	250 mL	VOC and VOA	G	HCl	3x40 mL
Turbidity	P	None	250 mL	VOC 8010/8020	G	HCl	3x40 mL
TPH-GC	G	None	2 L				
				Total Cyanide	P	NaOH[3]	250 mL
BNAs	G	None	2 L	Amenable Cyanide	P	NaOH	250 mL
BNA + Dioxin	G	None	2 L	Free Cyanide	P	NaOH	250 mL
PNA/PAH	G	None	2 L	Sulfide	P	Zn Acetate & NaOH	1 L
Pesticides	G	None	2 L	Formaldehyde	G	None	500 mL
Reactive Cyanide	P	None	1 L	Carbonate	P	None	250 mL
Reactive Sulfide	P	None	1 L	Bicarbonate	P	None	250 mL
PCB	G	None	2 L	TPH - Diesel (Ext.)	G	None	2 L

PRESERVATIVES, CONTAINERS, AND VOLUMES

Parameter	Container	Preservative[1,2]	Volume	Parameter	Container	Preservative [1,2]	Volume
Pesticides + PCBs	G	None	2 L	TPH - Gasoline (P&T)	G	HCl	2x40 mL
Herbicides	G	None	2 L	Glycols 8015	G	None	2x40 mL
OPPs	G	None	2 L	BTEX & MTBE	G	HCl	3x40 mL
				601/602	G	HCl	3x40 mL

* Filtered in field

[1] HCl, HNO_3, and H_2SO_4 to pH < 2 NaOH to pH > 12

[2] Temperature = 4°C ± 2°C except for aqueous metals

[3] Samples to be analyzed for Cyanide should be field-filtered for Residual Chlorine. If Residual Chlorine is detected, ascorbic acid (0.6 g) should be added.

17.1.4

Example

Internal Chain of Custody - CLP

STL North Canton

Sample Control Record

Client: _____ Case Number/SDG: _____

Storage Location: _____

Laboratory Sample Number	Transferred By	Date	Entered	Removed	Reason	Date Returned
1.						
2.						
3.						
4.						
5.						
6.						
7.						
8.						
9.						
10.						

17.1.5

Internal Chain of Custody

Regular Production-Organic

STL North Canton

Sample Control Record

Client: _____ Case Number/SDG: _____

Storage Location: _____

Laboratory Sample Number	Transferred By	Date	Entered	Removed	Reason	Date Returned
11.						
12						
13.						
14.						
15						
16						
17.						
18.						
19						
20						

17.1.6

Example

Sample Custodian Removal Request Form

(LIMS Generated)

PSR024 6/18/01 17:05:28 MT SAMPLE CUSTODIAN REMOVAL REQUEST PAGE 003

REQUESTED BY: KUHLEJ

METHOD: HL Nitrogen, Ammonia (ISE - 350.3)

STORAGE LOCATION	WORK ORDER #	PICKED CNTR#	CONTROL #	CLIENT #	ANALYSIS	LOTID	SMP#	SFX	MATRIX DESCRIPTION	QTY RCVD	QTY REQD
C100	EEHKF-1-AJ		694340	002962	I-88-HL	A1F070186	001		WATER	7	1
C100	EEHKR-1-AJ		694341	002962	I-88-HL	A1F070186	002		WATER	7	1
C102	EEKWW-1-AJ		694342	002962	I-88-HL	A1F080154	001		WATER	7	1
C102	EEKW7-1-AJ		694343	002962	I-88-HL	A1F080154	002		WATER	7	1
C102	EEKW8-1-AJ		694344	002962	I-88-HL	A1F080154	003		WATER	7	1
C102	EEKXC-1-AJ		694345	002962	I-88-HL	A1F080154	004		WATER	7	1
C111	EETJ0-1-AG		694353	057251	I-88-HL	A1F130158	019		WATER	3	1
C111 S76	EETJC-1-AG		694346	057251	I-88-HL	A1F130158	012		WATER	3	1
C111 S76	EETJK-1-AG		694347	057251	I-88-HL	A1F130158	013		WATER	3	1
C111 S76	EETJL-1-AT		694348	057251	I-88-HL	A1F130158	014		WATER	9	1
C111 S76	EETJM-1-AG		694349	057251	I-88-HL	A1F130158	015		WATER	3	1
C111 S76	EETJQ-1-AG		694350	057251	I-88-HL	A1F130158	016		WATER	3	1
C111 S76	EETJT-1-AG		694351	057251	I-88-HL	A1F130158	017		WATER	3	1
C111 S76	EETJW-1-AG		694352	057251	I-88-HL	A1F130158	018		WATER	3	1
C115	EETWR-1-AJ		694354	435004	I-88-HL	H1F130208	001		WATER	11	1
C95	EEF2T-1-AA		694339	056426	I-88-HL	A1F060238	001		WATER	2	1

RELINQUISHED BY	RECEIVED BY	DATE/TIME
		6-19-01

***** END OF REPORT *****

17.1.7

Example Sample Analysis Requisition

Severn Trent Laboratories, Inc
SAMPLE ANALYSIS REQUISITION

LABORATORY: STL Sacramento
880 Riverside Parkway
West Sacramento CA 95605,EZZ OL

NEED ANALYTICAL REPORT BY
7/23/01

ATTN:

LAB PURCHASE ORDER: SR031834

CLIENT CODE 406422 PROJECT MANAGER: David S. Heakin

NUMBER OF SAMPLES IN LOT: 0002

SAMPLE I D	SAMPLING DATE	ANALYSIS REQUIRED
A1F260180-001	6/25/01	Perchlorate (314 0)
EFHTA-1-AA		(ICCL04_I) METHOD: 314.0
A1F260180-002	6/25/01	Perchlorate (314.0)
EFHTD-1-AA		(ICCL04_I) METHOD: 314 0

NEED DETECTION LIMIT AND ANALYSIS DATE INCLUDED IN REPORT

SHIPPING METHOD: AIRBORNE DATE: 6/26/01

SEND REPORT TO: DAVE HEAKIN

SAMPLE RECEIVED BY: _____ DATE _____

PLEASE SEND A SIGNED COPY OF THIS FORM WITH REPORT AT COMPLETION OF ANALYSIS.

THANK YOU.

STL North Canton
INT: _____ 6/26/01 12:12:06

STL Sacramento
880 Riverside Parkway
West Sacramento CA 95605,EZZ OL

RELINQUISHED BY: [signature] DATE/TIME: 6/26/01 3:30

RELINQUISHED BY: _____ DATE/TIME _____

RECEIVED FOR LAB BY: _____ DATE/TIME: _____

PLEASE RETURN ORIGINAL SAMPLE ANALYSIS REQUISITION

17.1.8

Example Subcontracted PO Logbook

Severn Trent Laboratories, Inc
SAMPLE ANALYSIS REQUISITION

Laboratory: STL Austin

Lab Request SR031273 Need Analytical Report 2001-06-14

Client Code. 390133 Project Manager ALESIA DANFORD

Sample I D	Work Order Number	Client Sample ID	Sampling Date	Analysis Required	
A1E310129-1	ED6T6	HMW-2	2001-05-30	Dissolved Gases in Water	mg/L
A1E310129-1	ED6T6	HMW-2	2001-05-30	Dissolved Gases in Water	mg/L
A1E310129-2	ED6VR	HMW-3	2001-05-30	Dissolved Gases in Water	mg/L
A1E310129-2	ED6VR	HMW-3	2001-05-30	Dissolved Gases in Water	mg/L
A1E310129-3	ED6VT	HMW-3A	2001-05-30	Dissolved Gases in Water	mg/L
A1E310129-3	ED6VT	HMW-3A	2001-05-30	Dissolved Gases in Water	mg/L

Need detection limit and analysis date included in report

Shipping Method

Please send a signed copy of this form with the report at completion of analysis

Relinquished by [illegible] Date/Time 5/31/01 [illegible]

Relinquished by _____ Date/Time _____

Received for lab by _____ Date/Time _____

PLEASE RETURN ORIGINAL SAMPLE ANALYSIS REQUISITION

17.1.9

Laboratory Generated Bottle Label

CT656-001
A9C310142-001
3 VIALS
614MW001-4
MS

375241
3/30/99
8:42

APPROVAL:

Director, Quality Assurance

Vice President, Operations Services

Quanterra Incorporated®

POLICY NAME

COMPANY-WIDE

Quanterra® Quality Control Program

Rev. 2, 07/13/98
Supersedes: Revision 1

Policy #: QA-003

OBJECTIVE:

This policy describes the Quanterra® program of routine analytical quality control (QC) activities. The objective is to generate QC data that demonstrate that the analytical process is in control and that the data meet client and method requirements.

SCOPE:

This policy is to be enforced and followed throughout the company.

POLICY:

1.0 Assessments of QC data relative to control limits determine the acceptability of sample test results. Whenever control criteria are not met, the data must be evaluated to determine appropriate corrective action. The initial evaluation is made by the analyst, frequently in

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conjunction with data review software and /or senior analysts or supervisors. Further technical evaluation of the data or data review software output is conducted by second-party data reviewers. Corrective action decisions, particularly whether or not to reanalyze samples, should be done in consultation with the client to the extent possible when operating under project-specific QA plans. Requirements for assessment and corrective action are described in the attachments to this policy. Details concerning technical data review and documentation of the reviews are described in "Technical Data Review Requirements" (Policy QA-012).

2.0 Quanterra's® standard QC program is to be communicated to the client prior to acceptance of work. At the same time, every effort must be made to understand clients' special project requirements. Generally, laboratory project managers serve as a liaison between the clients and the laboratory staff to ensure that requirements are properly communicated in writing to both parties. In the event that alternative QC procedures are not specified by our clients, these standard QC protocols must be followed to ensure the generation of legally and scientifically defensible analytical data.

3.0 Successful implementation of this QC program requires that it is clearly understood by all Quanterra® staff. Training based on this policy will be conducted at each Quanterra® facility and provided to new personnel as appropriate for their functions.

4.0 Quanterra's® QC program applies to the following regulatory programs:

4.1 RCRA and SW-846 Methods - All routine analytical projects performed using SW-846 methods must comply with the requirements described in Quanterra's® Quality Assurance Management Plan (QAMP, Tables 8.4-2 through 8.4-6) and Attachment I to this policy. The Quality Control sections of analytical standard operating procedures (SOPs) referencing SW-846 methods must be consistent with the requirements in Attachment I

4.2 CWA and 40 CFR Part 136 Listed Methods - Any analytical work conducted in support of an NPDES permit or other Clean Water Act compliance activities, must meet the quality control specifications shown in Quanterra's® QAMP tables 8.4-2 through 8.4-6. The quality control requirements for the specific methods listed in the QAMP define the minimum requirements that must be given in laboratory analytical SOPs.

4.3 CERCLA and CLP Methods - Projects performed using USEPA Contract Laboratory Program (CLP) methods must comply with the quality control specifications shown in Quanterra's® Quality Assurance Management Plan (QAMP) table 8.4-7. The quality control sections of the SOPs referencing CLP protocols must be consistent with the QAMP and the relevant CLP Statement of Work.

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4.4 Other Programs or Projects with Clearly Defined QC Requirements

4.4.1 The differences between Quanterra's® standard QC program and special project requirements must be specified in project documents. These documents may include Quality Assurance Project Plans (QAPjPs), Quality Assurance Program Plans (QAPPs), Sampling and Analysis Plans (SAPs), project-specific Quality Assurance Summaries (QASs), SOPs, contracts, or other approved documents.

4.4.2 Documents describing special project requirements must be reviewed and approved by appropriate QA and operations staff.

4.4.3 If the special project requirements appear to result in modifications that contradict federal or state regulatory requirements, the variance must be noted in writing and communicated to the client. A record of this communication must be retained as a permanent part of the project file.

4.4.4 Any special client's project requirements must be communicated to Quanterra's® analysts in advance of releasing samples for analysis, and the work must be clearly differentiated in the analytical documentation, otherwise Attachment I requirements will be followed.

4.5. Projects Without Specific QC Requirements

Any projects for which no specific QC program is specified, regardless of the source of the analytical methods being used, must follow the requirements shown in Attachment I.

4.6 Radiochemistry QC

General QC requirements for radiochemistry analyses are provided in Attachment II.

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ATTACHMENT I
QUANTERRA® QUALITY CONTROL PROGRAM

1.0 Introduction

This quality control (QC) program is based on the requirements in "Test Methods for Evaluating Solid Waste", USEPA SW-846, Third Edition with promulgated updates. It applies whenever SW-846 analytical methods are used. It also applies in whole or in part whenever project requirements fail to specify some aspect of QC practices described here. It does not apply when other well defined QC programs (e.g. CLP, CLP-like, AFCEE, ACOE, or NFESC) are specified. This policy represents Quanterra's® base QC program for environmental analyses.

Details concerning instrument calibrations, tunes, and QC that are required for specific methods (e.g., interference check samples for ICP and isotopic spikes for dioxin procedures) are not given here. Refer to the method standard operating procedures (SOPs) for information about the frequency, assessment and corrective action required for additional QC elements.

2.0 Definitions

2.1 QC Batch - The QC batch is a set of up to 20 field samples plus associated laboratory QC samples that are similar in composition (matrix) and that are processed within the same time period using the same reagent and standard lots.

2.2 Surrogates - Surrogates are organic compounds similar in chemical behavior to the target analytes, but that are not normally found in environmental samples. Surrogates are added to all samples in a batch to monitor the effects of both the matrix and the analytical process on accuracy.

2.3 Method Blank - The method blank (MB) is a control sample prepared using the same reagents used for the samples. As part of a QC batch, it accompanies the samples through all steps of the analytical procedure. The method blank is used to monitor the level of contamination introduced to a batch of samples as a result of processing in the laboratory.

2.4 Instrument/Calibration Blank - The instrument blank is prepared using the same solvents and reagents (e.g. hexane, methylene chloride, or reagent water) used to dilute the prepared sample extracts or digests. Unlike the method blank, it is analyzed without being subject to the preparation steps of the analytical procedure. It is used to monitor laboratory or reagent contamination introduced at the instrumental analysis phase of work. For procedures without a separate preparation step, an instrument blank is equivalent to the method blank, and serves the same purpose.

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2.5 Laboratory Control Sample - A laboratory control sample (LCS) is prepared using a well characterized matrix (e.g. reagent water or Ottawa sand) that is spiked, with known amounts of representative analytes. Alternate matrices (e.g. glass beads) may be used for soil analyses when Ottawa sand is not appropriate. As part of a QC batch, it accompanies the samples through all steps of the analytical process. The LCS is used to monitor the accuracy of the analytical process independent of possible interference effects due to sample matrix.

2.6 Matrix Spike and Matrix Spike Duplicate

2.6.1 Matrix Spike - A matrix spike (MS) is a replicate portion of one field sample in the QC batch that is spiked with known amounts of target analytes. An MS is spiked with the same analytes at the same concentrations that are added to the LCS. As part of the QC batch, it accompanies the field samples through all steps of the analytical process.

2.6.2 Matrix Spike Duplicate - A matrix spike duplicate (MSD) consists of an additional portion of the same sample used to prepare the MS. This portion is spiked and processed exactly as is the MS.

2.6.3 The MS and MSD results are used to determine the effect of the sample matrix on the precision and accuracy of results. Due to the potential variability of the matrix of each sample, the MS and MSD results may not have immediate bearing on any samples except the one spiked.

2.7 Sample Duplicate - A sample duplicate (DU) is a second aliquot of an environmental sample, taken from the same sample container when possible, that is processed with the first aliquot of that sample. That is, sample duplicates are processed as independent samples within the same QC batch. The sample and DU results are compared to determine the effect of the sample matrix on the precision of the analytical process. As with the MS/MSD results, the sample/DU precision results are not necessarily representative of the precision for other samples in the batch.

2.8 Duplicate Control Sample - Duplicate laboratory control samples (LCS/LCSD, also called a DCS pair) consist of a pair of LCSs analyzed within the same QC batch to monitor precision and accuracy independent of sample matrix effects. This QC sample is prepared at the request of the client and/or when insufficient sample volume is received to prepare and analyze an MS/MSD pair. DCS is intended to provide information regarding the precision of the measurement process.

3.0 Batch QC Elements & Batch Processing

3.1 A QC batch is designed to determine the quality of the analytical results obtained for a

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group of up to 20 field samples in terms of accuracy and precision. With some exceptions as described in Sections 3.6 through 3.8 below, the minimum QC elements for each QC batch are

- one method blank (MB),
- one laboratory control sample (LCS),
- one matrix spike (MS), and
- one matrix spike duplicate (MSD).

3.2 The identity of each QC batch must be documented and traceable, i.e., each batch of field samples must be clearly associated with the applicable QC samples.

3.3 To the extent possible, samples that require a preparation step should be analyzed together with their associated QC samples. If the samples in a given QC batch require separate analytical runs, the minimum batch QC in each run is an acceptable MB or instrument/calibration blank. To the extent possible, the QC samples should not be analyzed independent of the field samples on a different instrument.

3.4 For analytical procedures that do not include a separate extraction or digestion (e.g., volatile organic analysis by purge and trap), the QC batch must be analyzed sequentially using the same instrument and instrument configuration within the same calibration event. That is, the same calibration curve, calibration factors, or response factors must be in effect throughout the analysis.

3.5 Field QC samples (e.g., trip blanks, equipment rinsates, and field duplicates) count as individual samples, therefore, they add to the QC batch count. Samples that require simple reanalysis (e.g., dilutions to adjust a sample extract to the working range of the instrument), as opposed to reextraction or digestion and reanalysis, do not count as additional samples in the QC batch. For procedures without a separate preparation, a reanalysis within the same calibration event (as defined in Section 3.4) does not add to the batch count.

3.6 MS/MSD pairs are not the only acceptable means of demonstrating precision.

3.6.1 As requested by clients or required by some methods, batch precision may also be demonstrated through the analysis of sample duplicates (DUs). However, the client should be advised that a DU is less likely to provide usable precision statistics depending on the likelihood of finding concentrations below reporting limits.

3.6.2 A duplicate LCS (DCS) may be used to demonstrate method batch precision independent of client's matrix when the client has not supplied sufficient sample quantity to prepare an MS, MSD or DU, if requested by the client.

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3.6.3 On-going monitoring of LCS results can be used to determine long-term (a.k.a., between batch) precision and accuracy for a method.

3.7 Some methods including isotope-dilution methods, pH and ignitability for example, do not use all of the QC elements listed in Section 3.1. Method exceptions to these requirements are listed in the QC tables of Quanterra's® QAMP and in the laboratory's analytical SOPs.

3.8 Deviations from these QC elements must either be noted in project planning documents (QAPPs, QAPjPs, SAPs, SOWs, QAS, or equivalent) or in a NCM.

4.0 Data Evaluation and Corrective Action

4.1 General Guidelines

4.1.1 Any QC component that is outside of established control limits is considered an out-of-control event. All out-of-control events must be documented and the associated data evaluated. Depending on the specific circumstances, evaluation can lead to a variety of actions. The following sections and the flowcharts describe the appropriate corrective action for the most common QC failures. However, it is not possible to address all possible data evaluation scenarios in this policy. The guiding principle for all evaluations is that the data and corrective action decisions must be defensible using Quanterra® policies, procedures or scientific evidence, and justified in the project records.

4.1.2 If reanalysis for QC failures is conducted and the second analysis confirms a QC problem that is outside of the laboratory's control, further testing is not necessary. The problem must be documented and the data properly qualified in the project report.

4.1.3 QC failures that are not corrected by reanalysis are documented in NCMs or using an electronic anomaly system as described in SOP # CORP-QA-0010. This does not include QC failures due to sample matrix interferences (particularly MS, MSD and surrogate failures). These failures are a function of the method used and are normally outside of the laboratory's control; trending via NCMs is not required. Other forms (for example, data review checklists) may be used to document matrix QC failures.

4.1.4 When ongoing, systematic problems are identified, work must stop until it can be demonstrated that the system is in control again.

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4.2 Method Blank (MB) Evaluation (also see Figure 1)

4.2.1 Method Blank Acceptance Criteria

The results of the method blank shall be one of the QC measures used to assess batch acceptance. Results are acceptable if all analyte concentrations in the MB meet the following criteria:

- The blank contamination is less than 1/10 of the measured concentration of any sample in the associated preparation batch , or
- The blank contamination is less than the concentration present in the samples and is less than 1/10 of the regulatory limit, or
- The same contaminants were not found in the associated samples, or
- MB results are less than or equal to the reporting limit.

Note: Positive method blank results slightly below the reporting limit should still be evaluated by the analyst for potential impact on sample results at or near the reporting limit.

4.2.2 Corrective Action for Method Blank Failure

- If the method blank does not meet the acceptance criteria, the source of contamination must be investigated and measures taken to correct, minimize or eliminate the problem. Samples associated with the contaminated blank shall be reprocessed for analysis or, under the following circumstances, may be reported as qualified (qualifier flags or narrative comments):
- MB contamination at a level less than the reporting limit with sample results at levels near the RL, based on analyst's judgement shall be flagged, or
- Analyte concentrations in samples are greater than 10 times blank contamination, or
- The contaminate is a common blank contaminate (see below) and the MB concentration is less than 5 times the RL for organics or less than 2 times the RL for inorganics.

Common Laboratory Contaminants:

Analyte	Method
Methylene Chloride	Volatile Organics (GC or GC/MS)
Acetone	Volatile Organics (GC or GC/MS)
2-Butanone	Volatile Organics (GC or GC/MS)
Phthalate Esters	Semi-Volatile Organics (GC or GC/MS)
Copper	Metals (ICP or GFAA)
Zinc	Metals (ICP or GFAA)
Iron	Metals (ICP or GFAA)
[illegible] :ad	Metals (Trace ICP or GFAA)

Revisions made on 10/01/99

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4.3 Laboratory Control Samples (LCS) Evaluation (also see Figure 2)

4.3.1 Acceptance Criteria
The LCS recovery for the control analytes must be within established control limits. The percent recovery is calculated as follows:

$$\text{LCS Percent Recovery} = \frac{X}{t} \times 100$$

Where: X = observed concentration
t = concentration of spike added

4.3.2 Corrective Action for LCS Failure
- check calculations,
- check instrument performance,
- reanalyze the LCS, and if still outside of control limits,
- reprepare and reanalyze all samples in the QC batch.

Notes: 1. It is acceptable to report the data, if the LCS recovery is out high and analyte of concern was not detected in any of the samples. Successful MS/MSD and surrogate recoveries may also provide evidence of control of accuracy, but this would be decided on a case-by-case basis and only with client approval.

2. In the case of volatile analyses, if the LCS fails, it may be reprepared and reanalyzed within the same tune period.

3. In the case where all target requested analytes are within control, but some other LCS compounds are out of control, the LCS may still be considered acceptable for reporting.

4.4 Duplicate Laboratory Control Samples (LCS/LCSD or DCS) Evaluation (also see Figure 2)

4.4.1 Acceptance Criteria
The recovery for each spike of the pair must be within established control limits. The formula used to calculate LCSD recoveries is the same as the formula for LCS spike recoveries. If a batch includes samples requiring LCS control and samples requiring DCS control, the LCS used will be the first LCS that passes control criteria.

The relative percent difference (RPD) for the pair is calculated as follows:

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$$RPD = \left[\frac{|X_1 - X_2|}{\frac{(X_1 + X_2)}{2}} \right] \times 100$$

Where: X_1 = first observed concentration

X_2 = second observed concentration

4.4.2 Corrective Action for LCS/LCSD Recovery (Accuracy) Failure

- check calculations,
- check instrument performance,
- reanalyze and/or reprepare and reanalyze all samples in the QC batch.

Note: If either LCS/LCSD spikes fails and the batch cannot be reanalyzed, the failure must be documented and noted in the final report.Also see notes under Section 4.3.2.

4.4.3 Corrective Action for LCSD Precision Failure

- check calculations;
- check instrument performance;
- if the RPD is out of control but both accuracy recoveries are within acceptance criteria, prepare an NCM, and qualify report.

Note: Because LCS/LCSD limits are based on the standard deviation of data collected over time and include long-term precision, it would be unusual to fail precision limits while meeting accuracy limits. If this occurs with any frequency, control limits should be reevaluated.

4.5 Surrogate Evaluation (also see Figure 3)

4.5.1 Acceptance Criteria

Surrogate recoveries must be within established control limits. Method QC (MB, LCS, and/or LCSD) results are not acceptable unless the surrogate recoveries for those QC samples are within control limits. If MS/MSD, DU or field samples require dilutions beyond the threshold stated in the analytical SOPs, routine surrogate control limits do not apply and recoveries are not evaluated. This should be noted in the final report. The recovery is calculated as follows:

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$$\text{Surrogate Percent Recovery} = \frac{X}{t} \times 100$$

Where: X = observed concentration
t = concentration of surrogate added

4.5.2 Corrective Action

4.5.2.1 Surrogate Failures in MB, LCS, or LCSD

- check calculation and instrument performance,
- reanalyze QC sample and/or reanalyze all samples in the QC batch.

Note: Unless otherwise specified by the client, it may be possible to report qualified results if method QC surrogate recoveries are biased high and analytes were not detected in the field samples. However, all other QC requirements would have to be met and the failure would have to be noted in the final report.

4.5.2.2 Surrogate Failures in Field Samples or MS/MSD

- check calculation and instrument performance;
- evaluate objective evidence of matrix interference (e.g. heterogeneous sample, interfering compounds seen on chromatograms, or interference demonstrated by prior analyses);
- document the failure and note it on the final report;

Note: Some client programs require reanalysis to confirm matrix interferences. Check special project instructions for this corrective action.

4.6 Matrix Spike and Matrix Spike Duplicates (MS/MSD) Evaluation (also see Figure 4)

4.6.1 Acceptance Criteria
MS and MSD recoveries and RPD should be within established control limits. If MS or MSD samples require dilutions beyond the threshold stated in the analytical SOPs, routine control limits do not apply and recoveries are not evaluated, but this should be noted in the final report. The MS and MSD recoveries are calculated as follows:

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$$\text{MS or MSD Percent Recovery} = \left[\frac{X_s - X}{t}\right] \times 100$$

Where: X = observed concentration in unspiked sample
X_s = observed concentration in spiked sample
t = concentration of spike added

Notes: 1. If sample result is ND, $X = 0$ when no values reported below RL. If sample result is reported as a value <RL, X = reported value.
2. CLP forms software uses observed recovery, not concentrations.

RPD is defined in Section 4.4.1.

4.6.2 Corrective Action for MS/MSD or MS/MSD RPD Failure (assuming that the LCS is in control)

- check calculation and instrument performance,
- consider objective evidence of matrix interference (e.g. heterogeneous sample, interfering compounds seen on chromatograms, or interference demonstrated by prior analyses);
- document the failure and note on final report;

Note: Some client programs require reanalysis to confirm matrix interferences. Check special project requirements for this corrective action.

4.7 Sample Duplicate (DU)

4.7.1 Acceptance Criteria
The RPD for the sample and its duplicate must be within established control limits. The RPD is the same as for the MS/MSD (see 4.6.1 above).

4.7.2 Corrective Action for DU Failure

- check calculation and instrument performance,
- document the QC failure and note on the final report.

5.0 Establishing QC Acceptance Limits

5.1 Selecting the Data Set
For new procedures, published method limits can be used until sufficient QC data are acquired (minimum of 20 to 30 data points recommended). However, the published limits may not be appropriate if they are based on a single-operator or single-laboratory study. In this case, the QA Manager may establish default limits until enough data is collected for laboratory established limits to be determined. For existing procedures, data collected

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over several months to a year or more can be used. Control tables or control charts are used together with the calculated mean and standard deviation to determine if the data set being considered are free of trends and are representative. If it appears that the data include gross outliers, outlier tests such as the Grubbs Test, Dixon Test (for 20 or fewer data points), or Rule-of-Huge-Error Test can be used to justify eliminating individual data points. Laboratory established limits must be reevaluated at least annually.

5.2 Calculating Laboratory Statistical Performance

Accuracy: mean recovery $\pm 3s$
Precision: zero to (mean RPD + 3s)

Where: s = standard deviation

If there are insufficient MS/MSD data available to calculate limits, LCS/LCSD limits may be used. If there are insufficient sample surrogate recovery data available to calculate limits, method limits may be used, if available. For methods, matrices, and/or analytes with very limited data, interim limits should be established using available data or by analogy to similar methods or matrices.

5.3 Setting Control Limits

The working control limits to be used by the laboratory are based on evaluation of the calculated laboratory statistical performance and available interlaboratory limits provided in the reference methods. Note that some SW-846 methods only supply single-operator or single-laboratory method performance data, which should be used for guidance only and may not be appropriate for routine lab operation.

The control limits should be evaluated for systematic trends and consistency of the performance of the analytical procedure at least annually or whenever new patterns of performance are observed in the laboratory data (i.e. new methods, equipment, etc.). When evaluating current "laboratory-generated limits" against historical "laboratory-generated limits", the laboratory QA manager should investigate any significant changes in "laboratory-generated mean" and "laboratory-generated range" and should attempt to identify the cause before making any changes to the laboratory limits. If the recalculated limits are consistent with the historical limits, the historical limits may remain unchanged.

Notes:
1. Laboratory-generated mean = statistical mean (i.e. $\Sigma x_i / n$)
   Laboratory-generated range = statistical ranges indicated in the previous section
2. If the laboratory-generated mean is within ± 10% of the historical mean, the two means are not significantly different and no investigation of cause of change would be necessary.
3. If the in-house calculated data lead to limits that are significantly tighter than both the guidance limits and/or the calibration acceptance criteria for the method, the laboratory

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can default to using the laboratory-generated mean ± calibration acceptance limit. Unreasonably tight statistical limits can result from the exclusion of unacceptable results from the database. If investigation demonstrates that this is happening, the laboratory's data entry systems should be improved. The lab should employ a statistical test for outlier values before excluding data points. (Reiterations of outlier tests lead to narrower limits and should be used with caution.)

4. If the decision is to use guidance limits from the method, the laboratory should investigate procedural improvements leading to better performance.

6.0 Reporting QC Data

The QC data routinely reported includes the LCS, method blank and surrogate standards. Matrix QC are reported on a project or client basis, and clients are encouraged to identify on the custody forms specific samples to be used for matrix spiking. Client reporting requirements are negotiated and documented as part of the project records. Ultimately, all reporting decisions should accommodate the client's requirements.

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Figure 1 - Method Blank Evaluation

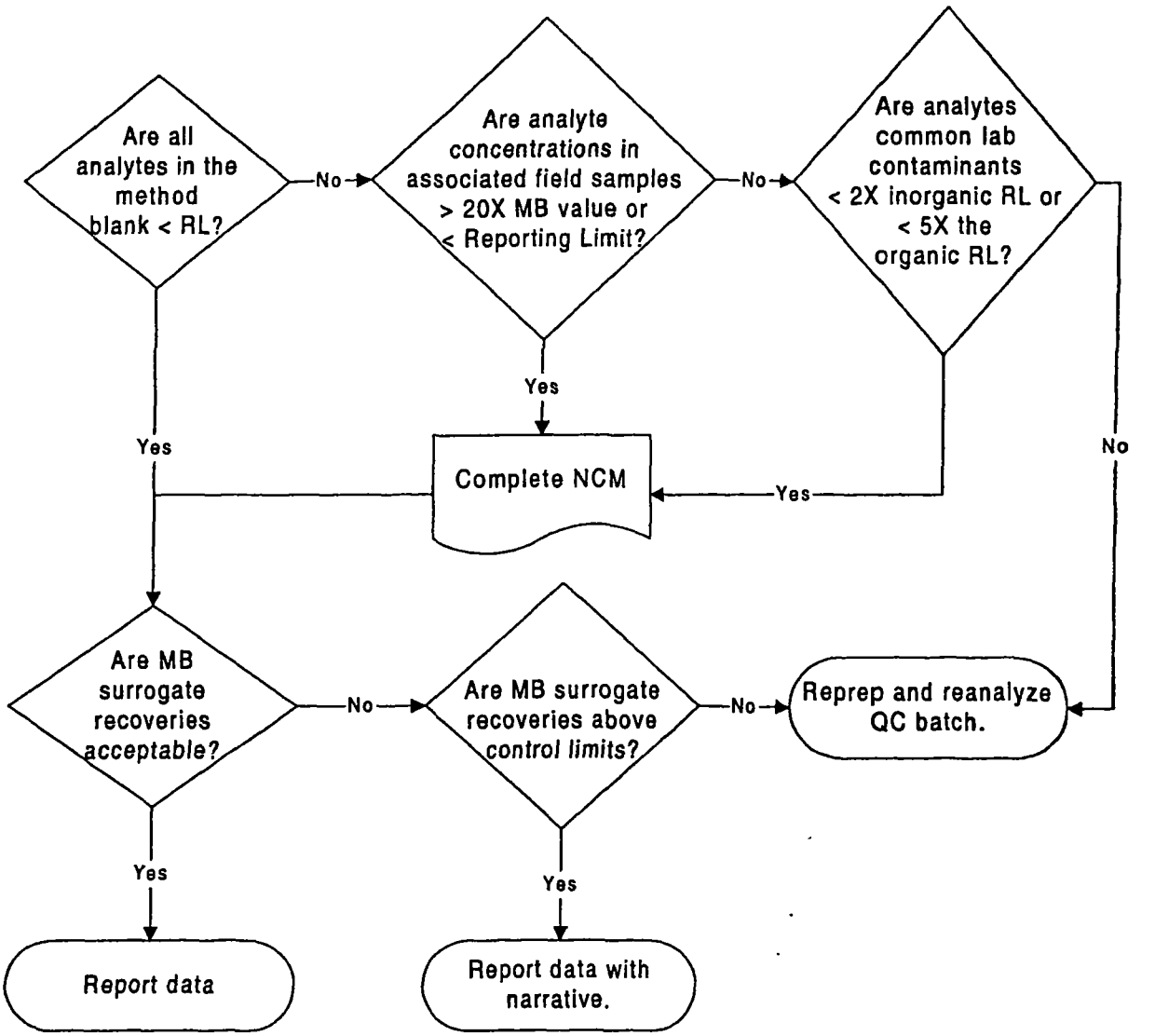


Figure 2 - LCS/LCSD Evaluation

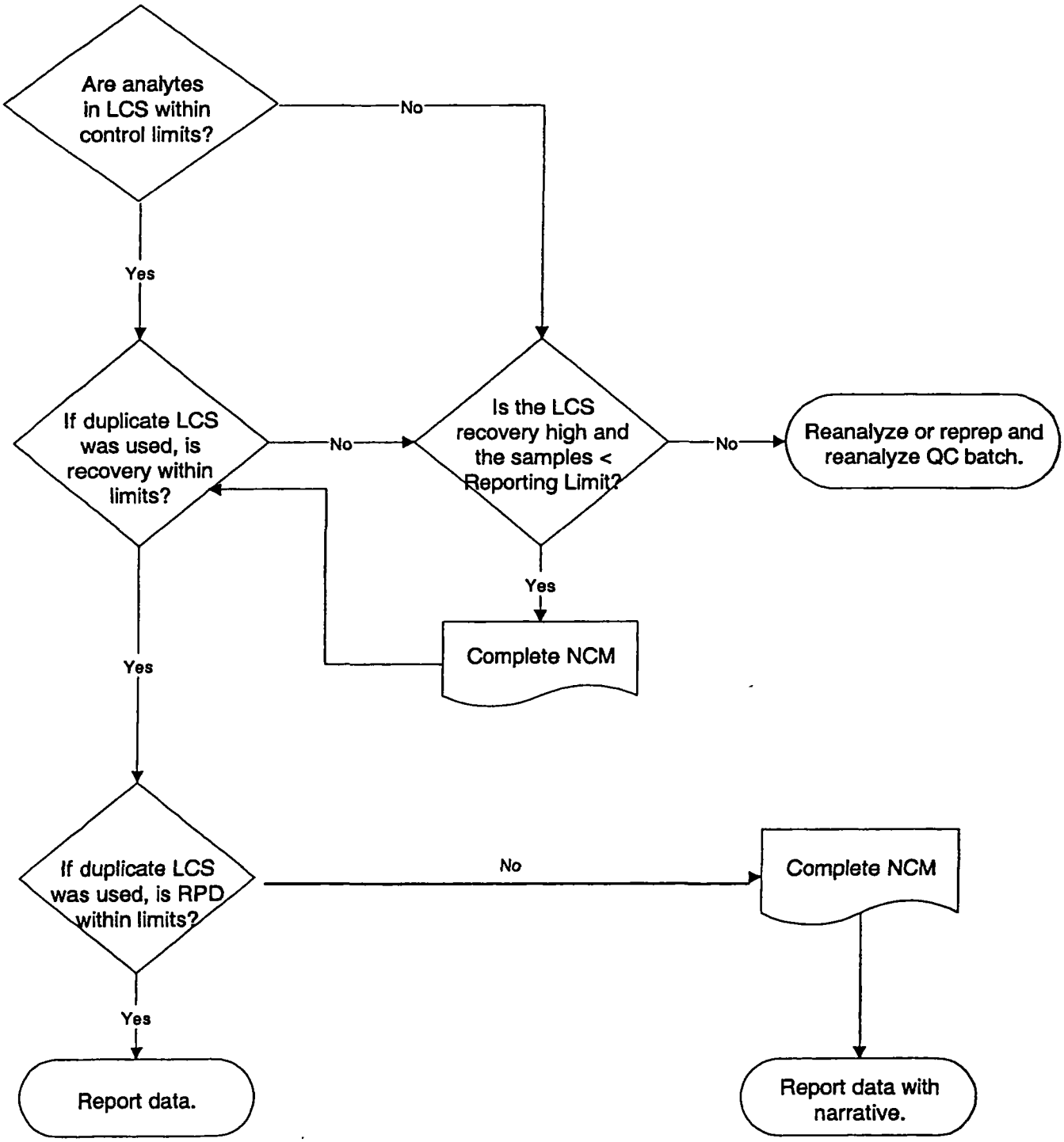


Figure 3 - Surrogate Evaluation

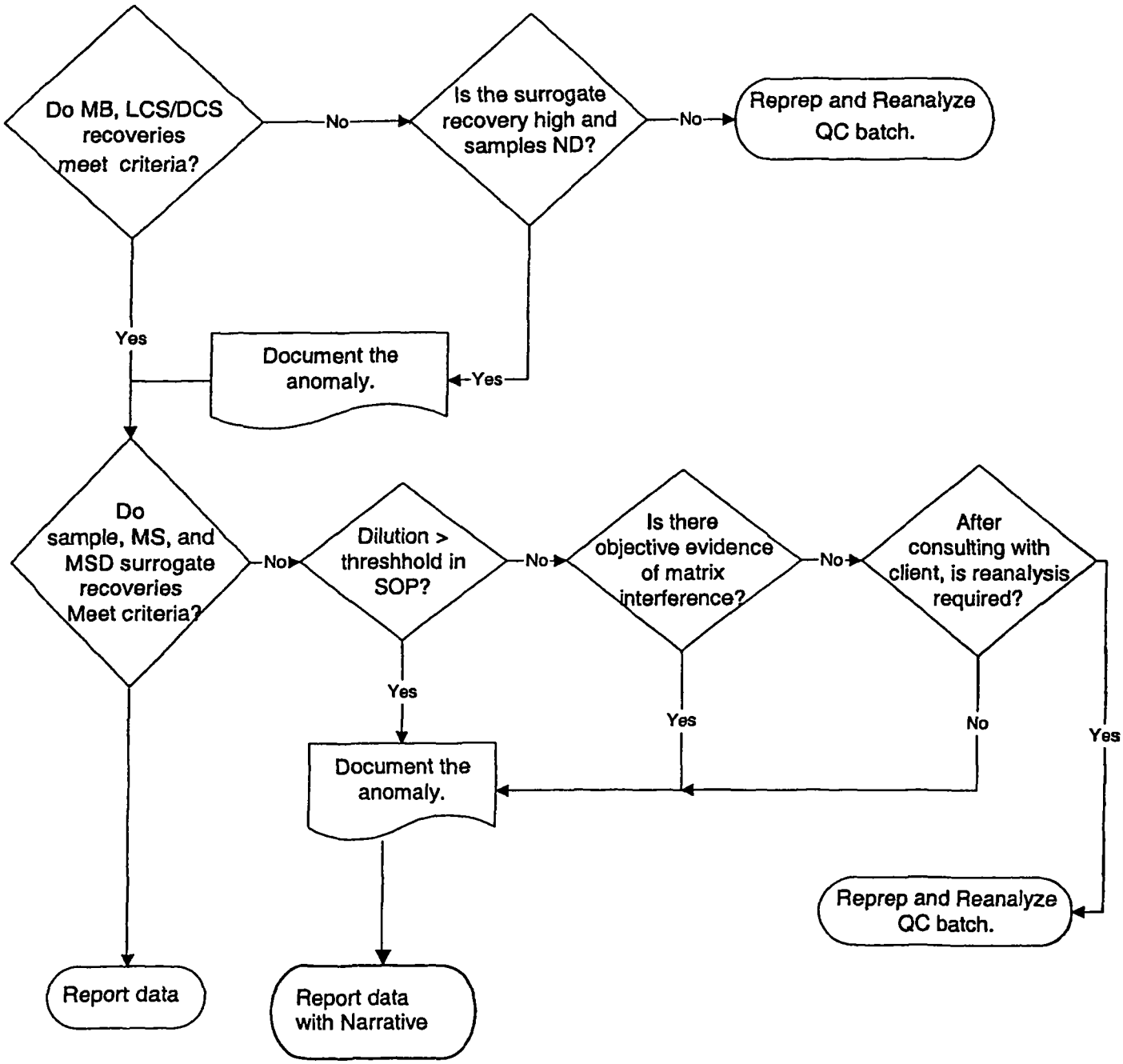
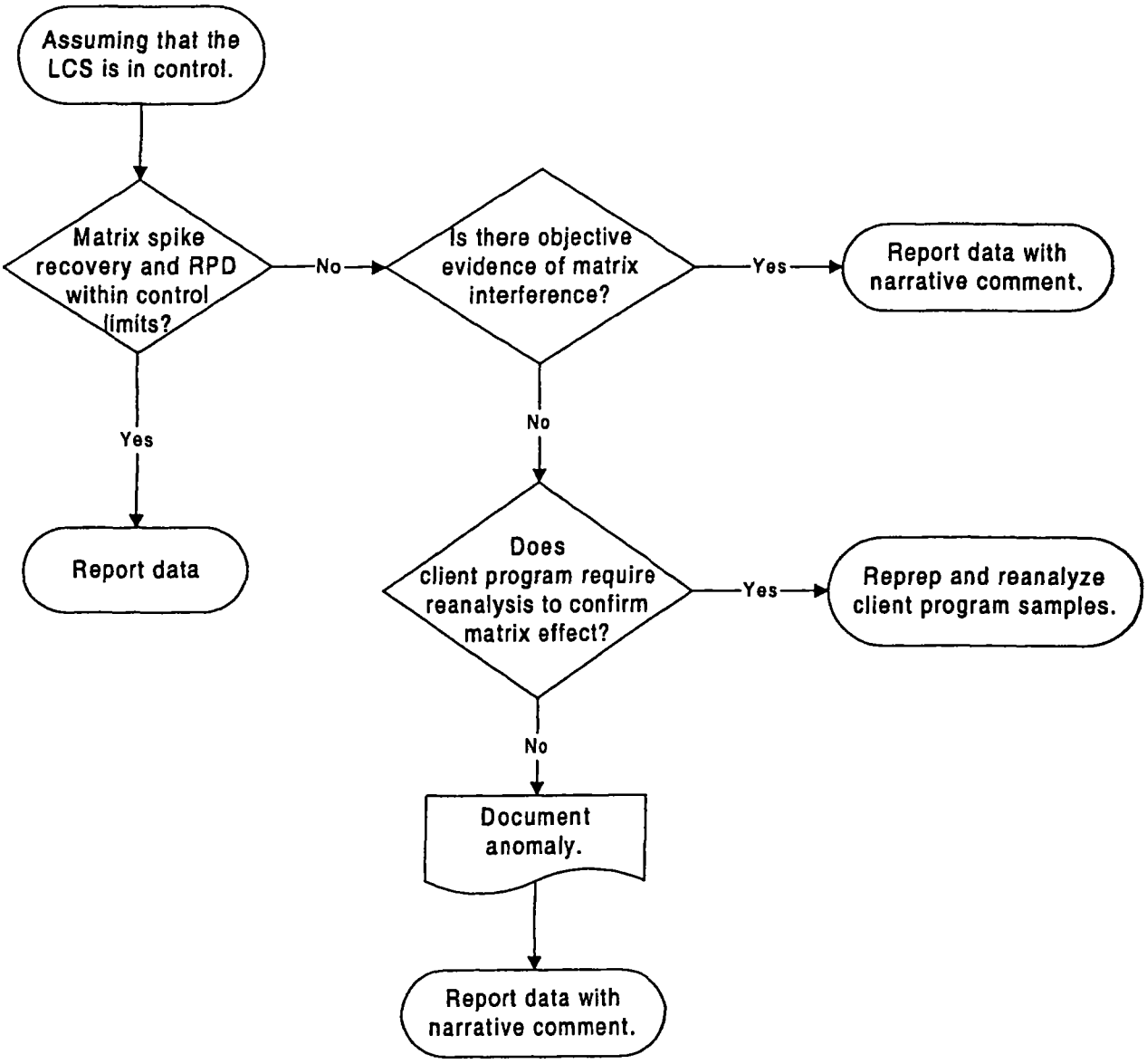


Figure 4 - Matrix Spike/Matrix Spike Duplicate Evaluation



ATTACHMENT 2
QUANTERRA® RADIOCHEMISTRY QUALITY CONTROL PROGRAM

1.0 Introduction

This Attachment describes the general quality control (QC) program in place to support radiochemical analyses performed in Quanterra® laboratories. Due to the lack of a national QC program which has been deemed to be the industry standard for radiochemistry, individual procedures may vary in their requirements. The program defined here should be taken as the minimum QC program. The details of the implementation and acceptability of the program are described in laboratory SOPs. The requirements of this Attachment may be superseded by a project Scope of work or QA program.

All data produced by the Quanterra® radiochemistry laboratories shall be reviewed by procedures described in the Quanterra® QAMP and facility SOPs. The review will be documented using a data review check list.

2.0 Quality Control Samples

2.1 Sample batches (defined in Attachment 1 of this policy) will be accompanied by laboratory prepared QC samples. The minimum QC samples required in a batch are as follows:

2.1.1 Method Blanks: carried through the entire preparation and analysis procedure, one for each batch.

2.1.2 Laboratory Control Samples: prepared and/or analyzed with the samples, one for each batch.

2.1.3 Sample Duplicates: one for each batch, assuming sufficient sample is received.

2.2 Additional Quality Control Samples may include matrix spikes and matrix spike duplicates (matrix spike duplicates will replace sample duplicates) which are performed when contractually required. Matrix spikes are not prepared for samples which are counted directly and are subject to homogenization restrictions, such as solid samples for gamma or alpha/beta analysis.

2.3 Tracers and carriers are added to every sample, blank, and QC sample when required by the analytical method. Tracers are radioisotopes usually with the same atomic number as the target analytes, when available. Carriers are non-radioactive compounds added to assist in isolation of the target analyte(s). Both tracers and carriers, when standardized can be used to correct counting results for actual recovery of the analyte when available radioactive tracers are NIST traceable.

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3.0 Acceptability Criteria/Corrective Action

3.1 In the absence of specific client instructions, the following criteria apply. However, individual cases allow for exceptions as stated below:

3.1.1 Re-counts - Client and/or QC samples are recounted if the acceptance criteria have not been met as indicated on the Data Review Checklist and as deemed necessary by the team leader/designee. Additionally, any blank, spike or client sample may be recounted to verify a result. If the re-count result is found to be within limits, the Data Reviewer accepts the re-count data. If the re-count result is found not to be within limits, the affected samples may need to be reanalyzed.

3.1.2 Reanalysis - If sample reanalysis is necessary and/or the client provides permission, the affected samples and associated quality control samples shall be reanalyzed providing sufficient sample is available. The data of the reanalysis set shall be reviewed using the same criteria as the original data set.

3.2 Method Blank: In general, method blanks may not contain concentrations of the analyte(s) of interest above the Reporting Limit (RL) or Client-Required Detection Limit (CRDL). Specific client requirements may require other criteria for the method blank. The occurrence of an unacceptable method blank requires investigation into the source of the contamination, followed by reanalysis of the associated batch of samples with an acceptable method blank unless the activity levels of the samples are significantly higher than the blank and or the MDA or MDC. The method blank may be water for all matrices unless client requirements specify otherwise

3.3 Yield Monitors: - For QC and sample data where gravimetric (chemical) or tracer recoveries are used for yield correction, the yield of the sample must meet, in the absence of specific limits, a yield monitor recovery greater than or equal to 20% and less than or equal to 115%. Unacceptable yields for method blanks or LCS require investigation and reanalysis of the associated sample batch with acceptable QC sample yields. Unacceptable yields for a sample require reanalysis of the sample in a batch with acceptable QC sample yields. Samples may be reported with unacceptable yield only if repeat analyses indicate that a matrix effect exists that prevents acceptable yield.

3.4 Laboratory Control Sample: Criteria for acceptability of Laboratory Control Samples are set by each procedure, and may utilize historical LCS recovery data. The occurrence of an unacceptable LCS requires investigation into the source of the nonconformance, followed by reanalysis of the associated batch of samples with an acceptable LCS.

3.5 Duplicate Samples: Acceptability criteria for duplicate sample results are stated in laboratory Standard Operating Procedures, and may utilize historical duplicate RPD data. Data associated with duplicate analyses that exceed the RPD criteria are evaluated for usability, and if reported without corrective action, are flagged and noted in client reports.

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3.6 Matrix Spike Recoveries: Acceptable matrix spike recovery is determined from laboratory historical data. Control limits are established for acceptability for each method and matrix at least annually. Samples with unacceptable matrix spike recoveries are flagged and noted in client reports unless the recovery can be shown to be due to laboratory error.

4.0 MDAs/MDCs

4.1 All radiochemical results are reported with both a sample-specific Minimum Detectable Activity (MDA) or Minimum Detectable Concentration (MDC) and an associated error. Formulas for calculating the MDA or MDC and the error are given in the Standard Operating Procedures. If the sample MDA/MDC is greater than the RL or CRDL, the Data Reviewer shall examine the sample volume/weight, counting time, and detector efficiency. The Data Reviewer shall decide if the sample should be recounted, reanalyzed, or the data accepted. If the sample activity exceeds the achieved MDA/MDC, no further action is necessary.

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STL STANDARD OPERATING PROCEDURE

TITLE: STATISTICAL EVALUATION OF DATA AND DEVELOPMENT OF CONTROL CHARTS

(SUPERSEDES: REVISION NO. 3)

Reviewed by:	Brenda R. Pettay-Koravetz	06/20/00 Date
Reviewed by:	Technology Specialist	6/20/00 Date
Approved by:	Quality Assurance Manager	6/19/00 Date
Approved by:	Stacey D. Campbell for Steve Jackson Environmental Health and Safety Coordinator	6/20/00 Date
Approved by:	Laboratory Director	6/21/00 Date

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1. PURPOSE

1.1. The purpose of this SOP is to describe the requirements for: (1) statistically establishing QC acceptance criteria and (2) long-term trend analysis of QC data using control charts at the STL-North Canton Laboratory.

1.2. The control chart is an effective tool for long-term trending because it records in real time the accuracy (bias) and precision of the appropriate parts of the measurement process. The control chart provides the means to demonstrate statistical control.

1.3. This document accurately reflects current standard operating procedures (SOP) as of the date above. All facility SOPs are maintained and updated as necessary by the laboratory QA department.

2. RESPONSIBILITIES

2.1. Analyst

2.1.1. All non-CLP QC data is entered into the Laboratory Information Management System (LIMS) for statistical evaluation for the generation of control charts. (Data entry may be automated or may be completed from the report generation software as part of the report or review group activities.)

2.1.2. Monitor method performance using established limits and identify any out-of-control situation. Respond to out-of-control conditions. QC Data results are considered out of control when recoveries exceed established control limits.

2.2. Group Leader/Supervisor

2.2.1. Respond to out-of-control conditions.

2.3. QA Department Staff

2.3.1. For analytical methods, coordinate updating of control limits annually. During this process, review control charts to detect any trends in routine analytical procedures.

2.3.2. Archive control charts and statistically derived QC acceptance data.

2.3.3. Each year at a minimum, publish statistically derived QC acceptance criteria.

2.3.4. Provide guidance in the development of control charts and in the application of QC samples and acceptance data.

2.3.5. With the Laboratory Director, ensure that Operations staff conforms to the requirements provided in this SOP.

2.4. Project Manager

2.4.1. Incorporate updated limits into project-specific QAPPs.

2.4.2. Submit project-specific control charts to the requesting client.

3. SAFETY

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

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

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

4. PROCEDURE

4.1. Empirical Establishment of QC Acceptance Limits

4.1.1. The assessment of QC sample data shall be performed by comparing precision and accuracy results against control limits. As defined in the following subsections, the control limits used for this comparison shall be either in-house (statistically generated using historical data) control limits or published limits from methods, contracts, or project QA plans.

4.1.2. In-house limits for all QC data must be determined and compared to those limits published in the methods for applicable matrices. Method limits will be employed until sufficient QC data are acquired. A minimum of 20 to 30 of the most recent data points should be used to establish in-house limits based on historical performance data for each major method. Periodically, QC data may need to be reviewed and house limits reestablished whenever a <u>significant</u> <u>change</u> in an analytical process occurs.

4.1.3. Control limits shall be generated for each matrix (i.e., aqueous and soil) for each preparative method using data from at least 20-30 of the most recent data points.

4.1.4. In-house control limits shall be established for the following samples:

4.1.4.1. Laboratory control sample (LCS) spike recoveries for method required analytes list.

4.1.4.2. Matrix Spike and Matrix Spike Duplicate (MS/MSD) spike recoveries for method required analytes list.

4.1.4.3. Surrogate spike recoveries in LCSs for organic analyses only.

4.1.5. Control limits shall be established for all methods except for CLP. For CLP-related projects, the acceptance criteria specified in the most current SOW shall be followed in evaluating data quality. CLP SOWs do not specify the generation of control charts.

4.1.6. The calculations used to generate the control limits for accuracy (%R) are described in the following subsections.

4.1.6.1. The %R is defined as the observed concentration in LCS divided by the theoretical concentration of the spike or LCS, times 100:

$$\%R = \frac{Found}{True} \times 100$$

4.1.6.2. The mean percent recovery and standard deviation is calculated using the following formulas:

$$\overline{\%R} = \frac{\sum_{i=1}^{n} \%R_i}{n}$$

$$S = \sqrt{\frac{\sum_{i=1}^{n}\left(\%R_i - \overline{\%R}\right)^2}{n-1}}$$

where:

%R	=	the mean percent recovery
$\%R_i$	=	the percent recovery of an LCS
n	=	the number of data points
S	=	the standard deviation of the data set of percent recoveries

4.1.6.3.The warning (95% or 2-sigma) and control limits (99% or 3-sigma) are then calculated from the following equations:

Upper Control Limit = $\overline{\%R} + 3\,s$

Lower Control Limit = $\overline{\%R} - 3\,s$

Upper Warning Limit = $\overline{\%R} + 2\,s$

Lower Warning Limit = $\overline{\%R} - 2\,s$

where:

$\overline{\%R}$	=	the mean percent recovery
S	=	the standard deviation of the data set

4.1.7. Control limits will be recalculated after excluding the following points from the calculations:

4.1.7.1. Samples with values outside control limits due to assignable cause.

4.1.7.2. True outliers as defined in the Grubbs test.

4.1.7.3. The LIMS is equipped to perform a Grubbs outlier test used to generate the control charts.

4.2. Monthly Trend Control Charts (Navy Only)

4.2.1. Control charts are required for LCSs only.

4.2.2. Control charts will be generated and reviewed on a monthly basis to keep current assessment of laboratory performance. Charts generated on a monthly basis will include a subset of parameters spiked as indicated in Table 4-1.

Table 4-1

Analyte	Analytical Method	Analyte	Analytical Method
Cyanide	Manual distillation/ automated analysis	Aluminum and Cadmium	Total Prep/ Inductively Coupled Plasma
Thallium	Total Prep, Graphite Furnace Atomic Absorption	Mercury	Manual digestion/ automated CVAA
Trichloroethene	Purge & Trap/ GC Volatile Hall	Toluene	Purge & Trap/ GC Volatile - PID
1,1-Dichloroethene, Benzene	Purge & Trap, GC Mass Spec Volatiles	1,2,4-Trichlorobenzene, 4-Nitrophenol	Liq/Liq, GC Mass Spec Semivolatile
Aldrin, Endrin	Liq/Liq, GC ECD	Aroclor 1016, Aroclor 1260	Liq/Liq, GC ECD
TCMX	Liq/Liq, GC ECD		

4.2.3. A control chart (X chart) is generated using the LIMS or a commercially available software to monitor accuracy and precision by plotting the LCS %R data in a graphical format as follows:

4.2.3.1. The average of the %R determinations for the original data set is established as the midpoint on the Y axis of the graph.

4.2.3.2. The upper and lower warning and control limits are plotted as solid horizontal lines across the graph at their respective points on the Y axis.

4.2.3.3. The calculated %R of each spiked sample is plotted chronologically on the graph to determine whether the recovery is within the warning and control limits of the control chart.

4.2.4. Control charts can be generated from any networked system (see network administrator) as follows:

4.2.4.1. From the Desktop, TraQAr double click the "Control limit " icon button.

4.2.4.2. Select "On-line Control Charts"

4.2.4.3. Select "QC Type"

4.2.4.4. Select "QuantIMS Method"

4.2.4.5. Select "QC Program" and write down spike list number

4.2.4.6. Select "Close Form"

4.2.4.7. Select QA Access button to create control charts and limits.

4.2.4.8. Select "location" (North Canton), "QC Type" (LCS/DCS, MS/MSD, LCS/DCS Surrogates, MS/MSD Surrogates, All Surrogates), "Start and End Date", "spike form" and then spike number.

4.2.4.9. Select "Collect Data" this screen will run and then the Control Limits Review screen comes up.

4.2.5. Control Limits Review screen

4.2.5.1. A "Grubbs test complete" sign comes up, select OK

4.2.5.2. A minimum of 20 - 30 points are required. If points are below 20 - 30 select close form and increase the start and end date to no more than one year.

4.2.5.3. If points are at least 30, select individual matrix.

4.2.5.4. Select "Grubbs Test"

4.2.5.5. A "Grubbs test complete" sign comes up, select OK

4.2.5.6. Select "Control Limits Rpt". Right click on report and select print.

4.2.5.7. Select "Control Charts Rpt". Right click on report and select print.

4.2.5.8. Close form and repeat 4.2.5.3. through 4.2.5.7.

4.2.5.9. This procedure can be used to demonstrate both "before" and "after" data sets used for control charts generation. An evaluation of the data excluded by a student-t test is useful to reveal existing problems (high volume of unused analyses, etc.).

4.2.6. The following information must be present on the control charts or in an associated table:

4.2.6.1. Parameter, Analytical Method and preparation procedure

4.2.6.2. LCS Batch ID allowing cross-reference to LIMS containing all analytical information.

4.2.6.3. Matrix

4.2.6.4. Number of points used

4.2.6.5. Mean

4.2.6.6. Standard Deviation

4.2.6.7. Percent recoveries

4.2.6.8. Upper and Lower warning and Control limits

4.2.6.9. Chart generation date.

4.2.6.10. An example of the Excel workbook output is provided in **Appendix A.**

4.3. Evaluation of Control Charts

4.3.1. When method, contract, or project plan requirements stipulate control limits which are more stringent than the laboratory generated limits, the more stringent limits shall be used to evaluate the quality control sample data.

4.3.2. If the laboratory-generated limits are more stringent than the method, contract, or project specific limits, the laboratory-generated limits shall be used to evaluate QC samples.

4.3.3. Criteria for an Out-of-Control Conditions

4.3.3.1. The causes for a shift or a trend in control charts could result from (1) incorrect preparation of a standard or a reagent, (2) sample contamination, (3) improper storage or preservation, (4) incorrect instrument calibration, (5) poor analytical technique, and (6) deviation from the analytical method. A measurement process for a particular analyte will be considered out-of-statistical-control when one of the following conditions occur:

4.3.3.1.1. A single point outside 3-sigma control limits

4.3.3.1.2. A series of eight consecutive points on the same side of the central line.

4.3.3.1.3. A series of three consecutive points between the warning limits and control limits.

4.3.3.1.4. A series of six consecutively increasing or decreasing points on the same side of the centerline.

4.3.3.1.5. A cyclic pattern of control values.

4.3.3.1.6. These conditions may indicate that the measurement system is out of statistical control. When this situation occurs, the data must be evaluated thoroughly to identify the most appropriate corrective action to be implemented. The problem and its solution may be documented through a Nonconformance Memo as appropriate. Exceeding warning limits will only require a close observation of the measurement system. In reviewing control charts, any significant changes in key analysts, instrumentation, standard

reference materials, or processes must be kept in mind to explain potential out-of-control situations. After thorough evaluation of the data and documentation of corrective actions taken, the QA Department must determine if the defensiveness of analytical results generated during the out of control situation has been jeopardized. If it is determined that data defensiveness has been compromised, the client will be notified of the out of control situation.

4.4. Setting Control Limits

4.4.1. The working control limits to be used by the laboratory are based on evaluation of the calculated laboratory statistical performance and available interlaboratory limits provided in the reference methods. Note that some SW-846 methods only supply single-operator or single-laboratory method performance data, which may not be appropriate.

Accuracy Evaluation

Lower Limit Evaluation	Upper Limit Evaluation	Accuracy Decision
Laboratory-generated Lower Limit > Guidance Limit	Laboratory-generated Upper Limit > Guidance Limit	Use laboratory-gen. Lower Limit & Guidance Upper Limit
Laboratory-generated Lower Limit > Guidance Limit	Laboratory-generated Upper Limit < Guidance Limit	Use laboratory-gen. Lower Limit & laboratory-generated Upper Limit
Laboratory-generated Lower Limit < Guidance Limit	Laboratory-generated Upper Limit > Guidance limit	Use guidance Lower Limit & guidance Upper Limit
Laboratory-generated Lower Limit < Guidance Limit	Laboratory-generated Upper Limit < Guidance limit	Use guidance Lower Limit & laboratory-generated Upper Limit

Precision Evaluation

Range Evaluation	Precision Decision
Laboratory-generated precision value > Guidance precision	Use guidance precision

Laboratory-generated precision < Guidance precision	Use laboratory-generated precision

Notes: If the decision is to use guidance limits from the method, the laboratory should investigate procedural improvements leading to better performance.

The following outlines other criteria:

Min/Max	Limit	Percentage	Inorganics	Organics
Minimum	**LCL**	**10%**	√	√
Maximum	**LCL**	**90%**	√	√
Minimum	**UCL**	**110%**	√	√
Maximum	**UCL**	**200%**	√	√
Minimum	**RPD**	**20%**	√	
Maximum	**RPD**	**99%**	√	√
Maximum	**RPD**	**30%**		√

NOTE: Best Practice limits may be utilized for a particular method/parameter based on laboratory and client approval. Best Practice limits combines the data from a group of laboratories (Knoxville, North Canton and Pittsburgh) to generate limits that are used between the laboratories. This allows for the ease in transfer of work between the laboratories including sharing large projects.

5. DEFINITIONS

5.1. Control Chart - A graphical QC tool to monitor method performance over time and to establish acceptance limits.

5.2. Relative Percent Difference (RPD) - a measure of intra-lab precision based on a duplicate sample analyses.

5.3. Grubbs Test – extension of sample sizes and percentage points for significant tests of outlying observations - a statistical outlier test.

5.4. Percent Recovery (%R) or Recovery - a measure of the accuracy (bias) of the measurement process based on a comparison of a measured value for a fortified (spiked) QC sample against the known spiked values.

5.5. Precision - a measure of mutual agreement (or variability) among individual measurements of the same property, usually under prescribed similar conditions.

5.6. Accuracy - the degree of agreement of a measurement (or an average of measurements of the same thing) with an accepted reference or true value. Accuracy is the measure of bias inherent in the system.

5.7. Bias - a systematic (consistent) error in test results. The difference between the population mean and the true or reference value, or as estimated from sample statistics; the difference between the sample average and the reference value.

5.8. X-chart - a control chart that plots a single measurement of a property (e.g., percent recovery) of quality control samples over time. The chart consists of a single line that is the mean of the statistic, warning limits at ± two standard deviations, and control limits at ± 3 sigma.

5.9. Assignable cause - a known reason for an outlying result (e.g., no spike added).

5.10. Duplicate: A second aliquot of a sample that is treated the same as the original sample in order to determine the precision of the method.

5.11. Laboratory Control Sample (LCS):

5.11.1. Organics: A LCS is a volume of deionized laboratory water (for water samples) or a suitable solid material (e.g., clean sand) (for soil/sediment samples) which is spiked with compounds of interest and subjected to the entire analytical procedure in order to estimate the accuracy of the method via percent spike recovery.

5.11.2. Inorganics: A well characterized liquid or solid sample which is prepared, digested or extracted along with each analytical batch of samples.

6. REFERENCES

6.1. STL Quality Management Plan, current revision.

6.1.1. STL Quality Management Plan, current revision.

6.1.2. Control Chart Generation SOP, NC-QA-0024

6.1.3. HAZWRAP Requirements for Quality Control of Analytical Data DOE/HWP-65/R1, July, 1990 or current revision.

6.1.4. Navy Installation Restoration Laboratory Quality Assurance Guide (Interim Guidance Document), February 1996.

6.1.5. Handbook for Analytical Quality Control in Water and Wastewater Laboratories, EMSL, US EPA, March 1977.

6.1.6. Test Methods for Evaluating Solid Waste, Third Edition, SW-846, US EPA, Final Update II, September 1994.

APPENDIX A

(Examples of Control Charts)

Calculated Control Limits

SEVERN TRENT SERVICES

North Canton
Spike List: 928: NC: 8082 Best Practice -LCS

QC Type: LCS/DCS
Analysis Dates: 05/25/2000 - 06/07/2000

Associated SrCs:

QC	*Method*	*Prep*
01	MY	1U
01	MY	2W
01	MY	57
01	MY	80
01	MY	61
01	MY	83
01	MY	77
01	OH	
2U	MY	61
50	OH	
72	OH	

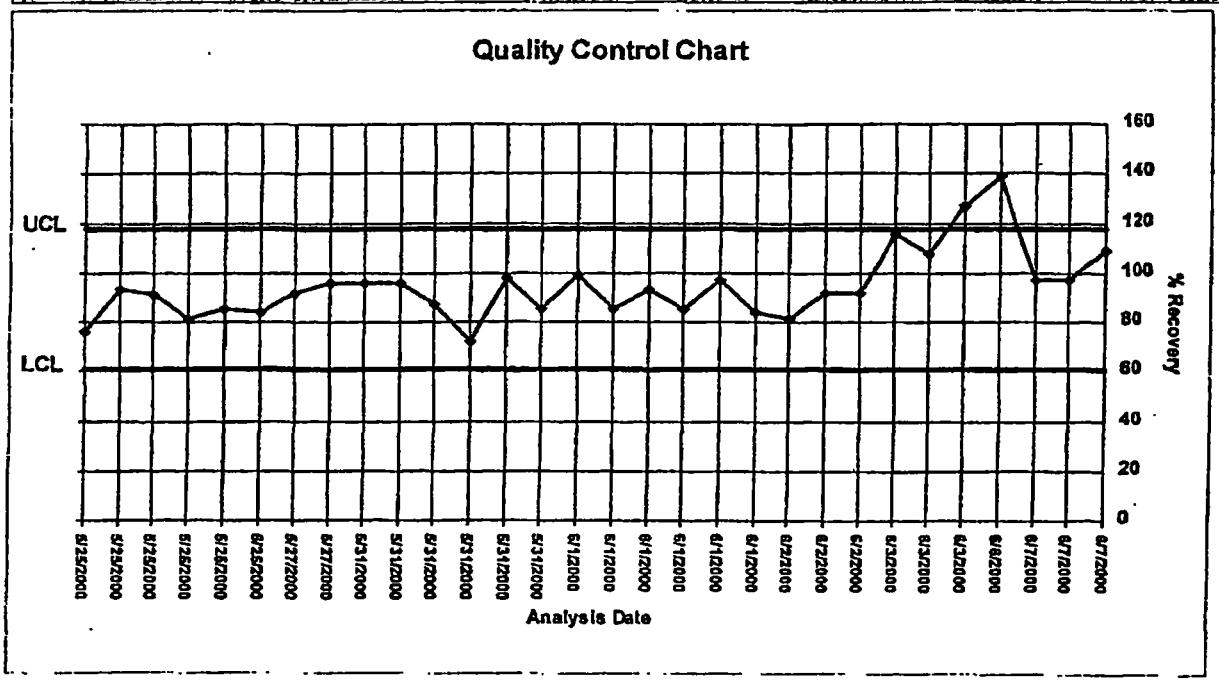
Aqueous

Constituent	*Spike Level*	*Units*	*N*	*Mean*	*Std. Dev.*	*QuantIMS LCL*	*QuantIMS UCL*	*QuantIMS RPD*	*Calculated LCL*	*Calculated UCL*	*Calculated RPD*
PCB-1016	10	ug/L	29	92.90	11.62	61	118	20	58	128	33
PCB-1260	10	ug/L	30	91.20	17.69	61	124	27	38	144	53

PCB-1016 Laboratory Control Sample Aqueous

QuantIMS Spike List: 928 (NC: 8082 Best Practice -LCS) **Analysis Dates:** 05/25/2000 - 06/07/200

Method	Method Description	Extraction
8081	Pesticides/PCBs (8081)	EXTRACTION, SOLID/SOLVENT (auto shaker) w/ACID STRIP (P
8081	Pesticides/PCBs (8081)	LIQ/LIQ, ACCEL ONE STEP w/ACID STRIP (PCB) - Nominal
8081	Pesticides/PCBs (8081)	LIQ/LIQ, CONT w/ACID STRIP (PCB) - Nominal
8081	Pesticides/PCBs (8081)	LIQ/LIQ, SEP FUNNEL w/ACID STRIP (PCB) - Nominal
8081	Pesticides/PCBs (8081)	SONICATION w/ACID STRIP (PCB)
8081	Pesticides/PCBs (8081)	SOXHLET (Na2SO4) w/ACID STRIP (PCB)
8081	Pesticides/PCBs (8081)	WASTE DILUTION w/ACID STRIP (PCB)
8082	PCBs (8082)	Not specified



Statistical Calculations

N	29
Mean %R:	92.897
Std. Dev.:	11.620
Spike Level:	10
Spike Units:	ug/L
QIMS LCL	
QIMS UCL	
CALC LWL	70
CALC UWL	116
CALC LCL	58
CALC UCL	128
N RPD	11
QIMS RPD	20
Calc RPD	0-310

Rejected data points are charted

Generated: 6/19/2000

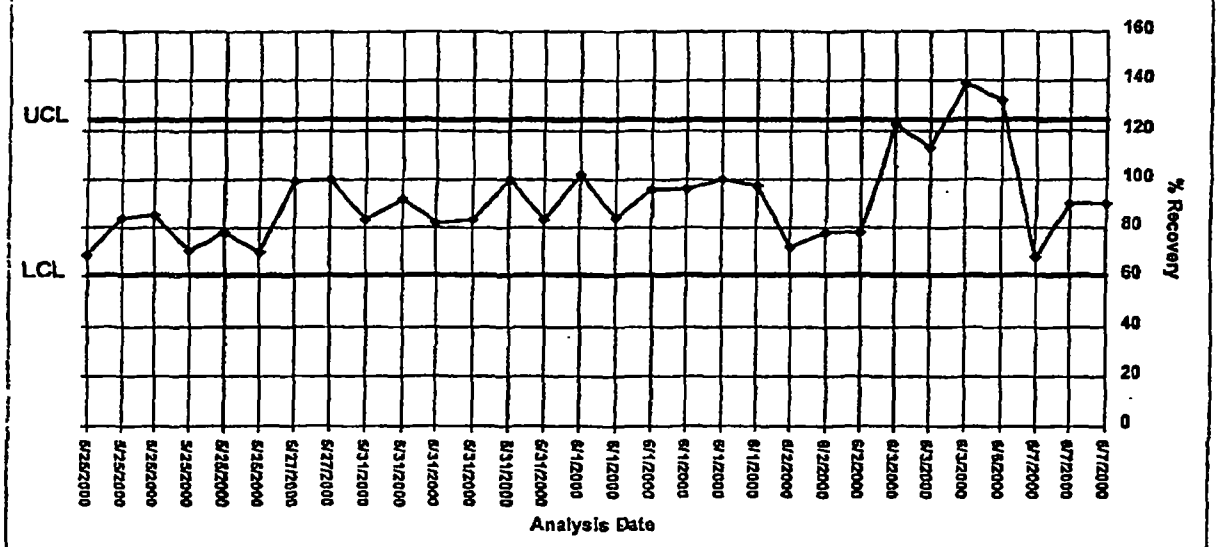
PCB-1260 — Laboratory Control Sample — Aqueous

QuantIMS Spike List: 928 (NC: 8082 Best Practice -LCS)

Analysis Dates: 05/25/2000 - 06/07/2000

Method	Method Description	Extraction
8081	Pesticides/PCBs (8081)	EXTRACTION, SOLID/SOLVENT (Auto shaker) w/ACID STRIP (P
8081	Pesticides/PCBs (8081)	LIQ/LIQ, ACCEL ONE STEP w/ACID STRIP (PCB) - Nominal
8081	Pesticides/PCBs (8081)	LIQ/LIQ, CONT w/ACID STRIP (PCB) - Nominal
8081	Pesticides/PCBs (8081)	LIQ/LIQ, SEP FUNNEL w/ACID STRIP (PCB) - Nominal
8081	Pesticides/PCBs (8081)	SONICATION w/ACID STRIP (PCB)
8081	Pesticides/PCBs (8081)	SOXHLET (Na2SO4) w/ACID STRIP (PCB)
8081	Pesticides/PCBs (8081)	WASTE DILUTION w/ACID STRIP (PCB)
8082	PCBs (8082)	Not specified

Quality Control Chart



Statistical Calculations

N	30
Mean %R:	91.2
Std Dev.:	17.69
Spike Level:	10
Spike Units:	ug/L
QIMS LCL	81
QIMS UCL	124
CALC LWL	56
CALC UWL	127
CALC LCL	36
CALC UCL	144
N RPD	12
QIMS RPD	27
Calc RPD	53.323

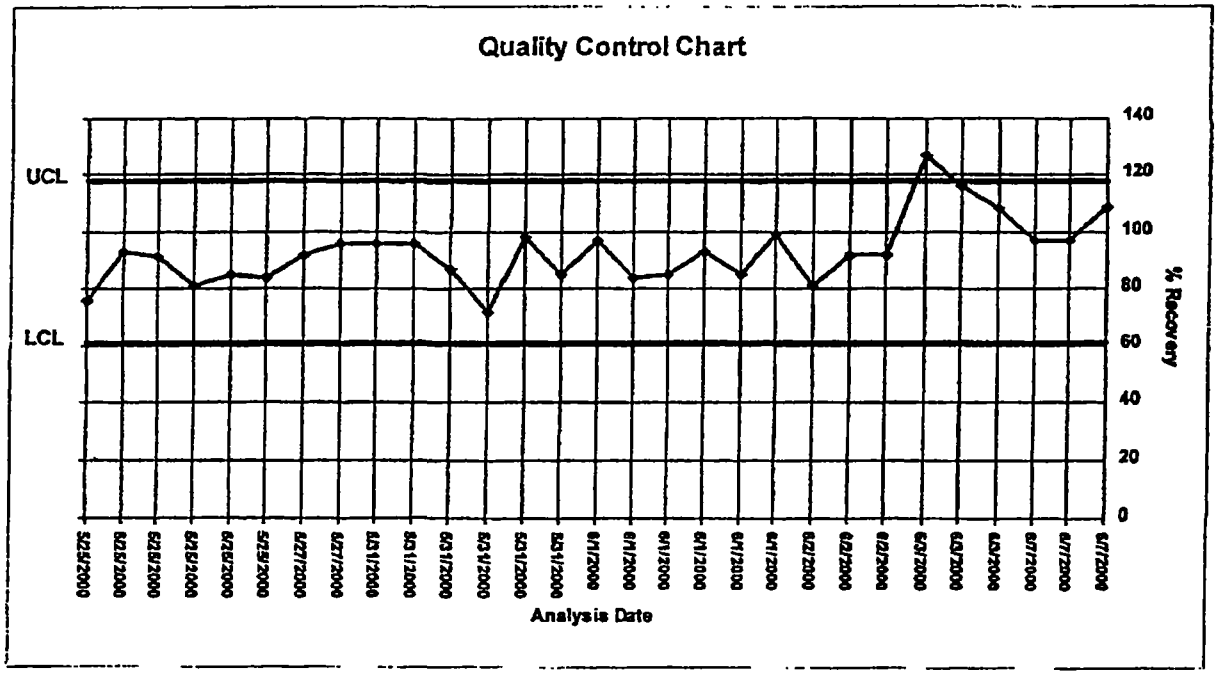
Rejected data points are charted

Generated: 6/19/2000

PCB-1016 — Laboratory Control Sample — Aqueous

QuantIMS Spike List: 928 (NC: 8082 Best Practice -LCS) **Analysis Dates: 05/25/2000 - 06/07/2000**

Method	Method Description	Extraction
8081	Pesticides/PCBs (8081)	EXTRACTION, SOLID/SOLVENT (Auto shaker) w/ACID STRIP (P
8081	Pesticides/PCBs (8081)	LIQ/LIQ, ACCEL ONE STEP w/ACID STRIP (PCB) - Nominal
8081	Pesticides/PCBs (8081)	LIQ/LIQ, CONT w/ACID STRIP (PCB) - Nominal
8081	Pesticides/PCBs (8081)	LIQ/LIQ, SEP FUNNEL w/ACID STRIP (PCB) - Nominal
8081	Pesticides/PCBs (8081)	SONICATION w/ACID STRIP (PCB)
8081	Pesticides/PCBs (8081)	SOXHLET (Na2SO4) w/ACID STRIP (PCB)
8081	Pesticides/PCBs (8081)	WASTE DILUTION w/ACID STRIP (PCB)
8082	PCBs (8082)	Not specified



Statistical Calculations

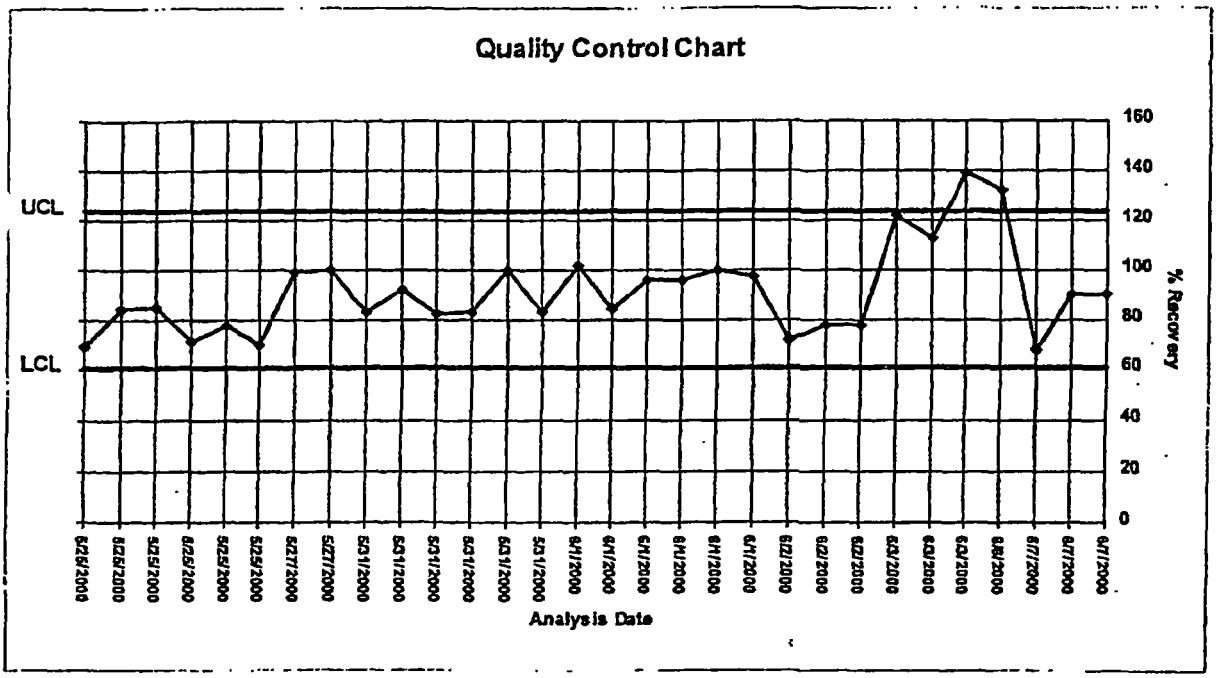
N	29
Mean %R:	92.897
Std. Dev.:	11.620
Spike Level:	10
Spike Units:	
QIMS LCL	61
QIMS UCL	118
CALC LWL	70
CALC UWL	116
CALC LCL	58
CALC UCL	128
N RPD	11
QIMS RPD	20
Calc RPD	33.319

Rejected data points are not charted

PCB-1260 Laboratory Control Sample Aqueous

QuantIMS Spike List: 928 (NC: 8082 Best Practice -LCS) **Analysis Dates: 05/25/2000 - 06/07/2000**

Method	Method Description	Extraction
8081	Pesticides/PCBs (8081)	EXTRACTION, SOLID/SOLVENT (Auto shaker) w/ACID STRIP (P
8081	Pesticides/PCBs (8081)	LIQ/LIQ, ACCEL ONE STEP w/ACID STRIP (PCB) - Nominal
8081	Pesticides/PCBs (8081)	LIQ/LIQ, CONT w/ACID STRIP (PCB) - Nominal
8081	Pesticides/PCBs (8081)	LIQ/LIQ, SEP FUNNEL w/ACID STRIP (PCB) - Nominal
8081	Pesticides/PCBs (8081)	SONICATION w/ACID STRIP (PCB)
8081	Pesticides/PCBs (8081)	SOXHLET (Na2SO4) w/ACID STRIP (PCB)
8081	Pesticides/PCBs (8081)	WASTE DILUTION w/ACID STRIP (PCB)
8082	PCBs (8082)	Not specified



Statistical Calculations

N	30
Mean %R:	91.2
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QIMS LCL	61
QIMS UCL	124
CALC LWL	56
CALC UWL	127
CALC LCL	38
CALC UCL	144
N RPD	12
QIMS RPD	27
Calc RPD	53.323

Rejected data points are not charted

STL NORTH CANTON STANDARD OPERATING PROCEDURE

TITLE: ACID DIGESTION OF SOILS, SW846 METHOD 3050B

(SUPERSEDES: REVISION 2.1 DATE 02/11/00)

Prepared by:		9/26/01 Date
Reviewed by:	Technology Specialist	9.26.1 Date
Reviewed by:	Quality Assurance Manager	9/25/01 Date
Reviewed by:	Environmental Health and Safety	9-27-01 Date
Reviewed by:	Laboratory Director	9-29-01 Date
Reviewed by:	Corporate Technology	Date

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1. SCOPE AND APPLICATION

1.1. This procedure describes the preparation of soil samples for the analysis of certain metals by Graphite Furnace Atomic Absorption (GFAA), Flame Atomic Absorption

(FLAA), Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP), and Inductively Coupled Plasma-Mass Spectrometry (ICP/MS) as specified in SW846 Method 3050B.

1.2. Samples prepared by the protocols detailed in this SOP may be analyzed by ICP, ICP/MS, FLAA or GFAA for the elements listed in Table I (Appendix A). Other elements and matrices may be analyzed following digestion by these protocols provided that the method performance criteria specified in Section 13.0 of this SOP are met.

1.3. This method is not a total digestion, but will dissolve almost all metals that could become "environmentally available". By design, metals bound in silicate structures are not dissolved by this procedure, as they are not usually mobile in the environment. This SOP can be applied to metals in solids, sludges, wastes and sediments.

1.4. This document accurately reflects current laboratory standard operating procedures (SOP) as of the date above. All facility SOPs are maintained and updated as necessary.

2. SUMMARY OF METHOD

A representative 1 gram (wet weight) portion of sample is digested in nitric acid and hydrogen peroxide. The digestate is refluxed with hydrochloric acid for ICP, FLAA or antimony by GFAA analysis. The digestates are then filtered and diluted to 100 mL/100 g.

3. DEFINITIONS

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

3.2. Total Metals: The concentration determined on an unfiltered sample following digestion. Note that this method is designed to determine the total *environmentally available* metals.

4. INTERFERENCES

4.1. There are numerous routes by which samples may become contaminated. Potential sources of trace metals contamination include: metallic or metal-containing labware (e.g., talc gloves which contain high levels of zinc), containers, impure reagents, dirty glassware, improper sample transfers, dirty work areas, atmospheric inputs such as dirt and dust, etc. Be aware of potential sources of contamination and take appropriate measures to minimize or avoid them.

4.2. The entire work area, including the bench top and fume hood, should be thoroughly cleaned on a routine schedule in order to minimize the potential for environmental contamination.

4.3. Boron and silica from the glassware will grow into the sample solution during and following sample processing. For critical low level determinations of boron and silica, only quartz and/or plastic labware should be used.

4.4. Physical interference effects may contribute to inaccuracies in the determinations of trace elements. Oils, solvents and other matrices may not be digested using these methods if they are not soluble with acids. If physical interferences are present, they should be documented.

4.5. Visual interferences or anomalies (such as foaming, emulsions, precipitates, etc.) must be documented.

4.6. Allowing samples to boil or go dry during digestion may result in the loss of volatile metals. If this occurs the sample must be reprepared. Antimony is easily lost by volatilization from hydrochloric media.

4.7. Specific analytical interferences are discussed in each of the determinative methods.

5. SAFETY

5.1. 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 protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately

5.3. The 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 and nitric acid.

5.3.2. The following materials are known to be **oxidizing agents**:

Nitric acid and hydrogen peroxide.

5.3.3. All heating of samples must be carried out in a fume hood.

5.4. The acidification of samples containing reactive materials may result in the release of toxic gases, such as cyanides or sulfides. Acidification of samples should be done in a fume hood. The analyst should also be aware of the potential for a vigorous reaction.

5.5. 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 operation will permit or under other means of mechanical ventilation.

5.7. 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.

5.8. Always carry bulk concentrated acid bottles in appropriate impact proof containers.

5.9. Acid/peroxide spills must be neutralized immediately, flushed with water and cleaned up using appropriate spill kits.

5.10. Discard chipped or broken beakers to prevent injury. Chipped glassware may be fire polished as an alternative to disposal.

5.11. Any and all accidents and spills must be reported to the lab supervisor or EH&S coordinator.

6. EQUIPMENT AND SUPPLIES

6.1. Hot plate, digestion block, steam bath or other heating source capable of maintaining a temperature of 90-99°C.

6.2. Calibrated thermometer that covers a temperature range of 0-200°C.

6.3. Griffin beakers of assorted sizes or equivalent.

6.4. Vapor recovery device (Watch glasses, ribbed or other device).

6.5. Whatman No. 41 filter paper or equivalent.

6.6. Funnels or equivalent filtration apparatus.

6.7. Centrifugation equipment (if desired method of removing particulates is centrifugation).

6.8. Graduated cylinder or equivalent capable of measuring 100 mL within 3% accuracy.

6.9. Analytical balance capable of accurately weighing to the nearest 0.01 grams.

6.10. Repippetors or suitable reagent dispensers.

6.11. Calibrated automatic pipettes with corresponding pipette tips or Class A glass volumetric pipettes.

6.12. Class A volumetric flasks.

6.13. pH indicator strips (pH range 0 - 6).

6.14. Plastic bottles.

7. REAGENTS AND STANDARDS

7.1. Reagent water must be produced by a Millipore DI system or equivalent. Reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks as defined in the determinative SOPs.

7.2. Laboratory Control Sample (LCS) and matrix spike (MS) solutions are purchased as custom STL North Canton solutions. All standards must be stored in FEP fluorocarbon or previously unused polyethylene or polypropylene bottles. Stock standard solutions must be replaced prior to the expiration date provided by the manufacturer. If no expiration date is provided, the stock solutions may be used for up to one year and must be replaced sooner if verification from an independent source indicates a problem.

7.3. Working ICP LCS/MS spike solution: Prepare the ICP LCS/MS working spike solutions from custom stock standards to the final concentration listed in Table II. The

working spike must be prepared in a matrix of 5% HNO_3. This acid (5 mL of concentrated HNO_3 per 100 mL) must be added to the volumetric flask before the addition of the stock standard aliquot. The working ICP LCS solution must be made fresh every three months.

7.4. Working GFAA LCS/MS spike solution: Prepare the GFAA working LCS/MS spike solutions by diluting the custom stock solution (7.2) 200x. The working spike solution must be prepared in a matrix of 5% HNO_3. This acid (5 mL of concentrated HNO_3 per 100 mL) must be added to the volumetric flask before the addition of the stock standard aliquot. The working GFAA LCS/MS solution must be made fresh every three months.

7.5. The LCS and MS samples must contain all the elements designated for analysis in each batch of samples. If a non-routine element is required that is not contained in the custom STL North Canton solution, the individual facility must purchase a solution from the designated vendor that will cover the additional analyte(s) of interest and provide for a final spike concentration that is appropriate to the determinative method.

7.6. Aqueous laboratory control samples (LCSW) and matrix spike samples are prepared as described in Sections 9.5 and 9.6. Refer to Tables II and III (Appendix A) for details regarding the stock, working standard and final digestate spike concentrations for ICP and GFAA LCS and matrix spike preparations.

7.7. Nitric acid (HNO_3), concentrated, trace metal grade or better.

7.8. Nitric acid, 1:1 - dilute concentrated HNO_3 with an equal volume of reagent water.

Note: When preparing diluted acids always add acid to water. If the water is added to the acid a violent reaction may occur.

7.9. Hydrochloric acid (HCl), concentrated, trace metal grade or better.

7.10. Hydrochloric acid, 1:1 - dilute concentrated HCl with an equal volume of reagent water.

Note: When preparing diluted acids always add acid to water. If the water is added to the acid a violent reaction may occur.

7.11. 30% Hydrogen peroxide (H_2O_2), reagent grade.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Sample holding time for metals included under the scope of this SOP is 180 days from the date of collection to the date of analysis.

8.2. Soil samples do not require preservation but must be stored at 4 °C ± 2 °C until the time of analysis.

9. QUALITY CONTROL

Table IV (Appendix A) provides a summary of quality control requirements including type, frequency, acceptance criteria and corrective action.

9.1. Initial Demonstration of Capability

Prior to analysis of any analyte using Method 3050B the following requirements must be met.

9.1.1. Method Detection Limit (MDL) - An MDL must be determined for each analyte/matrix prior to the analysis of any samples. The MDL is determined using seven replicates of reagent water, spiked with all the analytes of interest, that have been carried through the entire analytical procedure. MDLs must be redetermined on an annual basis in accordance with 40 CFR Part 136 Appendix B requirements or verified as detailed in STL North Canton QA Policy QA-005. The spike level must be between the calculated MDL and 10X the MDL to be valid. The result of the MDL determination must be below the STL North Canton reporting limit.

9.1.2. Initial Demonstration Study- this requires the analysis of four QC check samples. The QC check sample is a well characterized laboratory generated sample used to monitor method performance, which should contain all the analytes of interest. The results of the initial demonstration study must be acceptable before analysis of samples may begin. The results of the initial demonstration study may be used to extend a method for the analysis of other elements provided all acceptance criteria are met.

9.1.2.1. Four aliquots of the check sample (LCS) are prepared and analyzed using the procedures detailed in this SOP and the determinative SOPs.

9.1.2.2. Calculations and acceptance criteria for QC check samples are given in the determinative SOPs (CORP-MT-0001, CORP-MT-0003).

9.2. Preparation Batch - A group of up to 20 samples that are of the same matrix and are processed together using the same procedures and reagents. The preparation batch must contain a method blank, a LCS and a matrix spike/matrix spike duplicate. In some cases, at client request, it may be appropriate to process a matrix spike and sample duplicate in place of the MS/MSD. If clients specify specific samples for MS/MSD, the batch may contain multiple MS/MSD pairs.

9.3. Sample Count - Laboratory generated QC samples (method blanks, LCS, MS/MSD) are not counted towards the maximum 20 samples in a batch. Field QC samples are included in the batch count.

9.4. Method Blank (MB) - One method blank must be processed with each preparation batch. The method blank consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The method blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. Criteria for the acceptance of blanks are contained within the individual analytical method SOP's. If the method blank does not meet the criteria contained within the analytical method SOPs, the blank and all associated samples in the batch must be redigested.

9.5. Laboratory Control Sample (LCS) - One aqueous LCS must be processed with each preparation batch. The LCS must contain all analytes of interest and must be carried through the entire analytical procedure. The LCS is used to monitor the accuracy of the analytical process. On going monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines. Criteria for the acceptance of LCS results are contained within the individual analytical method SOP's. Corrective action when LCS results fail to meet control limits will be repreparation and reanalysis of the batch. Tables II and III provide the details regarding the stock, working standards and final spike concentrations for ICP and GFAA. Refer to Section 7.3 or 7.4 for instructions on preparation of the aqueous LCS.

9.5.1. The LCS is prepared by spiking a 1mL or 1 g aliquot of reagent water with 2 mL of the working LCS/MS spike solution (7.3 or 7.4). The LCS is then processed as described in either Section 11.10.

9.6. Matrix Spike/Matrix Spike Duplicate (MS/MSD) - One MS/MSD pair must be processed for each preparation batch. A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added. A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked identically as the MS) prepared and analyzed along with the sample and matrix spike. Some client specific data quality objectives (DQO's) may require the use of sample duplicates in place of or in

addition to MS/MSD's. The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Samples identified as field blanks cannot be used for MS/MSD analysis. If any analyte recovery or RPD falls outside the acceptance range, the recovery of that analyte must be in control for the LCS. If the recovery of the LCS is outside limits, corrective action must be taken. Corrective action will include repreparation and reanalysis of the batch. Corrective action when MS results fail to meet control limits does not include repreparation of samples unless the results indicate that a spiking error may have occurred. Tables II and III provide the details regarding the stock, working standards and final matrix spike concentrations for ICP and GFAA. Refer to Sections 7.3 and 7.4 for instructions on preparation of the working matrix spike solutions.

9.6.1. The soil matrix spike sample is prepared by spiking a 1 g aliquot of a sample with 2mL of the working LCS/MS spike solution (7.3 or 7.4). The matrix spike sample is then processed as described in either Section 11.10.

9.7. Quality Assurance Summaries - Certain clients may require specific project or program QC which may supersede the SOP requirements. Quality Assurance Summaries (QAS) should be developed to address these requirements.

10. CALIBRATION AND STANDARDIZATION

10.1. Hotplate or block temperature must be verified daily for each unit used and must be recorded on either the metals preparation log or in a hotplate temperature logbook. The hotplate temperature should be verified by measuring the temperature of a beaker of reagent water placed on each hotplate. For block digestors, use a tube containing water.

11. PROCEDURE

11.1. One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo and is approved by a Technical Specialist and QA Manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file.

11.2. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

11.3. The heating procedures are carried out in a properly functioning hood.

11.4. All samples are to be checked out of sample control with the chain of custody documentation filled out completely.

11.5. Proper sample identification is extremely important in any preparation procedure. Labeling of beakers and bottles must be done in a manner to ensure connection with the proper sample. The use of automatic label printing programs is recommended to reduce transcription errors (QuantIMS option).

11.6. Samples are typically logged in as either waters or soils. Wastes such as organic liquids or sludges and tissues (animal/vegetable) are usually logged in with solid test codes. When initiating prep, examine the sample to see if the sample matches the matrix designation. If the sample is logged in as aqueous but it appears more like a waste (biphasic, sludge like, organic liquid, lots of sediment etc.) contact the lab supervisor or project administrator for further instructions. In some cases it may be more appropriate to process these samples as solids.

11.7. If possible prepare all the samples of a project at the same time to minimize the QC required and streamline the flow of the project through the lab and reporting group.

11.8. In some cases, both AA and ICP digests are required on each sample. It is recommended that both aliquots be weighed out and processed at the same time.

11.9. Guidelines are provided in the appendices on procedures to minimize contamination of samples and standards.

11.10. Preparation of Soils, Sediments and Sludges for Analysis by GFAA, ICP, ICP/MS and FLAA.

11.10.1. Mix sample thoroughly by stirring with a clean plastic or wooden spoon or spatula.

11.10.2. For each digestion procedure required (i.e., ICP or GFAA), weigh a 1.0 portion of solid and record the exact weight to the nearest 0.01 g. A 2 g sample size may also be used if needed to meet the reporting limits.

11.10.3. Measure additional aliquots of the designated samples for the MS and MSD analyses.

11.10.4. Spike each of the MS and MSD aliquots with 2 mL of the working LCS/MS spiking solution (7.3 or 7.4).

11.10.5. Prepare a beaker for the method blank.

11.10.6. Prepare a beaker for the LCS. Add 2 mL of the working LCS/MS spiking solution (7.3 or 7.5).

11.10.7. Add 10 mL of 1:1 HNO_3 and mix the sample.

11.10.8. Heat sample to 95° ±4° C and reflux for 10 minutes without boiling, using a vapor recovery device.

Note: DO NOT ALLOW SAMPLE TO BOIL OR GO DRY during any part of the digestion. Doing so will result in the loss of analyte and the sample must be reprepared.

11.10.9. Allow sample to cool, if necessary.

11.10.10. Add 5 mL of concentrated HNO_3 and replace vapor recovery device.

11.10.11. Reflux at 95° ±4° C for 30 minutes. (Add reagent water as needed to ensure that the volume of solution is not reduced to less than 5 mL.)

11.10.12. If brown fumes are observed, repeat step 11.10.10 until no more fumes are evolved.

11.10.13. Allow the samples to cool, if necessary.

11.10.14. Add approximately 2 mL of reagent water and 1 mL of 30 % H_2O_2. Care must be taken to ensure that losses do not occur due to excessively vigorous effervescence.

11.10.15. Replace the vapor recovery device and heat sample until effervescence subsides.

11.10.16. Allow the sample to cool, if necessary.

11.10.17. Continue adding 30% H_2O_2 in 1 mL aliquots with warming until effervescence is minimal or sample appearance is unchanged.

Note: Do not add more than a total of 10 mL of 30 % H_2O_2.

11.10.18. Continue heating at 95° ±4° C for 75 minutes until the volume is reduced to approximately 5-10 mL. Alternatively the sample may be heated for 2 hours.

11.10.19. If the sample is being prepared for ICP or FLAA analyses add 10 mL of concentrated HCl and reflux for an additional 10 minutes without boiling. This step is omitted for analysis by ICP-MS and GFAA

Note: Antimony and silver have poor solubility in dilute nitric acid solution. Therefore it is strongly recommended that these elements are determined by the ICP procedure that includes HCl as the final digestion acid.

11.10.20. Allow the sample to cool.

11.10.21. Wash down beaker walls and vapor recovery device with reagent water.

11.10.22. Filter sample through Whatman 41 filter paper or equivalent into a graduated cylinder or equivalent or a pre-weighed bottle. Other measuring bottles (for example, Corning Snap Seals™) may be used if their accuracy is documented and is better than ± 2%. Rinse beaker and filter paper with reagent water to ensure complete sample transfer.

Note: In place of filtering, the samples, after dilution and mixing, may be centrifuged or allowed to settle by gravity overnight to remove insoluble material

11.10.23. Dilute sample to 100 mL or 100g with reagent water. The sample is now ready for analysis.

Note: This SOP allows for samples to be weighed instead of measured volumetrically. This assumes the density of the diluted sample is close to 1.0 g/mL (See Section 17.1.2).

12. DATA ANALYSIS AND CALCULATIONS

Not Applicable.

13. METHOD PERFORMANCE

13.1. Method performance is determined by the analysis of matrix spike and matrix spike duplicate samples as well as method blanks and laboratory control samples. In general, the matrix spike recovery should fall within +/- 20 % and the matrix spike duplicates should compare within 20% RPD. Method blanks must meet the criteria specified in the determinative SOPs. The laboratory control samples should recover within 20% of the true value until in house control limits are established. Acceptance criteria are given in the determinative SOPs.

13.2. The initial demonstration study as detailed in Section 9.1.2 must be acceptable before the analysis of field samples under this SOP may begin. The results of the initial demonstration study may be used to extend a method for the analysis of other elements provided all acceptance criteria are met.

13.3. Training Qualification:

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

14. POLLUTION PREVENTION

14.1. This method does not contain any specific modifications that serve to minimize or prevent pollution.

15. WASTE MANAGEMENT

15.1. 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.

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. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition, Final Update III, December 1996. Method 3050B.

16.2. CORP-MT-0001, Inductively Coupled Plasma-Atomic Emission Spectroscopy, Spectrometric Method for Trace Element Analysis of Water and Wastes, Method 6010B and Method 200.7.

16.3. CORP-MT-0003, Graphite Furnace Atomic Absorption Spectroscopy, SW846 Method 7000A and MCAWW 200 Series Methods.

16.4. NC-MT-0002, Inductively Coupled Plasma-Mass Spectrometry, EPA Methods 6020 and 200.8.

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. Chapter 1 of SW-846 states that the method blank should not contain any analyte of interest at or above the MDL. This SOP states that the method blank must not contain any analyte of interest at or above the reporting limit. Common lab contaminants, as defined in the determinative SOPs, are allowed up to two times the reporting limit in the blank following consultation with the client.

17.1.2. This SOP allows for aqueous samples to be weighed instead of measured volumetrically. This assumes the density of the sample is close to 1.0 g/mL. Samples with large amounts of sediment or suspended solids, sludges, non-aqueous liquids must be processed volumetrically. Weighing samples directly into the digestion vessel minimizes the potential for cross contamination, offers improved accuracy over the use of graduated cylinders (comparable to volumetric flask accuracy), uses less glassware and is more efficient.

17.2. Modifications from previous SOP

17.2.1. ICP/MS has been added as an appropriate determinative technique.

17.2.2. The approved analyte list may be modified provided that additional elements meet the requirements in section 13.

17.2.3. Directions for digestion for set time periods rather than reduction to set volumes have been added.

17.2.4. The order of two steps in the digestion has been changed. (See section 11.10.20)

17.2.5. Definition of the method as determining total environmentally available metals has been added.

17.3. Facility Specific SOPs

Each facility shall attach a list of facility specific SOPs or approved attachments (if applicable) which are required to implement this SOP or which are used in conjunction with this SOP. If no facility specific SOPs or amendments are to be attached, a statement must be attached specifying that there are none. Refer to the Appendices for any facility specific information required supporting this SOP.

17.4. Documentation and Record Management

The preparation benchsheet should, at a minimum, include the following information:

- Preparation date, analyst initials, matrix, prep type (ICP or GFAA), SOP reference.
- Sample ID; initial weight/volume and final weight/volume.
- Standards Documentation (source, lot, prep date, volume added).
- Analyst Signature.
- Reviewer's Signature and date.

Figure 1. Soil Sample Preparation (Section 11.10)

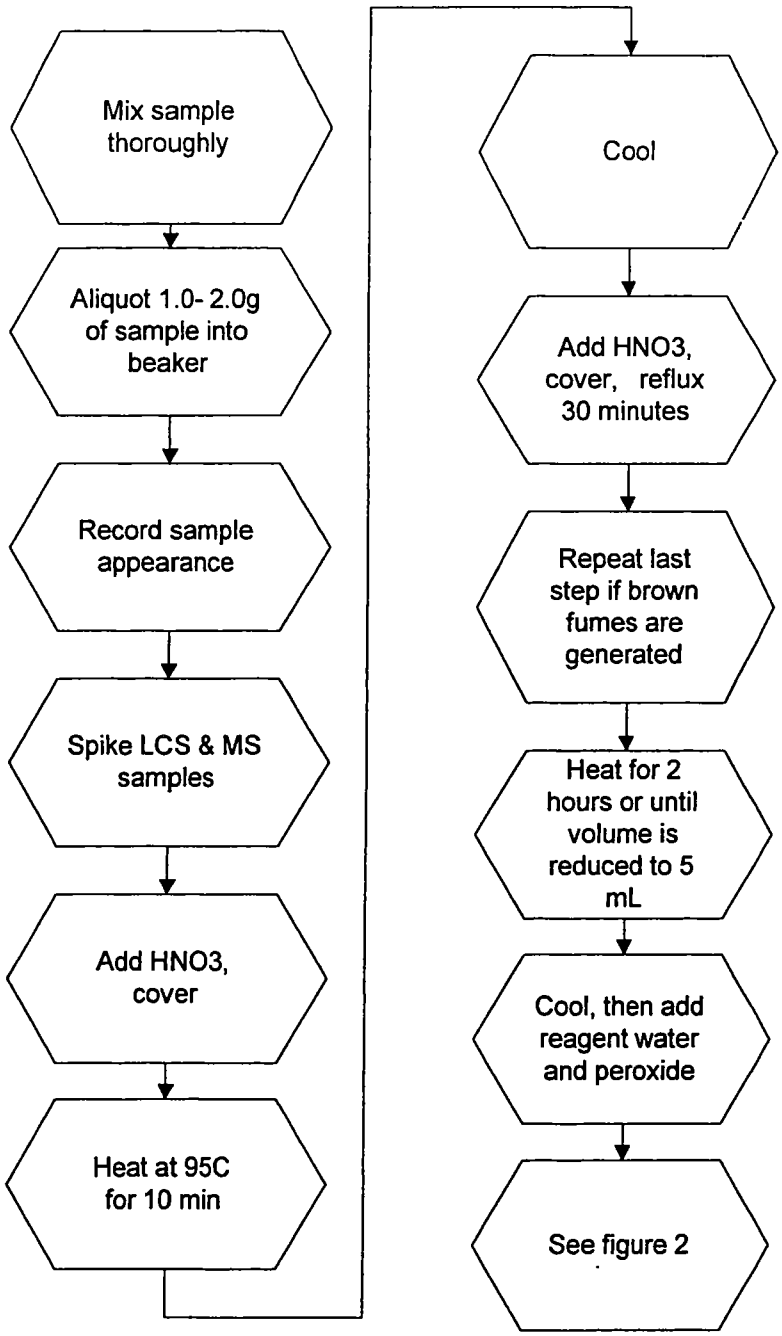
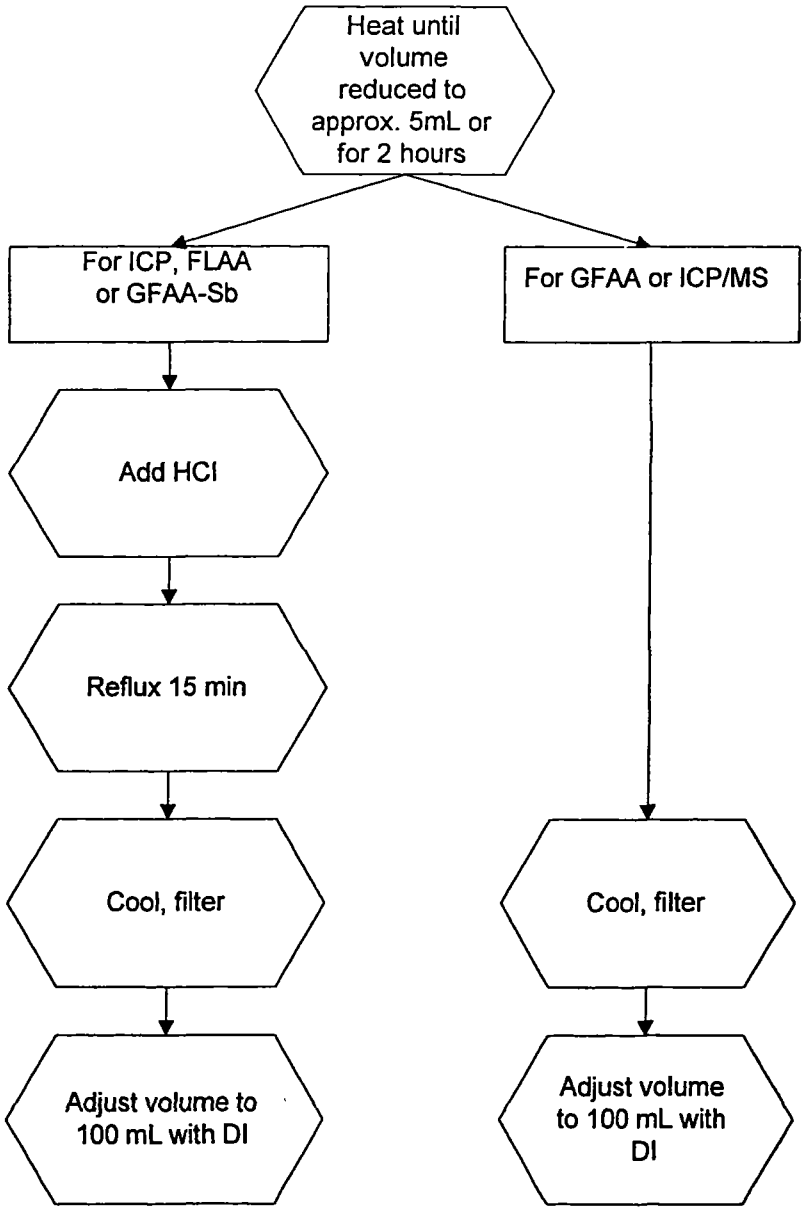


Figure 2. Soil Sample Preparation (continued)



APPENDIX A

TABLES

TABLE I. Method 3050A Approved Analyte List

ELEMENT	Symbol	CAS Number
Aluminum	Al	7429-90-5
Antimony	Sb	7440-36-0
Arsenic	As	7440-38-2
Barium	Ba	7440-39-3
Beryllium	Be	7440-41-7
Cadmium	Cd	7440-43-9
Calcium	Ca	7440-70-2
Chromium	Cr	7440-47-3
Cobalt	Co	7440-48-4
Copper	Cu	7440-50-8
Iron	Fe	7439-89-6
Lead	Pb	7439-92-1
Magnesium	Mg	7439-95-4
Manganese	Mn	7439-96-5
Molybdenum	Mo	7439-98-7
Nickel	Ni	7440-02-0
Potassium	K	7440-09-7
Selenium	Se	7782-49-2
Silver	Ag	7440-22-4
Sodium	Na	7440-23-5
Thallium	Tl	7440-28-0
Vanadium	V	7440-62-2
Zinc	Zn	7440-66-6

TABLE II. ICP and FLAA Soil Matrix Spike and Aqueous LCS Levels

ELEMENT	Working LCS/MS Standard (mg/L)	Aqueous LCS/MS Level* (ug/L)	Soil MS Level ** (mg/Kg)
Aluminum	100	2000	200
Antimony	25	500	50
Arsenic	100	2000	200
Barium	100	2000	200
Beryllium	2.5	50	5
Cadmium	2.5	50	5
Calcium	2500	50000	5000
Chromium	10	200	20
Cobalt	25	500	50
Copper	12.5	250	25
Iron	50	1000	100
Lead	25	500	50
Lithium	50	1000	100
Magnesium	2500	50000	5000
Manganese	25	500	50
Molybdenum	50	1000	100
Nickel	25	500	50
Potassium	2500	50000	5000
Selenium	100	2000	200
Silver	2.5	50	5
Sodium	2500	50000	5000
Strontium	50	1000	100
Thallium	100	2000	200
Vanadium	25	500	50
Zinc	25	500	50
Boron	50	1000	100
Tin	100	2000	200
Titanium	50	1000	100

* Levels shown indicate the spike concentration in the final digestate of the aqueous LCS or matrix spike based on the addition of 2.0 mL working spike (7.3) to 100 mL of sample.

** Final soil spike concentration based on the addition of 2.0 mL working spike (7.3) to 1.0 g of sample/100 mL final volume (assumes 100% solids).

TABLE III. ICPMS Soil Matrix Spike and Aqueous LCS Levels

ELEMENT	Working LCS/MS Standard (mg/L)	Aqueous LCS/MS Level* (ug/L)	Soil MS Level ** (mg/Kg)
Aluminum	10	1000	100
Antimony	10	100	10
Arsenic	10	100	10
Barium	10	100	10
Beryllium	10	100	10
Cadmium	10	100	10
Calcium	100	1000	100
Chromium	10	100	10
Cobalt	10	100	10
Copper	10	100	10
Iron	100	1000	100
Lead	10	100	10
Magnesium	100	1000	100
Manganese	10	100	10
Molybdenum	10	100	10
Nickel	10	100	10
Potassium	100	1000	100
Selenium	10	100	10
Silver	10	100	10
Sodium	100	1000	100
Strontium	10	100	10
Thallium	10	100	10
Vanadium	10	100	10
Zinc	10	100	10
Boron	10	100	10
Tin	10	100	10
Titanium	10	100	10
Zirconium	10	100	10

* Levels shown indicate the spike concentration in the final digestate of the aqueous LCS or matrix spike based on the addition of 1.0 mL working spike (7.4) to 100 mL of sample.

** Final soil spike concentration based on the addition of 1.0 mL working spike (7.4) to 1.0 g of sample/100 mL final volume (assumes 100% solids).

TABLE IV. GFAA Soil Matrix Spike and Aqueous LCS Spike Levels

ELEMENT	Stock LCS/MS Standard (mg/L)	Working LCS/MS Standard (ug/L)	Aqueous LCS/ MS Level * (ug/L)	Soil MS Level** (mg/Kg)
Arsenic	400	2000	40	4
Selenium	400	2000	40	4
Lead	400	2000	40	4
Thallium	400	2000	40	4
Antimony	400	2000	40	4
Cadmium	40	200	4	0.4
Chromium	100	500	10	1
Silver	50	250	5	0.5

* Levels shown indicate the spike concentration in the final digestate of the aqueous LCS or matrix spike based on the addition of 1.0 mL working spike (7.5) to 50 mL of sample.

** Final soil spike concentration based on the addition of 2.0 mL working spike (7.5) to 1.0 g of sample/100 mL final volume (assumes 100% solids).

TABLE V. Summary of Quality Control Requirements

QC PARAMETER	FREQUENCY	ACCEPTANCE CRITERIA	CORRECTIVE ACTION
Method Blank	One per sample preparation batch of up to 20 samples.	Refer to determinative SOPs: CORP-MT-0001 CORP-MT-0003	Redigest and reanalyze samples.
Laboratory Control Sample (LCS)	One per sample preparation batch of up to 20 samples.	Refer to determinative SOPs: CORP-MT-0001 CORP-MT-0003	Redigest and reanalyze all samples associated with the LCS.
Matrix Spike	One per sample preparation batch of up to 20 samples.	Refer to determinative SOPs: CORP-MT-0001 CORP-MT-0003	Reprep not required unless preparation error suspected.
Matrix Spike Duplicate	See Matrix Spike	Refer to determinative SOPs: CORP-MT-0001 CORP-MT-0003	See Corrective Action for Matrix Spike.

APPENDIX B

CONTAMINATION CONTROL GUIDELINES

APPENDIX B. CONTAMINATION CONTROL GUIDELINES

The following procedures are strongly recommended to prevent contamination:

All work areas used to prepare standards and spikes should be cleaned before and after each use.

All glassware should be washed with detergent and tap water and rinsed with 1:1 nitric acid followed by deionized water.

Proper laboratory housekeeping is essential in the reduction of contamination in the metals laboratory. All work areas must be kept scrupulously clean.

Powdered or latex gloves must not be used in the metals laboratory since the powder contains silica and zinc, as well as other metallic analytes. Only vinyl or nitrile gloves should be used in the metals laboratory.

Glassware should be periodically checked for cracks and etches and discarded if found. Etched glassware can cause cross contamination of any metallic analytes.

Autosampler trays should be covered to reduce the possibility of contamination. Trace levels of elements being analyzed in the samples can be easily contaminated by dust particles in the laboratory.

The following are helpful hints in the identification of the source of contaminants:

Reagents or standards can contain contaminants or be contaminated with the improper use of a pipette.

Improper cleaning of glassware can cause contamination.

Separate glassware if an unusually high sample is analyzed and soak with sulfuric acid prior to routine cleaning.

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Implementation Date:_____

SOP No. CORP-MT-0001NC
Revision No. 3.3
Revision Date: 12/05/01
Page 1 of 57

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)

Approved by: _____ 12/6/01
Date

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Technical Specialist Date

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Quality Assurance Manager Date

Approved by: _____ 12-10-01
Environmental, Health and Safety Coordinator Date

Approved by: _____ 12-10-01
Laboratory Manager Date

Approved by: _____ 1/30/01
Corporate Technology 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 <u>after</u> filtration).

3.2. Suspended Metals: Those elements which are retained by a 0.45 um membrane.

3.3. Total Metals: The concentration determined on an unfiltered sample following vigorous digestion.

3.4. Total Recoverable Metals: The concentration determined on an unfiltered sample following treatment with hot, dilute mineral acid.

4. INTERFERENCES

4.1. Spectral, physical and chemical interference effects may contribute to inaccuracies in the determinations of trace elements by ICP. Spectral interferences are caused by:

- Overlap of a spectral line from another element.
- Unresolved overlap of molecular band spectra.
- Background contribution from continuous or recombination phenomena.
- Stray light from the line emission of high concentration elements.

4.1.1. A background correction technique is required to compensate for variable background contribution to the determination of trace elements. Background correction is not required in cases where a background corrective measurement would actually degrade the analytical result.

4.1.2. Inter-element correction factors (IECs) are necessary to compensate for spectral overlap. Inter-element interferences occur when elements in the sample emit radiation at wavelengths so close to that of the analyte that they contribute significant intensity to the analyte channel. If such conditions exist, the intensity contributed by the matrix elements will cause an excessively high (or sometimes low) concentration to be reported for the analyte. Inter-element corrections IECs must be applied to the analyte to remove the effects of these unwanted emissions.

4.1.3. Physical interferences are generally considered to be effects associated with sample transport, nebulization and conversion within the plasma. These interferences may result in differences between instrument responses for the sample and the calibration standards. Physical interferences may occur in the transfer of solution to the nebulizer (e.g., viscosity effects), at the point of aerosol formation and transport to the plasma (e.g., surface tension) or during excitation and ionization processes within the plasma itself. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples containing high dissolved solids or high acid concentrations. If physical interferences are present, dilution of the sample, use of a peristaltic pump, mass flow controller, use of an internal standard and/or use of a high solids nebulizer can reduce the effect.

4.1.4. Chemical interferences are characterized by molecular compound formation, ionization effects and solute vaporization effects. Normally these effects are not significant with the ICP technique but if observed can be minimized by buffering the sample, matrix matching or standard addition procedures.

5. SAFETY

5.1. Procedures shall be carried out in a manner that protects the health and safety of all STL 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</u> <u>exposures</u> for each standard, field sample and QC sample is required. The average of the exposures is reported. For Trace ICP analyses, the results of the sum channel must be used for reporting.

11.3. Prior to calibration and between each sample/standard the system is rinsed with the calibration blank solution. The minimum rinse time between analytical samples is 60 seconds unless following the protocol outlined in 9.1.6 it can be demonstrated that a shorter rinse time may be used. Triton-X can be added to the rinse solution to facilitate the rinse process.

11.4. The use of an autosampler for all runs is strongly recommended.

11.5. The use of automated QC checks through the instrument software is highly recommended for all calibration verification samples (ICV,CCV), blanks

(ICB,CCB,PB), interference checks (ICSA,ICSAB) and field samples (linear range) to improve the data review process.

11.6. To facilitate the early identification of QC failures and samples requiring rerun it is strongly recommended that sample data be reviewed periodically throughout the run.

11.7. To facilitate the data review and reporting processes it is strongly recommended that all necessary dilutions be performed before closing out the instrument run.

11.8. 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:

<u>Original Run</u>: 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

12.1ICV percent recoveries are calculated according to the equation:

$$\%R = 100\left(\frac{Found(ICV)}{True(ICV)}\right)$$

12.2CCV percent recoveries are calculated according to the equation:

$$\%R = 100\left(\frac{Found(CCV)}{True(CCV)}\right)$$

12.3Matrix 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

12.4The 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

12.5The 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).

16.5QA-003, STL North Canton QC Program.

16.6QA-004, Rounding and Significant Figures.

16.7QA-005, Method Detection Limits.

17 MISCELLANEOUS (TABLES, APPENDICES, ETC.)

17.1Modifications/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.

17.2Modifications from previous SOP

Refer to revision 2 of this SOP.

17.3Facility-Specific SOPs

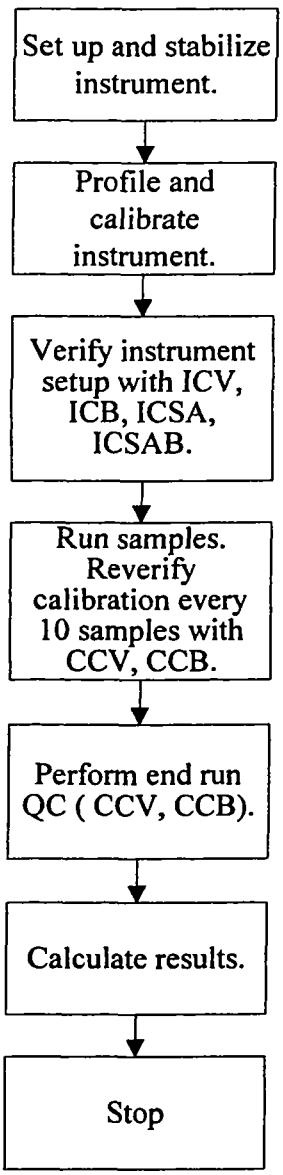
Each facility shall review and revise as appropriate this SOP to reflect any facility-specific requirements. If no facility-specific amendments are required, the SOP can be adopted as is.

17.4Documentation 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).

17.5Flow 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

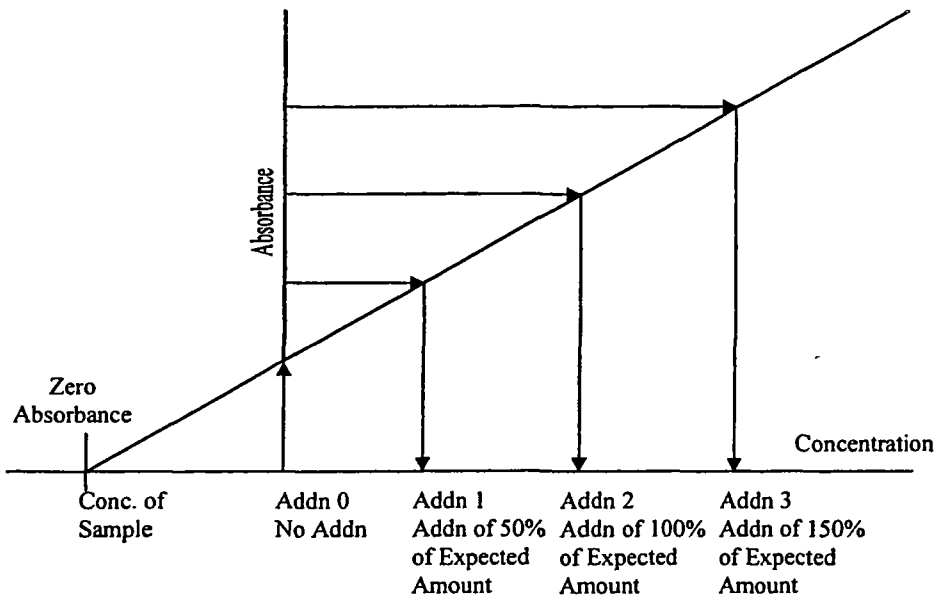
MSA GUIDANCE

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

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 3.6 (Dated 05/13/99))

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Approved by:	Corporate Technology	3/26/01 Date

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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:
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)	√		√		

EQUIPMENT AND SUPPLIES	Sep fun.	CLLE	Soni	Sox	Conc
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 (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 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.	√	√			

REAGENTS	Sep fun.	CLLE	Soni	Sox	Conc
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	√	√	√	√	√
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 $\leq 6^{o}C$. 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. 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

10.2. Extraction is initiated within 7 days of the sampling date for aqueous samples, 14 days for solid and waste samples.

20.2. 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 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 11.7 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.

11.3.1. 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.

11.3.2. 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.

11.3.3. 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 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.

11.3.3.1. 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

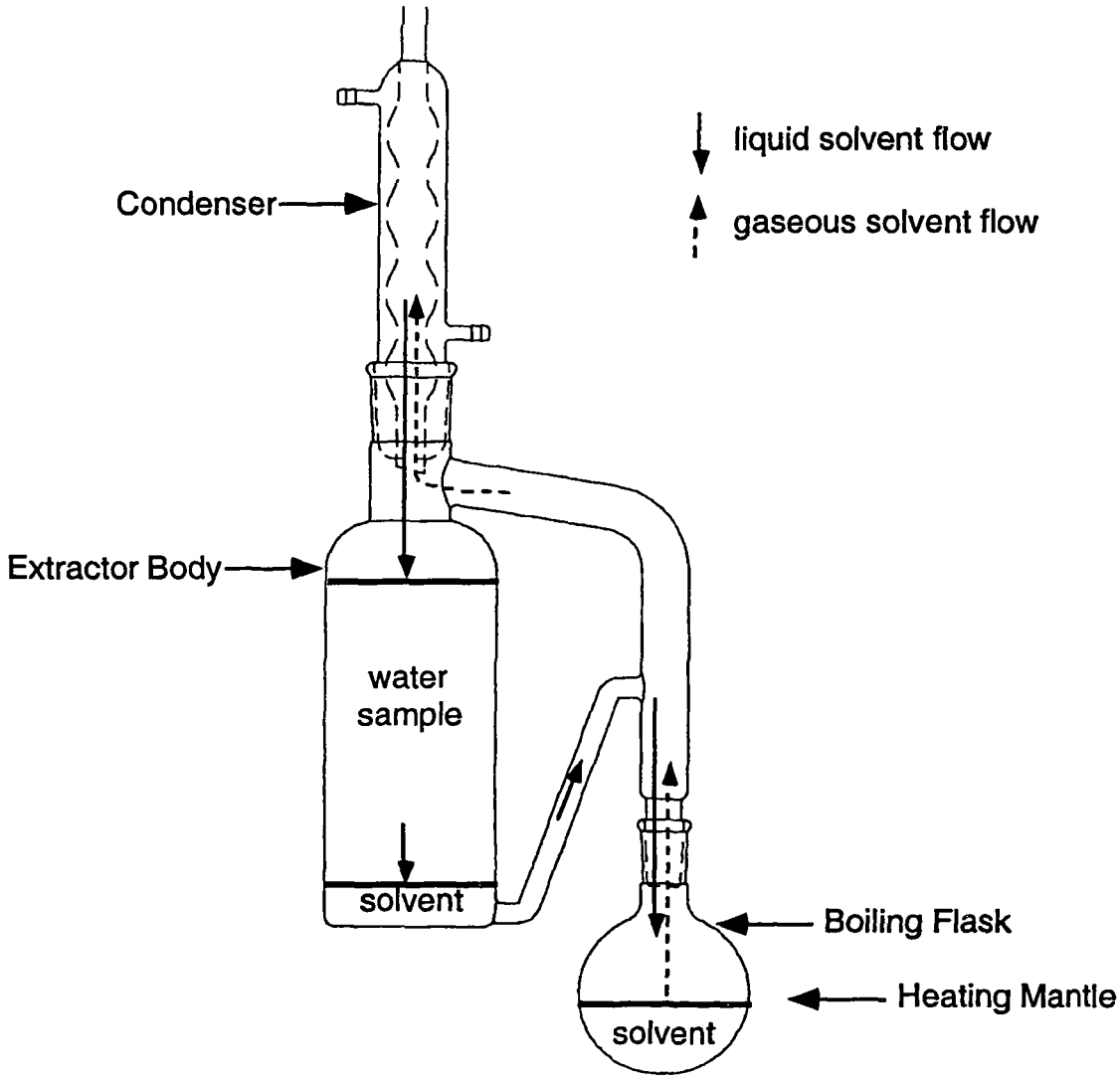
then measuring the volume of water required to fill the bottle to the meniscus after the sample is transferred. The former method is not recommended because of the risk of cross contamination while the latter is not recommended because of poor accuracy. However, either method may be necessary for specific client programs.

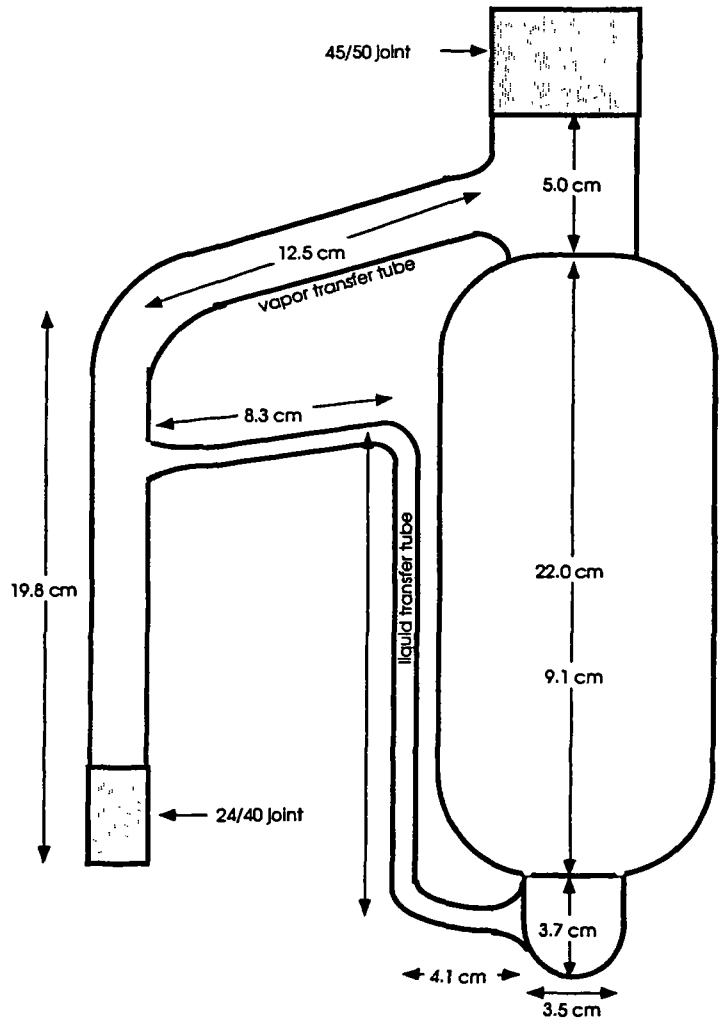
11.3.3.2. Prepare a method blank, LCS and MS/MSD for each batch as specified in section 9 of this SOP. Use 1 L of reagent water for method blanks and LCS. The method blank is spiked with the surrogates, the LCS and matrix spikes with the surrogates and matrix spiking solutions..

11.3.3.3. 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.

11.3.3.4. 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.

11.3.3.5. 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



11.3.4. 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. 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)

11.3.6. 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. Reattach the condenser and turn on heating mantle. Extract for 18-24 hours.

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 or 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

A flow chart for this procedure is included in Section 17.

11.4.1. 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.

$$\% \text{ Moisture} = \frac{(\text{weight of wet sample} - \text{weight of dry sample})}{\text{weight of wet sample}} \times 100$$

11.4.2. 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.

11.4.3. 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).

11.4.4. 11.4.4. Remove surrogate and matrix spiking solutions from refrigerator and allow to warm to room temperature.

11.4.5. 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.

11.4.6. 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)

11.4.7. Prepare a method blank, LCS and MS/MSD for each batch as specified in section 9 of this SOP.

11.4.8. 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.

11.4.9. Immediately add a minimum of 100 mL of solvent to the beaker.

Solvents:

Semivolatile GC/MS Organochlorine pesticides and PCBs	1:1 Methylene Chloride / Acetone
Hydrocarbons (DRO, PAH, etc.) and OPPs	Methylene Chloride

Note: Steps 11.4.5 - 11.4.9 should be performed rapidly to avoid loss of the more volatile extractables.

11.4.10. Place the bottom surface of the appropriate disrupter horn tip approximately ½ inch below the surface of the solvent, but above the sediment layer.

11.4.11. 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.

11.4.12. 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.

11.4.13. Place the prepared funnel on a collection apparatus (beaker or K-D Apparatus.

11.4.14. Decant and filter extracts through the prepared funnel into a clean beaker or K-D Apparatus.

11.4.15. 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 11.4.9).

Note: Alternatively, the three extracts may be collected together and then filtered through the sodium sulfate.

11.4.16. Cover with aluminum foil if the extract is not concentrated immediately. Refer to Section 11.7 for concentration and Section 11.8 for cleanup.

11.4.17. Sonicator Tuning.

11.4.17.1. Tune the sonicator according to manufacturer's instructions. The sonicator must be tuned at least every time a new horn is installed.

11.5. 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. 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 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.

11.5.6. Add the appropriate amount of surrogate and matrix spiking solution as indicated in Tables 3, 4, 5, and 6.

11.5.6.1. Sample weights less than 30 g but over 5 g may be used if the appropriate reporting limits can be met.

11.5.7. 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.

11.5.8. 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 Organochlorine pesticides and PCBs	1:1 Methylene Chloride / Acetone
Hydrocarbons (DRO, PAH, etc.) and OPPs	Methylene Chloride

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 approximately 1g of sample to the vial. Record the weight to the nearest 0.01 g.

11.6.4. Add 1 mL appropriate volume of surrogate solution (Table 3). 11.6.5. Dilute to 10 mL with the appropriate solvent. (Methylene Chloride for GC/MS and Hexane for pesticides pesticide and PCB analysis.)

11.6.6. Add 2 g + 0.1 g sodium sulfate to the sample. Cap and shake for 2 minutes.

11.6.7. Add 4-5 g sodium sulfate to a small funnel. The funnel can be plugged with glass wool or phase separation 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.

11.6.9. Label the sample, which is now ready for cleanup or analysis.

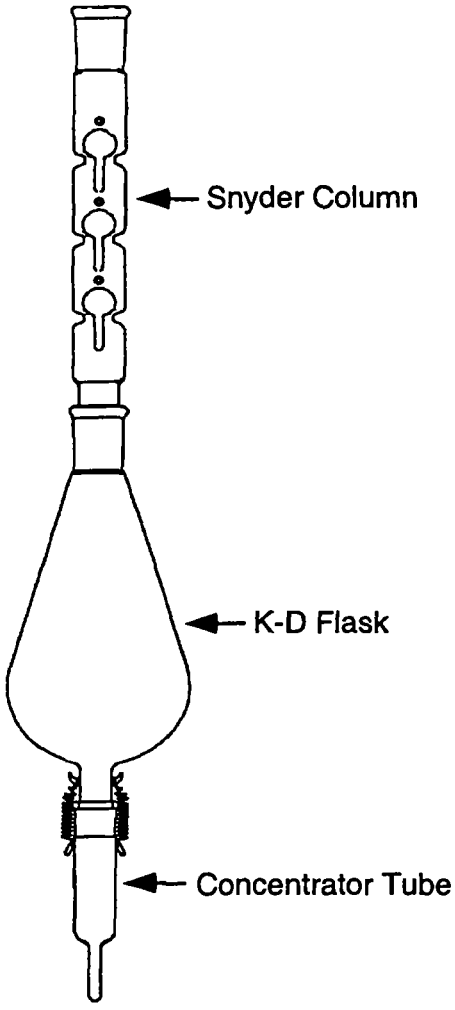
11.7. Concentration

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) Method:

11.7.1.1. 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.

11.7.1.2. 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).



11.7.1.3. 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.

11.7.1.4. 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.

11.7.1.5. 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.

11.7.1.6. 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 11.7.2

11.7.2. Nitrogen Evaporation to Final Concentration

11.7.2.1. 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.

11.7.2.2. 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

11.7.2.3. 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 the 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.

11.7.2.4. 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 11.7.1.1. 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.

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 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 11.7.2).

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.

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.

11.7.3.7. 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.

11.7.3.8. During the concentration rinse the Turbovap tube walls with a few mL of solvent 1 or 2 times.

11.7.3.9. Concentrate the extract to slightly less than the required final volume.

11.7.3.10. 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.

11.7.3.11. 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.

11.8. 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), 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.
Note: GPC used only for CLP Projects

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.
Note: GPC used only for CLP Projects
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.
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 11.8.5) is useful for separating organic acids and phenols from basic and neutral organics.

Fluorocarbon cleanup (Section 11.8.7) is used to remove hydrocarbons from water samples to be analyzed for water soluble alcohols.

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 ± 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 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.

11.8.1.4.2. 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 80-10120% 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.

11.8.1.5. 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 60%. 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. THIS IS NOT SPECIFIED OR REQUIRED BY THE SOW.

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.

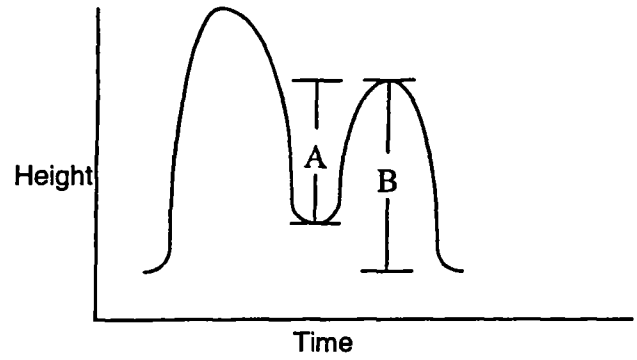
11.8.1.6.11. Solvent exchange pesticide/PCB sample extracts into hexane and concentrate to 5.0 mL. Refer to the concentration section 11.7.

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

Florisil cleanup is generally used for organochlorine pesticides, although it may be applied to other analytes. Sections 11.8.2.1 through 11.8.2.8 outline the procedure for organochlorine pesticides, while section 11.8.2.9 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.

11.8.2.1. 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.

11.8.2.9. Modifications for other analyte classes

11.8.2.9.1. 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.

11.8.3. 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 pipette 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 7.2 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. Shake or vortex for about thirty seconds 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. 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.

11.8.5.10. 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.

11.8.5.11. 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.

11.8.7. Fluorocarbon Cleanup

This procedure is appropriate for the removal hydrocarbons from water samples prior to analysis for water soluble alcohols

11.8.7.1. Transfer 1-2 mL of water sample to a 10 mL culture tube.

11.8.7.2. Add 1-2 mL of fluorocarbon solvent (PF-5080) to the culture and cap.

11.8.7.3. Shake for 30-60 seconds.

11.8.7.4. 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
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	1.0 or 5.0*
PCB	Hexane	10.0 for solids 5.0 for H2O **
Pesticides	Hexane	10.0 for solids 5.0 for H2O
PAH by HPLC	Acetonitrile	1.0 mL
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			
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 - OLM03.1
Semivolatiles	CH_2Cl_2	10 mL[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	100/150 ppm BNA	0.5
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	100 ppm BNA All-Analyte Spike	0.5
BNA TCLP	100 ppm BNA All-Analyte Spike	1.0
BNA NPDES	100 ppm BNA All-Analyte Spike	1.0
Pest	Pest NPDES Spike	1.0
Pest TCLP	Pest TCLP Spike	1.0
Pest NPDES	Pest NPDES 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	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	Methanol Acetone	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

Table 6

Matrix Spike Components

Type	Compounds	Solvent	Conc. (µg/mL)
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

Table 6

Matrix Spike Components

Type	Compounds	Solvent	Conc. (µg/mL)
	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

Table 6

Matrix Spike Components

Type	Compounds	Solvent	Conc. (µg/mL)
	2-Nitrophenol		100
	4-Nitrophenol		100
	Pentachlorophenol		100
	Phenol		100
	2,4,6-Trichlorophenol		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	Methanol Acetone	1.0
	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

Table 6			
Matrix Spike Components			
Type	Compounds	Solvent	Conc. (µg/mL)
	Endrin		1.0
	Heptachlor		1.0
	Heptachlor Epoxide		1.0

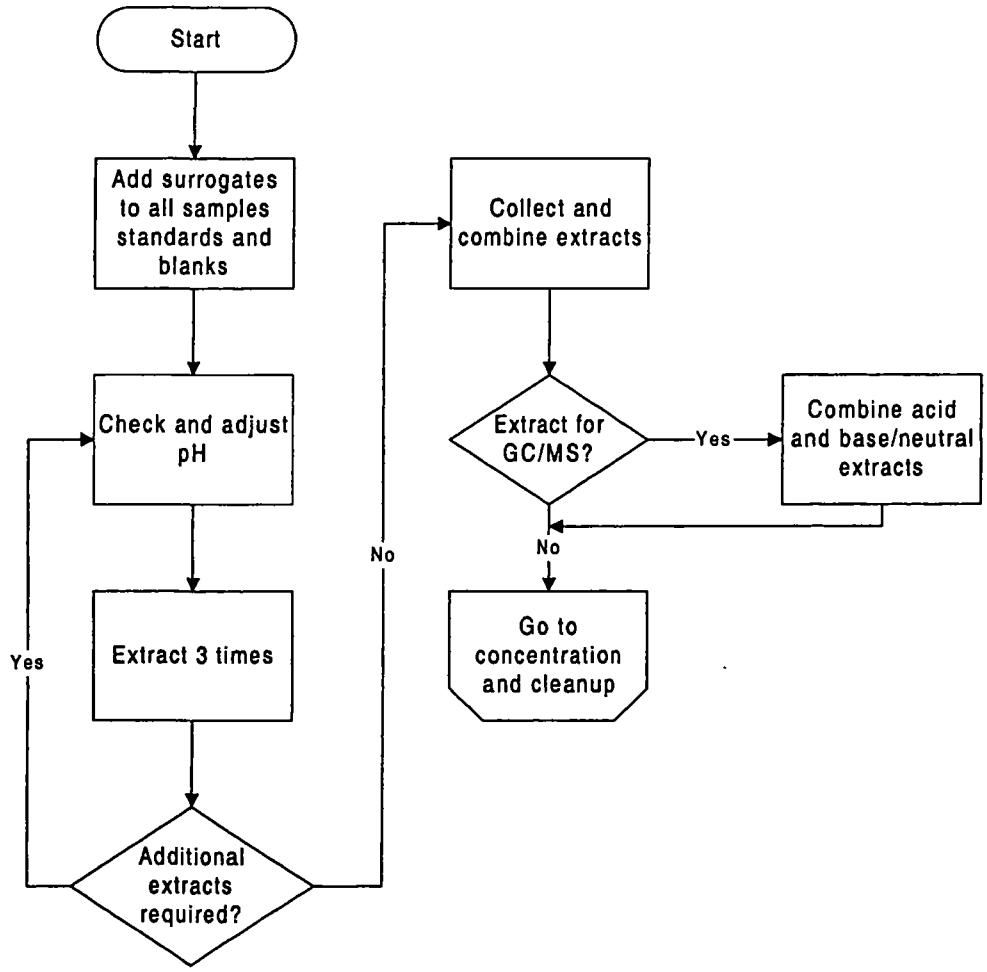
Diesel Range Organics (8015B) Spike	
Compound	**Final Concentration**
n-decane	50 µg/ml
n-dodecane	50 µg/ml
n-tetradecane	50 µg/ml
n-hexadecane	50 µg/ml
n-octadecane	50 µg/ml
n-eicosane	50 µg/ml
n-docosane	50 µg/ml
n-tetracosane	50 µg/ml
n-hexacosane	50 µg/ml
n-octacosane	50 µg/ml

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

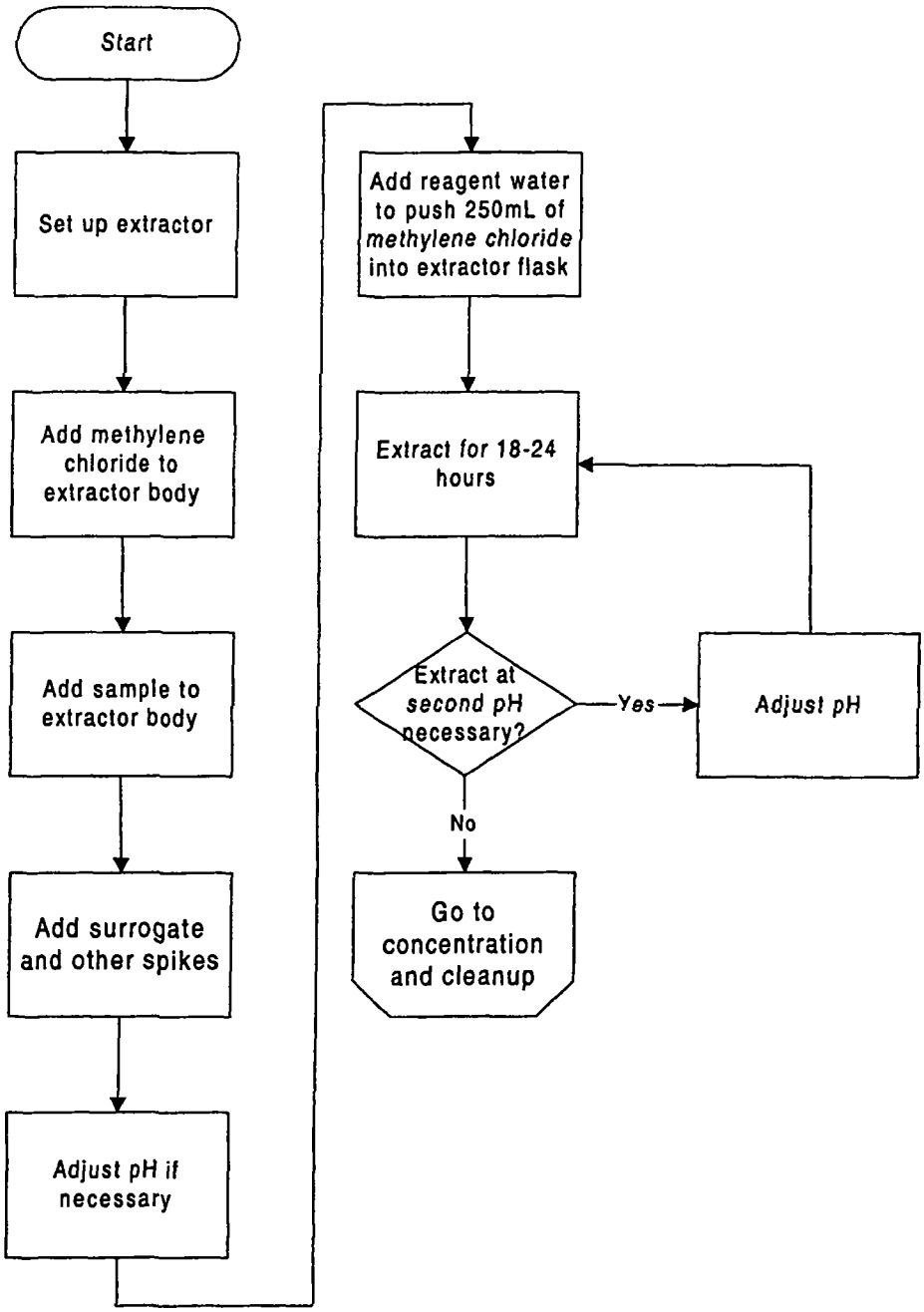
Polynuclear Aromatic Hydrocarbons (8310)	
Compound	**Final Concentration**
Acenaphthylene	10 µg/mL
Carbazole	10 µg/mL
Naphthalene	10 µg/mL
1-Methylnaphthalene	10 µg/mL
2-Methylnaphthalene	10 µg/mL
Acenaphthene	10 µg/mL
Fluorene	2 µg/mL
Phenanthrene	2 µg/mL
Anthracene	2 µg/mL
Fluoranthene	2 µg/mL
Pyrene	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

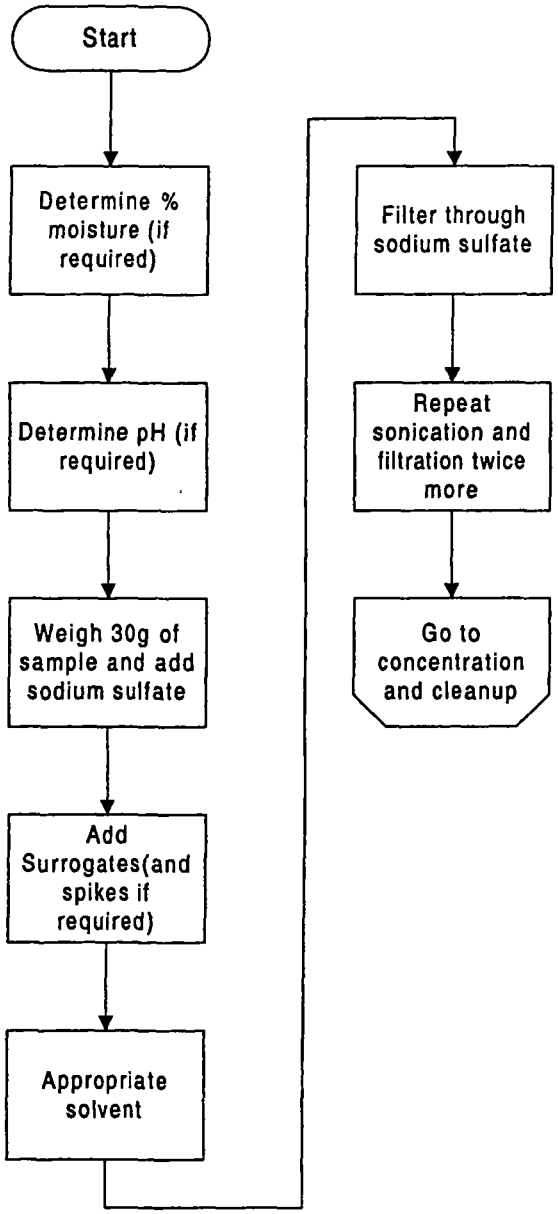
17.5.1. Separatory funnel extraction



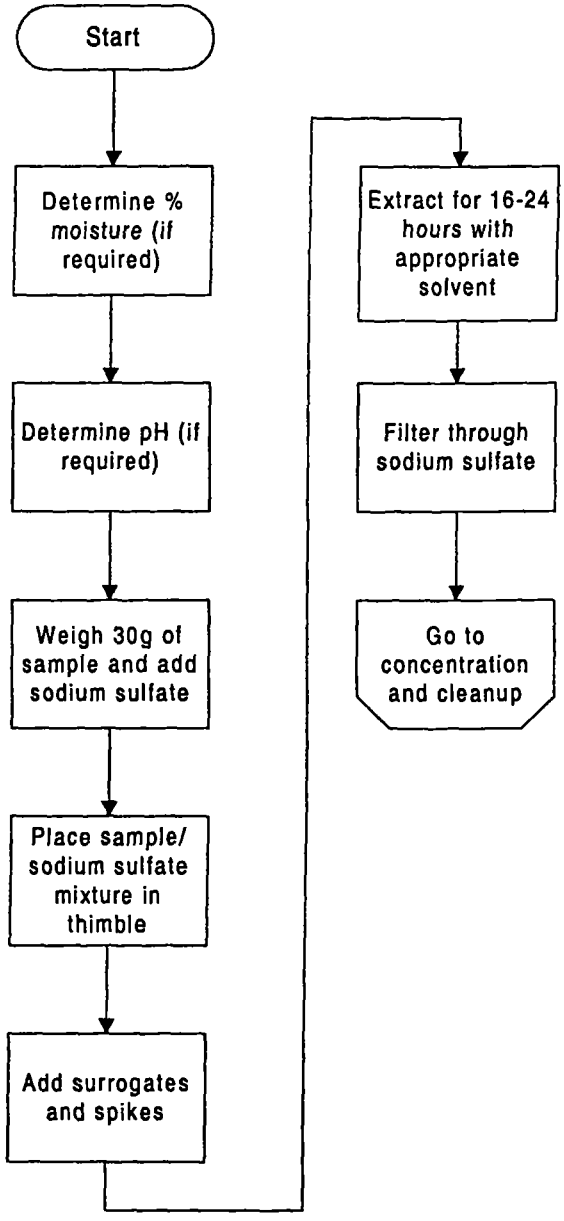
17.5.2. Continuous liquid/liquid extraction


Start
Set up extractor
Add methylene chloride to extractor body
Add sample to extractor body
Add surrogate and other spikes
Adjust pH if necessary
Add reagent water to push 250mL of methylene chloride into extractor flask
Extract for 18-24 hours
Extract at second pH necessary?
Yes
Adjust pH
No
Go to concentration and cleanup

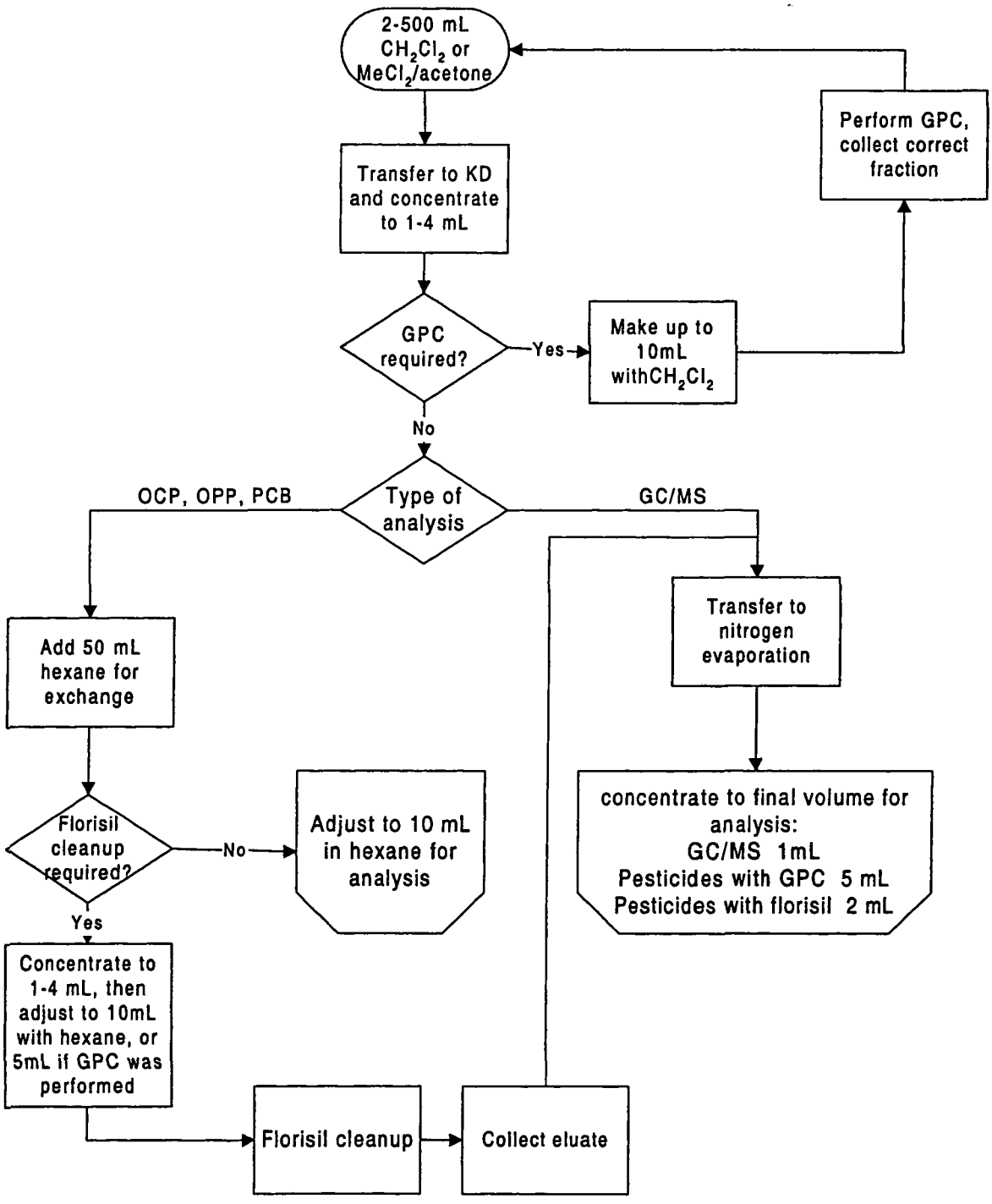
17.5.3. Sonication Extraction



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

23.3. EM Peroxide test strips

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. Sodium hydroxide solution, 10N. 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.

24.2.4. 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.

24.2.5. Diazald, 99% purity

24.2.7. 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 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.

24.2.8. Sodium Chloride, NaCl

24.2.9. 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).

24.2.10. Diethyl ether, reagent grade.

24.2.11. Methanol, reagent grade.

24.2.12. Silicic gel

24.2.13. 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 2 liter separatory funnel. 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 1 liter was used, reagent water may be added to make the volume up to 1 liter.

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 11.1.10.

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. If the whole contents of the sample bottle were not used, add 60 mL of methylene chloride to the separatory funnel.

28.1.7. Extract the sample by shaking or rotating vigorously for 2 minutes, venting as necessary. (An automatic shaker may be used. 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. Discard the **methylene chloride** phase.

28.1.9. 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.

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 2 minutes, venting as necessary. (An automatic shaker may be used. Place samples in tumbler and tumble for twenty (20) minutes for each extraction). 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.

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 11.5, 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). Decant and discard any water layer on a sediment/soil sample.

28.2.2. 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.

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. 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%.

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 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

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 $\leq$2 with 1:1 sulfuric acid.

28.2.19. Extract three times with 40 mL diethyl ether.

28.2.20. Proceed to section 11.3, Cleanup, if required, or Section 11.4, 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 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.

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 11.2.12 or 11.2.20, using a small separatory funnel. **Discard the organic phase.**

28.3.2. 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.

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 11.5, 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. Carefully disassemble the concentrator tube and rinse the lower glass joint with a small amount of diethyl ether.

28.5.5. The extract is now ready for esterification by either the diazomethane solution method (11.6) or the bubbler method (11.7)

28.7. Esterification (Bubbler Method)

28.7.1. Assemble the diazomethane apparatus (see figure below) 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.

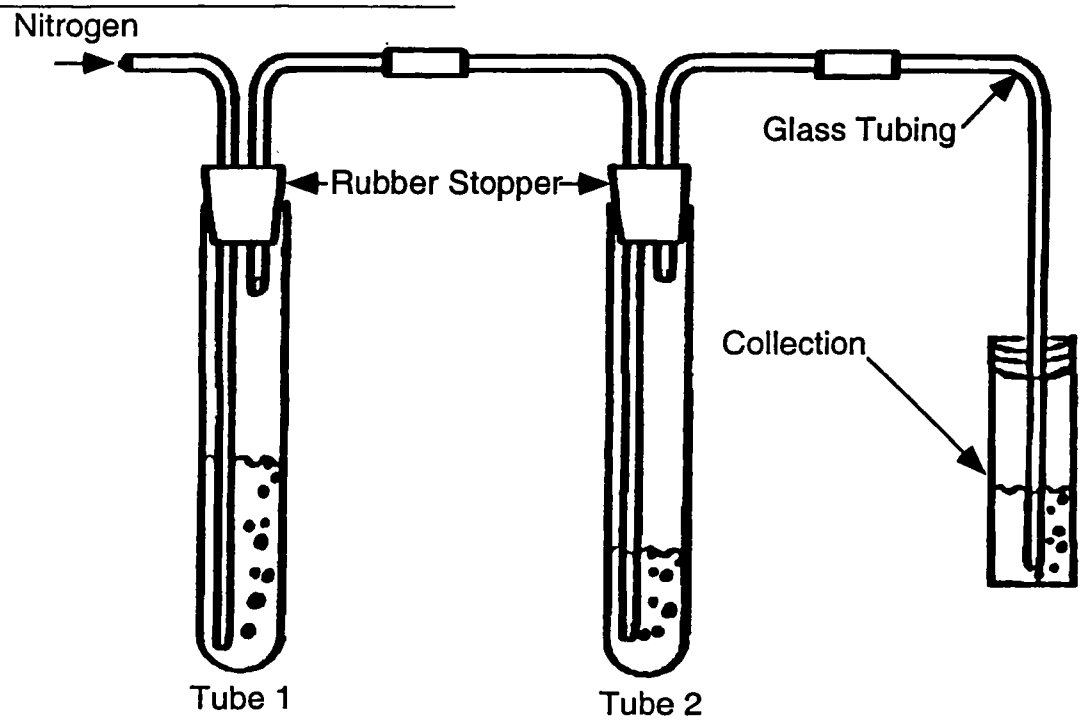
28.7.2. Place the tip of the disposable pipette into the vial containing the first sample extract. Apply nitrogen flow (approx. 10 mL/min) to bubble diazomethane through the sample extract for about 1 minute, or until the yellow color persists. Replace the disposable pipette and place the tip into the 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).

28.7.3. Allow the extracts to stand for 20 minutes, then add approximately 0.2 g of silicic gel to each extract. Allow to stand for an additional 20 minutes.

28.7.4. Adjust the volume to 10 mL with hexane. The sample is now ready for gas chromatography.

28.7.5 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.



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

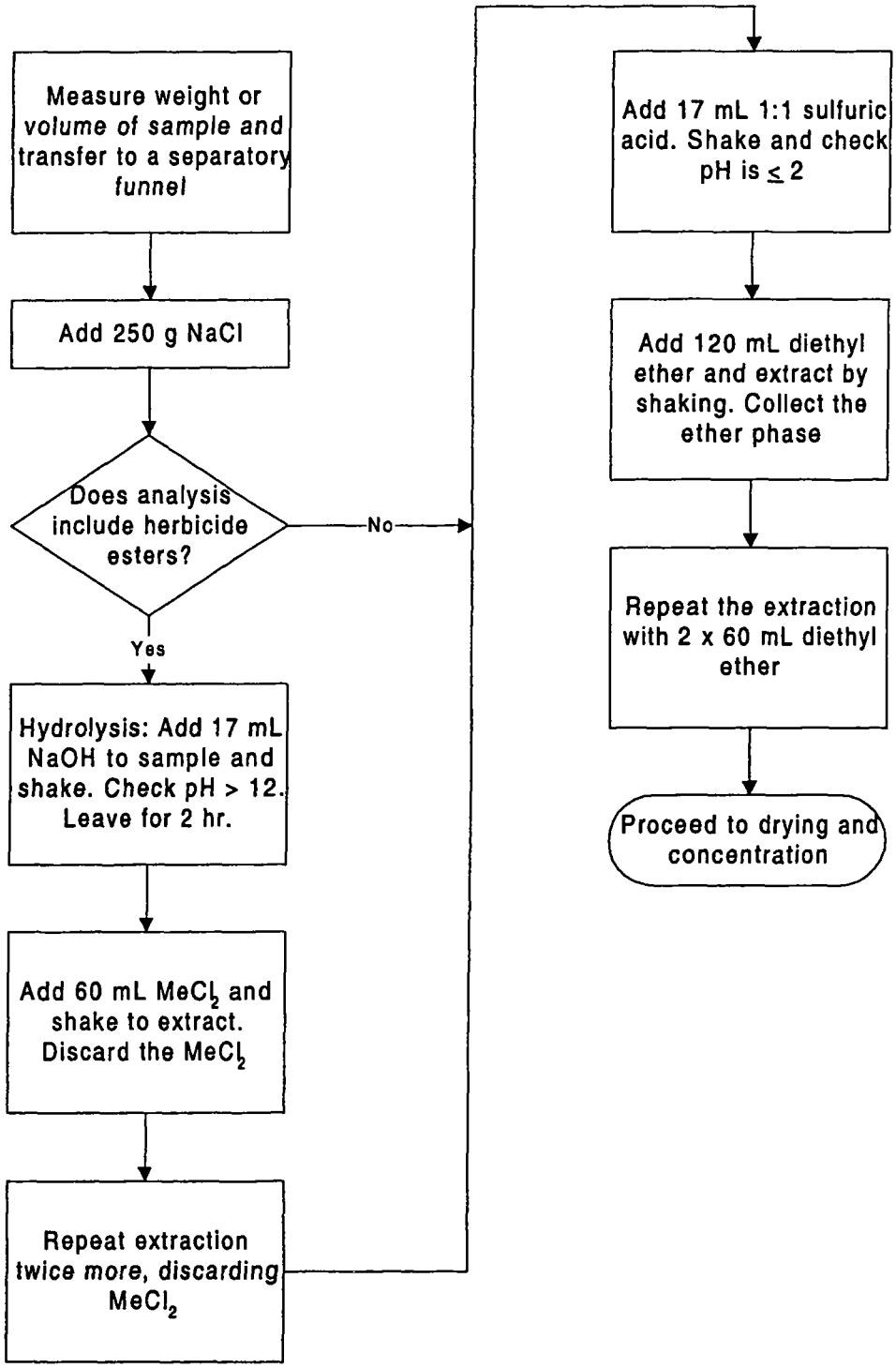
Table A3 Herbicide Surrogate Spike Components			
Type	Compounds[1]	Solvent	Conc. (ug/mL)
Herbicides SS	2,4-DCAA	Acetone Methanol	20

[1]The surrogate is spiked as the free acid

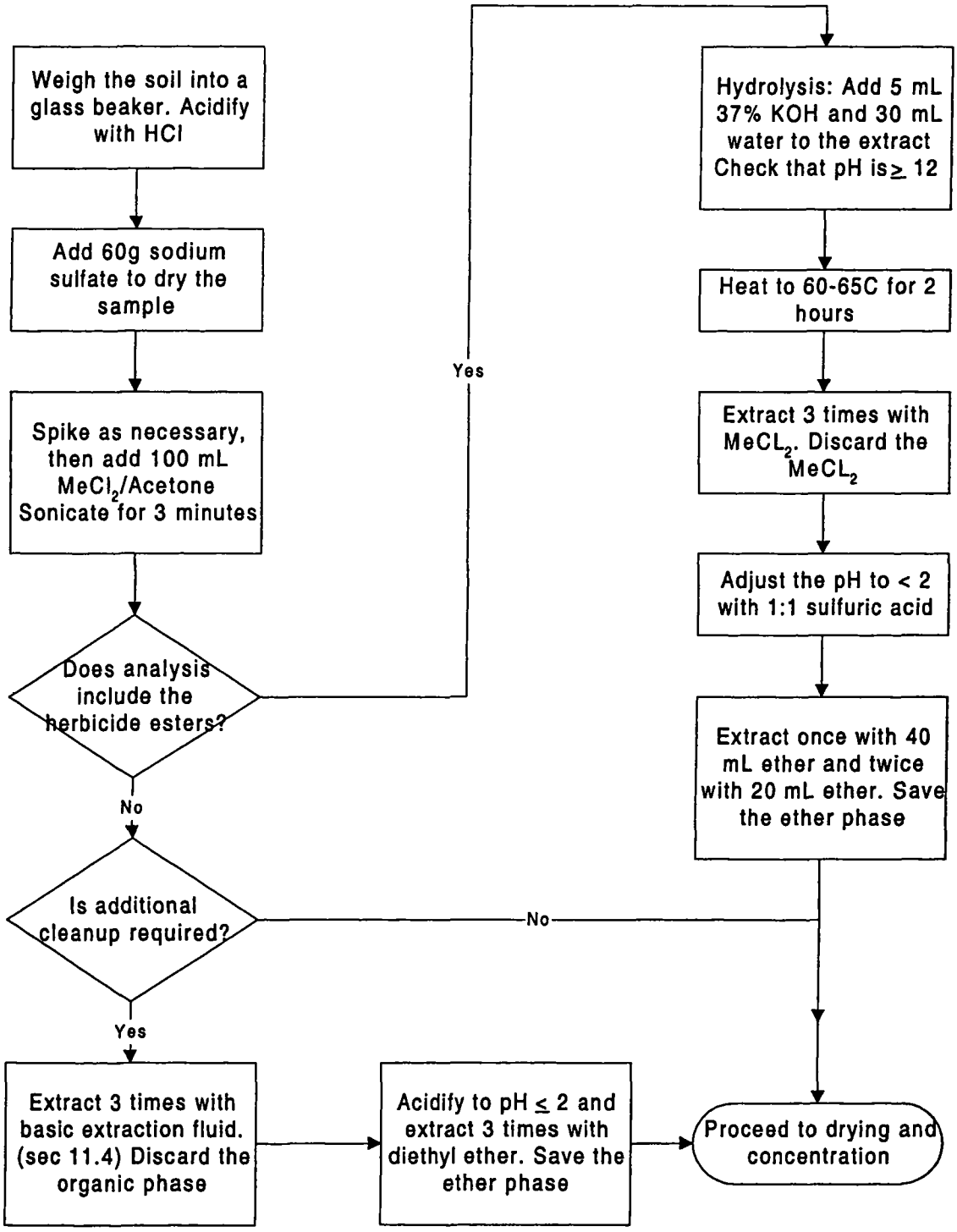
Table A4 Herbicide Matrix Spike Components				
Type	Compounds[1]	Compounds[1] Solvent	Soil Conc. (ug/mL) Solvent	Water Conc. (ug/mL)
Herbicides MS	2,4-D	Acetone	20 Methanol	2
	2,4-DB		20	2
	2,4,5-TP (Silvex)		5	0.5
	Dalapon		10	1
	Dicamba		10	1
	Dichloroprop		10	1
	Dinoseb		3	.3
	2,4,5-T		5	0.5

[1]The herbicide spiking solution contains the herbicides as the free acids.

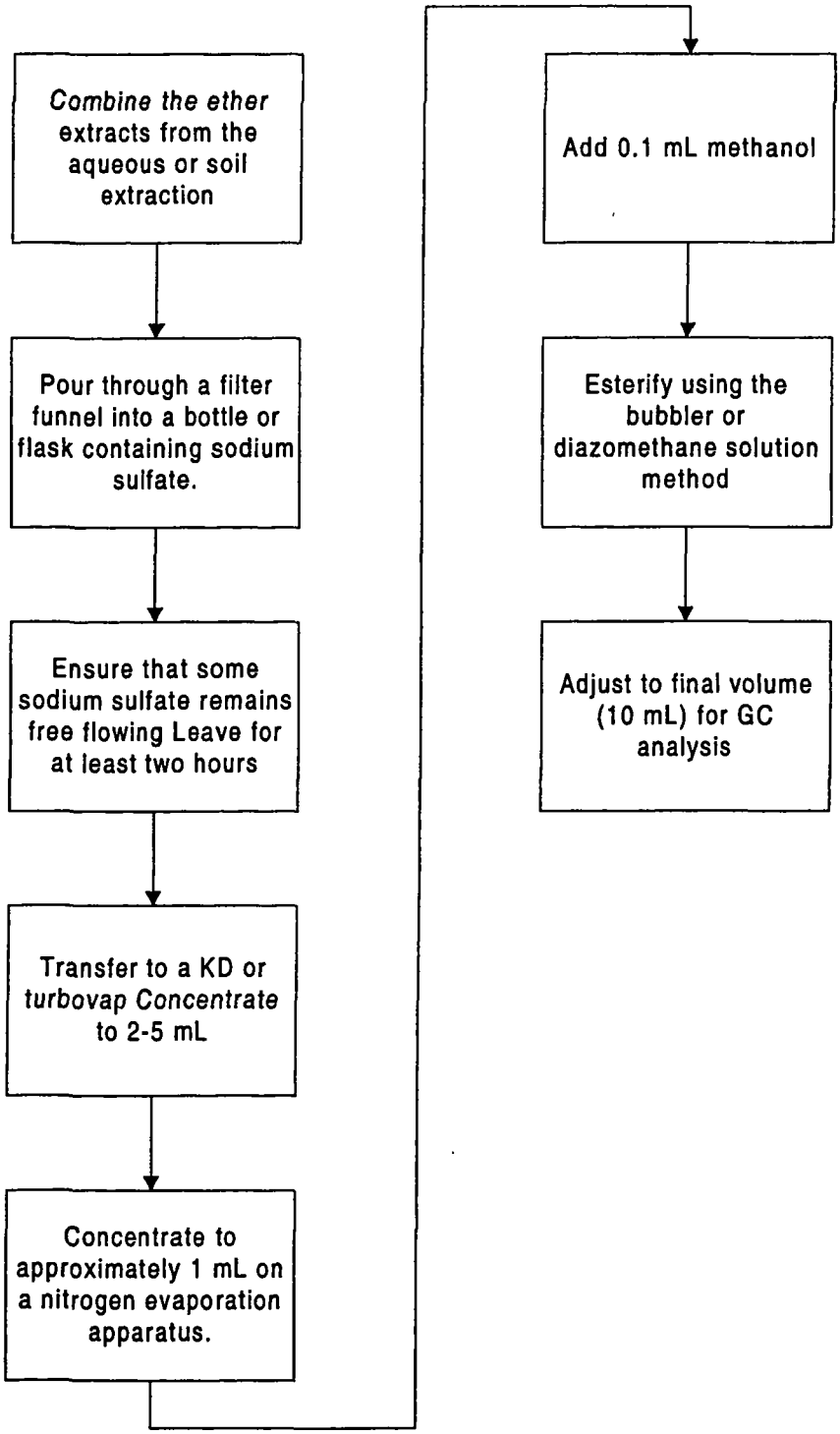
Extraction of Aqueous Samples



Extraction of Soils and Sediments



Drying, Concentration and Esterification



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SOP No: CORP-GC-0001NC
Revision No: 5.6
Revision Date: 05/25/01

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)

Prepared by:		5-25-01 Date
Approved by:	Technology Specialist	5-25-01 Date
Approved by:	Quality Assurance Manager	5/25/01 Date
Approved by:	Environmental Health and Safety	5-25-01 Date
Approved by:	Laboratory Director	5-25-01 Date
Approved by:	Corporate Technology	6-4-01 Date DK 6-5-01

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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 ≤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 ≤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 ± 15% corrective action must be taken. This may include clipping the column, changing the liner or other minor instrument adjustments, followed by reanalyzing the standard. If the overall average %D still varies by more than ± 15%, a new calibration curve must be prepared.

10.11.12.Corrective Action for Samples

For internal standard methods, any samples injected after a standard not meeting the calibration criteria must be 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 ≤ 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_t = 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

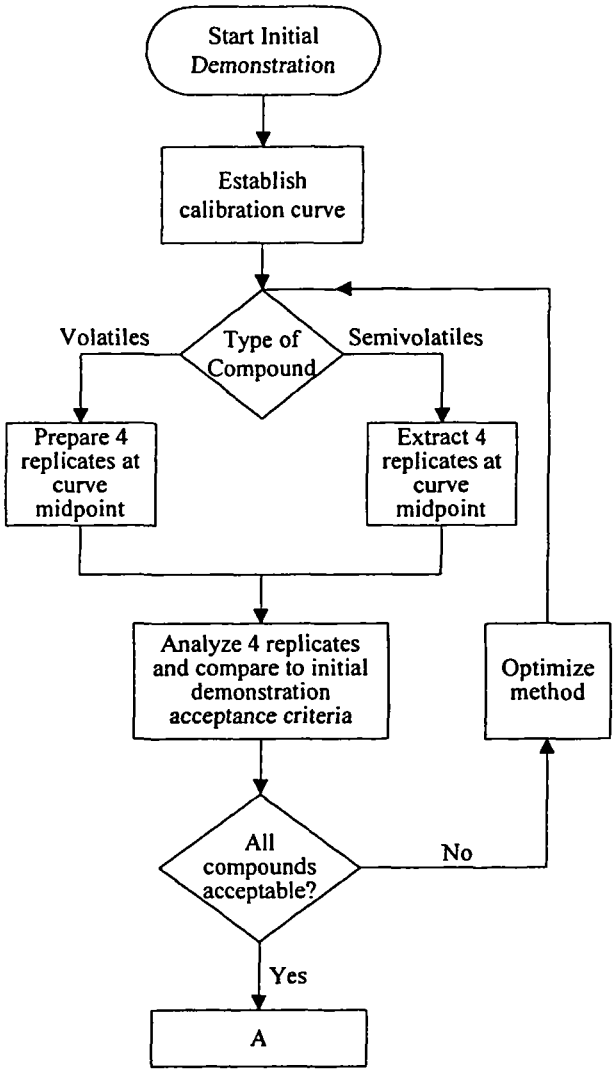
The calibration criteria in section 10.11 have been rewritten to improve consistency with SW-846 and to improve clarity.

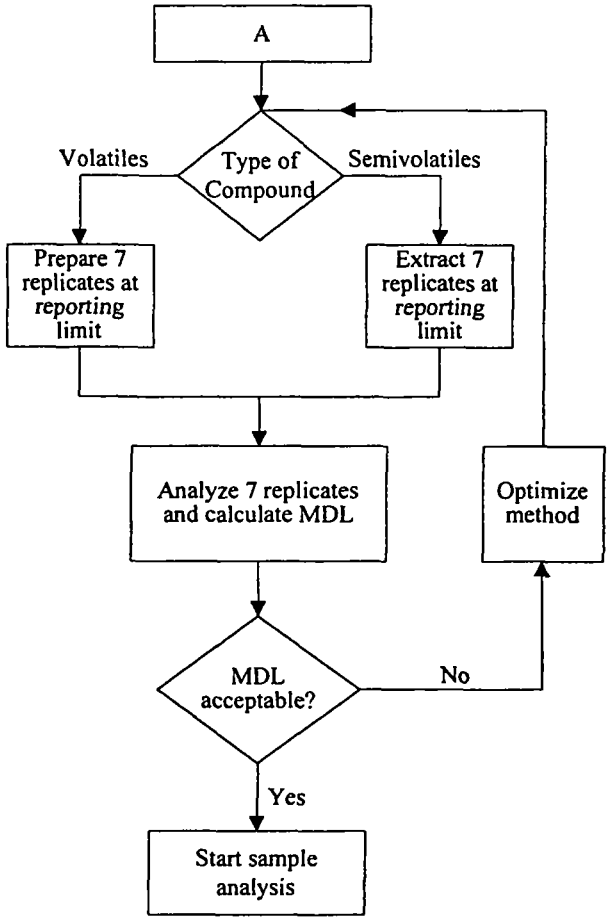
17.3. Facility Specific SOPs

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

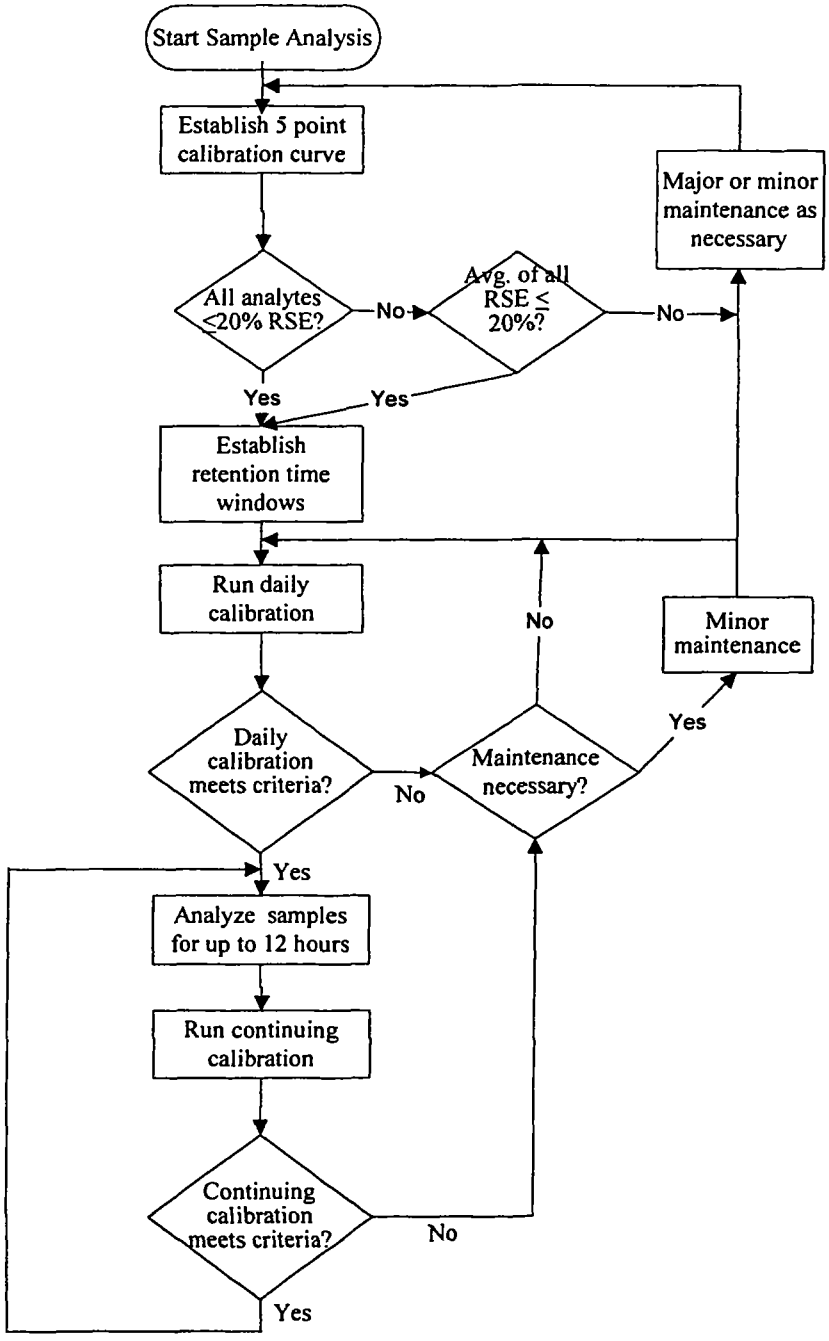
17.4.1. Initial demonstration and MDL[1]





[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.

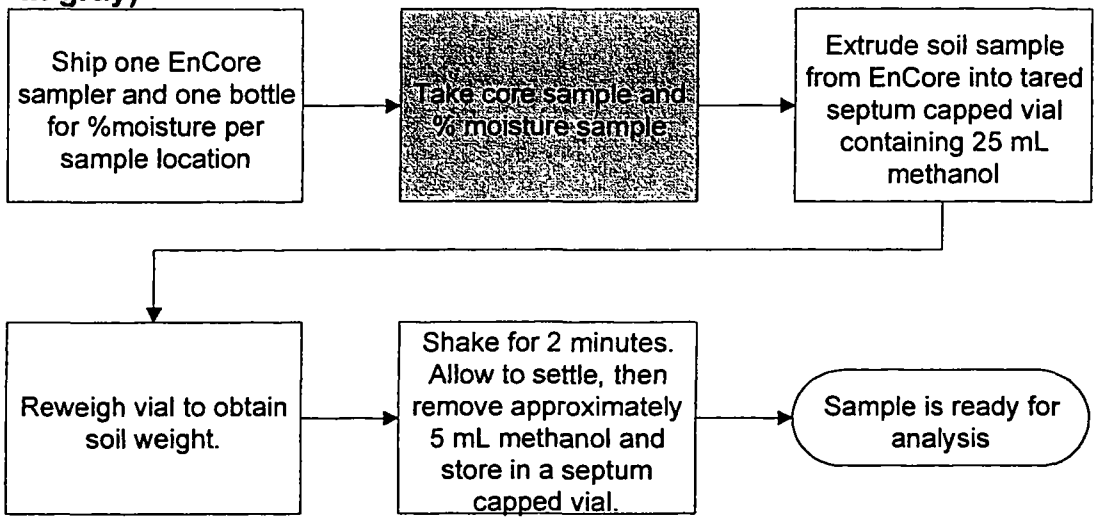
8.10. The maximum holding time is 14 days from sampling until the sample is analyzed. (Samples that are found to be unpreserved still have a 14 day holding time. However they should be analyzed as soon as

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.

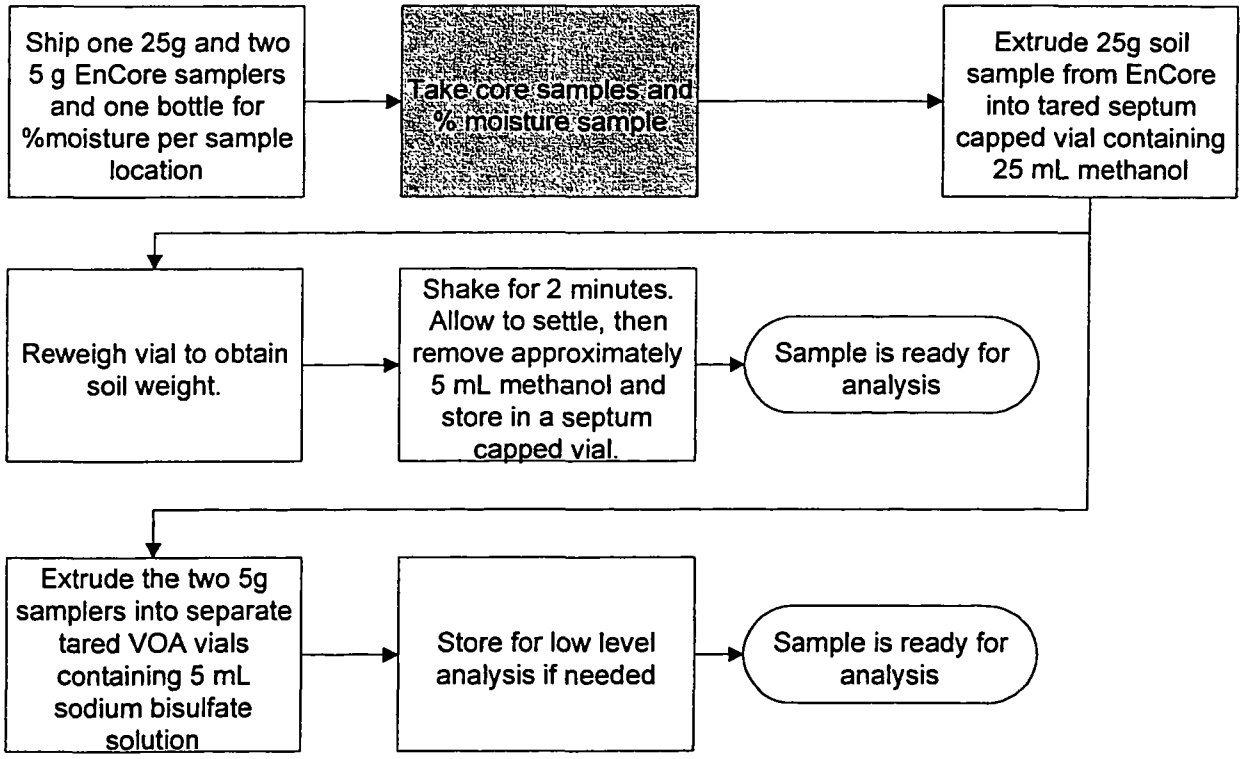
8.11. A holding blank is stored with the samples. This is analyzed and replaced if any of the trip blanks show any contamination. Otherwise it is replaced every 14 days.

Note: Freezing is not allowed for Ohio VAP solids.

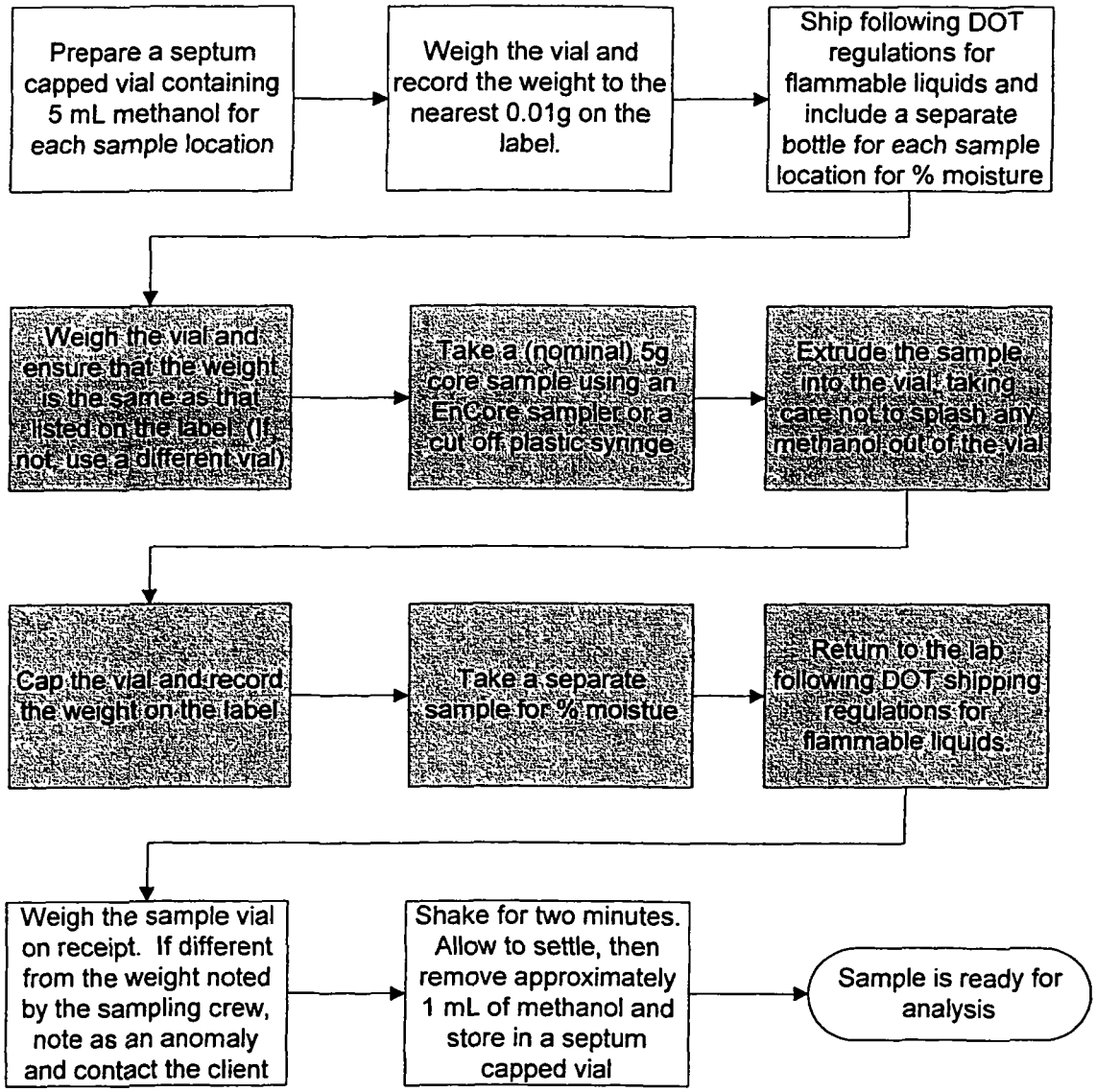
EnCore procedure when low level is not required (field steps in gray)



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 <u>after</u> the dilution is performed.

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

11.5.1. Units, which sample from the VOA vial, should be equipped with a module, which automatically adds surrogate and internal standard solution to the sample prior to purging the sample.

11.5.2. If the autosampler uses automatic IS/SS injection, no further preparation of the VOA vial is needed. Otherwise the internal and surrogate standards must be added to the vial. *Note:* Aqueous samples with high amounts of sediment present in the vial may not be suitable for analysis on this instrumentation, or they may need to analyzed as soils.

11.5.3. Sample remaining in the vial after sampling with one of these mechanisms is no longer valid for further analysis. A fresh VOA vial must be used for further sample analysis.

11.5.4. Check the pH of the sample remaining in the VOA vial after analysis is completed.

11.6. Low-Level Solids Analysis using discrete autosamplers

Note: This technique may seriously underestimate analyte concentration and must not be used except at specific client request for the purpose of comparability with previous data. It is no longer part of SW-846.

This method is based on purging a heated sediment/soil sample mixed with reagent water containing the surrogate and, if applicable, internal and matrix spiking standards. Analyze all reagent blanks and standards under the same conditions as the samples (e.g., heated). The calibration curve is also heated during analysis. Purge temperature is 40°C.

11.6.1. Do not discard any supernatant liquids. Mix the contents of the container with a narrow metal spatula.

11.6.2. Weigh out 5 g (or other appropriate aliquot) of sample into a disposable culture tube or other purge vessel. Record the weight to the nearest 0.1 g. If method sensitivity is demonstrated, a smaller aliquot may be used. Do not use aliquots less than 1.0 g. If the sample is contaminated with analytes such that a purge amount less than 1.0 g is appropriate, use the medium level method described in section 11.7.

11.6.3. Connect the purge vessel to the purge and trap device.

11.6.4. Rinse a 5 mL gas-tight syringe with organic free water, and fill. Compress to 5 mL. Add surrogate/internal standard (and matrix spike solutions if required.) (See Tables A-5, A-6, A-7 and A-8.) Add directly to the sample from 11.6.2.

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

11.6.6. Add the heater jacket or other heating device and start the purge and trap unit.

11.6.7. Soil samples that have low IS recovery when analyzed (<50%) should be reanalyzed once to confirm matrix effect. If external standard calibration is used, samples with surrogate recovery below the control limit should be reanalyzed once to confirm matrix effect.

11.7. Methanol Extract Soils

11.7.1. Rinse a gas-tight syringe with organic free water. Fill the syringe with the same volume of organic free water as used in the calibrations. Add no more than 2% (v/v) (100 µL for a 5 mL purge) methanolic extract (from Section 8.5 or 8.6) to the syringe. Add internal standard (if used). Load the sample onto the purge and trap device and analyze as for aqueous samples. If less than 5µL of methanolic extract is to be added to the water, dilute the methanolic extract such that a volume greater than 5µL will be added to the water in the syringe.

12. DATA ANALYSIS AND CALCULATIONS

Refer to section 12 of the 8000B section of this SOP.

13. METHOD PERFORMANCE

13.1. Performance limits for the four replicate initial demonstration of capability required under Section 13.1 of the 8000B section of this SOP.

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	Benzene	71-43-2	1.0	1.0	50
8021B	Ethyl Benzene	100-41-4	1.0	1.0	50
	Toluene	108-88-3	1.0	1.0	50
	Xylenes (total)	1330-20-7	1.0	1.0	50
Aromatic volatiles by 8021B	Benzene	71-43-2	1.0	1.0	50

Table A-1

Standard Analyte List

Test	Compound	CAS number	Reporting Limit, µg/L or µg/kg		
			Aqueous	Low Soil	Medium Soil
	Chlorobenzene	108-90-7	1.0	1.0	50
	1,2-Dichlorobenzene	75-34-3	1.0	1.0	50
	1,3-Dichlorobenzene	107-06-2	1.0	1.0	50
	1,4-Dichlorobenzene	75-45-4	1.0	1.0	50
	Ethyl Benzene	100-41-4	1.0	1.0	50
	Toluene	108-88-3	1.0	1.0	50
	Xylenes (total)	1330-20-7	1.0	1.0	50
Additional aromatic and unsaturated volatiles	1,2,4 Trimethylbenzene	95-63-6	1.0	1.0	50
	1,3,5 Trimethylbenzene	108-67-8	1.0	1.0	50
	Acetone	67-64-1	10	10	500
	MEK (2-butanone)	78-93-3	5.0	5.0	250
	MIBK (4-methyl-2-pentanone)	108-10-1	5.0	5.0	250
	Naphthalene	91-20-3	2.0	2.0	250
	Styrene	100-42-5	1.0	1.0	50
	Methyl tert-butyl ether (MTBE)	1634-04-4	1.0	1.0	50
Combined halogenated and aromatic volatiles by 8021B	Benzene	71-43-2	1.0	1.0	50
	Bromobenzene	108-86-1	1.0	1.0	50
	Bromochloromethane	74-97-5	1.0	1.0	50
	Bromodichloromethane	75-27-4	1.0	1.0	50
	Bromoform	75-25-2	1.0	1.0	50
	Bromomethane	74-83-9	1.0	1.0	50
	n-butylbenzene	104-51-8	1.0	1.0	50
	sec-Butylbenzene	135-98-8	1.0	1.0	50
	tert-Butylbenzene	98-06-6	1.0	1.0	50
	Carbon Tetrachloride	56-23-5	1.0	1.0	50
	Chlorobenzene	108-90-7	1.0	1.0	50
	Chlorodibromomethane	124-48-1	1.0	1.0	50
	Chloroethane	75-00-3	1.0	1.0	50
	Chloroform	67-66-3	1.0	1.0	50
	Chloromethane	74-87-3	1.0	1.0	50
	2-Chlorotoluene	95-49-8	1.0	1.0	50
	4-Chlorotoluene	106-43-4	1.0	1.0	50
	1,2-Dibromo-3-Chloropropane(DBCP)	96-12-8	1.0	1.0	50
	1,2-Dibromoethane(EDB)	106-93-4	1.0	1.0	50
	Dibromomethane	74-95-3	1.0	1.0	50
	1,2-Dichlorobenzene	95-50-1	1.0	1.0	50
	1,3-Dichlorobenzene	541-73-1	1.0	1.0	50
	1,4-Dichlorobenzene	106-46-7	1.0	1.0	50
	Dichlorodifluoromethane	75-71-8	1.0	1.0	50
	1,1-Dichloroethane	75-34-3	1.0	1.0	50
	1,2-Dichloroethane	107-06-2	1.0	1.0	50
	1,1-Dichloroethene	75-35-4	1.0	1.0	50
	cis-1,2-Dichloroethene	156-59-4	1.0	1.0	50
	trans-1,2-Dichloroethene	156-60-5	1.0	1.0	50
	1,2-Dichloropropane	78-87-5	1.0	1.0	50

Table A-1

Standard Analyte List

Test	Compound	CAS number	Reporting Limit, µg/L or µg/kg		
			Aqueous	Low Soil	Medium Soil
	1,3-Dichloropropane	142-28-9	1.0	1.0	50
	2,2-Dichloropropane	590-20-7	1.0	1.0	50
	1,1-Dichloropropene	563-58-6	1.0	1.0	50
	cis-1,3-Dichloropropene	10061-01-5	1.0	1.0	50
	trans-1,3-Dichloropropene	10061-02-6	1.0	1.0	50
	Ethylbenzene	100-41-4	1.0	1.0	50
	Hexachlorobutadiene	87-68-3	1.0	1.0	50
	Isopropylbenzene	98-82-8	1.0	1.0	50
	p-Isopropyltoluene	99-87-6	1.0	1.0	50
	Methylene Chloride	75-09-2	5.0	5.0	250
	Naphthalene	91-20-3	2.0	2.0	250
	n-Propylbenzene	10306501	1.0	1.0	50
	Styrene	100-42-5	1.0	1.0	50
	1,1,1,2-Tetrachloroethane	630-20-6	1.0	1.0	50
	1,1,2,2-Tetrachloroethane	79-34-5	1.0	1.0	50
	Tetrachloroethene	127-18-4	1.0	1.0	50
	Toluene	108-88-3	1.0	1.0	50
	1,2,3-Trichlorobenzene	87-61-6	1.0	1.0	50
	1,2,4-Trichlorobenzene	120-82-1	1.0	1.0	50
	1,1,1-Trichloroethane	71-55-6	1.0	1.0	50
	1,1,2-Trichloroethane	79-00-5	1.0	1.0	50
	Trichloroethene	79-01-6	1.0	1.0	50
	Trichlorofluoromethane	75-69-4	1.0	1.0	50
	1,2,3-Trichloropropane	96-18-4	1.0	1.0	50
	1,2,4-Trimethylbenzene	95-63-6	1.0	1.0	50
	1,3,5-Trimethylbenzene	108-67-8	1.0	1.0	50
	Vinyl Chloride	75-01-4	1.0	1.0	50
	Xylenes (total)	1330-20-7	1.0	1.0	50

Table A-2
Recommended Conditions for Aromatic Volatiles

Parameter	Recommended Conditions
Temperature program	50°C, 1min, 10°C/min to 200°C,1min
Column 1	Rtx-502.2 or DB-502.2 60m x 0.53mm 3.0um
Column 2	Rtx-1 or DB-1 60m x 0.53mm 3.0 um
Carrier gas	Helium or hydrogen
Purge Flow / time	40 mL/min, 11 minutes
Desorb Temp / time	180°C, 2 minutes (220°C for Vocarb 3000)
Bake Time / temp	200°C, 12 minutes (230°C for Vocarb 3000)
Transfer line / valve temp	115°C

Table A-3
Recommended Conditions for Method Halogenated Volatiles

Parameter	Recommended Conditions
Temperature program	35°C, 12 min, then 4°C/min to 200°C, hold for 5 min
Column 1	DB-VRX or RTX-502.2 105m x 0.53 mm id df = 3.0um
Column 2	DB-1 or RTX-1 105m x 0.53 mm ID df = 3.0um
Column 3	Rtx - Volatiles 120m x 0.53mm ID df=2.0um
Carrier gas	Helium
Purge Flow / time	40 mL/min, 11 minutes
Desorb Temp / time	180°C, 2 minutes (220°C for Vocarb 3000)
Bake Time / temp	200°C, 12 minutes (230°C for Vocarb 3000)
Transfer line / valve temp	115°C

Table A-4
Recommended Conditions for Method Combined Aromatic and Halogenated Volatiles

Parameter	Recommended Conditions
Temperature program	35°C, 12 min, then 4°C/min to 200°C, hold for 5 min
Column 1	DB-VRX or RTX-502.2 105m x 0.53 mm id df = 3.0um
Column 2	DB-1 or RTX-1 105m x 0.53 mm ID df = 3.0um
Column 3	Rtx - Volatiles 120m x 0.53mm ID df=2.0um
Carrier gas	Helium
Purge Flow / time	40 mL/min, 11 minutes
Desorb Temp / time	180°C, 2 minutes (220°C for Vocarb 3000)
Bake Time / temp	200°C, 12 minutes (230°C for Vocarb 3000)
Transfer line / valve temp	115°C

Table A-5
Surrogate and Internal Standard Concentrations

Standard	Components	Working Solution µg/mL	Spike amount µL (for 5 mL purge)	Final concentration µg/L (µg/kg)
Aromatic volatiles IS/SS	4-Chlorotoluene (SS) 1-Chloro-4-fluorobenzene (IS)	20 40	5	20 40
Halogenated volatiles IS/SS	4-chlorotoluene (SS) 1-Chloro-4-fluorobenzene (IS)	20 40	5	20 40
Combined Aromatic and halogenated volatiles IS/SS	Fluorobenzene (SS)	20	5	20
	1,4-Dichlorobutane (SS)	20	5	20
	1-Chloro-4-fluorobenzene (IS)	40	10	40

It may be necessary to select different surrogates in order to minimize sample interferences. 1-chloro-4-fluorobenzene and 4-chlorotoluene are fairly well resolved from analytes listed in this SOP. However 4-chlorotoluene may sometimes be requested as a target analyte. Other surrogates that may be considered, and issues associated with their use are:

Bromochloromethane: Elutes very close to chloroform and cis-1, 2-dichloroethene on the 502.2 column. May be a target analyte.

1,2-Bromochloroethane:

1-Chloro-2-fluorobenzene: Elutes close to ethylbenzene on DB-1 or Rtx-1 and close to m,p-xylene on 502.2

a,a,a-Trifluorotoluene: Good for aromatic volatiles, coelutes or very close to trichloroethene

Bromofluorobenzene: Close to 1,1,2,2-trichloroethane and 1,2,3-trichloropropane on the 502.2 column. Good on DB-1 or Rtx-1.

2-Bromo-1-chloropropane: May coelute with 1,1,2-trichloroethane

Table A-6
Concentrations for LCS and MS/MSD compounds

Standard	Components	Working Solution µg/mL	Spike amount µL (5 mL purge)	Final concentration µg/L (µg/kg)
Aromatic	Benzene	20	5	20
	Toluene	20		20
	Chlorobenzene	20		20
Halogenated	Chlorobenzene	20	5	20
	1,1-Dichloroethene	20		20
	Trichloroethene	20		20
Combination aromatic / halogenated	Benzene	20	5	20
	Toluene	20		20
	Chlorobenzene	20		20
	1,1-Dichloroethene	20		20
	Trichloroethene	20		20

1. SCOPE AND APPLICATION

This SOP Appendix describes procedures to be used when SW-846 Method 8081A is applied to the analysis of organochlorine pesticides by GC/ECD. This Appendix may also to be applied when discontinued SW-846 Method 8080A is requested, and is applicable to extracts derived from any matrix which are prepared according to the appropriate STL 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-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.	15	85	2.0 mL/m
	25 min.	5	95	2.0 mL/m
	30 min.	45	55	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
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

11.5.1. Record all analytical information in the analytical logbook/logsheet, including the analytical data from standards, blanks, LCSs, MS/MSDs, and any corrective actions or modifications to the method.

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

11.5.3. Documentation such as all associated instrument printouts (final runs, screens, reruns, QC samples, etc.) and daily calibration data corresponding to all final runs is available for each data file.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Refer to the 8000B section of this SOP for identification and quantitation of single component analytes.

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

13. METHOD PERFORMANCE

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

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
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

STL NORTH CANTON STANDARD OPERATING PROCEDURE

TITLE: GC/MS ANALYSIS BASED ON METHODS 8270C AND 625

(SUPERSEDES: Revision 2.3, 02/15/01)

Prepared by:_____
Date

Reviewed by:_____
Technology Specialist Date

Approved by:_____
Quality Assurance Manager Date

Approved by:_____
Environmental Health and Safety Date

Approved by:_____
Laboratory Director Date

Approved by:_____ 6/4/01
Coroporate Technology Date

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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, a continuous extractor or Accelerated One-Step™. Solid samples are extracted with methylene chloride / acetone using sonication, soxhlet, accelerated soxhlet or pressurized fluid extraction. Waste dilution is used for samples that are miscible with the solvent. The extract is dried, concentrated to a volume of 1 mL, and analyzed by GC/MS. Extraction procedures are detailed in SOP# CORP-OP-0001. Qualitative identification of the parameters in the extract is performed using the retention time and the relative abundance of characteristic ions. Quantitative analysis is performed using the internal standard technique with a single characteristic ion.

3 DEFINITIONS

3.1 CCC (Calibration Check Compounds) - A subset of target compounds used to evaluate the calibration stability of the GC/MS system. A maximum percent deviation of the CCC's is specified for calibration acceptance.

3.2 SPCC (System Performance Check Compounds) - Target compounds designated to monitor chromatographic performance, sensitivity, and compound instability or degradation on active sites. Minimum response factors are specified for acceptable performance.

3.3 Batch - The batch is a set of up to 20 samples of the same matrix processed using the same procedures and reagents within the same time period. The Quality Control batch must contain a matrix spike / spike duplicate (MS/MSD), a Laboratory Control Sample (LCS), and a method blank. In some cases, at client request, the MS/MSD may be replaced with a matrix spike and sample duplicate. Batches are defined at the sample preparation stage. Batches should be kept together through the whole analytical process to the extent possible, but it is not mandatory to analyze prepared extracts on the same instrument or in the same sequence. Refer to the STL 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 Chemicals that have been classified as carcinogens, or potential carcinogens, under OSHA include: Benzo(a)anthracene, benzidine, 3,3'-dichlorobenzidine, benzo(a)pyrene, dibenzo(a,h)anthracene, and n-nitrosodimethylamine. Primary standards should be purchased in solution. If neat materials must be obtained, they shall be handled in a hood.

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

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

6 EQUIPMENT AND SUPPLIES

6.1 Gas Chromatograph/Mass Spectrometer System: An analytical system complete with a temperature-programmable gas chromatograph suitable for split/splitless injection and all required accessories, including syringes, analytical columns, and gases. The capillary column should be directly coupled to the source.

6.2 Column: 30 m x 0.32 mm I.D. (or 0.25 mm I.D.) 0.5-µm film thickness silicon-coated fused-silica capillary column (J & W Scientific DB-5.625 or equivalent). Alternate columns are acceptable if they provide acceptable performance.

6.3 Mass Spectrometer: Capable of scanning from 35 to 500 AMU every one second or less, using 70 volts (nominal) electron energy in the electron impact ionization mode.

The mass spectrometer must be capable of producing a mass spectrum for decafluorotriphenylphosphine (DFTPP) which meets all of the criteria in Table 6 when 50 ng of the GC/MS tuning standard is injected through the GC.

6.4 GC/MS Interface: Any GC-to-MS interface that gives acceptable calibration points and achieves acceptable tuning performance criteria may be used.

6.5 Data System: A computer system must be interfaced to the mass spectrometer. The system must allow the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that can search any GC/MS data file for ions of a specific mass and that can plot such ion abundances versus time or scan number. This type of plot is defined as the Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundances in any EICP between specified time or scan-number limits. The most recent version of the EPA/NIH Mass Spectral Library is recommended.

6.6 Syringe: 10 µL Hamilton Laboratory grade syringes or equivalent.

6.7 Carrier gas: Ultra high purity helium.

7 REAGENTS AND STANDARDS

7.1 A minimum five point calibration curve is prepared. The low point should be at or below the reporting limit. Refer to Tables 12 and 13 for typical calibration levels for all analytes. Other calibration levels may be used, depending on instrument capability, but the low standard must support the reporting limit and the high standard defines the range of the calibration.

7.2 An Internal Standard solution is prepared. Compounds in the I.S. Mix are: acenaphthene-d10, chrysene-d12, 1,4-dichlorobenzene-d4, naphthalene-d8, perylene-d12, and phenanthrene-d10.

7.2.1 Internal Standards are added to all standards and extracts to result in 8 ng or 40ng injected onto the column. For example, if the volume of an extract used was 200 µL, 20 µL of a 400 µg/mL internal standard solution would be added for a 1 µL injection.

7.3 Surrogate Standard Spiking Solution: Prepare as indicated in the preparative methods. See appropriate preparation SOP. Surrogate compounds and levels are listed in Table 11.

7.4 GC/MS Tuning Standard: A methylene chloride solution containing 10 µg/mL or 50 µg/mL of decafluorotriphenylphosphine (DFTPP) is prepared. Pentachlorophenol,

benzidine, and DDT, should also be included in the Tuning Standard at 10 µg/mL or 50 µg/mL.

7.5 Laboratory Control Spiking Solution: Prepare as indicated in the preparative methods. See appropriate preparation SOP. LCS compounds and levels are listed in Tables 9 and 10.

7.6 Matrix Spike Solution: Prepare as indicated in the preparative methods. See preparation SOP. The matrix spike compounds and levels are the same as the LCS compounds.

7.7 The standards listed in 7.1 to 7.6 should be refrigerated at $\leq 6^{\circ}C$ when not in use. Refrigeration at $-10^{\circ}C$ to $-20^{\circ}C$ 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 $\leq 6^{\circ}C$.

8 SAMPLE PRESERVATION AND STORAGE

8.1 Reference appropriate facility SOP for sample bottle preservation and storage.

8.2 Samples are stored at $4 \pm 2^{\circ}C$. Samples and extracts should be stored in suitable glass containers with Teflon lined caps. (Extracts will normally be stored for 30 days after invoicing.)

8.3 Water samples are extracted within seven days of sampling and the extracts are analyzed within forty days of extraction. Solids, sludges, and organic liquids are extracted within fourteen days of sampling and the extracts are analyzed within forty days of extraction.

9 QUALITY CONTROL

9.1 Initial Demonstration of Capability

9.1.1 For the standard analyte list, the initial demonstration and method detection limit (MDL) studies described in section 13 must be acceptable before analysis of samples may begin. Refer to the flow chart in section 17.4.1.

9.1.2 For non-standard analytes an MDL study should be performed and calibration curve generated before analyzing any samples, unless lesser requirements are previously agreed to with the client. In any event, the minimum initial demonstration required is analysis of an extracted standard at the reporting limit and a single point calibration.

9.2 Control Limits

In-house historical control limits must be determined for surrogates, matrix spikes, and laboratory control samples (LCS). These limits must be determined at least annually. The recovery limits are mean recovery +/- 3 standard deviations for surrogates, MS and 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 unless the dilution is more than 5X.

9.2.2 All surrogate, LCS, and MS recoveries (except for dilutions) must be entered into QuantIMS (when available) or other database so that accurate historical control limits can be generated. For tests without a separate extraction, surrogates and matrix spikes will be reported for all dilutions.

9.2.3 Refer to the QC program document (QA-003) for further details of control limits.

9.3 Method Blank

A method blank is prepared and analyzed with each batch of samples. The method blank consists of reagent water for aqueous samples, and sodium sulfate for soil samples (Refer to SOP No. CORP-OP-0001 for details). Surrogates are added and the method blank is carried through the entire analytical procedure. The method blank must not contain any analyte of interest at or above the reporting limit (except common laboratory contaminants, see below) or at or above 5% of the measured concentration of that analyte in the associated samples, whichever is higher.

- If the analyte is a common laboratory contaminant (phthalate esters), the data may be reported with qualifiers if the concentration of the analyte is less than five times the RL. Such action must be taken in consultation with the client.

- Reanalysis of any samples with reportable concentrations of analytes found in the method blank is required unless other actions are agreed with the client.

- If there is no target analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. Such action should be taken in consultation with the client.

9.3.1 The method blank must have acceptable surrogate recoveries. If surrogate recoveries are not acceptable, the data must be evaluated to determine if the method blank has served the purpose of demonstrating that the analysis is free of contamination. If surrogate recoveries are low and there are reportable analytes in

the associated samples, re-extraction of the blank and affected samples will normally be required. Consultation with the client should take place.

9.3.2 If reanalysis of the batch is not possible due to limited sample volume or other constraints, the method blank is reported, all associated samples are flagged with a "B", and appropriate comments may be made in a narrative to provide further documentation.

9.3.3 Refer to the STL 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 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.

9.6 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 10 ng or 50 ng of the GC/MS tuning standard (Section 7.4) into the GC/MS system. Obtain a background-corrected mass spectra of DFTPP and confirm that all the key m/z criteria in Table 6 are achieved. If all the criteria are not achieved, the analyst must retune the mass spectrometer and repeat the test until all criteria are achieved. The performance criteria must be achieved before any samples, blanks, or standards are analyzed.

10.3.2 The GC/MS tuning standard should also be used to evaluate the inertness of the chromatographic system. Benzidine and pentachlorophenol should not exhibit excessive tailing. If DDT is an analyte of interest, it must be included in the tuning standard, and its breakdown must be < 20%. Refer to section 12 for the appropriate calculations.

10.4 Initial Calibration

10.4.1 Internal Standard Calibration Procedure: Internal standards are listed in Table 7. Use the base peak m/z as the primary m/z for quantitation of the standards. If interferences are noted, use one of the next two most intense masses for quantitation.

10.4.2 Compounds should be assigned to the IS with the closest retention time.

10.4.3 Prepare calibration standards at a minimum of five concentration levels for each parameter of interest. Six standards must be used for a quadratic least squares calibration. 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 or 40 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 ≤ 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.

10.4.8 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 form the initial curve, not the continuing calibration.

10.5 Continuing Calibration

10.5.1 At the start of each 12-hour period, the GC/MS tuning standard must be analyzed. A 10 ng or 50 ng injection of DFTPP must result in a mass spectrum for DFTPP which meets the criteria given in Table 6.

10.5.2 Following a successful DFTPP analysis the continuing calibration standard(s) are analyzed. The standards must contain all semivolatile analytes, including all required surrogates. A mid level calibration standard is used for the continuing calibration.

10.5.3 The following criteria must be met for the continuing calibration to be acceptable:

- The SPCC compounds must have a response factor of ≥ 0.05.
- The percent difference or drift of the CCC compounds from the initial calibration must be $\leq 20\%$. (see section 12 for calculations) In addition, the percent difference or drift of all analytes must be $\leq 50\%$, with allowance being made for up to six target compounds to have percent drift greater than 50%.
- The internal standard response must be within 50-200% of the response in the mid level of the initial calibration.
- The internal standard retention times must be within 30 seconds of the retention times in the mid-level of the initial calibration.
- 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.

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.)

NOTE: Additional compound analysis outside the TCL (Target Compound List) have no calibration criteria.

11 PROCEDURE

11.1 Sample Preparation

Samples are prepared following SOP CORP-OP-0001.

11.2 Sample Analysis Procedure

11.2.1 Calibrate the instrument as described in section 10. Depending on the target compounds required by the client, it may be necessary to use more than one calibration standard.

11.2.2 All samples must be analyzed using the same instrument conditions as the preceeding continuing calibration standard.

11.2.3 Add internal standard to the extract to result in 40 ng injected on column (for example, 8 µL or 50 µL internal standard solution in 0.5 mL of extract for a 1 µL injection). Mix thoroughly before injection into the instrument.

11.2.4 Inject the sample extract into the GC/MS system using the same injection technique as used for the standards.

11.2.5 The data system will determine the concentration of each analyte in the extract using calculations equivalent to those in section 12. Quantitation is based on the initial calibration, not the continuing calibration.

11.2.6 Identified compounds are reviewed for proper integration. Manual integrations are performed if necessary and are documented by the analyst or automatically by the data system.

11.2.7 Target compounds identified by the data system are evaluated using the criteria listed in section 12.1.

11.2.8 Library searches of peaks present in the chromatogram that are not target compounds (Tentatively Identified Compounds, TIC) may be performed if required by the client. They are evaluated using the criteria in section 12.3.

11.3 Dilutions

If the response for any compound exceeds the working range of the GC/MS system, a dilution of the extract is prepared and analyzed. An appropriate dilution should be in the upper half of the calibration range. Samples may be screened to determine the appropriate dilution for the initial run. If the initial diluted run has no hits or hits below 20% of the calibration range and the matrix allows for analysis at a lesser dilution, the sample must be reanalyzed at a dilution targeted to bring the largest hit above 50% of the calibration range.

11.3.1 Guidance for Dilutions Due to Matrix

If the sample is initially run at a dilution and the baseline rise is less than the height of the internal standards, or if individual non-target peaks are less than two times the height of the internal standards, the sample should be reanalyzed at a more concentrated dilution. This requirement is approximate and subject to analyst judgement. For example, samples containing organic acids may need to be analyzed at a higher dilution to avoid destroying the column.

11.3.2 Reporting Dilutions

The most concentrated dilution with no target compounds above the calibration range will be reported. Other dilutions will only be reported at client request.

11.4 Perform all qualitative and quantitative measurements. When the extracts are not being used for analyses, refrigerate them at $4 \pm 2^{\circ}C$, 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

$$\%RSD = \frac{SD}{\overline{RF}} \times 100$$

$RF =$ 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

R_{is}= Response for internal standard

C_{is}= Concentration of internal standard

A= Intercept

B= Slope

12.5.3.3 Quadratic fit

$$C_{ex} = A + B\left(\frac{R_x C_{is}}{R_{is}}\right) + C\left(\frac{R_x C_{is}}{R_{is}}\right)$$

C= Curvature

12.5.4 The concentration in the sample is then calculated.

12.5.4.1 Aqueous Calculation

$$\text{Concentration, } \mu g / L = \frac{C_{ex} V_t}{V_o}$$

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)

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.

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
2,4-Dinitrotoluene	121-14-2	10	330
2,6-Dinitrotoluene	606-20-2	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
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 formally 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[3]	2303-16-4	20	660
Dimethoate[2]	60-51-5	20	660
4-Aminobiphenyl	92-67-1	50	1600
Pentachloronitrobenzene	82-68-8	50	1600
Pronamide	23950-58-5	20	660
Disulfoton[2]	298-04-4	50	1600
2-secbutyl-4,6-dinitrophenol (Dinoseb)	88-85-7	20	660
*Methyl Parathion[2]	298-00-0	50	1600
4-Nitroquinoline-1-oxide	56-57-5	100	3300

Table 2

STL North Canton Appendix IX[1] Standard Reporting Limits

Semivolatiles	CAS Number	Standard Reporting Limits	
		Aqueous µg/L	Low Soil/Sediment µg/kg
*Parathion[2]	56-38-2	50	1600
Methapyrilene	91-80-5	50	1600
Aramite	140-57-8	20	660
*Isodrin[3]	465-73-6	10	330
*Kepone[2]	143-50-0	100	3300
Famphur[3]	52-85-7	100	3300
p-(Dimethylamino)azobenzene	60-11-7	20	660
p-Chlorobenzilate[3]	510-15-6	10	330
3,3'-Dimethylbenzidine	119-93-7	50	1600
2-Acetylaminofluorene	53-96-3	100	3300
Dibenz(a,j)acridine	224-42-0	20	660
7,12-Dimethylbenz(a)anthracene	57-97-6	20	660
3-Methylcholanthrene	56-49-5	20	660

[1] The Appendix IX standard contains additional analytes required for the Appendix IX list. The STL North Canton primary standard must also be analyzed to include all of the Appendix IX list

[2] May also be analyzed by method 8140 or 8141, which can achieve lower reporting limits.

[3] It is highly recommended that Famphur is analyzed by method 8081. It is a poor responder by 8270C.

* These compounds are analyzed by GC methods at STL North Canton.

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	4	330
Benzo(a)pyrene	50-32-8	4	330
Benzo(b)fluoranthene	205-99-2	4	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	4	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
Hexachloroethane	67-72-1	5	330

Table 2A
STL North Canton Michigan Program[1]

Semivolatile	CAS Number	Michigan Reporting Limits	
		Aqueous µg/L	Low Soil/Sediment µg/kg
Indeno(1,2,3-cd)pyrene	193-39-5	4	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.

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
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

Table 3

Reportable Analytes for STL North Canton Standard Tests, Primary Standard

Analyte	CAS Number	STL North Canton Standard List	TCLP	TCL	Appendix IX
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[4]	103-33-3				
4-Bromophenyl phenyl ether	101-55-3	X		X	X
Hexachlorobenzene	118-74-1	X	X	X	X
Pentachlorophenol	87-86-5	X	X	X	X
Phenanthrene	85-01-8	X		X	X
Anthracene	120-12-7	X		X	X
Carbazole	86-74-8	X		X	
Di-n-butyl phthalate	84-74-2	X		X	X
Fluoranthene	206-44-0	X		X	X
Benzidine	92-87-5				
Pyrene	129-00-0	X		X	X

Table 3

Reportable Analytes for STL North Canton Standard Tests, Primary Standard

Analyte	CAS Number	STL North Canton Standard List	TCLP	TCL	Appendix IX
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 formally known as bis(2-chloroisopropyl)ether

[2] Azobenzene is formed by decomposition of 1,2-diphenlyhydrazine. If 1,2-diphenylhydrazine is requested, it will be analyzed as azobenzene.

Table 4

Reportable analytes for STL 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[2]	126-68-1				X
a,a-Dimethyl-phenethylamine	122-09-8				X
2,6-Dichlorophenol	87-65-0				X
Hexachloropropene	1888-71-7				X
p-Phenylenediamine	106-50-3				X
n-Nitrosodi-n-butylamine	924-16-3				X
Safrole	94-59-7				X
1,2,4,5-Tetrachlorobenzene	95-94-3				X
Isosafrole	120-58-1				X
1,4-Dinitrobenzene	100-25-4				
1,4-Naphthoquinone	130-15-4				X
1,3-Dinitrobenzene	99-65-0				X
Pentachlorobenzene	608-93-5				X
1-Naphthylamine	134-32-7				X
2-Naphthylamine	91-59-8				X
2,3,4,6-Tetrachlorophenol	58-90-2				X
5-Nitro-o-toluidine	99-55-8				X
Thionazin[2]	297-97-2				X
1,3,5-Trinitrobenzene	99-35-4				X
Sulfotepp[2]	3689-24-5				X
Phorate[2]	298-02-2				X
Phenacetin	62-44-2				X
Diallate	2303-16-4				X
Dimethoate[2]	60-51-5				X
4-Aminobiphenyl	92-67-1				X
Pentachloronitrobenzene	82-68-8				X
Pronamide	23950-58-5				X
Disulfoton[2]	298-04-4				X
2-secbutyl-4,6-dinitrophenol (Dinoseb)[2]	88-85-7				X
*Methyl parathion[2]	298-00-0				X
4-Nitroquinoline-1-oxide	56-57-5				X

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
*Parathion[2]	56-38-2				X
*Isodrin[3]	465-73-6				X
*Kepone [2]	143-50-0				X
Famphur[2]	52-85-7				X
Methapyrilene	91-80-5				X
Aramite	140-57-8				X
p-(Dimethylamino)azobenzene	60-11-7				X
p-Chlorobenzilate[3]	510-15-6				X
3,3'-Dimethylbenzidine	119-93-7				X
2-Acetylaminofluorene	53-96-3				X
Dibenz(a,j)acridine	224-42-0				
7,12-Dimethylbenz(a)anthracene	57-97-6				X
3-Methylcholanthrene	56-49-5				X
Hexachlorophene[4]	70-30-4				X
Diphenylamine[5]	122-39-4				X

[2] May also be analyzed by method 8140 or 8141, which can achieve lower reporting limits.

[3] May also be analyzed by method 8080 or 8081, which can achieve lower reporting limits

[4] Hexachlorophene is a required analyte for Appendix IX. This compound is not stable, and therefore not included in the calibration standard. The characteristic ions for hexachlorophene are searched for in the chromatogram. (See section 12.2.1)

[5] Diphenylamine is a required compound for Appendix IX. N-nitrosodiphenylamine decomposes in the injection port to form diphenylamine. Therefore these two compounds cannot be distinguished. Diphenylamine is not included in the calibration standard.

* These compounds are analyzed by GC methods at STL North Canton.

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

Table 7

Analytes in Approximate Retention Time Order and Characteristic Ions, Primary Standard

Analyte	Primary	Secondary	Tertiary
Dimethylphthalate	163	194	164
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

Table 7

Analytes in Approximate Retention Time Order and Characteristic Ions, Primary Standard

Analyte	Primary	Secondary	Tertiary
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
Parathion	109	97	291

Table 8

Analytes in Approximate Retention Time Order and Characteristic Ions, Appendix IX Standard

Analyte	Primary	Secondary	Tertiary
Isodrin	193	66	195
Kepone	272	274	237
Famphur	218	125	93
Methapyrilene	97	58	
Aramite 1	185	319	
Aramite 2	185	319	
p-(Dimethylamino)azobenzene	120	225	77
p-Chlorobenzilate	251	139	253
3,3'-Dimethylbenzidine	212	106	
2-Acetylaminofluorene	181	180	223
Dibenz(a,j)acridine	279	280	
7,12-Dimethylbenz(a)anthracene	256	241	120
3-Methylcholanthrene	268	252	253

Table 9

8270C LCS Compounds

LCS Compounds	Spiking Level, ng/µL in extract[1]
1,2,4-Trichlorobenzene	100
Acenaphthene	100
2,4-Dinitrotoluene	100
Pyrene	100
N-Nitroso-di-n-propylamine	100
1,4-Dichlorobenzene	100
Pentachlorophenol	150
Phenol	150
2-Chlorophenol	150
4-Chloro-3-methylphenol	150
4-Nitrophenol	150

[1] Levels are 50 and 75 ng/µL if 2 µL injection is used

Table 10

TCLP LCS Compounds

LCS Compounds	Spiking Level, ng/µL in extract[1]
1,4-Dichlorobenzene	100
2,4-Dinitrotoluene	100
Hexachlorobenzene	100
Hexachlorobutadiene	100
Hexachloroethane	100
2-Methylphenol	100
3-Methylphenol	100
4-Methylphenol	100
Nitrobenzene	100
Pentachlorophenol	100
Pyridine	100
2,4,5-Trichlorophenol	100
2,4,6-Trichlorophenol	100

[1] Levels are 50 ng/µL if 2 µL injection is used

Recovery limits for the LCS and for matrix spikes are generated from historical data and are maintained by the QA department.

Table 11

8270C Surrogate Compounds

Surrogate Compounds	Spiking Level, ng/µL in extract[2]
Nitrobenzene-d5	100
2-Fluorobiphenyl	100
Terphenyl-d14	100
1,2-Dichlorobenzene-d4[1]	100
Phenol-d5	150
2-Fluorophenol	150
2,4,6-Tribromophenol	150
2-Chlorophenol-d4[1]	150

[1] Included in standard mix, but not routinely evaluated for method 8270B

[2] Levels are 50 and 75 ng/µL if 2 µL injection is used

Recovery limits for surrogates are generated from historical data and are maintained by the QA department.

Table 12[3]
Calibration Levels, Primary Standard, µg/mL

Analyte	Level 1	Level 2	Level 3	Level 4	Level 5
Pyridine	10	25	40	60	80
N-nitrosodimethylamine	10	25	40	60	80
Aniline	10	25	40	60	80
Phenol	10	25	40	60	80
Bis(2-chloroethyl)ether	10	25	40	60	80
2-Chlorophenol	10	25	40	60	80
1,3-Dichlorobenzene	10	25	40	60	80
1,4-Dichlorobenzene	10	25	40	60	80
Benzyl alcohol	10	25	40	60	80
1,2-Dichlorobenzene	10	25	40	60	80
2-Methylphenol	10	25	40	60	80
2,2'-oxybis(1-chloropropane)[1]	10	25	40	60	80
4-Methylphenol	10	25	40	60	80
N-Nitroso-di-n-propylamine	10	25	40	60	80
Hexachloroethane	10	25	40	60	80
Nitrobenzene	10	25	40	60	80
Isophorone	10	25	40	60	80
2-Nitrophenol	10	25	40	60	80
2,4-Dimethylphenol	10	25	40	60	80
Benzoic acid	10	25	40	60	80
Bis(2-chloroethoxy)methane	10	25	40	60	80
2,4-Dichlorophenol	10	25	40	60	80
1,2,4-Trichlorobenzene	10	25	40	60	80
Naphthalene	10	25	40	60	80
4-Chloroaniline	10	25	40	60	80
Hexachlorobutadiene	10	25	40	60	80
4-Chloro-3-methylphenol	10	25	40	60	80
2-Methylnaphthalene	10	25	40	60	80
Hexachlorocyclopentadiene	10	25	40	60	80
2,4,6-Trichlorophenol	10	25	40	60	80
2,4,5-Trichlorophenol	10	25	40	60	80
2-Chloronaphthalene	10	25	40	60	80
2-Nitroaniline	10	25	40	60	80
Dimethyl phthalate	10	25	40	60	80
Acenaphthylene	10	25	40	60	80
3-Nitroaniline	10	25	40	60	80
Acenaphthene	10	25	40	60	80
2,4-Dinitrophenol	10	25	40	60	80
4-Nitrophenol	10	25	40	60	80
Dibenzofuran	10	25	40	60	80
2,4-Dinitrotoluene	10	25	40	60	80
2,6-Dinitrotoluene	10	25	40	60	80
Diethylphthalate	10	25	40	60	80
4-Chlorophenyl phenyl ether	10	25	40	60	80
Fluorene	10	25	40	60	80
4-Nitroaniline	10	25	40	60	80
4,6-Dinitro-2-methylphenol	10	25	40	60	80

Table 12[3]
Calibration Levels, Primary Standard, µg/mL

Analyte	Level 1	Level 2	Level 3	Level 4	Level 5
N-Nitrosodiphenylamine	10	25	40	60	80
Azobenzene[2]	10	25	40	60	80
4-Bromophenyl phenyl ether	10	25	40	60	80
Hexachlorobenzene	10	25	40	60	80
Pentachlorophenol	10	25	40	60	80
Phenanthrene	10	25	40	60	80
Anthracene	10	25	40	60	80
Carbazole	10	25	40	60	80
Di-n-butyl phthalate	10	25	40	60	80
Fluoranthene	10	25	40	60	80
Benzidine	10	25	40	60	80
Pyrene	10	25	40	60	80
Butyl benzyl phthalate	10	25	40	60	80
3,3'-Dichlorobenzidine	10	25	40	60	80
Benzo(a)anthracene	10	25	40	60	80
Bis(2-ethylhexyl)phthalate	10	25	40	60	80
Chrysene	10	25	40	60	80
Di-n-octylphthalate	10	25	40	60	80
Benzo(b)fluoranthene	10	25	40	60	80
Benzo(k)fluoranthene	10	25	40	60	80
Benzo(a)pyrene	10	25	40	60	80
Indeno(1,2,3-cd)pyrene	10	25	40	60	80
Dibenz(a,h)anthracene	10	25	40	60	80
Benzo(g,h,i)perylene	10	25	40	60	80
Benzaldehyde	10	25	40	60	80
Caprolactam	10	25	40	60	80
1,1'-Biphenyl	10	25	40	60	80
Atrazine	10	25	40	60	80

[1] 2,2'oxybis(1-chloropropane) was formally known as bis(2-chloroisopropyl)ether

[2]Azobenzene is formed by decomposition of 1,2-diphenlyhydrazine. If 1,2-diphenylhydrazine is requested, it will be analyzed as azobenzene.

[3]Optional concentration levels = 1/5 of the listed concentrations for samples with a final volume of 5 mL.

Table 13[1]

Calibration Levels, Appendix IX Standard, µg/mL

Semivolatiles	Level 1	Level 2	Level 3	Level 4	Level 5
2-Picoline	10	25	40	60	80
N-Nitrosomethylethylamine	10	25	40	60	80
Methyl methanesulfonate	10	25	40	60	80
N-Nitrosodiethylamine	10	25	40	60	80
Ethyl methanesulfonate	10	25	40	60	80
Pentachloroethane	10	25	40	60	80
Acetophenone	10	25	40	60	80
N-Nitrosopyrrolidine	10	25	40	60	80
N-Nitrosomorpholine	10	25	40	60	80
o-Toluidine	10	25	40	60	80
3-Methylphenol	10	25	40	60	80
N-Nitrosopiperidine	10	25	40	60	80
o,o,o-Triethyl-Phosphorothioate	10	25	40	60	80
a,a-Dimethyl-phenethylamine	10	25	40	60	80
2,6-Dichlorophenol	10	25	40	60	80
Hexachloropropene	10	25	40	60	80
p-Phenylenediamine	10	25	40	60	80
n-Nitrosodi-n-butylamine	10	25	40	60	80
Safrole	10	25	40	60	80
1,2,4,5-Tetrachlorobenzene	10	25	40	60	80
Isosafrole 1 + 2	10	25	40	60	80
1,4-Dinitrobenzene	10	25	40	60	80
1,4-Naphthoquinone	10	25	40	60	80
1,3-Dinitrobenzene	10	25	40	60	80
Pentachlorobenzene	10	25	40	60	80
1-Naphthylamine	10	25	40	60	80
2-Naphthylamine	10	25	40	60	80
2,3,4,6-Tetrachlorophenol	10	25	40	60	80
5-Nitro-o-toluidine	10	25	40	60	80
Thionazin	10	25	40	60	80
1,3,5-Trinitrobenzene	10	25	40	60	80
Sulfotepp	10	25	40	60	80
Phorate	10	25	40	60	80
Phenacetin	10	25	40	60	80
Diallate 1 + 2	10	25	40	60	80
Dimethoate	10	25	40	60	80
4-Aminobiphenyl	10	25	40	60	80
Pentachloronitrobenzene	10	25	40	60	80
Pronamide	10	25	40	60	80
Disulfoton	10	25	40	60	80
2-secbutyl-4,6-dinitrophenol (Dinoseb)	10	25	40	60	80
*Methyl parathion	10	25	40	60	80
4-Nitroquinoline-1-oxide	10	25	40	60	80
*Parathion	10	25	40	60	80
*Isodrin	10	25	40	60	80

Table 13[1]

Calibration Levels, Appendix IX Standard, µg/mL

Semivolatiles	Level 1	Level 2	Level 3	Level 4	Level 5
*Kepone	10	25	40	60	80
Famphur	10	25	40	60	80
Methapyrilene	10	25	40	60	80
Aramite 1 and 2	10	25	40	60	80
p-(Dimethylamino)azobenzene	10	25	40	60	80
p-Chlorobenzilate	10	25	40	60	80
3,3'-Dimethylbenzidine	10	25	40	60	80
2-Acetylaminofluorene	10	25	40	60	80
Dibenz (a,j)acridine	10	25	40	60	80
7,12-Dimethylbenz(a)anthracene	10	25	40	60	80
3-Methylcholanthrene	10	25	40	60	80

* 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
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

Table 14
Initial demonstration recovery and precision limits

Compound	Spiking concentration µg/L	Limit for Relative Standard Deviation	Limit for average recovery, %
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
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 8080 at STL North Canton, they will not be included in the initial demonstration of capability for method 8270B.

ATTACHMENT A

MODIFICATIONS REQUIRED FOR ANALYSIS OF WASTEWATER FOLLOWING METHOD 625

18. REQUIREMENTS FOR METHOD 625

18.1 Method 625 is required for demonstration of compliance with NPDES wastewater discharge permits. The standard analyte list and reporting limits are listed in Table A-1.

18.2 This method can be applied only to aqueous matrices.

18.3 The tune period for this method is defined as 24 hours.

18.4 Initial calibration curve requirements:

18.4.1 The initial calibration curve for this method requires at least three points.

18.4.2 Target compounds must have RSD ≤ 35%.

18.4.3 If this requirement can not be met, a regression curve must be constructed for the non-compliant compounds.

18.5 Continuing calibration verification requirements: All target compounds must have %D ≤ 20%.

18.6 Matrix Spike and LCS requirements:

18.6.1 A full analyte spike is required for method 625. The spiking levels are given in Table A-2.

Table A-1. STL 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
Butyl benzyl phthalate	85-68-7	10

Analytes	CAS Number	Aqueous µg/L
3,3'-Dichlorobenzidine	91-94-1	50
Benzo(a)anthracene	56-55-3	10
Bis(2-ethylhexyl)phthalate	117-81-7	10
Chrysene	218-01-9	10
Di-n-octylphthalate	117-84-0	10
Benzo(b)fluoranthene	205-99-2	10
Benzo(k)fluoranthene	207-08-9	10
Benzo(a)pyrene	50-32-8	10
Indeno(1,2,3-cd)pyrene	193-39-5	10
Dibenz(a,h)anthracene	53-70-3	10
Benzo(g,h,i)perylene	191-24-2	10

Table A-2. Method 625 LCS and MS compounds and spike concentrations.

LCS Compounds	Spiking Level, ng/µL in extract[1]
Phenol	100
Bis(2-chloroethyl)ether	100
2-Chlorophenol	100
1,3-Dichlorobenzene	100
1,4-Dichlorobenzene	100
1,2-Dichlorobenzene	100
2,2'-oxybis(1-chloropropane)	100
N-Nitroso-di-n-propylamine	100
Hexachloroethane	100
Nitrobenzene	100
Isophorone	100
2-Nitrophenol	100
2,4-Dimethylphenol	100
Bis(2-chloroethoxy)methane	100
2,4-Dichlorophenol	100
1,2,4-Trichlorobenzene	100
Naphthalene	100
Hexachlorobutadiene	100
4-Chloro-3-methylphenol	100
Hexachlorocyclopentadiene	100
2,4,6-Trichlorophenol	100
2-Chloronaphthalene	100
Dimethyl phthalate	100
Acenaphthylene	100
Acenaphthene	100
2,4-Dinitrophenol	100
4-Nitrophenol	100
2,4-Dinitrotoluene	100
2,6-Dinitrotoluene	100
Diethylphthalate	100
4-Chlorophenyl phenyl ether	100
Fluorene	100
4,6-Dinitro-2-methylphenol	100
N-Nitrosodiphenylamine	100
4-Bromophenyl phenyl ether	100
Hexachlorobenzene	100
Pentachlorophenol	100
Phenanthrene	100
Anthracene	100
Di-n-butyl phthalate	100
Fluoranthene	100
Benzidine	100
Pyrene	100
Butyl benzyl phthalate	100
3,3'-Dichlorobenzidine	100
Benzo(a)anthracene	100

LCS Compounds	Spiking Level, ng/µL in extract[1]
Bis(2-ethylhexyl)phthalate	100
Chrysene	100
Di-n-octylphthalate	100
Benzo(b)fluoranthene	100
Benzo(k)fluoranthene	100
Benzo(a)pyrene	100
Indeno(1,2,3-cd)pyrene	100
Dibenz(a,h)anthracene	100
Benzo(g,h,i)perylene	100

[1] Levels are 50 and 75 ng/µL if 2 µL injection is used

STL STANDARD OPERATING PROCEDURE

TITLE: TOXICITY CHARACTERISTIC LEACHING PROCEDURE AND SYNTHETIC PRECIPITATION LEACHING PROCEDURE

(SUPERSEDES: REVISION 1, REVISION DATE 02/01/00)

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1. SCOPE AND APPLICATION

1.1. This SOP describes the application of the Toxicity Characteristic Leaching Procedure (TCLP), SW846 Method 1311. The Toxicity Characteristic (TC) of a waste material is established by determining the levels of 8 metals and 31 organic chemicals in the aqueous leachate of a waste. The TC is one of four criteria in 40 CFR Part 261 to determine whether a solid waste is classified as a hazardous waste. The other three are corrosivity, reactivity and ignitability. The TC Rule utilizes the TCLP method to generate the leachate under controlled conditions that were designed to simulate leaching through a landfill. EPA's "worst case" waste disposal model assumes mismanaged wastes will be exposed to leaching by the acidic fluids generated in municipal landfills. The EPA's model also assumes the acid/base characteristics of the waste will be dominated by the landfill fluids. The TCLP procedure directs the testing laboratory to use a more acidic leaching fluid if the sample is an alkaline waste, again in keeping with the model's assumption that the acid fluids will dominate leaching chemistry over time.

1.2. The specific list of TC analytes and regulatory limits may be found in Appendix A.

Note: The list in Appendix A does not include the December 1994 EPA rule for Universal Treatment Standards for Land Disposal Restrictions. Those requirements include 216 specific metallic and organic compounds and, in some cases, lower detection limit requirements (see 40 CFR 268.40). TCLP leachates are part of the new Universal Treatment Standards, but the conventional analytical methods will not necessarily meet the new regulatory limits. Consult with the client and with STL Technical Specialists before establishing the instrumental methods for these regulations.

1.3. This SOP also describes the application of the Synthetic Precipitation Leaching Procedure (SPLP) which was designed to simulate the leaching that would occur if a waste was disposed in a landfill and exposed only to percolating rain water. The procedure is based on SW846 Method 1312. The list of analytes for SPLP may extend beyond the toxicity characteristic compounds shown in Appendix A. With the exception of the use of a modified extraction fluid, the SPLP and TCLP protocols are essentially equivalent. Where slight differences may exist between the SPLP and TCLP they are distinguished within this SOP.

1.4. The procedure is applicable to liquid, solid, and multiphase wastes.

1.5. The results obtained are highly dependent on the pH of the extracting solution, the length of time that the sample is exposed to the extracting solution, the temperature

during extraction, and the particle size/surface area of the sample. These parameters must be carefully controlled.

1.6. The reporting limits are based on the individual samples as well as the individual analysis techniques. However, the sample is determined to be hazardous if it contains any analyte at levels greater than or equal to the regulatory limits.

1.7. If a total analysis of the waste demonstrates that individual analytes are not present in the waste, or that they are present but at such low concentrations that the appropriate regulatory levels could not possibly be exceeded, the procedure need not be run. If the total analysis results indicate that TCLP is not required, the decision to cease TCLP analysis should be remanded to the client.

1.8. If an analysis of any one of the liquid fractions of the procedure leachate indicates that a regulated compound is present at such a high concentration that, even after accounting for dilution from the other fractions of the leachate, the concentration would be equal to or above the regulatory level for that compound, then the waste is hazardous and it may not be necessary to analyze the remaining fractions of the leachate. However, the remaining analyses should not be terminated without the approval of the client.

1.9. Volatile organic analysis of the leachate obtained using a bottle extraction, normally used for extractable organics and metals, can be used to demonstrate that a waste is hazardous, but only the ZHE option can be used to demonstrate that the concentration of volatile organic compounds is below regulatory limits due to potential analyte loss into the headspace during the bottle extraction.

2. SUMMARY OF METHOD

2.1. For liquid wastes that contain less than 0.5% dry solid material, the waste, after filtration through 0.6 to 0.8 μm glass fiber filter, is defined as the TCLP leachate.

2.2. For wastes containing greater than or equal to 0.5% solids, the liquid, if any, is separated from the solids and stored for later analysis or recombination with the leachate. The particle size of the remaining solid phase is reduced, if necessary. The solid phase is extracted with an amount of extraction fluid equal to 20 times the weight of the solid phase. For TCLP, the extraction fluid employed for extraction of non-volatile analytes is a function of the alkalinity of the solid phase of the waste. For SPLP, the extraction fluid employed is a function of the region of the country where the sample site is located if the sample is a soil. If the sample is a waste or wastewater the extraction fluid employed is a pH 4.2 solution. Two leachates may be generated: a) one for analysis of non-volatile constituents (semi-volatile organics, pesticides, herbicides and metals and/or b) one from a Zero Headspace Extractor (ZHE) for

analysis of volatile organic constituents. Following extraction, the liquid leachate is separated from the solid phase by filtration through a 0.6 to 0.8 μm fiber filter.

2.3. If compatible (i.e., multiple phases will not form on combination), the initial liquid filtrate of the waste is added to the liquid leachate and these are prepared and analyzed together. If incompatible, the liquids are analyzed separately and the results are mathematically combined to yield a volume-weighted average concentration.

3. DEFINITIONS

3.1. "Leachate" is used to refer to the solutions generated from these procedures (TCLP, SPLP, deionized water leach).

3.2. "Wet Solids" is that fraction of a waste sample from which no liquid may be forced out by pressure filtration.

4. INTERFERENCES

4.1. Oily wastes may present unusual filtration and drying problems. If requested by the client and as recommended by EPA (see Figure 3), oily wastes can be assumed to be 100% liquid and analysis for total concentrations of contaminants will be performed. This applies specifically to samples containing viscous non-aqueous liquids that would be difficult to filter. Alternately, the oil may be subjected to pressure filtration. The portion that passes through the filter will be prepared and analyzed separately as an organic waste. The "wet solid" portion that remains behind on the filter will be subjected to leaching, prepared and analyzed. The results will then be mathematically combined.

4.2. Wastes containing free organic liquids (e.g., oil, paint thinner, fuel) usually require dilution prior to analysis to address the matrix interferences. In most instances this results in reporting limits elevated above the TCLP regulatory limits.

4.3. Solvents, reagents, glassware and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks as described in Section 9 and the individual determinative SOPs.

4.4. Glassware and equipment contamination may result in analyte degradation. Soap residue on glassware and equipment may contribute to this. All glassware and equipment should be rinsed very carefully to avoid this problem.

4.5. Phthalates may be eliminated by proper glassware cleanup and by avoiding plastics. Only glass, Teflon or Type 316 stainless steel tumblers may be used for leachates to be

analyzed for organics. Plastic tumblers may be used for leachates to be analyzed for the metals.

4.6. Overexposure of the sample to the environment will result in the loss of volatile components.

4.7. Potential interferences that may be encountered during analysis are discussed in the individual analytical methods.

5. SAFETY

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

5.2. Eye protection that satisfies ANSI Z87.1 (as per the Chemical Hygiene Plan), laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

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

5.3.1. Chemicals that have been classified as carcinogens, or potential carcinogens, under OSHA include:
Methylene chloride

5.3.2. Chemicals known to be flammable are:
Methanol

5.3.3. The following materials are known to be corrosive:
Hydrochloric acid, nitric acid, sulfuric acid, acetic acid, sodium hydroxide

5.3.4. The following materials are known to be oxidizing agents:
Nitric Acid.

5.4. Gas pressurized equipment is employed in this procedure. Be sure all valves and gauges are operating properly and that none of the equipment, especially tubing, is over-pressurized. CAUTION: Do not open equipment that has been pressurized until it has returned to ambient pressure.

5.5. A rotary agitation apparatus is used in this procedure. Certain samples may break the glass jars used in the procedure. For these samples, extra caution, including plastic or polyethylene overwraps of the glass jar, may be necessary. Turning the jar or bottle sideways rather than tumbling end over end may also reduce the chance of breakage. If sideways tumbling is used, note this change in the logbook comment section.

5.6. Secure tumbler and extraction apparatus before starting rotary agitation apparatus.

5.7. During sample rotation, pressure may build up inside the bottle. Periodic venting of the bottle will relieve pressure.

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

5.9. The preparation of standards and reagents and glassware cleaning procedures that involve solvents such as methylene chloride will be conducted in a fume hood with the sash closed as far as the operation will permit.

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

5.11. Due to the potential for ignition, flammability or production of noxious fumes, do not attempt to dry non-aqueous liquid samples in an oven. Use extended drying in a ventilation hood.

6. EQUIPMENT AND SUPPLIES

6.1. Extraction vessels

6.1.1. For volatile analytes - zero-headspace extraction (ZHE) vessel, gas-pressure actuated, Millipore YT3009OHW or equivalent (see Figure 2).

6.1.2. For metals - either borosilicate glass jars (2.5 L, with Teflon lid inserts) or 2.5 L HDPE (Nalgene or equivalent) bottles may be used.

6.1.3. For non-volatile organics - only borosilicate glass may be used.

6.2. Vacuum filtration apparatus and stainless steel pressure filtration apparatus (142 mm diameter), capable of 0 - 50 psi.

6.3. Borosilicate glass fiber filters, 0.6 - 0.8 μm (Whatman GF/F 14.2 cm, 9.0 cm, 4.7 cm, 0.7 μm or equivalent). When analyzing for metals, wash the filters with 1 N nitric acid and de-ionized water prior to use, or purchase pre-washed filters. Glass fiber filters are fragile and should be handled with care.

6.4. Rotary agitation apparatus, multiple-vessel, Associated Design and Manufacturing Company 3740-6 or equivalent (see Figure 1). The apparatus must be capable of rotating the extraction vessel in an end-over-end fashion at 30 ± 2 rpm.

6.5. ZHE Extract Collection Device: Gas-tight syringes, 50 or 100 mL capacity, Hamilton 0158330 or equivalent.

6.6. Top loading balance, capable of 0 - 4000 ± 0.01g (all measurements are to be within ± 0.1 grams).

6.7. pH meter and probe capable of reading to the nearest 0.01 unit, and with automatic temperature compensation.

6.8. pH probes.

6.9. Magnetic stirrer/hotplate and stirring bars.

6.10. VOA vials, 40 mL, with caps and septa.

6.11. Glass bottles, 1 liter, with Teflon lid-inserts.

6.12. Nalgene plastic bottles or equivalent, 1 liter.

6.13. Miscellaneous laboratory glassware and equipment.

7. REAGENTS AND STANDARDS

7.1. Reagent water for non-volatile constituents must be produced by a Millipore DI system or equivalent. For volatile constituents, water must be passed through an activated carbon filter bed (Milli-Q or tap water passed through activated carbon). Reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks.

7.2. Hydrochloric acid, 1 N: Carefully add 83 mL concentrated reagent grade HCl to 800 mL reagent water, cool and dilute to 1 liter with reagent water. Cap and shake to mix well.

7.3. Sodium hydroxide, 1 N: Carefully add 40 g reagent grade NaOH pellets to 800 mL reagent water, stir until the pellets are completely dissolved, cool and dilute to 1 liter with reagent water.

CAUTION: Heat is generated during this process.

7.4. Acetic acid, glacial: concentrated, reagent grade liquid (HOAc).

7.6. pH calibration solutions: buffered to a pH of 4, 7, and 10. Commercially available.

7.5. TCLP Leaching Fluids

7.5.1. General Comments

7.5.1.1. The pH of both solutions listed below should be monitored daily and the pH probes are to be calibrated prior to use.

7.5.1.2. The leaching fluids MUST be prepared correctly. If the desired pH range is not achieved and maintained, the TCLP may yield erroneous results due to improper leaching. If the pH is not within the specifications, the fluid must be discarded and fresh extraction fluid prepared.

7.5.1.3. Additional volumes of extraction fluids listed below may be prepared by multiplying the amounts of acetic acid and NaOH by the number of liters of extraction fluid required.

7.5.2. TCLP Fluid #1: Carefully add 5.7 mL glacial acetic acid and 64.3 mL of 1 N NaOH to 500 mL reagent water in a 1 liter volumetric flask. Dilute to a final volume of 1 L with reagent water, cap and shake to mix well. For 8 L of fluid use 45.6 mL glacial acetic acid and 514 mL 1N NaOH, dilute to 8 L with reagent water. When correctly prepared, the pH of this solution is 4.93 ± 0.05. The density of TCLP fluid #1 is 0.997 g/mL.

7.5.3. TCLP Fluid #2: Carefully add 5.7 mL glacial acetic acid to 500 mL reagent water in a 1 liter volumetric flask. Dilute to a final volume of 1 L with reagent water, cap and shake to mix well. For 8 L of fluid use 45.6 mL glacial acetic acid, dilute to 8 L with reagent water. When correctly prepared, the pH of this solution is 2.88 ± 0.05. The density of TCLP fluid #2 is 0.997 g/mL.

7.6. Nitric acid, 50% solution: Slowly and carefully add 500 mL concentrated HNO_3 to 500 mL reagent water. Cap and shake to mix well.

7.7. Sulfuric acid / nitric acid (60/40 weight percent mixture) H_2SO_4/HNO_3. Cautiously mix 60 g of concentrated sulfuric acid with 40 g of concentrated nitric acid.

7.8. SPLP Leaching fluids

7.8.1. SPLP solutions are unbuffered and exact pH may not be attained. The pH of TCLP and SPLP fluids should be checked prior to use. If not within specifications, the fluid should be discarded and fresh fluid prepared.

7.8.2. SPLP fluid #1: Add 60/40 weight percent mixture of sulfuric and nitric acids to reagent water until the pH is 4.20 ± 0.05 This fluid is used for soils from a site that is east of the Mississippi River and for wastes and wastewaters.

7.8.3. SPLP fluid #2: Add 60/40 weight percent mixture of sulfuric and nitric acids to reagent water until the pH is 5.00 ± 0.05. This fluid is used for soils from a site that is west of the Mississippi River.

7.8.4. SPLP fluid #3: This fluid is reagent water and is used for leaching of volatiles. Additionally, any cyanide-containing waste or soil is leached with fluid #3 because leaching of cyanide containing samples under acidic conditions may result in the formation of hydrogen cyanide gas.

7.9. Methanol and methylene chloride - used to aid in cleaning oil contaminated equipment.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Samples being analyzed for non-volatile organic compounds should be collected and stored in glass containers with Teflon lid liners. Chemical preservatives shall NOT be added UNTIL AFTER leachate generation.

8.2. Samples being analyzed for metals only can be collected in either glass or polyethylene containers.

8.3. When the waste is to be evaluated for volatile analytes, care should be taken to minimize the loss of volatiles. Samples shall be collected and stored in a manner intended to prevent the loss of volatile analytes (e.g., samples should be collected in Teflon lined septum capped vials with minimal headspace and stored at 4 ± 2°C). Samples should be opened only immediately prior to extraction.

8.4. Samples should be refrigerated to 4 ± 2°C unless refrigeration results in irreversible physical changes to the waste. If precipitation occurs, the entire sample (including precipitate) should be extracted.

8.5. The minimum TCLP sample collection size is determined by the physical state or states of the waste and the analytes of concern. The amount of waste required varies with the percent solids. The lower the percent solids, the more waste will be required for preliminary and final testing. For aqueous samples containing between 0.5 and 10% solids, several kilograms of sample are required to complete the analyses. The general minimal requirements when the samples are 100% solids include: 1 - 32 oz jar for semi-volatile organic analysis and metals, and 1 - 4 oz jar for volatile organic analysis. Low density sample materials, such as rags or vegetation, will require larger volumes of sample. For liquid samples (less than 50% solids), minimum requirements are 2 - 32 oz jars for semi-volatile organic analysis and metals, and 2 - 8 oz jars for volatile organic analysis. If volatile organic analysis is the only requested parameter, 2 separate jars are required. If matrix spike or duplicate control samples are requested, additional sample volume is required. If sufficient sample volumes were not received, analyses cannot be started and the client should be notified as soon as possible.

8.6. TCLP leachates should be prepared for analysis and analyzed as soon as possible following extraction. Leachates or portions of leachates for metallic analyte determinations must be acidified with nitric acid to a pH less than 2, unless precipitation occurs. If precipitation occurs upon addition of nitric acid to a small aliquot of the leachate, then the remaining portion of the leachate shall not be acidified and the leachate shall be analyzed as soon as possible. All other leachates should be stored under refrigeration (4 ± 2°C) until analyzed. ZHE leachates must be stored in VOA vials filled to eliminate all headspace.

8.7. Samples are subject to appropriate treatment within the following time periods:

Table 1 – Holding Times (days)

Parameter	Collection to Start of TCLP Leach	End of TCLP Tumble to Preparation	Start of TCLP Leach or Semi- volatile Prep Extraction to Analysis	Total Elapsed Time
Volatiles:	14	N/A	14	28
Semi-volatiles:	14	7	40	61
Mercury:	28	N/A	28	56
Other Metals:	180	N/A	180	360

NOTE: The initial holding time is measured from date of collection to date TCLP extraction started. (This should be the TCLP extraction date in QuanTims.) Semi-volatile method prep holding time is measured from the day tumbling is complete to the start of method extraction. Subsequent analysis holding times are measured from the date extraction (TCLP or method prep) starts. If sample holding times are exceeded, the values obtained will be considered minimal concentrations. Exceeding holding times is not acceptable in establishing that a waste does not exceed the regulatory level. Exceeding the holding time will not invalidate characterization if the waste exceeds the regulatory limit. The Total Elapsed Time is to be used as guidance. If preps are initiated at the last possible moment of a holding time, the elapsed times may be exceeded.

9. QUALITY CONTROL

9.1. Quality Control Batch (QC Batch) - QA-003 defines a QC Batch as a set of up to 20 field samples of similar matrix that behave similarly and are processed using the same procedures, reagents and standards within the same time period. The same lot of reagents must be used within a batch. A minimum of one TCLP extraction blank (Method Blank), one Laboratory Control Sample (LCS), one Matrix Spike (MS), and one Matrix Spike Duplicate (MSD) will be prepared with each TCLP leachate batch.

9.2. TCLP Extraction Blanks - A minimum of one blank (using the same extraction fluid as used for the samples) must be prepared and analyzed for every batch of samples extracted in a particular vessel type. The blanks are generated in the same way as the samples (i.e., blanks will be tumbled and filtered with the samples). ZHE Extraction vessels will be uniquely numbered. Consult the STL QC Program and the individual analysis SOPs for blank acceptance criteria.

9.3. Laboratory Control Sample (LCS) - A LCS is required with each batch of 20 or fewer samples. The LCS shall be generated after a batch of TCLP leachates have been generated (i.e., at the time of the preparative digestion or extraction) by spiking an aliquot of the appropriate extraction fluid used for that batch or reagent water. Consult the individual analysis SOPs for additional LCS guidance (i.e., spike amounts, spike levels, recovery criteria, etc.).

9.4. Matrix Spike (MS/MSD) - Matrix spikes are used to monitor the performance of the analytical methods on the matrix and to assess the presence of interferences. A MS/MSD pair are required with each batch of 20 or fewer samples.

9.4.1. Matrix spikes are to be added after filtration of the TCLP leachate. Spikes are not to be added prior to the TCLP leaching. For metals, matrix spikes are to be added before preservation with nitric acid.

9.4.2. Consult the individual analysis SOPs for additional guidance on spike compounds and levels.

9.5. Corrective Actions

9.5.1. Consult the STL QC Program and individual analysis SOPs for corrective action for blanks and LCS

9.5.2. Method of Standard Additions (MSA) shall be used for metals if all of the following conditions are met:

- Recovery of the analyte in matrix spike is not at least 50%,
- the concentration of the analyte does not exceed the regulatory level, and
- the concentration of the analyte measured in the sample is within 20% of the appropriate regulatory level.

If the matrix spike recovery is 5% or less due to dilution or matrix interference, contact the project manager and client for guidance. The client should also be contacted prior to initiation of any MSA steps. Refer to the individual analysis SOPs for details on how to perform MSA analysis.

10. CALIBRATION AND STANDARDIZATION

10.1. Refer to appropriate analysis SOPs.

11. PROCEDURE

11.1. GENERAL COMMENTS

11.1.1. One-time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented on a Nonconformance Memo kept in the project file and described in the final report. The variation must be approved by a project manager, Technical Specialist and QA Manager. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

11.1.2. All masses should be recorded to the nearest 0.1 g.

11.2. PRELIMINARY SAMPLE EVALUATIONS (Refer to Flow Chart #1, Appendix D)

11.2.1. Determine the total volume of TCLP leachate (solid phase leachate + liquid filtrate) that needs to be generated for analysis according to the following:

Table 2. Recommended TCLP Leachate Volume

Analysis	TCLP Required Volume (mL)	SPLP Required Volume (mL)
Volatiles	3 x 40	3 x 40
Semi-volatiles	500	1000

Pesticides	500	1000
Herbicides	500	1000
Metals	300	300

11.2.1.1. For TCLP and SPLP samples used for matrix spike and matrix spike duplicate analysis, two to three times the listed volumes are required.

11.2.2. Sample Description (determine sample matrix)

11.2.2.1.Solid - If the waste will obviously yield no free liquid when subjected to pressure filtration , then proceed to Section 11.2.5 or 11.4 (Bottle Extraction Procedure or ZHE Procedure).

11.2.2.2.Liquid - If the sample is a monophasic liquid, proceed to Section 11.2.3 (Percent Solid Determination).

11.2.2.3. Multiphasic – The sample has discernible layers (liquid/liquid or liquid/solid). If more than one container of multi-phasic materials is received from the field, each container might show different amounts of each phase. Consult client to determine sample selection alternatives (composite all sample containers, select one, resample, etc.) if this occurs.

11.2.3. Solids Determination

11.2.3.1.Determine Type of Filtration Apparatus and Process

11.2.3.1.1.Percent Solids and ZHE Extractions - The ZHE filtration apparatus cannot accurately determine percent solids less than 5%. If an extraction is to be performed solely for volatile organic compounds and the percent solids concentration is apparently greater than 5%, proceed to Section 11.4 (ZHE Extraction Procedure, Volatile Constituents). Otherwise, continue with Section 11.2.3.2. The aliquot of sample used here cannot be used again for the ZHE extraction.

11.2.3.1.2.If the sample is mostly a non-viscous liquid (water or non-viscous organic liquid) of low solids content (expected to be < 0.5%) , vacuum filtration should be used initially. Proceed to determination of percent dry solids (Section 11.2.3.2)

11.2.3.1.3.If the sample is viscous (sludge, oil, or is expected to have solids content > 0.5%), use pressure filtration. Proceed to determination of wet solids (Section 11.2.3.3).

11.2.3.2.Determination of percent dry solids

11.2.3.2.1.Measure and record the weight of the filter. Load the filter into the filter holder and assemble vacuum filter apparatus.

11.2.3.2.2.Homogenize the waste, then transfer 100 g subsample to a glass beaker. Record the sample weight in the percent dry solids section of the logbook.

11.2.3.2.3.Turn on vacuum source. Transfer the sample to the vacuum filtration device attempting to spread the waste sample evenly over the surface of the filter. Be sure to transfer all particulates from the beaker to the filter. Use a reagent water rinse if necessary.

11.2.3.2.4.Once all liquid has been pulled though the filter, remove the filter with the wet solids from the vacuum filtration apparatus.

11.2.3.2.5.Dry the filter and solid phase at 100 ± 20 ° C for approximately 15 minutes.

11.2.3.2.6.Remove the filter from the oven and allow to cool in a desiccator.

11.2.3.2.7.Weigh and record the dry weight of filter + particulates.

11.2.3.2.8.Calculate and record the percent dry solids.

11.2.3.2.9.If the percent dry solids is ≥ 0.5%, repeat the drying step. Weigh and record the second filter + particulates dry weight. If the two weighings do not agree within 1%, perform additional drying and weighing until successive weighings agree within 1%.

11.2.3.2.10.If the dry solids result is ≥ 0.5%, proceed to Section 11.2.3.3 using a fresh wet portion of the multiphase waste.

11.2.3.2.11.If the percent solids result is less than 0.5%, discard the solid phase. No leaching will be necessary. Filter sufficient

sample with either the pressure filtration system or ZHE system as described in Sections 11.3 and 11.4. The filtrate is the TCLP leachate.

11.2.3.3.Determination of wet solids

11.2.3.3.1.Assemble the pressure filtration apparatus (use blunt forceps to handle the 0.6 to 0.8 μm filter membrane).

11.2.3.3.2.Homogenize the waste, transfer a minimum of a 100 mL subsample to the glass beaker. Measure and record the gross weight (logbook column A).

11.2.3.3.3.Measure and record the tare weight of the filtrate collection bottle (logbook column D).

11.2.3.3.4.Transfer the sample to the filtration device attempting to spread the waste sample evenly over the surface of the filter. Measure and record the tare weight of the empty glass beaker and any residual sample (logbook column B).

11.2.3.3.5.Calculate and record the net weight of sample used for testing (logbook column C).

11.2.3.3.6.Slowly apply gentle pressure of 10 psi to the filtration apparatus. Allow the sample to filter until no SIGNIFICANT additional liquid has passed through the filter during a 2 minute period.

11.2.3.3.7.If necessary, repeat previous step by increasing the pressure in 10 psi increments until a maximum of 50 psi is reached. Stop the filtration when no additional filtrate is generated within a 2 minute period.

Note: Some samples will contain liquid material that does not filter (e.g., oil). Do not attempt to filter the sample again by exchanging filters. Viscous oils or any wastes which do not pass through the filter are classified by the method as a solid.

11.2.3.3.8.Remove the filtrate collection bottle, weigh and record the gross weight (logbook column E).

11.2.3.3.9.Calculate and record the net weight of filtrate (logbook column F). This result will be used in the percent solids calculation.

11.2.3.3.10.Pour the filtrate into an appropriately sized graduated cylinder. Measure and record the volume of the filtrate in the logbook.

11.2.3.3.11.Retain the filtrate for possible recombination with the leachate in Section 11.3.6. Retain the filter and wet solids for the leaching in Section 11.3.

11.2.3.3.12.For multiphase sample preparations, calculate the total weight of wet solids and record the result in logbook column G.

11.2.4. Particle-size Reduction for Fluid Selection

11.2.4.1.The subsample used for fluid selection must consist of particles less than approximately 1 mm in diameter (versus the less than 1 cm requirement for the material used for the actual extraction). The method requires a smaller particle size to partially compensate for the shorter duration of contact time with the leachate solution as compared to the full extraction. Inappropriate use of coarser materials could result in the selection of the wrong fluid type.

11.2.4.2.Surface area exclusion - size reduction is not required if the sample surface area is greater than or equal to 3.1 cm^2 per gram.

11.2.4.3.If the sample contains particles greater than approximately 1 mm in diameter, crush, cut, or grind the solids to the required size.

11.2.4.4.Consult a supervisor or manager when dealing with unusual sample matrices (e.g., wood, cloth, metal, brick).

11.2.5. Determination of Appropriate Extraction Fluid

11.2.5.1.If the solid content is greater than or equal to 0.5%, and if the sample is being analyzed for metals or nonvolatile organic compounds, the type of leaching solution must be determined.

11.2.5.2.Follow times, temperature, and particle size specified in this section as closely as possible. If reaction time between the acid solution and solid

waste is too short or too long, the procedure may produce false pH readings.

11.2.5.3.For SPLP, refer to Section 7.8 for fluid selection. Record the fluid type in the logbook.

11.2.5.4.The TCLP leaching fluid for all volatiles is TCLP Fluid #1.

11.2.5.5.TCLP leach fluid determination for non-volatile analytes

11.2.5.5.1.Calibrate the pH meter with fresh buffer solution in accordance with the pH SOP.

11.2.5.5.2.Weigh out a 5.0 ± 0.1 g subsample (less than 1 mm particle size) of the solid phase into a glass container, and record in the logbook. Note: If sample quantity is limited, consult supervisor or manager.

Note: Many multiphase samples have limited solids quantity . In these instances use a 5 g aliquot of the whole sample. Document this difference in the logbook comment section.

11.2.5.5.3.Add 96.5 ± 1.0 mL of reagent water, cover with a watchglass, and stir for 5 minutes.

11.2.5.5.4.Measure and record the pre-test sample pH in the logbook.

Note: To avoid damaging a glass pH probe when organic liquid is present, use narrow range pH indicator paper or an ISFET pH meter.

11.2.5.5.5.If the pH is less than or equal to 5.0, use TCLP Fluid #1.

1.1.1.1.6.If the fluid pH is greater than 5.0, add 3.5 mL 1 N HCl. Slurry the sample briefly. Clip thermometer to the inside edge of one sample in each pre-test sample group to monitor the temperature. All samples in the group must go on the hot plate at the same time in order for the temperature of the one monitored sample to represent the others. Heat to 50°C and maintain for 10 minutes.

Note: The heating cycle is a critical step. If the solid waste does not remain in contact with the acidic solution under specified

time and temperature conditions, an erroneous pH may be measured.

11.2.5.5.7.Cool to room temperature.

11.2.5.5.8.Measure and record the pH immediately after the sample has reached room temperature.

11.2.5.5.8.1.If the pH is less than or equal to 5.0, use TCLP Fluid #1. Record the buffer in the logbook.

11.2.5.5.8.2.If the pH is greater than 5.0, use TCLP Fluid #2. Record the buffer in the logbook.

11.2.6. For samples requiring analysis for semi-volatile organics, pesticides, herbicides or metals proceed to Section 11.3.

11.2.7. For samples requiring analysis for volatile organics (ZHE), proceed to Section 11.4.

11.3. BOTTLE EXTRACTION PROCEDURE: NON-VOLATILE CONSTITUENTS: SEMI-VOLATILES, PESTICIDES, HERBICIDES, METALS (Refer to Flow Chart #2, Appendix D)

11.3.1. Evaluate the solid portion of the waste for particle size. If it contains particles greater than 1 cm in size, prepare the solid portion of the waste for leaching by crushing, cutting, or grinding such that all particles are less than 1 cm in size (i.e., capable of passing through a 9.5 mm, 0.375 inch, standard sieve). Size reduction is not required if the sample surface area is greater than or equal to 3.1 cm^2 per gram. If particle size reduction was required, record this in comments column in logbook.

11.3.1.1.Consult your supervisor or manager when dealing with unusual sample matrices (e.g., wood, cloth, metal, brick). Scissors or shears may be used to cut cloth, plastic or sheet metal. Saws may be used for wood or solid metal. Determination of particle size reduction tools should take into account the requested analytes (e.g. avoid chromium steel tools when TCLP metals have been requested). Bricks, rocks, or other solids amenable to grinding may be subcontracted out for particle size reduction. (Contact PA or PM.) Note that size reduction to fine powder is not appropriate, and could invalidate results. If necessary, consult client for guidance.

11.3.2. Determine the minimum total volume of solid phase leachate that needs to be generated. Refer to Section 11.2.1.

11.3.3. Use 100 g of solid unless sample quantity is limited. If limited sample, divide the total volume of solid phase leachate required by 20 to determine the minimum mass of solid phase required for leaching. Round this mass UP to the nearest 5g. Client must be notified if less than 100 g of solid material is used.

Note: Solid phase material is often in limited quantity from multiphase samples. Generally all the *solid* phase material and the filter from Section 11.2.3.3.11 are transferred to the leaching bottle

11.3.4. Weigh the required mass of solid phase into an appropriate bottle (plastic for metals only, glass for all others) and **slowly** add 20 times its mass of appropriate leaching fluid (e.g., 100 g of sample would require 2000 mL of leaching fluid). Record the weight of the sample aliquoted for the extraction. Record the volume of extraction fluid added in the logbook if other than 2000 mL.

11.3.5. Ensure any effervescence has stopped before capping the bottle tightly. Secure in a rotary agitator and rotate end-over-end at 28-32 rpm for 16-20 hours. The temperature of the room should be 23 ± 2°C. Record the rotary agitator I.D. and the date and time extraction is started and completed in the logbook.

NOTE: As agitation continues, pressure may build up within the bottle for some types of wastes. To relieve excessive pressure, the bottle may be removed and opened periodically in a properly vented hood to relieve any built-up pressure

11.3.6. After tumbling in the rotary agitator is completed, remove the bottle and allow the solids to settle. Record the date and time the extraction is completed in the logbook. If sample was multiphase with an initial filtrate, drop a few drops of the filtrate (with a disposable glass pipette) into the extraction bottle and observe whether the filtrate is insoluble or forms a precipitate with the leachate. If so then the filtrate is not compatible with the leachate and must be bottled and analyzed separately. The results are normally mathematically recombined (Section 12.1.2). If the filtrate is compatible with the leachate (ie completely soluble) then pour the entire filtrate into the leachate bottle, recap and mix. Proceed with the leachate filtration step in the next section.

11.3.7. Filter the sample using pressure filtration by filtering through a new glass fiber filter. For final filtration of the TCLP leachate, the glass fiber filter may be

changed, if necessary, to facilitate filtration. Filters must be acid washed if metals are to be determined (see Section 6.3). The entire sample need not be filtered; however, sufficient volume should be generated to support the required analyses.

11.3.8. Measure the pH of the TCLP leachate and record in the logbook. (Use narrow range pH paper or ISFET pH meter to measure the pH of oily samples as a glass pH probe may be damaged .)

11.3.9. Prepare subsamples for metals for MS/MSD quality control testing using the appropriate TCLP spiking solution (do not spike for organics). Refer to the appropriate determinative SOPs for further guidance on the spike components, levels and action criteria.

11.3.10. Immediately preserve the leachate as follows:

Metals	pH < 2 w/ HNO_3 for aqueous filtrates and leachates (do not acidify oils and other non-aqueous liquids)
All others	Refrigerate to 4 ± 2 °C

Note: Refer to Section 8.6 if precipitation occurs upon preservation.

11.3.11. Label each sample with the appropriate information and submit to the appropriate analytical groups for prep and analysis. For multiphase samples requiring mathematical recombination provide copies of the TCLP preparation logbook sheets to the sample preparation and analysis groups. Most mathematically recombined samples will require data entry for the filtrate and leachate portions as well as for the mathematically recombined results. Contact the project manager to ensure the proper sample login is completed.

11.4. **ZHE EXTRACTION PROCEDURE: VOLATILE CONSTITUENTS** (Refer to Flow Chart #3, Appendix D)

11.4.1. Use the ZHE device to obtain a TCLP leachate for analysis of volatile compounds only. Leachate resulting from the use of the ZHE shall NOT be used to evaluate the mobility of non-volatile analytes (e.g., metals, pesticides, herbicides and semi-volatile organics).

11.4.2. Due to some shortcomings of the method, losses of volatile compounds may occur. Extra care should be observed during the ZHE procedure to ensure that such losses are minimized. Charge the ZHE with sample only once and do not open the device until the final extract has been collected. Do not allow the

waste, the initial liquid phase, or the extract to be exposed to the atmosphere any longer than necessary.

11.4.3. Install new O-rings and adjust the ZHE piston in the ZHE body to the appropriate height (slightly moisten the O-rings with leaching fluid if necessary).

11.4.4. If the preliminary evaluations indicated the need for particle size reduction, homogenize the waste, weigh out a sufficient size subsample and prepare for leaching by crushing, cutting, or grinding such that all particles are less than 1 cm in size as measured with a ruler (Do NOT sieve the sample). Size reduction is not required if the sample surface area is greater than or equal to 3.1 cm^2 per gram If particle size reduction was required record this in the comments column of the logbook.

Note: To minimize loss of volatiles, samples for volatiles that require particle size reduction should be kept in sample storage (at 4°C) until immediately before size reduction. Aggressive reduction which would generate heat should be avoided and exposure of the waste to the atmosphere should be avoided to the extent possible. Size reduction to a fine powder is not appropriate. Also see Section 11.3.1.

11.4.4.1. Consult your supervisor or manager when dealing with unusual sample matrices (e.g., wood, cloth, metal, brick). Scissors or shears may be used to cut cloth, plastic or sheet metal. Saws may be used for wood or solid metal. Bricks, rocks, or other solids amenable to grinding may be subcontracted out for particle size reduction (Contact PM).

11.4.5. Homogenize and transfer an appropriate size subsample of the waste into the ZHE and record the mass in the logbook.

11.4.5.1. For wastes that are solid, a 15 g sample is used.

11.4.5.2. For wastes containing < 0.5% solids, the liquid portion of the waste, after filtration, is defined as the TCLP leachate. Filter enough of the sample to support all of the volatile analyses required.

11.4.5.3. If the sample has ≥ 0.5% solids and has non-volatile TCLP/SPLP requested, the appropriate sample size should be estimated based on the wet solids content determined in Section 11.2.3.3. If ZHE only, use visual wet solids estimate to sample subaliquot.

Note: For wastes containing greater than 0.5% wet or dry solids, the "solids" value from the ZHE filtration process may be used to determine the volume of fluid to load into the ZHE. This approach is recommended since the solids value from Section 11.2.3.3 may differ from the ZHE filtration solids due to sample variability or differences in the filtration apparatus.

11.4.6. Carefully place the glass fiber filter between the support screens and secure to the ZHE. Tighten all the fittings.

11.4.7. Place the ZHE in a vertical position; open both the gas AND liquid inlet/outlet valves. Attach a gas line to the gas inlet/outlet valve.

11.4.8. If the waste is solid, slowly increase the pressure to a maximum of 50 psi to force out as much headspace as possible and proceed to Section 11.4.13.

11.4.9. If this is a mutliphase sample, carefully apply gentle pressure of 10 psi (or more, if necessary) to force all headspace slowly out of the ZHE. At the FIRST appearance of liquid from the liquid inlet/outlet valve, quickly close the valve and discontinue gas pressure.

11.4.10. Assemble a syringe and place the plunger in all the way. Attach the pre-weighed syringe to the liquid inlet/outlet valve and open the valve. Record the tare weight of the collection syringe in column D of the logbook. .

11.4.11. Carefully apply gas pressure of no more than 10 psi to force out the liquid phase. Allow the sample to filter until no SIGNIFICANT additional filtrate has passed in a 2 minute period.

Note: If the capacity of the syringe is reached, close the liquid inlet/outlet valve, discontinue gas pressure, remove the syringe, weigh, record weight in column E and filtrate volume in the logbook. Return to Section 11.4.10.

11.4.12. Repeat previous step increasing the pressure in 10 PSI increments until 50 psi is reached and no significant liquid has passed in a 2 minute period. Close the valve and discontinue gas pressure. Remove the collection device and record the total weight of the collection device with filtrate in column E and filtrate volume in the logbook. Transfer the filtrate to VOA vials and label appropriately. Calculate the weight of filtrate collected and record in column F in the logbook.

Notes: If the original waste contained less than 0.5% solids (Section 11.2.3.2), this filtrate is defined as the TCLP leachate and you may proceed to Section

11.4.22. Otherwise, save the vials by storing at 4°C under minimal headspace conditions, for recombination as in Section 11.4.21.

The material remaining in the ZHE is defined to be the "solid" phase. Calculate the weight of the solid phase and record in column G of the logbook by subtracting the weight of the filtrate from the weight of the sample.

11.4.13. Determine the amount of buffer to use. Solid samples use 300 mL of leach fluid (20 X 15 g). For multiphase samples use the wet solids (column G) amount and multiply by 20. Record the leach fluid volume in column H of the logbook.

Note: The TCLP ZHE prep uses only TCLP fluid #1; the SPLP ZHE prep uses only SPLP fluid #3.

11.4.14. Load the fluid transfer reservoir with an excess of Fluid #1 and preflush the transfer line to eliminate air pockets. Be sure the required volume remains.

11.4.15. Attach the transfer line to the liquid inlet/outlet valve and open the valve. Carefully pump the required volume into the ZHE and close the valve. Disconnect the transfer line.

11.4.16. Check the ZHE to make sure all the valves are closed and manually rotate the ZHE (end-over-end) 2 or 3 times. Reposition the ZHE in the vertical position.

11.4.17. Pressurize the ZHE to 5-10 psi. If the ZHE appears to be leaking, follow the corrective action protocols recommended by the manufacturer and repeat the analysis.

11.4.18. Slowly open the liquid inlet/outlet valve to bleed out any headspace that may have been introduced during the introduction of the Fluid. Upon the first sign of liquid from the valve, close the valve.

11.4.19. Repressurize the ZHE to 5-10 psi and place in the rotary agitator. Rotate at 28-32 rpm for 16-20 hours. Room temperature should be 23 ± 2 °C. The room temperature is recorded using a continuous temperature monitor.

11.4.20. Confirm that the pressure of 5-10 psi was maintained throughout the leaching. If it was NOT maintained, return to Section 11.4 and repeat the leachate with a new aliquot of sample.

11.4.21. If there is an initial liquid filtrate (Sec 11.4.12) determine if it is compatible with the leachate if the filtrate has not been previously tested (Sec. 11.3.6).

11.4.21.1.Remove the plunger from the syringe and attach the barrel to the ZHE vessel. Open the outlet valve and pressurize as necessary to transfer about 1 mL of leachate into the syringe. Close the outlet valve.

11.4.21.2.With a glass pipette transfer a few drops of initial filtrate into the open syringe barrel. Formation of separate layers or a precipitate indicates the filtrate and leachate are not compatible. Bottle the filtrate for separate preparation and analysis. The results are normally mathematically recombined.

11.4.21.3.If the filtrate is compatible gently pour the remainder of the filtrate into the syringe barrel. Install the plunger. Bleed any pressure in the ZHE piston. Open the inlet/outlet valve and depress the syringe plunger to inject the filtrate into the ZHE vessel. Do not inject the air bubble (if present) from the syringe.

11.4.21.4.Close the valve and rotate a few times to mix. Proceed with leachate filtration as described in the next section.

11.4.22.Attach an empty syringe to the outlet valve. Open the valve and pressurize the piston to expel the leachate from the ZHE vessel. Following collection, store the TCLP leachate in 2 or 3 40-mL VOA vials with minimal headspace at 4 ± 2 °C and prepare for analysis as soon as possible using the appropriate organic analysis procedure (see Section 16.3).

11.4.23.If the individual phases are analyzed separately, combine the results mathematically by using the recombination calculation in Section 12.1.2. . Provide copies of the TCLP preparation logbook sheets to the sample preparation and analysis groups. Most mathematically recombined samples will require data entry for the filtrate and leachate portions as well as for the mathematically recombined results. Contact the project manager to ensure the proper sample login is completed.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Calculations

12.1.1. Calculation of weight of extraction fluid to use:

Volume of extraction fluid = 20 X weight of wet solids to be extracted

12.1.2. Mathematical recombination of analytical results:

$$Final\ Analyte\ Concentration = \frac{(V_1 \times C_1) + (V_2 \times C_2)}{V_1 + V_2}$$

V_1 = total volume of the initial filtrate phase (L).
C_1 = analyte concentration in initial filtrate phase (mg/L).
V_2 = volume of the theoretical solid phase leachate (L).
C_2 = analyte concentration in solid phase leachate (mg/L).,

12.2. REPORTING REQUIREMENTS

12.2.1. Follow these reporting conventions for multi-phase samples:

12.2.1.1. If both phases have positive results, use the values from each phase to calculate the recombined result. Use the reporting limit for each phase to calculate the recombined reporting limit.

12.2.1.2. If both phases are "ND" (not detected) the recombined result is "ND," and the reporting limit is calculated from the reporting limit for each phase.

12.2.1.3. If one phase is "ND" and the other phase has a positive result, use the zero for the "ND" phase and the positive value for the other phase to calculate the combined result. This will produce a minimum known concentration. Alternatively, at client request, the maximum possible concentration can be calculated by using the reporting limit for the "ND" phase rather than zero. The combined reporting limit is based on the reporting limit for both phases

12.2.2. Units - regardless of the nature of the sample, all TCLP and SPLP results are reported in units of mg/L.

12.2.3. For limits and significant figures, consult the appropriate analytical methods (Section 16.3).

12.2.4. Anomalies - all anomalies observed during the leach procedure must be noted on the worksheet or an NCM form. Some examples of such anomalies are:

12.2.4.1. Sample was monolithic - particle size reduction not possible due to nature of matrix.

12.2.4.2. Insufficient sample - less than the required 100 g minimum was available.

12.3. REVIEW REQUIREMENTS

12.3.1. Review all applicable holding times. If a holding time was exceeded, confirm that a holding time violation was properly documented in an NCM.

12.3.2. If Total analysis results are available, those results may be compared with the TCLP analysis results according to the following:

$$Total \geq 20 \times TCLP$$

NOTE: Assumes the sample is 100% Solids.

12.3.3. Total constituent analysis results can be used to demonstrate the TCLP protocol is unnecessary. In performing a TCLP analysis, there is a 20:1 dilution of the original sample with the leaching solution. Thus, if the "total constituent" result is less than 20 times the TC level, it is impossible for the leachate to "fail" and the TCLP does not need to be performed. For example, the TC level for lead is 5.0 mg/L (ppm). Therefore, if a sample of lead-contaminated soil contains less than 100 ppm total lead, a TCLP test need not be run to demonstrate that lead is less than the TCLP limit.

13. METHOD PERFORMANCE

13.1. Refer to individual analysis SOPs.

13.2. Training Qualification:

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

14. POLLUTION PREVENTION

14.1. This method does not contain any specific modifications that serve to minimize or prevent pollution.

15. WASTE MANAGEMENT

15.1. Waste generated in this procedure must be segregated and disposed according to the facility's hazardous wastes procedures. The Environmental Health and Safety Director should be contacted if additional information is required.

16. REFERENCES

16.1. Method 1311, Toxicity Characteristic Leaching Procedure, Revision 0, July 1992, SW-846 Final Update I.

16.2. Method 1312, Synthetic Precipitation Leaching Procedure, Revision 0, November 1994, SW-846 Update II.

16.3. Related Documents

16.3.1. Toxicity Characteristic: Corrections to Final Rule. Method 1311, Federal Register, Vol. 55, No. 126, Friday, June 29, 1990.

16.3.2. Toxicity Characteristic: Final Rule. Method 1311, Federal Register, Vol. 55, No. 61, Thursday, March 29, 1990.

16.3.3. Technical Background Document and Response To Comments, Method 1311, Toxicity Characteristic Leaching Procedure, USEPA/OSW, April, 1989.

16.3.4. QA-003, Quality Control Program

16.3.5. CORP-IP-0003NC: Acid Digestion of Aqueous Samples by SW846 and MCAWW 200 Series Methods.

16.3.6. CORP-MT-0001NC: Inductively Coupled Plasma-Atomic Emission Spectroscopy, Spectrometric Method for Trace Element Analysis, Method 6010B and Method 200.7.

16.3.7. CORP-MT-0003NC: Graphite Furnace Atomic Absorption Spectroscopy, (Thallium only)

16.3.8. CORP-MT-0005NC: Preparation and Analysis of Mercury in Aqueous Samples by Cold Vapor Atomic Absorption, SW-846 7470A and MCAWW 245.1.

16.3.9. CORP-MS-0002NC: Determination of Volatile Organics by GC/MS based on Methods 8260B, 624, and 524.2.

16.3.10.CORP-MS-0001NC : GC/MS Analysis Based on Method 8270C and 625.

16.3.11. CORP-GC-0001NC: Gas Chromatographic Analysis Based on Methods 8000B, 8021B, 8081A, 8082, 8151A, 8310, 610, and 8141A.

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

17. MISCELLANEOUS

17.1. Modifications/Interpretations from Reference Methods

17.1.1. Section 11.2: Preliminary Evaluations. Section 7.1 of the source method 1311 states that the sample aliquot used for the preliminary evaluation "...may not actually undergo TCLP extraction." Section 7.1.5 of the source method indicates that the portion used for the preliminary evaluation may be used for either the ZHE or non-volatile extraction if the sample was 100% solid. Section 7.1.5 further indicates that if the sample was subjected to filtration (i.e., < 100% solid) that this aliquot may be used for the non-volatile extraction procedure only as long as sufficient sample is available (minimum 100 g). Samples which have been subjected to the oven drying step may not be used for TCLP extraction because solid phase degradation may result upon heating.

17.1.2. Sections 11.3.6 and 11.4.21: Determination of Filtrate/Extraction Fluid Compatibility. Section 7.2.13 of the source method provides no guidance as to how to make this determination. As a result, the procedure herein was developed.

17.1.3. Section 9.2: TCLP Extraction Blanks. Section 8.1 of the source method states that a minimum of one blank for every 20 extractions "...that have been conducted in an extraction vessel." STL has interpreted this to mean one blank per twenty samples leached per TYPE of leaching vessel (i.e., Bottle or ZHE) per leach fluid used.

17.1.4. Section 11.2.5.5.8.1: Determination of Appropriate Extraction Fluid. Method 1311 does not address the appropriate approach to take if the pH equals 5.0. This SOP requires that Fluid #1 must be used if the pH is less than or equal to 5.0.

17.1.5. Section 9.4: QA/QC - Matrix Spikes. Section 8.2 of the source method states "A matrix spike shall be performed for each waste type..." and "A minimum of one matrix spike must be analyzed for each analytical batch." Further, Section 8.2.3 of the source method also states "The purpose of the matrix spike is to monitor the performance of the analytical methods used, and to

determine whether matrix interferences exist." The standard STL LQM is designed to address the performance monitoring of analytical methodology through the LCS program. A minimum of one MS and MSD will be prepared for each TCLP leachate batch. The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Due to the potential variability of the matrix of each sample, the MS/MSD results have immediate bearing only on the specific sample spiked and not all samples in the batch.

17.1.6. Section 8.2.2 of the source method states that "In most cases, matrix spikes should be added at a concentration equivalent to the corresponding regulatory level." The method also states "If the analyte concentration is less than one half the regulatory level, the spike concentration may be as low as one half of the analyte concentration but may not be less than five times the method detection limit". For several analytes, spiking at the regulatory level is inappropriate to the range of analysis afforded by the determinative methods. Due to the wide range in these levels, STL spikes at the levels specified in the determinative SOPs.

17.2. Modifications from Previous SOP

17.3. Facility Specific SOPs

Each facility shall attach a list of facility specific SOPs or approved attachments (if applicable) which are required to implement this SOP or which are used in conjunction with this SOP. If no facility specific SOPs or amendments are to be attached, a statement must be attached specifying that there are none. Refer to the Appendices for any facility specific information required to support this SOP.

APPENDIX A

TABLES

Table 3 - Toxicity Characteristic Analytes and Regulatory Levels (Final Rule)

Contaminant	mg/L
Arsenic	5.0
Barium	100.0
Benzene	0.5
Cadmium	1.0
Carbon tetrachloride	0.5
Chlordane	0.03
Chlorobenzene	100.0
Chloroform	6.0
Chromium	5.0
o-Cresols	200.0
m-Cresols	200.0
p-Cresols	200.0
Total Cresols (used if isomers not resolved)	200.0
2,4-D	10.0
1,4-Dichlorobenzene	7.5
1,2-Dichloroethane	0.5
2,4-Dinitrotoluene	0.13
1,1-Dichloroethylene	0.7
Endrin	0.02
Heptachlor (& epoxide)	0.008
Hexachlorobenzene	0.13
Hexachlorobutadiene	0.5
Hexachloroethane	3.0
Lead	5.0
Lindane	0.4
Mercury	0.2
Methoxychlor	10.0
Methyl ethyl ketone	200.0
Nitrobenzene	2.0
Pentachlorophenol	100.0
Pyridine	5.0
Selenium	1.0
Silver	5.0
Tetrachloroethylene	0.7
Toxaphene	0.5
Trichloroethylene	0.5
2,4,5-Trichlorophenol	400.0
2,4,6-Trichlorophenol	2.0
2,4,5-TP (Silvex)	1.0
Vinyl chloride	0.2

APPENDIX B

FIGURES

Figure 1 & 2 - Rotary Agitation Apparatus and Zero Headspace Extraction Vessel (ZHE)

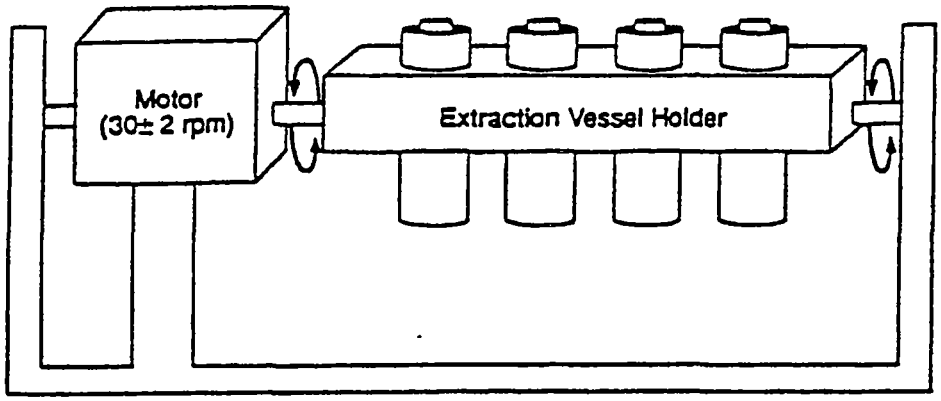

Figure 1. Rotary Agitation Apparatus

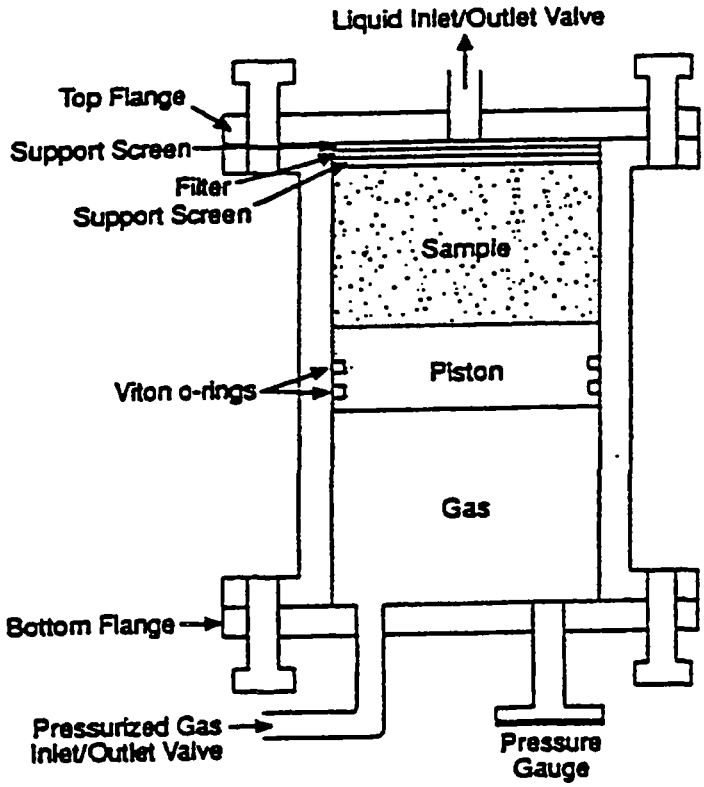

Figure 3 - US Environmental Protection Agency Memorandum #35, Page 1

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

OFFICE OF
SOLID WASTE AND EMERGENCY RESPONSE

MEMORANDUM # 35

DATE: June 12, 1992

SUBJECT: Notes on RCRA Methods and QA Activities

From: Gail Hansen, Chief
Methods Section (OS-331)

This memo addresses the following topics:

- 1992 Symposium on Waste Testing and Quality Assurance
- SW-846 Update
  - Final Rule for January 23, 1989 Proposed Rule
  - Notice, Proposed Rulemaking for the Second Update to the Third Edition
- Chlorofluorocarbon 113 (CFC-113) Solvent Replacement Update
- Environmental Monitoring Methods Index (EMMI)
- Sampling Work Group Formation
- MICE Update
- Oily Waste Analysis
- Electronic SW-846 Availability.

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Figure 3 - US Environmental Protection Agency Memorandum #35, Page 10

Oily Waste Analysis

One of the most frequently asked questions on the MICE Service concerns the application of the TCLP, Method 1311, to oily wastes. Many callers request technical guidance on the extraction of oily wastes due to the difficulty in the filtration on these types of waste. In many cases, an oily waste does not filter completely due to premature clogging of the glass fiber filter. This can result in the retention of standing liquid on the glass fiber filter. Material that do not pass through the glass fiber filter at the conclusion of the filtration step is defined by the method as the solid phase of the waste. The solid phase is then subjected to the leaching procedure of the TCLP. For oily wastes, clogging of the glass fiber filter can result in an overestimation of the amount of solid material available for leaching.

To solve this problem, the Agency recommends a conservative approach, one that probably will overestimate the amount of leaching. Rather than performing the TCLP extraction on the unfiltered portion of the oily waste, assume the waste is 100% liquid (e.g., will pass through the glass fiber filter) and perform a totals analysis on the oily waste to determine if the oil exceeds the appropriate regulatory level.

Filterable waste oil generated during the TCLP must be analyzed for a variety of organic and inorganic analytes. The OSW recognizes the difficulty in achieving acceptable performance for the analysis of waste oil using methods currently provided in SW-846. As a result, the Agency will provide several new methods for the preparation and analysis of oil samples to the Organic Methods Workgroup in July. In addition, a microwave assisted digestion procedure should improve the analysis of metals and will be proposed as part of the Second Update of the Third Edition of SW-846. Brief descriptions of these techniques are provided below, for additional information on the organic procedures contact Barry Lesnik at (202) 260-7459. For additional information on microwave digestion contact Ollie Fordham (202) 260-4778.

The use of purge-and-trap (Method 5030) for volatiles in oil generally results in severe contamination of analytical instrumentation. Traps, transfer lines and chromatography columns may become contaminated with oil. This leads to elevated baselines, hydrocarbon background in subsequent analyses, and cross-contamination. Headspace (Method 3810) is currently allowed only as a screening procedure in SW-846. The Agency is evaluating the use of headspace in conjunction with isotope dilution mass spectrometry for the quantitative analysis of volatiles in oil. Headspace reduces interference problems encountered with purge-and-trap. However, headspace quantitation can be questionable because the distribution of analytes is not

APPENDIX C

Logbook Pages

TCLP/SPLP ZHE Logbook

STL NORTH CANTON ZHE LOGBOOK

Sample Number	Extraction Vessel ID	Matrix	Sample Wt (g)	Extraction Buffer ID	Date On	Time On	Date Off	Time Off	Tumbler ID	Tumbler Speed 30±2 rpm	Extraction Fluid ID	Initial ZHE Pressure	Final ZHE Pressure	Comments

APPENDIX C – Logbook Pages

STL NORTH CANTON ZHE LOGBOOK

	A	B	C	D	E	F		G	H	
Sample Number	Weight of Container + Sample (g)	Weight of Container + Residue (g)	Difference (A – B) Sample Weight (g)	Weight of the Syringe (or vials) (g)	Weight of the Syringe (or vials) + Filtrate (g)	Difference (E – D) Filtrate Weight (g)	Volume of Filtrate* (mL)	Difference (C – F) Wet Solids Weight (g)	G x 20 Buffer Amount (mL)	Initials

* Filtrate volume only needed when filtrate is incompatible with leachate

TCLP/SPLP Bottle Extraction Logbook

SOP No.: NC-IP-0005

STL NORTH CANTON TCLP LOGBOOK

				Pre-Test			% Dry Solids				Leach Start					Leach Finish					
Pre-Prep Batch	Sample Number	Parameters	Matrix	Sample Wt (g)	pH after water	pH after heating	Sample Wt (g)	Filter Wt (g)	Filter + Particulates Wt (g)	% Dry Solids	Sample Wt (g)	Buffer # / ID	Date On	Time On	pH On	Date Off	Time Off	pH Off	Tumbler ID	Initials	Comments
		M B P H																			
		M B P H																			
		M B P H																			
		M B P H																			
		M B P H																			
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SOP No.: NC-IP-0005 STL NORTH CANTON TCLP LOGBOOK

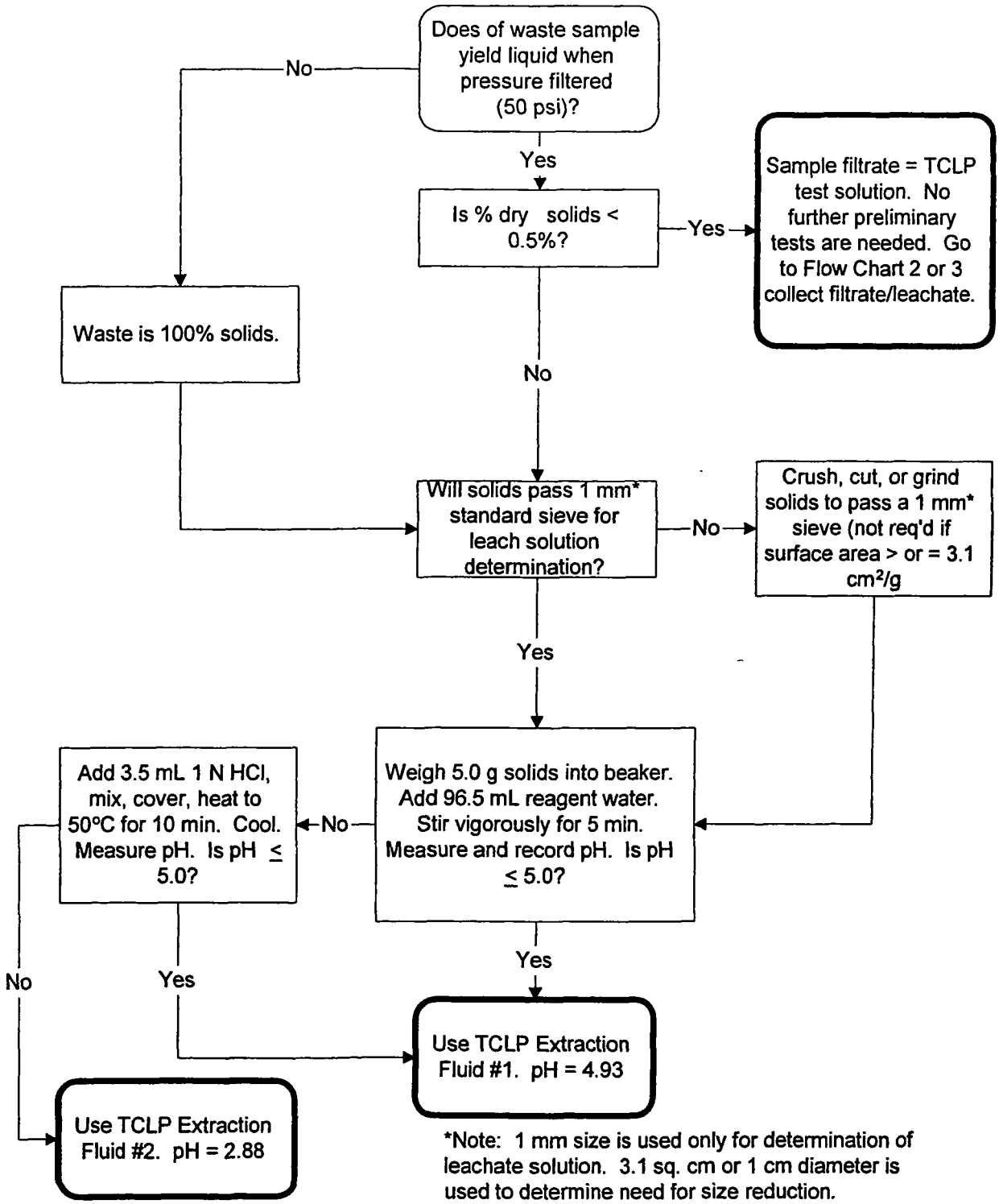
	A	B	C	D	E	F		G	H		
Sample Number	Weight of Container + Sample (g)	Weight of Container + Residue (g)	Difference (A – B) Sample Weight (g)	Weight of the Filtrate Bottle (g)	Weight of the Filtrate bottle + Filtrate(g)	Difference (E – D) Filtrate Weight (g)	Volume of Filtrate* (mL)	Difference (C – F) Wet Solids Weight (g)	G x 20 Buffer Amount (mL)	Initials	Comments

* Filtrate volume only needed when filtrate is incompatible with leachate

APPENDIX D

FLOW CHARTS

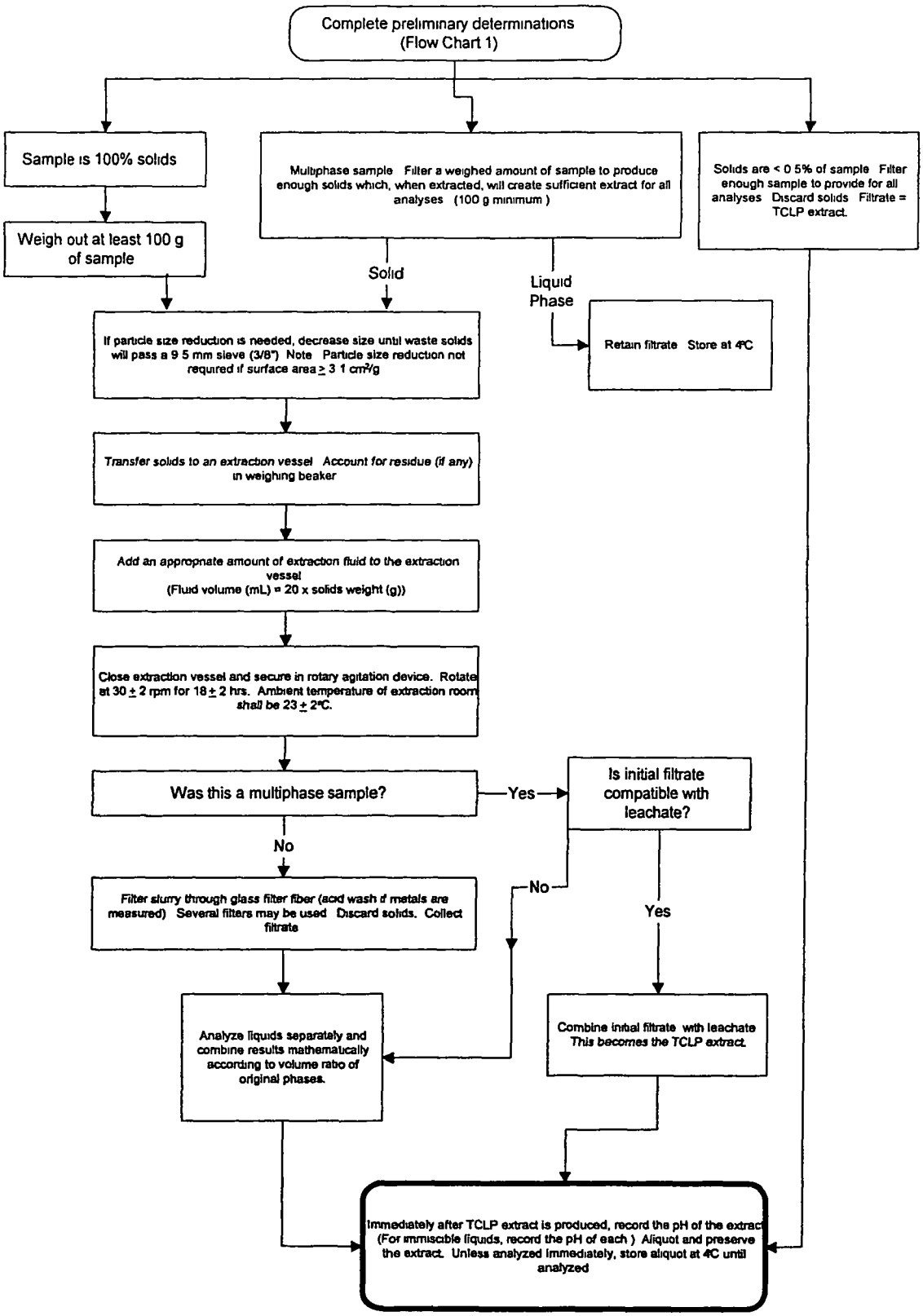
Flow Chart 1. Preliminary Sample Evaluation (Section 11.2)



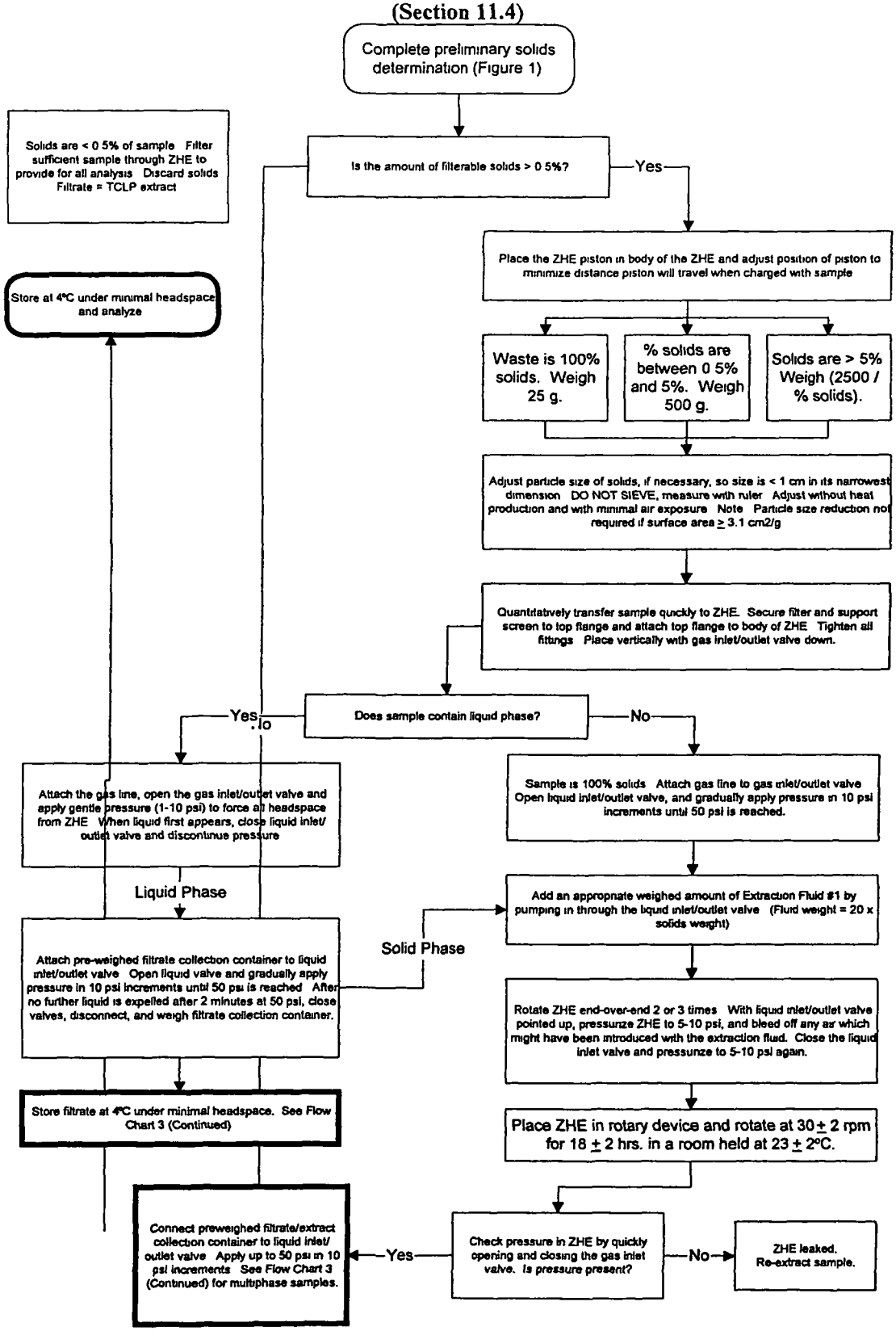
*Note: 1 mm size is used only for determination of leachate solution. 3.1 sq. cm or 1 cm diameter is used to determine need for size reduction.

x

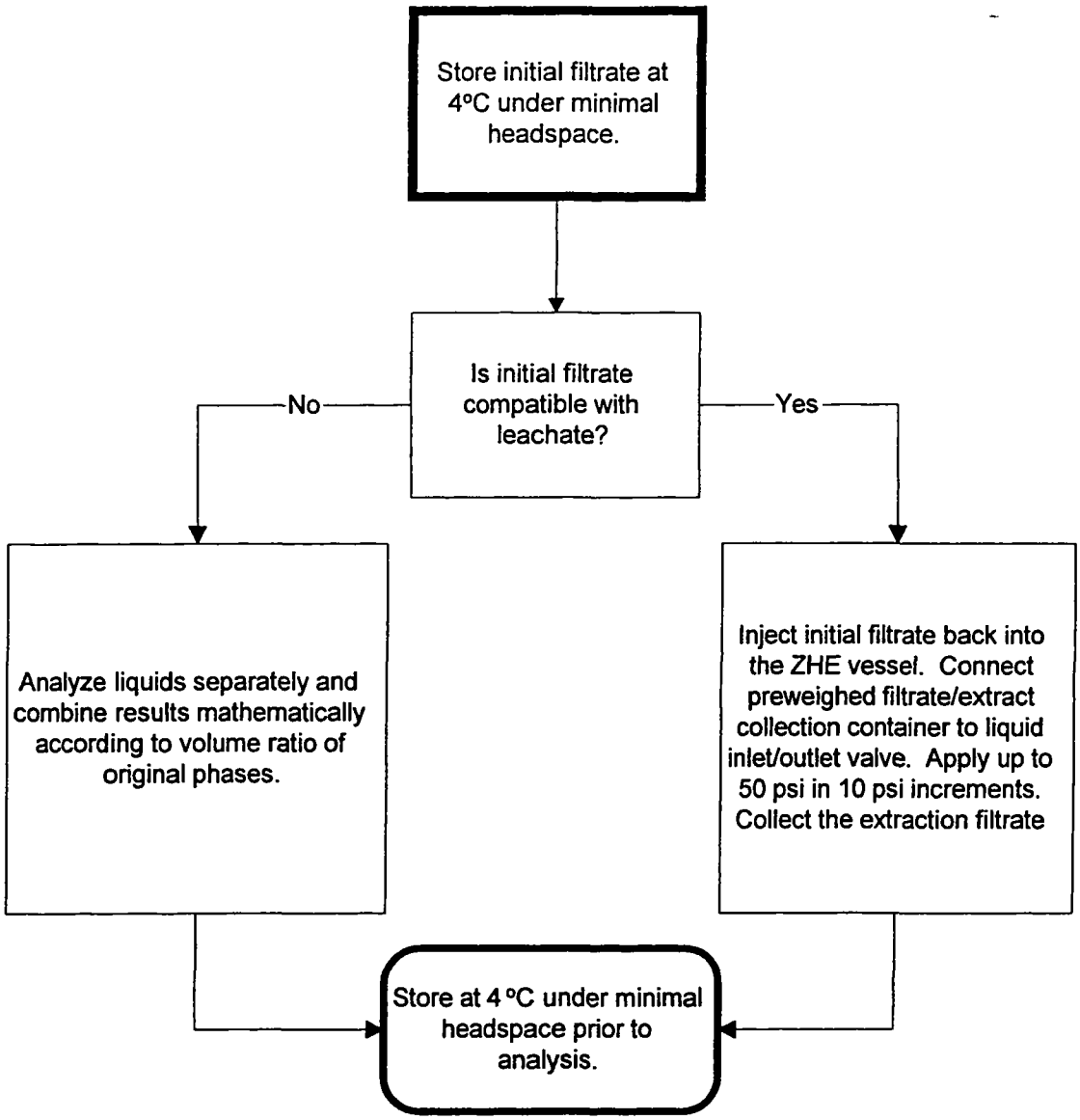
Flow Chart 2. Bottle Extraction, Non-Volatile Constituents (Section 11.3)



Flow Chart 3. ZHE Extraction, Volatile Constituents (Section 11.4)



Flow Chart 3. ZHE Extraction (Continued)



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Implementation Date: 06/05/01

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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APPENDIX A .....

ANALYSIS OF VOLATILE ORGANICS BY METHOD 624 55

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Table 11 SPCC Compounds and Minimum Response Factors

Table 12 CCC Compounds

Table 13 Characteristic Ions

Table A-1 Method 624 Analytes and Reporting Limits

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.

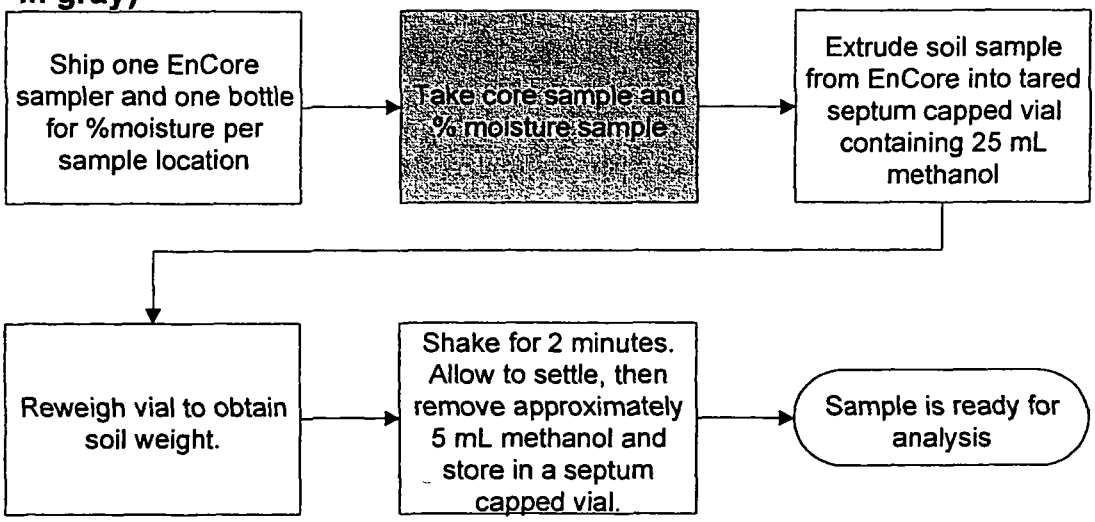
8.9. Aqueous samples are stored in glass containers with Teflon lined septa at 4°C +/- 2°C, with minimum headspace.

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.

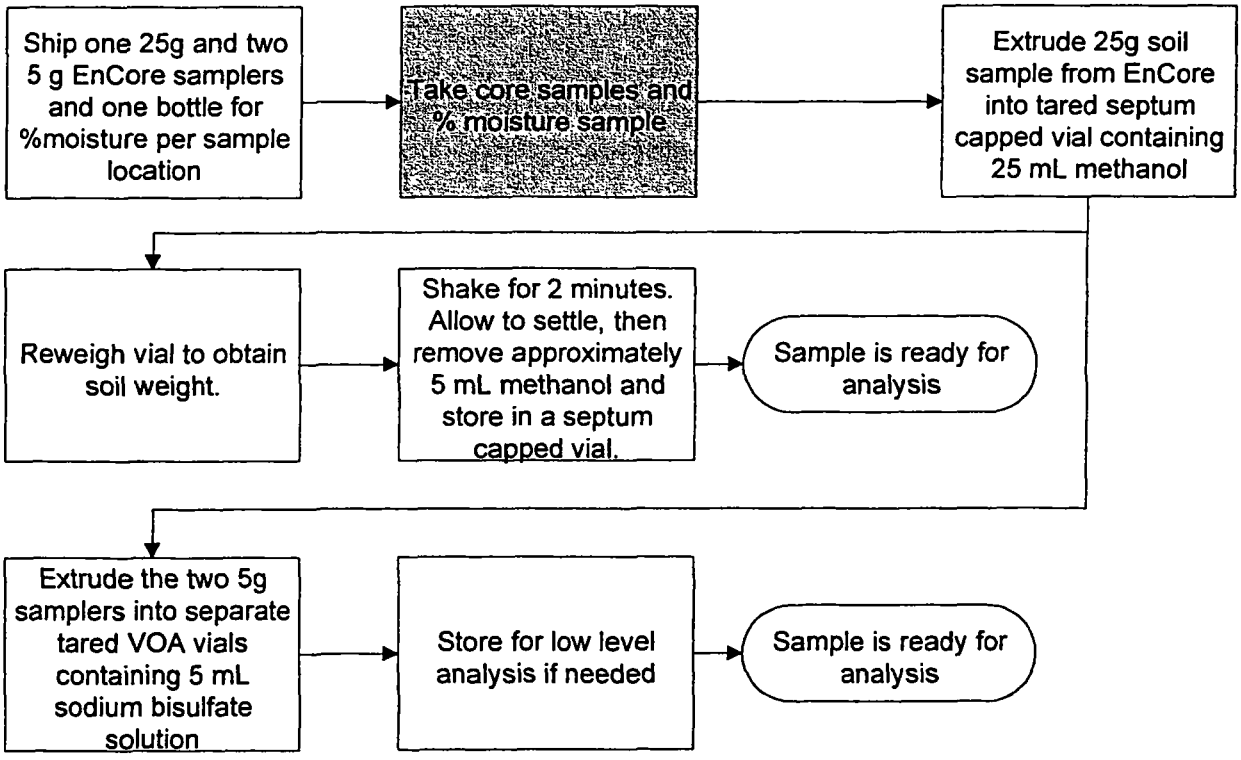
8.11. The maximum holding time is 14 days from sampling until the sample is analyzed. (Samples that are found to be unpreserved still have a 14 day holding time. However they should be analyzed as soon as possible. The lack of preservation should be addressed in the case narrative). Maximum holding time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

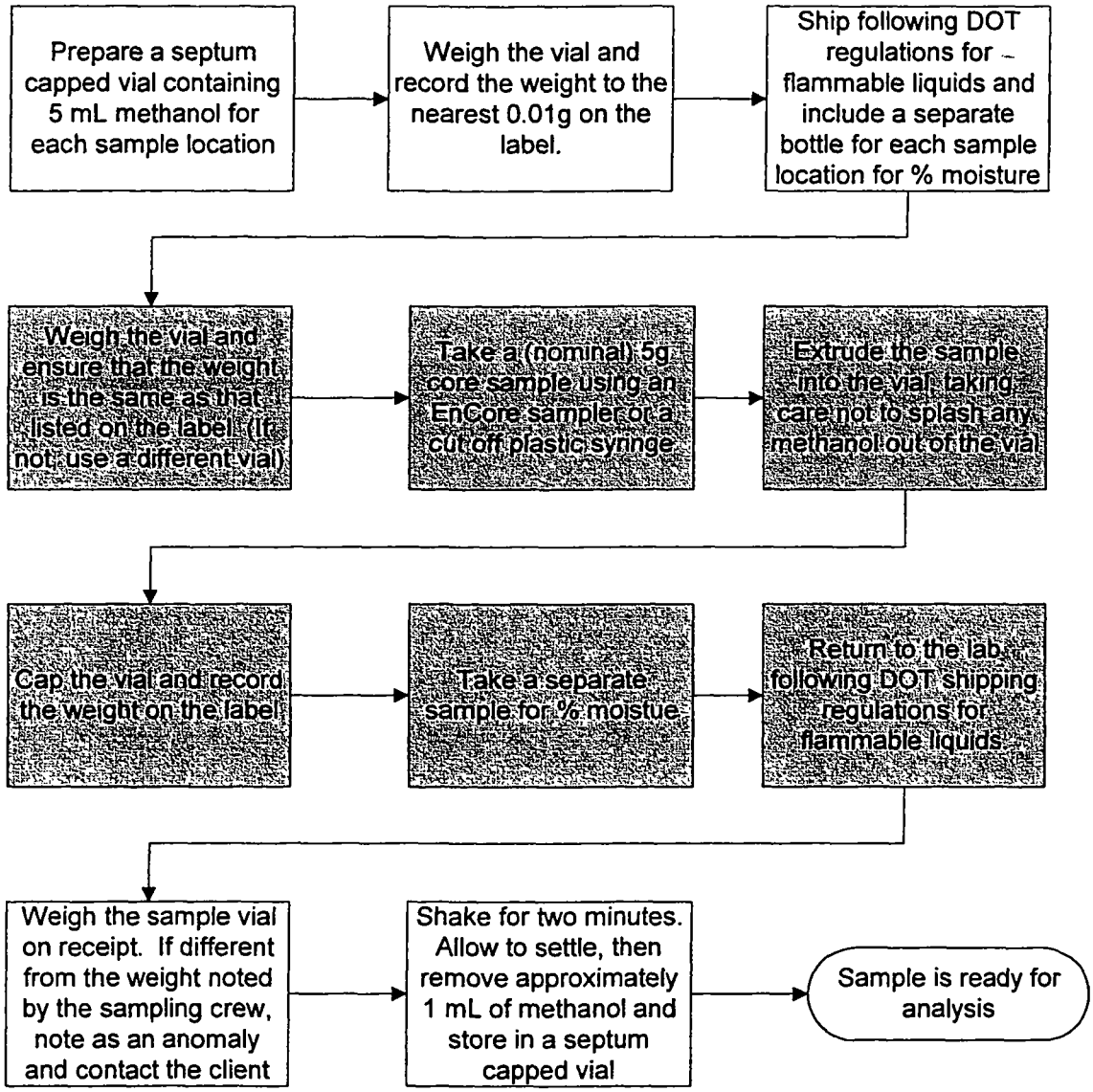
EnCore procedure when low level is not required (field steps in gray)



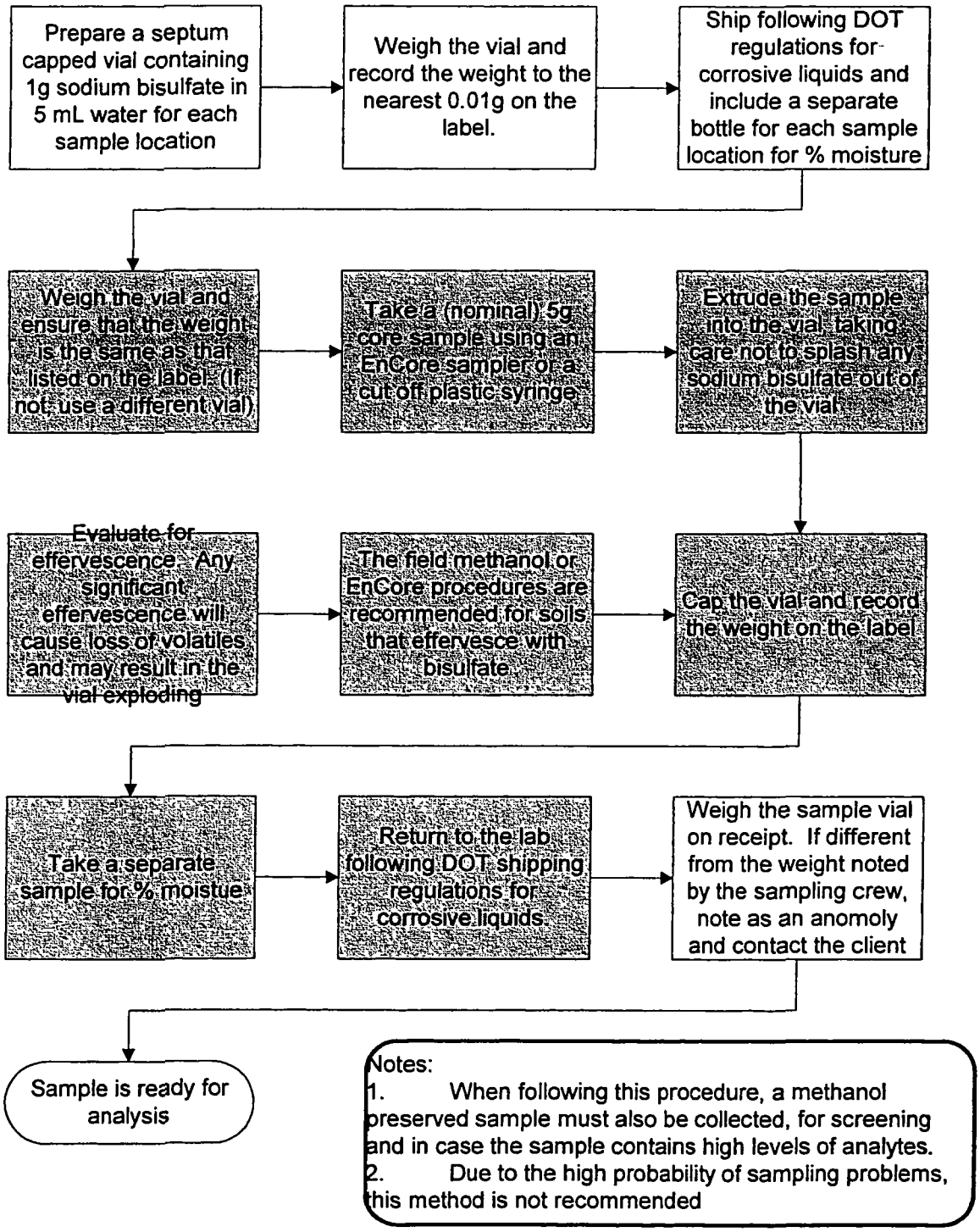
EnCore procedure when low level is required



Field methanol extraction procedure (field steps in gray)



Field bisulfate preservation procedure (field steps in gray)



Notes:
1. When following this procedure, a methanol preserved sample must also be collected, for screening and in case the sample contains high levels of analytes.
2. Due to the high probability of sampling problems, this method is not recommended

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 ≤ 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. $1/\text{Concentration}^2$ weighting (often called $1/X^2$ weighting) will improve accuracy at the low end of the curve and should be used if the data system has this capability.

10.4.8. If time remains in the 12-hour period initiated by the BFB injection before the initial calibration, samples may be analyzed. Otherwise, proceed to continuing calibration.

10.4.9. The calibration standards for the initial 5-point calibration for low level soils that are not preserved in sodium bisulfate (i.e. are preserved by freezing, or not preserved) must be heated to 40°C for purging. Using this calibration curve for water samples is acceptable as long as all calibration, QC, and samples are also heated to 40°C. A separate five point calibration must be prepared for analysis of low level soils that are preserved with sodium bisulfate. Low level soils analysis requires the use of a closed vial autosampler

such as the Varian Archon, O.I. 4552 or Tekmar Precept. Each standard for analysis of sodium bisulfate preserved samples is prepared by spiking the methanolic standard solution through the septum of a VOA vial containing 5 mL of water and 1 g sodium bisulfate. The standards are heated to 40°C for purging. All low-level soil samples, standards, and blanks must also be heated to 40°C for purging. 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

$$\%RSD = \frac{\textbf{Standard Deviation}}{\overline{RFi}} \times 100$$

$\overline{RFi}$ = **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 ≤ 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 ≤ 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

$$\textbf{Concentration } \mu g / L = A + Bx + Cx^2$$

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.

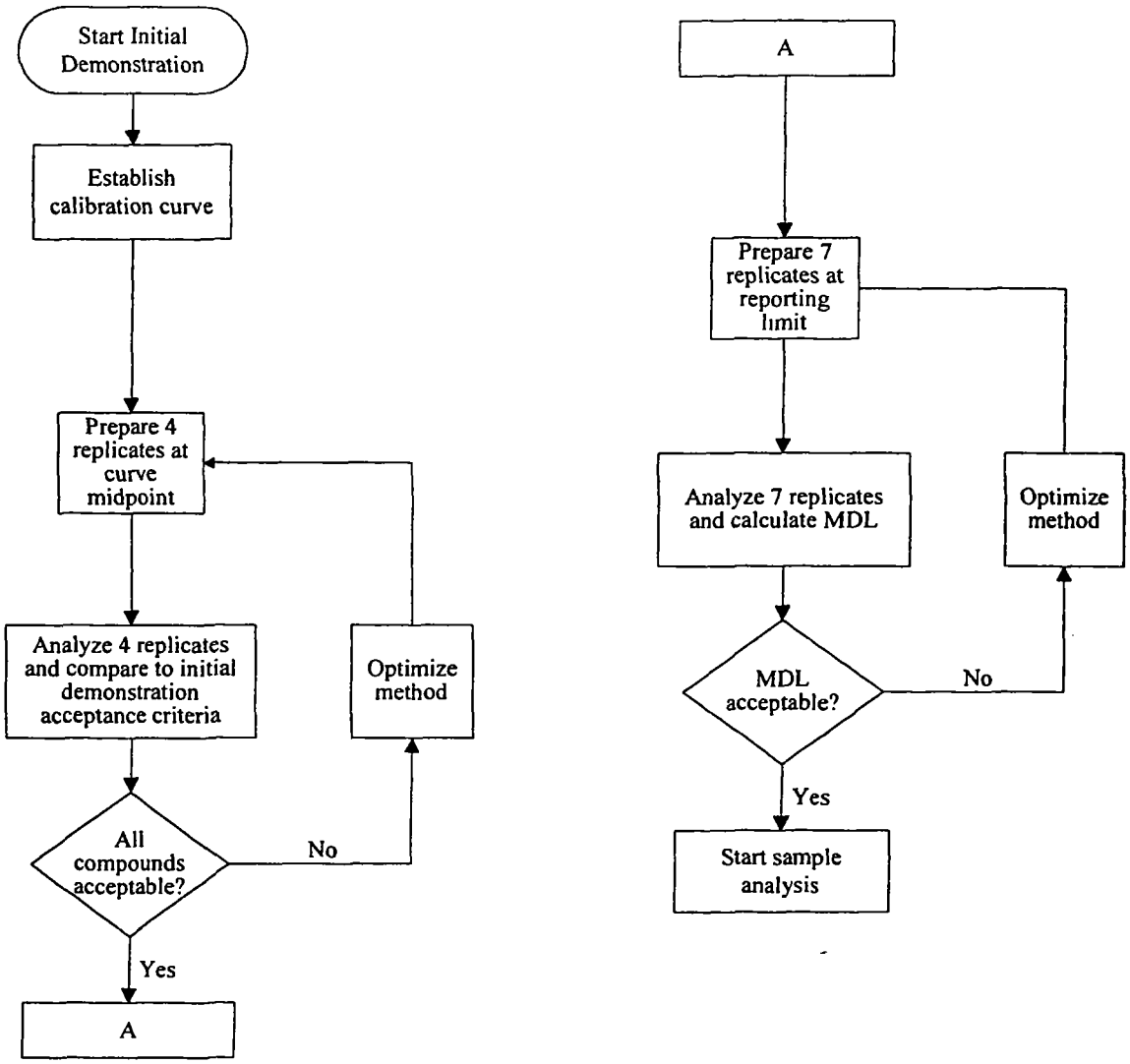

Start Initial Demonstration
Establish calibration curve
Prepare 4 replicates at curve midpoint
Analyze 4 replicates and compare to initial demonstration acceptance criteria
All compounds acceptable?
No
Optimize method
Yes
A
A
Prepare 7 replicates at reporting limit
Analyze 7 replicates and calculate MDL
MDL acceptable?
No
Optimize method
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

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
tert-Butylbenzene	5	20	50	100	200
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

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
1,4-Dioxane	50	250	500	1000	2000
Dibromomethane	1	5	10	20	40
Bromodichloromethane	1	5	10	20	40
2-Chloroethyl vinyl ether	2	10	20	40	80
cis-1,3-Dichloropropene	1	5	10	20	40
4-Methyl-2-pentanone	2	10	20	40	80
Toluene	1	5	10	20	40
trans-1,3-Dichloropropene	1	5	10	20	40
Ethyl Methacrylate	1	5	10	20	40
1,1,2-Trichloroethane	1	5	10	20	40
1,3-Dichloropropane	1	5	10	20	40
Tetrachloroethene	1	5	10	20	40
2-Hexanone	2	10	20	40	80
Dibromochloromethane	1	5	10	20	40
1,2-Dibromoethane	1	5	10	20	40
Chlorobenzene	1	5	10	20	40
1,1,1,2-Tetrachloroethane	1	5	10	20	40
Ethylbenzene	1	5	10	20	40
m + p-Xylene	2	10	20	40	80
Xylene-o	1	5	10	20	40
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

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-Dichlorobenzene	1	5	10	20	40
1,2-Dibromo-3-chloropropane	1	5	10	20	40
1,2,4-Trichlorobenzene	1	5	10	20	40
Hexachlorobutadiene	1	5	10	20	40
Naphthalene	1	5	10	20	40
1,2,3-Trichlorobenzene	1	5	10	20	40
Cyclohexane	1	5	10	20	40
Methyl Acetate	2	10	20	40	80
Methylcyclohexane	1	5	10	20	40
1,3,5-Trichlorobenzene	1	5	10	20	40

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

Table 3

STL Appendix IX Standard and Reporting Limits, 5 mL purge

Compound	CAS Number	Reporting Limits			
		5 mL Water µg/L	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-	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
	5					
Trichloroethene	79-01-6	X	X	X	X	X
Dibromochloromethane	124-48-1	X		X	X	X
1,2-Dibromoethane	106-93-4				X	X
1,2,3-Trichloropropane	96-18-4				X	X
1,1,2-Trichloroethane	79-00-5	X		X	X	X
Benzene	71-43-2	X	X	X	X	X
Ethylmethacrylate	97-63-2				X	X
trans-1,3-Dichloropropene	10061-02-6	X		X	X	X
Bromoform	75-25-2	X		X	X	X
4-Methyl-2-pentanone	108-10-1	X		X	X	X
2-Hexanone	591-78-6	X		X	X	
Tetrachloroethene	127-18-4	X	X	X	X	X
Toluene	108-88-3	X		X	X	X
1,1,2,2-Tetrachloroethane	79-34-5	X		X	X	X
2-Chloroethyl vinyl ether	110-75-8					
Vinyl acetate	108-05-4				X	
Chlorobenzene	108-90-7	X	X	X	X	X
Ethylbenzene	100-41-4	X		X	X	X
Styrene	100-42-5	X		X	X	
t-1,4-Dichloro-2-butene	110-57-6				X	
m and p Xylenes		X		X	X	X
o-xylene	95-47-6	X		X	X	X
Total xylenes	1330-20-7	X		X	X	X
1,3-Dichlorobenzene	541-73-1					
1,4-Dichlorobenzene	106-46-7					
1,2-Dichlorobenzene	95-50-1					

Table 6

Reportable Analytes for STL Standard Tests, Appendix IX standard

Compound	Number	STL Standard List	TCLP	TCL	Appendix IX	UTS
Allyl Chloride	107-05-1				X	
Acetonitrile	75-05-8				X	X
Dichlorofluoromethane	75-43-4					
Isopropyl ether	108-20-3					
Chloroprene	126-99-8				X	
n-Butanol	71-36-3					
Propionitrile	107-12-0				X	
Methacrylonitrile	126-98-7				X	X
Isobutanol	78-83-1				X	X
Methyl methacrylate	80-62-6				X	X
1,1,1,2-Tetrachloroethane	630-20-6				X	X
1,2-Dibromo-3-chloropropane	96-12-8				X	X
Ethyl ether	60-29-7					X
Ethyl Acetate	141-78-6					X
2-Nitropropane	79-46-9					
Cyclohexanone	108-94-1					X

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 from historical data and are maintained by the QA dedartment.

3) Full analyte spikes may also be used at the laboratories option or at client request.

Table 10

BFB Key Ion Abundance Criteria

Mass	Ion Abundance Criteria
50	15% to 40% of Mass 95
75	30% to 60% of Mass 95
95	Base Peak, 100% Relative Abundance
96	5% to 9% of Mass 95
173	Less Than 2% of Mass 174
174	Greater Than 50% of Mass 95
175	5% to 9% of Mass 174
176	Greater Than 95%, But Less Than 101% of Mass 174
177	5% to 9% of Mass 176

Table 11

SPCC Compounds and Minimum Response Factors

Compound	8260B, 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
1,1-Dichloroethene	96	61	98

Table 13

Characteristic ions

Compound	Primary*	Secondary	Tertiary
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
Tetrachloroethene	164	166	131

Table 13

Characteristic ions

Compound	Primary*	Secondary	Tertiary
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

Implementation Date: 06/05/01

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 2.2, DATED 02/05/01)

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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. Because of differences between various makes and models of CVAA instrumentation, no detailed operating instructions can be provided. Refer to the facility specific instrument operating SOP and the CVAA instrument manual for detailed setup and operation protocols.

11.2.2. All labs are required to detail the conditions/programs utilized for each instrument within the facility specific instrument operation SOP.

11.2.3. When ready to begin analysis, add 6 mL of sodium chloride-hydroxylamine hydrochloride solution to the samples to reduce the excess permanganate (the permanganate has been reduced when no purple color remains). Add this solution in 6-mL increments until the permanganate is completely reduced.

11.2.4. Manual determination:

11.2.4.1. Treating each sample individually, purge the 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:

$$mg/L = C \times D$$

Where:
C = Concentration (mg/L) from instrument readout
D = Instrument dilution factor

12.6. The LCS percent recovery is calculated according to the following equation:

$$\%R = 100\left(\frac{Found(LCS)}{True(LCS)}\right)$$

12.7. Appropriate factors must be applied to sample values if dilutions are performed.

12.8. Sample results should be reported with up to three significant figures in accordance with the STL 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. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition, Final Update II, Revision I, September 1994, Method 7470A (Mercury).

16.2. "Methods for the Chemical Analysis of Water and Wastes", EPA-600/4-79-020, U.S.EPA, August 1983, Method 245.1.

16.3. U.S.EPA Statement of Work for Inorganics Analysis, ILMO3.0 and ILMO4.0.

16.4. QA-003, STL North Canton QC Program.

16.5. QA-004, Rounding and Significant Figures.

16.6. QA-005, Method Detection Limits.

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

17.1. Modifications/Interpretations from reference method.

17.1.1. Modifications from both 7470A and 245.1.

17.1.1.1. The 200 series methods and Chapter 1 of SW846 specify the use of reagent water with a purity equivalent to ASTM Type II water. This SOP specifies the use of a Millipore DI system or equivalent

to produce reagent water. This SOP requires that reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks.

17.1.1.2. This SOP allows for the use of reduced sample volumes to decrease waste generation. Reagent levels are adjusted to maintain the same ratios as stated in the source methods. According to a letter from Robert Booth of EPA EMSL-Cinn to David Payne of EPA Region V, "Reduction in sample size and appropriate corresponding reduction in sample volume is not considered a significant change in the methodology."

17.1.1.3. The alternate run sequence presented in Section 11.2.12 is consistent with method requirements. An additional QC analysis (CRA) was added to accommodate the CLP protocol requirements.

17.1.2. Modifications from Method 7470A

17.1.2.1. Chapter 1 of SW-846 states that the method blank should not contain any analyte of interest at or above the MDL. This SOP states that the method blank must not contain any analyte of interest at or above the reporting limit.

17.1.2.2. Documentation is on file from EPA's Office of Solid Waste (Olliver Fordham 11/28/95) regarding the acceptance of the autoclave as an equivalent heating device to the water bath. In his letter, Mr. Fordham cited the CLP water protocol 245.1 CLP-M and therefore the operating parameters from that method were adopted for 7470A (15 minutes at 120 °C and 15 lbs.).

17.1.3. 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

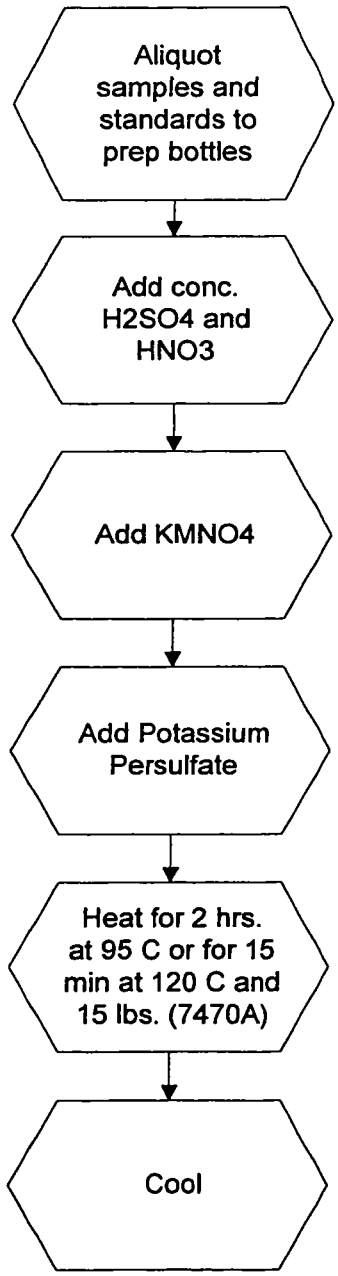
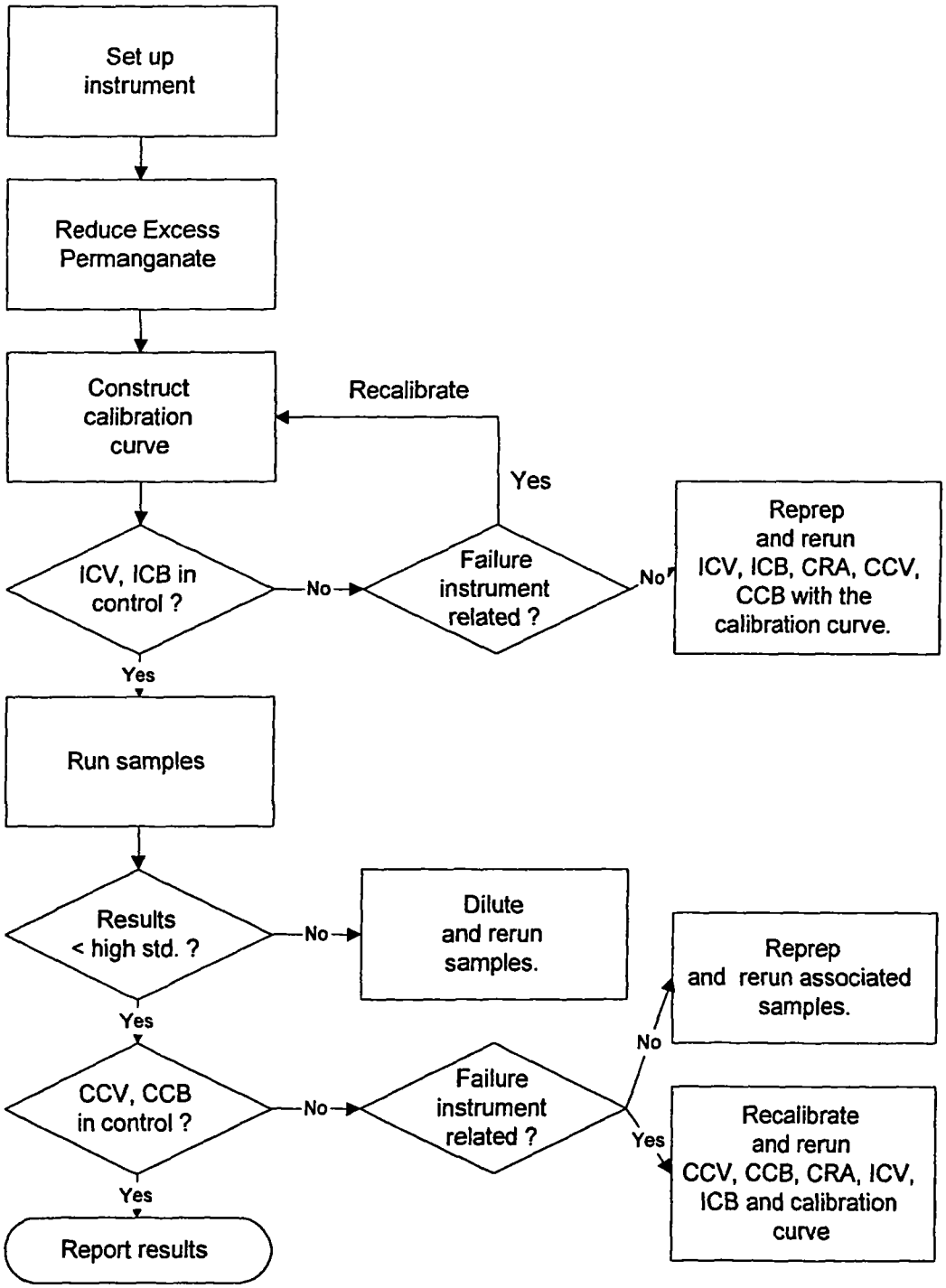


Figure 2. CVAA Mercury Analysis



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

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

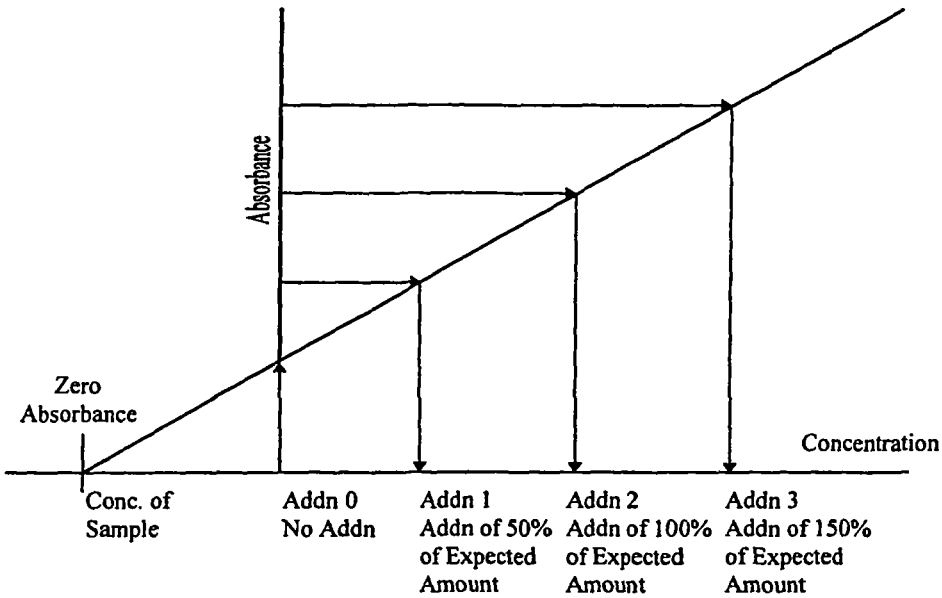
APPENDIX C. MSA GUIDANCE

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.

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.

QUANTERRA® STANDARD OPERATING PROCEDURE

TITLE: FLASHPOINT CLOSED CUP

(SUPERSEDES: ENSECO SOP #LM-WALN-1151 (REVISION 0))

Prepared by:		10/29/97 Date
Reviewed by:	Technology Specialist	10/29/97 Date
Approved by:	Quality Assurance Manager	11/3/97 Date
Approved by:	Environmental Health and Safety Coordinator	10-30-97 Date
Approved by:	Laboratory Director	11-4-97 Date

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QUANTERRA® STANDARD OPERATING PROCEDURE

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1. SCOPE AND APPLICATION

1.1. This method is applicable to the determination of Flashpoint by Pensky-Martens closed cup tester in a variety of wastes and liquids. It is based on ASTM Method D93-85 and SW846 Method 1010. Although the approximate working range is 20 - 200 °F, the test is generally considered complete when the temperature reaches 180°F without a measurable Flashpoint.

1.2. This document accurately reflects current laboratory standard operating procedures (SOP) as of the date above. All facility SOPs are maintained and updated as necessary by the laboratory QA department.

2. SUMMARY OF METHOD

2.1. The sample is heated at a slow constant rate with continual stirring if it is a liquid or water. A small test flame is directed into the sample cup at regular intervals. The Flashpoint is the lowest temperature at which the test flame causes the vapor above the sample to ignite.

3. DEFINITIONS

3.1. Refer to the glossary in the Quality Assurance Management Plan (QAMP).

4. INTERFERENCES

4.1. Not Applicable

5. SAFETY

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

5.2. Eye protection that satisfies ANSI Z87.1 (as per the Chemical Hygiene Plan), laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

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

5.3.1. Chemicals known to be **flammable** are: **p-Xylene**

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

5.5. The preparation of standards and reagents will be conducted in a fume hood with the sash closed as far as the operation will permit.

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

6. EQUIPMENT AND SUPPLIES

6.1. Pensky-Martens closed cup tester with stirrer and stirring motor

6.2. Flash point sample cup

6.3. Thermometer: 20 - 200°F range (made for the Pensky-Martens)

6.4. Barometer: cm

7. REAGENTS AND STANDARDS

7.1. Reagents

7.1.1. p-Xylene

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Samples are not chemically preserved.

8.2. Samples are stored in glass containers at 4°C ± 2°C. Samples are not to be stored in plastic containers since volatile materials may diffuse through the walls of the enclosure.

9. QUALITY CONTROL

9.1. Batch Definition

9.1.1. A batch is a group of no greater than 20 samples excluding QC samples (LCS, Method Blank, MS, MSD) which are processed similarly, with respect to the procedure. All sample setups must be initiated within a 24 hour period from the initial preparation or extraction and without interruption of the process. All samples

within the batch must be treated with the same lots of reagents and the same processes.

9.2. Duplicates

9.2.1. Sample duplicates are performed at a minimum frequency of 10% (or one per analytical batch) and must meet laboratory-specific limits for precision.

10. CALIBRATION AND STANDARDIZATION

10.1. Calibration of tester

10.1.1. Determine the flash point of p-xylene following the procedures outlined in 11.4

10.1.2. The tester is operating properly when a value of 81± 2°F is obtained.

11. PROCEDURE

11.1. One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo and is approved by a Technical Specialist and QA Manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file.

11.2. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

11.3. Sample Preparation Procedure

11.3.1. Not Applicable

11.4. Sample Analysis Procedure

11.4.1. Operate the Pensky-Martens tester according to the manufacturer's specifications, in a well-ventilated area away from flammable materials and significant air movement. Performing this analysis under a hood is the best approach - ensure that the air intake and hood lights are turned off. Fill the sample cup to the designated line with sample and assemble the tester as directed.

11.4.2. A flash check must be analyzed with each analytical batch of samples. The compound p-Xylene is used to provide the analyst a reference true flash. The flash

temperature is recorded on the analytical logsheet. The true flash temperature for p-Xylene is 80°F.

11.4.3. Begin mixing the sample (90 to 130 rpm - turn the knob to 4-5 on the control box to accomplish this) and record the initial temperature. Stirring can not be accomplished on a solid matrix so the stirring apparatus should be removed. Light the ignition flame and with this light the test flame. Adjust test flame to approximately 1/4 inch diameter. Apply heat such that the temperature rise is 9 to 11° F per minute. Shut off the stirrer. Apply the test flame to sample and remove it. The total time of the application should take 1.5 seconds. Restart the stirrer. Repeat this process every 2°F rise in temperature until the temperature reaches 180°F. A Flashpoint is the temperature at which the vapors ignite. A true flashpoint is indicated by a whitish-blue flame which is rapidly emitted and is accompanied by an audible "whoosh" sound. Record the temperature at which the flash occurred on the analytical logsheet. If the temperature reaches 180°F and no flash occurs, shut off the heater and stirrer and record > 180°F as the Flashpoint on the analytical logsheet.

11.4.4. Some wastes that contain halogenated solvents may exhibit an apparent flash which is referred to as a "false flash". This is detected by a green color or halo in the test flame, but is not due to the ignition of the vapors from the sample.

11.4.5. Record the barometric pressure.

11.4.6. If solvents are used to clean sample cups, be sure to clean thoroughly with reagent water to prevent contamination. Be sure to read the thermometer prior to applying the test flame, because reading it after a flash may give an erroneous high result due to the flash.

NOTE: Some samples may burn, but not flash. Record DNF (does not flash) along with the initial temperature at which it burns.

Some samples have a Flashpoint below room temperature. If this is known, the sample should be chilled to just above freezing and then analyzed promptly to confirm a true Flashpoint.

False flashes should not be confused with true flashes. False flashes give off a green to green-blue flame with no pronounced noise. A true flash produces a flame which is bright and, most important, loud. Only record flashes that are visually and audibly pronounced as true flashes; however, record any other anomalies.

11.5. Analytical Documentation

11.5.1. Record all analytical information in the analytical logsheet, including the analytical data from standards, and any corrective actions or modifications to the method.

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

11.5.3. Documentation such as all associated instrument printouts (final runs, screens, reruns, QC samples, etc.) and daily calibration data corresponding to all final runs is available for each data file.

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

12. DATA ANALYSIS AND CALCULATIONS

12.1. Use the following equation to calculate the Flashpoint:

$$\textbf{Flash} = F + [0.6\ (76 - BP)]$$

Where: F = *observed flash temperature, °F*

BP = *barometric pressure, cm*

12.2. If the sample did not flash, report > 180°F

13. METHOD PERFORMANCE

13.1. Each laboratory must have initial demonstration of performance data on file and corresponding method detection limit files.

13.2. Training Qualifications:

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

14. POLLUTION PREVENTION

14.1. This method does not contain any specific modifications that serve to minimize or prevent pollution.

15. WASTE MANAGEMENT

15.1. Solvent waste must be disposed of in clearly labeled waste cans.

15.2. Solid materials (gloves, soiled paper products, etc.) are placed in the solid debris container. Do not put liquids in the solid waste container.

15.3. Refer to the Laboratory Sample and Waste Disposal plan.

15.4. Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices of Quanterra. They must have training on the hazardous waste disposal practices upon initial assignment to these tasks, followed by an annual refresher training.

16. REFERENCES

16.1. References

16.1.1. Annual Book of ASTM Standards, ASTM Method D93-85, Flashpoint by Pensky-Martens Closed Tester, Volume 5.01, 1987

16.1.2. SW846, Test Methods for Evaluating Solid Waste, Third Edition, Pensky-Martens Closed Cup Method for Determining Ignitability, Method 1010

16.1.3. Quanterra® Quality Assurance Management Plan (QAMP), current revision

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

17.1. Troubleshooting guide

17.1.1. Some matrices will not mix. If this is the case, the Open Cup Flashpoint Method (NC-WC-0002) is preferred.

LABORATORY-SPECIFIC

STL NORTH CANTON STANDARD OPERATING PROCEDURE

TITLE: PH ELECTROMETRIC METHOD

(SUPERSEDES: REVISION 4.0; DATED 01/04/99)

Prepared by:	Susan A Macurzak	11/28/00 Date
Reviewed by:	Kurt C. Ill Technology Specialist	11/28/00 Date
Approved by:	Carol Ann Palm Quality Assurance Manager	11/29/00 Date
Approved by:	[signature] Environmental Health and Safety Coordinator	12-4-00 Date
Approved by:	Christopher F. Oprandi Laboratory Director	11/28/00 Date

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LABORATORY-SPECIFIC

STL NORTH CANTON STANDARD OPERATING PROCEDURE

TITLE: PH ELECTROMETRIC METHOD

(SUPERSEDES: REVISION 4.0; DATED 01/04/99)

Prepared by: _____ Date

Reviewed by: _____
Technology Specialist Date

Approved by: _____
Quality Assurance Manager Date

Approved by: _____
Environmental Health and Safety Coordinator Date

Approved by: _____
Laboratory Director Date

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1. SCOPE AND APPLICATION

1.1. This method is applicable to the determination of pH in waters, wastewaters, and solids. It is based on SW846 Methods 9040B and 9045C and EPA Method 150.1. The approximate working range is 1 - 14 pH units. Samples with a pH of < 1 are reported as < 1.

1.2. The associated method codes are PU (9040B), OZ (9045C), and AJ (150.1). The preparation codes are 88 and 1C.

1.3. This document accurately reflects current laboratory standard operating procedures (SOP) as of the date above. All facility SOPs are maintained and updated as necessary.

2. SUMMARY OF METHOD

2.1. The pH is determined electrometrically by using an electrode. The pH meter is calibrated with a series of known pH buffers.

3. DEFINITIONS

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

4. INTERFERENCES

4.1. Samples with very low or very high pH may give incorrect readings on the meter. For samples with a true pH of >10, the measured pH may be incorrectly low. This error can be minimized by using a low-sodium-error electrode.

5. SAFETY

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

5.2. Eye protection that satisfies ANSI Z87.1 (as per the Chemical Hygiene Plan), laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.3. The health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the Material Safety Data Sheets (MSDS) maintained in the laboratory.

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

5.5. The preparation of standards and reagents will be conducted in a fume hood with the sash closed as far as the operation will permit.

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

6. EQUIPMENT AND SUPPLIES

6.1. pH meter with electrode(s) and temperature compensation

6.2. Beakers: various

6.3. Top loading balance: Capable of accurately weighing ±0.01 g

6.4. Stir plate and stir bars

6.5. Shaker or mechanical tumbler

7. REAGENTS AND STANDARDS

7.1. Standards

7.1.1. Target Calibration Standards

7.1.1.1. pH 4, 7, and pH 10 buffers, purchased

7.1.1.2.Fresh buffers are poured and used each working day.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Samples are not chemically preserved.

8.2. Samples are stored in plastic or glass containers at 4°C ± 2°C.

8.3. Samples should be analyzed as soon as possible after sampling, but not to exceed twenty-four hours.

9. QUALITY CONTROL

9.1. Batch Definition

9.1.1. A batch is a group of no greater than 20 samples excluding QC samples (LCS, Method Blank, MS, MSD) which are processed similarly, with respect to the procedure. All sample setups must be initiated within a 24 hour period from the initial preparation or extraction and without interruption of the process. All samples within the batch must be treated with the same lots of reagents and the same processes.

9.2. Duplicates

9.2.1. Sample duplicates are performed at a minimum frequency one per analytical batch and must meet laboratory-specific limits for precision.

9.3. Laboratory Control Sample (LCS)

9.3.1. One aqueous LCS must be processed with each analytical batch. The LCS must be carried through the entire analytical procedure. The LCS is used to monitor the accuracy of the analytical process. On-going monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines.

9.3.2. A commercially available (Environmental Resource Associates or equivalent) control standard will be analyzed. Recovery must be within +/- 2% of true value.

9.3.3. Corrective Action for LCS

9.3.3.1. If the pH is outside the established control limits the system is out of control and corrective action must occur.

9.3.3.2. Corrective action consists of identification and correction of the cause for the out of control situation and reanalysis of all effected samples.

10. CALIBRATION AND STANDARDIZATION

10.1. Initial Calibration

10.1.1. Refer to the manufacturer's manual for instrumental calibration.

10.1.2. The following procedure is applicable for use with the Orion 240 pH meter.

10.1.2.1.Rinse the electrodes with reagent water and place in the pH 4.0 buffer. Press "Cal". Allow the value to stabilize and then, using the arrow keys, adjust the value up or down to read 4.00. Press Enter.

10.1.2.2.Rinse the electrodes and place in the pH 7.0 buffer. Allow the value to stabilize and then, using the arrow keys, adjust the value up or down to read 7.00. Press Enter.

10.1.2.3.Calibration Check: Rinse the electrodes and place in the pH 10.0 buffer. Allow value to stabilize. The pH should be between 9.95 and 10.05 or recalibration is necessary.

NOTE: When analyzing drinking water samples, calibrate as described in section 10.1.2, using the pH 7.0 and pH 10.0 buffers for calibration and the pH 4.0 buffer for the calibration check.

10.1.3The pH meter should be calibrated daily. The calibration is recorded on the analytical logsheet.

10.1.4If the pH meter has been turned off, it must be calibrated prior to use.

10.2. Continuing Calibration

10.2.1. A pH 7 buffer is analyzed before analysis and every ten samples to ensure the calibration remains linear.

10.2.2. The pH meter must be recalibrated if the buffer deviates by more than± 2% If this range is exceeded, reanalyze all samples analyzed since the last pH buffer that met criteria.

11. PROCEDURE

11.1. One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo and is approved by a Technical Specialist and QA Manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file.

11.2. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

11.3. Sample Preparation

11.3.1. Waters

11.3.1.1. No preparation necessary for waters and wastewaters.

11.3.2. Solids and Soils

11.3.2.1. Place 20 g (± 0.5 g) of sample in a beaker or other suitable container.

11.3.2.2. Add 20 mL of reagent water and mix for five minutes.

11.3.2.3. Allow sample to stand for one hour to allow the solids to settle out.

11.4. Sample Analysis

11.4.1. Waters

11.4.1.1. Place the sample in a clean beaker using a sufficient volume to cover the sensing elements of the electrode(s). Allow the pH to stabilize (swirling or stirring may quicken stabilization). Record the pH on the analytical logsheet. Remove the electrodes from the sample. Rinse and gently dab off the electrodes between each measurement. Store the electrodes in pH 7 buffer when not in use.

11.4.2. Solids

11.4.2.1. Immerse the pH electrodes in the supernatant layer of the sample - be careful not to stir up solids. Allow pH to stabilize and record it on the analytical logsheet. Remove and rinse the electrodes between each measurement. Store electrodes in the pH 7.0 buffer.

NOTE: If the sample contains oil or other substances that will coat or damage the electrodes, the pH should be analyzed following SOP# NC-WC-0009, pH - Paper Method.

11.5. Analytical Documentation

11.5.1. Record all analytical information in the analytical logbook/logsheet, including the analytical data from standards and any corrective actions or modifications to the method.

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

11.5.3. Documentation such as all associated instrument printouts (final runs, screens, reruns, QC samples, etc.) and daily calibration data corresponding to all final runs is available for each data file.

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

12. DATA ANALYSIS AND CALCULATIONS

12.1. Not Applicable

13. METHOD PERFORMANCE

13.1. Each laboratory must have initial demonstration of performance data on file and corresponding method detection limit files.

13.2. Training Qualifications:

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

14. POLLUTION PREVENTION

14.1. This method does not contain any specific modifications that serve to minimize or prevent pollution.

15. WASTE MANAGEMENT

15.1. Solid materials (gloves, soiled paper products, etc.) are placed in the solid debris container. Do not put liquids in the solid waste container.

15.2. Refer to the Laboratory Sample and Waste Disposal plan.

15.3. Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices of Quanterra. They must have training on the hazardous waste disposal practices upon initial assignment to these tasks, followed by an annual refresher training.

16. REFERENCES

16.1. References

16.1.1. SW846, Test Methods for Evaluating Solid Waste, 3rd Edition, pH Electrometric Measurement, Method 9040B

16.1.2. EPA 600, Methods for Chemical Analysis of Water and Wastes, pH (Electrometric), Method 150.1

16.1.3. SW846, Test Methods for Evaluating Solid Waste, 3rd Edition, Soil pH, method 9045C.

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

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

17.1. Reporting limits

17.1.1. A minimum reporting limit is not listed in LIMS. Units are reported as No Units.

STL NORTH CANTON STANDARD OPERATING PROCEDURE

TITLE: REACTIVE CYANIDE

(SUPERSEDES: REVISION 1, 05/18/99)

Prepared by:	Susan A. Macenzah	10/12/00 Date
Approved by:	Kurt C. Sell Technology Specialist	10/12/00 Date
Approved by:	[signature] Quality Assurance Manager	10/12/00 Date
Approved by:	[signature] Environmental Health and Safety Coordinator	10-16-00 Date
Approved by:	[signature] Laboratory Director	10-16-00 Date

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STL NORTH CANTON STANDARD OPERATING PROCEDURE

TITLE: REACTIVE CYANIDE

(SUPERSEDES: REVISION 1, 05/18/99)

Prepared by: _____
Date

Approved by: _____
Technology Specialist Date

Approved by: _____
Quality Assurance Manager Date

Approved by: _____
Environmental Health and Safety Coordinator Date

Approved by: _____
Laboratory Director Date

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1. SCOPE AND APPLICATION

1.1. This method is applicable to the determination of Reactive Cyanide in all wastes, with the condition that wastes combined with acids do not form explosive mixtures. It is based on SW846 Section 7.3.3.2 The working linear range is 10 to 1000 mg/kg. The EPA guidance level is 250 mg HCN/Kg waste (Total releasable cyanide).

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 applicable LIMs method code is GI. The preparation code for samples is 08.

2. SUMMARY OF METHOD

2.1. An aliquot of sample is acidified in a closed system. The gas generated is trapped in a sodium hydroxide solution and then analyzed using the titration method for Cyanide.

2.2. This test measures only the hydrocyanic acid evolved under the test conditions. It is not intended to measure forms of cyanide other than those that are evolvable under the test conditions.

3. DEFINITIONS

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

4. INTERFERENCES

4.1. Method interfererences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus that lead to discrete artifacts. All of these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. Specific selection of reagents may be required to avoid introduction of contaminants.

4.2. Sulfide interferes with analysis and can be precipitated out using cadmium carbonate prior to titration.

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 (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: Sulfuric Acid, Sodium Hydroxide.**

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

5.5. The preparation of standards and reagents will be conducted in a fume hood with the sash closed as far as the operation will permit.

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

6. EQUIPMENT AND SUPPLIES

6.1. Round Bottom Reactivity flask: 3-neck, 500 mL minimum capacity

6.2. Separatory funnel: 250 mL pressure-equalizing

6.3. Stir plate and stir bars

6.4. Compressed Nitrogen and two-way regulator, with flexible tubing.

6.5. Scrubber and absorber tube: 50 mL capacity

6.6. Buret: 10 mL Class A

6.7. Erlenmeyer flasks: various

6.8. Volumetric flasks: various

6.9. Graduated cylinders: various

6.10. Whatman filter paper #4

6.11. Analytical balance, capable of accurately weighing ±0.001g.

7. REAGENTS AND STANDARDS

7.1. Reagents

7.1.1. Sulfuric Acid: (H_2SO_4), concentrated, reagent grade

7.1.2. 0.05 M H_2SO_4: Add 2.8 mL concentrated H_2SO_4 to 900 mL reagent water and dilute to 1 liter with reagent water.

7.1.3. 0.005 M H_2SO_4 (0.01N): Add 100 mL 0.05 M H_2SO_4 to 800 mL reagent water and dilute to 1 liter with reagent water.

7.1.4. Sodium Hydroxide: (NaOH), reagent grade

7.1.5. 1.25 N NaOH: Add 50 g NaOH to 900 mL reagent water and dilute to 1 liter with reagent water.

7.1.6. 0.25 N NaOH: Add 200 mL 1.25 N NaOH to 700 mL reagent water and dilute 1 liter with reagent water.

7.1.7. 0.0192 N Silver Nitrate Solution: reagent grade

7.1.8. Rhodanine Indicator: Dimethylaminobenzalrhodanine, reagent grade

7.1.9. Acetic acid: (CH_3COOH), concentrated, reagent grade

7.1.10. Kaolin: reagent grade

7.1.11. Cadmium Carbonate: ($CdCO_3$), reagent grade

8. SAMPLE PRESERVATION AND STORAGE

8.1. Samples are stored in plastic or glass containers at 4° ± 2°C, with no headspace.

8.2. Solid and water samples are not chemically preserved.

8.3. The holding time is fourteen days from sampling to analysis (based on the Total Cyanide holding time). There is no defined holding time.

9. QUALITY CONTROL

9.1. Batch Definition

9.1.1. A batch is a group of no greater than 20 samples excluding QC samples (LCS, MS, MSD, Method Blanks) which are processed similarly, with respect to the procedure. All samples within the batch must be treated with the same lots of reagents and the same processes. All samples within the batch must be treated with the same processes.

9.2. Method Blank (MB)

9.2.1. One method blank (MB) must be processed with each preparation batch. The method blank consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The method blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. The method blank should not contain any analyte of interest at or above the reporting limit.

9.2.2. A blank consisting of 10 g Kaolin or other inert solid must be reacted and analyzed with each analytical batch of samples.

9.2.3. Corrective Action for Blanks

9.2.3.1. If the analyte level in the method blank exceeds the reporting limit for the analytes of interest in the sample, all associated samples are reprepared and reanalyzed. If this is not possible due to limited sample quantity or other considerations, the corresponding sample data **must be taken in consultation with the client and must be addressed in the project narrative.**

9.2.3.2. If there is no analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. **Such action must be taken in consultation with the client and must be addressed in the project narrative.**

9.3. Duplicate Sample

9.3.1. Sample duplicates are performed at a min frequency of one per analytical batch and must meet laboratory-specific limits for precision.

9.4. QC Acceptance Criteria

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

10. CALIBRATION AND STANDARDIZATION

10.1. Not Applicable.

11. PROCEDURE

11.1. Summary

11.1.1. The sample is acidified in a closed system and liberated Cyanide gas is trapped in 0.25 N NaOH.

11.2. Sample Preparation Procedure

11.2.1. Add 50 mL 0.25 N NaOH to the absorber tube and connect the scrubber.

11.2.2. Add 10 g ± 0.05 g approximately of sample (waters and non-waters) to the reactivity flask with closed stop cock.

11.2.3. Add 250 mL of 0.005 M H_2SO_4 to the addition funnel.

11.2.4. Close the entire system and begin the flow of nitrogen. The flow should be 60 mL/minute.

11.2.5. Begin sample stirring and start adding the acid by opening the stopcock on the separatory funnel. **NOTE:** The stirring should not be fast enough to create a vortex and should be at a constant speed.

11.2.6. Allow the sample to react (while mixing) for thirty minutes. Document mixing time.

11.2.7. After the thirty minute reacting period, disconnect the system and shut off the nitrogen.

11.2.8. Pour the scrubber contents into a 250 mL volumetric flask. Rinse the scrubber with 0.25N NaOH and pour the rinsate into the 250 mL volumetric flask. Dilute to volume with 0.25N NaOH.

11.3. Preparation Documentation

11.3.1. Record all the necessary information on the analytical logsheet.

11.4. Sample Analysis Procedure

11.4.1. After the 100 mL aliquot has been removed (and checked and/or analyzed) for sulfide, if necessary, add one scoop (1 - 2 g) of $CdCO_3$ powder to the volumetric flask and mix. If the precipitate turns yellow, add another scoop until white precipitate forms. This removes sulfide which interferes with the titration. If the results of the sulfide analysis are "ND", go to section 11.4.2. Filter 100 mLs of treated scrubber solution through a #4 Whatman filter paper into an Erlenmeyer flask.

11.4.2. Add 10-12 drops of rhodanine indicator to the Erlenmeyer flask. The solution should turn yellow. Titrate with 0.0192 N silver nitrate until a orange-peach color develops. Record the volume of titrant used on the analytical logsheet.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Calculations

$$\frac{A(1000)}{B} \times \frac{250}{C} = mg / L \text{ Cyanide in scrubber solution}$$

Where:

A = mL of titrant used

B = Volume of sample titrated

C = mL of scrubber solution titrated (usually 100 mL)

$$\frac{(X)(L)}{(W)(S)} = \text{(R) Rate of release}$$

Where:

X = Conc. Cyanide from previous equation

L = Total volume of scrubber solution in liters (0.25 l)

W = Weight of original sample used in kg (10 g = 0.1 kg)

S = Time of reaction in seconds (30 minute = 1800 seconds)

R = Rate of release from second equation

12.2. Report Documentation

12.2.1. Record all analytical information on the analytical logsheet, including the analytical data from standards, blanks, and LCSs.

12.2.2. All standards are logged onto the departmental standard logsheet. All standards are assigned in an unique number for identification. Logbooks are reviewed by the supervisor or designee.

12.2.3. The documentation such as all associated instrument printouts (final runs, screens, reruns, QC samples, ect.) and daily calibration data corresponding to all final runs is available for each data file.

12.2.4. Sample results and associated QC are entered into the LIMS after final technical review.

13. METHOD PERFORMANCE

13.1. Each laboratory must have initial demonstration of performance data on file and corresponding method detection limit files.

13.2. Training Qualifications:

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

14. POLLUTION PREVENTION

14.1. This method does not contain any specific modifications that serve to minimize or prevent pollution.

15. WASTE MANAGEMENT

15.1. Acid waste must be collected in the clearly labeled acid waste containers.

15.2. Solid materials (soil, gloves, soiled paper products) are placed in the solid debris container. Do not put liquids in the solid waste container.

15.3. Refer to the Laboratory Sample and Waste Disposal plan.

15.4. Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices of STL North Canton. They must have training on the hazardous waste disposal practices upon initial assignment to these tasks, followed by annual refresher training.

16. REFERENCES

16.1. References.

16.1.1. SW846, Test Methods for Evaluating Solid Waste, Reactivity, Method 7.3.3.2 for Cyanide Reactivity, and its Updates.

16.1.2. SW846, Test Methods for Evaluating Solid Wastes, Reactivity, Method 9012A for Cyanide Analysis, and its Updates.

16.2. Associated SOPs

16.2.1. Cyanide, Total NC-WC-0031

16.2.2. Reactive Sulfide, NC-WC-0061

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

16.2.4. STL North Canton Laboratory Quality Manual (LQM), current version.

16.3. Withdrawal of Reactive Cyanide and Sulfide, USEPA Office of Solid Waste and Emergency Response Abstract, April 21, 1998.

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

17.1. Troubleshooting Guide

17.1.1. If the sample turns black while titrating, sulfide is present. See Sample Analysis Procedure 11.4.1 for removal. Use the remaining aliquot.

17.2. Method Deviation

17.2.1. A rotometer for monitoring nitrogen gas flow rate is not utilized by the laboratory.

17.2.2. A cyanide reference solution is not utilized by the laboratory.

STL NORTH CANTON STANDARD OPERATING PROCEDURE

TITLE: REACTIVE SULFIDE

(SUPERSEDES: (REVISION 0, DATED 06/03/98))

Prepared by:	Susan A Macaugah	10/11/00 Date
Reviewed by:	Kurt C. Ill Technology Specialist	10/11/00 Date
Approved by:	Opal Rai Fahm Quality Assurance Manager	10/11/00 Date
Approved by:	[signature] Environmental Health and Safety Coordinator	10-16-00 Date
Approved by:	Christoph N Oprandi Laboratory Director	10-16-00 Date

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STL NORTH CANTON STANDARD OPERATING PROCEDURE

TITLE: REACTIVE SULFIDE

(SUPERSEDES: (REVISION 0, DATED 06/03/98))

Prepared by: _____ Date

Reviewed by: _____
Technology Specialist Date

Approved by: _____
Quality Assurance Manager Date

Approved by: _____
Environmental Health and Safety Coordinator Date

Approved by: _____
Laboratory Director Date

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1. SCOPE AND APPLICATION

1.1. This method is applicable to the determination of Reactive Sulfide in all wastes, with the condition that wastes combined with acids do not form explosive mixtures. It is based on SW846 Section 7.3.4.2. The lower detection limit is 200 mg/kg. The EPA guidance level is 500 mg H2S/Kg waste (Total releasable sulfide).

1.2. This document accurately reflects current laboratory standard operating procedures (SOP) as of the date above. All facility SOPs are maintained and updated as necessary.

1.3. The QuantIMs associated method code is GJ. The preparation code for samples is 08.

2. SUMMARY OF METHOD

2.1. An aliquot of sample is acidified in a closed system. The gas is generated and trapped in a sodium hydroxide solution and then analyzed using the titration method for Sulfide.

2.2. This procedure releases only the hydrogen sulfide evolved under the test conditions. It is not intended to measure forms of sulfide other than those that are evolvable under the test conditions.

3. DEFINITIONS

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

4. INTERFERENCES

4.1. Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus that lead to discrete artifacts. All of these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. Specific selection of reagents may be required to avoid introduction of contaminants.

4.2. Oxidizers and reducers interfere with Sulfide analysis.

5. SAFETY

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

5.2. Eye protection that satisfied 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, Sodium Hydroxide, and Sulfuric Acid**

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

5.5. The preparation of standards and reagents will be conducted in a fume hood with the sash closed as far as the operation will permit.

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

6. EQUIPMENT AND SUPPLIES

6.1. Reactivity round bottom flask: 3-neck, 500 mL min. capacity

6.2. Separatory funnel: 250 mL pressure-equalizing

6.3. Stir plate and stir bars

6.4. Compressed nitrogen and Two-way regulator with flexible tubing

6.5. Scrubber and absorber tube: 50 mL capacity

6.6. Burettes: 10 mL and 25 mL Class A

6.7. Erlenmeyer Flasks: various

6.8. Pipettes: various

6.9. Graduated cylinders: various

6.10. Analytical balance, capable of accurately weighing ± 0.001g

6.11. 250 mL volumetric flasks

7. REAGENTS AND STANDARDS

7.1.1. Sulfuric Acid, 0.05 M H_2SO_4: Add 2.8 mL concentrated sulfuric acid to a 1 liter volumetric flask containing 900 mL reagent water and bring to volume with reagent water.

7.1.2. Sulfuric Acid, 0.005 M H_2SO_4 (0.01N): Add 100 mL 0.05 M H_2SO_4 to a 1 liter volumetric flask and bring to volume with reagent water.

7.1.3. Sodium Hydroxide, 1.25 N NaOH: Add 50 g sodium hydroxide to a 1 liter volumetric flask and bring to volume with reagent water.

7.1.4. Sodium Hydroxide, 0.25 N NaOH: Add 200 mL 1.25 N NaOH to a 1 liter volumetric flask and bring to volume with reagent water.

7.1.5. Iodine Solution, 0.025 N: Manufactured, or add 20 g KI (potassium iodide) and 3.2 g iodine to a 1 liter volumetric flask. Add 500 - 700 mL of reagent water and dissolve. Dilute to volume with reagent water. Store in a dark container.

7.1.5.1. Standardization 0.025N Iodine Solution: Prepare three (3) method blanks using 250 mL of reagent water. Follow the analysis procedure and calculate an average normality.

$$\text{Normality Iodine} = \frac{(\text{Normality } Na_2S_2O_3)(\text{mL of titrant } Na_2S_2O_3)}{20 \text{ mL Iodine}}$$

7.1.6. Sodium Thiosulfate, 0.025 N: Manufactured, or add 0.4 g of NaOH and 6.205 g of sodium thiosulfate ($Na_2S_2O_3 \bullet 5H_2O$) to 500 mL of reagent water in a 1 liter volumetric flask. Dilute to volume with reagent water. Store in a dark container.

7.1.6.1. Standardization of 0.025 N Sodium Thiosulfate Solution: To make 0.025N Biodate Solution, dissolve 0.4062 g $KH(IO_3)_2$ in 500 mL reagent water. Weigh 2 g KI in a 500 mL Erlenmeyer flask. Add 100 to 150 mL reagent water, 5 drops H_2SO_4, and 20 mL biodate solution using a volumetric pipet. Dilute to 200 mL with reagent water. Titrate with Sodium Thiosulfate. When a pale straw yellow color is reached, add 1-2

mL starch. Continue titrating from a blue to a clear end point. Repeat two (2) more times. Calculate an average normality.

$$Na_2S_2O_3 \text{ Normality} = \frac{(a)(b)}{c}$$

where:

a = mLs Biodate (20mL)

b = Normality Biodate (0.025N)

c = mLs of $Na_2S_2O_3$ used to titrate

7.1.7. Starch Indicator: Add 10 mL reagent water to 5 g potato starch and mix. Add mixture to 500 mL boiling reagent water, mix, and cool.

7.1.8. Hydrochloric Acid, 6 N: Add 250 mL concentrated hydrochloric acid to 250 mL reagent water.

7.1.9. Zinc Acetate Solution: Add 220 g Zinc Acetate to a 1000 mL volumetric flask and dilute to volume with reagent water.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Samples are unpreserved.

8.2. Samples are stored in glass containers at 4°C ± 2°C with no headspace.

8.3. There is no defined holding time.

9. QUALITY CONTROL

9.1. Batch Definition

9.1.1. A batch is a group of no greater than 20 samples excluding QC samples (Method Blank, Sample Duplicate) which are processed similarly, with respect to the procedure. All sample setups must be initiated within a 24 hour period from the initial preparation or extraction and without interruption of the process. All samples within the batch must be treated with the same lots of reagents and the same processes.

9.2. Method Blank

9.2.1. One method blank (MB) must be processed with each preparation batch. The method blank consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The method blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. The method blank should not contain any analyte of interest at or above the reporting limit.

9.2.2. A blank consisting of 10 g of Kaolin must be reacted and analyzed with each analytical batch of samples.

9.2.3. Corrective Action for Blanks

9.2.3.1. If the analyte level in the method blank exceeds the reporting limit for the analytes of interest in the sample, all associated samples are reprepared and reanalyzed. If this is not possible due to limited sample quantity or other considerations, the corresponding sample data **must be addressed in the project narrative.**

9.2.3.2. If there is no analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. **Such action must be taken in consultation with the client and must be addressed in the project narrative.**

9.3. Sample Duplicate

9.3.1. Sample duplicates are performed at a minimum frequency of one per analytical batch and must meet laboratory-specific limits for precision.

9.4. QC Acceptance Criteria

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

10. CALIBRATION AND STANDARDIZATION

10.1. Not Applicable

11. PROCEDURE

11.1. One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo and is approved by a Technical Specialist and QA Manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file.

11.2. Any unauthorized deviations from this procedure must also be documents as a nonconformance, with a cause and corrective action described.

11.3. Sample Preparation

11.3.1. Summary

11.3.1.1. The sample is acidified in a closed system and liberated Sulfide gas is trapped in 0.25 N NaOH.

11.3.2. Sample Preparation Procedure

11.3.2.1. Add 50 mL 0.25 N NaOH to the absorber tube and connect the scrubber.

11.3.2.2. Add 10 g ± 0.05 g of sample to the reactivity flask.

11.3.2.3. Add 250 mL of 0.005 M H_2SO_4 to the addition funnel.

11.3.2.4. Close the entire system and begin the flow of nitrogen. The flow should be 60 mL/minute.

11.3.2.5. Begin sample stirring and start the addition of acid to the flask.

NOTE: The stirring should not be fast enough to create a vortex and should be at a constant speed.

11.3.2.6. Begin timing for thirty minutes. Document mixing time.

11.3.2.7. After the thirty minute reacting period, disconnect the system and shut off the nitrogen.

11.3.2.8. Pour the scrubber contents into a 250 mL volumetric flask. Rinse the scrubber with 0.25N NaOH and pour the rinsate into the 250 mL volumetric flask. Bring to volume with 0.25N NaOH.

11.4. Sample Analysis

11.4.1. Pour 100 mL of scrubber into a 500 mL Erlenmeyer flask and add 150 mL of reagent water. Add 1-2 mL of zinc acetate solution, 20.0 mL of 0.025 N iodine, 2-3 mL of 1:1 HCl, and 2 - 3 mL of starch indicator to solution and mix. Titrate with 0.025 N sodium thiosulfate until blue color disappears. Record the volume of titrant used.

11.4.2. Preliminary Evaluation

11.4.2.1. The color of the scrubber solution should be a golden color after the addition of the iodine and HCl; if it is not, a lesser volume of sample (25 mL is recommended) is titrated.

11.5. Analytical Documentation

11.5.1. Record all analytical information in the analytical logbook/logsheet, including the analytical data from standards, blanks, LCSs, MS/MSDs, and any corrective actions or modifications to the method.

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

11.5.3. Documentation such as all associated instrument printouts (final runs, screens, reruns, QC samples, etc.) and daily calibration data corresponding to all final runs is available for each data file.

11.5.4. Sample results and associated QC are entered into the LIMS after final technical review.

12. DATA ANALYSIS AND CALCULATIONS

12.1. ***mg / L Sulfide in scrubber solution*** $= \dfrac{[(A \bullet a) - (B \bullet b)]16{,}000}{C}$

Where:

A = mL of iodine used

a = N of iodine

B = mL titrant used

b = N of titrant

C = mL of scrubber solution titrated

12.2. ***Rate of release (R)*** $= \dfrac{(X)(L)}{(W)(S)}$

Where:

X = Concentrated Sulfide from 12.1 or 12.2

L = Total volume of scrubber solution in liters (0.25 L)

W = Weight of original sample used in kg (10 g = 0.1 kg)

S = time of reaction in seconds (30 minute = 1800 seconds)

12.3. ***mg / kg Reactive Sulfide = R x 1800***

Where:

R = Rate of release from second equation

13. METHOD PERFORMANCE

13.1. Each laboratory must have initial demonstration of performance data on file and corresponding method detection limit files.

13.2. Training Qualifications:

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

14. POLLUTION PREVENTION

14.1. This method does not contain any specific modifications that serve to minimize or prevent pollution.

15. WASTE MANAGEMENT

15.1. Solvent waste must be disposed of in clearly labeled waste cans.

15.2. Acid waste must be collected in clearly labeled acid waste containers.

15.3. Solid materials (gloves, soiled paper products, etc.) are placed in the solid debris container. Do not put liquids in the solid waste container.

15.4. Refer to the Laboratory Sample and Waste Disposal plan.

15.5. Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices of STL. They must have training on the hazardous waste disposal practices upon initial assignment to these tasks, followed by an annual refresher training.

16. REFERENCES

16.1. References

16.1.1. SW846, Test methods for Evaluating Solid Wastes, 3rd Edition, Reactivity, Method 7.3.4.2 for Sulfide.

16.1.2. SW846, Test Methods for Evaluating Solid Wastes, 3rd Edition,

16.1.3. Reactivity, Method 9030A for Sulfide.

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

16.2. Associated SOPs

16.2.1. Sulfide, NC-WC-0060

16.2.2. Reactive Cyanide, NC-WC-0033

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

16.3. Withdrawal of Reactive Cyanide and Sulfide, USEPA Office of Solid Waste and Emergency Response Abstract, April 21, 1998.

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

17.1. Reporting limits

17.1.1. The lower reporting limit (RL) is 200 mg/kg Reactive Sulfide.

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

17.2. Method Deviation

17.2.1. A rotometer for monitoring nitrogen gas flow rate is not utilized by the laboratory.

17.2.2. A sulfide reference solution is not utilized by the laboratory.

STL NORTH CANTON STANDARD OPERATING PROCEDURE

TITLE: PAINT FILTER

(SUPERSEDES: (REVISION 0; DATED 06/08/95)

Prepared by: _____

Reviewed by: _____
Technology Specialist

Approved by: _____
Quality Assurance Manager

Approved by: _____
Environmental Health and Safety Coordinator

Approved by: _____
Laboratory Director

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QUANTERRA STANDARD OPERATING PROCEDURE

TITLE: PAINT FILTER

(SUPERSEDES: ENSECO SOP #LM-WALN-1230 (REVISION 0))

Prepared by: Joanne Hancock

Reviewed by: Bruce Hart
Technology Specialist

Approved by: _____
Quality Assurance Manager

Approved by: _____
Environmental Health and Safety Coordinator

Approved by: _____
Laboratory Director

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1. SCOPE AND APPLICATION

1.1. This method is applicable to the determination of the presence of free liquid in a variety of wastes. It is based on SW846 Method 9095.

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.

2. SUMMARY OF METHOD

2.1. An aliquot of sample is placed in a paint filter. If any portion of the material passes through the filter in five minutes, the sample is deemed to contain free liquids.

3. DEFINITIONS

3.1. Refer to the glossary in the Quality Assurance Management Plan (QAMP).

4. INTERFERENCES

4.1. Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus that lead to discrete artifacts. All of these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. Specific selection of reagents may be required to avoid introduction of contaminants.

4.2. Some samples may contain very small particles of solid which will pass through the filter; this is not a positive paint filter.

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.

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

5.5. The preparation of standards and reagents will be conducted in a fume hood with the sash closed as far as the operation will permit.

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

6. EQUIPMENT AND SUPPLIES

6.1. Conical paint filter: Mesh 60

6.2. Glass funnel

6.3. Ring stand

6.4. Graduated cylinders: various

7. REAGENTS AND STANDARDS

7.1. Not Applicable

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Samples are not chemically preserved.

8.2. Samples are stored in glass containers at 4°C ± 2°C.

8.3. Holding Times - Not Applicable

9. QUALITY CONTROL

9.1. Not Applicable

10. CALIBRATION AND STANDARDIZATION

10.1. Not Applicable

11. PROCEDURE

11.1. One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo and is approved by a Technical Specialist and QA Manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file.

11.2. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

11.3. Sample Preparation

11.3.1. Not Applicable

11.4. Sample Analysis

11.4.1. Place an aliquot of representative sample in the paint filter which is placed in the glass funnel above a graduated cylinder.

11.4.2. Allow the sample to drain for five minutes into the graduated cylinder. If any free liquid is collected in the graduated cylinder, the sample is considered positive. If no free liquid is collected, the sample is negative.

NOTE: If sample quantity is limited, a visual procedure may be performed and documented accordingly.

11.5. Analytical Documentation

11.5.1. Record all analytical information in the analytical logbook/logsheet, including the analytical data from standards, blanks, LCSs, MS/MSDs, and any corrective actions or modifications to the method.

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

11.5.3. Documentation such as all associated instrument printouts (final runs, screens, reruns, QC samples, etc.) and daily calibration data corresponding to all final runs is available for each data file.

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

12. DATA ANALYSIS AND CALCULATIONS

12.1. Not Applicable

13. METHOD PERFORMANCE

13.1. Each laboratory must have initial demonstration of performance data on file and corresponding method detection limit files.

13.2. Training Qualifications:

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

14. POLLUTION PREVENTION

14.1. This method does not contain any specific modifications that serve to minimize or prevent pollution.

15. WASTE MANAGEMENT

15.1. Solid materials (gloves, soiled paper products, etc.) are placed in the solid debris container. Do not put liquids in the solid waste container.

15.2. Refer to the Laboratory Sample and Waste Disposal plan.

15.3. Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices of STL North Canton. They must have training on the hazardous waste disposal practices upon initial assignment to these tasks, followed by an annual refresher training.

16. REFERENCES

16.1. References

16.1.1. SW846, Test Methods for Evaluating Solid Waste, Third Edition, Paint Filter Liquids Test, Method 9095.

16.1.2. STL North Canton Laboratory Quality Management Plan (LQMP), current version.

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

STL STANDARD OPERATING PROCEDURE

TITLE: DETERMINATION OF INORGANIC ANIONS BY ION CHROMATOGRAPHY

(SUPERSEDES: REVISION (2))

Prepared by:	Deborah N Marcum	10-5-00 Date
Reviewed by:	Technology Specialist	10/5/00 Date
Approved by:	Quality Assurance Manager	10/5/00 Date
Approved by:	Environmental Health and Safety Coordinator	10-10-00 Date
Approved by:	Laboratory Director	10/11/00 Date

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1. SCOPE AND APPLICATION

1.1. This method covers the determination of fluoride, chloride, nitrite, bromide, nitrate, ortho-phosphate and sulfate in drinking water, surface water, mixed domestic and industrial wastewaters, groundwater, reagent waters, solids (after extraction 11.7) and leachates (when no acetic acid is used).

1.2. A listing of associated LIMs method codes is located in Section 8.2.

1.3. This document accurately reflects current laboratory standard operating procedures (SOP) as of the date above. All facility SOPs are maintained and updated as necessary.

2. SUMMARY OF METHOD

2.1. A 25 uL volume of sample is introduced into the ion chromatograph. The sample is pumped through three different ion exchange columns and into a conductivity detector. The first two columns, a precolumn or guard column and a separator column, are packed with low-capacity, strongly basic anion exchange resin. Ions are separated into discrete bands based on their affinity for the exchange sites of the resin. The last column is a suppresser column that reduces the background conductivity of the eluent to a low or negligible level and converts the anions in the sample to their corresponding acids. The separated anions in their acid form are measured using an electrical conductivity cell. Anions are identified based on their retention times compared to known standards. Quantitation is accomplished by measuring the peak height or area and comparing it to a calibration curve generated from known standards.

3. DEFINITIONS

3.1. Refer to the glossary in the Laboratory Quality Manual (LQM).

4. INTERFERENCES

4.1. Interferences can be caused by substances with retention times that are similar to and overlap those of the anion of interest. Large amounts of an anion can interfere with the peak resolution of an adjacent anion. Sample dilution and/or fortification can be used to solve most interference problems associated with retention times.

4.2. The water dip or negative peak that elutes near, and can interfere with, the fluoride peak can usually be eliminated by the addition of concentrated eluent to each standard and sample.

4.3. Method interferences may be caused by contaminants in the reagent water, reagents, glassware and other sample processing apparatus that lead to discrete artifacts or an elevated baseline in the ion chromatograms.

4.4. Any anion that is not retained by the column or only slightly retained will elute in the area of fluoride and interfere. Known coelution is caused by carbonate and other small organic anions. At concentrations of fluoride above 1.5 mg/L, this interference may not be significant; however, it is the responsibility of the user to generate precision and accuracy information in each sample matrix.

4.5. The acetate anion elutes early during the chromatographic run. The retention times of the anions also seem to differ when large amounts of acetate are present. Therefore, this method is not recommended for leachates of solid samples when acetic acid is used for pH adjustment.

5. SAFETY

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

5.2. Eye protection that satisfied ANSI Z87.1 (as per the Chemical Hygiene Plan), laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.3. The health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the Material Safety Data Sheets (MSDS) maintained in the laboratory.

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

5.5. The preparation of standards and reagents will be conducted in a fume hood with the sash closed as far as the operation will permit.

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

6. EQUIPMENT AND SUPPLIES

6.1. Balance -- Analytical, capable of accurately weighing to the nearest 0.0001 g.

6.2. Ion Chromatograph -- Analytical system complete with ion chromatograph and all required accessories including analytical columns, compressed gases and detectors.

6.2.1. Anion guard column: A protector of the separator column. If omitted from the system the retention times will be shorter. Usually packed with same substrate as the separator column. 4 x 50 mm, Dionex IonPac AG14 P/N 46134, or equivalent.

6.2.2. Anion separator column: The separation shown in Figure 1 was generated using a Dionex IonPac AS14 column (P/N 46134). Equivalent column may be used if comparable resolution is obtained, and the requirements of Sect. 9.2 can be met.

6.2.3. Anion suppresser device: Dionex anion micro membrane suppresser (P/N 37106) or ASRS-Ultra Self-Regenerating Suppressor (4mm) P/N 53946 or equivalent.

6.2.4. Detector -- Conductivity cell: approximately 1.25 uL internal volume, Dionex, or equivalent.

6.2.5. Dionex –PeakNet 5.1Data Chromatography Software or equivalent.

6.3. Assorted laboratory glassware (pipettes, volumetric flasks, etc.).

7. REAGENTS AND STANDARDS

7.1. Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2. Reagent water: Distilled or deionized water, free of the anions of interest. Water should contain particles no larger than 0.20 microns.

7.3. Eluent solution: sodium bicarbonate (CASRN 144-55-8) 1.0 mM, sodium carbonate (CASRN 497-19-8) 3.5 mM. Dissolve 1.680 g sodium bicarbonate ($NaHCO_3$) and 7.417 g of sodium carbonate (Na_2CO_3) in reagent water (7.2) and dilute to 100 mL in a volumetric flask. Take 10 mL of this concentrated eluent solution and dilute to 2 L for

use as the working eluent solution or dissolve the entire bicarbonate/carbonate amount in 20 L of reagent water.

7.4. Stock solutions (1,000 mg/L): All stocks may be prepared as described below or purchased from commercial sources. Primary and secondary sources are required for each target analyte.

7.4.1. Fluoride stock solution (1.00 mL = 1.00 mg F^-): In a 1 liter volumetric flask, dissolve 2.2100 g of sodium fluoride (NaF) in reagent water, and dilute to volume with reagent water. Store in chemical- resistant glass or polyethylene.

7.4.2. Chloride stock solution (1.00 mL = 1.00 mg Cl^-): Dry sodium chloride (NaCl) for 12 hours at 105°C, and cool in a desiccator. In a 1 liter volumetric flask, dissolve 1.6485 g of the dry salt in reagent water and dilute to volume with reagent water.

7.4.3. Nitrite stock solution (1.00 mL = 1.00 mg NO_2^- - N): Place approximately 10.0 g of sodium nitrite (KNO_2) in a 125 mL beaker and dry to constant weight (about 24 hours) in a desiccator. In a 1 liter volumetric flask, dissolve 6.0790 g of the dried salt in reagent water and dilute to volume with reagent water. Store in a sterilized glass bottle. Refrigerate and prepare monthly.

- Nitrite is easily oxidized, especially in the presence of moisture, and only fresh reagents are to be used.
- Prepare sterile bottles for storing nitrite solutions by heating for 1 hour at 170°C in an air oven.

7.4.4. Bromide stock solution (1.00 mL = 1.00 mg Br^-): Dry approximately 5.0 g of sodium bromide (NaBr) for 12 hours at 105°C, and cool in a desiccator. In a 1 liter volumetric flask, dissolve 1.2876 g of the dried salt in reagent water and dilute to volume with reagent water.

7.4.5. Nitrate stock solution (1.00 mL = 1.00 mg NO_3^- - N): Dry approximately 10.00 g of sodium nitrate (KNO_3) at 105°C for 24 hours . In a 1 liter volumetric flask, dissolve 7.2200 g of the dried salt in reagent water and dilute to volume with reagent water.

7.4.6. Phosphate stock solution (1.00 mL = 1.00 mg PO_4 - P): Dry approximately 10.00 g of potassium dihydrogen phosphate (KH_2PO_4) for 1 hour at 105°C and cool in a desiccator. In a 1 liter volumetric flask, dissolve 4.3937 g of the dry salt in reagent water and dilute to volume with reagent water.

7.4.7. Sulfate stock solution (1.00 mL = 1.00 mg SO_4^{--2}): Dry approximately 5.00 g of potassium sulfate (K_2SO_4) at 105°C for 1 hour and cool in a desiccator. In a 1 liter volumetric flask, dissolve 1.8141 g of the dried salt in reagent water and dilute to volume with reagent water.

7.4.8. Commercial stock solution A: F^- - 25 mg/L, Cl^- - 500 mg/L, Br^-- 100 mg/L, NO_3^- - N- 25 mg/L, PO_4 – P - 25 mg/L, SO_4^{--2}- 500 mg/L

7.4.9. Commercial stock solution B: NO_2^- - N- 25 mg/L

7.4.10. Commercial IC Spike solution A: : F^- - 125 mg/L, Cl^- - 2500 mg/L, Br^-- 500 mg/L, NO_3^- - N- 125 mg/L, PO_4 – P - 125 mg/L, SO_4^{--2}- 2500 mg/L

7.4.11. Commercial IC Spike solution B: NO_2^- - N- 125 mg/L

7.5. Working standards: Prepare calibration standard #5 in a 10 mL volumetric flask and transfer to a vial. Adjust the amount of stock solution used to prepare the working standards if the stock concentration differs from 1000 mg/L as assumed Alternatively prepare Cal standard #5 by mixing 4.0 mL commercial stock A, 4.0 mL commercial stock B and 2.0 mL of reagent water.

Calibration Standard #5

Analyte	mL of Stock	Final Conc.
Fluoride	0.10mL	10.0 mg/L
Chloride	2.0 mL	200. mg/L
Nitrite	0.10 mL	10.0 mg/L
Bromide	0.40 mL	40.0 mg/L
Nitrate	0.10 mL	10.0 mg/L
Ortho-Phosphate	0.10 mL	10.0 mg/L
Sulfate	2.0 mL	200. mg/L

7.5.1. In 5 mL PolyVials prepare the following calibration standards in reagent grade water. Final concentrations of working standards are shown below.

Calibration Standard #4: take 2.50 mL of calibration standard #5 and add 2.50 mL of reagent water.

Calibration Standard #2: take 250 µL of calibration standard #5 and add 4.75 mL of reagent water.

Calibration Standard #1: take 25.0 µL of calibration standard #5 and add 4.95 mL of reagent water.

Calibration Standard #3: take 1.25 mL of calibration standard #5 and add 3.75 mL of reagent water.

Calibration Standard #1

Analyte	25.0 µL of Cal Std #5	Final Conc
Fluoride		0.05 mg/L
Chloride		1.0 mg/L
Nitrite		0.05 mg/L
Bromide		0.20 mg/L
Nitrate		0.05 mg/L
Ortho-Phosphate		0.05 mg/L
Sulfate		1.0 mg/L

Calibration Standard #2

Analyte	250 µL of Cal Std #5	Final Conc.
Fluoride		0.5 mg/L
Chloride		10. mg/L
Nitrite		0.5 mg/L
Bromide		2.0 mg/L
Nitrate		0.5 mg/L
Ortho-Phosphate		0.5 mg/L
Sulfate		10. mg/L

Calibration Standard #3

Analyte	1.25 mL of Cal Std #5	Final Conc.
Fluoride		2.5 mg/L
Chloride		50. mg/L
Nitrite		2.5 mg/L
Bromide		10. mg/L
Nitrate		2.5 mg/L
Ortho-Phosphate		2.5 mg/L
Sulfate		50. mg/L

Calibration Standard #4

Analyte	2.5 mL of Cal Std #5	Final Conc.

Fluoride		5.0 mg/L
Chloride		100 mg/L
Nitrite		5.0 mg/L
Bromide		40. mg/L
Nitrate		5.0 mg/L
Ortho-Phosphate		5.0 mg/L
Sulfate		100 mg/L

7.5.2. Prepare or purchase a secondary stock standard(s) using a standards source other than that used for the primary standards as described in Section 7.5. Dilute these stock standards to as indicated in the table below to prepare the mixture to be used for the LCS and CCV solution. Alternatively prepare this solution by mixing 0.50 mL commercial stock A, 0.50 mL commercial stock B and 4.0 mL of reagent water.

LCS & Continuing Calibration Verification Solution

Analyte	Final Conc. (V_f=5ml)
Fluoride	2.5 mg/L
Chloride	50. mg/L
Nitrite	2.5 mg/L
Bromide	10. mg/L
Nitrate	2.5 mg/L
Ortho Phosphate	2.5 mg/L
Sulfate	50. mg/L

7.5.3. Prepare or purchase a secondary stock standard(s) using a standards source other than that used for the primary standards as described in Section 7.5. Dilute these stock standards to prepare the mixture to be used for the Matrix Spike solution. Alternatively purchase these mixes (ready to use) from a commercial source. Add 100 uL of each IC Spike solution to 5 mL of sample when preparing the MS/MSD. Dilute as needed after spiking the sample.

Matrix Spike "True" Values

Analyte	Final Conc.
Fluoride	2.5 mg/L
Chloride	50. mg/L
Nitrite	2.5 mg/L
Bromide	10. mg/L
Nitrate	2.5 mg/L
Ortho Phosphate	2.5 mg/L
Sulfate	50. mg/L

NOTE: Stock standards, calibration standard #5 and LCS standard should be stored in the dark at 4° ± 2°C. Replace these standards when instrument response indicates target analyte degradation may have occurred or after the standard has expired (12 months commercial mix or 6 months in house mix), which ever occurs first. Nitrite and ortho-phosphate are particularly light and oxygen sensitive.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Samples should be collected in plastic or glass bottles. All bottles must be thoroughly cleaned and rinsed with reagent water. The volume collected should be sufficient to ensure a representative sample, allow for replicate analysis, if required, and minimize waste disposal.

8.2. Sample preservation and holding times for the anions that can be determined by this method for water samples are as follows:

QuanTIMs Method Code		Analyte	Preservation	Holding Time
EPA 300.0A	SW846 9056A	Fluoride	4° ± 2°C	28 days
C8	3C			
CX	3D	Chloride	4° ± 2°C	28 days
GO	3E	Nitrite	4° ± 2°C	48 hours
GM	3F	Bromide	4° ± 2°C	28 days
C9	3G	Nitrate	4° ± 2°C	48 hours
DO	3H	Ortho Phosphate	4° ± 2°C	48 hours
CY	3I	Sulfate	4° ± 2°C	28 days

Note: Soil leachates will follow the same preservation and holding times as the water samples; starting from the time of extraction.

9. QUALITY CONTROL

9.1. The STL QC Program document provides further details of the QC and corrective action guidelines presented in this SOP. Refer to this document if additional guidance is required.

9.2. Table I provides a summary of quality control requirements including type, frequency, acceptance criteria and corrective action.

9.3. Initial Demonstration of Capability

9.3.1. Prior to the analysis of any samples by Ion Chromatography, the following requirements must be meet:

9.3.1.1. Method Detection Limit (MDL): An MDL must be determined prior to analysis of any samples. The MDL is determined using seven replicates of reagent water spiked with the anions of interest that has been carried through the entire analytical procedure. MDLs must be redetermined on an annual basis. The spike level must be greater than the calculated MDL

but less than or equal to 10x the MDL. The result of the MDL determination must be below the STL reporting limit.

9.4. Batch definition: Preparation and QC batch definitions are provided in the STL QC Policy.

9.5. Method Blank (MB): One method blank must be processed with each preparation batch. The method blank consists of reagent grade water that has been taken through the entire preparation and analytical process. The method blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. The method blank should not contain any analyte of interest above the reporting limit.

9.6. Laboratory Control Sample (LCS): One LCS must be processed with each preparation batch and must be carried through the entire analytical procedure. The LCS is used to monitor the accuracy of the analytical process. On-going monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines. If the result is outside established control limits the system is out of control and corrective action must occur. Until in-house limits are established, a control limit of 90 - 110% recovery must be applied. Corrective action will be repreparation and reanalysis of the batch unless the client agrees that other corrective action is acceptable. The LCS consists of reagent grade water containing a known amount of target analytes that has been injected into the ion chromatography system. The LCS is prepared from a separate stock standard, or neat material, of a different manufacturer than the stock, or neat material, used to prepare the calibration standard.

9.7. Matrix Spike/Matrix Spike Duplicate (MS/MSD): One MS/MSD pair must be processed for each QC batch. A matrix spike (MS) is a field sample to which a known concentration of target analyte has 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 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. Spiking levels will be the same as the LCS values.

- If the MS/MSD recovery or RPD falls outside the acceptance range, the recovery of the analyte must be in control for the LCS. Until in-house control limits are established, a control limit of 90-110% recovery and 20% RPD must be applied to the MS/MSD.

- If the native analyte concentration in the MS/MSD exceeds 4x the spike level for that analyte, the recovery data are reported as NC (i.e. not calculated).

- If the LCS recovery is within limits, then the laboratory operation is in control and the results may be accepted.

- If the recovery of the LCS is outside the limits, corrective action must be taken. Corrective action will include repreparation and reanalysis of the batch.

- If a MS/MSD is not possible due to limited sample volume then a LCS duplicate must be analyzed. The RPD of the LCS and LCSD must be compared to the matrix spike limits.

9.8. Continuing Calibration Verification (CCV/CCB): Continuing calibration is verified by analyzing the calibration standard after every ten (10) samples . The CCV must fall within +/- 10% of the true value for each target analyte. A CCB is analyzed immediately following the CCV to monitor low level accuracy and system cleanliness. The CCB result must be below the reporting limit for that analyte. If either the CCV or CCB fail to meet criteria, the analysis must be terminated, the problem corrected and repreparation and analysis of all samples following the last CCV and CCB which were in control.

10. CALIBRATION AND STANDARDIZATION

10.1. Establish ion chromatographic operating parameters equivalent to those indicated in table 2. Refer to Table 3 for typical standard run retention times. Other than the presence of the analytical column the instrument conditions are the same.

10.2. For each analyte of interest, prepare a **minimum** of 3 calibration standards and a blank by adding accurately measured volumes of one or more stock standards to a volumetric flask and dilution to volume with reagent water. If a sample analyte concentration exceeds the calibration range the sample may be diluted to fall within the range. If this is not possible then three new calibration concentrations must be chosen, two of which must bracket the concentration of the sample analyte of interest. Each attenuation range of the instrument used to analyze a sample must be calibrated individually.

10.3. Using an injection volume of 25 uL of each calibration standard, tabulate peak height or area responses against the concentration. The results are used to prepare a calibration curve for each analyte. During this procedure, retention times must be recorded. All

analytes will be calibrated using a quadratic regression forced through the origin. Correlation coefficients (R^2) must be 0.995 or better.

11. PROCEDURE

11.1. One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo and is approved by a Technical Specialist and QA Manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file.

11.2. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

11.3. Table 2 summarizes the recommended operating conditions for the ion chromatograph. Included in this table are estimated retention times that can be achieved by this method. Other columns, chromatographic conditions, or detectors may be used if the requirements of Sect. 9.2 are met.

11.4. Check system calibration daily as outlined in Table 1 and, if required, recalibrate as described in Sect 10.

11.5. Load and inject a fixed amount (25 uL) of settled & filtered sample. If the sample is cloudy then it should be filtered prior to loading into the autosampler polyvial. Flush injection loop thoroughly, using each new sample. Use the same size loop for standards and samples. Record the resulting peak size in area or peak height units. An automated constant volume injection system may also be used.

11.6. The width of the retention time window used to make identifications should be based upon measurements of actual retention time variations of various concentration. Three times the standard deviation of a retention time can be used to calculate a suggested window size for each analyte. However, the experience of the analyst should weigh heavily in the interpretation of chromatograms since retention time is concentration dependent for most analytes..

11.7. If the response for the peak exceeds the working range of the system, dilute the sample with an appropriate amount of reagent water and reanalyze.

11.8. If the resulting chromatogram fails to produce adequate resolution, or if identification of specific anions is questionable, fortify the sample with an appropriate amount of standard and reanalyze.

NOTE: Retention time is affected by concentration. Nitrate and sulfate exhibit the greatest amount of change, although all anions are affected to some degree. See Table 3. In some cases this peak migration may produce poor resolution or identification.

11.9. The following extraction should be used for solid materials: Add an amount of reagent water equal to ten times the weight of dry solid material taken as a sample. This slurry is mixed for one hour using a magnetic stirring device or tumbler. Filter the resulting slurry before injecting using a 0.45 um membrane type filter. This can be the type that attaches directly to the end of the syringe

11.10. Should more complete resolution be needed between peaks the eluent (7.3) can be diluted. This will spread out the run but will also cause the later eluting anions to be retained longer. The analyst must determine to what extent the eluent is diluted. This dilution should not be considered a deviation from the method.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Prepare a calibration curve for each analyte by plotting instrument response against standard concentration. Compute sample concentration by comparing sample response with the standard curve. Multiply answer by appropriate dilution factor.

12.2. Report only those values that fall between the lowest and the highest calibration standards. Samples exceeding the highest standard should be diluted and reanalyzed.

12.3. Report results in mg/L for aqueous samples and mg/Kg for 1 hour leachates and mg/L for 18 hour leachates of solid samples.

12.4. Report NO_2^- as N

NO_3^- as N

$HPO_4^=$ as P

13. METHOD PERFORMANCE

13.1. The reporting limits for the following analytes are based on a 25 uL injection volume:

Analyte	Water RL	Soil RL
Fluoride	1.0 mg/L	10 mg/kg
Chloride	1.0 mg/L	10 mg/kg
Nitrite	0.5 mg/L	5 mg/kg
Bromide	0.5 mg/L	5 mg/kg
Nitrate	0.05 mg/L	0.5 mg/kg
O-Phosphate	0.5 mg/L	5 mg/kg
Sulfate	1.0 mg/L	10 mg/kg

13.2. The group/team leader has the responsibility to ensure that this procedure is performed by an analyst who has been properly trained in its use and has the required experience. The analyst must be given two blind performance samples to analyze or process for analysis. Upon successful completion of the performance evaluation (PE) samples, these analyses will be documented as initial qualification,. Requalification must be performed annually thereafter for this procedure. The group/team leader must document the training and PE performance and submit the results to the QA Manager for inclusion in the associate's training files.

14. POLLUTION PREVENTION

14.1. This method does not contain any specific modifications that serve to minimize or prevent pollution.

15. WASTE MANAGEMENT

15.1. Waste generated in this procedure must be segregated, and disposed of according to the facility hazardous waste procedures. The Environmental Health and Safety Director should be contacted if additional information is required.

16. REFERENCES

16.1. Method 300.0, "Determination of Inorganic Anions by Ion Chromatography", Environmental Monitoring Systems Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Cincinnati, Ohio, Revision 2.1, August 1993.

16.2. Method 9056A, "Determination of Inorganic Anions by Ion Chromatography", SW846, Test Methods for Evaluating Solid Waste, Third Edition, Draft Revision 1, September 1999.

16.3. STL North Canton Laboratory Quality Manual (LQM), current version.

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

17.1. Attachment #1, method Flow Chart

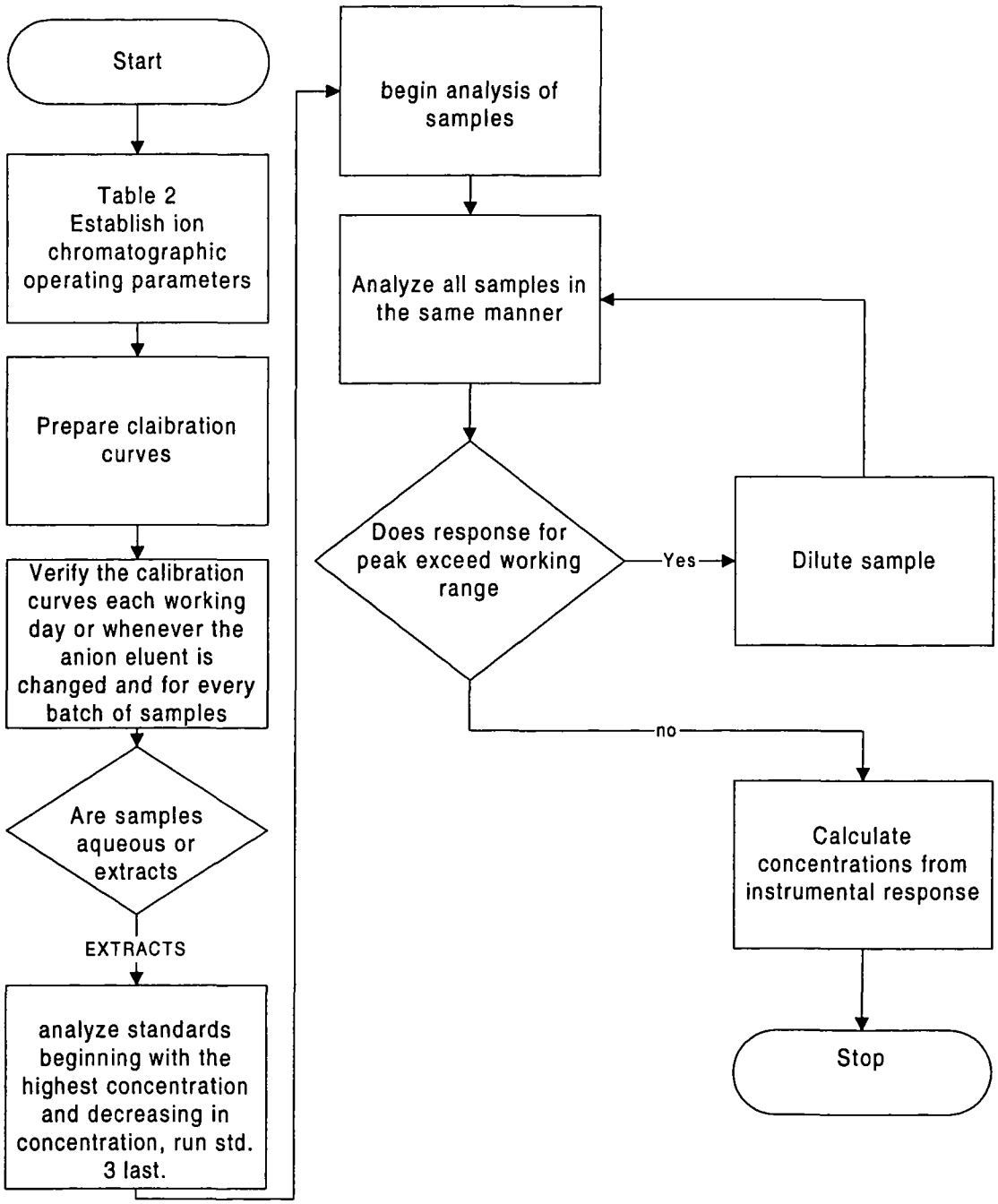
17.2. Table 1, Quality Control Samples

17.3. Table 2, Standard Instrument Operating Parameters

17.4. Table 3, Retention Time Matrix

17.5. Figure 1, Example Chromatogram

Determination Of Inorganic Anions By Ion Chromatography



ATTACHMENT #1

TABLE 1

QUALITY CONTROL SAMPLES

QC Samples	Frequency	Acceptance Criteria	Corrective Action
Initial Calibration Verification (ICV)	At the start of each day following calibrating prior to sample analysis	+/- 10% of true value	Recalibrate and reanalyze
Initial Calibration Blank (ICB)	After Initial Calibration Verification and prior to sample analysis	< the Reporting Limit	Reprepare and reanalyze
Laboratory Control Sample (LCS)	1 per batch of 20 samples	Meets laboratory historical limits	Reanalyze all samples associated with unacceptable LCS
Matrix Spike Sample (MS/MSD)	1 MS/MSD pair per batch or 20 samples	Meets laboratory historical limits	Supervisor's technical judgment
Continuing Calibration Verification (CCV)	Between each group of 10 injections and at the end of the analytical sequence	+/- 10% of true value	Recalibrate and reanalyze all samples since the last acceptable CCV
Continuing Calibration Blank (CCB)	Between each group of 10 injections and at the end of the analytical sequence	< the Reporting Limit	Recalibrate and reanalyze all samples since the last acceptable CCB

TABLE 2

Standard Instrument Operating Parameters

Standard Conditions:

Eluent Pump Rate:	1.20 mL/min (DX-120 and DX-320)
Sample Loop:	25 uL
Eluent:	1.0mM sodium bicarbonate, 3.5mM sodium carbonate
Detector output	Baseline conductivity should be 15 - 20 uS prior to sample analysis.

TABLE 3

Standard Run Retention Time Matrix (minutes)*

	Concentration (mg/L)													
Analyte	0.05	0.2	0.5	1	2	2.5	5	10	20	40	50	100	200	RT window
F^-	2.75		2.75			2.75	2.75	2.75						
Cl^-				3.97				3.98			4.03	4.08	4.17	
NO_2^-	4.80		4.80			4.78	4.78	4.80						
Br^-		6.15			6.13			6.10	6.08	6.07				
NO_3^-	7.33		7.27			7.17	7.13	7.07						
$o\text{-}PO_4^{2-}$	9.53		9.53			9.52	9.50	9.48						
SO_4^{2-}				11.50				11.48			11.43	11.38	11.27	

* Analyte retention time is concentration dependent for most anions. Retention time increases with increasing concentration for chloride. Retention time decreases with increasing concentration for bromide, nitrate, ortho-phosphate and sulfate.

EXAMPLE ION CHROMATOGRAM

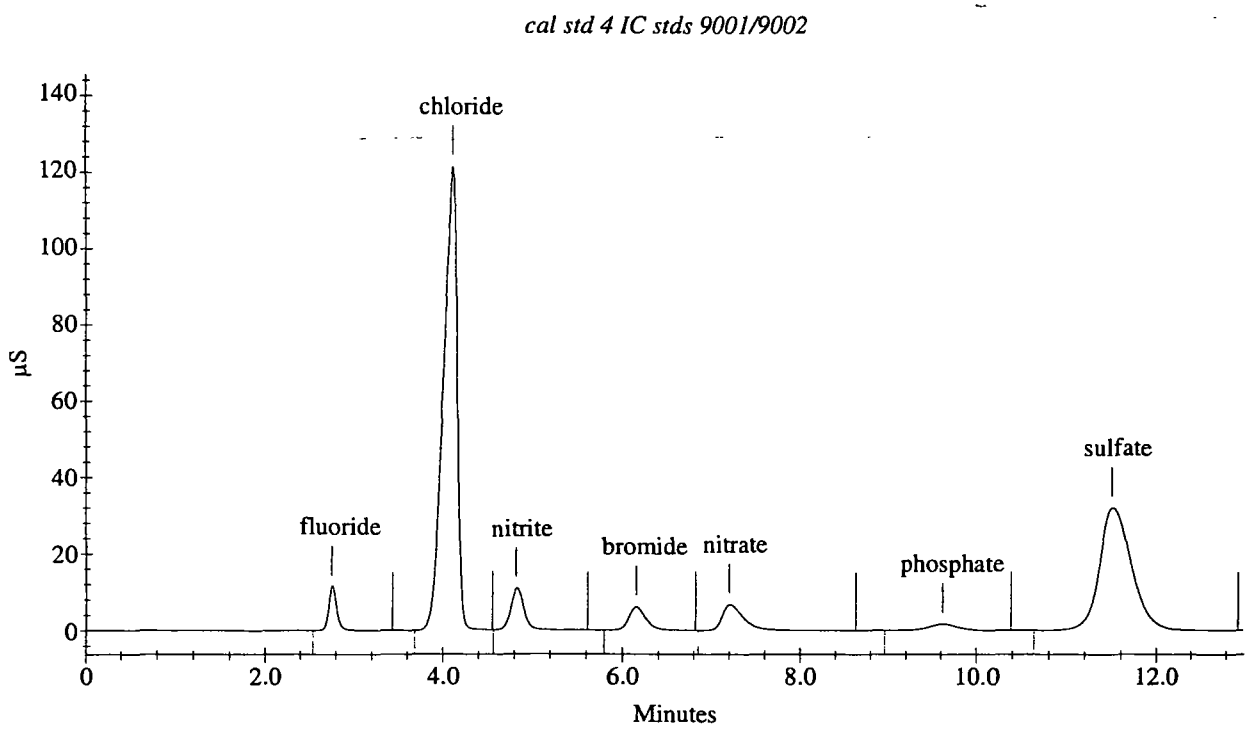


Figure #1

STL NORTH CANTON STANDARD OPERATING PROCEDURE

TITLE: SULFIDE

(SUPERSEDES: REVISION 0; DATED 02/14/96)

Prepared by:	Laurel E. Wood	11/20/00 Date
Reviewed by:	Technology Specialist	11/20/00 Date
Approved by:	Quality Assurance Manager	11/20/00 Date
Approved by:	Environmental Health and Safety Coordinator	11-20-00 Date
Approved by:	Laboratory Director	11-20-00 Date

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1. SCOPE AND APPLICATION

1.1. This method is applicable to the determination of the concentration of Sulfide in waters, liquids, solids, and sludges. It is based on SW846 Method 9030A and Methods for Chemical Analysis of Water and Wastes (MCAWW) 376.1. The working range is 1 to 30 mg/L for waters and 50 to 1500 mg/kg for solids and sludges.

1.2. This document accurately reflects current laboratory standard operating procedures (SOP) as of the date above. All facility SOPs are maintained and updated as necessary by the laboratory QA department.

1.3. The associated QuantIMS method codes are P3 (9030), FG (9030A), and CT (376.1).

2. SUMMARY OF METHOD

2.1. An excess of iodine is added to a sample which oxidizes the Sulfide to sulfur under acidic conditions. The excess iodine is back titrated with sodium thiosulfate.

3. DEFINITIONS

3.1. Refer to the glossary in the Laboratory Quality Manaual (LQM).

4. INTERFERENCES

4.1. Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus that lead to discrete artifacts. All of these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. Specific selection of reagents may be required to avoid introduction of contaminants.

4.2. Reducing substances such as thiosulfite, sulfites, and various organic compounds cause interferences, but treatment with zinc acetate solution will eliminate some of these interferences. (Use approximately 15 drops of 2 N zinc acetate per 500 mL of sample if not already preserved with it.)

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 Aicd, Sodium Hydroxide**

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

5.5. The preparation of standards and reagents will be conducted in a fume hood with the sash closed as far as the operation will permit.

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

6. EQUIPMENT AND SUPPLIES

6.1. Volumetric pipets: various

6.2. Buret: 25 mL Class A

6.3. Erlenmeyer flasks: 500 mL

6.4. Graduated cylinder: 250 mL

6.5. Top loading balance: capable of accurately weighing ± 0.01 g

6.6. Volumetric flasks: various

6.7. Vacuum pump, filter and flask

6.8. Whatman 934-AH filters

6.9. Dessicator

7. REAGENTS AND STANDARDS

7.1. Reagents

7.1.1. (1:1) Hydrochloric Acid: Add 250 mL concentrated hydrochloric acid (HCl) to 250 mL of reagent water.

7.1.2. Starch Indicator: Add 10 mL of reagent water to 5 g starch (potato) and mix. Add starch mixture to 500 mL of boiling reagent water. Mix, cool, and store in a well-labeled squirt bottle. Alternately, use purchased starch solution.

7.1.3. 0.025 N Sodium Thiosulfate (stored in dessicator): Add 0.4 g NaOH and 6.205 g of sodium thiosulfate ($Na_2S_2O_3 \bullet 5H_2O$) to 500 mL of reagent water in a 1 liter volumetric. Dilute to volume with reagent water. Store in a dark container. Also available commercially.

7.1.3.1. Standardization of 0.025 N Sodium Thiosulfate Solution: To make 0.025N Biodate Solution, dissolve 0.462 g $KH(IO_3)_2$ in 500 mL with reagent water. Weigh 2 g KI in a 500 mL Erlenmeyer flask. Add 100 to 150 mL reagent water, 5 drops H_2SO_4 and 20 mL biodate solution using a volumetric pipet. Dilute to 200 mL with reagent water. Titrate with Sodium Thiosulfate. When a pale straw yellow color is reached, add 1-2 mL starch. Continue titrating from a blue to a clear end point.

Calculation

$$Na_xS_2O_3\ Normality = \frac{(a)\ (b)}{c}$$

a = *mLs Biodate (20 mL)*

b = *Normality Biodate (0.025N)*

c = *mLs of $Na_2S_2O_3$ used to titrate*

Repeat two more times

7.1.4. 0.025 N Iodine Solution: Add 20 g KI (potassium iodide) and 3.2 g iodine to a 1 liter volumetric flask. Add 500 - 700 mL of reagent water and dissolve. Dilute to volume with reagent water. Store in a dark container. Also available commercially.

7.1.4.1. Standardization 0.025 N Iodine Solution: Perform three method blanks. Refer to method blank section in SOP.

Calculation

$$\textit{Normality Iodine} = \frac{(\textit{Normality } Na_2S_2O_3)(\textit{mL of titrant } Na_2S_2O_3)}{\textit{20 mL Iodine}}$$

7.1.5. 2N Zinc Acetate: Dissolve 220 g of zinc acetate in 870 mL of reagent water and dilute to 1 liter with reagent water.

7.2. Standards

7.2.1. Laboratory Control Sample

7.2.1.1. 2000 ppm Sulfide: Add 3.5 g of sodium sulfide to 100 mL of reagent water in a 250mL volumetric flask. Dilute to volume with reagent water. Sulfide standard must be made fresh daily.

7.2.2. Matrix Spike Standard

7.2.2.1. Prepare a midrange matrix spike standard as described in 7.2.1 for use as a MS/MSD.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Waters are preserved to a pH > 9 with NaOH and zinc acetate. Non-water samples are unpreserved. All matrices are stored at 4°C ± 2°C in plastic or glass containers.

8.2. The holding time is seven days from sampling to analysis.

9. QUALITY CONTROL

9.1. Batch Definition

9.1.1. A batch is a group of no greater than 20 samples excluding QC samples (LCS, Method Blank, MS, MSD) which are processed similarly, with respect to the procedure. All sample setups must be initiated within a 24 hour period from the initial preparation or extraction and without interruption of the process. All samples within the batch must be treated with the same lots of reagents and the same processes.

9.2. Method Blank

9.2.1. One method blank (MB) must be processed with each preparation batch. The method blank consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The method blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. The method blank should not contain any analyte of interest at or above the reporting limit.

9.2.2. A reagent water blank consisting of 250 mL of reagent water must be analyzed with each analytical batch of samples.

9.2.3. Corrective Action for Blanks

9.2.3.1. If the analyte level in the method blank exceeds the reporting limit for the analytes of interest in the sample, all associated samples are reprepared and reanalyzed. If this is not possible due to limited sample quantity or other considerations, the corresponding sample data **must be addressed in the project narrative.**

9.2.3.2. If there is no analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. **Such action must be taken in consultation with the client and must be addressed in the project narrative.**

9.3. Laboratory Control Sample (LCS)

9.3.1. One aqueous LCS must be processed with each preparation batch. The LCS must be carried through the entire analytical procedure. The LCS is used to monitor the accuracy of the analytical process. On-going monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines.

9.3.2. A midrange LCS is prepared by adding 2.5 mL of 2000ppm sulfide standard to a 250mL volumetric flask and bringing to final volume with reagent water. This standard must be analyzed with each analytical batch of samples.

9.3.3. Corrective Action for LCS

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

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

9.4. Matrix Spike/Matrix Spike Duplicate (MS/MSD)

9.4.1. One MS/MSD pair must be processed for each batch. A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added. A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked identically as the MS) prepared and analyzed along with the sample and matrix spike. Some client specific data quality objectives (DQO's) may require the use of sample duplicates in place of or in addition to MS/MSD's. The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Due to the potential variability of the matrix of each sample, these results may have immediate bearing only on the specific sample spiked. Samples identified as field blanks cannot be used for MS/MSD analysis.

9.4.2. A MS/MSD consisting of 5 g or 250 mL of the sample and 2.5mL of 2000 ppm sulfide standard should be analyzed with every 20 samples.

9.4.3. Corrective action for MS/MSDs

9.4.3.1. If the analyte recovery or RPD falls outside the acceptance range, the recovery of that analyte must be in control for the LCS. If the LCS recovery is within limits, then the laboratory operation is in control and the results may be accepted. If the recovery of the LCS is outside limits, corrective action must be taken. Corrective action will include repreparation and reanalysis of the batch.

9.4.3.2. If the native analyte concentration in the MS/MSD exceeds 4x the spike level for that analyte, the recovery data is reported as DIL (diluted out).

9.4.3.3. If an MS/MSD is not possible due to limited sample volume then a laboratory control sample duplicate (LCSD) should be analyzed. The

RPD of the LCS and LCSD must be compared to the matrix spike RPD limits.

10. CALIBRATION AND STANDARDIZATION

10.1. Not Applicable

11. PROCEDURE

11.1. One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo and is approved by a Technical Specialist and QA Manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file.

11.2. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

11.3. Sample Preparation

11.3.1. Water Samples

11.3.1.1. Using the vacuum apparatus, filter 250 mL (or a lesser aliquot) of well homogenized sample. Discard the filtrate and analyze the pad and solids following section 11.4. Record volume filtered on the analytical logsheet.

11.3.2. Non-Water Samples

11.3.2.1. No preparation necessary.

11.4. Sample Analysis

11.4.1. Summary

11.4.1.1. Excess iodine is added to a sample and under acidic conditions is back titrated with sodium thiosulfate from a blue to a clear color.

11.4.2. Sample Analysis Procedure

11.4.2.1. Place the pad from the filtered water sample (section 11.3.1) or 5 g of non-water sample in a 500 mL Erlenmeyer flask. At this time, add any spiking solutions if necessary. Add 20.0 mL .025 Iodine solution and 1-2 mL 1:1 HCl solution (watch for fumes). Add 250 mL reagent water and mix. Add 1 squirt (1-2 mL) of starch indicator and mix. Titrate from blue to clear with .025 N sodium thiosulfate titrant. Record the amount of titrant used on the analytical logsheet.

NOTE: Some matrices may be turbid or colored and the color change from blue to clear may not be easily seen. In this case, look for a shade change.

11.5. Analytical Documentation

11.5.1. Record all analytical information in the analytical logbook/logsheet, including the analytical data from standards, blanks, LCSs, MS/MSDs, and any corrective actions or modifications to the method.

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

11.5.3. Documentation such as all associated instrument printouts (final runs, screens, reruns, QC samples, etc.) and daily calibration data corresponding to all final runs is available for each data file.

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

12. DATA ANALYSIS AND CALCULATIONS

12.1. Calculations

$$\textit{Sulfide, mg / L or mg / kg} = \frac{[(A \times B) - (C \times D)] \times 16{,}000}{\textit{mL or g of sample used}}$$

Where:

A	=	***mL of iodine solution***
B	=	***Normality of iodine solution***
C	=	***mL of sodium thiosulfate titrant***
D	=	***Normality of sodium thiosulfate titrant***

$$\textit{Sulfide, mg / L or mg / kg} = \frac{(20 - \textit{mL titrant}) \times 400}{\textit{mL or g of sample used}}$$

12.1.1.

$$LCS\ \%\ \text{Recovery} = \frac{\text{mg/L (from 12.1.1)}}{\text{20 (true)}} \times 100$$

12.1.2.

$$\text{MS/MSD \% Recovery} = \frac{\text{A - B}}{\text{20 (waters) or 1000 (solids)}} \times 100$$

Where:

A	=	***(20 - mL titrant for MS/MSD) x 400***
B	=	***Concentration from 12.1.1 x mL or g of sample used***

13. METHOD PERFORMANCE

13.1. Each laboratory must have initial demonstration of performance data on file and corresponding method detection limit files.

13.2. Training Qualifications:

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

14. POLLUTION PREVENTION

14.1. This method does not contain any specific modifications that serve to minimize or prevent pollution.

15. WASTE MANAGEMENT

15.1. All aqueous sample preparations can be rinsed down the drain with copious amounts of water.

15.2. Solvent waste must be disposed of in clearly labeled waste cans.

15.3. Acid waste must be collected in clearly labeled acid waste containers.

15.4. Solid materials (gloves, soiled paper products, etc.) are placed in the solid debris container. Do not put liquids in the solid waste container.

15.5. Refer to the Laboratory Sample and Waste Disposal plan.

15.6. Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices of STL North Canton. They must have training on the hazardous waste disposal practices upon initial assignment to these tasks, followed by an annual refresher training.

16. REFERENCES

16.1. References

16.1.1. SW846, Test Methods of Evaluating Solid Waste, Third Edition, Sulfide, Method 9030A.

16.1.2. EPA 600, Methods for Chemical Analysis of Waters and Wastes, Sulfide (Titrimetric, Iodine), Method 376.1

16.1.3. Standard Methods Eighteenth Edition, Sulfide Method 4500-5^2-E

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

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

17.1. Reporting limits

17.1.1. The lower reporting limits (RL) are 1 mg/L for waters and 50 mg/kg for solids.

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

17.1.3. The lab does not perform the distillation procedure described in Method SW846 9030A.

17.2. Troubleshooting guide

17.2.1. Samples that contain strong oxidizers or reducers will interfere with this method.

17.2.2. Samples that are not water miscible (oils, various solvents) cannot be analyzed using this method.

17.2.3. The iodine should turn a yellow-orange color when added to the sample after the addition of the reagent water. If it does not, the sample may be high in sulfide and less sample should be used.

ATTACHMENT 2

EXAMPLE FIELD FORMS

STRATIGRAPHY LOG (OVERBURDEN)

PAGE ____ OF ____

PROJECT NAME _____
PROJECT NUMBER _____
CLIENT _____
LOCATION _____

DRILLING CONTRACTOR _____
DRILLER _____
SURFACE ELEVATION _____
WEATHER (A.M.) _____
(P.M.) _____

HOLE DESIGNATION _____
DATE/TIME STARTED _____
DATE/TIME COMPLETED _____
DRILLING METHOD _____
CRA SUPERVISOR _____

STRATIGRAPHIC INTERVALS (DEPTHS IN ft/m BGS)			SAMPLE DESCRIPTION	SAMPLE DETAILS									
FROM	AT	TO	ORDER OF DESCRIPTORS: SOIL TYPE SYMBOL(S) – MAIN COMPONENT(S), (NATURE OF DEPOSIT), SECONDARY COMPONENTS, RELATIVE DENSITY/CONSISTENCY, GRAIN SIZE/PLASTICITY, GRADATION/STRUCTURE, COLOUR, MOISTURE CONTENT, SUPPLEMENTARY DESCRIPTORS NOTE: PLASTICITY DETERMINATION REQUIRES THE ADDITION OF MOISTURE IF THE SAMPLE IS TOO DRY TO ROLL (INDICATE IF MOISTURE WAS ADDED OR NOT).	SAMPLE #	SAMPLING METHOD	PENETRATION RECORD SPLIT SPOON BLOWS (RECORD N-VALUES & RECOVERIES) 6"	6"	6"	6"	SAMPLE INTERVAL	PID / FID (ppm)	CHEMICAL ANALYSIS	GRAIN SIZE

NOTES AND COMMENTS

DEPTH OF BOREHOLE CAVING _____ DEPTH OF FIRST GROUNDWATER ENCOUNTER _____ TOPSOIL THICKNESS _____

WATER LEVEL IN OPEN BOREHOLE ON COMPLETION _____, AFTER ____ HOURS ____

COMPLETION DETAILS: _____

NOTE: FOR EACH SPLIT-SPOON SAMPLE, RECORD BLOW COUNTS, N-VALUE, SAMPLE RECOVERY LENGTH, AND SAMPLE INTERVAL.

CRA

SOIL CLASSIFICATION SYSTEM (MODIFIED U.S.C.S.)

MAJOR DIVISIONS			GROUP SYMBOL	TYPICAL DESCRIPTION
HIGHLY ORGANIC SOILS			PT	PEAT AND OTHER HIGHLY ORGANIC SOILS
COARSE-GRAINED SOILS (MORE THAN HALF BY WEIGHT LARGER THAN NO. 200 SIEVE SIZE)	GRAVELS MORE THAN HALF OF COARSE FRACTION LARGER THAN NO. 4 SIEVE SIZE	CLEAN GRAVELS	GW	WELL GRADED GRAVEL, GRAVEL-SAND MIXTURES, < 5% FINES
			GP	POORLY GRADED GRAVELS AND GRAVEL-SAND MIXTURES, < 5% FINES
		DIRTY GRAVELS	GM	SILTY GRAVELS, GRAVEL-SAND-SILT MIXTURES, > 12% FINES
			GC	CLAYEY GRAVELS, GRAVEL-SAND-CLAY MIXTURES, > 12% FINES
	SANDS MORE THAN HALF OF COARSE FRACTION SMALLER THAN NO. 4 SIEVE SIZE	CLEAN SANDS	SW	WELL GRADED SANDS, GRAVELLY SANDS, < 5% FINES
			SP	POORLY GRADED SANDS, OR GRAVELLY SAND, < 5% FINES
		DIRTY SANDS	SM	SILTY SANDS, SAND-SILT MIXTURES > 12% FINES
			SC	CLAYEY SANDS, SAND-CLAY MIXTURES > 12% FINES
FINE-GRAINED SOILS (MORE THAN HALF BY WEIGHT PASSES NO. 200 SIEVE SIZE)	SILTS BELOW "A" LINE ON PLASTICITY CHART; NEGLIGIBLE ORGANIC CONTENT		ML	INORGANIC SILTS AND VERY FINE SAND, ROCK FLOUR, SILTY SANDS OF SLIGHT PLASTICITY
			MH	INORGANIC SILTS, MICACEOUS OR DIATOMACEOUS, FINE SANDY OR SILTY SOILS
	CLAYS ABOVE "A" LINE ON PLASTICITY CHART; NEGLIGIBLE ORGANIC CONTENT		CL	INORGANIC CLAYS OF LOW PLASTICITY, GRAVELLY, SANDY, OR SILTY CLAYS, LEAN CLAYS
			CI	INORGANIC CLAYS OF MEDIUM PLASTICITY, SILTY CLAYS
			CH	INORGANIC CLAYS OF HIGH PLASTICITY, FAT CLAYS
	ORGANIC SILTS & ORGANIC CLAYS BELOW "A" LINE ON PLASTICITY CHART		OL	ORGANIC SILTS AND ORGANIC SILTY CLAYS OF LOW PLASTICITY
			OH	ORGANIC CLAYS OF HIGH PLASTICITY

CONVENTIONAL SOIL DESCRIPTIONS

NON-COHESIVE (GRANULAR) SOIL

RELATIVE DENSITY	BLOWS PER FOOT (N-VALUE)
Very loose	less than 5
Loose	5 to 9
Compact	10 to 29
Dense	30 to 50
Very Dense	greater than 50

COHESIVE (CLAYEY) SOIL

CONSISTENCY	BLOWS PER FOOT (N-VALUE)
Very Soft	0 to 2
Soft	3 to 4
Firm	5 to 8
Stiff	9 to 15
Very Stiff	16 to 30
Hard	greater than 30

GRAIN SIZE CLASSIFICATION

COBBLES	Greater than 3 inches (76 mm)
GRAVEL	3 in. to No. 4 (4.76 mm)
Coarse Gravel	3 in. to 3/4 in.
Fine Gravel	3/4 in. to No. 4 (4.76 mm)
SAND	No. 4 (4.76 mm) to No. 200 (0.074 mm)
Coarse Sand	No. 4 (4.76 mm) to No. 10 (2.0 mm)
Medium Sand	No. 10 (2.0 mm) to No. 40 (0.42 mm)
Fine Sand	No. 40 (0.42 mm) to No. 200 (0.074 mm)
SILT	No. 200 (0.074 mm) to 0.002 mm
CLAY	Less than 0.002 mm

NOTE: The "No. ___ " refers to the standard sieve sizes.

COMPONENT PERCENTAGE DESCRIPTORS

Noun(s) (e.g. SAND and GRAVEL)	35 to 50%
Adjective (e.g. SANDY)	20 to 35%
With	10 to 20%
Trace	Less than 10%

SOIL STRUCTURE TERMS

Stratified	Blocky
Laminated	Lenses/Seams
Fissured	Homogeneous

CRA

TEST PIT STRATIGRAPHY LOG

PAGE ____ OF ____

PROJECT NAME _____
PROJECT NUMBER _____
CLIENT _____
LOCATION _____

CONTRACTOR _____
SURFACE ELEVATION _____
WEATHER (A.M.) _____
(P.M.) _____

TEST PIT DESIGNATION _____
DATE/TIME STARTED _____
DATE/TIME COMPLETED _____
TEST PIT METHOD _____
CRA SUPERVISOR _____

STRATIGRAPHIC INTERVALS (DEPTHS IN ft/m BGS)			SAMPLE DESCRIPTION	SAMPLE DETAILS			GEOLOGIC PROFILE
FROM	AT	TO	ORDER OF DESCRIPTORS: SOIL TYPE SYMBOL(S) - MAIN COMPONENT(S), (NATURE OF DEPOSIT), SECONDARY COMPONENTS, RELATIVE DENSITY/CONSISTENCY, GRAIN SIZE/PLASTICITY, GRADATION/STRUCTURE, COLOUR, MOISTURE CONTENT, SUPPLEMENTARY DESCRIPTORS NOTE: PLASTICITY DETERMINATION REQUIRES THE ADDITION OF MOISTURE IF THE SAMPLE IS TOO DRY TO ROLL (INDICATE IF MOISTURE WAS ADDED OR NOT).	SAMPLE #	SAMPLE	INTERVAL	PID/FID (ppm)	

NOTES AND COMMENTS

CRA

CONESTOGA-ROVERS & ASSOCIATES
JOB NAME: Waukegan Manufactured Gas and Coke Plant
JOB NO: 19023
PRESERVED? YES NO (Circle)

HNO_3 HCl NaOH H_2SO_4 NaOH/ZnOAc Other

MONTH/DAY/YEAR: _____ TIME: _____

SAMPLE ID: _____

SAMPLER'S SIGNATURE: _____

LAB SAMPLE ID: _____

EXAMPLE SAMPLE LABEL

CRA
CONESTOGA-ROVERS & ASSOCIATES
8615 West Bryn Mawr Ave. · Chicago, IL 60631

EXAMPLE CUSTODY SEAL

FedEx Express USA Airbill

FedEx Tracking Number 831889446147

Form ID No. 0215

SPG13

1 From *Please print and press hard.*

Date Example

Sender's FedEx Account Number [redacted]

Sender's Name Joe Sampler Phone (773) 380-9933

Company CONESTOGA-ROVERS & ASSOC INC

Address 8615 W BRYN MAWR AVE

Dept./Floor/Suite/Room

City CHICAGO State IL ZIP 60631

2 Your Internal Billing Reference
First 24 characters will appear on invoice

3 To

Recipient's Name Sample Receiving Phone (330) 497-0772

Company STL

Address 4101 Shuffel Drive, NW

To "HOLD" at FedEx location, print FedEx address — We cannot deliver to P.O. boxes or P.O. ZIP codes

Dept./Floor/Suite/Room

City North Canton State OH ZIP 44720

By using this Airbill you agree to the service conditions on the back of this Airbill and in our current Service Guide, including terms that limit our liability

Questions? Visit our Web site at fedex.com
or call 1 800 Go.FedEx® 800.463.3339.

0198317575

4a Express Package Service — *Packages up to 150 lbs.* Delivery commitment may be later in some areas

- [x] FedEx Priority Overnight — Next business morning
- [ ] FedEx Standard Overnight — Next business afternoon
- [ ] FedEx First Overnight — Earliest next business morning delivery to select locations
- [ ] FedEx 2Day — Second business day
- [ ] FedEx Express Saver — Third business day
- [ ] FedEx Extra Hours — Later drop-off with next business afternoon delivery for select locations

FedEx Envelope rate not available. Minimum charge: One pound rate

4b Express Freight Service — *Packages over 150 lbs.* Delivery commitment may be later in some areas

- [ ] FedEx 1Day Freight* — Next business day
- [ ] FedEx 2Day Freight — Second business day
- [ ] FedEx 3Day Freight — Third business day

* Call for Confirmation.

5 Packaging — * Declared value limit $500

- [ ] FedEx Envelope*
- [ ] FedEx Pak* — Includes FedEx Small Pak, FedEx Large Pak, and FedEx Sturdy Pak
- [x] Other Pkg. — Includes FedEx Box, FedEx Tube, and customer pkg.

6 Special Handling

- [ ] SATURDAY Delivery — FedEx Priority Overnight and FedEx 2Day to select ZIP codes
- [ ] HOLD Weekday at FedEx Location — FedEx First Overnight
- [ ] HOLD Saturday at FedEx Location — FedEx Priority Overnight and FedEx 2Day to select locations

Does this shipment contain dangerous goods?

- [ ] No
- [ ] Yes — As per attached Shipper's Declaration
- [ ] Yes — Shipper's Declaration not required
- [ ] Dry Ice — Dry Ice - 9, UN 1845 ____ x ____ kg

Dangerous Goods (incl. Dry Ice) cannot be shipped in FedEx packaging or with FedEx Extra Hours service

- [ ] Cargo Aircraft Only

7 Payment *Bill to:*

- [ ] Sender — Acct. No. in Section 1 will be billed
- [ ] Recipient
- [ ] Third Party
- [ ] Credit Card
- [ ] Cash/Check

FedEx Acct. No. / Credit Card No. — Exp. Date

Total Packages	Total Weight	Total Declared Value†
		$ ____ .00

†Our liability is limited to $100 unless you declare a higher value. See back for details.

FedEx Use Only

8 Release Signature *Sign to authorize delivery without obtaining signature*

By signing you authorize us to deliver this shipment without obtaining a signature and agree to indemnify and hold us harmless from any resulting claims.

447

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CRA
CONESTOGA-ROVERS & ASSOCIATES
8615 W. Bryn Mawr Avenue
Chicago, Illinois 60631 (773)380-9933

CHAIN OF CUSTODY RECORD

SHIPPED TO (Laboratory Name):

REFERENCE NUMBER:

PROJECT NAME:

SAMPLER'S SIGNATURE: _____ PRINTED NAME: _____

SEQ. No.	DATE	TIME	SAMPLE No.	SAMPLE MATRIX	No. OF CONTAINERS	PARAMETERS										REMARKS
			TOTAL NUMBER OF CONTAINERS													

EXAMPLE

RELINQUISHED BY: ① _____	DATE: TIME:	RECEIVED BY: ② _____	DATE: TIME:
RELINQUISHED BY: ② _____	DATE: TIME:	RECEIVED BY: ③ _____	DATE: TIME:
RELINQUISHED BY: ③ _____	DATE: TIME:	RECEIVED BY: ④ _____	DATE: TIME:

METHOD OF SHIPMENT: AIR BILL No.

White —Fully Executed Copy
Yellow —Receiving Laboratory Copy
Pink —Shipper Copy
Goldenrod —Sampler Copy

SAMPLE TEAM: _____ _____

RECEIVED FOR LABORATORY BY: _____

DATE: _____ TIME: _____

5258

1001(FORMS)-OCT 24/96-REV 0-(C)(F-01)

APPENDIX D

HEALTH AND SAFETY PLAN

TABLE OF CONTENTS

		Page
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1.0 GENERAL

Conestoga-Rovers & Associates (CRA) has prepared this Health & Safety Plan (HASP) to be implemented at the Waukegan Manufactured Gas and Coke Plant in Waukegan, Illinois (Site). The activities outlined in the Remedial Design Scope of Work (SOW) will involve drilling, excavating, and sampling within the limits of the Site. While conducting these activities, CRA personnel may come in contact with soils, groundwater and debris which potentially contain hazardous materials. To ensure that any direct contact with potentially contaminated material by CRA Site personnel is minimized, this Site-specific Health and Safety Plan (HASP) was developed. Contractors and subcontractors shall develop HASPs which are specific to their SOW.

This HASP is designed to ensure the following:

i) that CRA's Site personnel are not adversely exposed to the compounds of concern as well as the physical and biological hazards present on Site;

ii) that public welfare or the environment are not adversely impacted by off-Site migration of contaminated materials due to work activities at the Site; and

iii) that CRA's operations, procedures and equipment at the Site will meet the requirements of 29 CFR 1910.120, Hazardous Waste Operations and Emergency Response, and the applicable subparts of 29 CFR 1926 and 29 CFR 1910.

For the purpose of this HASP, all remedial design activities carried out on Site involving contact with potentially contaminated materials will be considered contaminated operations requiring personal protective equipment (PPE). Similar activities occurring off Site are considered non-contaminated operations requiring a modified level of PPE from that for on-Site work.

All remedial design operations at the Site will be conducted in accordance with the provisions of the HASP. Cost and/or scheduling considerations will not be considered as justification for modifying this plan.

2.0 SITE CHARACTERIZATION AND HAZARD ANALYSIS

The Site is located in Waukegan, Illinois, on the peninsula separating Waukegan Harbor from Lake Michigan as depicted in Figure D.1.1. Access to and egress from the Site can be obtained from Sea Horse Drive. A Site plan is provided as Figure D.1.2.

The plant was built in 1928, operated through 1969, and was demolished in 1972. The soil and groundwater at the Site have been adversely impacted by past activities at the plant. The soil is contaminated with coal tar and arsenic. The groundwater contains elevated concentrations of arsenic, phenols, and ammonia.

A summary of the contaminants of concern and their related health effects are presented in Table D.1 of this HASP.

The activities to be performed as part of the remedial design SOW will include:

- groundwater monitoring activities;
- oversight of test pit and soil excavation;
- soil solidification/treatability study;
- oversight of surveying activities; and
- sampling activities.

Risks associated with these activities will be minimized by implementing engineering controls, safe work practices, and the proper use of personal protective equipment. Table D.2 summarizes the potential hazards associated with activities at the Site.

A hospital route map is provided on Figure D.1.3.

3.0 BASIS

The Occupational Safety and Health Administration (OSHA) Standards and Regulations contained in Title 29, CFR, Parts 1910 and 1926 (29 CFR 1910 and 1926) including the amended sections in 29 CFR 1910.120 and current Recommended Exposure Limits (RELs) as provided by the National Institute for Occupational Safety and Health (NIOSH) provide the basis for this Health and Safety Plan. Some of the specifications within this section are in addition to OSHA regulations and reflect the positions of the United States Environmental Protection Agency (USEPA), the National Institute for Occupational Safety and Health (NIOSH) and the United States Coast Guard (USCG) regarding procedures required to ensure safe operations at potential hazardous waste sites.

The safety and health of the public and on-Site personnel and the protection of the environment will take precedence over cost and schedule considerations for all project work.

4.0 RESPONSIBILITIES AND ADMINISTRATION

The following individuals are designated to carry out stated job responsibilities related to this project.

-Project Manager:	Alan Van Norman
-Project Coordinator:	Steve Wanner
-Field Coordinator:	Walter Pochron
-Project Industrial Hygienist:	Matthew Lazaric

An on-Site individual shall be designated as the Site Health and Safety Officer (HSO). The HSO will supervise the implementation of the Health and Safety Plan and will make all decisions regarding operations and work stoppages due to health and safety considerations.

The responsibilities of the HSO are as follows:

i) be responsible for controlling and maintaining Site access;

ii) be responsible for implementation of the HASP at the initiation of Site work;

iii) conduct the pre-entry safety briefing for all on-Site personnel with regard to the HASP and other safety requirements to be observed during field work, including:

   a) potential hazards,

   b) personal hygiene principles,

   c) personal protective equipment,

   d) respiratory protection equipment usage, and

   e) emergency response procedures.

iv) be responsible to hold "tailgate" meetings to discuss health and safety issues during each part of the days work;

v) review and modify the HASP as more information becomes available concerning the hazardous materials involved;

vi) supervision and enforcement of safety equipment usage;

vii) supervision and inspection of equipment cleaning;

viii) personnel training in safety equipment usage and emergency procedures;

ix) monitoring of the health and safety program under direction of an industrial hygienist;

x) suspend work activity if unsafe working conditions develop;

xi) inform workers of the nature of chemical exposure risk as required by the "Right-to-Know" Law;

xii) recommend a medical examination when a worker appears to require it;

xiii) coordination of the Emergency Response Plan;

xiv) assure that safety equipment is provided, maintained and accessible to Site personnel;

xv) maintain a log with a sign in/out sheet for personnel performing activities and visitors entering the Site;

xvi) assure that workers comply with the "buddy system" while working on Site; and,

xvii) investigate all accidents, injuries, illnesses, spills, fires, incidents, and near misses.

5.0 MEDICAL SURVEILLANCE

In accordance with requirements detailed in 29 CFR 1910.120(f), all CRA Site personnel (including contractors and/or subcontractors) who may be exposed to potentially contaminated materials will have received, within one year prior to starting field activities, medical surveillance by a licensed physician or physician's group.

Medical records for all on-Site personnel will be maintained by their respective employers. The medical records will detail the tests that were taken and will include a copy of the consulting physician's statement regarding the tests and the employee's suitability for work.

Each employer will ensure that its personnel involved in on-Site work will have all necessary medical examinations prior to commencing work which requires respiratory protection or exposure to hazardous materials. Personnel not obtaining medical certification will not perform work within contaminated areas.

Interim medical surveillance will be completed if an individual exhibits poor health or high stress responses due to on-Site activity or when accidental exposure to elevated concentrations of contaminants occurs.

6.0 TRAINING

All Site personnel are required, prior to entering the Site, to complete training sessions in accordance with 29 CFR 1910.120(e). This training shall consist of a minimum of 40 hours of instruction off Site and three days of actual field experience under the direct supervision of a trained, experienced supervisor. Each employer will maintain documentation stating that its on-Site personnel have complied with this regulation.

Prior to commencing Site activities, a Site-specific pre-entry safety briefing will be conducted. Topics covered during the pre-entry safety briefing will include:

i) Site-specific health and safety hazards;

ii) level of PPE required;

iii) safe use of equipment;

iv) decontamination procedures; and

v) emergency response procedures.

All personnel who attend this briefing will sign the Health and Safety Plan Acknowledgment Form presented as Attachment A.

All personnel working on Site shall attend regular safety ("tailgate") meetings. These meetings will be conducted by the HSO, and will cover specific health and safety issues, Site activities, changes in Site conditions, and a review of topics covered in the Site-specific pre-entry briefing. Topics discussed in the safety meetings will be documented along with the signatures of personnel who attend. -

7.0 WORK AREAS

Specific work areas, as defined below, will be delineated by temporary fencing or a flagged line.

a) Exclusion Zone (EZ) - This zone will include all areas where potentially contaminated soils or materials are to be handled and all areas where contaminated equipment or personnel travel.

b) Contaminant Reduction Zone (CRZ) - This zone will occur at the interface of the EZ and Support Zone and will provide access for the transfer of construction materials and Site equipment to the EZ, the decontamination of vehicles prior to leaving the EZ, the decontamination of personnel and clothing prior to entering the Support Zone, and for the physical segregation of the Support Zone and EZ.

c) Support Zone (SZ) - This area is the portion of the Site defined as the area outside the zone of significant air and soil contamination. The Support Zone will be clearly delineated and procedures implemented to prevent active or passive migration of contamination from the work Site.

8.0 PERSONAL PROTECTIVE EQUIPMENT

Engineering controls and work practices designed to reduce and maintain employee exposure at or below the permissible exposure limits (PELs) for the contaminants of concern will be implemented. Whenever engineering controls and work practices are not feasible, a reasonable combination of engineering controls, work practices and PPE shall be used to reduce and maintain employee exposure at or below the permissible exposure limits for the contaminants of concern.

All on-Site personnel shall be equipped with PPE appropriate for the nature of work being completed. All safety equipment and protective clothing shall be kept clean, well-maintained, and intact.

Safety equipment and apparel as required will be Level D, Modified Level D and Level C personal protective equipment (as determined by the action levels set forth in Section 9.0) within the Exclusion Zone.

Level D PPE

Type	*Properties*	*Item*
Foot protection	Steel-toe/reinforced shank	Boots
Head protection	Meets ANSI Z89.1 standard	Hard hat
Hand protection	Puncture/tear resistant	Leather/cotton gloves
Eye protection	Meets ANSI Z87.1 standard	Glasses/goggles with side shields

Modified Level D PPE

Type	*Properties*	*Item*
Foot protection	Steel-toe/reinforced shank	Boots
Foot protection	Chemical resistant (latex)	Overboots
Head protection	Meets ANSI Z89.1 standard	Hard hat
Hand protection	Chemical resistant (nitrile)	Inner gloves
Hand protection	Chemical resistant, puncture/ tear resistant (nitrile)	Outer gloves
Eye protection	Meets ANSI Z-87.1 standard	Glasses/goggles with side shields
Body protection	Chemical resistant (tyvek)	Coverall

Level C PPE

Type	*Properties*	*Item*
Foot protection	Steel-toe/reinforced shank	Boots
Foot protection	Chemical resistant (latex)	Overboots
Head protection	Meets ANSI Z89.1 standard	Hard hat
Hand protection	Chemical resistant (nitrile)	Inner gloves
Hand protection	Chemical resistant, puncture/ tear resistant (nitrile)	Outer gloves
Body protection	Chemical resistant (tyvek)	Coverall
Respiratory protection	NIOSH approved	Full-face air- purifying respirator with organic vapor/acid gas/HEPA filter

Additional protective equipment guidelines to be implemented include:

i) prescription eyeglasses in use on the Site will be safety glasses with side shields;

ii) contact lenses will not be permitted on the site;

iii) protective gloves (leather palm) will be worn over nitrile gloves by Site personnel involved in any drilling activities;

iv) during periods of respirator usage, respirator cartridges and filters will be changed daily, or upon breakthrough, whichever occurs first;

v) on-Site personnel who have not passed a respirator fit test will not be permitted to enter or work in the Exclusion Zone;

vi) personnel required to wear a respirator will not be permitted to have beards, or long sideburns or mustaches that interfere with the proper fit of the respirator;

vii) all PPE worn on Site will be decontaminated or discarded at the end of each work day;

viii) duct tape will be used to ensure that disposable coveralls and gloves are tightly secured when personnel are working within the Exclusion Zone; and

ix) no watches or other accessories will be permitted during drilling and sampling activities; rings are not allowed in the plant.

9.0 RESPIRATOR PROGRAM

Prior to arriving at the Site, all on-Site personnel will have received training in the use of, and have been fit tested for a full-facepiece respirator. Companies employing individuals required to perform intrusive work at the Site shall have a written respiratory program that complies with 29 CFR 1910.134.

During intrusive activities, a photoionization detector (PID) will be used to determine if organic vapors and some inorganic gases are present in the breathing space; a particulate monitor (miniram or equivalent) will be used to determine the level of particulates present in the breathing zone. A background reading will be established prior to commencing work activities at each work location.

Sustained (greater than 5 minutes) meter readings to determine the level of respiratory protection necessary during field activities will be:

Sustained Photoionization Organic Vapor Reading Above Background	*Protection Level*
0 - 1 ppm	Level D
1 - 25 ppm	Level C
>25 ppm	shut down activities

Sustained Particulate Reading Above Background	*Protection Level*
0 – 0.1 mg/m^3	Level D
0.1 – 2.5 mg/m^3	Level C
>2.5 mg/m^3	shut down activities

Work will be stopped and the work area will be allowed to vent if monitoring indicates that any of the following conditions exist:

i) organic vapors or particulate are present at concentrations which present Immediate Danger to Life and Health (IDLH) conditions, or in excess of the protection factor afforded by the air purifying respirator (whichever is lower);

ii) the oxygen content of the air is less than 19.5 percent or above 22.5 percent;

iii) organic vapor concentrations in the breathing zone exceed 25 ppm;

Air monitoring should continue, at a safe distance, if operations are stopped due to action level exceedences, to determine if a threat to the surrounding community exists.

Any changes to the protection level will be communicated to the HSO prior to continuation of the work.

10.0 JUSTIFICATION

These action levels assume that all NIOSH criteria for using an air purifying respirator (APR) have been met. An APR can typically be worn in concentrations of up to 50 times the TLV for a given contaminant. All of the contaminants of concern have TLVs or PELs higher than 1 ppm or 0.1 mg/m^3. Because of differences in sensitivities with direct reading instruments, a 50 percent safety factor is included when determining action levels. Therefore, the calculation to determine when a respirator could no longer be used would be:

1 ppm (TLV) x 50 (protection factor) x 0.5 (50% safety factor) = 25 ppm

1 mg/m^3 (TLV) x 50 (protection factor) x 0.5 (50% safety factor) = 2.5 mg/m^3

The primary routes of exposure of contaminants to individuals performing field investigative tasks include direct contact, ingestion and inhalation. The risk of exposure due to direct contact and ingestion will be minimized through the proper use of PPE as described in Section 8.0 and by exercising ordinary caution during sampling activities. In order to minimize exposure by the inhalation pathway, the respirator and air monitoring programs discussed in Sections 9.0 and 12.0 will be undertaken.

11.0 PERSONAL HYGIENE

All personnel performing or supervising work within the Exclusion Zone shall adhere to the personal hygiene-related provisions of this section.

On-Site personnel found to be disregarding the personal hygiene-related provisions of this HASP will, at the discretion of the HSO, be barred from the Site.

The following equipment/facilities shall be available for the personal hygiene of all on-Site personnel:

i) suitable disposable outerwear, gloves, respiratory protection and footwear on a daily basis for the use of on-Site personnel;

ii) disposal containers for used disposable outerwear; and

iii) potable water and a suitable sanitation facility.

The following regulations for personnel actively participating in the field sampling program shall be enforced:

i) on-Site personnel will wear appropriate PPE when in the Exclusion Zone;

ii) used disposable outerwear will not be reused if deemed to be unsuitable to provide the necessary protection, and when removed, will be placed inside disposal containers provided for that purpose;

iii) smoking, eating and drinking will be prohibited within the Exclusion Zone. These activities will be permitted only within designated areas; and

iv) on-Site personnel will thoroughly cleanse their hands, face, neck area and other exposed areas before smoking, eating or drinking and before leaving the Site.

12.0 AIR MONITORING

During the progress of intrusive work, air quality will be monitored on a continuous basis. During non-intrusive work air monitoring will be conducted on a periodic basis.

The air monitoring program will consist of monitoring with a PID for organic vapors and a particulate monitor for particulates in the breathing space. Operation and calibration procedures will be according to manufacturers' instructions. Calibration and maintenance records will be kept in the field log.

Identification of volatile organic vapor or particulate levels in excess of the action levels cited in Section 9.0 shall be reported to the HSO who will determine when PPE should be upgraded or operations be shut down and restarted.

If work is stopped because action levels have been exceeded, air monitoring will continue from a safe distance to determine if there is a threat to the surrounding community.

13.0 COMMUNICATIONS

Emergency numbers including the police department, fire department, ambulance, hospital and appropriate Regulatory agencies (Table 3) will be prominently posted near the Site telephone(s). In the event of an emergency, Outboard Marine Corporation's (OMC's) on-duty guard will be notified to coordinate necessary emergency response actions with the plant.

Prior to initiating Site activities, the route to the emergency medical facility will be verified to ensure preparedness to respond to any Site-related injuries.

14.0 EMERGENCY AND FIRST AID EQUIPMENT

Safety equipment will be available for use by Site personnel and will be located and maintained on Site. The safety equipment will include, but is not limited to, the following:

i) a portable emergency eye wash;

ii) one ABC type dry chemical fire extinguisher; and

iii) a first-aid kit for a minimum of 10 personnel.

15.0 EMERGENCY RESPONSE PLAN

Prior to commencing work, an emergency contingency plan shall be developed. The plan is intended to provide immediate response to a serious Site occurrence such as injury, explosion or fire. A list of emergency contact numbers is presented as Table D.3 of this HASP. A hospital route map is provided in Figure D.1.3.

In the event of injury to on-Site personnel, the following protocol will be followed:

i) notify the Health and Safety Officer;

ii) evacuate all personnel upwind;

iii) exit Site;

iv) notify the OMC's guard on duty to coordinate contact the designated hospital and describe the injury;

v) decontaminate personnel if possible, and administer appropriate first aid. If personnel cannot be decontaminated, alert hospital to possible problems of contamination; and

vi) transport personnel to the medical facility along a predefined route.

16.0 EQUIPMENT AND PERSONNEL DECONTAMINATION

During the initiation of the remedial design program, procedures will be implemented to reduce the amount of contact of both personnel and equipment with potentially contaminated materials. These procedures include the following:

i) proper work practices that will lead to minimal direct contact with potentially contaminated material; and

ii) use of disposable equipment and clothing as much as practicable.

All equipment used for the collection of samples for chemical analysis will be cleaned according to the following protocol:

- wash and scrub with low phosphate detergent;
- tap water rinse and steam clean;
- thorough rinse with deionized distilled water;
- air dry; and
- wrap in aluminum foil for transport.

Tap water may be used from any municipal water treatment system. The use of an untreated potable water supply is not an acceptable substitute.

All cleaned equipment will be placed on polyethylene sheeting or aluminum foil in order to avoid contacting a contaminated surface before use.

All personnel will remove their protective clothing and wash their hands, face, neck area and other exposed areas before entering the lunch and break areas to eat, drink or smoke.

17.0 CONTAMINATION MIGRATION CONTROL

All vehicles and equipment used within the Exclusion Zone will be decontaminated on Site as determined necessary by the HSO prior to leaving the Site. Decontamination, when required, will consist of the thorough cleaning of those parts of the equipment which come in contact with potentially contaminated material. The HSO will certify that each piece of equipment is clean or has been decontaminated prior to removal from the Site.

Personnel engaged in vehicle decontamination will wear protective equipment including suitable disposable clothing, respiratory protection and face shields.

ATTACHMENT A

HEALTH AND SAFETY PLAN
ACKNOWLEDGMENT FORM

ATTACHMENT A

HEALTH AND SAFETY PLAN ACKNOWLEDGEMENT FORM

The following employees have read and understood the attached Health and Safety Plan:

Name	*Employer*	*Date*

ATTACHMENT B

RESPIRATORY PROTECTION PROGRAM

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1.0 RESPIRATORY PROTECTION

1.1 PRACTICE

The primary control of respiratory hazards shall be accomplished, whenever feasible, through the use of engineering controls, hazard substitution, revised work practices or other administrative controls. However, when such controls are not feasible, appropriate respiratory protection shall be used in accordance with the procedures established in this SOP. Any deviation from the requirements set forth must have approval from an IH.

1.1.1 AUTHORIZATION

Employees requiring respiratory protection must have authorization from an IH. Office management shall notify an IH of respirator needs. The work situation will then be assessed and a respirator will be issued based on the hazard(s) the individual is exposed to. Reassessment of the hazard and the individual's needs will be repeated periodically.

1.1.2 MEDICAL SURVEILLANCE

All personnel designated to use respirators must successfully complete a physical exam as part of the medical requirements placed on persons exposed to hazardous substances and for users of respiratory protection (29 CFR 1910.134 and 1910.120). The medical exam will be repeated annually. All medical data will be reviewed by a consulting occupational physician. The physician will generate a written opinion on the suitability of the employee to wear a respirator.

1.1.3 AIR QUALITY

When air supplied respirators are used, the breathing air shall meet the Compressed Gas Association (CGA-CG7.1) Standards for Grade D breathing air or better.

1.1.4 AIR CYLINDERS

Cylinders used to supply breathing air are tested and maintained as prescribed in Shipping Container Specifications (49 CFR 178). SCBA cylinders are approximately

2400 psi pressure when full. Compressed air cylinders are visually inspected annually and hydrostatically tested once every five years for steel cylinders and once every three years for composite cylinders. These test dates are stamped on the cylinder for future reference.

1.2 FIT TESTING

1.2.1 QUALITATIVE OR QUANTITATIVE FIT TESTING

Fit testing of the respirator will be conducted by an IH or other designated, trained personnel following the medical evaluation. All users of respirators must be fit tested to assure proper protection. Only the brand and size a person is fitted for is allowed to be used in the field. DO NOT SUBSTITUTE RESPIRATORS FOR A BRAND AND SIZE THAT YOU HAVE NOT BEEN PROPERLY FITTED FOR. The fit test will be accomplished quantitatively for full face APRs. After fit testing, the employee will be issued an authorization card. This card serves as a reference for the proper type of respirator to use as well as prima facie proof of proper medical and training clearance for regulatory purposes.

1.2.2 POSITIVE & NEGATIVE FIT TESTING

All personnel will be instructed in the proper method of testing respirator fit by use of the **Positive & Negative** pressure test. This test is to be done by the user each and every time a respirator is donned. This test is performed to help the wearer assess respirator function and find gross leaks between the face and facepiece. This positive-negative pressure test checks the presence and functioning of the respirator valves as well as leakage that may occur due to improper cartridge seal or respirator face fit.

1.2.2.1 POSITIVE PRESSURE

1) Block off the exhalation valve cover openings.

   MSA: Exhalation valve cover can be blocked with the palm of the hand.

   Scott: Exhalation valve covers have front openings as well as four small side openings. These openings are difficult to block off with the hands. However, a small piece of flexible material such as Saran wrap or latex can be used.

North: Exhalation valve cover has long narrow openings around its perimeter. These can be blocked by encircling the fingers around the valve cover.

2) The person exhales gently, creating a slight positive pressure within the facepiece. The positive pressure should be maintained for at least 10 seconds.

3) If no outward leakage is detected, the person has passed the test.

4) If leakage is detected (usually felt as a cool sensation against the skin or a loss of pressure), the respirator is either malfunctioning or a gross leak between the face and facepiece is present. The following should be done when a failure occurs: Re-don or readjust the respirator.

If the facepiece continues to lose pressure, although previous positive or negative pressure tests performed with that respirator had passed, it is probably malfunctioning. Consult Industrial Hygiene. It is also possible that there are new scars or wrinkles, beard growth, missing teeth or dentures, significant weight gain or loss, etc. to cause gross leakage into the facepiece. When such new conditions exist, reevaluation of the respirator in a test atmosphere is necessary.

1.2.2.2 NEGATIVE PRESSURE

1) Block off the respirator cartridge inlet openings.

MSA: Cartridges can be blocked with the palms of the hands or with disposable latex gloves.

Scott: Cartridges can be blocked by using the palms of the hands or with gloves.

North: Cartridges can be blocked only with gloves.

2) Inhale gently, holding the negative pressure for at least 10 seconds.

3) If no inward leakage of air is detected, the person has passed the test.

4) If leakage is detected, see 4 above.

1.2.3 EXCEPTIONS

1.2.3.1 FACIAL HAIR

Any individual with facial hair which protrudes into the sealing surface of the masks will be refused fitting. Fitting, issuance and use will be based on clean shaven faces only. Employees with facial hair which interferes with respirator fit are not permitted to work at sites where respiratory protection must be worn.

1.2.3.2 GLASSES

Employees who wear prescription glasses and must wear a full face respirator shall be fitted with special eyeglass adapters. Contact lenses are not permitted to be worn with any type of respiratory protection.

1.3 TRAINING

Proper training of respirator users is required to insure that all respirators will provide adequate protection against respiratory hazards and so that the user will understand the device's limitations. The training will include the following elements:

1) An explanation of the nature of respiratory hazards and what may happen if the respirator is not used properly.
2) A description of what engineering and administrative controls may be utilized to reduce the effects of the respiratory hazard and why respirators are required.
3) An explanation of the various types of respirators and why specific types have been selected.
4) A discussion of the function, capabilities and limitations of respirator cartridges.
5) Instruction in the inspection, fit and maintenance of the respirator.
6) Instructions in recognizing and handling emergency situations.

1.4 MAINTENANCE AND CARE OF RESPIRATORS

A program for the maintenance and care of respirators will include the following:

1) Inspection for defects;
2) Cleaning and disinfecting;
3) Repair/miscellaneous maintenance; and
4) Storage.

1.4.1 INSPECTION FOR DEFECTS

Employees shall inspect their respirators before each use. A respirator that is not routinely used but is kept ready for emergency use shall be inspected after each use and at least monthly to assure that it is in satisfactory condition. SCBA shall be inspected monthly if kept for emergency response (i.e., long duration site remediation).

Inspection shall include a check of the tightness of the connections and the condition of the face piece, headbands, valves, breathing tubes and canisters. Rubber or elastic parts shall be inspected for pliability and signs of deterioration. Any respirator with worn or defective parts will be immediately taken out of service.

Before and after each use, respirators will be inspected for the following:

1) Tightness of connections and condition of the facepiece;
2) The headstraps or head harness should be examined for: breaks, loss of elasticity, broken or malfunctioning buckles and attachments, and excessively worn head-harness serrations that might permit slippage;
3) Valves and valve seats;
4) Connecting tube and canisters, air or oxygen cylinders;
5) Rubber or elastomer parts for pliability and deterioration; and
6) Regulators, fittings and gauges.

The following contains inspection information for various types of respirators.

Air Purifying Respirators

1) Check rubber facepiece for dirt, pliability of rubber, deterioration and cracks, tears, holes or distortion from improper storage.
2) Check straps for breaks, tears, loss of elasticity, broken snaps and proper tightness.

3) Check valves (exhalation and inhalation) for holes, warpage, cracks, etc. After removing its cover, the exhalation valve should be examined for: foreign material, distortion, defective or missing valve cover or improper installation of valve into the valve seat.

4) Check filters or cartridges for dents, corrosion, etc. (loose or missing gaskets, improperly seated cartridges).

5) Check for cracked or badly scratched lenses in full facepieces; incorrectly mounted lens, broken or missing mounting clips.

Atmosphere-Supplying Respirators

1) Check appropriate items above.

2) Check air supply system for breaks or kinks in supply hoses and detachable coupling attachments.

3) Follow manufacturer's recommendations for the specific equipment.

4) Check air supply level and warning devices.

1.4.2 CLEANING AND DISINFECTING

The respirator must be washed after each day's use. If the respirator is shared it must also be disinfected according to the manufacturer's instructions. Organic solvents of any kind must not be used for cleaning. Air purifying filters must not be wetted.

1.4.2.1 CLEANING

1) Remove any filters, cartridges or canisters and, if required by the manufacturer, straps and speaking diaphragms from the facepiece. Remove regulators on airline or SCBA.

2) Wash respirator parts excluding cartridges and canisters in warm (not to exceed 140°F), soapy water or in a product specifically designed by respirator manufacturers for this purpose. A plastic bristle hand brush may be helpful in removing dirt from respirator parts.

3) Rinse all parts thoroughly in warm water.

4) Air dry all parts.

5) Reassemble the respirator and insert new cartridges if needed.

6) Place the respirator in a plastic bag or container and seal it for storage. The respirator facepiece should be stored in its normal position so as not to distort the elastomer.

1.4.2.2 DISINFECTION

1) Disinfection should be done with a cleaner/disinfection agent purchased from the respirator vendor. If that material is not available the following NIOSH procedures can be followed:

   a) Immerse the respirator body for two minutes in a 50 ppm chlorine solution (about 2 ml bleach to 1 liter of water). Rinse thoroughly in clean water and air dry.

   b) Immerse the respirator body for two minutes in an aqueous solution of iodine (add 0.8 ml of iodine in 1 liter water). The iodine is about 7% ammonium and potassium iodide, 45% alcohol and 48% water. Rinse thoroughly in clean water and air dry.

2) Immersion times have to be limited to minimize damage to the respirator. The solutions can age rubber and rust metal parts.

   NOTE: The air-purifying elements must be removed from the respirator prior to cleaning and sanitizing the respirator. Never allow the air-purifying elements to come in contact with water or cleaning/sanitizing solution.

1.4.3 STORAGE

Respirators must be stored to protect them from contamination and mechanical damage at all times when not in use. New, cleaned or reconditioned respirators are to be kept in a clean, sealed plastic bag or container, stored in a normal position. The plastic bag should be labeled with the users name. A suitable cabinet or drawer should be used to protect respirators and supplies from dirt, extremes of temperature or bright sunlight. They are not to be left in vehicles or on site perimeter fences, in change sheds, etc.

ATTACHMENT C

HEAT STRESS AND COLD STRESS PROCEDURES

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1.0 COLD STRESS

1.1 OVERVIEW

Fatal exposures to cold have been reported in employees failing to escape from low environmental air temperatures or from immersion in low temperature water. Hypothermia, a condition in which the body's deep core temperature falls significantly below 98.6°F, can be life threatening. A drop in core temperature to 95°F or lower must be prevented.

Air temperature is not sufficient to determine the cold hazard of the work environment. The wind-chill must be considered as it contributes to the effective temperature. The body's physiologic defense against cold includes constriction of the blood vessels, inhibition of the sweat glands to prevent loss of heat via evaporation, glucose production and involuntary shivering to produce heat by rapid muscle contraction.

The frequency of accidents increases with cold temperature exposures as the body's nerve impulses slow down, individuals react sluggishly and numb extremities make for increased clumsiness. Additional safety hazards include ice, snow blindness, reflections from snow and possible skin burns from contact with cold metal.

There are certain predisposing factors that make an individual more susceptible to cold stress. It is the responsibility of the project team members to inform the Health and Safety Officer to monitor an individual, if necessary, or use other means of preventing/reducing the individual's likelihood of experiencing a cold related illness or disorder.

1.2 PREDISPOSING FACTORS

Predisposing factors that will increase an individual's susceptibility to cold stress are listed below:

- Dehydration: The use of diuretics and/or alcohol, or diarrhea can cause dehydration. Dehydration reduces blood circulation to the extremities.
- Fatigue During Physical Activity: Exhaustion reduces the body's ability to constrict blood vessels. This results in the blood circulation occurring closer to the surface of the skin and the rapid loss of body heat.

- Age: Some older and very young individuals may have an impaired ability to sense cold.
- Alcohol Consumption: Alcohol dilates the blood vessels near the skin surface resulting in excessive body heat loss.
- Sedative Drugs: Sedatives may interfere with the transmission of impulses to the brain, thereby interfering with the body's physiological defense against cold. Some prescription drugs may react the same way.
- Poor Circulation: Vasoconstriction of peripheral vessels reduces blood flow to the skin surface.
- Heavy Work Load: Heavy work loads generate metabolic heat and make an individual perspire even in extremely cold environments. If perspiration is absorbed by the individual's clothing and is in contact with the skin, cooling of the body will occur.
- The Use of PPE: PPE usage which traps sweat inside the PPE may increase an individual's susceptibility to cold stress.
- Lack of Acclimatization: Acclimatization, the gradual introduction of workers into a cold environment, allows the body to physiologically adjust to cold working conditions.
- History of Cold Injury: Previous injury from cold exposures may result in increased cold sensitivity.

1.3 PREVENTION OF COLD STRESS

There are a variety of measures that can be implemented to prevent or reduce the likelihood of employees developing cold related ailments and disorders. These include acclimatization, fluid and electrolyte replenishment, eating a well balanced diet, wearing warm clothing, the provision of shelter from the cold, thermal insulation of metal surfaces, adjusting work schedules and employee education.

- Acclimatization: Acclimatization is the gradual introduction of workers into the cold environment to allow their bodies to physiologically adjust to cold working conditions. However, the physiologic changes are usually minor and require repeated uncomfortably cold exposures to induce them.
- Fluid and Electrolyte Replenishment: Cold, dry air can cause employees to lose significant amounts of water through the skin and lungs. Dehydration affects

the flow of blood to the extremities and increases the risk of cold injury. Warm, sweet, caffeine-free, non-alcoholic drinks and soup are good sources to replenish body fluids.

- Eating a Well-Balanced Diet: Restricted diets including low salt diets can deprive the body of elements needed to withstand cold stress. Eat high energy foods throughout the day.
- Warm Clothing: It is beneficial to maintain air space between the body and outer layers of clothing in order to retain body heat. However, the insulating effect provided by such air spaces is lost when the skin or clothing is wet.

The parts of the body most important to keep warm are the feet, hands, head and face. As much as 40 percent of body heat can be lost when the head is exposed.

Recommended clothing includes:

- Inner layers (t-shirts, shorts, socks) should be of a thin, thermal insulating material.
- Wool or thermal trousers. Denim is not a good protective fabric.
- Felt-lined, rubber-bottomed, leather-upper boots with a removable felt insole is preferred. Change socks when wet.
- Wool shirts/sweaters should be worn over inner layer.
- A wool cap is good head protection. Use a liner under a hard hat.
- Mittens are better insulators than gloves.
- Face masks or scarves are good protection against wind.
- Tyvek/poly-coated Tyvek provides good wind protection.
- Wear loose fitting clothing, especially footwear.
- Carry extra clothing in your vehicle.
- Shelters with heaters should be provided for the employees' rest periods if possible. Sitting in a heated vehicle is a viable option. Care should be taken that the exhaust is not blocked and that windows are partially open to provide ventilation.
- At temperatures of 30°F (-1°C) or lower, cover metal tool handles with thermal insulating material if possible.

- Schedule work during the warmest part of the day if possible, rotate personnel and adjust the work/rest schedule to enable employees to recover from the effects of cold stress.

1.3.1 EMPLOYEE EDUCATION

Employees have already been trained to recognize and treat the effects of cold stress during their 40-hour training. Signs, symptoms and treatment of cold stress should be reviewed in project safety meetings where applicable. The buddy system will help in preventing cold stress once the employees are trained to recognize the signs and symptoms of cold stress.

1.3.2 COLD STRESS PREVENTION GUIDELINES

It may not be practically feasible to implement all the above prevention measures. Follow the guidelines given below when the ambient air temperature is -5°F (-20°C) or lower:

- Contact the project manager or the industrial hygienist to determine if the project team should be on-site in such temperatures;
- Dress warm;
- Replenish fluids and electrolytes at regular intervals;
- Provide shelter from the cold; and
- Adjust work/rest schedules.

1.3.3 ADJUST WORK-REST SCHEDULES

Follow the work/rest schedule on Table C.1. It is based on the cooling power of air which is a function of wind speed and ambient air temperature.

1.4 FIRST-AID TREATMENT GUIDELINES

The following describes symptoms of different stages in cold stress and the related first-aid treatment guidelines.

1.4.1 FROSTBITE

Stages

Incipient (frost nip)	May be painless. Tips of ears, nose, cheeks, fingers, toes, chin affected. Skin blanched white.
Superficial	Affects skin/tissue just beneath skin; turns purple as it thaws. Skin is firm, waxy; tissue beneath is soft, numb.
Deep	Tissue beneath skin is solid, waxy, white with purplish tinge. Entire tissue depth is affected.

First-Aid

Incipient	Warm by applying firm pressure - blow warm breath on spot or submerge in warm water (102°F to 110°F) (39°C to 43°C). Do not rub the area.
Superficial	Provide dry coverage, steady warmth; submerge in warm water.
Deep	Hospital care is needed. Do not thaw frostbitten part if needed to walk on. Do not thaw if there is danger of refreezing. Apply dry clothing over frostbite. Submerge in water; do not rub.

1.4.2 GENERAL HYPOTHERMIA

Stages

- Shivering
- Indifference
- Decreased Consciousness
- Unconsciousness

- Death

Symptoms

- Muscle Tension
- Uncontrollable Shivering
- Glassy Stare
- Decreased Muscle Function
- Speech Distortion
- Blue, Puffy Skin
- Slow Pulse
- Shallow Breathing
- Coordination Loss
- Stumbling
- Forgetfulness
- Freezing Extremities
- Dilated Pupils
- Fatigue

Emergency Response

- Keep person dry; replace wet clothing
- Apply external heat to both sides of patient using available heat sources, including other bodies.
- Give warm liquids - not coffee or alcohol - after shivering stops and if conscious.
- Handle gently.
- Transport to medical facility as soon as possible.
- If more than 30 minutes from a medical facility, warm person with other bodies.

2.0 HEAT STRESS

2.1 OVERVIEW

Heat induced occupational illnesses, injuries and reduced productivity occur in situations in which the total heat load (environmental plus metabolic) exceeds the body's capacities to maintain normal body functions without excessive strain. Heat stress is the sum of the heat generated in the body plus the heat gained from the environment minus the heat lost from the body to the environment. The body's response to heat stress is called heat strain. The level of heat stress at which excessive heat strain will result depends on the heat tolerance of the individual. Certain predisposing factors may reduce an individual's ability to tolerate heat stress.

Using PPE may put a hazardous waste worker at an increased risk of developing heat stress. Health effects may range from heat rash or heat fatigue to serious illness or death. Heat stress is caused by a number of interacting factors, including environmental conditions such as temperature and relative humidity, protective clothing which limits natural heat loss through perspiration, workload and the individual characteristics of the worker.

It is the responsibility of the project team members to inform the HSO or industrial hygienist if any of the predisposing factors listed below apply to them. This enables the HSO to monitor the individual if necessary, or use other means of preventing/reducing the individual's likelihood of experiencing a heat related illness or disorder.

2.2 PREDISPOSING

Predisposing factors that will increase the individual's susceptibility to heat stress are listed below:

- Lack of Physical Fitness: Such individuals experience more physiological strain including a higher heart rate, a higher body temperature, less efficient sweating and slightly higher oxygen consumption as compared to fit individuals.
- Obesity: Overweight individuals produce more heat per unit surface area than thin individuals and have a lowered ability to dissipate heat.
- Age: Older individuals may have a decreased ability to cope with heat stress.
- Dehydration: Dehydrated individuals will have a decreased ability to cool the body by sweating. Diarrhea can cause dehydration.

- Alcohol, Medications and Drug Use: Alcohol consumption may dehydrate individuals and certain medications/drugs may act as diuretics. Hence, the individual may have a decreased ability to lose heat by sweating.
- Infection, Sunburn, Illness and Certain Chronic Diseases: These factors may interfere with the body's normal mechanisms to lose heat.
- Heart Conditions or Circulatory Problems: Heat stress may place an additional strain on the heart and circulatory system that could harm the individual as well as decrease the individual's physiologic response.
- Low Salt Diet: Could affect the individual's electrolyte balance.
- Pregnancy
- Previous History of Heat Stroke or Heat Exhaustion: May increase the individual's susceptibility to heat stress.
- Heavy Work Load: Will generate metabolic heat thereby increasing the heat stress placed on the individual
- The Use of PPE Over Light Summer Clothing: This will decrease the ability of an individual to lose heat by sweating as evaporative cooling can no longer occur.
- Lack of Acclimatization: Acclimatization is the gradual introduction of workers into a hot environment to allow their bodies to physiologically adjust to hot working conditions. Acclimatized individuals generally have lower heart rates and lower body temperatures. In addition, they sweat sooner and more profusely and even have more dilute sweat (thereby losing less electrolytes) than non-acclimatized individuals.

2.3 PREVENTION OF HEAT STRESS

There are a variety of measures that can be implemented to prevent or reduce the likelihood of employees developing heat stress related disorders. These include fluid and electrolyte replenishment, the provision of shelter from the sun and heat, work schedule adjustment, the use of cooling devices, acclimatization, heat stress monitoring and employee education, as discussed below:

- Fluid and Electrolyte Replenishment: Personnel should drink about 16 ounces of water before starting work and drink water at every break. To encourage water consumption, cool water and disposable cups should be made available. The normal thirst mechanism is not sensitive enough to ensure that enough water

will be drunk to replace lost sweat. When heavy sweating occurs, personnel should be encouraged to drink more. Replacing body fluids with Gatorade is an option. It is advisable to have Gatorade on-site if the air temperature is 70°F (21°C) or more and the workers are performing tasks with a moderate to heavy work load in chemical resistant clothing.

- Shelter From the Sun and Heat: Air-conditioned (if possible) or shaded areas should be made available for rest periods. Sitting in an air-conditioned truck is an acceptable option.
- Work Schedule Adjustment: Scheduling work for early mornings and/or late afternoons will avoid the hottest parts of the day and reduce the heat stress placed on personnel. Rotation of personnel will help reduce overexertion of workers and adjusting the work-rest schedule will help personnel recover from the effects of heat stress periodically.
- Use of Cooling Devices: The use of cooling devices like field showers, hose-down areas or cooling vests should be considered for project tasks that involve heavy work loads in chemical resistant clothing.
- Acclimatization: Acclimatization is the gradual introduction of workers into a hot environment to allow their body to physiologically adjust to hot working conditions. Acclimatized individuals generally have lower heart rates and lower body temperatures. In addition, they sweat sooner and more profusely and even have more dilute sweat (thereby losing less electrolytes) than non-acclimatized individuals.
- Heat Stress Monitoring: Monitoring hot environments for potential heat stress should be initiated when the ambient air temperature is in excess of 70°F (21°C). There are several ways to monitor heat stress: measuring heart rate, oral temperature, loss of body weight and the Wet Bulb Globe Temperature using a Reuter-Stokes or Quest Electronics heat stress monitor.
- Employee Education: Workers have already been trained to recognize and treat the effects of heat stress during the 40-hour training course. Signs, symptoms and treatment of heat stress should be discussed in site safety meetings. The buddy system will help in preventing heat stress once the employees are trained to recognize the signs and symptoms of heat stress.

2.3.1 PREVENTION PRACTICES

It may not be practically feasible to implement all of the above prevention measures. The following has been developed as a field guide for use in actual field situations.

Ambient air temperature is 70°F (21°C) or more:

- Replenish fluids and electrolytes. Drink cool (50°F to 60°F/10°C to 15°C) fluids hourly. The fluids should be caffeine-free and non-alcoholic. Do not wait until you are thirsty. Your normal thirst mechanism is not sufficient to overcome the effects of dehydration. If you feel thirsty, you are already becoming dehydrated.
- Provide shelter from the sun and heat.

Ambient air temperature is 70°F (21°C) or more and chemical-resistant clothing is being used:

- Same as above;
- Adjust work schedules if feasible; and
- Initiate heat stress monitoring and/or the use of cooling devices.

2.3.2 HEAT STRESS MONITORING

Heat stress monitoring may be performed by monitoring the heart rate. Heart rate should be measured at the beginning of the work shift, at regular intervals and at the start of each rest period.

1) If the heart rate is <110 beats per minute (bpm), personnel may continue the current work/rest schedule.
2) If the heart rate is >110 bpm, take a 10 minute break. Monitor heart rate at the end of the rest period. If not <110 bpm, rest until the heart rate is <110 bpm. Reduce the current work time between breaks by approximately one hour. If the next scheduled monitoring session shows a heart rate of >110 bpm once again, reduce the work time between breaks by one hour.

2.4 HEAT STRESS FIRST AID

2.4.1 HEAT CRAMPS

Cause: Excessive water loss/electrolyte imbalance.

Symptoms	First-Aid Guidelines
Muscular pain in arms, legs, abdomen Faintness, dizziness, exhaustion Normal temp, cool moist skin	Administer sips of Gatorade (1/2 glass every 15 minutes) Do not massage cramping muscles Relax person

2.4.2 HEAT EXHAUSTION

Cause: Large amount of water loss; blood circulation diminishes.

Symptoms	First-Aid Guidelines
Moist, clammy, skin, usually pale Dilated pupils Weak, dizzy, nauseous, headache Normal or low body temperature	Move to a cool place Apply cold, wet compresses to skin Raise feet 8 to 12 inches Administer sips of Gatorade (1/2 glass every 15 minutes) Get medical attention

2.4.3 HEAT STROKE

Cause: Body overheats; temperature rises; no sweating occurs

Symptoms	First-Aid Guidelines
No sweating occurs	Get emergency medical assistance ASAP
Dry, hot skin, usually red	Remove from sunlight
Constricted pupils	Wet down body with cool water or rubbing alcohol
Hot body temperature (105°F to 110°F/40.5°C to 43.5°C)	Elevate head/shoulders
Strong, rapid pulse	Wrap in wet, cold wrapping
Unconsciousness may occur	Once cooled to 102°F (38.9°C), stop cooling measures
Muscular twitching	

TABLE C.1

WORK/REST SCHEDULE
FOR AN EIGHT HOUR WORK SHIFT

Air Temperature with Sunny Sky		*Work/Break Schedule (Minutes)*				
°F	*°C*	*No Wind*	*5 mph Wind*	*10 mph Wind*	*15 mph Wind*	*20 mph Wind*
-05 to -09	-20 to -23	110/10	110/10	75/10	55/10	40/10
-10 to -14	-23 to -26	110/10	75/10	55/10	40/10	30/10
-15 to -19	-26 to -28	75/10	55/10	40/10	30/10	Stop
-20 to -24	-29 to -31	55/10	40/10	30/10	Stop	Stop
-25 to -29	-32 to -34	40/10	30/10	Stop	Stop	Stop
-30 to -34	-35 to -37	30/10	Stop	Stop	Stop	Stop
-35 & Below	-38 & Below	Stop	Stop	Stop	Stop	Stop

Note:

This table addresses the health hazards related to cold weather work. The practicality of working under a work/rest schedule, together with the ability of the necessary equipment to function properly in cold weather, may be more restrictive than the health hazards and also need to be considered.

The cold stress schedule applies to light or sedentary work activities. Light to moderate work activities can be moved down one level, moderate to heavy work activities can be moved down two levels if workers are acclimated, have proper protective clothing and show no signs of cold stress.

0 - 5 mph Winc Light flag moves.
15 mph Wind: Raises newspaper sheet.
10 mph Wind: Light flag fully extended.
20 mph Wind: Blowing and drifting snow.

ATTACHMENT D

SEVERE WEATHER EMERGENCY PROCEDURES

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4.0 WINTER STORMS 4

SEVERE WEATHER

1.0 SCOPE

As most projects are conducted outside, the potential for severe weather must be considered. Thunderstorms, tornadoes, and winter storms can develop quickly, jeopardizing worker safety. The following emergency procedures are to be followed in case of severe weather.

2.0 THUNDERSTORMS AND LIGHTNING

Monitor weather conditions at all times while working. Monitor for a sign of an impending storm such as increased cloudiness, darkened skies, and increased wind. If any of these signs are observed, listen to a radio for the latest weather information or contact a local weather reporting service.

When a thunderstorm accompanied by lightning is in the project area, cease work immediately. All powered equipment, such as drill rigs, are to be shut down.

Seek shelter inside nearby buildings or trailers. If there are no buildings nearby, seek shelter inside your vehicle.

If you are caught outside, do not stand beneath tall, isolated trees or telephone poles. Avoid areas projecting above the landscape such as hilltops. In open areas, go to a low place such as a ravine or valley. Stay away from open water, metal equipment, wire fences, and metal pipes. If you are in a group of people in the open, spread out, staying several yards apart.

If you are caught in a level field or open area far from shelter and you feel your hair stand on end, lightning may be about to strike you. Drop to your knees and bend forward, putting your hands on your knees. **DO NOT LIE FLAT ON THE GROUND.**

If someone has been struck by lightning, monitor life signs and begin administering mouth-to-mouth resuscitation or cardiopulmonary resuscitation as needed. Send for help. Check conscious victims for burns, especially at the fingers and toes and next to buckles and jewelry. Administer first aid for shock. Do not let the victim walk around.

3.0 TORNADOES

Tornadoes usually develop from thunderstorms and normally occur at the trailing edge of the storm. Most tornadoes occur in the months of April, May, June, and July in the late afternoon and early evening hours.

When storms are predicted for the project area, monitor weather conditions on a radio. A tornado watch is issued when favorable conditions exist for the development of a tornado. A tornado warning is issued by the local weather service office whenever a tornado has actually been sighted or is strongly indicated by radar.

If a tornado warning is issued, seek shelter immediately. If there are permanent buildings located on site, go there immediately, moving toward interior hallways or small rooms on the lowest floor.

If a tornado warning is issued and you are in a vehicle or a site trailer, leave and go to the nearest building. If there are no buildings nearby, go in the nearest ditch, ravine, or culvert, with your hands shielding your head.

If a tornado is sighted or a warning issued while you are in open country, lie flat in a ditch or depression. Hold onto something on the ground, such as a bush or wooden fence post, if possible.

Once a tornado has passed the site, site personnel are to assemble at the designated assembly area to determine if anyone is missing. Administer first aid and seek medical attention as needed.

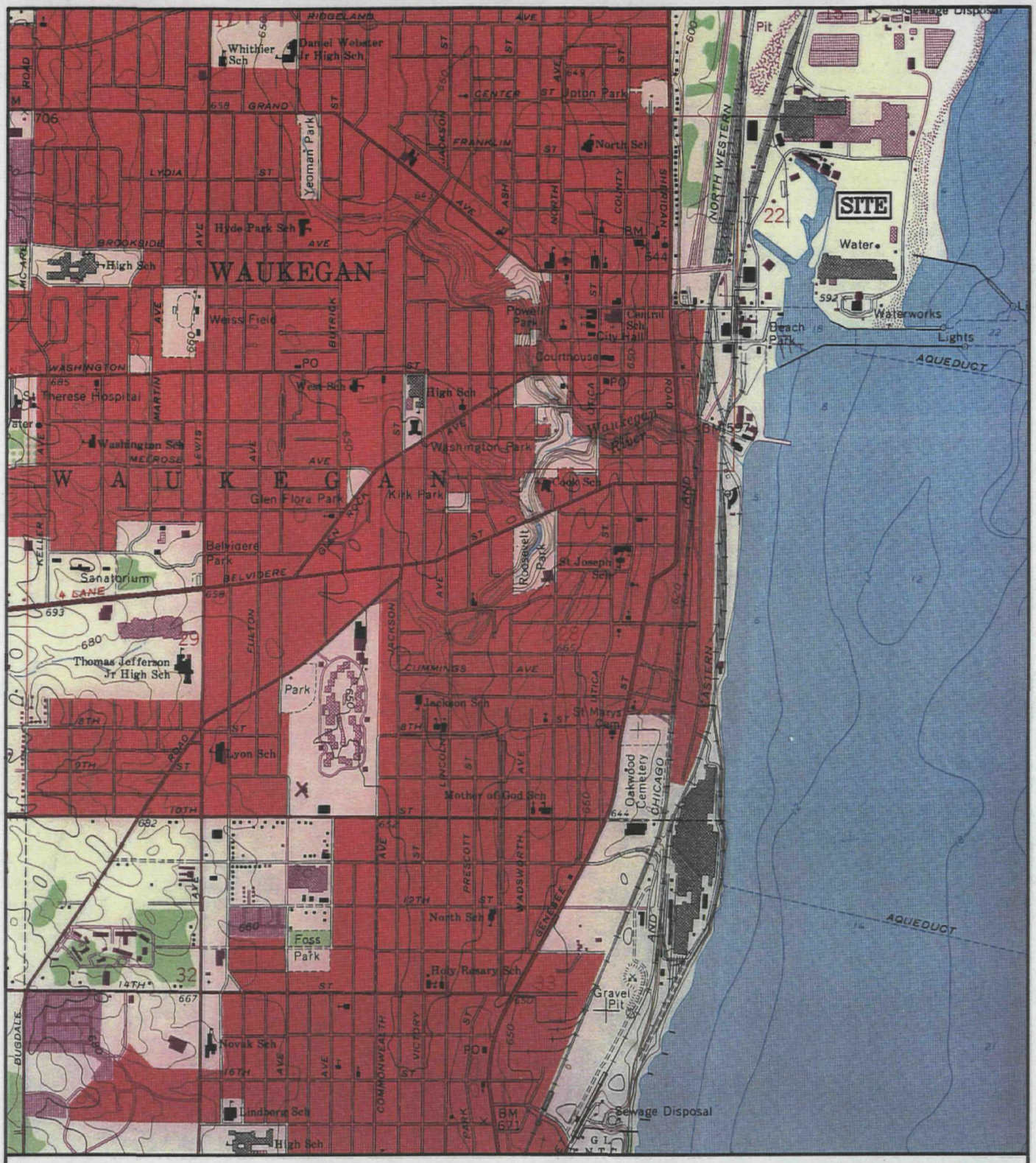
4.0 WINTER STORMS

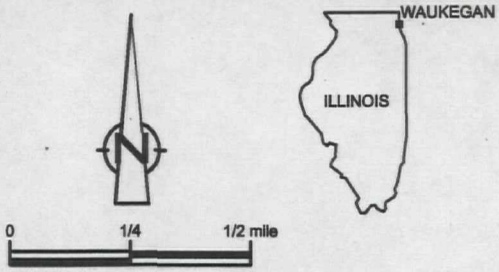
When snow or ice storms are predicted for the project area, site personnel should monitor weather conditions on a radio. A winter storm watch is issued when a storm has formed and is approaching the area. A winter storm warning is issued when a storm is imminent and immediate action is to be taken.

When a storm watch is issued, monitor weather conditions and prepare to halt site activities. Notify the project manager (PM) of the situation. Seek shelter at site buildings or leave the site and seek warm shelter. If you are caught in a severe winter storm while traveling, seek warm shelter if road conditions prevent safe travel.

If you are stranded in a vehicle during a winter storm:

- STAY IN THE VEHICLE, disorientation comes quickly in blowing and drifting snow;
- wait for help;
- keep a window open an inch or so to avoid carbon monoxide poisoning;
- run the engine and heater sparingly;
- keep watch - do not let everyone sleep at the same time; and
- exercise occasionally.





BASE SOURCE: USGS 7.5 MINUTE TOPOGRAPHIC QUADRANGLE; WAUKEGAN, ILLINOIS 1960

figure D.1.1

SITE LOCATION
WAUKEGAN COKE PLANT
Waukegan, Illinois

CRA

19023-00(002)GN-CO011 MAY 10/2002

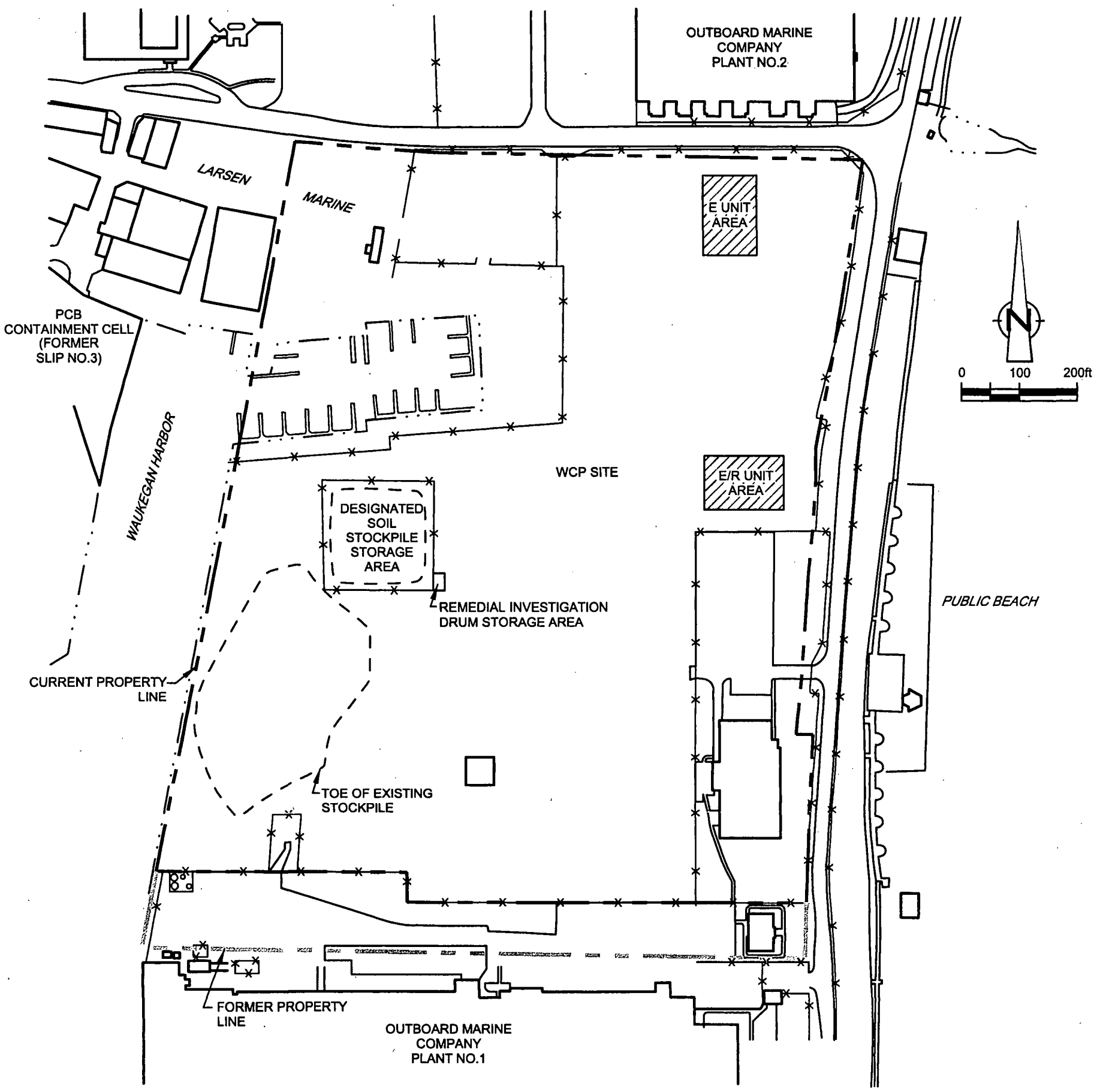


figure D.1.2

SITE PLAN
WAUKEGAN MANUFACTURED GAS AND COKE PLANT
Waukegan, Illinois

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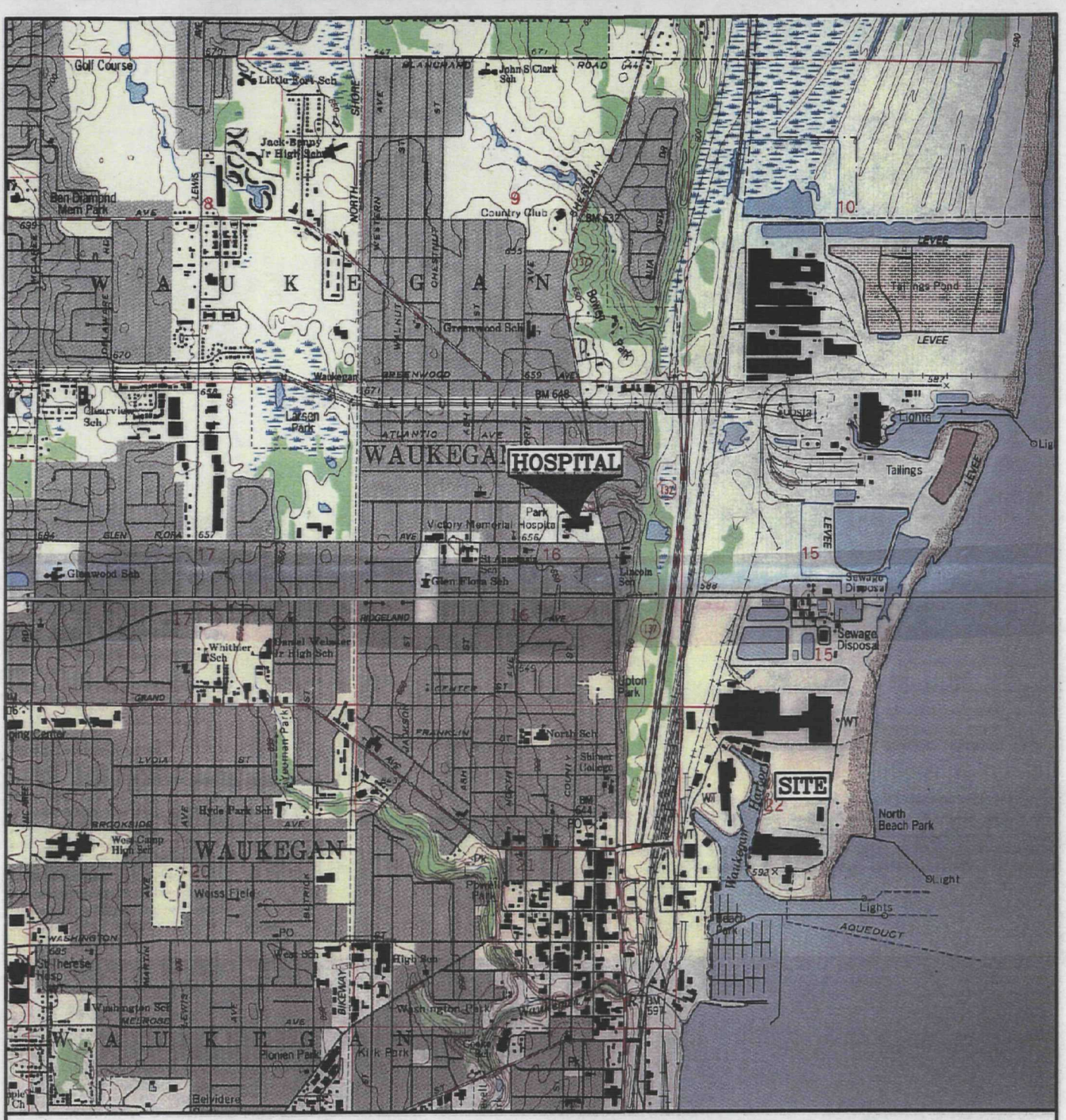

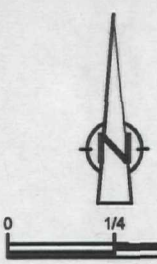

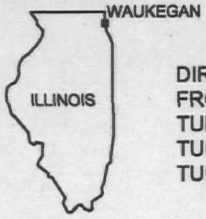

BASE SOURCE: USGS 7.5 MINUTE TOPOGRAPHIC QUADRANGLE; WAUKEGAN, ILLINOIS 1960

DIRECTIONS TO THE HOSPITAL
FROM THE SEA HORSE DRIVE TURN RIGHT ONTO E. CLAYTON STREET (0.1 miles)
TURN RIGHT ONTO PERSHING ROAD (0.1 miles)
TURN LEFT ONTO MATHON DRIVE. (0.2 miles)
TURN RIGHT ONTO N. SHERIDAN ROAD (1.0 miles)

figure D.1.3

HOSPITAL ROUTE MAP
WAUKEGAN MANUFACTURED GAS AND COKE PLANT
Waukegan, Illinois

CRA

19023-00(002)GN-CO013 MAY 10/2002

TABLE D.1

CONTAMINANTS OF CONCERN
WAUKEGAN MANUFACTURED GAS AND COKE PLANT
WAUKEGAN , ILLINOIS

Contaminant	*REL*	*PEL*	*IDLH*	*IP (eV)*	*Flammability Range*	*Routes of Exposure*	*Symptoms of Exposure*	*Other*
Arsenic	0.002 mg/m3	0.010 mg/m3	5 mg/m3	NA	NA	Inhalation, Ingestion, Contact	Ulceration of nasal septum, dermatitis, gastrointestinal disturbances, peripheral neuropathy, respiratory irritation, hyperpigmentation of skin	Potential occupational carcinogen
Coal Tar Pitch Volatiles	0.1 mg/m3	0.2 mg/m3	80 mg/m3	NA	NA	Inhalation, Ingestion, Contact	Dermatitis, bronchitis	Potential occupational carcinogen

NA - Not Applicable
REL - Recommended Exposure Limit
PEL - Permissible Exposure Limit
IDLH - Immediate Danger to Life and Health
IP - Ionization Potential
ppm - parts per million
mg/m3 - milligrams per cubic meter
eV - electron volts

TABLE D.2

SITE HAZARD ANALYSIS
WAUKEGAN MANUFACTURED GAS AND COKE PLANT
WAUKEGAN , ILLINOIS

Site Activities	*Hazards*	*Prevention*
Soil Boring Advancement and Test Pit Excavation Oversight	Chemical hazards due to inhalation and dermal contact	Proper use of PPE
	Exposure to temperature extremes	Monitor for heat or cold stress
	Physical hazards associated with operation of excavation equipment	Maintain a safe distance from equipment
		Avoid overhead power lines (20 feet)
		Check and mark underground utilities
	Physical hazards including steep grades and unstable surfaces while transporting heavy equipment	Use "buddy system" during Site activities
	Biological Hazards	Proper PPE, exercising ordinary caution, use of buddy system during Site activities
	High noise level	Use hearing protection
	Slip, trip, fall	Clean mud, snow or grease from shoes and equipment
Groundwater Monitoring and Sampling Activities	Exposure to temperature extremes	Monitor for heat or cold stress
	Physical hazards including steep grades and unstable surfaces	Use "buddy system" during Site activities
	Biological Hazards	Proper PPE, exercising ordinary caution, use of buddy system during Site activities
Soil Solidification/Treatability Study	Chemical hazards due to inhalation and dermal contact	Proper use of PPE
	Exposure to temperature extremes	Monitor for heat or cold stress

TABLE D.3

EMERGENCY CONTACTS
WAUKEGAN MANUFACTURED GAS AND COKE PLANT
WAUKEGAN, ILLINOIS

Agency/Firm	*Emergency Telephone Number*	*Business Telephone Number*
Local Emergency Services		
Fire Department	911	
Police Department	911	
Ambulance	911	
Hospital (Victory Memorial) 1324 North Sheridan Road Waukegan, IL 60085		(847) 360-3000
Illinois Emergency Services & Disaster Agency		(800) 782-7860
National Poison Center		(800) 942-5969
National Response Center		(800) 424-8802
CRA Industrial Hygiene - Matthew Lazaric		(773) 380-9933
CRA Project Manager - Alan Van Norman		(773) 380-9933
CRA Project Coordinator - Steve Wanner		(773) 380-9933

Directions to the Hospital: From Sea Horse Drive turn right onto E. Clayton Street (0.1 miles)
Turn right onto Pershing Road. (0.1 miles)
Turn left onto Mathon Drive. (0.2 miles)
Turn right onto N. Sheridan Road (1.0 miles)

ATTACHMENT A

HEALTH AND SAFETY PLAN
ACKNOWLEDGMENT FORM

ATTACHMENT A

HEALTH AND SAFETY PLAN ACKNOWLEDGEMENT FORM

The following employees have read and understood the attached Health and Safety Plan:

Name	*Employer*	*Date*

ATTACHMENT B

RESPIRATORY PROTECTION PROGRAM

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1.0 RESPIRATORY PROTECTION

1.1 PRACTICE

The primary control of respiratory hazards shall be accomplished, whenever feasible, through the use of engineering controls, hazard substitution, revised work practices or other administrative controls. However, when such controls are not feasible, appropriate respiratory protection shall be used in accordance with the procedures established in this SOP. Any deviation from the requirements set forth must have approval from an IH.

1.1.1 AUTHORIZATION

Employees requiring respiratory protection must have authorization from an IH. Office management shall notify an IH of respirator needs. The work situation will then be assessed and a respirator will be issued based on the hazard(s) the individual is exposed to. Reassessment of the hazard and the individual's needs will be repeated periodically.

1.1.2 MEDICAL SURVEILLANCE

All personnel designated to use respirators must successfully complete a physical exam as part of the medical requirements placed on persons exposed to hazardous substances and for users of respiratory protection (29 CFR 1910.134 and 1910.120). The medical exam will be repeated annually. All medical data will be reviewed by a consulting occupational physician. The physician will generate a written opinion on the suitability of the employee to wear a respirator.

1.1.3 AIR QUALITY

When air supplied respirators are used, the breathing air shall meet the Compressed Gas Association (CGA-CG7.1) Standards for Grade D breathing air or better.

1.1.4 AIR CYLINDERS

Cylinders used to supply breathing air are tested and maintained as prescribed in Shipping Container Specifications (49 CFR 178). SCBA cylinders are approximately

2400 psi pressure when full. Compressed air cylinders are visually inspected annually and hydrostatically tested once every five years for steel cylinders and once every three years for composite cylinders. These test dates are stamped on the cylinder for future reference.

1.2 FIT TESTING

1.2.1 QUALITATIVE OR QUANTITATIVE FIT TESTING

Fit testing of the respirator will be conducted by an IH or other designated, trained personnel following the medical evaluation. All users of respirators must be fit tested to assure proper protection. Only the brand and size a person is fitted for is allowed to be used in the field. DO NOT SUBSTITUTE RESPIRATORS FOR A BRAND AND SIZE THAT YOU HAVE NOT BEEN PROPERLY FITTED FOR. The fit test will be accomplished quantitatively for full face APRs. After fit testing, the employee will be issued an authorization card. This card serves as a reference for the proper type of respirator to use as well as prima facie proof of proper medical and training clearance for regulatory purposes.

1.2.2 POSITIVE & NEGATIVE FIT TESTING

All personnel will be instructed in the proper method of testing respirator fit by use of the **Positive & Negative** pressure test. This test is to be done by the user each and every time a respirator is donned. This test is performed to help the wearer assess respirator function and find gross leaks between the face and facepiece. This positive-negative pressure test checks the presence and functioning of the respirator valves as well as leakage that may occur due to improper cartridge seal or respirator face fit.

1.2.2.1 POSITIVE PRESSURE

1) Block off the exhalation valve cover openings.

   MSA: Exhalation valve cover can be blocked with the palm of the hand.

   Scott: Exhalation valve covers have front openings as well as four small side openings. These openings are difficult to block off with the hands. However, a small piece of flexible material such as Saran wrap or latex can be used.

North: Exhalation valve cover has long narrow openings around its perimeter. These can be blocked by encircling the fingers around the valve cover.

2) The person exhales gently, creating a slight positive pressure within the facepiece. The positive pressure should be maintained for at least 10 seconds.

3) If no outward leakage is detected, the person has passed the test.

4) If leakage is detected (usually felt as a cool sensation against the skin or a loss of pressure), the respirator is either malfunctioning or a gross leak between the face and facepiece is present. The following should be done when a failure occurs: Re-don or readjust the respirator.

If the facepiece continues to lose pressure, although previous positive or negative pressure tests performed with that respirator had passed, it is probably malfunctioning. Consult Industrial Hygiene. It is also possible that there are new scars or wrinkles, beard growth, missing teeth or dentures, significant weight gain or loss, etc. to cause gross leakage into the facepiece. When such new conditions exist, reevaluation of the respirator in a test atmosphere is necessary.

1.2.2.2 NEGATIVE PRESSURE

1) Block off the respirator cartridge inlet openings.

MSA: Cartridges can be blocked with the palms of the hands or with disposable latex gloves.

Scott: Cartridges can be blocked by using the palms of the hands or with gloves.

North: Cartridges can be blocked only with gloves.

2) Inhale gently, holding the negative pressure for at least 10 seconds.

3) If no inward leakage of air is detected, the person has passed the test.

4) If leakage is detected, see 4 above.

1.2.3 EXCEPTIONS

1.2.3.1 FACIAL HAIR

Any individual with facial hair which protrudes into the sealing surface of the masks will be refused fitting. Fitting, issuance and use will be based on clean shaven faces only. Employees with facial hair which interferes with respirator fit are not permitted to work at sites where respiratory protection must be worn.

1.2.3.2 GLASSES

Employees who wear prescription glasses and must wear a full face respirator shall be fitted with special eyeglass adapters. Contact lenses are not permitted to be worn with any type of respiratory protection.

1.3 TRAINING

Proper training of respirator users is required to insure that all respirators will provide adequate protection against respiratory hazards and so that the user will understand the device's limitations. The training will include the following elements:

1) An explanation of the nature of respiratory hazards and what may happen if the respirator is not used properly.
2) A description of what engineering and administrative controls may be utilized to reduce the effects of the respiratory hazard and why respirators are required.
3) An explanation of the various types of respirators and why specific types have been selected.
4) A discussion of the function, capabilities and limitations of respirator cartridges.
5) Instruction in the inspection, fit and maintenance of the respirator.
6) Instructions in recognizing and handling emergency situations.

1.4 MAINTENANCE AND CARE OF RESPIRATORS

A program for the maintenance and care of respirators will include the following:

1) Inspection for defects;
2) Cleaning and disinfecting;
3) Repair/miscellaneous maintenance; and
4) Storage.

1.4.1 INSPECTION FOR DEFECTS

Employees shall inspect their respirators before each use. A respirator that is not routinely used but is kept ready for emergency use shall be inspected after each use and at least monthly to assure that it is in satisfactory condition. SCBA shall be inspected monthly if kept for emergency response (i.e., long duration site remediation).

Inspection shall include a check of the tightness of the connections and the condition of the face piece, headbands, valves, breathing tubes and canisters. Rubber or elastic parts shall be inspected for pliability and signs of deterioration. Any respirator with worn or defective parts will be immediately taken out of service.

Before and after each use, respirators will be inspected for the following:

1) Tightness of connections and condition of the facepiece;
2) The headstraps or head harness should be examined for: breaks, loss of elasticity, broken or malfunctioning buckles and attachments, and excessively worn head-harness serrations that might permit slippage;
3) Valves and valve seats;
4) Connecting tube and canisters, air or oxygen cylinders;
5) Rubber or elastomer parts for pliability and deterioration; and
6) Regulators, fittings and gauges.

The following contains inspection information for various types of respirators.

Air Purifying Respirators

1) Check rubber facepiece for dirt, pliability of rubber, deterioration and cracks, tears, holes or distortion from improper storage.
2) Check straps for breaks, tears, loss of elasticity, broken snaps and proper tightness.

3) Check valves (exhalation and inhalation) for holes, warpage, cracks, etc. After removing its cover, the exhalation valve should be examined for: foreign material, distortion, defective or missing valve cover or improper installation of valve into the valve seat.

4) Check filters or cartridges for dents, corrosion, etc. (loose or missing gaskets, improperly seated cartridges).

5) Check for cracked or badly scratched lenses in full facepieces; incorrectly mounted lens, broken or missing mounting clips.

Atmosphere-Supplying Respirators

1) Check appropriate items above.

2) Check air supply system for breaks or kinks in supply hoses and detachable coupling attachments.

3) Follow manufacturer's recommendations for the specific equipment.

4) Check air supply level and warning devices.

1.4.2 CLEANING AND DISINFECTING

The respirator must be washed after each day's use. If the respirator is shared it must also be disinfected according to the manufacturer's instructions. Organic solvents of any kind must not be used for cleaning. Air purifying filters must not be wetted.

1.4.2.1 CLEANING

1) Remove any filters, cartridges or canisters and, if required by the manufacturer, straps and speaking diaphragms from the facepiece. Remove regulators on airline or SCBA.

2) Wash respirator parts excluding cartridges and canisters in warm (not to exceed 140°F), soapy water or in a product specifically designed by respirator manufacturers for this purpose. A plastic bristle hand brush may be helpful in removing dirt from respirator parts.

3) Rinse all parts thoroughly in warm water.

4) Air dry all parts.

5) Reassemble the respirator and insert new cartridges if needed.

6) Place the respirator in a plastic bag or container and seal it for storage. The respirator facepiece should be stored in its normal position so as not to distort the elastomer.

1.4.2.2 DISINFECTION

1) Disinfection should be done with a cleaner/disinfection agent purchased from the respirator vendor. If that material is not available the following NIOSH procedures can be followed:

   a) Immerse the respirator body for two minutes in a 50 ppm chlorine solution (about 2 ml bleach to 1 liter of water). Rinse thoroughly in clean water and air dry.

   b) Immerse the respirator body for two minutes in an aqueous solution of iodine (add 0.8 ml of iodine in 1 liter water). The iodine is about 7% ammonium and potassium iodide, 45% alcohol and 48% water. Rinse thoroughly in clean water and air dry.

2) Immersion times have to be limited to minimize damage to the respirator. The solutions can age rubber and rust metal parts.

   NOTE: The air-purifying elements must be removed from the respirator prior to cleaning and sanitizing the respirator. Never allow the air-purifying elements to come in contact with water or cleaning/sanitizing solution.

1.4.3 STORAGE

Respirators must be stored to protect them from contamination and mechanical damage at all times when not in use. New, cleaned or reconditioned respirators are to be kept in a clean, sealed plastic bag or container, stored in a normal position. The plastic bag should be labeled with the users name. A suitable cabinet or drawer should be used to protect respirators and supplies from dirt, extremes of temperature or bright sunlight. They are not to be left in vehicles or on site perimeter fences, in change sheds, etc.

ATTACHMENT C

HEAT STRESS AND COLD STRESS PROCEDURES

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1.0 COLD STRESS

1.1 OVERVIEW

Fatal exposures to cold have been reported in employees failing to escape from low environmental air temperatures or from immersion in low temperature water. Hypothermia, a condition in which the body's deep core temperature falls significantly below 98.6°F, can be life threatening. A drop in core temperature to 95°F or lower must be prevented.

Air temperature is not sufficient to determine the cold hazard of the work environment. The wind-chill must be considered as it contributes to the effective temperature. The body's physiologic defense against cold includes constriction of the blood vessels, inhibition of the sweat glands to prevent loss of heat via evaporation, glucose production and involuntary shivering to produce heat by rapid muscle contraction.

The frequency of accidents increases with cold temperature exposures as the body's nerve impulses slow down, individuals react sluggishly and numb extremities make for increased clumsiness. Additional safety hazards include ice, snow blindness, reflections from snow and possible skin burns from contact with cold metal.

There are certain predisposing factors that make an individual more susceptible to cold stress. It is the responsibility of the project team members to inform the Health and Safety Officer to monitor an individual, if necessary, or use other means of preventing/reducing the individual's likelihood of experiencing a cold related illness or disorder.

1.2 PREDISPOSING FACTORS

Predisposing factors that will increase an individual's susceptibility to cold stress are listed below:

- Dehydration: The use of diuretics and/or alcohol, or diarrhea can cause dehydration. Dehydration reduces blood circulation to the extremities.
- Fatigue During Physical Activity: Exhaustion reduces the body's ability to constrict blood vessels. This results in the blood circulation occurring closer to the surface of the skin and the rapid loss of body heat.

- Age: Some older and very young individuals may have an impaired ability to sense cold.
- Alcohol Consumption: Alcohol dilates the blood vessels near the skin surface resulting in excessive body heat loss.
- Sedative Drugs: Sedatives may interfere with the transmission of impulses to the brain, thereby interfering with the body's physiological defense against cold. Some prescription drugs may react the same way.
- Poor Circulation: Vasoconstriction of peripheral vessels reduces blood flow to the skin surface.
- Heavy Work Load: Heavy work loads generate metabolic heat and make an individual perspire even in extremely cold environments. If perspiration is absorbed by the individual's clothing and is in contact with the skin, cooling of the body will occur.
- The Use of PPE: PPE usage which traps sweat inside the PPE may increase an individual's susceptibility to cold stress.
- Lack of Acclimatization: Acclimatization, the gradual introduction of workers into a cold environment, allows the body to physiologically adjust to cold working conditions.
- History of Cold Injury: Previous injury from cold exposures may result in increased cold sensitivity.

1.3 PREVENTION OF COLD STRESS

There are a variety of measures that can be implemented to prevent or reduce the likelihood of employees developing cold related ailments and disorders. These include acclimatization, fluid and electrolyte replenishment, eating a well balanced diet, wearing warm clothing, the provision of shelter from the cold, thermal insulation of metal surfaces, adjusting work schedules and employee education.

- Acclimatization: Acclimatization is the gradual introduction of workers into the cold environment to allow their bodies to physiologically adjust to cold working conditions. However, the physiologic changes are usually minor and require repeated uncomfortably cold exposures to induce them.
- Fluid and Electrolyte Replenishment: Cold, dry air can cause employees to lose significant amounts of water through the skin and lungs. Dehydration affects

the flow of blood to the extremities and increases the risk of cold injury. Warm, sweet, caffeine-free, non-alcoholic drinks and soup are good sources to replenish body fluids.

- Eating a Well-Balanced Diet: Restricted diets including low salt diets can deprive the body of elements needed to withstand cold stress. Eat high energy foods throughout the day.
- Warm Clothing: It is beneficial to maintain air space between the body and outer layers of clothing in order to retain body heat. However, the insulating effect provided by such air spaces is lost when the skin or clothing is wet.

The parts of the body most important to keep warm are the feet, hands, head and face. As much as 40 percent of body heat can be lost when the head is exposed.

Recommended clothing includes:

- Inner layers (t-shirts, shorts, socks) should be of a thin, thermal insulating material.
- Wool or thermal trousers. Denim is not a good protective fabric.
- Felt-lined, rubber-bottomed, leather-upper boots with a removable felt insole is preferred. Change socks when wet.
- Wool shirts/sweaters should be worn over inner layer.
- A wool cap is good head protection. Use a liner under a hard hat.
- Mittens are better insulators than gloves.
- Face masks or scarves are good protection against wind.
- Tyvek/poly-coated Tyvek provides good wind protection.
- Wear loose fitting clothing, especially footwear.
- Carry extra clothing in your vehicle.
- Shelters with heaters should be provided for the employees' rest periods if possible. Sitting in a heated vehicle is a viable option. Care should be taken that the exhaust is not blocked and that windows are partially open to provide ventilation.
- At temperatures of 30°F (-1°C) or lower, cover metal tool handles with thermal insulating material if possible.

- Schedule work during the warmest part of the day if possible, rotate personnel and adjust the work/rest schedule to enable employees to recover from the effects of cold stress.

1.3.1 EMPLOYEE EDUCATION

Employees have already been trained to recognize and treat the effects of cold stress during their 40-hour training. Signs, symptoms and treatment of cold stress should be reviewed in project safety meetings where applicable. The buddy system will help in preventing cold stress once the employees are trained to recognize the signs and symptoms of cold stress.

1.3.2 COLD STRESS PREVENTION GUIDELINES

It may not be practically feasible to implement all the above prevention measures. Follow the guidelines given below when the ambient air temperature is -5°F (-20°C) or lower:

- Contact the project manager or the industrial hygienist to determine if the project team should be on-site in such temperatures;
- Dress warm;
- Replenish fluids and electrolytes at regular intervals;
- Provide shelter from the cold; and
- Adjust work/rest schedules.

1.3.3 ADJUST WORK-REST SCHEDULES

Follow the work/rest schedule on Table C.1. It is based on the cooling power of air which is a function of wind speed and ambient air temperature.

1.4 FIRST-AID TREATMENT GUIDELINES

The following describes symptoms of different stages in cold stress and the related first-aid treatment guidelines.

1.4.1 FROSTBITE

Stages

Incipient (frost nip)	May be painless. Tips of ears, nose, cheeks, fingers, toes, chin affected. Skin blanched white.
Superficial	Affects skin/tissue just beneath skin; turns purple as it thaws. Skin is firm, waxy; tissue beneath is soft, numb.
Deep	Tissue beneath skin is solid, waxy, white with purplish tinge. Entire tissue depth is affected.

First-Aid

Incipient	Warm by applying firm pressure - blow warm breath on spot or submerge in warm water (102°F to 110°F) (39°C to 43°C). Do not rub the area.
Superficial	Provide dry coverage, steady warmth; submerge in warm water.
Deep	Hospital care is needed. Do not thaw frostbitten part if needed to walk on. Do not thaw if there is danger of refreezing. Apply dry clothing over frostbite. Submerge in water; do not rub.

1.4.2 GENERAL HYPOTHERMIA

Stages

- Shivering
- Indifference
- Decreased Consciousness
- Unconsciousness

- Death

Symptoms

- Muscle Tension
- Uncontrollable Shivering
- Glassy Stare
- Decreased Muscle Function
- Speech Distortion
- Blue, Puffy Skin
- Slow Pulse
- Shallow Breathing
- Coordination Loss
- Stumbling
- Forgetfulness
- Freezing Extremities
- Dilated Pupils
- Fatigue

Emergency Response

- Keep person dry; replace wet clothing
- Apply external heat to both sides of patient using available heat sources, including other bodies.
- Give warm liquids - not coffee or alcohol - after shivering stops and if conscious.
- Handle gently.
- Transport to medical facility as soon as possible.
- If more than 30 minutes from a medical facility, warm person with other bodies.

2.0 HEAT STRESS

2.1 OVERVIEW

Heat induced occupational illnesses, injuries and reduced productivity occur in situations in which the total heat load (environmental plus metabolic) exceeds the body's capacities to maintain normal body functions without excessive strain. Heat stress is the sum of the heat generated in the body plus the heat gained from the environment minus the heat lost from the body to the environment. The body's response to heat stress is called heat strain. The level of heat stress at which excessive heat strain will result depends on the heat tolerance of the individual. Certain predisposing factors may reduce an individual's ability to tolerate heat stress.

Using PPE may put a hazardous waste worker at an increased risk of developing heat stress. Health effects may range from heat rash or heat fatigue to serious illness or death. Heat stress is caused by a number of interacting factors, including environmental conditions such as temperature and relative humidity, protective clothing which limits natural heat loss through perspiration, workload and the individual characteristics of the worker.

It is the responsibility of the project team members to inform the HSO or industrial hygienist if any of the predisposing factors listed below apply to them. This enables the HSO to monitor the individual if necessary, or use other means of preventing/reducing the individual's likelihood of experiencing a heat related illness or disorder.

2.2 PREDISPOSING

Predisposing factors that will increase the individual's susceptibility to heat stress are listed below:

- Lack of Physical Fitness: Such individuals experience more physiological strain including a higher heart rate, a higher body temperature, less efficient sweating and slightly higher oxygen consumption as compared to fit individuals.
- Obesity: Overweight individuals produce more heat per unit surface area than thin individuals and have a lowered ability to dissipate heat.
- Age: Older individuals may have a decreased ability to cope with heat stress.
- Dehydration: Dehydrated individuals will have a decreased ability to cool the body by sweating. Diarrhea can cause dehydration.

- Alcohol, Medications and Drug Use: Alcohol consumption may dehydrate individuals and certain medications/drugs may act as diuretics. Hence, the individual may have a decreased ability to lose heat by sweating.
- Infection, Sunburn, Illness and Certain Chronic Diseases: These factors may interfere with the body's normal mechanisms to lose heat.
- Heart Conditions or Circulatory Problems: Heat stress may place an additional strain on the heart and circulatory system that could harm the individual as well as decrease the individual's physiologic response.
- Low Salt Diet: Could affect the individual's electrolyte balance.
- Pregnancy
- Previous History of Heat Stroke or Heat Exhaustion: May increase the individual's susceptibility to heat stress.
- Heavy Work Load: Will generate metabolic heat thereby increasing the heat stress placed on the individual
- The Use of PPE Over Light Summer Clothing: This will decrease the ability of an individual to lose heat by sweating as evaporative cooling can no longer occur.
- Lack of Acclimatization: Acclimatization is the gradual introduction of workers into a hot environment to allow their bodies to physiologically adjust to hot working conditions. Acclimatized individuals generally have lower heart rates and lower body temperatures. In addition, they sweat sooner and more profusely and even have more dilute sweat (thereby losing less electrolytes) than non-acclimatized individuals.

2.3 PREVENTION OF HEAT STRESS

There are a variety of measures that can be implemented to prevent or reduce the likelihood of employees developing heat stress related disorders. These include fluid and electrolyte replenishment, the provision of shelter from the sun and heat, work schedule adjustment, the use of cooling devices, acclimatization, heat stress monitoring and employee education, as discussed below:

- Fluid and Electrolyte Replenishment: Personnel should drink about 16 ounces of water before starting work and drink water at every break. To encourage water consumption, cool water and disposable cups should be made available. The normal thirst mechanism is not sensitive enough to ensure that enough water

will be drunk to replace lost sweat. When heavy sweating occurs, personnel should be encouraged to drink more. Replacing body fluids with Gatorade is an option. It is advisable to have Gatorade on-site if the air temperature is 70°F (21°C) or more and the workers are performing tasks with a moderate to heavy work load in chemical resistant clothing.

- Shelter From the Sun and Heat: Air-conditioned (if possible) or shaded areas should be made available for rest periods. Sitting in an air-conditioned truck is an acceptable option.
- Work Schedule Adjustment: Scheduling work for early mornings and/or late afternoons will avoid the hottest parts of the day and reduce the heat stress placed on personnel. Rotation of personnel will help reduce overexertion of workers and adjusting the work-rest schedule will help personnel recover from the effects of heat stress periodically.
- Use of Cooling Devices: The use of cooling devices like field showers, hose-down areas or cooling vests should be considered for project tasks that involve heavy work loads in chemical resistant clothing.
- Acclimatization: Acclimatization is the gradual introduction of workers into a hot environment to allow their body to physiologically adjust to hot working conditions. Acclimatized individuals generally have lower heart rates and lower body temperatures. In addition, they sweat sooner and more profusely and even have more dilute sweat (thereby losing less electrolytes) than non-acclimatized individuals.
- Heat Stress Monitoring: Monitoring hot environments for potential heat stress should be initiated when the ambient air temperature is in excess of 70°F (21°C). There are several ways to monitor heat stress: measuring heart rate, oral temperature, loss of body weight and the Wet Bulb Globe Temperature using a Reuter-Stokes or Quest Electronics heat stress monitor.
- Employee Education: Workers have already been trained to recognize and treat the effects of heat stress during the 40-hour training course. Signs, symptoms and treatment of heat stress should be discussed in site safety meetings. The buddy system will help in preventing heat stress once the employees are trained to recognize the signs and symptoms of heat stress.

2.3.1 PREVENTION PRACTICES

It may not be practically feasible to implement all of the above prevention measures. The following has been developed as a field guide for use in actual field situations.

Ambient air temperature is 70°F (21°C) or more:

- Replenish fluids and electrolytes. Drink cool (50°F to 60°F/10°C to 15°C) fluids hourly. The fluids should be caffeine-free and non-alcoholic. Do not wait until you are thirsty. Your normal thirst mechanism is not sufficient to overcome the effects of dehydration. If you feel thirsty, you are already becoming dehydrated.
- Provide shelter from the sun and heat.

Ambient air temperature is 70°F (21°C) or more and chemical-resistant clothing is being used:

- Same as above;
- Adjust work schedules if feasible; and
- Initiate heat stress monitoring and/or the use of cooling devices.

2.3.2 HEAT STRESS MONITORING

Heat stress monitoring may be performed by monitoring the heart rate. Heart rate should be measured at the beginning of the work shift, at regular intervals and at the start of each rest period.

1) If the heart rate is <110 beats per minute (bpm), personnel may continue the current work/rest schedule.
2) If the heart rate is >110 bpm, take a 10 minute break. Monitor heart rate at the end of the rest period. If not <110 bpm, rest until the heart rate is <110 bpm. Reduce the current work time between breaks by approximately one hour. If the next scheduled monitoring session shows a heart rate of >110 bpm once again, reduce the work time between breaks by one hour.

2.4 HEAT STRESS FIRST AID

2.4.1 HEAT CRAMPS

Cause: Excessive water loss/electrolyte imbalance.

Symptoms	First-Aid Guidelines
Muscular pain in arms, legs, abdomen Faintness, dizziness, exhaustion Normal temp, cool moist skin	Administer sips of Gatorade (1/2 glass every 15 minutes) Do not massage cramping muscles Relax person

2.4.2 HEAT EXHAUSTION

Cause: Large amount of water loss; blood circulation diminishes.

Symptoms	First-Aid Guidelines
Moist, clammy, skin, usually pale Dilated pupils Weak, dizzy, nauseous, headache Normal or low body temperature	Move to a cool place Apply cold, wet compresses to skin Raise feet 8 to 12 inches Administer sips of Gatorade (1/2 glass every 15 minutes) Get medical attention

2.4.3 HEAT STROKE

Cause: Body overheats; temperature rises; no sweating occurs

Symptoms	First-Aid Guidelines
No sweating occurs	Get emergency medical assistance ASAP
Dry, hot skin, usually red	Remove from sunlight
Constricted pupils	Wet down body with cool water or rubbing alcohol
Hot body temperature (105°F to 110°F/40.5°C to 43.5°C)	Elevate head/shoulders
Strong, rapid pulse	Wrap in wet, cold wrapping
Unconsciousness may occur	Once cooled to 102°F (38.9°C), stop cooling measures
Muscular twitching	

TABLE C.1

WORK/REST SCHEDULE
FOR AN EIGHT HOUR WORK SHIFT

Air Temperature with Sunny Sky		*Work/Break Schedule (Minutes)*				
°F	*°C*	*No Wind*	*5 mph Wind*	*10 mph Wind*	*15 mph Wind*	*20 mph Wind*
-05 to -09	-20 to -23	110/10	110/10	75/10	55/10	40/10
-10 to -14	-23 to -26	110/10	75/10	55/10	40/10	30/10
-15 to -19	-26 to -28	75/10	55/10	40/10	30/10	Stop
-20 to -24	-29 to -31	55/10	40/10	30/10	Stop	Stop
-25 to -29	-32 to -34	40/10	30/10	Stop	Stop	Stop
-30 to -34	-35 to -37	30/10	Stop	Stop	Stop	Stop
-35 & Below	-38 & Below	Stop	Stop	Stop	Stop	Stop

Note:

This table addresses the health hazards related to cold weather work. The practicality of working under a work/rest schedule, together with the ability of the necessary equipment to function properly in cold weather, may be more restrictive than the health hazards and also need to be considered.

The cold stress schedule applies to light or sedentary work activities. Light to moderate work activities can be moved down one level, moderate to heavy work activities can be moved down two levels if workers are acclimated, have proper protective clothing and show no signs of cold stress.

0 - 5 mph Winc Light flag moves.
15 mph Wind: Raises newspaper sheet.
10 mph Wind: Light flag fully extended.
20 mph Wind: Blowing and drifting snow.

ATTACHMENT D

SEVERE WEATHER EMERGENCY PROCEDURES

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SEVERE WEATHER

1.0 SCOPE

As most projects are conducted outside, the potential for severe weather must be considered. Thunderstorms, tornadoes, and winter storms can develop quickly, jeopardizing worker safety. The following emergency procedures are to be followed in case of severe weather.

2.0 THUNDERSTORMS AND LIGHTNING

Monitor weather conditions at all times while working. Monitor for a sign of an impending storm such as increased cloudiness, darkened skies, and increased wind. If any of these signs are observed, listen to a radio for the latest weather information or contact a local weather reporting service.

When a thunderstorm accompanied by lightning is in the project area, cease work immediately. All powered equipment, such as drill rigs, are to be shut down.

Seek shelter inside nearby buildings or trailers. If there are no buildings nearby, seek shelter inside your vehicle.

If you are caught outside, do not stand beneath tall, isolated trees or telephone poles. Avoid areas projecting above the landscape such as hilltops. In open areas, go to a low place such as a ravine or valley. Stay away from open water, metal equipment, wire fences, and metal pipes. If you are in a group of people in the open, spread out, staying several yards apart.

If you are caught in a level field or open area far from shelter and you feel your hair stand on end, lightning may be about to strike you. Drop to your knees and bend forward, putting your hands on your knees. **DO NOT LIE FLAT ON THE GROUND.**

If someone has been struck by lightning, monitor life signs and begin administering mouth-to-mouth resuscitation or cardiopulmonary resuscitation as needed. Send for help. Check conscious victims for burns, especially at the fingers and toes and next to buckles and jewelry. Administer first aid for shock. Do not let the victim walk around.

3.0 TORNADOES

Tornadoes usually develop from thunderstorms and normally occur at the trailing edge of the storm. Most tornadoes occur in the months of April, May, June, and July in the late afternoon and early evening hours.

When storms are predicted for the project area, monitor weather conditions on a radio. A tornado watch is issued when favorable conditions exist for the development of a tornado. A tornado warning is issued by the local weather service office whenever a tornado has actually been sighted or is strongly indicated by radar.

If a tornado warning is issued, seek shelter immediately. If there are permanent buildings located on site, go there immediately, moving toward interior hallways or small rooms on the lowest floor.

If a tornado warning is issued and you are in a vehicle or a site trailer, leave and go to the nearest building. If there are no buildings nearby, go in the nearest ditch, ravine, or culvert, with your hands shielding your head.

If a tornado is sighted or a warning issued while you are in open country, lie flat in a ditch or depression. Hold onto something on the ground, such as a bush or wooden fence post, if possible.

Once a tornado has passed the site, site personnel are to assemble at the designated assembly area to determine if anyone is missing. Administer first aid and seek medical attention as needed.

4.0 WINTER STORMS

When snow or ice storms are predicted for the project area, site personnel should monitor weather conditions on a radio. A winter storm watch is issued when a storm has formed and is approaching the area. A winter storm warning is issued when a storm is imminent and immediate action is to be taken.

When a storm watch is issued, monitor weather conditions and prepare to halt site activities. Notify the project manager (PM) of the situation. Seek shelter at site buildings or leave the site and seek warm shelter. If you are caught in a severe winter storm while traveling, seek warm shelter if road conditions prevent safe travel.

If you are stranded in a vehicle during a winter storm:

- STAY IN THE VEHICLE, disorientation comes quickly in blowing and drifting snow;
- wait for help;
- keep a window open an inch or so to avoid carbon monoxide poisoning;
- run the engine and heater sparingly;
- keep watch - do not let everyone sleep at the same time; and
- exercise occasionally.