WORK PLAN

General Motors Corporation
Grand Rapids Metal Plant
Wyoming, Michigan

NOVEMBER 2002
REF. NO. 17360 (2)

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1.0 INTRODUCTION

This Work Plan describes the Scope of Work (SOW) that will be performed during the collection and analysis of groundwater, air, and light non-aqueous phase liquid (LNAPL) samples during the investigation conducted at the General Motors Corporation (GM) Grand Rapids Metal Plant located at 300 36th Street in Wyoming, Michigan (Site). Figure 1.1 presents the Site location.

1.1 SITE BACKGROUND

The Grand Rapids Metal Plant is a metal fabrication and assembly plant for GM consisting of approximately 45 acres of production activities on approximately 88 acres of land. A Site plan is presented on Plan 1.

Current operations conducted at the Site include the manufacture of quarter panels, floor pans, roof panels, deck lids, doors, and center pillars for assembly plant use. In addition, the Site constructs the dies, fixtures, mechanical devices, and manufacturing aids used internally to produce the aforementioned parts. The Site consists of a main manufacturing building, with several outbuildings including a baler house, wastewater treatment plant (WWTP), powerhouse, and other ancillary structures. The remainder of Site areas consist of asphalt/concrete paved areas and landscaped areas. The Site is relatively flat, with little or no significant topographic relief.

Numerous environmental investigations have been conducted at the Site to date. Based on the review of available documentation regarding environmental investigations previously conducted at the Site, two areas of interest were identified: an oil release from a press pit sump pan formerly located near Column B-35 and chlorinated compounds in soil and groundwater beneath the Site. In addition, LNAPL was observed in groundwater in monitoring wells located in the northeast portion of the plant.

Contamination from a release of water soluble oil from a press pit sump pan was identified in soil and groundwater at the Site in 1981. Based on analytical results from soil and groundwater samples collected in the vicinity of the release and a review of the material safety data sheet (MSDS) for the oil, no chemicals of concern were detected in the soil and groundwater samples collected above the applicable regulatory limits at the time that the samples were collected.

From 1953 to 1979, the Site conducted degreasing operations inside the facility utilizing chlorinated compounds near Column A-15. This area is the suspected source of chlorinated compound contamination to soil and groundwater beneath the facility. Numerous subsurface investigations were conducted at the Site between 1985 and 1989 to identify and delineate the chlorinated compound contamination and the geological/hydrogeological conditions at the Site and on the area located hydraulically downgradient of the Site. Chlorinated volatile organic compounds (VOCs) have been identified in groundwater on-Site and off-Site at concentrations above the Michigan Act 451, Part 201 Residential Drinking Water Criteria (RDWC). Semi-volatile organic compounds (SVOCs) have been identified in groundwater on-Site at concentrations above the Michigan Act 451, Part 201 Industrial Groundwater Volatilization to Indoor Air Criteria (CGVIAC). Based on the results of the investigations, a remediation system, consisting of a combination soil vapor extraction (SVE) system and a groundwater extraction system was constructed in 1989 and is currently in place at the facility to remediate the soil and groundwater at the Site. Quarterly monitoring activities are conducted at the Site and reported to the Michigan Department of Environmental Quality (MDEQ).

LNAPL was identified in monitoring wells located in the northeast portion of the plant in 1985 during plant expansion activities. Subsequent investigations continued to monitor on a regular basis for the presence of LNAPL in select monitoring wells. The nature and extent of the LNAPL has not been determined.

1.2 PURPOSE OF WORK PLAN

The purpose of this Work Plan is to outline the activities necessary to further evaluate and delineate chlorinated compound impacts to groundwater above the Michigan Act 451, Part 201 Residential Cleanup Criteria; to further define hydrogeologic conditions at the Site; to evaluate the extent and nature of the LNAPL identified at the Site; evaluate potential groundwater and indoor air impact associated with the identified LNAPL; and evaluate the current effectiveness of the existing SVE and groundwater extraction systems.

2.0 CURRENT CONDITIONS

2.1 NATURE AND EXTENT OF CONTAMINATION

During the previous environmental investigations conducted at the Site, samples of soil, groundwater, and soil gas were collected and submitted for various chemical analyses. Chemical analysis included VOCs, total organic carbon (TOC), oil and grease, SVOCs, Polynuclear Aromatic Hydrocarbons (PNAs), and metals.

Historically, chlorinated compounds and SVOCs have been identified in groundwater at concentrations above the Michigan Act 451, Part 201 Residential and/or Industrial Cleanup Criteria and a combination SVE groundwater remediation system is currently in place at the Site (see Section 1.1). Quarterly monitoring events are currently conducted at the Site, including the collection of groundwater samples from select monitoring wells and air samples from the SVE system influent, intermediate, and effluent for chemical analysis. In addition, monthly inspections are conducted on the remediation system equipment and groundwater samples are collected from the influent, intermediate, and effluent and the stormwater retention pond outfall in accordance with the National Pollution Discharge Elimination System (NPDES) permit issued for the Site. Based on recent quarterly groundwater results, the extent of the chlorinated compound plume has not been defined to Michigan Act 451, Part 201 Residential Drinking Water Cleanup Criteria.

A preliminary evaluation of the existing remediation systems was conducted in spring 2002. Based on the preliminary evaluation, the SVE system was determined to have removed significant contaminant mass historically; however, TCE influent concentrations have remained consistently at low levels for approximately the last 10 years. Based on the long term evidence of steady state function and very low TCE concentrations in the SVE system influent during constant operation of the SVE system, it may be appropriate to consider decommissioning of the SVE system at this time; however, additional data collection is proposed to support such a conclusion.

2.2 SITE GEOLOGY AND HYDROGEOLOGY

Information regarding the geologic conditions at the Site was collected during previous environmental investigations. Numerous soil borings were installed at the Site between 1981 and 1993.

Regional overburden in the vicinity of the Site consists of glacial outwash sand and gravel, and postglacial alluvium from the Paleozoic Upper Mississippian Meramecian Series. Based on the review of stratigraphic boring logs generated during previous investigations at the Site, the glacial outwash, consisting of sands and gravels, has been observed at varying depths between 40 and 90 feet below ground surface (bgs). The outwash is underlain by a clay layer that has been observed to generally slope to the west-northwest at a gradient of approximately 1 foot in 15 feet. Bedrock was not encountered during previous investigations conducted at the Site. Bedrock in the area of the Site is encountered at approximately 100 feet bgs. The upper bedrock is part of the Michigan formation, which is underlain by Marshall sandstone. The Michigan formation is approximately 100 feet thick, and consists of interbedded layers of shale, gypsum, and limestone. To better understand the surficial geology at the Site, three cross-sections have been prepared. Locations of the cross-sections are presented on Figure 2.1. Cross-sections A-A', B-B', and C-C' are presented on Figures 2.2, 2.3, and 2.4 respectively.

Groundwater was encountered during the environmental investigations at approximately 20 feet bgs. Groundwater level measurements were recorded during the environmental investigations and during subsequent quarterly monitoring events. Based on the July 26, 2002 water levels, the approximate groundwater flow direction is to the north-northwest, towards Cole Drain. This groundwater flow direction is consistent with historical groundwater elevation data. Figure 2.5 presents the July 26, 2002 groundwater elevations and flow direction.

3.0 SCOPE OF WORK

The SOW for this Work Plan includes the installation of 7 soil borings and 7 monitoring wells, the collection and analysis of approximately 56 groundwater samples, including QA/QC samples, and the collection and analysis of one LNAPL sample. In addition, the SOW includes analysis of soil samples if warranted, the collection and analysis of air samples from the existing SVE system, and conducting a LNAPL recovery test. The investigation field work will adhere to the methods and procedures specified in this Work Plan, including the Quality Assurance Project Plan (QAPP) presented in Appendix A.

3.1 SOIL BORING AND MONITORING WELL INSTALLATION

Proposed soil boring and monitoring well locations for this Work Plan are presented in Figure 3.1. Soil borings and monitoring wells will be installed as outlined below.

3.1.1 SOIL BORING INSTALLATION/VERTICAL AQUIFER SAMPLING

Seven soil borings, HP1-02 through HP7-02, will be advanced at the Site during the implementation of this Work Plan.

Three soil borings, HP1-02 though HP3-02, will be installed upgradient/cross-gradient from the former degreaser location to further delineate the extent of the chlorinated compound contamination in groundwater and evaluate the potential of additional sources of contamination. Three soil borings, HP4-02 though HP6-02, will be installed downgradient from the former degreaser location to further delineate the extent of the chlorinated compound contamination. One soil boring, HP7-02, will be installed immediately downgradient to evaluate the area of influence that purge well, PWDISCH, encompasses to further evaluate the effectiveness of the existing groundwater extraction system.

Soil borings shall be advanced at the designated locations using a rotary drill rig equipped with a 4 ¼-inch inside diameter hollow stem auger (HSA). Concrete coring of approximately 10 to 12-inch thick concrete will be performed, as necessary. Concrete will be patched after completion of drilling activities.

Soil samples will be collected continuously using 2-foot long, 2-inch outside diameter split spoon samplers at each location, as presented in Section 4.1. Soil samples will be collected from the borings in accordance with the Standard Penetration Test Method, ASTM D1586 and as presented in Section 4.1. The split spoon samples will be examined by a CRA geologist for visual/olfactory evidence of impact and screened with a PID. If visual/olfactory evidence of impact or high PID readings are observed, at the discretion of CRA field personnel, additional soil samples will be collected and submitted to the laboratory for chemical analysis. Additionally, discrete groundwater samples will be collected from each soil boring utilizing vertical aquifer sampling (VAS) via a hydropunch as presented in Section 4.2.

Soil cuttings will be screened with an 11.7 eV bulb photoionization detector (PID) and examined for visual/olfactory indication of contamination. All soil cuttings will be containerized in Department of Transportation (DOT) approved 55-gallon drums and labeled for future characterization.

Upon completion of discrete groundwater sample collection, each borehole will be abandoned. All soil borings will be abandoned using the tremie-method to backfill the borehole annulus with a high solids bentonite grout to ground surface.

3.1.2 MONITORING WELL INSTALLATION

Seven monitoring wells, MW1-02 through MW7-02, will be installed at the Site during the implementation of this Work Plan.

Monitoring wells will be installed utilizing a 4 ¼-inch HSA. Split spoon samples will not be collected during monitoring well installation. Monitoring wells will be installed adjacent to the soil borings and it can be assumed that the stratigraphy will be the same as that of the monitoring wells. A confirmation split spoon sample will be collected upon reaching depth during the installation of the monitoring well.

Soil cuttings will be screened with an 11.7 eV bulb photoionization detector (PID) and examined for visual/olfactory indication of contamination. All soil cuttings will be containerized in DOT approved 55-gallon drums and labeled for future characterization.

Monitoring wells will be constructed using Schedule 40 PVC risers and 10-foot long, 0.01-inch slot Schedule 40 PVC screen through the augers as a 2-inch diameter installation. During completion of the installation, the riser pipe shall be temporarily

capped to prevent entrance of foreign materials during overburden monitoring well installation. The screen and casing will be joined utilizing flush threaded joints. The depths of the monitoring well screens will be determined based on the analytical results from the VAS. Monitoring well screens will be set at the interval identified during the VAS sampling to exhibit the highest concentrations of the chemicals of concern. If no chemicals of concern are identified during the VAS, the monitoring well will be set to straddle the water table to further evaluate the groundwater flow regime across the Site.

An inert silica sandpack will be placed to a height of three vertical feet above the top of the screen using a flush-threaded 1-inch diameter tremie pipe as the augers are withdrawn from the borehole. If bridging of the silica sand occurs, the bridged material will be mechanically broken prior to the addition of more silica sand.

The remainder of the annulus will be filled with a high solids bentonite grout using a flush-threaded 1-inch diameter tremie pipe to within two feet of the ground surface. The grout will be set in one continuous operation with the entire amount placed before the initial set occurs. Once the grout has set, the remaining portion of the unfilled annulus will be filled with concrete and a flushmount protective surface casing will be installed at each well. The protective flushmounted casing will be centered over the riser and extend into the concrete collar 1-foot. The riser pipe will be capped with an expandable locking cap.

Each monitoring well will be clearly labeled with a unique identification number. The number will be located on the well protector in an area where the number is protected from possible tampering.

The stratigraphic boring logs from newly installed monitoring wells will be used in conjunction with the stratigraphic boring logs from previous drilling activities to supplement previous data to further determine geologic conditions across the extent of the identified impacted areas.

3.1.3 MONITORING WELL DEVELOPMENT

Groundwater level measurements and corresponding bottom depths will be recorded for MW1-02 through MW7-02. The well volumes of MW1-02 through MW7-02 will be calculated and each well will be developed by surging the well with a stainless steel bailer for a minimum of five minutes and then purged with a submersible pump. Each well will be developed by removing a minimum of five well volumes until groundwater

is developed to a silt-free condition, if possible, and the turbidity, pH, temperature, and conductivity of the groundwater have stabilized.

In addition, monitoring wells 86-1 and 87-10 will be re-developed by surging the well with a stainless steel bailer for a minimum of five minutes and by removing a minimum of ten well volumes. Bottom depth measurements will be re-collected for these wells, and if the screens are obstructed, additional surging will be conducted and an additional five well volumes will be removed.

All generated development water will be visually examined and screened with a PID. Purge and development groundwater will be containerized in DOT approved 55-gallon drums and labeled for future characterization.

3.1.4 SURVEYING

A survey of the Site will be completed for all new soil boring and monitoring well locations. Soil boring locations and monitoring well locations and elevations will be surveyed, with elevations to the nearest 0.01-foot. These elevations will be referenced to an above mean sea level benchmark. Monitoring well elevations will be used to determine groundwater elevations, which will be used to develop Site groundwater contours, flow direction, and flow velocities.

3.1.5 DECONTAMINATION

Upon mobilization to the Site and prior to drilling commencement, the drill rig and all associated equipment will be thoroughly cleaned using a high pressure, low volume steam wash and inspected. Before initiating drilling at each subsequent location, the augers, drill rod, and other associated equipment will be decontaminated to prevent cross-contamination. Decontamination of sampling equipment is presented in Section 4.4.

All generated decontamination water will be visually examined and screened with a PID. All decontamination water will be containerized in DOT approved 55-gallon drums and labeled as to where it was generated and the initial accumulation date.

3.2 LNAPL RECOVERY TEST

To evaluate the potential extent of the LNAPL, a recovery test will be conducted. Measurements of LNAPL and groundwater levels will be collected from monitoring wells, 85-3, 85-5b, 85-6, and 86-1, which are currently monitored on a monthly, quarterly, or annual basis in the area of the identified LNAPL, utilizing an oil-water interface probe.

Based on the observed levels of LNAPL in the above monitoring wells, a LNAPL recovery test will be conducted on all monitoring wells determined to contain LNAPL. LNAPL will be removed from the well utilizing a dedicated polyethylene bailer or a peristaltic pump with dedicated polyethylene tubing, dependent upon the levels of LNAPL observed, and an oil-water interface probe will be used to record recovery at specific intervals over a 12-hour period. Initial readings will be monitored at 1 minute, 5 minutes, 15 minutes, 30 minutes, 45 minutes, and one hour. Dependent upon the recovery, at the discretion of CRA field staff, these intervals may be increased or decreased in duration. After one hour, if no significant product recovery has occurred, recovery will be monitored on an hourly basis. If recovery occurs prior to the end of the 12-hour period, the recovery test will cease. Intervals at which the readings are monitored will vary dependent upon recovery levels observed in the field, at the discretion of CRA field staff.

3.3 SVE SYSTEM TESTING

Based on the review of historical quarterly sampling results, it has been identified that the mass of TCE being captured by the SVE system is insignificant and has remained at a steady state for approximately 10 years. To further evaluate the current effectiveness of the SVE system, the SVE system will be shutdown on an intermittent schedule and influent air samples will be collected as presented below.

3.3.1 INITIAL SVE SYSTEM TESTING

During the month of July, the SVE system experienced an electrical problem and was shutdown for a period of approximately 8 weeks for repair. CRA calculated the volume of air contained within the air purge well system and used that information in

conjunction with the flow rate of the air through the system to determine the time required to purge one volume of air from the system.

Upon re-start of the SVE system, CRA collected 3 air samples from the treatment system influent, at one, five, and ten purge volumes, respectively. Air samples were grab-type samples collected using laboratory provided pre-cleaned and pressurized Summa air canisters. The samples were collected from the SVE system by connecting the sample port to the canister using tygon tubing. The canister was allowed to de-pressurize and fill with air from the sample port. Upon completion, the pressure in each of the canisters was checked to confirm the sample had been collected. Air samples were analyzed for chloroethane, 1,1-dichloroethene (DCE), cis-1,2-DCE, trans-1,2-DCE, vinyl chloride (VC), TCE, tetrachloroethene (PCE), and 1,1,1-trichloroethane (TCA).

Analytical results indicated detections of 1,1,1-TCA, TCE, and PCE in all three air samples. 1,1,1-TCA was detected in the samples at concentrations of 0.0077 mg/m^3, 0.0084 mg/m^3, and 0.0084 mg/m^3, respectively. TCE was detected in the samples at concentrations of 2.9 mg/m^3, 2.8 mg/m^3, and 2.9 mg/m^3, respectively. PCE was detected in the samples at concentrations of 0.0098 mg/m^3, 0.0097 mg/m^3, and 0.010 mg/m^3, respectively. Based on the detected concentrations of chlorinated VOCs observed in the SVE system influent after the initial intermittent period of shutdown, additional evaluation of the effects of system shutdown are proposed.

3.3.2 ADDITIONAL SVE SYSTEM TESTING

Based on the results presented in Section 3.2.2, additional intermittent testing of the SVE system will be conducted on a quarterly basis for the period of one year. The SVE system will be shutdown except for each quarterly sampling event (i.e., for a three month period and sampled each quarter). Sample collection will be conducted as outlined in Section 4.5.

4.0 SAMPLING PROCEDURES

Proposed sample locations are presented on Figure 3.1. All sampling will be performed in accordance with the procedures outlined below.

4.1 SOIL SAMPLE COLLECTION

Soil samples will be collected continuously utilizing 2-foot long, 2-inch diameter split spoon samplers from all soil borings. Split spoon samples will be examined by a CRA geologist for visual/olfactory evidence of impact and screened with a PID meter. If visual/olfactory evidence of impact or high PID meter readings are observed, at the discretion of CRA field personnel, soil samples will be collected and submitted to the laboratory for chemical analysis.

4.2 DISCRETE GROUNDWATER SAMPLE COLLECTION

Vertical aquifer sampling (VAS) will be conducted at HP1-02 through HP7-01 at 10-foot intervals beginning at the water table, at approximately 20 feet bgs, 30 feet bgs, 40 feet bgs, and 50 feet bgs or until the clay confining layer is encountered. 15-foot intervals may be utilized at the discretion of the CRA field geologist, dependent upon conditions encountered in the field (i.e., review of previous stratigraphic logs in the vicinity of the soil boring location indicate that the clay confining layer is anticipated to be encountered at a depth greater than 50 feet bgs).

A 5-foot long, 2-inch diameter stainless steel hydropunch sampler with a 0.01-inch slotted screen and a well point will be driven through the undisturbed material through a 4 ¼-inch HSA. The well point will detach from the hydropunch sampler at the correct sample depth and groundwater will flow into, and fill the hydropunch sampler. The amount of time required to fill the hydropunch is dependent upon many factors including type of sample media (i.e., sand vs. clay) and depth below groundsurface (i.e., increasing water pressure with increasing depth).

After sufficient time to fill the hydropunch sampler has passed, the sampler will be removed from the soil boring, the screen broken off, and the discrete groundwater sample will be collected from the sampler.

Approximately 36 discrete groundwater samples, including QA/QC samples, will be collected and analyzed for TCL VOCs on a 48-hour turnaround time. Table 3.1 presents the Sampling and Analysis Plan.

Discrete groundwater samples will be placed into pre-cleaned laboratory provided containers, properly labeled, and submitted to the laboratory under proper chain-of-custody (COC) protocol.

4.3 GROUNDWATER SAMPLE COLLECTION

One groundwater sample will be collected from each of the newly installed monitoring wells and from all existing monitoring wells currently sampled during the quarterly monitoring program.

Prior to sample collection, water level measurements along the bottom depth will be collected and recorded to the nearest 0.01-foot below top of riser. Based on the results of the water level measurements, well volumes will be calculated, the wells will be purged a minimum of five well volumes, and field measurements of temperature, pH, conductivity, dissolved oxygen (DO), oxidation-reduction potential (ORP), turbidity, and dissolved iron (Fe(II)) will be recorded.

Approximately 29 groundwater samples, including QA/QC samples, will be collected and analyzed for TCL VOCs and select natural attenuation parameters (TOC, nitrate, nitrite, manganese, sulfate, sulfide, methane, alkalinity, calcium, carbonate hardness, hardness, magnesium, chloride, ethane, and ethene) on a 2-week turn-around-time using low flow purging techniques. In addition, one groundwater sample will be collected from monitoring well 85-3 and analyzed for SVOCs on a 2-week turn-around-time. Table 3.1 presents the Sampling and Analysis Plan.

Groundwater samples will be placed into a pre-cleaned laboratory-provided container, properly labeled, and submitted under proper COC protocol to the laboratory.

4.4 LNAPL SAMPLE COLLECTION

One LNAPL sample will be collected by slowly lowering a dedicated polyethylene bailer into monitoring wells identified as potentially containing LNAPL. The LNAPL sample will be analyzed for TCL VOCs, TCL SVOCs, Target Analyte List (TAL) metals, diesel

range organics (DRO), and gasoline range organics (GRO). Based on the amount of LNAPL present, insufficient volume may be available for analysis. If an insufficient volume of LNAPL is available, collection of sample for analysis will be done in the following order: SVOCs, DRO and GRO, TAL metals, and TCL VOCs. Table 3.1 presents the Sampling and Analysis Plan.

4.5 AIR SAMPLE COLLECTION

During the first quarterly sampling event, a total of 3 air samples will be collected from the SVE system influent at one, five, and ten system purge volumes, consistent with the initial sample collection, for analysis for TCE. The SVE system will be operated at its minimum design flow rate during system purging and sampling. In addition, the first quarter sampling event will include the collection of four additional influent air samples at half-hour intervals over a 2 hour time period after the tenth purge volume to determine whether TCE concentrations in the SVE influent stream begin to decrease within the volume purged during this period. Based on the results of the first quarterly sampling event, sampling time periods/purge volumes will be established for the subsequent second, third, and fourth quarter sample collection.

Air samples will be collected as grab-type samples using laboratory provided pre-cleaned and pressurized Summa air canisters. The samples will be collected from the SVE system by connecting the sample port to the canister using tygon tubing. The canister will be allowed to de-pressurize and fill with air from the sample port. Upon completion, the pressure in each of the canisters will be checked to confirm the sample had been collected. Air samples will be submitted for analysis for TCE on a two week turnaround time. Table 3.1 presents the Sampling and Analysis Plan.

4.6 DECONTAMINATION

All non-disposable sampling equipment will be decontaminated prior to each use by using an Alconox wash, potable water rinse, followed by a deionized water rinse and allowed to air dry. This includes split spoon samplers, the hydropunch, hand sampling tools, bailers, etc.

All generated decontamination water will be visually examined and screened with a PID. All decontamination water will be containerized in DOT approved 55-gallon drums and labeled as to where it was generated and the initial accumulation date.

4.7 WASTE CHARACTERIZATION

All generated soil cuttings and decontamination/development water will be visually examined and screened with a PID. All generated soil cuttings and decontamination/development water will be containerized in DOT approved 55-gallon drums and labeled as to where it was generated and the initial accumulation date.

Two soil and two groundwater waste characterization samples will be collected from the drums and analyzed for Toxicity Characteristic Leaching Procedure (TCLP) metals, TCLP VOCs, TCLP SVOCs, reactivity, corrosivity, and ignitability (RCI), and total VOCs on a 2-week TAT for off-Site disposal. Table 3.1 presents the Sampling and Analysis Plan.

5.0 ANALYTICAL PROTOCOLS

Groundwater samples will be analyzed for TCL VOCs, SVOCs, and/or natural attenuation parameters. LNAPL samples will be analyzed for DRO and GRO, TAL metals, TCL VOCs, and TCL SVOCs. Air samples will be analyzed for TCE. All samples will be analyzed using the United States Environmental Protection Agency approved methods set forth in "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods", SW-846, 3rd Edition and Promulgated Update, November 1986. Quality Control/Quality Assurance samples will be collected for data and sample quality assessment in accordance with the QAPP. The QAPP is presented in Appendix A.

Following receipt of final analytical data, a data quality assessment and validation will be prepared by a CRA chemist, in accordance with the QAPP presented in Appendix A.

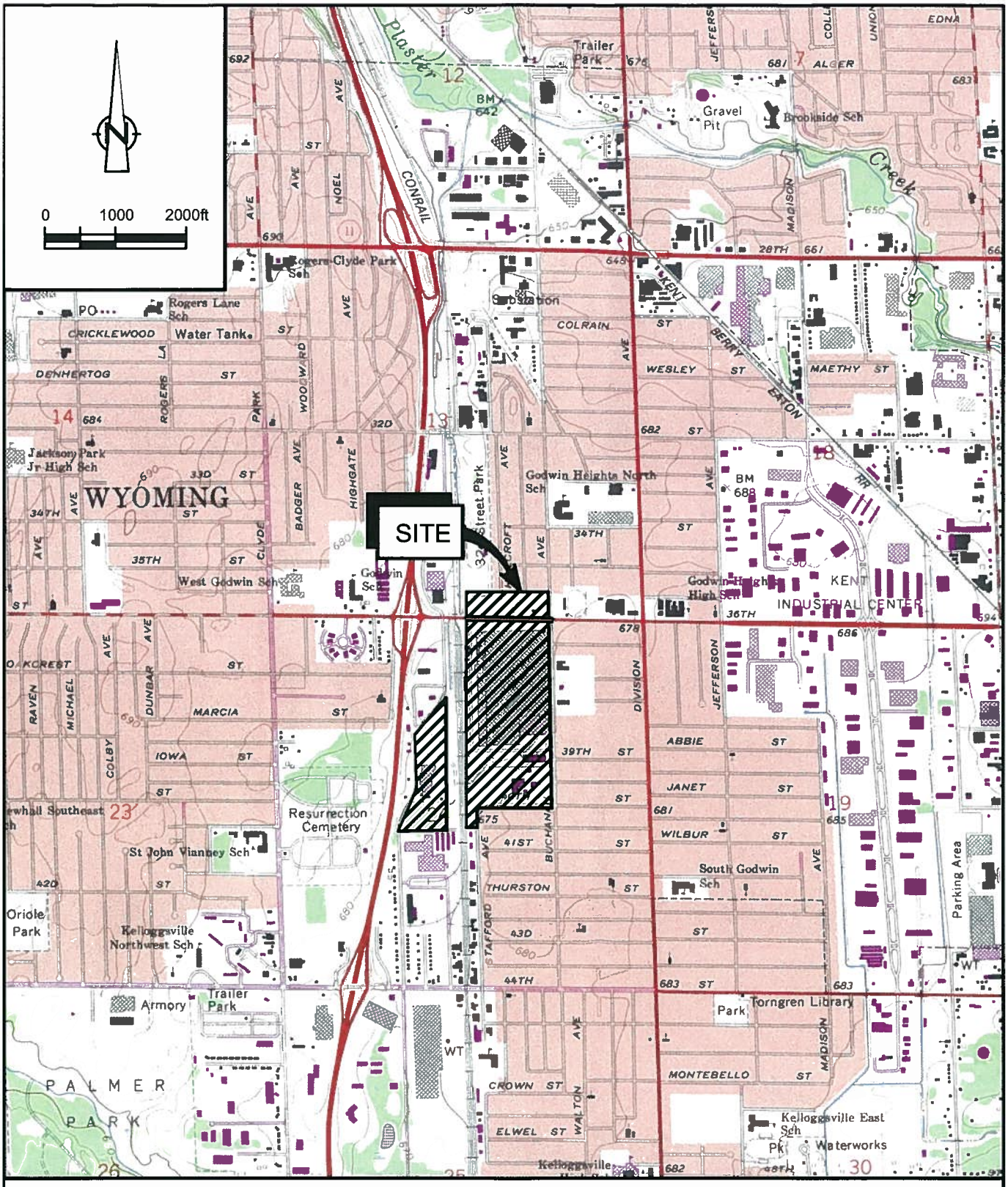
6.0 REPORTING

Upon completion of the field activities, receipt of final analytical results, and data quality assessment and validation, a report summarizing the results will be generated.

7.0 SCHEDULE

Access agreements for off-Site locations are currently being negotiated with off-Site property owners. It is anticipated that field activities will be initiated in March 2003, dependent upon weather conditions and securement of access to off-Site locations. A generalized proposed schedule for the implementation of the field activities and reporting is presented below. A more detailed schedule will be provided upon verification of start date.

- Implementation of Field Activities – Approximately 5 to 7 weeks;
- Preparation of Data Report – Analysis of samples will be conducted on a standard turnaround time with preliminary analytical results received within 2 weeks and final data received within one week of preliminary data receipt. Data validation will take approximately 2 weeks to complete. Preparation of the data report will take approximately 30 days following receipt of all final analytical data.



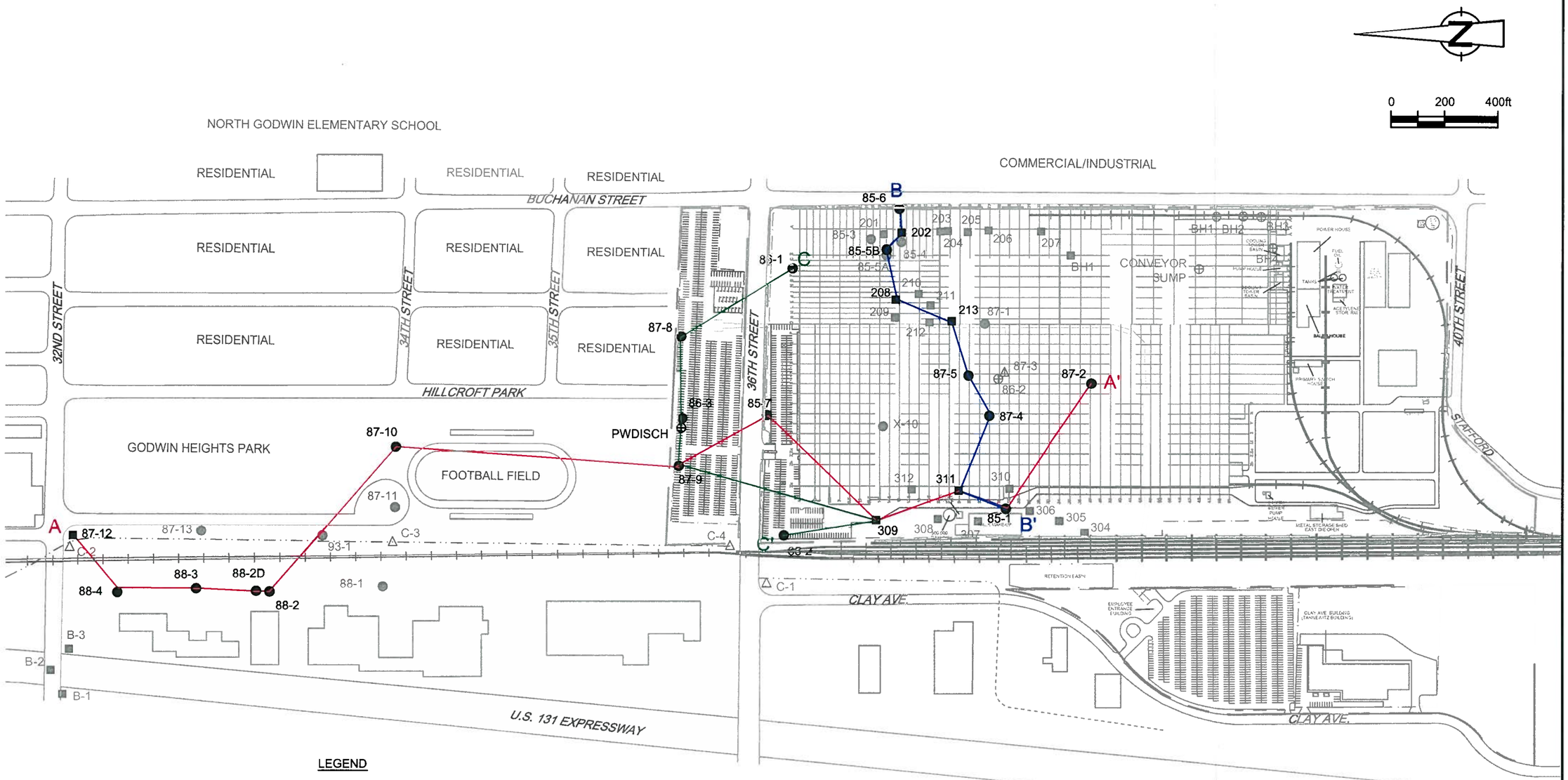
SOURCE: USGS QUADRANGLE MAP;
GRAND RAPIDS WEST, MICHIGAN



figure 1.1

SITE LOCATION
GRAND RAPIDS METAL PLANT
Wyoming, Michigan

17360-01(002)GN-DE001 DEC 03/2002

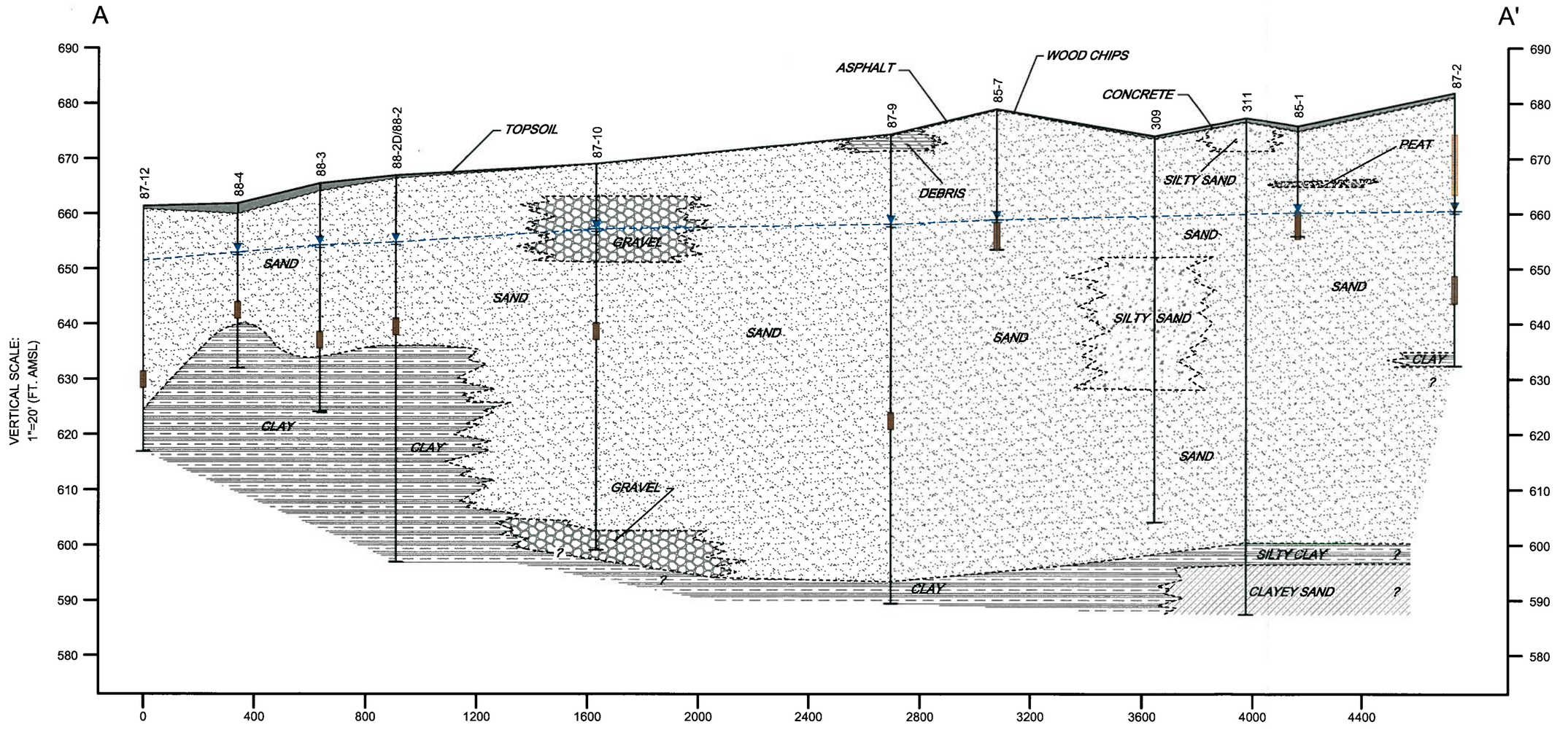


SOURCE: EDI ENGINEERING & SCIENCE, JUNE 1987 AND JUNE 1988 AND EARTH TECH, SEPTEMBER 2001.

figure 2.1

CROSS SECTION LOCATIONS
GRAND RAPIDS METAL PLANT
Wyoming, Michigan

17360-01(002)GN-DE010 DEC 03/2002



HORIZONTAL SCALE:
1"=400'

LEGEND

- MARCH 28, 2002 STATIC WATER LEVEL
- UNSATURATED ZONE SCREEN
- SATURATED ZONE SCREEN
- INTERPRETIVE WATER TABLE
- INTERPRETIVE CONTACT
- KNOWN CONTACT
- ASPHALT/TOPSOIL/WOOD CHIPS/ WOOD FLOOR BLOCK/CONCRETE
- DEBRIS
- GRAVEL
- SAND
- CLAY
- SILTY SAND
- CLAYEY SAND
- PEAT

figure 2.2

CROSS SECTION A-A'
GRAND RAPIDS METAL PLANT
Wyoming, Michigan

17360-01(002)GN-DE003 DEC 03/2002

B

B'

VERTICAL SCALE:
1"=20' (FT. AMSL)

700
690
680
670
660
650
640
630
620
610
600
590
580
570

WOOD FLOOR BLOCK/ CONCRETE

WOOD FLOOR BLOCK/ CONCRETE

WOOD FLOOR BLOCK/ CONCRETE

85-6
202
85-5B
208
213
87-5
87-4
311
85-1

SAND
GRAVEL
SAND
SAND
DEBRIS
SILTY SAND
PEAT
SAND
SAND
SAND
SAND
SILTY CLAY
SANDY SILT
SILTY SAND
CLAYEY SILT
SILTY CLAY
SILTY CLAY
SILTY CLAY
CLAY
SILTY CLAY
CLAYEY SAND
SAND
SAND & GRAVEL
?
?
SANDY SILT
SILTY CLAY

0
120
240
360
480
600
720
840
960
1080
1200
1320
1440
1560

HORIZONTAL SCALE:
1"=120'

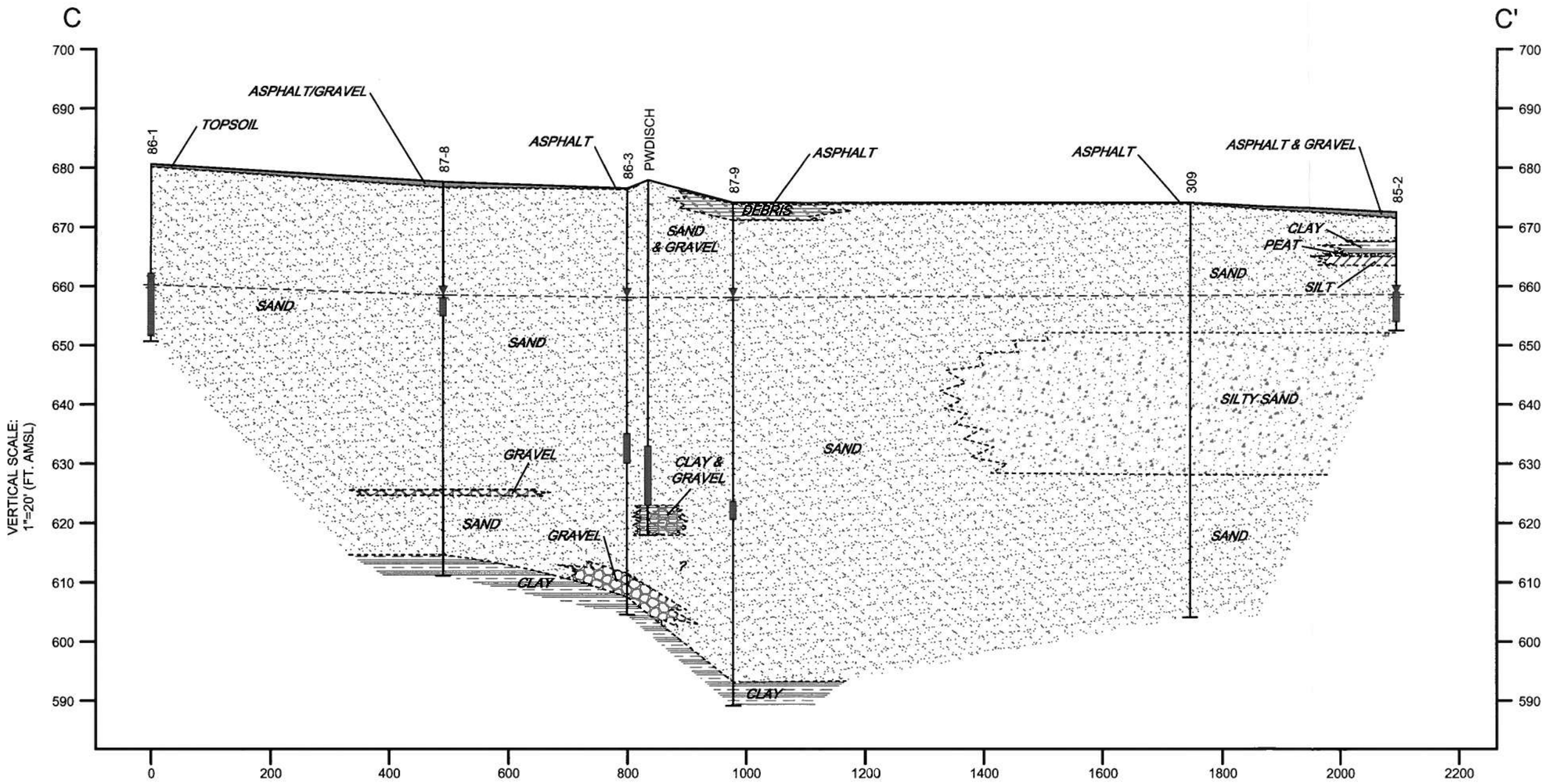
LEGEND

- MARCH 28, 2002 STATIC WATER LEVEL
- UNSATURATED ZONE SCREEN
- SATURATED ZONE SCREEN
- INTERPRETIVE WATER TABLE
- INTERPRETIVE CONTACT
- KNOWN CONTACT
- WOOD FLOOR BLOCK/CONCRETE
- DEBRIS
- GRAVEL
- SAND
- CLAY
- PEAT
- CLAYEY SILT
- SANDY SILT
- SILTY SAND
- CLAYEY SAND

figure 2.3

CROSS SECTION B-B'
GRAND RAPIDS METAL PLANT
Wyoming, Michigan

17360-01(002)GN-DE004 DEC 03/2002



HORIZONTAL SCALE:
1"=200'

LEGEND

- MARCH 28, 2002 STATIC WATER LEVEL
- UNSATURATED ZONE SCREEN
- SATURATED ZONE SCREEN
- INTERPRETIVE WATER TABLE
- INTERPRETIVE CONTACT
- KNOWN CONTACT
- WOOD FLOOR BLOCK/CONCRETE/PEAT
- DEBRIS
- GRAVEL
- SAND
- CLAY
- SILT
- SILTY SAND
- PEAT

figure 2.4

CROSS SECTION C-C'
GRAND RAPIDS METAL PLANT
Wyoming, Michigan

17360-01(002)GN-DE005 DEC 03/2002

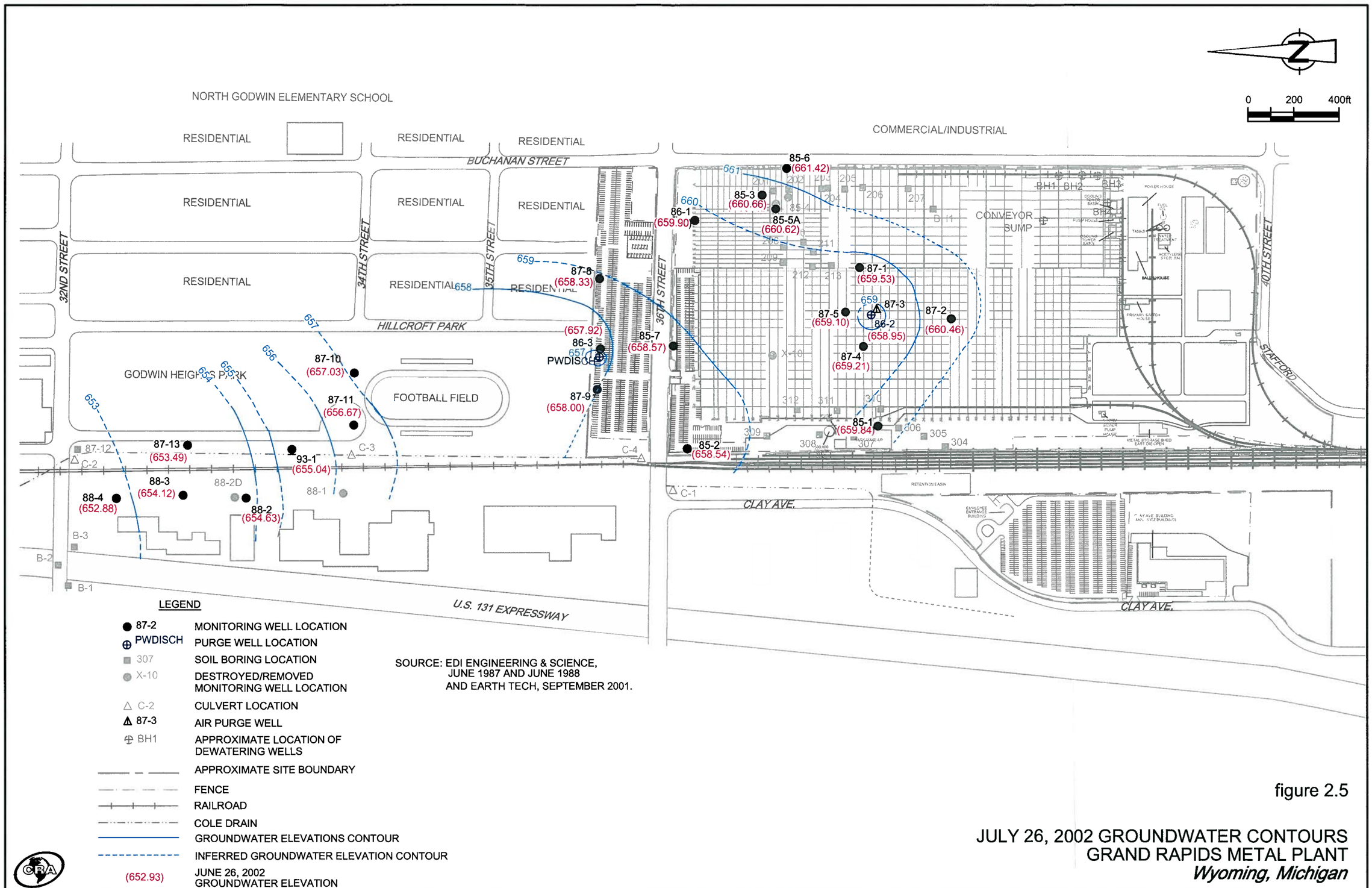
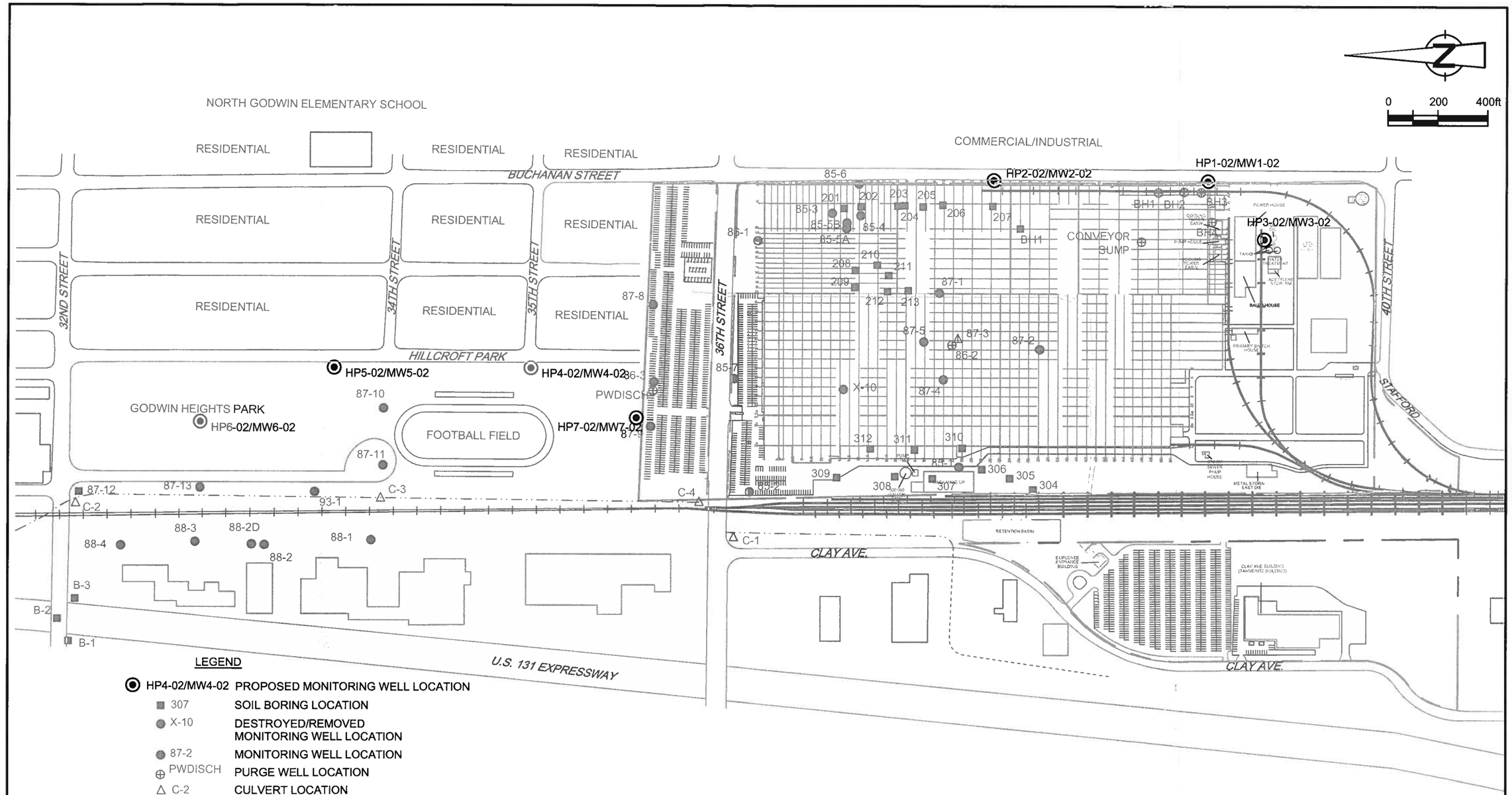


figure 2.5

JULY 26, 2002 GROUNDWATER CONTOURS
GRAND RAPIDS METAL PLANT
Wyoming, Michigan

17360-01(002)GN-DE006 DEC 03/2002



LEGEND

HP4-02/MW4-02	PROPOSED MONITORING WELL LOCATION
307	SOIL BORING LOCATION
X-10	DESTROYED/REMOVED MONITORING WELL LOCATION
87-2	MONITORING WELL LOCATION
PWDISCH	PURGE WELL LOCATION
C-2	CULVERT LOCATION
87-3	AIR PURGE WELL
BH1	APPROXIMATE LOCATION OF DEWATERING WELLS
	APPROXIMATE SITE BOUNDARY
	FENCE
	RAILROAD
	COLE DRAIN

SOURCE: EDI ENGINEERING & SCIENCE, JUNE 1987 AND JUNE 1988 AND EARTH TECH, SEPTEMBER 2001.

figure 3.1

PROPOSED SOIL BORING AND MONITORING WELL LOCATIONS
GRAND RAPIDS METAL PLANT
Wyoming, Michigan

17360-01(002)GN-DE007 DEC 03/2002

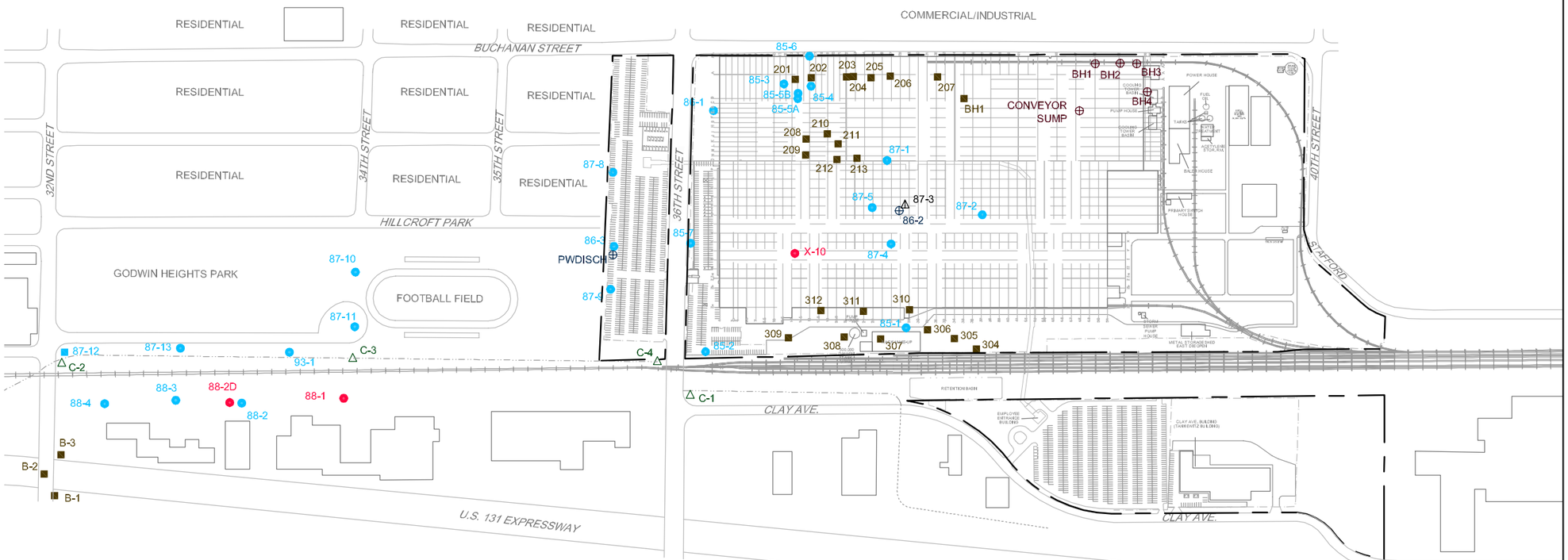
TABLE 3.1

SAMPLING AND ANALYSIS PLAN
WORK PLAN
GENERAL MOTORS CORPORATION
GRAND RAPIDS METAL PLANT
WYOMING, MICHIGAN

Proposed Investigation Activity	*Reason for Activity*	*Quantity of Sample Locations*	*Quantity of Samples*	*Sample Matrix*	*Sample Interval*	*Analysis*
Vertical Aquifier Sampling	Vertical/horizontal delineation	7	36 [1]	groundwater	discrete vertical intervals of the water bearing unit	TCL VOCs
Collection of Groundwater Samples	Vertical/horizontal delineation	21	29 [1]	groundwater	--	TCL VOCs and Natural Attenuation Parameters
		1	1	groundwater	--	TCL SVOCs
Collection of LNAPL sample	Characterization	1	1	LNAPL	--	DRO, GRO, TCL VOCs, TAL metals, TCL SVOCs
Collection of SVE system influent samples	System Evaluation	1	16 [2]	air	--	TCE
Collection of waste characterization samples	Disposal	2 [3]	2 [3]	soil	--	TCLP metals, VOCs, SVOCs, RCI, total VOCs
		2 [3]	2 [3]	wastewater	--	TCLP metals, VOCs, SVOCs, RCI, total VOCs

Notes:

[1] Number of samples includes Quality Assurance/Quality Control samples.
[2] Seven air samples to be collected the first quarter, and three air samples each quarter thereafter.
[3] Number of samples to be determined in the field.
TCL - Target Compound List
VOCs - Volatile Organic Compounds
TCLP - Toxicity Characteristic Leaching Procedure
SVOCs - Semi-volatile Organic Compounds
RCI - Reactivity, Corrosivity, and Ignitability
TAL - Target Analyte List
DRO - Diesel Range Organics
GRO - Gasoline Range Organics



No	Revision	Date	Initial

0 150 250ft

LEGEND

307	SOIL BORING LOCATION
X-10	DESTROYED/REMOVED MONITORING WELL LOCATION
87-2	MONITORING WELL LOCATION
PWDISCH	PURGE WELL LOCATION
C-2	CULVERT LOCATION
87-3	AIR PURGE WELL
BH1	APPROXIMATE LOCATION OF DEWATERING WELLS
	APPROXIMATE SITE BOUNDARY
	FENCE
	RAILROAD
	COLE DRAIN

SOURCE: EDI ENGINEERING & SCIENCE, JUNE 1987 AND JUNE 1988 AND EARTH TECH, SEPTEMBER 2001.

SCALE VERIFICATION

THIS BAR MEASURES 1" ON ORIGINAL. ADJUST SCALE ACCORDINGLY.

Approved

DRAWING STATUS

Status	Date	Initial

GRAND RAPIDS METAL PLANT

WYOMING, MICHIGAN

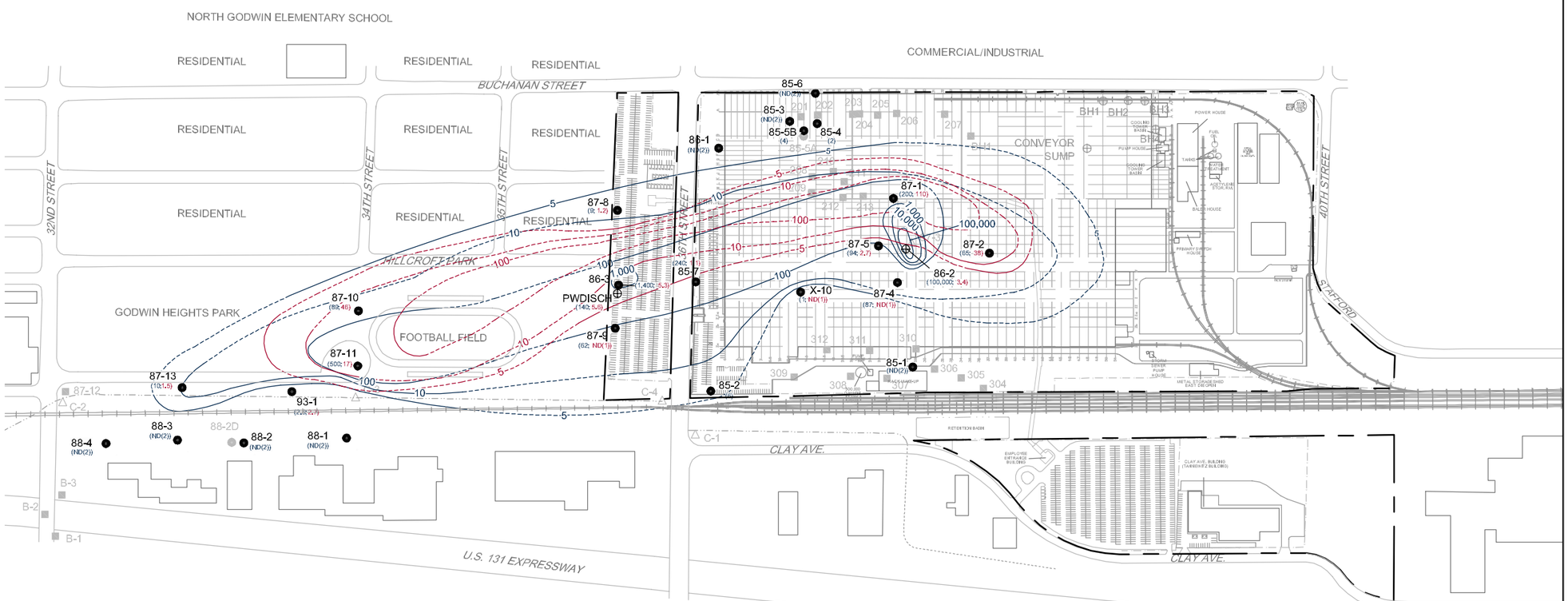
SITE PLAN

CONESTOGA-ROVERS & ASSOCIATES

Source Reference:

Project Manager:	Reviewed By:	Date:	
G.K.	J.O.	MAY 2002	
Scale: 1"=250'	Project No: 17360-01	Report No: 002	Drawing No: 1

17360-01(002)GN-DE008 DEC 03/2002



No	Revision	Date	Initial

0 150 250ft

LEGEND

■ 307	SOIL BORING LOCATION
● X-10	ABANDONED MONITORING WELL LOCATION
● 87-2	MONITORING WELL LOCATION
⊕ PWDISCH	PURGE WELL LOCATION
△ C-2	CULVERTS USED TO MEASURE WATER LEVELS IN COLE DRAIN
⚠ 87-3	AIR PURGE WELL
⊕ BH1	APPROXIMATE LOCATION OF DEWATERING WELLS
	FENCE
	RAILROAD
	COLE DRAIN
10	INITIAL SAMPLE TCE CONCENTRATIONS (ug/L) (SAMPLES COLLECTED BETWEEN 1985 AND 1993)
10	DECEMBER 2001 TCE CONCENTRATIONS (ug/L)

SCALE VERIFICATION

THIS BAR MEASURES 1" ON ORIGINAL. ADJUST SCALE ACCORDINGLY.

Approved

DRAWING STATUS

Status	Date	Initial

GRAND RAPIDS METAL PLANT

WYOMING, MICHIGAN

HISTORICAL AND CURRENT CONCENTRATIONS OF TCE IN GROUNDWATER

CONESTOGA-ROVERS & ASSOCIATES

Source Reference:

Project Manager:	Reviewed By:	Date:	
G.K.	J.O.	MAY 2002	
Scale: 1"=250'	Project No: 17360-01	Report No: 002	Drawing No: 2

17360-01(002)GN-DE009 DEC 03/2002

APPENDIX A
QUALITY ASSURANCE PROJECT PLAN (QAPP) WORK PLAN

General Motors Corporation
Grand Rapids Metal Plant
Wyoming, Michigan

NOVEMBER 2002
REF. NO. 17360 (2)

QUALITY ASSURANCE PROJECT PLAN (QAPP)

GENERAL MOTORS CORPORATION
GRAND RAPIDS METAL PLANT
WYOMING, MICHIGAN
REVISION NUMBER 0
NOVEMBER 22, 2002

Prepared By: Conestoga-Rovers & Associates (CRA)

Prepared For: General Motors Corporation (GM)

Approved By: Kurt D. Blizzard Date: 11/27/02
Kurt Blizzard
GM Project Manager

Approved By: Gary Klepper Date: 11/27/02
Gary Klepper
CRA Project Manager

Approved By: Date: 11/22/02
Paul Wiseman
CRA QA Officer

Approved By: Jennifer Quigley Date: 11/27/02
Jennifer Quigley
CRA Field QA Officer

Approved By: Amy McCormick Date: 11-22-02
Amy McCormick
STL Project Manager

Approved By: Mary Beth Lambert Date: 11-22-02
Mary Beth Lambert
STL QA Officer

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ATTACHMENT 5 LABORATORY AUDIT CHECKLIST

1.0 PROJECT DESCRIPTION

The following outlines the scope of the investigation to be performed at the General Motors Corporation (GM) Grand Rapids Metal Plant located 300 36th Street in Wyoming, Michigan (Site) for the Site.

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

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

1.1 INTRODUCTION

This Quality Assurance Project Plan (QAPP) has been prepared on behalf of GM. The QAPP is a component of the Work Plan for the Site.

1.1.1 PROJECT OBJECTIVES AND DECISION STATEMENT

The primary objectives for data collection activities include:

i) Further evaluate and delineate chlorinated VOC impacts to groundwater at the Site above the Michigan Act 451, Part 201 Residential Cleanup Criteria;

ii) Further define hydrogeologic conditions at the Site;

iii) Evaluate the extent and nature of the light non-aqueous phase liquid (LNAPL) identified at the Site;

iv) Evaluate potential groundwater and indoor air impacts associated with the identified LNAPL; and

v) Evaluate current effectiveness of the existing soil vapor extraction (SVE) and groundwater extraction systems.

The Decision Statement for the investigation is as follows:

i) Determine whether current remedial actions are required or sufficient to achieve Michigan Act 451, Part 201 Residential Cleanup Criteria.

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

1.1.2 PROJECT STATUS/PHASE

The project status and investigation approach is presented in the Work Plan. Section 1.1 summarizes the Site background. Section 3.0 describes the proposed scope of work for the investigation at the Site. Section 5.0 describes how the data evaluation procedures for this project will be conducted.

1.1.3 QAPP PREPARATION GUIDELINES

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

1.2 SITE DESCRIPTION

The general Site description is provided and is incorporated here by reference to the following Work Plan Sections.

Location	Work Plan Section 1.0
Site Dimensions/Borders	Work Plan Section 1.1
Natural and Manmade Features	Work Plan Section 1.1
Topography	Work Plan Section 1.1
Local Geology and Hydrology	Work Plan Section 2.2

1.3 SITE HISTORY

The Site history is provided in Sections 1.1 and 2.1 of the Work Plan and incorporated here by reference.

General History	Work Plan Section 1.1
Past Data Collection Activities	Work Plan Section 1.1 and 2.1
Current Status	Work Plan Section 2.1

1.4 PROJECT OBJECTIVES AND INTENDED DATA USE

1.4.1 TARGET PARAMETER LIST

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

1.4.1.1 FIELD PARAMETERS

Concurrent with sample collection, several field parameters will be determined by the field sampling personnel. For soils and solid matrices, these field parameters will include visual observations, odor identification, and VOC screening using handheld monitoring equipment. For aqueous samples (groundwater), at a minimum, the following parameters

will be determined with field testing equipment: pH, specific conductivity, and temperature. The low-flow purging techniques utilized for groundwater sampling, will include additional field parameters including temperature, pH, conductivity, turbidity, dissolved oxygen, oxidation/reduction potential (ORP), and dissolved iron (Fe(II)) will be measured.

1.4.1.2 LABORATORY PARAMETERS

The laboratory parameters for groundwater samples include target compound list (TCL) volatile organic compounds (VOCs), TCL semi-volatile organic compounds (SVOCs), and select natural attenuation parameters (total organic carbon (TOC), nitrate, nitrite, manganese, sulfate, sulfide, methane, alkalinity, calcium, carbonate hardness, hardness, magnesium, chloride, ethane, and ethene) in groundwater and soil samples. The basis for the selected parameter list is provided in Section 5.0 of the Work Plan.

Table 1.2 presents the estimated quantitation limits (EQL) and method detection limits (MDL) for each compound or analyte for vertical aquifer and groundwater samples. MDL studies have been performed by Severn Trent Laboratories (STL) in accordance with the procedures established in the Federal Register, Volume 49, number 209, October 26, 1984 pp. 198-199, the results of these MDL studies are presented in Attachment 3.

In addition to the groundwater sampling, LNAPL samples will be analyzed for TCL VOCs, TCL SVOCs, gasoline range organics (GRO), diesel range organics (DRO) and target analyte list (TAL) metals, presented with EQLs in Table 1.3; air samples from the SVE system will be analyzed for trichloroethene (TCE), presented with EQLs in Table 1.4; waste characterization will be completed on soil cuttings and purge/decontamination water as presented with EQLs in Table 1.5.

1.5 SAMPLING LOCATIONS

The Work Plan provides a summary and rationale for the location of groundwater samples at the Site. It is possible, however, that depending on the nature of encountered field conditions, sampling locations may change. The person responsible for making such decisions will be the Field Quality Assurance (QA) Officer whose responsibilities are described in Section 2.0 of this QAPP. Any change of the sampling strategy will only be implemented after approval from the GM Project Manager.

2.0 PROJECT ORGANIZATION AND RESPONSIBILITIES

The GM Project Manager will have the primary responsibility for the implementation of the Work Plan. STL's laboratory in North Canton, Ohio will perform the analyses of environmental samples collected at the Site. This section defines the roles and responsibilities of the individuals who will perform the Work Plan activities.

2.1 MANAGEMENT RESPONSIBILITIES

A description of the key project personnel responsibilities is presented in the following sections. Management responsibilities are as follows:

Kurt Blizzard - GM Project Manager

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

Gary Klepper - CRA Project Manager

The Project Manager is responsible for managing the implementation of the Work Plan and coordinating the collection of data pertaining to the Investigation. The Project Manager is responsible for technical quality control and project oversight. The Project Manager also provides approval of the QAPP.

Jennifer Quigley - CRA Project Coordinator

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

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

2.2 QUALITY ASSURANCE RESPONSIBILITIES

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

Paul Wiseman – CRA Quality Assurance (QA) Officer

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

i) Assuring the application and effectiveness of the QAPP by the analytical laboratory and the project staff;
ii) Conducting internal QA/QC of the investigation activities;
iii) Providing input to the Project Manager and the Project Engineer as to corrective actions required resulting from the above-mentioned evaluations;
iv) Preparation and review of data validation and audit reports; and
v) Approval of the QAPP.

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

2.3 LABORATORY RESPONSIBILITIES

STL will provide laboratory services in support of the Work Plan.

Amy McCormick - STL Laboratory Project Manager

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

Opal Davis-Johnson - STL Laboratory Operations Manager

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

Mary Beth Lambert - STL Laboratory QA Officer

The Laboratory QA Officer will have sole responsibility for review and validation of the analytical laboratory data generated as part of the investigation. The Laboratory QA Officer will sign all final laboratory data reports provided from the analysis of the project samples and will provide Case Narrative descriptions of any data quality issues encountered during the analyses conducted by the laboratory. The QA Officer will also define appropriate QA procedures, overview QA/QC documentation, and approve this QAPP.

Lois Ezzo - STL Laboratory Sample Custodian

The Laboratory Sample Custodian will report to the Laboratory Operations Manager and will be responsible for the following:

i) Receiving and inspecting the incoming sample containers;
ii) Recording the condition of the incoming sample containers;
iii) Signing appropriate documents;
iv) Verifying chain-of-custody and its correctness;

v) Notifying the Project Manager and Operations Manager of sample receipt and inspection;
vi) Assigning a unique identification number and customer number, and entering each into the sample receiving log;
vii) Initiating transfer of samples to lab sections; and
viii) Controlling and monitoring access/storage of samples and extracts.

Laboratory Technical Personnel

The laboratory technical staff will have the primary responsibility in the performance of sample analysis and the execution of the QA procedures developed to determine the data quality. These activities will include the proper preparation and analysis of the project samples in accordance with the contract laboratory's Quality Assurance Manual and associated Standard Operating Procedures (SOPs).

Data Validation Staff

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

2.4 FIELD RESPONSIBILITIES

Jennifer Quigley - CRA Field QA Officer

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

i) Developing and implementing field-related work plans, ensuring schedule compliance, and adhering to management-developed project requirements;
ii) Coordinating and managing field staff, including sampling and drilling;
iii) Performing field system audits;

iv) Overseeing quality control for technical data provided by the field staff;
v) Preparing, and approving of text and graphics required for field team efforts;
vi) Coordinating and overseeing technical efforts of subcontractors assisting the field team;
vii) Identifying problems in the field, resolving difficulties in consultation with the, Project QA Officer and CRA Project Manager, implementing and documenting corrective action procedures;
viii) Approving the QAPP; and
ix) Participating in preparation of the final reports.

Field Team Personnel

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

i) Performance of field activities as detailed in the Work Plan and in compliance with the DQO outlined in this QAPP; and

ii) Immediately reporting any accidents and/or unsafe conditions to the Site Health & Safety Officer and taking all reasonable precautions to prevent injury.

3.0 QUALITY ASSURANCE OBJECTIVES FOR MEASUREMENT DATA

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

i) A mechanism for ongoing control of measurements and evaluation of data quality.

ii) A measure of data quality in terms of precision, accuracy, representativeness, completeness, and comparability.

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

3.1 PRECISION

3.1.1 DEFINITION

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

3.1.2 FIELD PRECISION SAMPLE OBJECTIVES

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

3.1.3 LABORATORY PRECISION SAMPLE OBJECTIVES

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

3.2 ACCURACY

3.2.1 DEFINITION

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

3.2.2 FIELD ACCURACY OBJECTIVES

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

Field equipment rinsate blanks will be collected by passing laboratory purified water over and/or through the respective field equipment utilized during each sampling effort. One rinsate blank will be collected every 20 investigative samples. However, at a minimum one equipment rinsate blank sample will be collected per day for each type of field equipment used for the sampling effort. Field rinsate blanks will be analyzed for each target parameter for the respective sampling effort for which environmental media have been collected. (Note: If dedicated or disposable sampling equipment is used, equipment rinsate samples may not be collected as part of that field effort.)

Trip blank samples will be prepared by the laboratory and provided with each cooler that includes VOC analysis containers. Trip blank samples will be analyzed for each VOC for which environmental media have been collected for analysis.

3.2.3 LABORATORY ACCURACY SAMPLE OBJECTIVES

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

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

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

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

3.3 REPRESENTATIVENESS

3.3.1 DEFINITION

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

3.3.2 MEASURES TO ENSURE REPRESENTATIVENESS OF FIELD DATA

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

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

3.3.3 MEASURES TO ENSURE REPRESENTATIVENESS OF LABORATORY DATA

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

3.4 COMPLETENESS

3.4.1 DEFINITION

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

3.4.2 FIELD COMPLETENESS OBJECTIVES

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

3.4.3 LABORATORY COMPLETENESS OBJECTIVES

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

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

3.5 COMPARABILITY

3.5.1 DEFINITION

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

3.5.2 MEASURES TO ENSURE COMPARABILITY OF FIELD DATA

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

3.5.3 MEASURES TO ENSURE COMPARABILITY OF LABORATORY DATA

Comparability of laboratory data will also be measured with the results from the analysis of Standard Reference Materials (SRM) obtained from either EPA Cooperative Research and Development Agreement (CRADA) suppliers or the National Institute of Standards and Technology (NIST) for instrument initial and continuing calibration verification. The reported analytical data will be presented in standard units of mass of contaminant within a known volume or mass of environmental media.

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

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

3.6 LEVEL OF QUALITY CONTROL EFFORT

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

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

Trip blanks are used to assess the potential for contamination during sample storage and shipment. The trip blank consists of laboratory purified water that has been purged with an inert gas by the laboratory and provided with the sample containers to be used for the sampling of VOCs. Trip blanks will be preserved and handled in the same manner as the investigation samples. One trip blank will be included along with each shipment cooler containing project samples to be analyzed for VOCs.

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

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

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

4.0 SAMPLING PROCEDURES

Samples of groundwater, air, soil, and LNAPL will be obtained during the investigation program. The sampling procedures for the investigation will be consistent for the objectives of the project. The Work Plan describes each of the sampling tasks and objectives.

Refer to the Work Plan for the field investigation standard operating procedures.

4.1 SAMPLE CONTAINERS

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

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

4.2 SAMPLE LABELING

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

Example: S-17360-MMDDYY-XX-001

S	- designates types of sample (S-soil, GW-groundwater, A-air)
17360	- Site reference number
MMDDYY	- designates date of collection presented as month/day/year
XX	- sampler's initials
01	- 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.

4.3 FIELD QC SAMPLE COLLECTION

4.3.1 EQUIPMENT RINSATE BLANK SAMPLE COLLECTION

Equipment rinsate blank samples will be collected when non-dedicated or non-disposable sampling equipment is used to collect samples. Equipment rinsate blanks consist of laboratory purified water that has been routed through decontaminated sampling equipment and collected into the appropriate containers. The containers will be filled in order of decreasing analyte volatility (i.e., VOCs first, SVOCs second, which are followed by the containers for the remaining analyses).

4.3.2 FIELD DUPLICATE SAMPLE COLLECTION

4.3.2.1 WATER SAMPLES

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

4.3.2.2 SOIL SAMPLES

Soil field duplicates, if necessary, will be collected concurrently with the investigative sample using the procedures identified in the Work Plan.

4.3.3 MS/MSD SAMPLE COLLECTION

MS/MSD sample collection for aqueous samples requires triple the sample volume for VOC analysis and double the volume for all remaining parameters. The sampling procedure specified in Section 4.3.2.1 is used to collect aqueous samples. Soil MS/MSD samples

require triple volume for VOC analyses. No additional volume is required for remaining soil parameters. Section 4.3.2.2 describes the sampling procedures for soil sample collection.

5.0 CUSTODY PROCEDURES

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

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

1. the item is in actual possession of a person;

2. the item is in the view of the person after being in actual possession of the person;

3. the item was in actual possession but is stored to prevent tampering; or

4. the item is in a designated and identified secure area.

5.1 FIELD CUSTODY PROCEDURES

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

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

i) Date,
ii) Start ,time

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

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

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

5.1.1 FIELD PROCEDURES

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

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

i) Upon collection samples are placed in the proper containers. In general, samples collected for organic analysis will be placed in pre-cleaned glass containers, and samples collected for inorganic analysis will be placed in pre-cleaned plastic (polyethylene) bottles. The sample container, preservation methods, shipping, and packaging requirements are presented in Table 4.1.

ii) Samples will be assigned a unique sample number and will be affixed to a sample label. The information to be placed on the sample label will include the sample ID number, the sample type, the sampler's name, date collected, preservation technique, and analytical parameter and method to be performed. Information on the labels will be completed with a ballpoint pen or indelible marker.

iii) Samples will be properly and appropriately preserved by field personnel in order to minimize loss of the constituent(s) of interest due to physical, chemical or biological mechanisms. Sample aliquots that require preservation (pH adjustment) will be checked with pH paper at the time of preservation. Confirmation of preservation will include capping of the preserved sample, inverting the sample three times, uncapping and confirming the sample pH. If required, additional preservative will be added and the procedure repeated until proper preservation is achieved. Samples for VOC analysis will be collected in pre-preserved containers and will not undergo this procedure.

iv) Appropriate volumes will be collected to ensure that the EQLs can be successfully achieved and that the required QC Sample Analyses can be completed.

5.1.2 TRANSFER OF CUSTODY AND SHIPMENT PROCEDURES

i) A chain-of-custody (COC) record will be completed during sample collection and will accompany each shipment identifying the contents of the shipment. The COC record will accompany the samples to the laboratory. The field personnel collecting the samples will be responsible for the custody of the samples until the samples are relinquished to the laboratory. Sample transfer will require the individuals relinquishing and receiving the samples to sign, date and note the time of sample transfer on the COC record. As few people as possible should handle the samples.

ii) Samples will be shipped or delivered in a timely fashion to the laboratory so that holding-times and/or analysis times as prescribed by the methodology can be met.

iii) Samples will also be transported in containers (coolers) packed with ice to maintain the temperatures prescribed in Table 4.1. Samples will be packaged for shipment and shipped to the appropriate laboratory for analysis with a separate signed chain-of-custody record enclosed in each sample cooler. Water VOC samples will be placed in bubble wrap bags that contain three containers per bag while soil VOC samples will be placed in sealed sample pouches. The remaining samples in glass containers will be wrapped in bubble wrap and placed in the sample cooler. Samples in polyethylene containers will be placed upright directly in the sample cooler. All samples will be placed in an upright position and limited to one layer of samples per each cooler. Additional bubble wrap or packaging material will be

added to fill the cooler. Shipping containers will be secured with strapping tape and custody tape for shipment to the laboratory.

iv) When samples are split with the U.S. EPA and Site representatives, a separate chain-of-custody will be prepared for the samples and marked to indicate to whom the samples are being split. The person relinquishing the samples to the U.S. EPA or the Site will require the representatives signature acknowledging sample receipt.

v) If samples are sent by a commercial carrier, a bill of lading will be used. A copy of the bill of lading will be retained as part of permanent documentation. Commercial carriers are not required to sign the custody record as long as the custody record is sealed inside the sample cooler and the custody tape remains intact.

vi) Samples will be picked up by a laboratory courier or transported overnight by a courier to the laboratory the same day they are collected unless collected on a weekend or holiday. In these cases, the samples will be stored in a secure location until delivery to the lab. Additional ice will be added to the cooler as needed to maintain proper preservation temperatures.

5.2 LABORATORY CHAIN-OF-CUSTODY PROCEDURES

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

Consistent with the analyses requested on the chain-of-custody form, analyses by the laboratory's analysts will begin in accordance with the appropriate methodologies. Samples

will be removed from secure storage only after internal chain-of-custody sign-out procedures have been followed.

5.3 STORAGE OF SAMPLES

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

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

5.4 FINAL PROJECT FILES CUSTODY PROCEDURES

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

The final project file will include:

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

x) Final report.

The laboratory will be responsible for maintaining analytical logbooks, laboratory data and sample chain of custody documents. Raw laboratory data files and copies of hard copy reports will be inventoried and maintained by the laboratory for a period of six (6) years at which time the laboratory will contact CRA regarding the disposition of the project related files.

6.0 CALIBRATION PROCEDURES AND FREQUENCY

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

6.1 FIELD INSTRUMENT CALIBRATION PROCEDURES

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

The field instruments are likely to include dissolved oxygen meters, pH meters, turbidity meters, specific conductance meters and PIDs. Field instruments will be used for real-time sample measurement during monitoring well sampling and organics screening for both on-site screening of soil samples and for health and safety air monitoring, as described in the Work Plan. On-site air monitoring for health and safety purposes and the screening of soil samples may be accomplished using PIDs.

Field instruments will be calibrated prior to use and the calibration will be verified after a maximum of 10 measurements. Specific information concerning calibration frequency, acceptance criteria, and the conditions that require more frequent calibration is contained in the field SOPs in Attachment 1.

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

6.2 LABORATORY INSTRUMENT CALIBRATION PROCEDURES

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

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

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

All solid chemicals and acids/bases used by the laboratory will be reagent grade or better. All gases will be high purity or better. All Standard Reference Materials (SRMs) or Performance Evaluation (PE) Materials will be obtained from approved vendors of the National Institute of Standards and Technology (formerly National Bureau of Standards), the U.S. EPA Environmental Monitoring Support Laboratories (EMSL), or reliable Cooperative Research and Development Agreement (CRADA) certified commercial sources.

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

7.0 ANALYTICAL PROCEDURES

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

7.1 FIELD ANALYTICAL PROCEDURES

Field analytical procedures include the measurement of pH/temperature, specific conductivity, dissolved oxygen, turbidity, ORP and Fe (II) during sampling of groundwater, and the qualitative measurement of VOC during the collection of soil samples at the Site. Specific guidance in the measurement of these parameters is presented in the SOPs provided in Attachment 1 of this QAPP.

7.2 LABORATORY ANALYTICAL PROCEDURES

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

i) "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods", SW-846 EPA, U.S. EPA Office of Solid Waste, 3rd Edition and promulgated updates, 1986;
ii) "Methods for Chemical Analysis of Water and Wastes", EPA-600/4-79-020, March 1983;
iii) "Compendium of Methods for the Determination Toxic Organic Compounds in Ambient Air", EPA/625/R-96/010b, Second Edition, January 1999.; and
iv) "Standard Operating Procedure RSK 175", U.S. EPA Robert S. Kerr Environmental Research Laboratory, Ada OK.

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

7.2.1 LIST OF PROJECT TARGET COMPOUNDS AND LABORATORY DETECTION LIMITS

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

7.2.2 LIST OF METHOD SPECIFIC QUALITY CONTROL (QC) CRITERIA

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

8.0 INTERNAL QUALITY CONTROL CHECKS

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

8.1 FIELD QUALITY CONTROL

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

8.1.1 EQUIPMENT RINSATE BLANKS

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

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

8.1.2 TRIP BLANKS

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

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

8.1.3 FIELD DUPLICATE SAMPLES

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

8.2 LABORATORY PROCEDURES

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

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

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

9.0 DATA REDUCTION, VALIDATION AND REPORTING

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

9.1 DATA REDUCTION

9.1.1 FIELD DATA REDUCTION PROCEDURES

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

9.1.2 LABORATORY DATA REDUCTION PROCEDURES

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

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

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

9.2 DATA VALIDATION

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

9.2.1 PROCEDURES USED TO EVALUATE FIELD DATA

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

9.2.2 PROCEDURES TO VALIDATE LABORATORY DATA

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

"U.S. EPA Contract Laboratory Program National Functional Guidelines for Organic Data Review", EPA-540/R-99/008, October 1999 and the "U.S. EPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review ", EPA-540/R-01-008, July 2002 (CLP National Functional Guidelines).

The specific data qualifiers used will be as presented and defined in the CLP National Functional Guidelines. Data review and validation will consist of two tiers of assessment that incorporates an approach similar to "Innovative Approaches to Data Validation", U.S. EPA Region III, June 1995.

Tier I data validation will be performed on 100% of the laboratory data deliverables associated with the Monitoring Well Sampling and will consist of the following components:

Organic Analysis

i) technical holding times;
ii) GC/MS instrument performance check;
iii) initial and continuing calibration;
iv) internal standard performance
v) method, trip and field blanks;
vi) system monitoring compounds (surrogate spikes);
vii) MS/MSD results;
viii) laboratory control samples; and
ix) field duplicate samples.

Inorganic Analysis

i) technical holding times;
ii) initial calibration;
iii) initial and continuing calibration verification;
iv) blanks;
v) ICP interference check samples;
vi) ICP serial dilutions;
vii) laboratory control samples;
viii) MS/MSD and matrix duplicate results; and
ix) field duplicate.

Tier II validation will be completed on 10 percent of the expanded deliverables during the initial investigation activities. The Tier II validation will include the evaluation of all raw data and mass spectra to validate the above components as well as verify sample results.

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

9.3 DATA REPORTING

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

9.3.1 FIELD DATA REPORTING

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

9.3.2 LABORATORY DATA REPORTING

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

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

i) Title Page
- project name and number;
- laboratory project or lot number;
- signature of the Laboratory QA Officer or his designee; and
- date issued.

ii) Table of Contents - laboratory report contents

iii) Case Narrative
- number of samples and respective matrices;;
- laboratory analysis performed;
- any deviations from intended analytical strategy;

- definition of data qualifiers used;
- QC procedures utilized and references to the acceptance criteria;
- condition of samples "as received";
- discussion of whether or not sample holding times were met;
- discussion of technical problems or other observations which may have created analytical difficulties; and
- discussion of laboratory QC checks which failed to meet project criteria.

iv) Analytical Methods Summary - methods of sample preparation and analyses for samples.

v) Analytical Sample Summary - cross-reference table of laboratory sample to project sample identification numbers.

vi) Shipping and Receiving Documents
- sample container documentation; and
- sample reception information and original chain of custody record.

vii) Chemistry Data Package by Analysis
- Sample Results
  - sample quantitation (report) limits (RL), reporting MDL and estimated values between the RL and MDL,
  - methods of sample preparation and analyses for samples,
  - raw data for sample results (dated chromatograms, parameter specific quantitation reports, mass spectra and instrument printouts;

- QC Summary Data with Current Control Limits
  - matrix spike and matrix spike duplicate recoveries, laboratory control samples, method blank results, surrogate recoveries, GC/MS tuning results, and internal standards (organics),
  - matrix spike recoveries and matrix duplicate relative percent differences, laboratory control sample, serial dilutions, method blank results, and reagent blank results and interference check standards (inorganics);

- Standard Data
  - initial calibration data, initial calibration checks, continuing calibration verification/check standards,

  - initial and continuing calibration blanks,
  - raw data for calibration data (dated chromatograms, parameter specific quantitation reports, mass spectra and instrument printouts;

- Raw QC Data - dated chromatograms, parameter specific quantitation reports, mass spectra and instrument printouts of QC samples;

- Miscellaneous Data
  - instrument run logs,
  - sample preparation records, and
  - instrument conditions.

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

The final laboratory data reports associated with the vertical aquifer sampling, LNAPL, SVE air monitoring and waste characterization samples will include a reduced deliverable report. These laboratory data reports will not include standard data, QC and raw sample data and the miscellaneous data identified in the expanded deliverables report.

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

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

10.0 PERFORMANCE AND SYSTEM AUDITS

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

10.1 FIELD PERFORMANCE AND SYSTEM AUDITS

10.1.1 INTERNAL FIELD AUDIT RESPONSIBILITIES

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

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

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

10.1.2 EXTERNAL FIELD AUDIT RESPONSIBILITIES

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

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

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

10.2 LABORATORY PERFORMANCE AND SYSTEM AUDITS

10.2.1 INTERNAL LABORATORY AUDIT RESPONSIBILITIES

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

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

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

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

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

10.2.2 EXTERNAL LABORATORY AUDIT RESPONSIBILITIES

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

External audits may include any of the following:

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

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

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

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

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

11.0 PREVENTATIVE MAINTENANCE

11.1 FIELD INSTRUMENT PREVENTATIVE MAINTENANCE

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

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

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

11.2 LABORATORY INSTRUMENT PREVENTATIVE MAINTENANCE

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

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

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

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

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

12.1 FIELD MEASUREMENTS

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

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

12.2 LABORATORY DATA

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

12.2.1 PRECISION

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

12.2.2 ACCURACY

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

12.2.3 COMPLETENESS

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

12.3 STATISTICAL EVALUATIONS

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

12.3.1 PERCENT RECOVERY

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

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

where:

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

12.3.2 RELATIVE PERCENT DIFFERENCE

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

$$RPD = \frac{(R_1 - R_2)}{\frac{R_1 + R_2}{2}} \times 100$$

where:

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

13.0 CORRECTIVE ACTION

13.1 FIELD CORRECTIVE ACTION

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

The corrective action procedures will be as follows:

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

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

13.2 LABORATORY CORRECTIVE ACTION

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

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

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

13.3 CORRECTIVE ACTION DURING DATA VALIDATION AND DATA ASSESSMENT

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

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

14.0 QUALITY ASSURANCE (QA) REPORTS

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

QA reports to management include:

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

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

15.0 REFERENCES

1. United States Environmental Protection Agency, (1999). EPA Requirements for Quality Assurance Project Plans for Environmental Data Operations. EPA QA/R-5 Interim Final, November 1999.

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3. United States Environmental Protection Agency (1991). Preparation Aids for the Development of Category I Quality Assurance Project Plans. U.S. EPA/600/8-91/003, Risk Reduction Engineering Laboratory, Office of Research and Development, Cincinnati, Ohio, February 1991.

4. United States Environmental Protection Agency, (1993). Data Quality Objectives Process for Superfund Interim Final Guidance. U.S. EPA/540/R-93-071, Office of Solid Waste and Emergency Response (OSWER), September 1993.

5. United States Environmental Protection Agency, (1992). Specifications and Guidance for Contaminant-Free Sample Containers. OSWER Directive 9240.0-05A, April 1992.

6. United States Environmental Protection Agency. U.S. EPA Contract Laboratory Program National Functional Guidelines for Organic Data Review. U.S. EPA 540/R-99-012.

7. United States Environmental Protection Agency. U.S. EPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review. U.S. EPA 540/R-01-008.

8. United States Environmental Protection Agency. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods Office of Solid Waste, U.S. EPA, SW-846, November 1986, with updates.

TABLE 1.1

SUMMARY OF SAMPLING AND ANALYSIS PROGRAM
WORK PLAN
GRAND RAPIDS METAL PLANT
WYOMING, MICHIGAN

Investigation Activity	*Sample Matrix*	*Field Parameters*	*Laboratory Parameters*	*Investigative Samples*	*Quality Control Samples (1)*			*Total*
					Field Blanks (2)	*Field Duplicates*	*MS/MSD (3)*	
Vertical Aquifer Sampling	Soil	PID VOC Screen	TCL VOC	(4)	1/20	1/20	1/20	(5)
	Groundwater	pH/Temperature, DO, Specific Conductivity, Turbidity, ORP	TCL VOC	30	1/20	1/20	1/20	(5)
Monitoring Well Sampling	Groundwater	pH/Temperature, DO, Specific Conductivity, Turbidity, ORP	TCL VOC, Select NA Parameters (6) TCL SVOC (7)	22	1/20	1/20	1/20	(5)
LNAPL Characterization	LNAPL	None	GRO, DRO, TCL VOC, TCL SVOC, TAL Metals	1	0	0	0	1
SVE System Evaluation	Air	PID VOC Screen	Trichloroethene	16	0	0	0	16
Waste Characterization	Waste	None	TCL VOC, TCLP VOC, TCLP SVOC, TCLP Metals, Corrosivity, Ignitability, Reactivity	(8)	0	0	0	(8)

Notes:

(1) - A laboratory trip blank will be submitted with each shipment of samples for TCL VOC analysis.
(2) - Field blank samples will not be required if dedicated or disposable sampling equipment is used.
(3) - Matrix Spike/Matrix Spike duplicate (MS/MSD) analyses are required for samples submitted for organic and inorganic analyses are to be analyzed at a frequency of one per group of twenty (20) or fewer investigative samples for the activities detailed above.
(4) - Collection of soil samples and laboratory analysis will be at the discretion of CRA's field personnel based on field conditions.
(5) - The frequency of Field Blanks and Field Duplicates will be one per 20 investigative samples and will be combined from multiple investigation activities. The total sample quantity will vary depending on which activity the QC samples are collected from.
(6) - NA = Natural Attenuation, select list includes Total Organic Carbon, Calcium, Manganese, Magnesium, Alkalinity, Carbonate Hardness, Hardness, Chloride, Nitrate, Nitrite, Sulfate, Sulfide, Methane, Ethane, and Ethene.
(7) - TCL SVOCs will be analyzed at one location.
(8) - The quantity of waste samples will be based on volume of waste generated and quantity of drums.

SVE = Soil Vapor Extraction
TCL = Target Compound List
TAL = Target Analyte List
TCLP = Toxic Characterics Leaching Procedure
LNAPL = Light Non-aqueous Phase Liquid
VOC = Volatile Organic Compounds
SVOC = Semi-volatile Organic Compounds
GRO = Gasoline Range Organics
PID = Photoionization Detector
DO = Dissolved Oxygen
ORP = Oxidation-Reduction Potential
DRO = Diesel Range Organics

TABLE 1.2

VERTICAL AQUIFER AND MONITORING WELL PARAMETER LIST
WORK PLAN
GRAND RAPIDS METAL PLANT
WYOMING, MICHIGAN

Compound	Estimated Quantitation Limits (TQL)[1] Water (µg/L)	Estimated Quantitation Limits (TQL)[1] Soil (µg/kg)	Method Detection Limits (MDL)[2] Water (µg/L)	Method Detection Limits (MDL)[2] Soil (µg/kg)
Target Compound List (TCL) Volatile Organic Compounds (VOC)[3]				
Acetone	25	750	1.1	48
Benzene	1	50	0.37	6.9
Bromodichloromethane	1	100	0.32	8.2
Bromoform	1	100	0.37	11
Bromomethane	1	250	0.3	42
2-Butanone	25	750	0.59	52
Carbon disulfide	5	250	0.24	4.5
Carbon tetrachloride	1	50	0.37	14
Chlorobenzene	1	50	0.38	5.8
Chloroethane	1	250	0.29	47
Chloroform	1	50	0.35	12
Chloromethane	1	250	0.49	14
Cyclohexane	1	1,200	0.33	6.2
Dibromochloromethane	1	50	0.37	11
1,2-Dibromo-3-chloropropane	1	250	0.82	23
1,2-Dibromoethane	1	250	0.34	7.6
1,2-Dichlorobenzene	1	100	0.38	6.9
1,3-Dichlorobenzene	1	100	0.38	8.3
1,4-Dichlorobenzene	1	100	0.38	8.6
Dichlorodifluoromethane	1	100	0.49	23
1,1-Dichloroethane	1	50	0.3	11
1,2-Dichloroethane	1	50	0.28	13
1,1-Dichloroethene	1	50	0.31	7.9
cis-1,2-Dichloroethene	1	50	0.35	7.8
trans-1,2-Dichloroethene	1	50	0.33	10
1,2-Dichloropropane	1	50	0.41	13
cis-1,3-Dichloropropene	1	50	0.35	7.7
trans-1,3-Dichloropropene	1	50	0.35	5.3
Ethylbenzene	1	50	0.41	6.5
2-Hexanone	50	2,500	0.58	16
Isopropylbenzene	5	250	0.39	8.5
Methyl acetate	10	1,200	0.54	24
Methylene chloride	5	250	0.29	16
Methylcyclohexane	1	1,200	0.42	8.92
4-Methyl-2-pentanone	50	2,500	0.26	24
Methyl tert-butyl ether	5	250	0.27	8.2
Styrene	1	50	0.35	7.2
1,1,2,2-Tetrachloroethane	1	100	0.4	10
Tetrachloroethene	1	50	0.42	11
Toluene	1	100	0.39	5.6
1,2,4-Trichlorobenzene	5	250	0.4	11
1,1,1-Trichloroethane	1	50	0.39	8.9

Compound	Estimated Quantitation Limits (TQL)[1] Water (µg/L)	Estimated Quantitation Limits (TQL)[1] Soil (µg/kg)	Method Detection Limits (MDL)[2] Water (µg/L)	Method Detection Limits (MDL)[2] Soil (µg/kg)
TCL VOC (continued)				
1,1,2-Trichloroethane	1	50	0.36	7.9
Trichloroethene	1	50	0.42	8.7
Trichlorofluoromethane	1	100	0.54	8.8
1,1,2-Trichloro-1,2,2-trifluoroethane	1	250	0.32	29

TABLE 1.2

VERTICAL AQUIFER AND MONITORING WELL PARAMETER LIST
WORK PLAN
GRAND RAPIDS METAL PLANT
WYOMING, MICHIGAN

Vinyl chloride	1	100	0.36	18
Xylenes (total)	3	150	0.44	49
TCL Semi-Volatile Organic Compounds (SVOC) [3]				
Acenaphthene	5	330	0.8	14
Acenaphthylene	5	330	0.71	19
Acetophenone	5	330	2.6	20
Anthracene	5	330	0.68	17
Atrazine	5	330	2.5	22
Benzaldehyde	10	330	2.8	14
Benzo(a)anthracene	4	330	0.7	23
Benzo(a)pyrene	4	330	0.73	15
Benzo(b)fluoranthene	4	330	0.94	20
Benzo(g,h,i)perylene	5	330	0.85	16
Benzo(k)fluoranthene	5	330	0.84	16
1,1'-Biphenyl	10	330	2.6	18
4-Bromophenylphenyl ether	5	330	0.88	15
Butylbenzylphthalate	5	330	0.88	21
di-n-Butylphthalate	5	330	0.67	23
Caprolactam	10	330	2.5	28
Carbazole	10	330	0.82	19
4-Chloroaniline	20	1,700	0.61	20
bis(2-Chloroethoxy)methane	5	330	0.87	26
bis(2-Chloroethyl)ether	4	330	0.97	18
2,2'-oxibis(1-Chloropropane)	5	330	0.78	27
4-Chloro-3-methylphenol	5	330	0.99	19
2-Chloronaphthalene	5	330	0.85	17
2-Chlorophenol	5	330	1	18
4-Chlorophenyl phenyl ether	5	330	0.79	17
Chrysene	5	330	0.75	22
Dibenz(a,h)anthracene	4	330	0.79	18
Dibenzofuran	5	330	1.1	17
3,3'-Dichlorobenzidine	4	2,000	0.93	18

	Targeted Quantitation Limits (TQL) [1]		*Method Detection Limits (MDL)* [2]	
Compound	*Water (µg/L)*	*Soil (µg/kg)*	*Water (µg/L)*	*Soil (µg/kg)*
TCL Semi-Volatile Organic Compounds (cont'd)				
2,4-Dichorophenol	10	330	0.85	16
Diethylphthalate	5	330	0.65	19
2,4-Dimethylphenol	5	330	0.85	18
Dimethylphthalate	5	330	0.76	17
4,6-Dinitro-2-methylphenol	20	1,700	1.3	48
2,4-Dinitrophenol	20	1,700	3	47
2,4-Dinitrotoluene	5	330	0.79	22
2,6-Dinitrotoluene	5	330	0.57	15
bis(2-Ethylhexyl)phthalate	5	330	2.7	13
Fluoranthene	5	330	0.81	16
Fluorene	5	330	1	15
Hexachlorobenzene	5	330	0.74	22
Hexachlorobutadiene	5	330	0.73	16
Hexachlorocyclopentadiene	5	330	1.1	10
Hexachloroethane	5	330	0.74	17
Indeno(1,2,3-cd)pyrene	4	330	0.63	19
Isophorone	5	330	0.63	22
2-Methylnaphthalene	5	330	0.64	17
2-Methylphenol	5	330	1.1	21
4-Methylphenol	5	330	1.3	20
Naphthalene	5	330	0.75	17

TABLE 1.2

VERTICAL AQUIFER AND MONITORING WELL PARAMETER LIST
WORK PLAN
GRAND RAPIDS METAL PLANT
WYOMING, MICHIGAN

2-Nitroaniline	20	1,700	0.7	13
3-Nitroaniline	20	1,700	0.71	22
4-Nitroaniline	20	1,700	1.3	17
Nitrobenzene	4	330	0.81	24
2-Nitrophenol	5	330	2.1	21
4-Nitrophenol	20	1,700	1.9	53
N-Nitroso-di-n-propylamine	5	330	0.67	15
N-Nitrosodiphenylamine (diphenylamine)	5	330	1.4	19
di-n-Octylphthalate	5	330	1.1	64
Pentachlorophenol	20	800	2.4	60
Phenanthrene	5	330	0.82	21
Phenol	5	330	2.6	18
Pyrene	5	330	1.1	21
2,4,5-Trichlorophenol	5	330	1.2	15
2,4,6-Trichlorophenol	4	330	1.7	19

	Estimated Quantitation Limits (TQL) [1]		*Method Detection Limits (MDL)* [2]	
Compound	*Water (mg/L)*	*Soil (mg/kg)*	*Water (mg/L)*	*Soil (mg/kg)*
Select Natural Attenuation (NA) Parameters				
Alkalinity	5	--	1.3	--
Chloride	1	--	0.094	--
Hardness (total)	5	--	2.1	--
Hardness (carbonate)	5	--	2.1	--
Nitrate Nitrogen	0.1	--	0.0076	--
Nitrite Nitrogen	0.1	--	0.02	--
Sulfate	1	--	0.11	--
Sulfide	1	--	0.25	--
Total Organic Carbon	1	--	1	--
NA Metals				
Calcium	5	--	0.059	--
Magnesium	5	--	0.035	--
Manganese	0.015	--	0.00068	--
Dissolved Gasses				
Ethane	0.5 µg/L	--	0.3	--
Ethene	0.5 µg/L	--	0.29	--
Methane	0.5 µg/L	--	0.39	--

Notes:

[1] - Please note that these are targeted quantitation limits and are presented for guidance only. Actual quantitation limits are highly matrix dependent and may be elevated due to matrix effects, QA/QC problems and high concentrations of target and non-target analytes.

[2] - Method Detection Limits (MDL) are also presented for guidance only. Actual MDLs will vary depending on sample specific preparation factors. The MDLs are also highly matrix dependant and may be elevated due to matrix effects, QA/QC problems and high concentrations of target and non-target analytes. Laboratory

TABLE 1.2

VERTICAL AQUIFER AND MONITORING WELL PARAMETER LIST
WORK PLAN
GRAND RAPIDS METAL PLANT
WYOMING, MICHIGAN

MDLs are updated on a periodic basis and the MDLs in effect when the samples are analyzed will be used for reporting purposes.

[3] - U.S. EPA Contract Laboratory Program, "Statement of Work for Organic Analysis, Multi-Media, Multi-Concentration", OLM4.2, May 1999 Target Compound List.

TABLE 1.3

LNAPL PARAMETER LIST
WORK PLAN
GRAND RAPIDS METAL PLANT
WYOMING, MICHIGAN

Compound	*Estimated Quantitation Limits (TQL)* [1] *(µg/kg)*	*Method Detection Limits (MDL)* [2] *(µg/kg)*
Target Compound List (TCL) Volatile Organic Compounds (VOC) [3]		
Acetone	2,500	48
Benzene	620	6.9
Bromodichloromethane	620	8.2
Bromoform	620	11
Bromomethane	1,200	42
2-Butanone	2,500	52
Carbon disulfide	620	4.5
Carbon tetrachloride	620	14
Chlorobenzene	620	5.8
Chloroethane	1,200	47
Chloroform	620	12
Chloromethane	1,200	14
Cyclohexane	2,500	6.2
Dibromochloromethane	620	11
1,2-Dibromo-3-chloropropane	1,200	23
1,2-Dibromoethane	620	7.6
1,2-Dichlorobenzene	1,200	6.9
1,3-Dichlorobenzene	1,200	8.3
1,4-Dichlorobenzene	1,200	8.6
Dichlorodifluoromethane	1,200	23
1,1-Dichloroethane	620	11
1,2-Dichloroethane	620	13
1,1-Dichloroethene	620	7.9
cis-1,2-Dichloroethene	310	7.8
trans-1,2-Dichloroethene	310	10
1,2-Dichloropropane	620	13
cis-1,3-Dichloropropene	620	7.7
trans-1,3-Dichloropropene	620	5.3
Ethylbenzene	620	6.5
2-Hexanone	2,500	16
Isopropylbenzene	1,200	8.5
Methyl acetate	1,200	24
Methylene chloride	620	16
Methylcyclohexane	620	8.92
4-Methyl-2-pentanone	2,500	24
Methyl tert-butyl ether	2,500	8.2
Styrene	620	7.2
1,1,2,2-Tetrachloroethane	620	10
Tetrachloroethene	620	11
Toluene	620	5.6
1,2,4-Trichlorobenzene	620	11
1,1,1-Trichloroethane	620	8.9

TABLE 1.3

LNAPL PARAMETER LIST
WORK PLAN
GRAND RAPIDS METAL PLANT
WYOMING, MICHIGAN

Compound	*Estimated Quantitation Limits (TQL)* [1] *(µg/kg)*	*Method Detection Limits (MDL)* [2] *(µg/kg)*
TCL VOC (continued)		
1,1,2-Trichloroethane	1,200	7.9
Trichloroethene	620	8.7
Trichlorofluoromethane	1,200	8.8
1,1,2-Trichloro-1,2,2-trifluoroethane	2,500	29
Vinyl chloride	1,200	18
Xylenes (total)	620	49
TCL Semi-Volatile Organic Compounds (SVOC)		
Acenaphthene	330	14
Acenaphthylene	330	19
Acetophenone	330	20
Anthracene	330	17
Atrazine	330	22
Benzaldehyde	330	14
Benzo(a)anthracene	330	23
Benzo(a)pyrene	330	15
Benzo(b)fluoranthene	330	20
Benzo(g,h,i)perylene	330	16
Benzo(k)fluoranthene	330	16
1,1'-Biphenyl	330	18
4-Bromophenylphenyl ether	330	15
Butylbenzylphthalate	330	21
di-n-Butyphthalate	330	23
Caprolactam	330	28
Carbazole	330	19
4-Chloroaniline	1,700	20
bis(2-Chloroethoxy)methane	330	26
bis(2-Chloroethyl)ether	330	18
2,2'-oxibis(1-Chloropropane)	330	27
4-Chloro-3-methylphenol	330	19
2-Chloronaphthalene	330	17
2-Chlorophenol	330	18
4-Chlorophenyl phenyl ether	330	17
Chrysene	330	22
Dibenz(a,h)anthracene	330	18
Dibenzofuran	330	17
3,3'-Dichlorobenzidine	2,000	18
2,4-Dichorophenol	330	16
Diethylphthalate	330	19
2,4-Dimethylphenol	330	18
Dimethylphthalate	330	17
4,6-Dinitro-2-methylphenol	1,700	48

TABLE 1.3

LNAPL PARAMETER LIST
WORK PLAN
GRAND RAPIDS METAL PLANT
WYOMING, MICHIGAN

Compound	*Estimated Quantitation Limits (TQL)*[1] *(µg/kg)*	*Method Detection Limits (MDL)*[2] *(µg/kg)*
TCL Semi-Volatile Organic Compounds (cont'd)		
2,4-Dinitrophenol	1,700	47
2,4-Dinitrotoluene	330	22
2,6-Dinitrotoluene	330	15
bis(2-Ethylhexyl)phthalate	330	13
Fluoranthene	330	16
Fluorene	330	15
Hexachlorobenzene	330	22
Hexachlorobutadiene	330	16
Hexachlorocyclopentadiene	330	10
Hexachloroethane	330	17
Indeno(1,2,3-cd)pyrene	330	19
Isophorone	330	22
2-Methylnaphthalene	330	17
2-Methylphenol	330	21
4-Methylphenol	330	20
Naphthalene	330	17
2-Nitroaniline	1,700	13
3-Nitroaniline	1,700	22
4-Nitroaniline	1,700	17
Nitrobenzene	330	24
2-Nitrophenol	330	21
4-Nitrophenol	1,700	53
N-Nitroso-di-n-propylamine	330	15
N-Nitrosodiphenylamine (diphenylamine)	330	19
di-n-Octylphthalate	330	64
Pentachlorophenol	800	60
Phenanthrene	330	21
Phenol	330	18
Pyrene	330	21
2,4,5-Trichlorophenol	330	15
2,4,6-Trichlorophenol	330	19

TABLE 1.3

LNAPL PARAMETER LIST
WORK PLAN
GRAND RAPIDS METAL PLANT
WYOMING, MICHIGAN

Compound	*Estimated Quantitation Limits (TQL)* [1] *(mg/kg)*	*Method Detection Limits (MDL)* [2] *(mg/kg)*
TAL Metals		
Aluminum	20	4.80
Antimony	6	0.230
Arsenic	1	0.28
Barium	20	0.066
Beryllium	0.5	0.068
Cadmium	0.5	0.016
Chromium	1	0.13
Cobalt	5	0.053
Copper	2.5	0.14
Iron	10	3.6
Lead	0.3	0.3
Manganese	1.5	0.071
Mercury	0.1	0.016
Nickel	4	0.15
Selenium	0.5	0.43
Silver	1	0.1
Thallium	1	0.58
Vanadium	5	0.069
Zinc	2	1.5
Gasoline Range Organics (GRO)	10	0.017
Diesel Range Organics (DRO)	3	1.3

Notes:

[1] - Please note that these are targeted quantitation limits and are presented for guidance only. Actual quantitation limits are highly matrix dependent and may be elevated due to matrix effects, QA/QC problems and high concentrations of target and non-target analytes.

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

[3] - U.S. EPA Contract Laboratory Program, "Statement of Work for Organic Analysis, Multi-Media, Multi-Concentration", OLM4.2, May 1999 Target Compound List.

TABLE 1.4

SVE AIR SAMPLE PARAMETER LIST
WORK PLAN
GRAND RAPIDS METAL PLANT
WYOMING, MICHIGAN

Compound	*Estimated Quantitation Limits (TQL)* [1] *Water* ($\mu g/M^3$)	*Method Detection Limits (MDL)* [2] *Water* ($\mu g/M^3$)
Volatile Organic Compounds (VOC)		
Trichloroethene	1	0.42

Notes:

[1] - Please note that these are targeted quantitation limits and are presented for guidance only. Actual quantitation limits are highly matrix dependent and may be elevated due to matrix effects, QA/QC problems and high concentrations of target and non-target analytes.

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

TABLE 1.5

WASTE CHARACTERIZATION PARAMETER LIST
WORK PLAN
GRAND RAPIDS METAL PLANT
WYOMING, MICHIGAN

	Estimated Quantitation Limits (TQL)[1]		*Method Detection Limits (MDL)*[2]	
Compound	*Water (µg/L)*	*Soil (µg/kg)*	*Water (µg/L)*	*Soil (µg/kg)*
Target Compound List (TCL) Volatile Organic Compounds (VOC)[3]				
Acetone	25	750	1.1	48
Benzene	1	50	0.37	6.9
Bromodichloromethane	1	100	0.32	8.2
Bromoform	1	100	0.37	11
Bromomethane	1	250	0.3	42
2-Butanone	25	750	0.59	52
Carbon disulfide	5	250	0.24	4.5
Carbon tetrachloride	1	50	0.37	14
Chlorobenzene	1	50	0.38	5.8
Chloroethane	1	250	0.29	47
Chloroform	1	50	0.35	12
Chloromethane	1	250	0.49	14
Cyclohexane	1	1,200	0.33	6.2
Dibromochloromethane	1	50	0.37	11
1,2-Dibromo-3-chloropropane	1	250	0.82	23
1,2-Dibromoethane	1	250	0.34	7.6
1,2-Dichlorobenzene	1	100	0.38	6.9
1,3-Dichlorobenzene	1	100	0.38	8.3
1,4-Dichlorobenzene	1	100	0.38	8.6
Dichlorodifluoromethane	1	100	0.49	23
1,1-Dichloroethane	1	50	0.3	11
1,2-Dichloroethane	1	50	0.28	13
1,1-Dichloroethene	1	50	0.31	7.9
cis-1,2-Dichloroethene	1	50	0.35	7.8
trans-1,2-Dichloroethene	1	50	0.33	10
1,2-Dichloropropane	1	50	0.41	13
cis-1,3-Dichloropropene	1	50	0.35	7.7
trans-1,3-Dichloropropene	1	50	0.35	5.3
Ethylbenzene	1	50	0.41	6.5
2-Hexanone	50	2,500	0.58	16
Isopropylbenzene	5	250	0.39	8.5
Methyl acetate	10	1,200	0.54	24
Methylene chloride	5	250	0.29	16
Methylcyclohexane	1	1,200	0.42	8.92
4-Methyl-2-pentanone	50	2,500	0.26	24
Methyl tert-butyl ether	5	250	0.27	8.2
Styrene	1	50	0.35	7.2
1,1,2,2-Tetrachloroethane	1	100	0.4	10
Tetrachloroethene	1	50	0.42	11
Toluene	1	100	0.39	5.6
1,2,4-Trichlorobenzene	5	250	0.4	11
1,1,1-Trichloroethane	1	50	0.39	8.9

TABLE 1.5

WASTE CHARACTERIZATION PARAMETER LIST
WORK PLAN
GRAND RAPIDS METAL PLANT
WYOMING, MICHIGAN

Compound	Estimated Quantitation Limits (TQL)[1] Water (µg/L)	Estimated Quantitation Limits (TQL)[1] Soil (µg/kg)	Method Detection Limits (MDL)[2] Water (µg/L)	Method Detection Limits (MDL)[2] Soil (µg/kg)
TCL VOC (continued)				
1,1,2-Trichloroethane	1	50	0.36	7.9
Trichloroethene	1	50	0.42	8.7
Trichlorofluoromethane	1	100	0.54	8.8
1,1,2-Trichloro-1,2,2-trifluoroethane	1	250	0.32	29
Vinyl chloride	1	100	0.36	18
Xylenes (total)	3	150	0.44	49

Compound	Estimated Quantitation Limits (TQL)[1] Leachate (mg/L)
Toxic Characteristics Leachate Procedure (TCLP) VOC	
Benzene	0.025
2-Butanone	0.05
Carbon tetrachloride	0.025
Chlorobenzene	0.025
Chloroform	0.025
1,2-Dichloroethane	0.025
1,1-Dichloroethene	0.07
Tetrachloroethene	0.07
Trichloroethene	0.05
Vinyl chloride	0.05
TCLP Base-Neutral/Acid Extractables	
Cresols, total	0.15
1,4-Dichlorobenzene	0.05
2,4-Dinitrotoluene	0.05
Hexachlorobenzene	0.05
Hexachlorobutadiene	0.05
Hexachloroethane	0.05
Nitrobenzene	0.05
Pentachlorophenol	0.1
Pyridine	0.1
2,4,5-Trichlorophenol	0.25
2,4,6-Trichlorophenol	0.05

TABLE 1.5

WASTE CHARACTERIZATION PARAMETER LIST
WORK PLAN
GRAND RAPIDS METAL PLANT
WYOMING, MICHIGAN

Compound	*Estimated Quantitation Limits (TQL)* [1] *Leachate (mg/L)*	
TCLP Metals		
Arsenic	0.5	
Barium	10	
Cadmium	0.1	
Chromium	0.5	
Lead	0.5	
Mercury	0.002	
Selenium	0.25	
Silver	0.5	
Characteristics		
Cyanide, Reactive	200	mg/kg
Sulfide, Reactive	500	mg/kg
Ignitablilty (flashpoint)	-	deg. F
Corrosivity (pH)	-	no units

Notes:

[1] - Please note that these are targeted quantitation limits and are presented for guidance only. Actual quantitation limits are highly matrix dependent and may be elevated due to matrix effects, QA/QC problems and high concentrations of target and non-target analytes.

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

[3] - U.S. EPA Contract Laboratory Program, "Statement of Work for Organic Analysis, Multi-Media, Multi-Concentration", OLM4.2, May 1999 Target Compound List.

TABLE 4.1

CONTAINER, PRESERVATION, SHIPPING AND PACKAGING REQUIREMENTS
WORK PLAN
GRAND RAPIDS METAL PLANT
WYOMING, MICHIGAN

Analyses	*Sample Containers*[1]	*Preservation*	*Maximum Holding Time from Sample Collection*[2]	*Volume of Sample*	*Shipping*	*Normal Packaging*
WATER (Groundwater)						
Volatile Organic Compounds (VOC)	Three 40 mL teflon-lined septum vials per analysis	HCl to pH < 2 Iced, 4 ± 2° C	14 days for analysis	Fill completely, no air bubbles	Overnight or Hand Deliver	Foam Liner or Bubble-wrap
SVOC	Two 1 liter amber glass bottles per analysis	Iced, 4 ± 2° C	7 days for extraction 40 days after extraction for analysis	Fill to neck of bottle	Overnight or Hand Deliver	Foam Liner or Bubble-wrap
Dissolved Gases	Three 40 mL teflon-lined septum vials	Iced, 4 ± 2° C	14 days for analysis	Fill completely, no air bubbles	Overnight or Hand Deliver	Foam Liner or Bubble-wrap
Metals & Hardness	One 500-ml plastic bottle	HNO_3 to pH < 2 Iced, 4 ± 2° C	180 days for analysis	Fill to neck of bottle	Overnight or Hand Deliver	Bubble Pack or Foam Chips
Total Organic Carbon (TOC)	Two 40 mL teflon-lined septum vials	H_2SO_4 to pH <2 Iced, 4 ± 2° C	14 days for analysis	Fill completely, no air bubbles	Overnight or Hand Deliver	Foam Liner or Bubble-wrap
Sulfide	One 500-ml plastic bottle	NaOH to pH ≥ 9, Zinc Acetate and Iced, 4 ± 2° C	7 days for preparation and analysis	Fill to neck of bottle	Overnight or Hand Deliver	Bubble Pack or Foam Chips
Alkalinity, Chloride, Sulfate, Nitrate, Nitrite	One 1-liter plastic bottle	Iced, 4 ± 2° C	Alkalinity - 14 days, Chloride and Sulfate - 28 days, Nitrate and Nitrite - 48 hours for analysis	Fill to shoulder of bottle	Overnight or Hand Deliver	Bubble Pack or Foam Chips
SOLID (Soil)						

TABLE 4.1

CONTAINER, PRESERVATION, SHIPPING AND PACKAGING REQUIREMENTS
WORK PLAN
GRAND RAPIDS METAL PLANT
WYOMING, MICHIGAN

Analyses	*Sample Containers*[1]	*Preservation*	*Maximum Holding Time from Sample Collection*[2]	*Volume of Sample*	*Shipping*	*Normal Packaging*
VOC	One 25g EnCore Sampler™ per analysis[3]	Iced, 4 ± 2° C	48 hours for extraction 14 days for analysis	Fill completely	Overnight or Hand Deliver	Bubble Pack or Foam Chips
LNAPL						
Gasoline Range Organics (GRO), VOC	One 4-ounce glass jar[4]	Iced, 4 ± 2° C	14 days for analysis	Fill completely	Overnight or Hand Deliver	Bubble Pack or Foam Chips
Diesel Range Organics (DRO), Semi-volatile Organic Compounds (SVOC)	One 4-ounce glass jar[4]	Iced, 4 ± 2° C	14 days for extraction 40 days after extraction for analysis	Fill to shoulder of jar	Overnight or Hand Deliver	Bubble Pack or Foam Chips
Metals	One 4-ounce glass jar[4]	Iced, 4 ± 2° C	180 days (mercury 28 days) for analysis	Fill to shoulder of jar	Overnight or Hand Deliver	Bubble Pack or Foam Chips
Air (Soil Vapor Extraction)						
Trichloroethene	One 6 L Summa Canister™ per analysis	Iced, 4 ± 2° C	14 days for analysis	Grab Sample 90 percent of Canister Capacity	Overnight or Hand Deliver	Cardboard Box
Waste (Solid)						
VOC (totals)	One 4-ounce glass jar[4]	Iced, 4 ± 2° C	14 days for analysis	Fill completely	Overnight or Hand Deliver	Bubble Pack or Foam Chips
Waste (Solid) (Cont'd)						

TABLE 4.1

CONTAINER, PRESERVATION, SHIPPING AND PACKAGING REQUIREMENTS
WORK PLAN
GRAND RAPIDS METAL PLANT
WYOMING, MICHIGAN

Analyses	*Sample Containers*[1]	*Preservation*	*Maximum Holding Time from Sample Collection*[2]	*Volume of Sample*	*Shipping*	*Normal Packaging*
VOC (TCLP)	One 4-ounce glass jar[4]	Iced, 4 ± 2° C	14 days for extraction 14 days for analysis	Fill completely	Overnight or Hand Deliver	Bubble Pack or Foam Chips
SVOC (TCLP)	One 4-ounce glass jar[4]	Iced, 4 ± 2° C	14 days for TCLP extraction 14 days for SVOC extraction 40 days after extraction for analysis	Fill to shoulder of jar	Overnight or Hand Deliver	Bubble Pack or Foam Chips
Metals (TCLP)	One 4-ounce glass jar[4]	Iced, 4 ± 2° C	180 days (mercury 28 days) for extraction 180 days (mercury 28 days) for analysis	Fill to shoulder of jar	Overnight or Hand Deliver	Bubble Pack or Foam Chips
Corrosivity (pH) and Ignitability (flash point), Reactivity (Cyanide and Sulfide)	One 4-ounce glass jar[4]	Iced, 4 ± 2° C	As soon as practical	Fill to should of jar	Overnight or Hand Deliver	Bubble Pack or Foam Chips
Waste (Liquid)						
VOC (totals)	Three 40 mL teflon-lined septum vials per analysis	HCl to pH <2 Iced, 4 ± 2° C	14 days for analysis	Fill completely, no air bubbles	Overnight or Hand Deliver	Foam Liner or Bubble-wrap
Waste (Liquid) (Cont'd)						
VOC (TCLP)	Two 40 mL teflon-lined septum vials	Iced, 4 ± 2° C	7 days for extraction 14 days for analysis	Fill completely, no air bubbles	Overnight or Hand Deliver	Foam Liner or Bubble-wrap

TABLE 4.1

CONTAINER, PRESERVATION, SHIPPING AND PACKAGING REQUIREMENTS
WORK PLAN
GRAND RAPIDS METAL PLANT
WYOMING, MICHIGAN

Analyses	*Sample Containers*[1]	*Preservation*	*Maximum Holding Time from Sample Collection*[2]	*Volume of Sample*	*Shipping*	*Normal Packaging*
SVOC (TCLP)	One 1 liter amber glass bottle per analysis[4]	Iced, 4 ± 2° C	7 days for TCLP extraction 7 days for SVOC extraction 40 days after extraction for analysis	Fill to neck of bottle	Overnight or Hand Deliver	Foam Liner or Bubble-wrap
Metals (TCLP)	One 1 liter amber glass bottle per analysis[4]	Iced, 4 ± 2° C	180 days (mercury 28 days) for extraction 180 days (mercury 28 days) for analysis	Fill to neck of bottle	Overnight or Hand Deliver	Foam Liner or Bubble-wrap
Corrosivity (pH) and Ignitability (flash point), Reactivity (Cyanide and Sulfide)	One 1 liter amber glass bottle[4]	Iced, 4 ± 2° C	As soon as practical	Fill to neck of bottle	Overnight or Hand Deliver	Foam Liner or Bubble-wrap

Notes:

[1] - Multiple parameters on a single sample may be combined into one single 16 ounce glass jar.

[2] - These are technical holding times, i.e., are based on time elapsed from time of sample collection.

[3] - Soil VOC samples will require in addition to the EnCore an additional container of sample for dry weight determination if no other analyses are required. Sediment samples if non-cohesive, may require standard bulk sampling techniques using a 4 ounce glass jar with no head space.

[4] - The NAPL and Waste Characterization samples may be combined into single containers of different volume depending on the parameters required and the material sampled.

TABLE 7.1

SUMMARY OF ANALYTICAL METHODS
WORK PLAN
GRAND RAPIDS METAL PLANT
WYOMING, MICHIGAN

Parameter[1]	*Preparation Method*[2]	*Laboratory Preparation SOP*	*Analytical Method*[2]	*Laboratory Analytical SOP*
Groundwater Samples				
VOC	SW-846 5030B	CORP-MS-0002NC	SW-846 8260B	CORP-MS-0002NC
SVOC	SW-846 3520C	CORP-OP-0001NC	SW-846 8270C	CORP-MS-0001NC
Alkalinity	SM 2320 B	NC-WC-0003	SM 2320B	NC-WC-0003
Chloride	SW-846 9056	NC-WC-0084	SW-846 9056	NC-WC-0084
Hardness (total & carbonate)	EPA-MCA 130.2	NC-WC-0036	EPA-MCA 130.2	NC-WC-0036
Nitrate Nitrogen	SW-846 9056	NC-WC-0084	SW-846 9056	NC-WC-0084
Nitrite Nitrogen	SW-846 9056	NC-WC-0084	SW-846 9056	NC-WC-0084
Sulfate	SW-846 9056	NC-WC-0084	SW-846 9056	NC-WC-0084
Sulfide	SW-846 9030A	NC-WC-0060	SW-846 9030A	NC-WC-0060
Total Organic Carbon	SW-846 9060	NC-WC-0017	SW-846 9060	NC-WC-0017
Dissolved Gasses	EPA-RSK 175	NC-GC-0032	EPA-RSK 175	NC-GC-0032
NA Metals	SW-846 3010A	CORP-IP-0003	SW-846 6010B	CORP-MT-0001NC
Soil Samples				
VOC	SW-846 5035[4]	CORP-MS-0002NC	SW-846 8260B	CORP-MS-0002NC
Air Samples				
Trichloroethene	EPA-AA TO14	COI-MS-0007	EPA-AA TO14	COI-MS-0007
LNAPL Samples				
VOC	SW-846 5030B	CORP-MS-0002NC	SW-846 8260B	CORP-MS-0002NC
SVOC	SW-846 3550B	CORP-OP-0001NC	SW-846 8270C	CORP-MS-0001NC
GRO	SW+846 8011M	NC-GC 0025	SW-846 8011M	NC-GC-0025
DRO	SW-846 3550B	CORP-OP-0001NC	SW-846 8011M	CORP-GC-0001
Metals				
ICP Metals	SW-846 3050A	CORP-IP-0002NC	SW-846 6010B	CORP-MT-0001NC
Mercury	SW-846 7471A	CORP-MT-0007NC	SW-846 7471A	CORP-MT-0007NC
Waste Characterization Samples				
TCLP Extraction	SW-846 1311	CORP-IP-0004NC	NA	NA
VOC	SW-846 5030B/5035[4]	CORP-MS-0002NC	SW-846 8260B	CORP-MS-0002NC
SVOC	SW-846 3520C	CORP-OP-0001NC	SW-846 8270C	CORP-MS-0001NC
Metals				
ICP Metals	SW-846 3010A	CORP-IP-0002NC	SW-846 6010B	CORP-MT-0001NC
Mercury	SW-846 7470A	CORP-MT-0007NC	SW-846 7470A	CORP-MT-0007NC
Cyanide, Reactive	SW-846 Sect. 7	NC-WC-0033	SW-846 Sect. 7	NC-WC-0033
Sulfide, Reactive	SW-846 Sect. 7	NC-WC-0061	SW-846 Sect. 7	NC-WC-0061
Ignitablilty (flashpoint)	SW-846 1010	NC-WC-0034	SW-846 1010	NC-WC-0034
Corrosivity (pH)	SW-846 9045C	NC-WC-0010	SW-846 9045C	NC-WC-0010

TABLE 7.1

SUMMARY OF ANALYTICAL METHODS
WORK PLAN
GRAND RAPIDS METAL PLANT
WYOMING, MICHIGAN

Notes:

[1] Refer to Table 1.2 for the compounds/elements of each parameter group.

[2] Preperation and Analytical Method References:
- SW-846 - "Test Methods for Evaluating Solid Wastes, Physical/Chemical Methods ", SW-846, 3rd Edition, and Promulgated Updates, November 1986.
- EPA-RSK - EPA Internal Standard Operating Procedure, from the R.S. Kerr Laboratory, August 11, 1994.
- EPA-MCA - "Methods for Chemical Analysis of Water and Wastes", EPA-600/4-79-020, Revised March 1983.
- EPA-AA - "Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air", EPA/625/R-96/010b, Second Edition, January 1999.

[4] Sediment and sludge samples may be collected as bulk samples which will be prepared in accordance with SW-846 Method 5030B.

VOC = Volatile Organic Compounds
GRO = Gasoline Range Organics
DRO = Diesel Range Organics
TCLP = Toxic Characterics Leachate Procedure
SVOC = Semi-Volatile Organic Compounds

ATTACHMENT 1

FIELD ANALYTICAL STANDARD OPERATING PROCEDURES

ATTACHMENT 1

FIELD ANALYTICAL STANDARD OPERATING PROCEDURES

	Title	SOP ID
1.	pH/Temperature	17360-PHT-02
2.	Specific Conductance	17360-SC-02
3.	Dissolved Oxygen	17360-DO-02
4.	Oxidation Reduction Potential	17360-ORP-02
5.	Turbidity	17360-NTU-02
6.	Soil VOC Screening	17360-VOC-02

DISSOLVED OXYGEN

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

Method: Potentiometric

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

Sensitivity: 0.1 mg/L as O_2

Optimum Range: 0.1 mg/L to 20 mg/L O_2

Sample Handling: Determined on site

Reagents and Apparatus:

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

Setting Up DO Sensor:

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

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

Calibration:

1. Remove wetting cap from tip of sensor. Switch on meter.

2. For first calibration point, place sensor in zero oxygen solution. Allow sufficient time for sensor to stabilize.

3. Move the sensor in a gentle circular motion.

4. Make sure sensor is immersed to a depth of 40 mm to cover the temperature-sensing element.

5. Press "CAL" key. CAL 1 is displayed on meter and after endpointing, the display automatically updates to zero.

6. For second calibration point, hold sensor in air. Press "CAL" key. CAL 2 is displayed. After endpointing, the display automatically updates to 100% O_2.

7. To adjust oxygen calibration for salinity and barometric pressure, press "Mode" key. In mg/L O_2 mode, press "CAL" key and 100 is displayed. Use down arrow and up arrow on the keypad to adjust the display according to the salinity and barometric pressure tables contained on the operating instruction leaflet.

Procedure:

1. Calibrate meter using calibration procedure.

2. Pour the sample into clean sample jar or plastic cup.

3. Place sensor in sample. After following the immersion, stirring and stabilization steps referred to during calibration, press "READ" key to obtain sample result.

4. Record result in the field logbook.

5. Repeat steps 2 through 4 for each sample.

Quality Control:

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

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

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

2. Calibration check results must be within 10% of the true value. If the result is outside of 10%, rinse electrodes and check solution again. If still outside the control limit, recalibrate the meter and reanalyze all samples analyzed since the last in control calibration.

3. All glassware is to be soap and water washed, tap rinsed and distilled or deionized water rinsed prior to analyses unless pre-cleaned sample jars are used.

Interferences:

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

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

TURBIDITY

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

Method: Nephalometric

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

Sensitivity: 0.01 Nephalometric Turbidity Unit (NTU)

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

Sample Handling: Determined on site

Reagents and Apparatus:

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

Calibration Check and Operation

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

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

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

3. With the light shield in place over the well, adjust the Reference Adjust knob to cause the meter to read the reference standard value on the scale. The unit is now ready for use in either range.

4. To make a measurement of a sample, clean one of the cuvettes and fill to within approximately 3/4" from the top with sample. Place the top on the cuvette and carefully clean the outside surface of the cuvette with a lint free wiper such as KimWipes. Place the sample in the well and place the light shield over the well. Select the appropriate range for best readability. Record results in field logbook.

5. Repeat steps 3 and 4 for each sample.

Quality Control:

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

   If the results are outside of the control limits, clean cuvettes and repeat analysis. If results are still outside of the control limits, recollect samples and repeat analysis. If the results are still outside of the control limits, check calibration and recalibrate if necessary (see item 2, below).

2. Calibration check results must be ±10% of the true value. If the result is outside of ±10%, clean cuvettes and check solution again. If still outside the control limit, recalibrate the meter and reanalyze all samples analyzed since the last in-control calibration.

3. All glassware is to be soap and water washed, tap rinsed and distilled or deionized water rinsed prior to analyses.

Interferences:

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

OXIDATION-REDUCTION POTENTIAL (ORP)

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

Method: Potentiometric

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

Sensitivity: 1 mV

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

Sample Handling: Determined on site

Reagents and Apparatus:

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

Calibration:

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

7. The displayed mV values are not temperature compensated and should be corrected to 25°C at 1.3 mV/°C. The temperature coefficient is in reverse proportion to the temperature.

8. Correct the value to 25°C using the following equation:

   Actual Value mV = Display Value + [(Display Temp. - 25°C) x (1.3 mV)]

Procedure:

1. Calibrate meter using calibration procedure.

2. Set up meter as outlined in the instruction manual.

3. Record temperature and ORP of the sample in the field logbook.

4. Correct ORP to 25°C using the formula presented above.

5. Record corrected ORP in the field logbook.

6. Repeat steps 3 through 6 for each sample.

7. Recheck calibration with ZoBell solution after every ten or fewer samples and after the last sample.

8. Store electrode in soaker bottle when not in use.

Quality Control:

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

   If the results are outside of the control limits, rinse electrodes and repeat analysis. If results are still outside of the control limits, recollect samples and repeat analysis. If the results are still outside of the control limits, check calibration and recalibrate if necessary (see item 2, below). If drift is suspected to be the cause of the problem, clean the electrode and recalibrate. If drift is still apparent, replace electrode.

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

Interferences:

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

1. Soft coatings should be removed by use of a wash bottle of water or by gently wiping with a soft cloth. Remove the bulb guard if necessary. Be careful not to scratch the platinum.

2. Hard coatings or organic chemicals should be removed by an appropriate chemical solvent, by gently scrubbing with a very fine cleansing powder such as "Softscrub", or by gently polishing with 600 grade wet silicon carbide paper. Wet a piece of the paper with water and gently polish the electrode with a circular twisting motion.

Note:

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

pH/TEMPERATURE

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

Method: Potentiometric

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

Sensitivity: 0.01 pH unit; 0.1 °C

Optimum Range: pH 1.00 to 12.00; temperature -5 to 50 °C

Sample Handling: Determined on site

Reagents and Apparatus:

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

Calibration:

1. Switch On/Off key to on. Before connecting the pH electrode, zero the electronics with the shorting cap attached to the meter. Turn on the meter and set the pH function switch to pH. Connect the shorting cap to the pH-input jack and set the manual temperature compensation knob to 25°C. Adjust the CAL control to indicate 7.00 ±0.01 on the pH-mV display. Disconnect the shorting cap from the pH input and connect it to the mV-input jack. The monitor is now zeroed.

2. Test the pH electrode for noise and offset as follows: Rinse the Temperature Probe with pH 7.00 buffer to remove any contaminants. Connect to the pH-input jack and to the TEMP input jack. Pour pH 7.00 buffer into a 50 mL sample cup then immerse both of the sensors into the buffer at 25.0 ±0.1°C (use the °C display to confirm the temperature). Allow the sensors to equilibrate. A display value other than 7.00 shows electrode background noise and offset. The background noise and offset at pH 7.00 should not exceed ±0.2 pH units at 25°C. Replace pH probe if background noise exceeds this tolerance.

3. Set the function switch to pH ATC. Connect to the pH ATC input jack. The pH ATC function will not work unless it is connected to the pH ATC input.

4. Rinse the Temperature Probe with pH 7.00 buffer to remove any contaminants. Connect to the pH-input jack and to the TEMP input jack. Pour pH 7.00 buffer into a 50 ml sample cup; immerse both of the sensors into the buffer. Allow the sensors to equilibrate in the buffer until a stable reading is obtained. Read the temperature and adjust the pH manual temperature compensation knob to the same value. Adjust the CAL control knob for 700 ±0.01 pH units in the display and discard the buffer. Rinse the sensors with deionized or distilled water, followed by a rinse of the next desired buffer (typically pH 4.00 or 10.00). Half fill another disposable 50 ml sample cup with the next buffer for calibration and immerse the sensors. Allow the sensors to equilibrate until a stable reading is obtained. The temperature of the two buffers should not differ by more than ±0.1°C. Adjust the SLOPE control until the display is within 0.01 pH units of the buffers, stated value. Discard the buffers. The pH system is now calibrated and ready for use.

Procedure:

1. Calibrate meter using calibration procedure.

2. Set up meter as outlined in the operating manual.

3. Pour the sample into clean sample jar or plastic cup.

4. Record temperature and pH of the sample in the logbook.

5. Rinse with water and pH 7.00 buffer.

6. Repeat steps 3 through 5 for each sample.

7. Recheck calibration with pH 7.00 buffer solution after every 10 or fewer samples and after the last sample.

8. Store pH electrode in soaker bottle when not in use.

Quality Control:

1. Duplicate 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate is still required. Duplicates must be ±0.2 pH units.

   If the results are outside of the control limits, rinse electrodes and repeat analysis. If results are still outside of the control limits, recollect samples and repeat analysis. If the results are still outside of the control limits, check calibration and recalibrate if necessary (see item 2, below). If drift is suspected to be the cause of

the problem, clean the electrode and recalibrate. If drift is still apparent, replace electrode.

2. Calibration check results must be ±0.10 pH unit of the true value. If the result is outside of ±0.10 pH unit, rinse electrodes and check solution again. If still outside the control limit, recalibrate the meter and reanalyze all samples analyzed since the last in-control calibration.

3. All glassware is to be soap and water washed, tap water rinsed and distilled or deionized water rinsed prior to analyses.

Interferences:

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

SPECIFIC CONDUCTANCE

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

Method: Specific Conductance

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

Sensitivity: 0.1 mmhos/cm

Optimum Range: 0 - 100.0 mmhos/cm

Sample Handling; Determine on site

Reagents and Apparatus:

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

Notes:

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

Calibration Check

Connect the cell and the Temperature Probe, and remove them from the sample chamber. Set the conductivity function switch to 2 ATC. Rinse the inside and outside of the cell and the probe with about 1/3 the calibration solution. Place both of the sensors into the remainder of the solution in the bottle and allow them to come to temperature equilibrium. Make sure that the body is immersed so that the liquid level is half way up the knurled portion of the cell. Read the displayed value and determine if the cell/instrument is within specified accuracy. The displayed value is corrected to 25°C automatically and should be 1.000 ±070 mmho/cm. If the value is not within specification replace cell.

Procedure:

1. Check calibration of meter.

2. Set up meter as outlined in the operating manual.

3. Before any conductivity cell is used, it should be soaked in distilled or deionized water for at least one hour. To make conductivity measurements, connect a YSI Flow-Through Conductivity Cell to the monitoring system. Set the conductivity function switch to 2 and observe the displayed value after the reading is stable. The display reads out in mmho/cm.

4. If the overrange signal (1._____) is displayed, the conductivity of the water being measured is greater than 1.999 mmho/cm. Reset the function switch to 20. If the overrange signal is still displayed, reset to 100. If the overrange signal is still displayed, either the conductivity is greater than 100.0 mmho/cm and the YSI Water Quality Monitor can not be used for conductivity determinations.

5. Record conductance readings in field logbook.

6. Repeat steps 3 through 5 for remaining samples.

Quality Control:

1. The quality control calibration check standard must be analyzed initially, after every 10 or fewer samples and after the last sample. If less than 10 samples are analyzed, the calibration standard is still required to be analyzed. The standard must be within ±10 percent of the true value or the samples run after the last acceptable check standard are to be reanalyzed. Record the calibration standard in the field logbook.

2. Duplicate a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate is still required. Duplicate values are to be within ±15% of each other. If outside of this range, reanalyze the samples. If still outside the acceptance range, recollect sample and reanalyze. If still out, replace probe.

SOIL VOC SCREENING

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

Method: Photoionization

Sensitivity: Approximately 0.5 ppm depending on background

Optimum Range: Background to 2,000 ppm

Sample Handling: Determined on site

Reagents and Apparatus:

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

Calibration:

A) Calibration of the HNu

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

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

   Turn the function switch to the STANDBY position.

2. With the SPAN setting and the function switch at the same positions as listed in the Application Data Sheet or Calibration Report, open the valve on the cylinder until a steady reading is obtained.

3. If the reading is the same as the recorded data, the analyzer calibration for the original species of interest is still correct.

4. If the reading has changed, adjust the SPAN setting until the reading is the same.

5. Shut off the cylinder as soon as the reading is established.

6. Record and maintain this new SPAN setting.

7. Background organic vapor readings should be measured prior to any soil screening.

B) Calibration of MicroTip

1. Connect the supplied regulator to the span gas cylinder. Hand tighten the fittings. Observe proper handling techniques for all gases.

2. Open the valve on the gasbag by turning the valve stem fully counterclockwise.

3. Attach the nut to the regulator. Hand tighten the fittings.

4. Turn the regulator knob counterclockwise about half a turn to start the flow of gas.

5. Fill the gasbag about half full and then close the regulator fully clockwise to turn off the flow of gas.

6. Disconnect the bag from the adapter and empty it. Flush the bag a few times with the span gas and then fill it.

7. Close the gasbag by turning the valve clockwise.

8. Press SETUP and select the desired Cal Memory with the arrow keys and press ENTER. Press EXIT to leave Setup.

9. Press CAL and enter the desired response factor. Use Table 2 from the manual to find the correct response factor. If the compound is not in Table 2 or you are not looking specifically for one compound then enter 1.00.

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

10. Expose MicroTIP to zero air. Press ENTER and MicroTIP sets its zero point.

11. MicroTIP then asks for the span gas concentration. Enter the known span gas concentration and then connect the span gas bag adapter to the inlet.

12. Press ENTER and MicroTIP sets its sensitivity.

13. When MicroTIP's display reverts to normal, MicroTIP is calibrated and ready for use. Remove the span gasbag from the inlet.

Procedure:

1. Calibrate meter using the correct calibration procedure for the meter used.

2. The samples for VOC headspace screening will be prepared in the field by filling a 4-ounce soil jar to one-half its volume and sealing with a teflon-lined closure. The remaining sample will be placed in the appropriate jars for the analyses required.

3. Allow the sample for VOC headspace screening to remain at ambient temperature for a minimum of 10 minutes. This will allow for VOCs in the soil to reach equilibrium in the headspace of the jar.

4. Remove the lid of the soil jar slightly and insert the probe of the meter into the headspace.

5. Take the highest reading from the meter or readout of the instrument.

6. Record the reading in the field logbook.

7. Recheck calibration with calibration gas after a minimum of every 10 samples and after the last sample.

Quality Control:

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

2. Duplicate samples are not analyzed since the headspace VOC readings will vary considerably as the soil VOCs volatilize.

Interferences and Limitations:

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

ATTACHMENT 2

LABORATORY ANALYTICAL STANDARD OPERATING PROCEDURES

ATTACHMENT 2

LABORATORY ANALYTICAL STANDARD OPERATING PROCEDURES

Title	SOP ID
A. Organic Procedures	
1. Determination of Volatile Organics by GC/MS Based on Method 8260B, 8260A, and 624	CORP-MS-0002NC
2. Extraction and Cleanup of Organic Compounds from Waters and Soils, Based on SW-846 3500 Series, 3600 Series, 8151A and 600 Series Methods	CORP-OP-0001NC
3. Gas Chromatographic Analysis Based on Method 8000B, 8021B, 8081A, 8082, 8151A, 8310, 8141A, 8015B, 608, 610 and Wisconsin DNR Modified DRO Method	CORP-GC-0001NC
4. GC/MS Analysis Based on Methods 8270C and 625	CORP-MS-0001NC
5. Analysis of Dissolved Gases in Groundwater by Modified Method RSK-175	NC-GC-0032
6. Volatile Petroleum Hydrocarbons as Gasoline by Purge and Trap Gas Chromatography	NC-GC-0025
7. Determination of Low-Level Volatile Organics (VOCS) in Ambient Air by GC/MS - Scan Mode using EPA Methods TO-14A & TO-15	COI-MS-007
B. Metals Procedures	
1. Acid Digestion of Soils, SW 846 Method 3050B	CORP-IP-0002NC
2. Acid Digestion of Aqueous Samples by SW 846 and MCAQQ 200 Series Methods	CORP-IP-0003NC
3. Inductively Coupled Plasma-Atomic Emission Spectroscopy, Spectrometric Method for Trace Element Analyses, SW-846 Method 6010B and EPA Method 200.7	CORP-MT-0001NC
4. Inductively Coupled Plasma-Mass Spectrometry, EPA Methods 6020 and 200.8	NC-MT-0002

ATTACHMENT 2

LABORATORY ANALYTICAL STANDARD OPERATING PROCEDURES

Title	SOP ID
5. Preparation and Analysis of Mercury in Aqueous Samples by Cold Vapor Atomic Absorption, SW846 7470A and MCAQQ 245.1	CORP-MT-0005NC
6. Preparation and Analysis of Mercury in Solid Samples by Cold Vapor Atomic Absorption Spectroscopy, SW846 7471A and MCAWW 245.5	CORP-MT-0007NC
C. Inorganic Procedures	
1. Carbonate, Bicarbonate, Hydroxide Alkalinity	NC-WC-0003
2. Determination of Inorganic Anions by Ion Chromatography	NC-WC-0084
3. Total Hardness (MG/L $CACO_3$), Titrimetric	NC-WC-0036
4. Sulfide	NC-WC-0060
5. Total Organic Carbon (TOC) and Total Inorganic Carbon (TIC)	NC-WC-0017
D. Waste Characterization Procedures	
1. Toxicity Characteristic Leaching Procedure and Synthetic Precipitation Leaching Procedure	CORP-IP-004NC
2. Reactive Cyanide	NC-WC-0033
3. Reactive Sulfide	NC-WC-0061
4. Flashpoint Closed Cup	NC-WC-0034
5. pH Electrometric Method	NC-WC-0010

SEVERN TRENT SERVICES

STL Los Angeles

SOP No. COI-MS-0007
Revision No. 1
Revision Date: 03/15/01
Effective Date: 04/01/01
Page: 1 of 24

STANDARD OPERATING PROCEDURE

TITLE: DETERMINATION OF LOW-LEVEL VOLATILE ORGANICS (VOCS) IN AMBIENT AIR BY GC/MS - SCAN MODE USING EPA METHODS TO-14A & TO-15

(SUPERSEDES: COI-MS-0007 REV. 0)

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1. SCOPE AND APPLICATION

1.1. This method is applicable to the GC/MS determination of low-level volatile organic compounds (VOCs) in ambient air samples collected in SUMMA canisters or Tedlar Bags. This method is based on EPA methods TO14A and TO15.

1.2. Target analytes and reporting limits are listed in Table 1.

1.3. Applicable matrices - air, vapor

2. SUMMARY OF METHOD

2.1. An air sample and internal standards are metered through a mass flow controller and concentrated onto a cryogenically cooled glass bead trap. The trap is heated and the contents are transferred to a Tenax trap to remove water. The Tenax trap is heated and the analytes are transferred to a cryofocusing module. The cryofocuser is heated to transfer the analytes to the CG column for separation and detection by a mass spectrometer operated in the SCAN mode.

3. DEFINITIONS

3.1. Batch

An analytical batch is defined as a set of 20 or fewer samples of the same matrix processed using the same procedures and reagents within the same time period. A batch must contain a Laboratory Control Sample (LCS), a laboratory control sample duplicate (LCSD), and a method blank. Refer to the STL LQM for further details of the batch definition.

3.2. Method Blank

A method blank consisting of all reagents added to the samples must be analyzed with each batch of samples. The method blank is used to identify any background interference or contamination of the analytical system that may lead to the reporting of elevated concentration levels or false positive data.

3.3. Laboratory Control Samples (LCS/LCSD)

Laboratory control samples are laboratory-generated samples used to monitor the laboratory's day-to-day performance. 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. LCS is prepared from a source independent of the calibration standards. LCS spiking compounds are listed in Table 1.

3.4. Surrogates

Surrogates are organic compounds which are similar to the target analytes in chemical composition and behavior in the analytical process, but which are not normally found in environmental samples. Each sample, blank, and LCS is spiked with surrogate standards. Surrogate spike recoveries may be evaluated against project specific requirements by determining whether the concentration (measured as percent recovery) falls within the required limits. Surrogate compounds are listed in Table 1.

3.5. Reporting Units

Routinely, calibration and sample results are calculated in part-per-billion volume/volume [ppb (v/v)] units. Client-specific requirements may require conversion to mass/volume units.

4. INTERFERENCES

4.1. Gas regulators are cleaned by the manufacturer using Freon 113, which is one of the target compounds. Before using ultra high purity (UHP) Nitrogen (N_2), Hydrocarbon (HC) free air, Internal Standard (IS), or a target compound standard mix, each regulator should be purged a minimum of three times with the appropriate gas.

4.2. Contamination may occur in the sampling system if canisters are not properly cleaned prior to use. Canisters should not be used for the collection of samples until a batch blank analysis indicates that no target compounds are present above the reporting limit, or a level previously agreed upon by STL and the Client. (Further information regarding the cleaning and certification of canisters can be found in the SOP COI-QA-0005) All other sampling equipment including pumps, flow controllers and filters must be thoroughly cleaned to ensure that the filling apparatus will not contaminate samples.

4.3. Carry over may occur when samples with high levels of contaminants are analyzed. The sample immediately following a high level sample should be reanalyzed if carryover is suspected.

4.4. Tedlar bags may contain low levels of target analytes.

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 should 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. 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. 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. At no time should SUMMA canisters be pressurized over 30 psig.

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

6. EQUIPMENT AND SUPPLIES

6.1. Gas chromatograph - capable of subambient temperature programming and electronic pressure control.

6.2. Mass-selective detector - equipped with computer and appropriate software (Hewlett Packard 5972/5973)

6.3. Sample concentrator – equipped with a cryogenic trap and appropriate systems for the control of moisture (Entech 7000 or equivalent)

6.4. Electronic mass flow controller – device used to accurately meter gas flow in sample concentrators.

6.5. Chromatographic grade stainless steel or nickel tubing and stainless steel plumbing fittings.

6.6. Chromatographic column – Rtx-Volatiles, 0.32 mm ID, 1.5um df, 60 meter length, methyl polysilicate liquid phase (Restek Corporation) or equivalent.

6.7. Stainless steel vacuum/pressure gauge capable of measuring from 30" of mercury (Hg) to 40 psig (Span Instruments) or equivalent.

6.8. High precision vacuum gauge - for making daily standards. (Wallace & Tiernan Pennwalt)

6.9. Pressure regulators for carrier gas and standards - 2 stage, stainless steel diaphragm (single stage acceptable for standards).

6.10. SUMMA passivated canisters 6 L or 15 L (Scientific Instrumentation Specialists, Anderson Instruments) or equivalent.

6.11. 7 micron filters (Nupro), or equivalent.

6.12. Variable Flow Regulator (VFR) – used during composite air sampling with SUMMA canisters.

6.13. Tedlar Bag – an inert plastic like bag used as an alternative to SUMMA canisters for sample collection.

6.14. Diaphragm type vacuum pump to draw sample through mass flow controller.

7. REAGENTS AND STANDARDS

7.1. Reagents

7.1.1. High purity (UHP) Nitrogen. UHP Nitrogen is used for method blanks and making dilutions of samples and standards. All method blanks are humidified with 50ul of distilled water.

7.1.2. UHP Helium used as the GC carrier gas.

7.1.3. Pressurized air source for Entech 7000 heater gas.

7.2. Standards

7.2.1. Gas calibration stock standards containing the target compounds are purchased from commercial sources or prepared from neat in SUMMA canisters. Suppliers are required to provide certification of the analyte concentrations.

7.2.2. Internal/surrogate stock standard mix at 250 ppbv. See tables 1 and 7 for surrogates and internal standard compound list.

7.2.3. Expiration dates for standards and reagents are based on vendor specification. Expiration dates must be documented on the gas cylinders.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Samples should be collected in precleaned and batch analyzed SUMMA passivated canisters. A 7-micron filter should be placed on the inlet of the can to protect the valve from particulates. Canisters should never be pressurized over 40 psig.

8.2. The absolute pressure of the canister should be recorded before and after sample collection. See Section 11.3.1 for sample preparation.

8.3. Samples must be kept within the temperature range of 20 to 30 °C.

8.4. Tedlar bag samples should be protected from sunlight.

8.5. Canister samples should be analyzed within 30 days of collection.

8.6. Tedlar Bag samples should be analyzed within 3 days of collection.

9. QUALITY CONTROL

9.1. Demonstration of Capability

9.1.1. STL Los Angeles will 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 specified in 40 CFR part 136, Appendix B, and further defined in QA Policy #QA-005.

9.1.2. In addition to the MDL study, the laboratory must complete the analysis of four LCSs (or 2 sets of LCSD) with acceptable accuracy and precision for each analyte.

9.1.3. For non-standard analytes, an MDL study can be performed and calibration curve generated prior to sample analysis, unless lesser requirements are acceptable to the client. The minimum initial demonstration required is analysis of a single point calibration.

9.2. Control Limits

If the reference methods do not specify accuracy and precision limits, in-house historical control limits must be generated for surrogates and the LCS results. These limits should be updated at least annually. The recovery limits are determined as the mean recovery plus or minus three standard deviations for surrogates and LCS.

9.3. Surrogates

Surrogate recoveries in samples, blanks and QC samples may be assessed to ensure that recoveries are within established limits. If any surrogates are outside limits and if surrogates are a project-specific requirement, the following corrective actions must take place:

- 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.
- 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 reanalyze a sample once to demonstrate that poor surrogate recovery is due to matrix effect, unless the analyst has reason to believe that the repeated out of control results are due to problems other than matrix effect.

9.4. Method Blanks

For each batch of samples an acceptable method blank must be analyzed. The method blank is analyzed after the calibration standards and LCS prior to sample analysis. 6-liter blank cans are humidified with 50ul of water and carried through the entire analytical sequence.

9.4.1. The method blank must not contain any analyte of interest above the reporting limit. A method blank that does not meet this criterion must be reanalyzed unless no reportable concentrations of target analytes are present in the associated samples.

9.4.2. If surrogates are a project-specific requirement then 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, reanalysis of the blank and affected samples will normally be required. Consultation with the client should take place.

9.5. Laboratory Control Samples (LCS/LCSD)

For each batch of samples an LCS/LCSD pair must be analyzed. The LCS/LCSD is analyzed after the calibration standard and before the method blank and samples. The LCS should contain a representative subset of the analytes of interest (See Table 1) although client specific requirements may require additional compounds. If any analyte is outside the established control limits, the analysis is out of control and corrective action must be taken. Corrective action will normally be reanalysis of the batch. LCS compounds and acceptance criteria are given in Table 1.

- If the batch is not reanalyzed the reasons for accepting the batch must be clearly stated in the case narrative.

- If the analytes in the LCS exceed the upper control limit and no analytes are detected in any of the samples; they may be reported without qualification. Positive bias is not expected to impact ND results.

9.6 Internal standard

The internal standard (IS) areas are monitored for each shift by comparing the IS areas in each sample with those of the associated Continuing Calibration Verification Standard (CCV). Sample IS areas are considered acceptable if they fall between ±40% of the CCV IS areas for TO-15 and –50% to +100% for TO-14A low level. Any sample exceeding this criterion must be reanalyzed. If the IS area(s) fails upon reanalysis, it is documented in a Non-Conformance Memo (NCM) and discussed in the report narrative. Internal standards are listed in Table 7.

10. CALIBRATION AND STANDARDIZATION

10.1. Prior to the analysis of samples and blanks, each GC/MS system must be tuned and calibrated. Hardware tuning is checked to establish that the system meets the standard mass spectral abundance criteria. This is done through the analysis of 50ng of BFB and must meet the acceptance criteria listed in tables 3 or 4.

10.2. Standard Preparation

Static dilutions of the stock standard gas mixtures is made in 6 or 15 liter summa canisters to create working standards. A high precision vacuum gauge is flushed with UHP Nitrogen and attached to the top valve of a clean, evacuated canister, and the absolute pressure is recorded. Depending on the concentration of each stock standard gas mixture, a particular pressure of each is added to the canister to achieve the desired concentration in the working standard. Care should be taken to flush each regulator and transfer line with standard prior to transfer to the canister. After all the stock standard mixes are added the standard canister is pressurized with UHP nitrogen to achieve the appropriate concentration.

Currently the daily standard has a nominal concentration of 25ppbv and is created by adding 1 psia each of the two 1 ppmv stock standard mixes and adding UHP nitrogen to the canister to achieve a final pressure of 40 psia.

10.3. Initial Calibration and Continuing Calibration Verification

10.3.1. An initial calibration curve consisting of a minimum of 5 points (ICAL) is analyzed to determine the linear working range of the system for each compound. An average response factor (RF) and per-cent relative standard deviation (%RSD) are calculated for each target analyte using the calculation in section 12. The ICAL is considered acceptable if less than 90% of the target analytes have a %RSD less than or equal to 30% and the average of the %RSD for all target compounds is less than 30%. All compounds must have a relative response factor greater than or equal to 0.05.

10.3.2. The nominal concentrations of the standards are typically 0.2, 0.4, 1.25, 5.0, 10 and 50 ppbv. The standards are run by varying the trapped volume of the two working standards from the "default" volume of 250 ml. For example, the 0.2, 0.5, and 1.25 ppbv standards are analyzed by trapping 40, 100 and 250 ml of a 1.25 ppbv-working standard.

10.3.3. Each new five-point ICAL must be verified using a second source standard, if available. Since the regulatory agencies have not provided guidance on second source verification, the following acceptance criterion is typically used: ± 35% for target analytes with warning limits of ± 35 - 55% for poor performers. These limits are provided as guidance. If this criterion is not met: (1) rerun the second source check standard, (2) reprepare or acquire new standard, (3) evaluate instrument conditions, and (4) regenerate a new ICAL.

10.3.4. Analyte quantitation must be performed off the initial calibration and not from daily continuing calibration standard analysis. Test results must be qualified in reports when analyte quantitation is based on the CCV at the client's request.

10.3.5. For each QC batch or every 24 hours of operation, a Continuing Calibration Verification Standard (CCV) is analyzed to verify the ICAL average RF. The percent difference (%D) of the CCV RF from the ICAL average RF is calculated for each compound. The CCV is considered acceptable if less than 90% of the target analytes have a %D less than or equal to 30% and the average of the %D for all target compounds is less than 30%. If the criteria are not met the CCV or the ICAL must be reanalyzed prior to sample analysis.

10.3.5.1. For projects requiring NELAC accreditation, the concentration for the CCV standard must be varied within the working range of the initial instrument calibration. This will be done at least once per year.

11. PROCEDURE

11.1. Procedural Variations

Any variation must be completely documented using the nonconformance database (Clouseau) and shall be approved by the Supervisor, PM, and QA Manager.

11.2. Sample Analysis Procedure

All analysis conditions for samples must be the same for the CCV, including flow rates, desorb time and temperature, column temperatures, multiplier setting etc.

11.3. Sample Preparation

11.3.1. The initial pressure of the sample canister is checked and recorded by attaching a vacuum/pressure gauge to the canister. The gauge should be rinsed before use with zero grade nitrogen by physically holding against the air outlet and flushing for a few seconds. If the pressure is less than approximately 6 psig, pressurize the canister to 10 psig with zero grade nitrogen and record the final pressure. Pressures should be recorded in the sample pressurizing log and on the individual canister field sheets.

11.3.2. If the canister pressure is increased, a dilution factor (DF) is calculated and applied to results:

$$DF = \frac{Y_a}{X_a}$$

Where:

X_a = *absolute canister pressure before dilution (initial pressure)*
Y_a = *absolute canister pressure after dilution (final pressure)*

The pressure dilution factor (pDF) must be compensated for by trapping more sample. For example a sample received at 12.0 psia and pressurized to 24.6 psia has a pDF of 2.05. If the default volume is 250 ml, then 513ml should be trapped (the volume is rounded up to three significant figures).

11.3.3. If it is suspected that a sample may contain significant contamination, the canister is screened using GC/FID analysis or other screening method to determine a proper dilution. A sample that requires only a small dilution can be analyzed by trapping a volume less than the standard volume. The minimum volume that can be trapped is 40ml. Larger dilutions will require the transfer of an aliquot of sample to a Tedlar bag and diluting with UHP nitrogen. Bag dilutions should be analyzed within 24 hours. Dilution to Tedlar bag can be used for reporting the analytes that exceed calibration range in the original analysis but not as a single reportable analysis due to low level contamination in Tedlar bag.

11.3.4. If non-standard reporting limits are required, the standard sample volume can be adjusted. The maximum trapped volume is 1500ml.

11.4. Initial/Daily GC/MS Tuning

11.4.1. At the beginning of each 24-hour shift, prior to any analytical runs, the GC/MS system must be verified that acceptable tune performance criteria are achieved. If any of the key ions fail the abundance criteria listed in tables 5 or

6, the system is considered out of tune and any subsequent sample/standard analysis should be considered unacceptable.

11.4.2. Using the BFB method in the cryotrap software trap the internal standard mixture volume required to put 50ng of BFB on column (currently 28ml of 250 ppbv standard). The MS software will evaluate the average of the spectra of the peak apex and the scans immediately before and after.

11.5. Analysis

11.5.1. Each canister is attached to the autosampler (A/S) and recorded in the instrument logbook. A sequence is created in the GC/MS software to prepare the instrument for data acquisition. The sequence information controls the GC/MS method, data file creation, sample parameters, and report output. A second sequence must be created in the A/S control software to control the sampling process, such as, line position, sample volume, trap temperatures, flow rates, and times.

11.5.2. The valves are opened on all canisters and the A/S and GC/MS sequences are started.

11.5.3. For routine analysis the A/S will follow this sequence of events:

- Glass bead trap (Module 1) cooled to –150C.
- Trap internal standard.
- Trap sample.
- The Tenax trap (Module 2) is cooled to –10 C and the glass bead trap is heated. The sample is transferred to Module 2 by passing helium through Module 1. This step is designed to remove water from the sample.
- When GC is ready, the cryofocuser (Module 3) is cooled to –150 C. Module 2 is heated. The sample is transferred to Module 3
- Module 3 is heated and the GC/MS column flow is routed through Module 3 to inject the sample and begin the run.
- The system is pre-flushed with the next sample and the system is baked to limit carryover.

11.5.4. Upon completion of the analytical sequence, the concentrator generates a QA/QC report that records data from the sampling event (i.e. actual volume trapped, temperature at the time of trapping, sample pressure, etc.)

12. DATA INTERPRETATION

12.1. Qualitative Analyses

12.1.1. Two criteria must be satisfied to verify positive identification: (1) Elution of sample component at the same GC relative or absolute retention time as those of the standard component and (2) correspondence of the sample component and the standard component mass spectra.

12.1.1.1. The sample component relative retention time (RRT) must compare within ± 0.06 RRT units of the RRT of the standard component. As an option, RT must compare within 0.33 minutes of the standard component absolute retention time (RT). For reference, the RT standard must be run within the same 24-hour shift as the sample.

12.1.1.2. (1) All ions present in the standard mass spectra at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100%) must be present in the sample spectrum. (2) The relative intensities of ions specified in (1) must agree within plus or minus 30% between the standard reference and sample spectra. (Example: For an ion with an abundance of 50% in the reference spectra, the corresponding sample abundance must be between 20 and 80 percent.

12.1.1.3. If a compound cannot be verified by all of the criteria in the above paragraphs but in the technical judgment of the analytical chemist the identification is correct, then the compound may be reported.

12.1.2. Tentatively Identified Compounds (TICs)

12.1.2.1. 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 analysis being conducted. 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 ± 30%. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 20 and 80%).

- 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 co-eluting 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.

- Only peaks having a total ion current greater than 10% of the nearest eluting Internal Standard total ion current will be evaluated for reporting.

12.1.2.2. Semi-quantitative results will be calculated for tentatively identified compounds using total ion current areas and assuming a relative response factor of 1.0.

12.1.2.3. 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 with the nearest library searches will the mass spectral interpretation specialist assign a tentative identification.

12.2. Quantitative Analysis:

12.2.1. When a compound has been identified, the quantification of that compound will be based on the integrated abundance from the EICP of the primary characteristic ion. Quantification will take place using the internal standard technique. A summary table of primary and secondary ions for target

compounds and internal standards is listed in Table 4. The calculation for quantitation of sample is found in section 12.3.

12.3. Calculations

12.3.1. The HP data system automatically quantitates the sample results based on a "standard" sample size of 250 ml. The default result units are in ppbv. If a sample size other than 250 ml was used and/or a canister sample was pressurized, the result must be adjusted as shown below:

$$Final\ result\ ppbv = raw\ result ppbv X \frac{250mL}{sample volume injected} X \frac{final psia}{initial psia}$$

12.3.2. Calculation for Relative Response Factor (RRF):

$$RRF = \frac{Area\ cpd\ in\ Std.}{Area\ I.S.} X \frac{Conc.\ I.S.}{Conc.\ cpd\ in\ Std.}$$

The area of the primary quantitation ion is used in the calculation.
I.S.: Internal Standard

12.3.3. Calculation for Percent Relative Standard Deviation (%RSD):

$$\%RSD = \frac{Std.\ Dev.\ of\ RRFs}{Mean\ of\ RRFs} X 100$$

12.3.4. Calculation for Percent Difference (%D):

$$\%D = \frac{Average\ RRF\ from\ initial\ curve\ RRF\ cpd.}{Average\ RRF\ from\ initial\ curve} X 100$$

12.3.5. Calculation for Determining Concentration of Compounds:

$$Conc.Cpd(ppbv) = \frac{Area cpd in sample}{Area I.S. in sample} X \frac{Conc.I.S.}{RRF ICAL.} X Dil.Factor$$

The area of the primary quantitation ion is used in the calculation.
I.S.: Internal Standard

12.3.6. Calculation for Percent Recovery (%Rec):

$$\%\,Rec = \frac{Amount\ cpd.\ recovered}{Amount\ cpd.\ spiked} X 100\%$$

12.3.7. Calculation for Relative Percent Difference (RPD):

$$RPD = \frac{Value\ A - Value\ B}{Average\ of\ Values} X 100$$

13. REPORTING

13.1. Standard reporting units are ppb v/v. If results are to be reported in ng/L or ug/m^3 use the following equation:

$$result\ ppbv\ X \frac{Molecular\ weight\ of\ compound}{24.5} = results\ ng/L\ or\ ug/m^3$$

Note: 24.5 is the molar volume of ideal gas at 25° Centigrade and 1 atm.

13.2. Reporting limits

13.2.1. See Table 1. All reporting limits and MDLs must be derived on GC/MS systems at the STL laboratory and are updated annually.

13.2.2. "J" values (results below the normal reporting limit but above the MDL) are reported on request only.

13.3. Significant figures

13.3.1. All results should be reported to two significant figures.

13.4. No conversion of the analytical results to standard conditions is made.

14. METHOD PERFORMANCE

14.1. Method performance is controlled through the measurement of accuracy and precision. Analysis of a LCS and LCSD are preformed to measure both accuracy and precision. The control limits established for the LCS and LCSD are used to maintain method performance within a well-defined set of criteria.

14.2. Monitoring of background contamination by the analysis of method blanks, trip blanks, and system blanks is also critical to method performance.

15. POLLUTION PREVENTION & WASTE MANAGEMENT

15.1. Ambient air analysis does not generate any solid or liquid hazardous waste.

16. REFERENCES

16.1. Method Source

16.1.1. "EPA Compendium Method TO-14A. Determination of Volatile Organic Compounds (VOCs) in Ambient Air using Specially Prepared Canisters With Subsequent Analysis Gas Chromatographic Analysis." January 1999.

16.1.2. "EPA Compendium Method TO-15. The Determination of Volatile Organic Compounds (VOCs) in Air Collected in Specially-Prepared Canisters and Analyzed by Gas Chromatography/Mass Spectrometry (GC/MS)." January 1999.

16.2. Laboratory Quality Manual (LQM), current revision.

16.3. Deviations from Method

16.3.1. Nitrogen is used for dilution/pressurization purposes.

16.3.2. TO-14A describes the use of a Nafion dryer to remove excess moisture from air matrices. STL does not use a Nafion dryer since polar compounds may be lost during this removal step.

16.3.3. TO-14A and TO-15 describe the use of SUMMA passivated steel canisters for sampling and analysis. No mention is made of Tedlar sampling bags. STL analyzes samples in Tedlar bags for VOCs using the same procedures described herein. A modification to the method is noted in the narrative of the final report.

16.3.4. TO-15 describes a shelf life of thirty days for Primary working standards. STL maintains these standards for longer periods of time as determined by the manufacturer's recommendation and the results of stability monitoring.

16.3.5. The methods indicate that for initial and continuing calibrations all samples must have a %RSD and %D less than or equal to 30%. STL Los Angeles uses criteria of 90% of compounds and the average less than or equal to 30% for the ICAL and the 90% of compounds and the average %D less than or equal to 30% for the CCV. This is to account for analytical issues that arise for poor performing analytes.

16.3.6. TO-15 sets method performance criteria of accuracy of plus or minus 30% and precision less than or equal to 25%. STL uses project-specific QC criteria or control limits bases on historical data.

17. MISCELLANEOUS (TABLES, APPENDICES, ETC.)

Table 1. VOC Target Compounds and Reporting Limits

Compound	RL ppb v/v	QC Limits (%R)	Precision (RPD)
Acetone	0.8		20
Benzene	0.2		20
Benzyl chloride	0.4		20
Bromodichloromethane	0.2		20
Bromoform	0.2		20
Bromomethane	0.2		20
2-Butanone (MEK)	1		20
Carbon disulfide	1		20
Carbon tetrachloride	0.2		20
Chlorobenzene	0.2		20
Dibromochloromethane	0.2		20
Chloroethane	0.4		20
Chloroform	0.2		20
Chloromethane	0.4		20
1,2-Dibromoethane (EDB)	0.2		20
1,2-Dichlorobenzene	0.2		20
1,3-Dichlorobenzene	0.2		20
1,4-Dichlorobenzene	0.2		20
Dichlorodifluoromethane	0.2		20
1,1-Dichloroethane	0.2		20
1,2-Dichloroethane	0.2		20
cis-1,2-Dichloroethene	0.2		20
trans-1,2-Dichloroethene	0.2		20
1,1-Dichloroethene*	0.2	80 - 130	20
1,2-Dichloropropane	0.2		20
cis-1,3-Dichloropropene	0.2		20
trans-1,3-Dichloropropene	0.2		20
1,2-Dichloro-1,1,2,2-tetrafluoroethane	0.2		20
Ethylbenzene	0.2		20

Compound	RL ppb v/v	QC Limits (%R)	Precision (RPD)
4-Ethyltoluene	0.4		20
Hexachlorobutadiene	0.4		20
2-Hexanone	0.4		20
Methylene chloride*	0.2	80 - 125	20
4-Methyl-2-pentanone (MIBK)	0.4		20
Styrene	0.2		20
1,1,2,2-Tetrachloroethane*	0.2	60 - 130	20
Tetrachloroethene	0.2		20
Toluene*	0.3	80 - 125	20
1,2,4-Trichlorobenzene	0.8		20
1,1,1-Trichloroethane	0.2		20
1,1,2-Trichloroethane	0.2		20
Trichloroethene*	0.2	80 - 135	20
Trichlorofluoromethane	0.4		20
1,1,2-Trichloro-1,2,2-trifluoroethane	0.4		20
1,2,4-Trimethylbenzene	0.4		20
1,3,5-Trimethylbenzene	0.4		20
Vinyl acetate	1		20
Vinyl chloride	0.2		20
m-Xylene & p-Xylene	0.5		20
o-Xylene	0.2		20
Xylenes (total)	0.5		20
4-Bromofluorobenzene**	--	70 - 130	--
1,2-Dichloroethane-d4**	--	70 - 130	--
Toluene-d8**	--	70 - 130	--

* LCS/LCSD Spiking compound

** Surrogate compound

TABLE 2. BFB GC Operating Conditions

Method file: TO14BFB

METHOD FILE LIST

Method file:		GC Type: 5890	Run type: SCAN,GC,E1	
		Column: Cap	Splitless: Yes	
Temperature:	Inj.P	Intfc	Source	
	150	280	NA	
GC/DIP		LEVEL A	LEVEL B	POST RUN
Temp 1	150	150	0.0	
Time 1	1.0	0.0	0.0	
Rate		11	0.0	
Temp 2		210	0.0	
Time		2.5	0.0	

Oven equilibration Time. 0 min

Run time: ~9 mins
Scan Start time 8 mins

Scan Parameters:	Mass Range:	34 to 300		
	Multiplier voltage:	varies	Number of samples:	2
	Threshold:	150 counts		

TABLE 3. GC Analytical Method

Method file: LOWTO14

METHOD FILE LIST

Method file:		GC Type: 5890 Column: Cap	Run type: SCAN,GC,E1 Splitless: Yes	
Temperature:	Inj.P 150	Intfc 280	Source NA	
GC/DIP		LEVEL A	LEVEL B	POST RUN
Temp 1	35	35		
Time 1	5.5	0.0		
Rate		11		
Temp 2		210		
Time		7.6		

Oven equilibration Time. 0 min

Run time: ~29 mins
Scan Start time 3.8 mins

Scan Parameters:	Mass Range:	34 to 300		
	Multiplier voltage:	varies	Number of samples:	2
	Threshold:	150 counts		

TABLE 4. VOC Key Ions

Compound	Primary	Secondary		
Bromochloromethane I.S. #1	49	130	128	
Dichlorodifluoromethane (Freon 12)	85	87,	50	
Chloromethane	50	52		
1,2-Dichloro-1,1,2,2-tetrafluoroethane (Freon 114)	85	135	87	
Vinyl Chloride	62	64		
Bromomethane	94	96,	79	
Chloroethane	64	66,	49	
Trichlorofluoromethane (11)	101	103	66	
1,1-Dichloroethene	61	96,	63,	
Carbon Disulfide	76	78,		
1,1,2-Trichloro-1,2,2-trifluoroethane (Freon 113)	151	101	103	
Acetone	43	58		
Methylene Chloride	49	84	86	
trans-1,2-Dichloroethene	96	61,	98,	
1,1-Dichloroethane	63	65,	83	
Vinyl Acetate	43	42	86,	
cis-1,2-Dichloroethene	96	61,	98,	
2-Butanone	72 *	57,	43	
Chloroform	83	85,	47	
1,1,1-Trichloroethane	97	99,	61	
Carbon Tetrachloride	117	119	121	
1,4-Difluorobenzene I.S. #2	114	63,	88	
Benzene	78	50,	52,	
1,2-Dichloroethane	62	64,	49,	
Trichloroethene	130	95,	132	
1,2-Dichloropropane	63	62,	39	
Bromodichloromethane	83	85,	129	
cis-1,3-Dichloropropene	75	77,	39	
4-Methyl-2-pentanone	43	58,	100	
Toluene	91	65,	92	
Chlorobenzene-d5 I.S. #3	117	54	82	
trans-1,3-Dichloropropene	75	77,	39	
1,1,2-Trichloroethane	97	83,	61	
Tetrachloroethene	166	164	131	
2-Hexanone	58	43	100	
Dibromochloromethane	129	127	131	
1,2-Dibromoethane	107	109	188	
Chlorobenzene	112	77,	114	

TABLE 4. VOC Key Ions

Compound	Primary	Secondary		
Ethylbenzene	91	106		
1,4-and 1,3-(p,m)Xylene	91	106		
1,2-(ortho)Xylene	91	106		
Styrene	104	78	103	
Bromoform	173	171	175	
1,1,2,2-Tetrachloroethane	83	85	60	
Benzyl Chloride	91	126	63	
4-Ethyltoluene	105	120	77	
1,3,5-Trimethylbenzene	105	120	77	
1,2,4-Trimethylbenzene	105	120	77	
1,3-Dichlorobenzene	146	148	111	
1,4-Dichlorobenzene	146	148	111	
1,2-Dichlorobenzene	146	148	111	
1,2,4-Trichlorobenzene	180	182	145	
Hexachlorobutadiene	225	227	223	

* Quant ion for 2-Butanone is different from those listed in Method TO-15. STL Los Angeles expects this ion to be subject to less interference.

Table 5. TO14A BFB 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	5.0 to 9.0% of mass 95
173	<2.0% of mass 174
174	>50% of mass 95
175	5.0 to 9.0% of mass 174
176	>95% but <101% of mass 174
177	5.0 to 9.0% of mass 176

Table 6. TO15 BFB Criteria

Mass	Ion Abundance Criteria
50	8.0 to 40% of mass 95
75	30 to 66% of mass 95
95	Base Peak, 100% Relative Abundance
96	5.0 to 9.0% of mass 95
173	<2% of mass 174
174	50 to 120% of mass 95
175	4.0 to 9.0% of mass 174
176	93% to 101% of mass 174
177	5.0 to 9.0% of mass 176

Table 7. Internal Standards

Bromochloromethane
1,4-Difluorobenzene
Chlorobenzene-d5

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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)

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1. SCOPE AND APPLICATION

This SOP describes procedures for analysis of organic analytes by Gas Chromatography (GC). The procedures are based on SW-846 methodology and are applicable for measurements made to comply with the Resource Conservation and Recovery Act (RCRA). Individual analytes and methods are described in the appendices. Appendices B, C, and E include criteria for the analysis of wastewater by Methods 608 and 610. Appendix G describes procedures for the analysis of petroleum hydrocarbons by SW-846 methodology and the Wisconsin DNR Modified DRO method. Appendix H includes criteria for the analysis of non-halogenated organic compounds by Method 8015B, Direct Injection. Appendix I describes the analysis of Phillips 66 analytes by Method 8015B.

2. SUMMARY OF METHOD

In general, semivolatile analytes in aqueous samples are prepared for analysis using continuous or separatory funnel liquid / liquid extraction or solid phase extraction (SOP # CORP-OP-0001NCNC) Solid samples are prepared using sonication, Soxhlet or pressurized fluid extraction (SOP # CORP-OP-0001NC). Volatile analytes are prepared for analysis using purge and trap methodology (Appendix A).

After the initial preparation step, the sample is introduced to the GC and concentrations of target analytes are measured by the detector response within a defined retention time window, relative to the response to standard concentrations. Internal or external standardization procedures are used as specified in the method appendices.

3. DEFINITIONS

Definitions of terms used in this SOP may be found in the glossary of the STL North Canton Laboratory Quality Manual (LQM), current version.

4. INTERFERENCES

Contamination by carryover can occur when a low concentration sample is analyzed after a high concentration sample. In addition, some purge and trap autosamplers are susceptible to port specific contamination. Co-elution of target analytes with non-targets can occur, resulting in false positives or biased high results. In particular, this is a problem with non-selective detectors such as the Flame Ionization Detector (FID). See the appendices for interferences specific to individual tests and suggested corrective actions.

5. SAFETY

5.1. Procedures shall be carried out in a manner that protects the health and safety of all STL North Canton associates. The following requirements must be met:

Eye protection that prevents spalsh, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have become contaminated will be removed and discarded; other gloves will be cleaned immediately. Refer to the STL North Canton Chemical Hygiene plan for a complete description of personal protection equipment.

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

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

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

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

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

6. EQUIPMENT AND SUPPLIES

An analytical system complete with a gas chromatograph is required. A data system capable of measuring peak area and/or height is required. Recommended equipment and supplies for individual methods are listed in each method appendix.

7. REAGENTS AND STANDARDS

7.1. Stock Standards

Stock standards are purchased as certified solutions or prepared from pure solutions. Stock standards for method 8021B are stored at -10 to -20°C. Other stock standard solutions are stored as recommended by the manufacturer. All stock standards must be protected from light. Stock standard solutions should be brought to room temperature before using.

Semivolatile stock standard solutions must be replaced after one year. Stock standards of gases must be replaced at least every week, unless the acceptability of the standard is demonstrated (Less than 20% drift from the initial calibration is an acceptable demonstration). Other volatile stock standards must be replaced every 6 months or sooner if comparison with check standards prepared from an independent source indicates a problem.

7.1.1. Expiration times for all standards are measured from the time the standard is prepared or from the time that the standard ampoule is opened, if the standard is supplied in a sealed ampoule. If a vendor-supplied standard has an earlier expiration date then that date is used.

7.2. Calibration Standards

7.2.1. Volatile Calibration Standards

The procedure for preparation of volatile standards is given in Appendix A.

7.2.2. Semivolatile Calibration Standards

Semivolatile calibration standards are prepared as dilutions of the stock standards. Surrogates and internal standards are used as specified in the method appendices. Semivolatile calibration solutions must be refrigerated at $\leq$6°C and protected from light. The standards must be replaced at least every six months or sooner if comparison with check standards indicates a problem.

7.3. Gases for carrier and make-up: Hydrogen, Helium, Nitrogen, Argon/Methane.

7.4. Quality control (QC) Standards

QC standards (matrix spiking and LCS standards) are prepared and stored in the same way as calibration standards. They must be made from a stock independent from the calibration standards.

8. SAMPLE PRESERVATION AND STORAGE

Semivolatile extracts must be refrigerated at $\leq$6°C and analyzed within 40 days of the end of the extraction. Volatile sample storage conditions and holding times are given in Appendix A.

9. QUALITY CONTROL

9.1. Initial Demonstration of Capability

9.1.1. For the standard analyte list, the initial demonstration and method detection limit (MDL) studies described in Section 13 must be acceptable before analysis of samples may begin.

9.1.2. For non-standard analytes, a MDL study must be performed and calibration curve generated before analyzing any samples, unless lesser requirements are previously agreed to with the client. In any event the minimum initial demonstration required is analysis of an extracted standard at the reporting limit and a single point calibration.

9.2. Batch Definition

Batches are defined at the sample preparation stage. Batches should be kept together through the whole analytical process as far as possible, but it is not mandatory to analyze prepared extracts on the same instrument or in the same sequence. Refer to the STL North Canton QC Program document (QA-003) for further details of the batch definition.

9.2.1. Quality Control Batch

The batch is a set of up to 20 samples of the same matrix processed using the same procedures and reagents within the same time period. The Quality Control batch must contain a matrix spike / spike duplicate (MS/MSD), a Laboratory Control Sample (LCS), and a method blank. Laboratory generated QC samples (Blank, LCS, MS/MSD) do not count towards the maximum 20 samples in a batch. Field QC samples are included in the batch count. In some cases, at client request, the MS/MSD may be replaced with a matrix spike and sample duplicate. If insufficient sample is available for an MS/MSD a LCSD may be substituted.

9.3. Control Limits

In-house historical control limits must be determined for surrogates, matrix spikes, and laboratory control samples (LCS). These limits must be determined at least annually. The recovery limits are mean recovery +/- 3 standard deviations, unless that limit is tighter than the calibration criteria, in which case limits may be widened. Refer to policy QA-003 for more details.

9.3.1. These limits do not apply to dilutions (except for tests without a separate extraction), but surrogate and matrix spike recoveries will be reported unless the dilution is more than 5X.

9.3.2. All surrogate, LCS, and MS recoveries (except for dilutions) must be entered into QuantIMS (when available) or other database so that accurate historical control limits can be generated. For tests without a separate extraction, surrogates and matrix spikes will be reported for all dilutions.

9.3.3. Refer to the QC Program document (QA-003) for further details of control limits.

9.4. Surrogates

All methods must use surrogates to the extent possible. Surrogate recoveries in samples and QC samples must be assessed to ensure that recoveries are within established limits. If any surrogates are outside limits, the following corrective actions must take place (except for dilutions):

- Check all calculations for error.
- Ensure that instrument performance is acceptable.
- Recalculate the data and/or reanalyze the extract if either of the above checks reveal a problem.

- Reprepare and reanalyze the sample or flag the data as "Estimated Concentration" if neither of the above resolves the problem. Repreparation is not necessary is there is obvious chromatographic interference.
- The decision to reanalyze or flag the data should be made in consultation with the client. It is only necessary to reprepare / reanalyze a sample once to demonstrate that poor surrogate recovery is due to matrix effect, unless the analyst believes that the repeated out of control results are not due to matrix effect.

9.4.1. If dual column analysis is used the choice of which result to report is made in the same way as for samples (Section 12.1.2) unless one column is out of control, in which case the in-control result is reported.

9.4.2. If the surrogates are out of control for the sample, matrix spike, and matrix spike duplicate, then matrix effect has been demonstrated for that sample and repreparation is not necessary. If the sample is out of control and the MS and/or MSD is in control, then repreparation or flagging of the data is required.

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

9.5. Method Blanks

For each batch of samples, analyze a method blank. The method blank consists of reagent water for aqueous semivolatile samples, and sodium sulfate for semivolatile soils tests (Refer to SOP No. CORP-OP-0001NCNC for details). For low level volatiles, the method blank consists of reagent water. For medium level volatiles, the method blank consists of methanol as described in Appendix A. Surrogates are added and the method blank is carried through the entire analytical procedure. The method blank must not contain any analyte of interest at or above the reporting limit (except common laboratory contaminants, see below) or at or above 5% of the measured concentration of that analyte in the associated samples, whichever is higher.

If the analyte is a common laboratory contaminant (methylene chloride, acetone, 2-butanone, phthalate esters) the data may be reported with qualifiers if the concentration of the analyte is less than five times the reporting limit. Such action must be taken in consultation with the client.

Re-extraction and reanalysis of samples associated with an unacceptable method blank is required when reportable concentrations are determined in the samples.

If there is no target analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. Such action should be taken in consultation with the client.

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

9.6. Instrument Blanks

9.6.1. An instrument blank must be analyzed during any 12-hour period of analysis that does not contain a method blank.

9.6.2. An instrument blank consists of the appropriate solvent with internal standards added. If internal standards are not used the surrogates should be added.

9.6.3. Control criteria are the same as for the method blank, except that only reanalysis of affected samples would be required, not re-extraction.

9.7. Laboratory Control Samples (LCS)

For each batch of samples, analyze a LCS. The LCS contains a representative subset of the analytes of interest, and must contain the same analytes as the matrix spike. The LCS may also contain the full set of analytes with a subset of control analytes. If any control analyte or surrogate is outside established control limits, the system is out of control and corrective action must occur. Corrective action will normally be repreparation and reanalysis of the batch; however, if the matrix spike and matrix spike duplicate are within limits; the batch may be acceptable.

9.7.1. Refer to the STL North Canton QC Program document (QA-003) for further details of the corrective action.

9.7.2. If dual column analysis is used the choice of which result to report is made in the same way as for samples (Section 12.1.2) unless one column is out of control, in which case the in control result is reported.

9.7.3. LCS compound lists are included in the appendices.

9.8. Matrix Spikes

For each QC batch, analyze a matrix spike and matrix spike duplicate. Spiking compounds and levels are given in the appendices. Compare the percent recovery and relative percent difference (RPD) to those in the laboratory specific historically generated limits.

- If any individual recovery or RPD falls outside the acceptable range, corrective action must occur. The initial corrective action will be to check the recovery of that analyte in the Laboratory Control Sample (LCS). Generally, if the recovery of the analyte in the LCS is within limits, then the laboratory operation is in control and analysis may proceed.
- If the recovery for any component is outside QC limits for both the Matrix spike / spike duplicate and the LCS, the laboratory is out of control and corrective action must be taken. Corrective action will normally include repreparation and reanalysis of the batch.
- If a MS/MSD is not possible due to limited sample, then a LCS duplicate should be analyzed.
- The matrix spike / duplicate must be analyzed at the same dilution as the unspiked sample, unless the matrix spike components would then be above the calibration range.

9.8.1. If dual column analysis is used the choice of which result to report is made in the same way as for samples (Section 12.1.2) unless one column is out of control, in which case the in control result is reported.

9.9. Quality Assurance Summaries

Certain clients may require specific project or program QC that may supersede these method requirements. Quality Assurance Summaries should be developed to address these requirements.

9.10. STL North Canton QC Program

Further details of QC and corrective action guidelines are presented in the STL QC Program document (QA-003). Refer to this document if in doubt regarding corrective actions.

10. CALIBRATION AND STANDARDIZATION

Internal or external calibration may be used. Internal calibration is recommended unless the sample matrix is likely to interfere with the quantitation of the internal standard. In either event prepare standards containing each analyte of interest at a minimum of five concentration levels. The low level standard should be at or

below the reporting limit. The other standards define the working range of the detector. Recommended calibration levels are given in the appendices.

10.1. A new calibration curve must be generated after major changes to the system or when the continuing calibration criteria cannot be met. Major changes include new columns, changing PID lamps or FID jets or replacing the ECD detector. A new calibration is not required after clipping the column, replacing the septum or syringe, or other minor maintenance.

10.2. With the exception of 10.3 below, it is NOT acceptable to remove points from a calibration curve for the purpose of meeting criteria, unless the points are the highest or lowest on the curve AND the reporting limit and/or linear range is adjusted accordingly. In any event, at least 5 points must be included in the calibration curve. Quadratic (second order) calibrations require at least six points. Third order calibrations require at least seven points.

10.3. A level may be removed from the calibration if the reason can be clearly documented, for example a broken vial or no purge run. A minimum of five levels must remain in the calibration. The documentation must be retained with the initial calibration. Alternatively, if the analyst believes that a point on the curve is inaccurate, the point may be reanalyzed and the reanalysis used for the calibration. All initial calibration points must be analyzed without any changes to instrument conditions, and all points must be analyzed within 24 hours.

10.4. External standard calibration

Quantitation by the external standard method assumes a proportional relationship between the calibration run and the analyte in the sample. To use this approach, introduce each calibration standard into the GC using the technique that will be used for samples. The ratio of the peak height or area response to the mass or concentration injected may be used to prepare a calibration curve.

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

Some data systems may use the inverse of this formula. This is acceptable so long as the same formula is used for standards and samples. It is also possible to use the concentration of the standard rather than the mass injected. (This would require changes in the equations used to calculate the sample concentrations). Use of peak area or height must be consistent. However, if matrix interferences would make quantitation using peak area inaccurate for a particular sample, then peak height may be used as a substitute.

10.5. Internal standard calibration

10.5.1. The internal standard approach assumes that variations in instrument sensitivity, amount injected etc. can be corrected by determining the ratio of the response of the analyte to the response of an internal standard that has been added to the extract. To use this approach, select one or more internal standard(s) that are similar in analytical behavior to the compounds of interest. Recommended internal standards are given in the appendices. The analyst must demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. If the sample matrix interferes with quantitation of the internal standard, then the external standard approach must be used instead. In this event use the response factors from the previous continuing calibration to quantitate the analytes in the sample with the interference (applies only to the sample with the interference).

10.5.2. Introduce each calibration standard into the GC using the technique that will be used for samples. Response factors (RF) for each compound are calculated as follows:

$$RF = \frac{As \times Cis}{Ais \times Cs}$$

Where:

A_s = Response for the analyte to be measured
A_{is} = Response for the internal standard
C_{is} = Concentration of internal standard
C_s = Concentration of the analyte to be determined in the standard

10.6. Calibration curve fits

Average response factor, linear regression, or quadratic curves may be used to fit the data. Average response factor may be used if the average % RSD of the response factors or calibration factors of all the analytes in the calibration standard taken together is ≤ 20%. The average %RSD is calculated by summing the RSD value for each analyte and dividing by the total number of analytes.

10.6.1. In general, for environmental analysis, average response factors are the most appropriate calibration model. Linear or curved regression fits should only be used if the analyst has reason to believe that the average RF model does not fit the normal concentration/response behavior of the detector.

10.6.2. Average response factor

The average response factor may be used if the average percent relative standard deviation (%RSD) of all the response factors taken together is ≤ 20%.

The equation for average response factor is:

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

Where: n = Number of calibration levels

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

10.6.3. Linear regression

The linear fit uses the following functions:

10.6.3.1. External Standard

$$y = ax + b$$

or

$$x = \frac{(y - b)}{a}$$

Where: y = Instrument response
x = Concentration
a = Slope
b = Intercept

10.6.3.2. Internal Standard

$$C_s = \frac{\left[\frac{A_s C_{is}}{A_{is}} - b\right]}{a}$$

Where: C_s = Concentration in the sample
A_s = Area of target peak in the sample
A_{is} = Area of internal standard in the sample
C_{is} = Concentration of the internal standard

10.6.4. Quadratic curve

The quadratic curve uses the following functions:

10.6.4.1. External standard

$$y = ax + cx^2 + b$$

Where c is the curvature

10.6.4.2. Internal Standard

$$y = a\left(\frac{A_s \times C_{is}}{A_{is}}\right) + c\left(\frac{A_s \times C_{is}}{A_{is}}\right)^2 + b$$

10.7. Evaluation of calibration curves

10.7.1. The percent relative standard error (%RSE) from the calibration curve is used to evaluate the initial calibration. This provides a measure of how much error is associated with using the calibration curve for quantitation.

10.7.2. The least squares regression line is calculated and used to calculate the predicted concentration for each level. The percent relative standard error is calculated as follows:

$$\%\ RSE = 100\% \times \sqrt{\frac{\sum_{i=1}^{N}\left[\frac{C_i - PC_i}{C_i}\right]^2}{(N-P)}}$$

Where:
N = Number of points in the curve
P = Number of parameters in the curve (= 1 for average response factor, 2 for linear, 3 for quadratic)
C_i = True concentration for level i
PC_i = Predicted concentration for level i

Note that when average response factors are used, %RSE is equivalent to %RSD.

10.8. The following requirements must be met for any calibration to be used:

- Response must increase with increasing concentration.
- If a curve is used, the intercept of the curve at zero response must be less than ± the reporting limit for the analyte.
- The average Relative Standard Error (RSD for average response factors) of the calibration points from the curve used must be ≤ 20%.
- Some data systems will not measure the %RSE from a linear or quadratic fit. For the linear case, the correlation coefficient may be used as an alternative to the %RSE, and must be greater than or equal to 0.990. For the quadratic case the Coefficient of Determination may be used, and must be greater or equal to 0.990.

Note: The Relative Standard Error (RSE) is superior to the Correlation Coefficient (r) and Coefficient of Determination (r^2) for testing the fit of a set of calibration points to a line. The lower points on a curve have little effect on r. As a result a curve may have a very good correlation coefficient (>0.995), while also having > 100% error at the low point.

10.9. Weighting of data points

10.9.1. In linear and quadratic calibration fits, the points at the lower end of the calibration curve have less absolute variance than points at the high concentration end of the curve. This can cause severe errors in quantitation at the low end of the calibration. However, in environmental analysis, accuracy at the low end of the curve is very important. For this reason it is preferable to increase the weighting of the lower concentration points. $1/Concentration^2$ weighting (often called $1/X^2$ weighting) will improve accuracy at the low end of the curve and should be used if the data system has this capability.

10.10. Non-standard analytes are sometimes requested. For these analytes, it may be acceptable to analyze a single standard at the reporting limit with each continuing calibration rather than a five point initial calibration. This action must be with client approval. If the analyte is detected in any of the samples, a five point initial calibration must be generated and the sample(s) reanalyzed for quantitation.

10.11. Calibration Verification

10.11.1. 12 hour Calibration

The working calibration curve or RF must be verified by the analysis of a mid point calibration standard at the beginning, after every 12 hours, and at the end of the analysis sequence. The center of each retention time window is updated with each 12-hour calibration or calibration verification.

10.11.2. Calibration Verification

It may be appropriate to analyze a mid point standard more frequently than every 12 hours. If these calibration verification standards are analyzed, requirements are the same as the 12-hour calibration with the exception that retention times are not updated.

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

10.11.4. It is not necessary to run a calibration verification standard at the beginning of the sequence if samples are analyzed immediately after the completion of the initial calibration.

10.11.5. Samples quantitated by external standard methods must be bracketed by calibration verification standards that meet the criteria listed above. The bracketing standards on the column used for calibration must meet the same criteria as the opening standards. Bracketing is not necessary for internal standard methods.

10.11.6. If the analyst notes that a CCV has failed and can document the reason for failure (e.g. no purge, broken vial, carryover from the previous sample etc.) then a second CCV may be analyzed without any adjustments to the instrument. If this CCV meets criteria then the preceding samples have been successfully bracketed. If adjustments to the instrument are performed before the repeat CCV then the proceeding samples have not been successfully bracketed but analysis may continue.

10.11.7. In general, it is not advisable to analyze repeat CCVs on unattended runs. If repeat CCVs are analyzed then the first will serve as the bracketing standard for the preceding samples and the last will serve as the CCV for the following samples.

10.11.8. If highly contaminated samples are expected it is acceptable to analyze blanks or primers at any point in the run.

10.11.9. % Difference calculation

% Difference for internal and external methods is calculated as follows

Internal Standard:

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

External standard:

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

Where RF_c and CF_c are the response and calibration factors from the continuing calibration

$\overline{RF}$ and $\overline{CF}$ are the average response and calibration factors from the initial calibration

10.11.10. % Drift calculation

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

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

10.11.11. Corrective Actions for Continuing Calibration

If the overall average %D of all analytes is greater than $\pm$ 15% corrective action must be taken. This may include clipping the column, changing the liner or other minor instrument adjustments, followed by reanalyzing the standard. If the overall average %D still varies by more than $\pm$ 15%, a new calibration curve must be prepared.

10.11.12. Corrective Action for Samples

For internal standard methods, any samples injected after a standard not meeting the calibration criteria must be re-injected.

For external standard methods, any samples injected after the last good continuing calibration standard must be re-injected.

If the average %D for all the analytes in the calibration is over 15%, but all of the analytes requested for a particular sample have %D $\leq$ 15%, then the analysis is acceptable for that sample.

11. PROCEDURE

11.1. Extraction

Extraction procedures are referenced in the appendices.

11.2. Cleanup

Cleanup procedures are referenced in the appendices.

11.3. Gas Chromatography

Chromatographic conditions for individual methods are presented in the appendices.

11.4. Sample Introduction

In general, volatiles analytes are introduced using purge and trap as described in Appendix A. Semivolatile analytes are introduced by direct injection of the extract. Samples, standards, and QC must be introduced using the same procedure.

11.5. Analytical Sequence

An analytical sequence starts with an initial calibration or a daily calibration. Refer to the individual method appendices for method specific details of daily calibrations and analytical sequences.

11.5.1. The daily calibration includes analysis of standards containing all single response analytes and updating the retention time windows.

11.5.2. If there is a break in the analytical sequence of greater than 12 hours, a new analytical sequence must be started with a daily calibration.

11.6. Retention Time Windows

11.6.1. Retention time windows must be determined for all analytes. Make an injection of all analytes of interest each day over a three-day period. Calculate the standard deviation of the three retention times for each analyte (relative retention times may also be used). For multi-response analytes (e.g., Aroclors) use the retention time of major peaks. Plus or minus three times the standard deviation of the retention times of each analyte defines the retention time window.

11.6.2. The center of the retention time window is the retention time from the last of the three standards. The centers of the windows are updated with the mid- point of the initial calibration and each 12-hour calibration. The widths of the windows will remain the same until new windows are generated following the installation of a new column.

11.6.3. If the retention time window as calculated above is less than +/- 0.05 minutes, use +/- 0.05 minutes as the retention time window. This allows for slight variations in retention times caused by sample matrix.

11.6.4. The laboratory must calculate new retention time windows each time a new column is installed. The new windows must be generated within one week of the installation of the new column. Until these standards have been run on the new column, the retention time windows from the old column may be used, updated with the retention times from the new initial calibration.

11.6.5. Corrective Action for Retention Times

The retention times of all compounds in the 12 hour calibration or calibration verification standard must be within the retention time window. If this condition is not met, all samples analyzed after the last compliant standard must be reanalyzed unless the following conditions are met for any compound that elutes outside the retention time window:

The retention time of that compound in the standard must be within a retention time range equal to twice the original window.

No peak that would be reportable may be present on the sample chromatogram within an elution time range equal to three times the original retention time window.

11.7. Daily Retention Time Windows

The center of the retention time windows determined in Section 11.6 are adjusted to the retention time of each analyte as determined in the 12 hour calibration standards or continuing calibration verification standards. (See the method 8081A and 8082 appendices for exceptions for multi-response components.) The retention time windows must be updated at the beginning of each analytical sequence and with each 12-hour calibration or continuing calibration verification.

11.8. Percent Moisture

Analytical results may be reported as dry or wet weight, as required by the client. Percent moisture must be determined if results will be reported as dry weight. Refer to SOP CORP-OP-0001NC for determination of percent moisture.

11.9. Procedural Variations

Procedural variations are allowed only if deemed necessary in the professional judgment of the supervisor to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo and approved by a supervisor and QA/QC manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file. The nonconformance is also addressed in the case narrative. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Qualitative Identification

12.1.1. Tentative identification occurs when a peak is found within the retention time window for an analyte, at a concentration above the reporting limit, or above the MDL if J flags are required. Normally confirmation is required on a second column, but if the detector is sufficiently specific or if the sample matrix is well enough defined, single column analysis may be adequate. In some cases GC/MS confirmation may be required. Client specific requirements may also define the need for second column confirmation and / or GC/MS confirmation. Refer to the appendices for test specific requirements for confirmation. Identification is confirmed if a peak is also present in the retention time window for that analyte on the confirmatory column, at a concentration greater than the reporting limit (MDL if J flag confirmation required).

12.1.2. Dual column quantitation

For confirmed results, two approaches are available to the analyst.
A) The primary column approach
Or
B) The better result approach
Both are acceptable to avoid the reporting of erroneous or unconfirmed data.

12.1.2.1. Primary column approach:

The result from the primary column is normally reported. The result from the secondary column is reported if any of the following three bulleted possibilities are true.

- There is obvious chromatographic interference on the primary column
- The result on the primary column is > 40% greater than the result on the secondary column
- Continuing or bracketing standard fails on the primary column but is acceptable on the secondary column. (If the primary column result is > 40% higher than the secondary and the primary column calibration fails, then the sample must be evaluated for reanalysis.)

12.1.2.2. Better result approach

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

- There is obvious chromatographic interference on the column with the lower result
- The continuing or bracketing calibration on the column with the lower result fails. (If the higher result is > 40% higher and the calibration on the column with the lower result fails, then the sample must be evaluated for reanalysis.)

12.1.3. If the Relative percent difference (RPD) between the response on the two columns is greater than 40%, or if the opinion of an experienced analyst is that the complexity of the matrix is resulting in false positives, the confirmation is suspect and the results are qualified. RPD is calculated using the following formula:

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

Where R=Result

12.1.4. Multi-response Analytes

For multi-response analytes, the analyst should use the retention time window, but should rely primarily on pattern recognition. The pattern of peaks will normally serve as confirmation.

12.1.5. The experience of the analyst should weigh heavily in the interpretation of the chromatogram. For example, sample matrix or laboratory temperature fluctuation may result in variation of retention times.

12.2. Calibration Range

If concentrations of any analytes exceed the working range as defined by the calibration standards, then the sample must be diluted and reanalyzed. Dilutions should target the most concentrated analyte in the upper half (over 50% of the high level standard) of the calibration range. It may be necessary to dilute samples due to matrix.

12.3. Dilutions

Samples may be screened to determine the appropriate dilution for the initial run. If the initial diluted run has no hits or hits below 20% of the calibration range and the matrix allows for analysis at a lesser dilution, then the sample must be reanalyzed at a dilution targeted to bring the largest hit above 50% of the calibration range.

12.3.1. Guidance for Dilutions Due to Matrix

If the sample is initially run at a dilution and only minor matrix peaks are, then the sample should be reanalyzed at a more concentrated dilution. Analyst judgement is required to determine the most concentrated dilution that will not result in instrument contamination.

12.3.2. Reporting Dilutions

The most concentrated dilution with no target compounds above the calibration range will be reported. Other dilutions may be reported at client request, if the lower dilutions will not cause detector saturation, column overload, or carryover. Analyst judgement and client site history will factors in the reporting of dual dilutions.

12.4. Interferences

If peak detection is prevented by interferences, further cleanup should be attempted. If no further cleanup is reasonable, then elevation of reporting levels and/or lack of positive identification must be addressed in the case narrative.

12.5. Internal Standard Criteria for Continuing Calibration

If internal standard calibration is used, then the internal standard response in a continuing calibration standard must be within 50 to 150% of the response in the mid level of the initial calibration.

12.6. Calculations

Capabilities of individual data systems may require the use of different formulas than those presented here. When this is the case, the calculations used must be shown to be equivalent and must be documented in an appendix attached to this document.

12.6.1. External Standard Calculations

12.6.1.1. Aqueous samples

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

Where:

A_x = Response for the analyte in the sample
V_i = Volume of extract injected, µL
D_f = Dilution factor
V_t = Volume of total extract, µL
V_s = Volume of sample extracted or purged, mL
CF = Calibration factor, area or height/ng, Section 10.1

12.6.1.2. Non-aqueous Samples

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

Where:

W = Weight of sample extracted or purged, g

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

12.6.2. Internal Standard Calculations

12.6.2.1. Aqueous Samples

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

Where:

C_{is} = Amount of internal standard added, ng
A_{is} = Response of the internal standard
RF = Response factor for analyte

12.6.2.2. Non-aqueous Samples

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

12.6.3. Surrogate Recovery

Concentrations of surrogate compounds are calculated using the same equations as for the target compounds. The response factor from the initial calibration is used. Surrogate recovery is calculated using the following equation:

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

13. METHOD PERFORMANCE

13.1. Method Detection Limit

Each laboratory must generate a valid method detection limit for each analyte of interest. The MDL must be below the reporting limit for each analyte. The procedure for determination of the method detection limit is given in 40 CFR Part 136, Appendix B, and further defined in QA Policy #: QA-005.

13.2. Initial Demonstration

Each laboratory must make a one time initial demonstration of capability for each individual method. Demonstration of capability for both soils and water matrices is required. This requires analysis of QC check samples containing all of the standard analytes for the method. For some tests it may be necessary to use more than one QC check mix to cover all analytes of interest.

13.2.1. Four aliquots of the QC check sample are analyzed using the same procedures used to analyze samples, including sample preparation. The concentration of the QC check sample should be equivalent to a mid-level calibration.

13.2.2. Calculate the average recovery and standard deviation of the recovery for each analyte of interest. Compare these results with the acceptance criteria given in each appendix.

13.2.3. If any analyte does not meet the acceptance criteria, the test must be repeated. Only those analytes that did not meet criteria in the first test need to be evaluated. Repeated failure for any analyte indicates the need for the laboratory to evaluate the analytical procedure and take corrective action.

13.3. Training Qualification

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

14. POLLUTION PREVENTION

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

15. WASTE MANAGEMENT

Waste generated in this procedure will be segregated and disposed according to the facility hazardous waste procedures. The Environmental Health and Safety Director should be contacted if additional information is required.

16. REFERENCES

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

17. MISCELLANEOUS

17.1. Modifications from Reference Method

17.1.1. Chapter 1 of SW-846 states that the method blank should not contain any analyte of interest at or above the Method Detection Limit. This SOP states that the Method Blank must not contain any analyte of interest at or above the reporting limit. Common lab contaminants are allowed to be up to 5 times the reporting limit in the blank following consultation with the client.

17.2. Modifications from Previous Revision

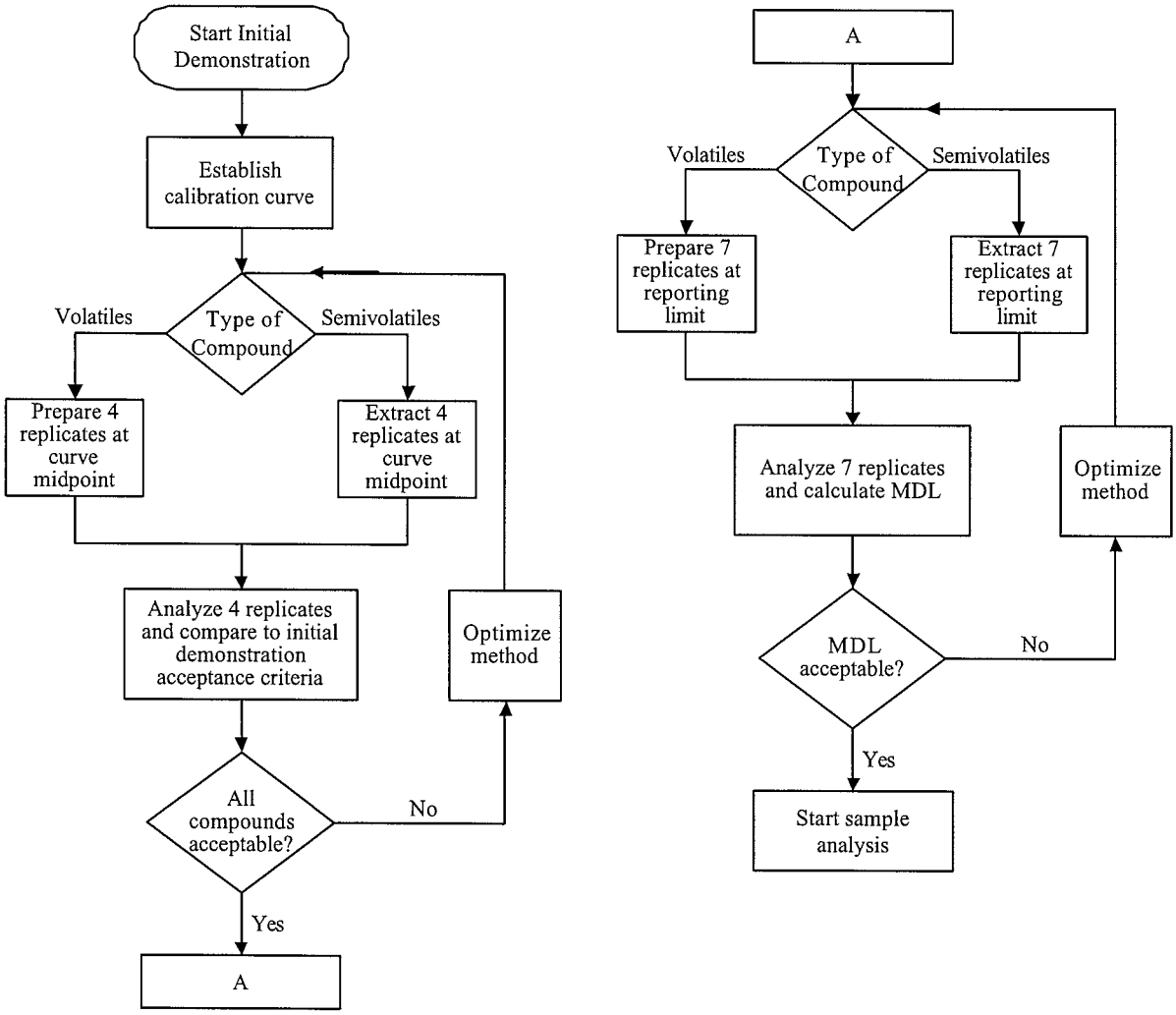
The calibration criteria in section 10.11 have been rewritten to improve consistency with SW-846 and to improve clarity.

17.3. Facility Specific SOPs

Each facility shall attach a list of facility specific SOPs or approved attachments (if applicable) which are required to implement this SOP or which are used in conjunction with this SOP. If no facility specific SOPs or amendments are to be attached, a statement must be attached specifying that there are none.

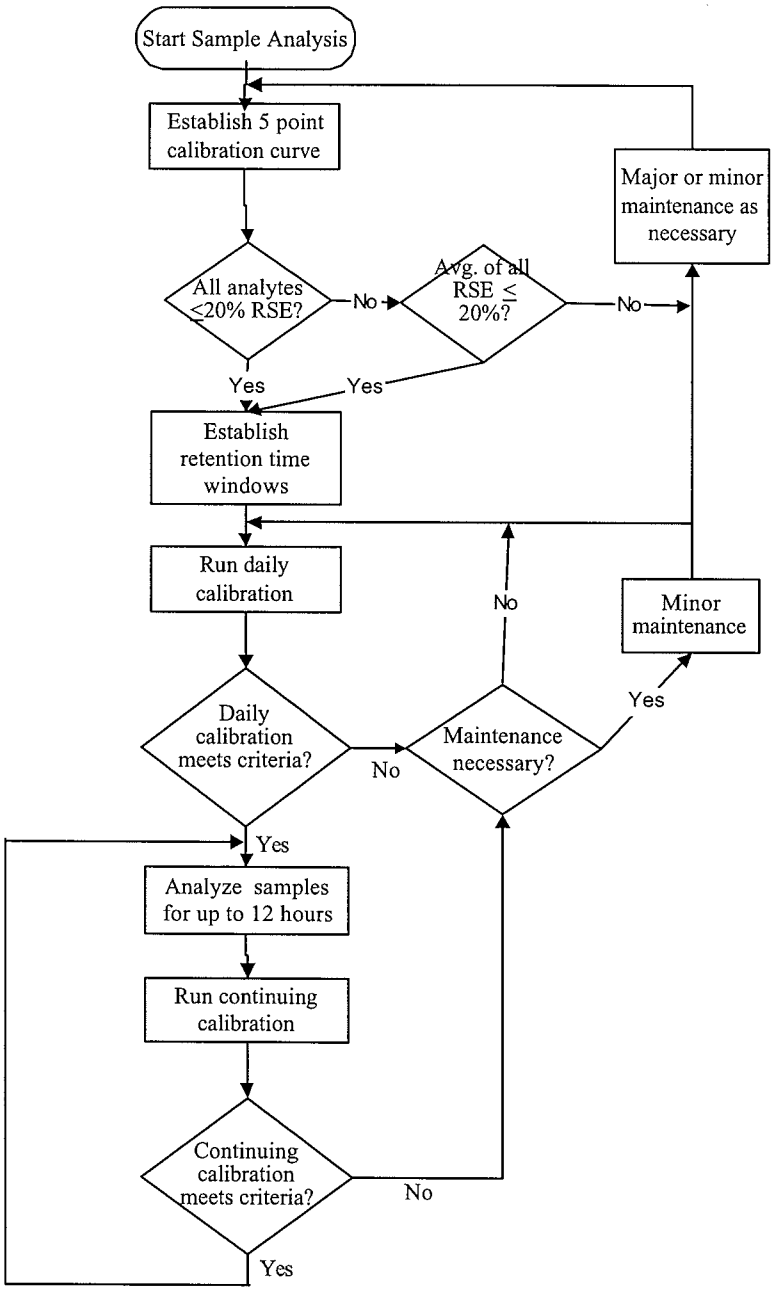
17.4. Flow Diagrams

17.4.1. Initial demonstration and MDL[1]



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

17.4.2. Sample Analysis [1]



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

1. SCOPE AND APPLICATION

1.1. This method describes sample preparation and extraction for the analysis of volatile organics by a purge and trap procedure, following method 8021B. However, where required by a client QAPP this section may also be used to analyze aromatic volatiles by discontinued methods 8020A and 8010B. All requirements of the 8000B section of this SOP must be met except when superseded by this Appendix. Refer to Table A-1 for the individual analytes normally determined by these procedures.

1.2. Compounds within the scope of this method have boiling points below 200°C and are soluble or slightly soluble in water. Classes of compounds best suited to purge-and-trap analysis include low molecular weight halogenated hydrocarbons, aromatics, ketones, nitriles, acetates, acrylates, ethers, and sulfides.

1.3. Water samples and soils samples with low levels of contamination may be analyzed directly by purge-and-trap extraction and gas chromatography. Higher concentrations of these analytes in soil may be determined by the medium level methanol extraction procedure.

1.4. This method also describes the preparation of water-miscible liquids, non-water-miscible liquids, solids, wastes, and soils/sediments for analysis by the purge-and-trap procedure.

1.5. The associated LIMS method code is QR.

2. SUMMARY OF METHOD

2.1. An inert gas is bubbled through the sample at ambient temperature or at 40°C (40°C required for low-level soils), and the volatile components are transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent column where the volatile components are adsorbed. After purging is completed, the sorbent column is heated and back-flushed with inert gas to desorb the components onto a gas chromatographic column. Analytes are detected using a photoionization Detector, an electrolytic conductivity detector or a combination of both.

2.2. For soil samples, a portion of the sample is dispersed in methanol to dissolve the volatile organic constituents. A portion of the methanolic solution is combined with water. It is then analyzed by purge-and-trap GC following the normal water method. If very low detection limits are needed for soil samples then direct purge using sodium bisulfate preservation may be necessary.

3. DEFINITIONS

Refer to the STL North Canton Laboratory Quality Manual (LQM), current version, for definitions of terms used in this SOP.

4. INTERFERENCES

4.1. Refer to section 4 of the method 8000B part of this SOP for general information on chromatographic interferences.

4.2. Impurities in the purge gas, and from organic compounds out-gassing from the plumbing ahead of the trap, account for the majority of contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running laboratory reagent blanks. The use of non-TFE plastic tubing, non-TFE thread sealants, or flow controllers with rubber components in the purging device should be avoided.

4.3. Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride and fluorocarbons) through the septum seal of the sample vial during shipment and storage. A trip blank

prepared from organic-free reagent water and carried through sampling and handling protocols serves as a check on such contamination.

4.4. Contamination by carryover can occur whenever high-concentration and low-concentration samples are analyzed sequentially. Whenever an unusually concentrated sample is analyzed, it should be followed by an analysis of organic-free reagent water to check for cross-contamination. The trap and other parts of the system are subject to contamination. Therefore, frequent bake-out and purging of the system may be required.

4.5. When utilizing an autosampler system, which has multiple ports for sample analysis, it is likely that only a single stage or port may be contaminated by a highly concentrated sample. If a port is suspect, a water blank should be analyzed to verify lack of contamination. If the water blank and subsequent blanks on that port show contamination consistent with the concentrated sample, further maintenance is required. This may include replacing or cleaning the multi-port valve, transfer lines, etc.

4.6. A holding blank is kept in the sample refrigerator. This is analyzed and replaced every 14 days. If the holding blank does not meet the method blank criteria, the source of contamination must be found and corrected. Evaluation of all samples analyzed in the 14-day period prior to the analysis of the contaminated holding blank is required.

4.7. Acidification of samples may result in hydrolysis of 2-chloroethyl-vinyl ether.

5. SAFETY

5.1. Refer to section 5 of the Method 8000B section of this SOP for general safety requirements.

5.2. Often, purge vessels on purge-and-trap instrumentation are pressurized by the time analysis is completed. Therefore, vent the pressure prior to removal of these vessels to prevent the contents from spraying out.

5.3. The toxicity or carcinogenicity of each chemical used in this procedure has not been fully defined. Additional health and safety information can be obtained from the MSDS files maintained in the laboratory. The following specific hazards are known:

Methanol -- Flammable and toxic

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

5.5. Methanol shall not be used in a CaptAir hood.

6. EQUIPMENT AND SUPPLIES

6.1. Microsyringes -- 10µL, 25µL, 100µL, 250µL, 500µL, and 1000µL. These should be equipped with a 20 gauge (0.006" ID) needle. These will be used to measure and dispense methanolic solutions and aqueous samples.

6.2. Gas tight syringes -- 5 mL and 25 mL. Used for measuring sample volumes.

6.3. Purge and Trap Apparatus -- A device capable of extracting volatile compounds, trapping on a sorbent trap, and introducing onto a gas chromatograph.

6.4. Purge and Trap Autosampler -- In order to maintain high sample throughput, an autosampler is highly recommended.

6.5. Trap -- The trap used is dependent on the class of compound to be analyzed. Refer to Table A-2 for suggested traps for specific tests.

6.6. Purge Vessels -- These are dependent on the purge and trap unit/autosampler used. Both disposable culture tubes (needle sparge units) and specially designed vessels with fritted bottoms may be used. Follow the manufacturer's suggestions for configuration.

6.7. Columns - Refer to Table A-2 for details of columns.

6.8. Volumetric flasks, Class A: 5 mL to 250 mL

6.9. pH paper

6.10. Balance capable of weighing to 0.01g for samples.

7. REAGENTS AND SUPPLIES

7.1. Refer to the method 8000B section of this SOP for general requirements for reagents and supplies.

7.2. Organic Free Water

Organic free water is defined as water in which an interferent is not observed at the reporting limit of the compounds of interest. Suggested methods for generating organic free water include:

- Filtration through a carbon bed.
- Continuously sparging water with helium or nitrogen.
- Use of commercial water purification systems.

Other methods may be used, so long as the requirement that the water show no interference is met. The procedure used should be documented in a lab specific attachment.

7.3. Sodium Bisulfate

7.4. Methanol -- Purge and Trap Grade

7.5. Standards

Refer to tables A-5 and A-6 for details of surrogate, matrix spiking and internal standards. Calibration standard levels are not specified, since they may depend on the sensitivity and linear range of specific detectors. However, the low level standard must be equivalent to the reporting limits specified in Table A-1.

7.5.1. Volatile standards are prepared by injecting a measured volume of the stock standard into a syringe containing the appropriate volume of organic free water. The calibration standard is then loaded into the purge device.

8. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1. Holding times for all volatile analysis are 14 days from sample collection.

8.2. Water samples are normally preserved at pH < 2 with 1:1 hydrochloric acid. If residual chlorine is present, 2 drops of 10% sodium thiosulfate are added.

8.3. Solid samples are field preserved with sodium bisulfate solution for low level analysis, or with methanol for medium level analysis. Soil samples can also be taken using the EnCore™ sampler and preserved in the lab within 48 hours of sampling. At specific client request, unpreserved soil samples may be accepted.

8.4. There are several methods of sampling soil. The recommended method, which provides the minimum of field difficulties, is to take an EnCore sample. (The 5 g or 25 g sampler can be used, depending on client preference). Following shipment back to the lab the soil is preserved in methanol. This is the medium level procedure. If very low detection limits are needed (< 50 µg/kg for most analytes) then it will be necessary to use two additional 5 g EnCore samplers or to use field preservation.

8.5. Sample collection for medium level analysis using EnCore samplers.

8.5.1. Ship one 5 g (or 25 g) EnCore sampler per field sample position.

8.5.2. An additional bottle must be shipped for percent moisture determination.

8.5.3. When the samples are returned to the lab, extrude the (nominal) 5g (or 25 g) sample into a tared VOA vial containing 5 mL methanol (25 mL methanol for the 25 g sampler). Obtain the weight of the soil added to the vial and note on the label.

8.5.4. Add the correct amount of surrogate spiking mixture. (Add 100 µL of 250 µg/mL solution for a nominal 25 g sample, 20µL for a nominal 5 g sample.)

8.5.5. Add the correct amount of matrix spiking solution to the matrix spike and matrix spike duplicate samples. (Add 100 µL of 250 µg/mL solution for a nominal 25 g sample, 20µL for a nominal 5 g sample.) The addition of spike introduces a slight error, (0.4%) which can be neglected, into the calculations.

8.5.6. Prepare an LCS for each batch by adding the correct amount of matrix spiking solution to clean methanol. (100 µL of spike to 25 mL methanol or 20 µL spike to 5 mL methanol).

8.5.7. Shake the samples for two minutes to distribute the methanol throughout the soil.

8.5.8. Allow to settle, then remove a portion of methanol and store in a clean Teflon capped vial at 4+2°C until analysis.

8.6. Sample collection for medium level analysis using field methanol preservation

8.6.1. Prepare a VOA vial by adding 5 mL purge and trap grade methanol. (If a 25 g sample is to be used, add 25 mL methanol to the VOA vial).

8.6.2. Seal the bottle and attach a label.

8.6.3. Weigh the bottle to the nearest 0.01g and note the weight on the label.

8.6.4. Ship with appropriate sampling instructions.

8.6.5. Each sample will require an additional bottle with no preservative for percent moisture determination.

8.6.6. At client request, the methanol addition and weighing may also be performed in the field.

8.6.7. When the samples are returned to the lab, obtain the weight of the soil added to the vial and note on the label.

8.6.8. Add the correct amount of surrogate spiking mixture. (Add 100 µL of 250 µg/mL solution for a nominal 25 g sample, 20µL for a nominal 5 g sample.)

8.6.9. Add the correct amount of matrix spiking solution to the matrix spike and matrix spike duplicate samples. (Add 100 µL of 250 µg/mL solution for a nominal 25 g sample, 20µL for a nominal 5 g sample.) The addition of spike introduces a slight error, (0.4%) which can be neglected, into the calculations.

8.6.10. Prepare an LCS for each batch by adding the correct amount of matrix spiking solution to clean methanol. (100 µL of spike to 25 mL methanol or 20 µL spike to 5 mL methanol).

8.6.11. Shake the samples for two minutes to distribute the methanol throughout the soil.

8.6.12. Allow to settle, then remove a portion of methanol and store in a clean Teflon capped vial at 4+2°C until analysis.

8.7. Low level procedure

8.7.1. If low detection limits are required (typically < 50 µg/kg) sodium bisulfate preservation must be used. However, it is also necessary to take a sample for the medium level (methanol preserved) procedure, in case the concentration of analytes in the soil is above the calibration range of the low-level procedure.

8.7.2. A purge and trap autosampler capable of sampling from a sealed vial is required for analysis of samples collected using this method. (Varian Archon or O.I. 4552).

8.7.3. The soil sample is taken using a 5g EnCore sampling device and returned to the lab. It is recommended that two EnCore samplers be used for each field sample position, to allow for any reruns than may be necessary. A separate sample for % moisture determination is also necessary.

8.7.4. Prepare VOA vials by adding a magnetic stir bar, approximately 1 g of sodium bisulfate and 5 mL of reagent water.

8.7.5. Seal the vial and attach a label. The label must not cover the neck of the vial or the autosampler will malfunction.

8.7.6. Weigh the vial to the nearest 0.01g and note the weight on the label.

8.7.7. Extrude the soil sample from the EnCore sampler into the prepared VOA vial. Reweigh the vial to obtain the weight of soil and note on the label.

8.7.8. **Note:** Soils containing carbonates may effervesce when added to the sodium bisulfate solution. If this is the case at a specific site, add 5 mL of water instead, and freeze at ≥ -10°C until analysis.

8.7.9. Alternatively the sodium bisulfate preservation may be performed in the field. Ship at least two vials per sample. The field samplers must determine the weight of soil sampled. Each sample will require an additional bottle with no preservative for percent moisture determination, and an additional bottle preserved with methanol for the medium level procedure.

8.8. Aqueous samples are stored in glass containers with Teflon lined septa at 4°C +/- 2°C, with minimum headspace.

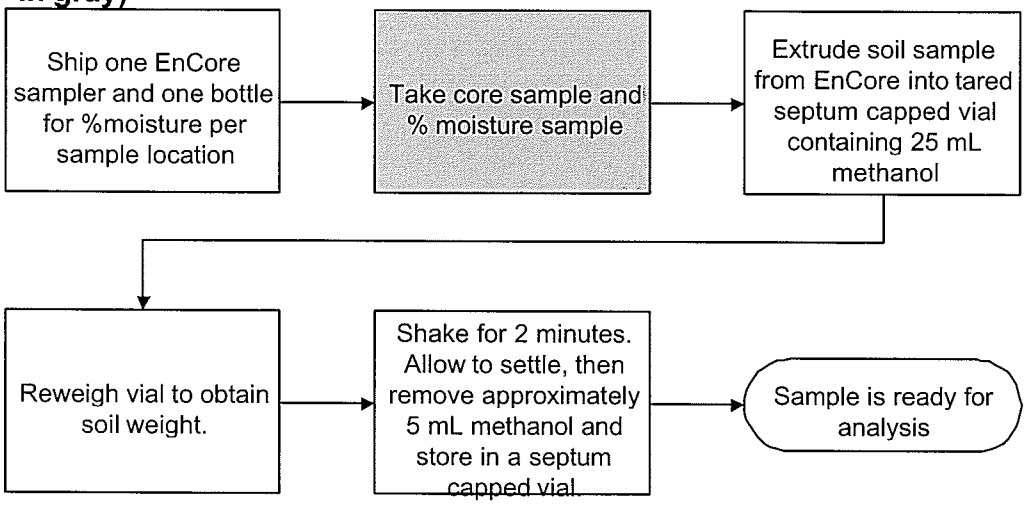
8.9. Medium level solid extracts are aliquoted into 2 - 5 mL glass vials with Teflon lined caps and stored at 4°C +/- 2°C. The extracts are stored with minimum headspace.

8.10. The maximum holding time is 14 days from sampling until the sample is analyzed. (Samples that are found to be unpreserved still have a 14 day holding time. However they should be analyzed as soon as possible. The lack of preservation should be addressed in the case narrative). Maximum holding time for the EnCore sampler (before the sample is added to methanol or sodium bisulfate) is 48 hours.

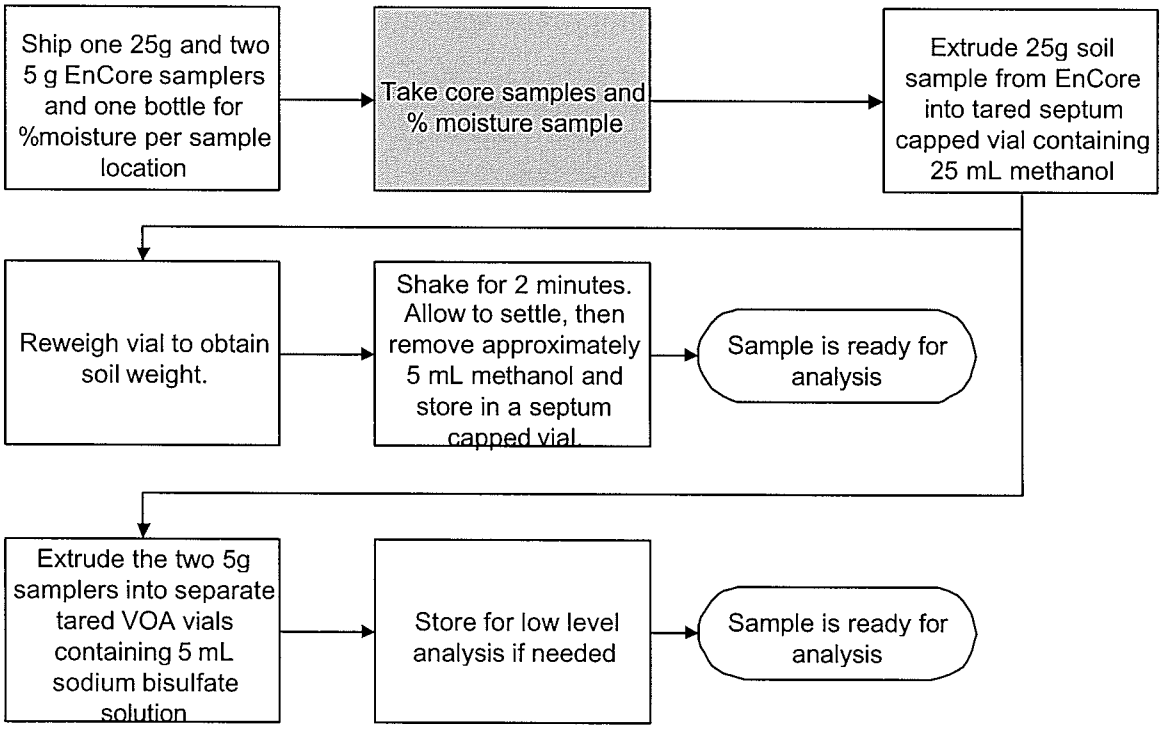
8.11. A holding blank is stored with the samples. This is analyzed and replaced if any of the trip blanks show any contamination. Otherwise it is replaced every 14 days.

Note: Freezing is not allowed for Ohio VAP solids.

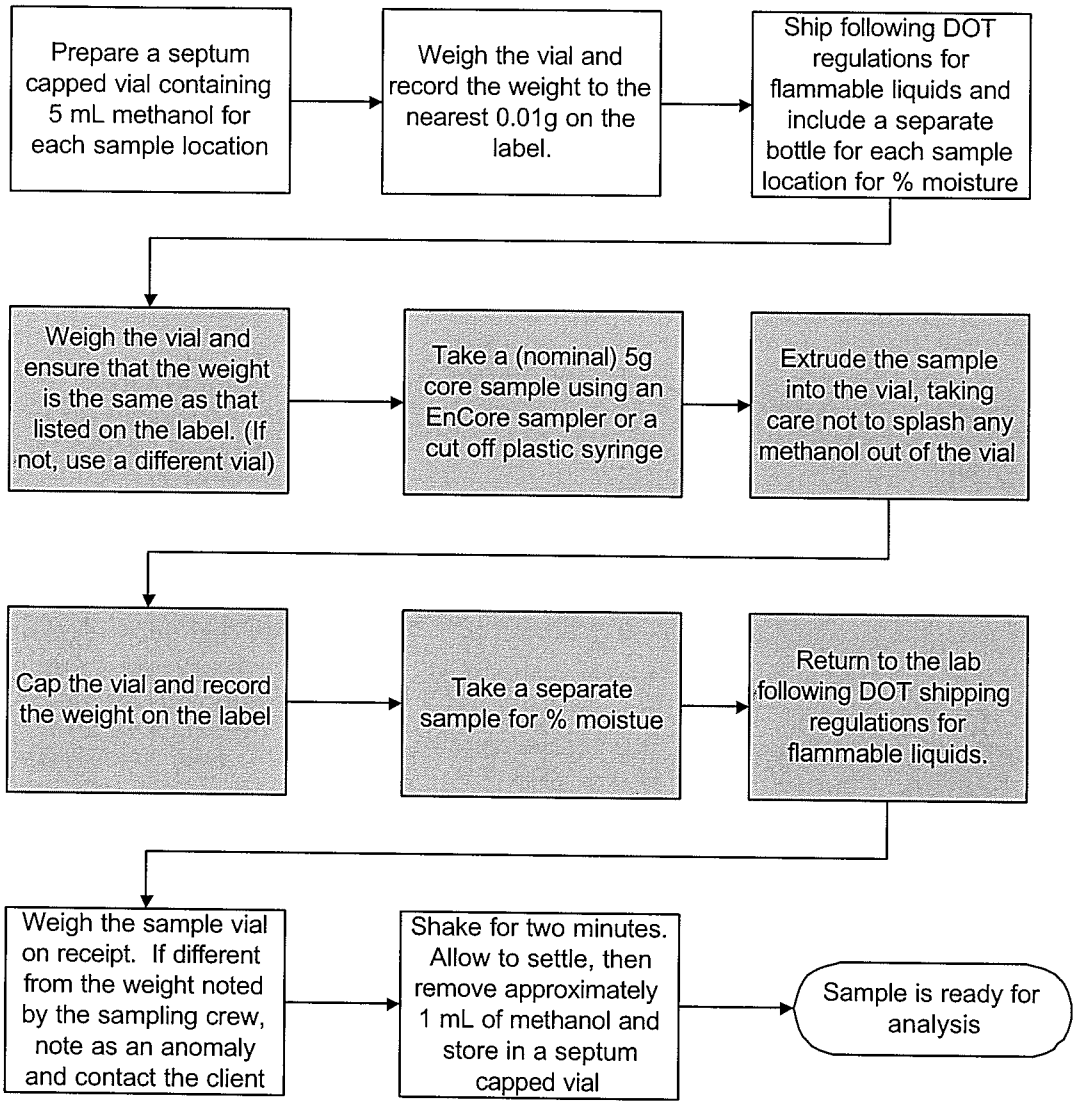
EnCore procedure when low level is not required (field steps in gray)



EnCore procedure when low level is required



Field methanol extraction procedure (field steps in gray)



9. QUALITY CONTROL

9.1. Refer to the method 8000B section of this SOP, section 9, for general quality control procedures, including batch definition, requirements for method blanks, LCS, matrix spikes, surrogates, and control limits.

10. CALIBRATION AND STANDARDIZATION

10.1. Refer to the method 8000B section of this SOP, section 10, for general calibration procedures.

10.2. Gas Chromatograph Operating Conditions

Various column configurations are possible. If dual column confirmation is necessary, the sample may be split using a Y splitter at the injector end to direct the sample to two columns and two detectors. For simultaneous determination of aromatic and halogenated volatiles, a single column is used and the PID and ELCD detectors are connected in series.

10.2.1. Refer to Table A-2, A-3 and A-4 for GC operating conditions.

10.3. Initial Calibration

10.3.1. Refer to Section 10 of the 8000B section of this SOP for details of initial calibration criteria.

10.3.2. Low level soil samples must be purged at 40°C; therefore the calibration curve must also be purged at 40°C. In addition, the low level soil calibration solutions should contain approximately the same amount of sodium bisulfate as the samples.

10.3.3. The low level calibration must be at the reporting limit or below. The remaining standards encompass the working range of the detector.

10.3.4. Calibrate the instrument using the same volume that will be used during sample analysis.

10.4. Calibration Verification

10.4.1. A mid level calibration standard is used for the calibration verification. The gases have 20 % D criteria rather than the 15% used for other analytes.

10.4.2. A calibration verification run is performed after every 10 samples for this method.

10.4.3. Bracketing of samples with calibration verification runs is only necessary for external standard analysis.

11. PROCEDURE

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

11.2. Analytical Sequence

The analytical sequence starts with an initial calibration of at least five points, or a 12 hour calibration that meets % difference criteria from an existing initial calibration.

11.3. Confirmation

The PID and ELCD detectors are sufficiently selective that second column confirmation is not always necessary. Requirements for second column confirmation should be decided in consultation with the

client. If the PID and ELCD are used in series confirmatory information for many analytes can be gained by comparing the relative response from the two detectors.

11.4. Aqueous Sample Analysis (Purge and Trap units using sparge vessels)

11.4.1. Depending on the sensitivity of the instrument and capabilities of the purge and trap device, 5, 10, 20, or 25 mL sample volumes may be analyzed. A 5 mL sample volume is recommended.

11.4.2. Rinse a 5 mL (or 25 mL for larger sample volumes) gas-tight syringe with organic free water. Fill the syringe with the sample to be analyzed, and compress to volume.

11.4.3. Check and document the pH of the sample remaining in the VOA vial after loading the syringe.

11.4.4. This procedure invalidates the contents of the VOA vial for further analysis, unless an aliquot is transferred to a smaller VOA vial with no headspace (e.g., 20 mL) at the same time the analysis aliquot is removed.

11.4.5. Spike with the appropriate volume of surrogate/internal standard solution and spike solution (if required) through the barrel of the syringe. The method blank is spiked with surrogates only, the LCS and matrix spikes with the surrogate and matrix spiking solutions. Refer to Tables A-5 and A-6 for volumes and concentrations of spiking solutions.

11.4.6. Load onto the purge and trap device and start the run.

11.4.7. If the initial analysis of a sample or a dilution of the sample has a concentration of analytes that exceeds the initial calibration range, the sample must be reanalyzed at a higher dilution. When a sample has a high response for a compound, an organic free water blank should follow analysis. It is recognized that during automated unattended analysis, this may not occur. If any potential carryover hits are present in samples following highly contaminated samples, the sample must be reanalyzed to determine if any of these hits are a result of carryover or are actually present in the sample.

11.4.8. Dilutions may be made in gas tight syringes unless the volume of sample used is less than 5 µL, in which case dilution in volumetric flasks will be necessary.

11.4.8.1. Spike with the same volume of surrogate/internal standard solution as used for undiluted samples prior to loading onto the purge and trap device.

11.4.8.2. For Matrix spike / matrix spike duplicates where the sample requires dilution, the sample is spiked after the dilution is performed.

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

11.5.1. Units, which sample from the VOA vial, should be equipped with a module, which automatically adds surrogate and internal standard solution to the sample prior to purging the sample.

11.5.2. If the autosampler uses automatic IS/SS injection, no further preparation of the VOA vial is needed. Otherwise the internal and surrogate standards must be added to the vial. *Note:* Aqueous samples with high amounts of sediment present in the vial may not be suitable for analysis on this instrumentation, or they may need to analyzed as soils.

11.5.3. Sample remaining in the vial after sampling with one of these mechanisms is no longer valid for further analysis. A fresh VOA vial must be used for further sample analysis.

11.5.4. Check the pH of the sample remaining in the VOA vial after analysis is completed.

11.6. Low-Level Solids Analysis using discrete autosamplers

Note: This technique may seriously underestimate analyte concentration and must not be used except at specific client request for the purpose of comparability with previous data. It is no longer part of SW-846.

This method is based on purging a heated sediment/soil sample mixed with reagent water containing the surrogate and, if applicable, internal and matrix spiking standards. Analyze all reagent blanks and standards under the same conditions as the samples (e.g., heated). The calibration curve is also heated during analysis. Purge temperature is 40°C.

11.6.1. Do not discard any supernatant liquids. Mix the contents of the container with a narrow metal spatula.

11.6.2. Weigh out 5 g (or other appropriate aliquot) of sample into a disposable culture tube or other purge vessel. Record the weight to the nearest 0.1 g. If method sensitivity is demonstrated, a smaller aliquot may be used. Do not use aliquots less than 1.0 g. If the sample is contaminated with analytes such that a purge amount less than 1.0 g is appropriate, use the medium level method described in section 11.7.

11.6.3. Connect the purge vessel to the purge and trap device.

11.6.4. Rinse a 5 mL gas-tight syringe with organic free water, and fill. Compress to 5 mL. Add surrogate/internal standard (and matrix spike solutions if required.) (See Tables A-5, A-6, A-7 and A-8.) Add directly to the sample from 11.6.2.

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

11.6.6. Add the heater jacket or other heating device and start the purge and trap unit.

11.6.7. Soil samples that have low IS recovery when analyzed (<50%) should be reanalyzed once to confirm matrix effect. If external standard calibration is used, samples with surrogate recovery below the control limit should be reanalyzed once to confirm matrix effect.

11.7. Methanol Extract Soils

11.7.1. Rinse a gas-tight syringe with organic free water. Fill the syringe with the same volume of organic free water as used in the calibrations. Add no more than 2% (v/v) (100 µL for a 5 mL purge) methanolic extract (from Section 8.5 or 8.6) to the syringe. Add internal standard (if used). Load the sample onto the purge and trap device and analyze as for aqueous samples. If less than 5µL of methanolic extract is to be added to the water, dilute the methanolic extract such that a volume greater than 5µL will be added to the water in the syringe.

12. DATA ANALYSIS AND CALCULATIONS

Refer to section 12 of the 8000B section of this SOP.

13. METHOD PERFORMANCE

13.1. Performance limits for the four replicate initial demonstration of capability required under Section 13.1 of the 8000B section of this SOP.

14. POLLUTION PREVENTION

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

15. WASTE MANAGEMENT

15.1. Waste generated in this procedure will be segregated and disposed according to the facility hazardous waste procedures. The Environmental Health and Safety Director should be contacted if additional information is required.

16. REFERENCES

16.1. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW846, 3rd Edition, Final Update III, December 1996, Sections 5000, 5030B, 5035 and 8021B

17. MISCELLANEOUS

17.1. Modifications from Reference Method

17.2. Modifications from previous revision

17.2.1. No revisions were made to this appendix.

17.3. Facility Specific SOPs

Each facility shall attach a list of facility specific SOPs or approved attachments (if applicable) which are required to implement this SOP or which are used in conjunction with this SOP. If no facility specific SOPs or amendments are to be attached, a statement must be attached specifying that there are none.

17.4. Tables

Table A-1

Standard Analyte List

Test	Compound	CAS number	Reporting Limit, µg/L or µg/kg		
			Aqueous	Low Soil	Medium Soil
Halogenated volatiles by 8021B	Bromodichloromethane	75-27-4	1.0	1.0	50
	Bromoform	75-25-2	1.0	1.0	50
	Bromomethane	74-83-9	1.0	1.0	50
	Carbon Tetrachloride	56-23-5	1.0	1.0	50
	Chlorobenzene	108-90-7	1.0	1.0	50
	Chloroethane	70-00-3	1.0	1.0	50
	2-Chloroethyl vinyl ether	110-75-8	5.0	5.0	250
	Chloroform	67-66-3	1.0	1.0	50
	Chloromethane	74-87-3	1.0	1.0	50
	Dibromochloromethane	124-48-1	1.0	1.0	50
	1,2-Dichlorobenzene	95-50-1	1.0	1.0	50
	1,3-Dichlorobenzene	541-73-1	1.0	1.0	50
	1,4-Dichlorobenzene	106-46-7	1.0	1.0	50
	Dichlorodifluoromethane	75-71-8	1.0	1.0	50
	1,1-Dichloroethane	75-34-3	1.0	1.0	50
	1,2-Dichloroethane	107-06-2	1.0	1.0	50
	1,1-Dichloroethene	75-45-4	1.0	1.0	50
	cis-1,2 Dichloroethene	156-59-4	1.0	1.0	50
	trans-1,2-Dichloroethene	156-60-5	1.0	1.0	50
	Dichloromethane(DCM)	75-09-2	5.0	5.0	250
	1,2-Dichloropropane	78-87-5	1.0	1.0	50
	cis-1,3-Dichloropropene	10061-01-5	1.0	1.0	50
	trans-1,3-Dichloropropene	10061-02-6	1.0	1.0	50
	1,1,2,2-Tetrachloroethane	79-34-5	1.0	1.0	50
	Tetrachloroethene	127-18-4	1.0	1.0	50
	1,1,1-Trichloroethane	71-55-6	1.0	1.0	50
	1,1,2-Trichloroethane	79-00-5	1.0	1.0	50
	Trichloroethene	79-01-6	1.0	1.0	50
	Trichlorofluoromethane	75-69-4	1.0	1.0	50
	Vinyl Chloride	75-01-4	1.0	1.0	50
Additional halogenated volatiles	Benzyl Chloride	100-44-7	5.0	5.0	250
	Bromobenzene	108-86-1	1.0	1.0	50
	Dibromomethane	74-95-3	1.0	1.0	50
	1,1,1,2-Tetrachloroethane	630-20-6	1.0	1.0	50
	Freon 113	76-13-1	1.0	1.0	50
	1,2,3-Trichloropropane	96-18-4	1.0	1.0	50
BTEX by 8021B	Benzene	71-43-2	1.0	1.0	50
	Ethyl Benzene	100-41-4	1.0	1.0	50
	Toluene	108-88-3	1.0	1.0	50
	Xylenes (total)	1330-20-7	1.0	1.0	50
Aromatic	Benzene	71-43-2	1.0	1.0	50

Table A-1

Standard Analyte List

Test	Compound	CAS number	Reporting Limit, µg/L or µg/kg		
			Aqueous	Low Soil	Medium Soil
volatiles by 8021B					
	Chlorobenzene	108-90-7	1.0	1.0	50
	1,2-Dichlorobenzene	75-34-3	1.0	1.0	50
	1,3-Dichlorobenzene	107-06-2	1.0	1.0	50
	1,4-Dichlorobenzene	75-45-4	1.0	1.0	50
	Ethyl Benzene	100-41-4	1.0	1.0	50
	Toluene	108-88-3	1.0	1.0	50
	Xylenes (total)	1330-20-7	1.0	1.0	50
Additional aromatic and unsaturated volatiles	1,2,4 Trimethylbenzene	95-63-6	1.0	1.0	50
	1,3,5 Trimethylbenzene	108-67-8	1.0	1.0	50
	Acetone	67-64-1	10	10	500
	MEK (2-butanone)	78-93-3	5.0	5.0	250
	MIBK (4-methyl-2-pentanone)	108-10-1	5.0	5.0	250
	Naphthalene	91-20-3	2.0	2.0	250
	Styrene	100-42-5	1.0	1.0	50
	Methyl tert-butyl ether (MTBE)	1634-04-4	1.0	1.0	50
Combined halogenated and aromatic volatiles by 8021B	Benzene	71-43-2	1.0	1.0	50
	Bromobenzene	108-86-1	1.0	1.0	50
	Bromochloromethane	74-97-5	1.0	1.0	50
	Bromodichloromethane	75-27-4	1.0	1.0	50
	Bromoform	75-25-2	1.0	1.0	50
	Bromomethane	74-83-9	1.0	1.0	50
	n-butylbenzene	104-51-8	1.0	1.0	50
	sec-Butylbenzene	135-98-8	1.0	1.0	50
	tert-Butylbenzene	98-06-6	1.0	1.0	50
	Carbon Tetrachloride	56-23-5	1.0	1.0	50
	Chlorobenzene	108-90-7	1.0	1.0	50
	Chlorodibromomethane	124-48-1	1.0	1.0	50
	Chloroethane	75-00-3	1.0	1.0	50
	Chloroform	67-66-3	1.0	1.0	50
	Chloromethane	74-87-3	1.0	1.0	50
	2-Chlorotoluene	95-49-8	1.0	1.0	50
	4-Chlorotoluene	106-43-4	1.0	1.0	50
	1,2-Dibromo-3-Chloropropane(DBCP)	96-12-8	1.0	1.0	50
	1,2-Dibromoethane(EDB)	106-93-4	1.0	1.0	50
	Dibromomethane	74-95-3	1.0	1.0	50
	1,2-Dichlorobenzene	95-50-1	1.0	1.0	50
	1,3-Dichlorobenzene	541-73-1	1.0	1.0	50
	1,4-Dichlorobenzene	106-46-7	1.0	1.0	50
	Dichlorodifluoromethane	75-71-8	1.0	1.0	50
	1,1-Dichloroethane	75-34-3	1.0	1.0	50
	1,2-Dichloroethane	107-06-2	1.0	1.0	50
	1,1-Dichloroethene	75-35-4	1.0	1.0	50

Table A-1
Standard Analyte List

Test	Compound	CAS number	Reporting Limit, µg/L or µg/kg		
			Aqueous	Low Soil	Medium Soil
	cis-1,2-Dichloroethene	156-59-4	1.0	1.0	50
	trans-1,2-Dichloroethene	156-60-5	1.0	1.0	50
	1,2-Dichloropropane	78-87-5	1.0	1.0	50
	1,3-Dichloropropane	142-28-9	1.0	1.0	50
	2,2-Dichloropropane	590-20-7	1.0	1.0	50
	1,1-Dichloropropene	563-58-6	1.0	1.0	50
	cis-1,3-Dichloropropene	10061-01-5	1.0	1.0	50
	trans-1,3-Dichloropropene	10061-02-6	1.0	1.0	50
	Ethylbenzene	100-41-4	1.0	1.0	50
	Hexachlorobutadiene	87-68-3	1.0	1.0	50
	Isopropylbenzene	98-82-8	1.0	1.0	50
	p-Isopropyltoluene	99-87-6	1.0	1.0	50
	Methylene Chloride	75-09-2	5.0	5.0	250
	Naphthalene	91-20-3	2.0	2.0	250
	n-Propylbenzene	10306501	1.0	1.0	50
	Styrene	100-42-5	1.0	1.0	50
	1,1,1,2-Tetrachloroethane	630-20-6	1.0	1.0	50
	1,1,2,2-Tetrachloroethane	79-34-5	1.0	1.0	50
	Tetrachloroethene	127-18-4	1.0	1.0	50
	Toluene	108-88-3	1.0	1.0	50
	1,2,3-Trichlorobenzene	87-61-6	1.0	1.0	50
	1,2,4-Trichlorobenzene	120-82-1	1.0	1.0	50
	1,1,1-Trichloroethane	71-55-6	1.0	1.0	50
	1,1,2-Trichloroethane	79-00-5	1.0	1.0	50
	Trichloroethene	79-01-6	1.0	1.0	50
	Trichlorofluoromethane	75-69-4	1.0	1.0	50
	1,2,3-Trichloropropane	96-18-4	1.0	1.0	50
	1,2,4-Trimethylbenzene	95-63-6	1.0	1.0	50
	1,3,5-Trimethylbenzene	108-67-8	1.0	1.0	50
	Vinyl Chloride	75-01-4	1.0	1.0	50
	Xylenes (total)	1330-20-7	1.0	1.0	50

Table A-2
Recommended Conditions for Aromatic Volatiles

Parameter	Recommended Conditions
Temperature program	50°C, 1min, 10°C/min to 200°C,1min
Column 1	Rtx-502.2 or DB-502.2 60m x 0.53mm 3.0um
Column 2	Rtx-1 or DB-1 60m x 0.53mm 3.0 um
Carrier gas	Helium or hydrogen
Purge Flow / time	40 mL/min, 11 minutes
Desorb Temp / time	180°C, 2 minutes (220°C for Vocarb 3000)
Bake Time / temp	200°C, 12 minutes (230°C for Vocarb 3000)
Transfer line / valve temp	115°C

Table A-3 Recommended Conditions for Method Halogenated Volatiles	
Parameter	Recommended Conditions
Temperature program	35°C, 12 min, then 4°C/min to 200°C, hold for 5 min
Column 1	DB-VRX or RTX-502.2 105m x 0.53 mm id df = 3.0um
Column 2	DB-1 or RTX-1 105m x 0.53 mm ID df = 3.0um
Column 3	Rtx - Volatiles 120m x 0.53mm ID df=2.0um
Carrier gas	Helium
Purge Flow / time	40 mL/min, 11 minutes
Desorb Temp / time	180°C, 2 minutes (220°C for Vocarb 3000)
Bake Time / temp	200°C, 12 minutes (230°C for Vocarb 3000)
Transfer line / valve temp	115°C

Table A-4 Recommended Conditions for Method Combined Aromatic and Halogenated Volatiles	
Parameter	Recommended Conditions
Temperature program	35°C, 12 min, then 4°C/min to 200°C, hold for 5 min
Column 1	DB-VRX or RTX-502.2 105m x 0.53 mm id df = 3.0um
Column 2	DB-1 or RTX-1 105m x 0.53 mm ID df = 3.0um
Column 3	Rtx - Volatiles 120m x 0.53mm ID df=2.0um
Carrier gas	Helium
Purge Flow / time	40 mL/min, 11 minutes
Desorb Temp / time	180°C, 2 minutes (220°C for Vocarb 3000)
Bake Time / temp	200°C, 12 minutes (230°C for Vocarb 3000)
Transfer line / valve temp	115°C

Table A-5
Surrogate and Internal Standard Concentrations

Standard	Components	Working Solution µg/mL	Spike amount µL (for 5 mL purge)	Final concentration µg/L (µg/kg)
Aromatic volatiles IS/SS	4-Chlorotoluene (SS) 1-Chloro-4-fluorobenzene (IS)	20 40	5	20 40
Halogenated volatiles IS/SS	4-chlorotoluene (SS) 1-Chloro-4-fluorobenzene (IS)	20 40	5	20 40
Combined Aromatic and halogenated volatiles IS/SS	Fluorobenzene (SS)	20	5	20
	1,4-Dichlorobutane (SS)	20	5	20
	1-Chloro-4-fluorobenzene (IS)	40	10	40

It may be necessary to select different surrogates in order to minimize sample interferences. 1-chloro-4-fluorobenzene and 4-chlorotoluene are fairly well resolved from analytes listed in this SOP. However 4-chlorotoluene may sometimes be requested as a target analyte. Other surrogates that may be considered, and issues associated with their use are:

Bromochloromethane: Elutes very close to chloroform and cis-1, 2-dichloroethene on the 502.2 column. May be a target analyte.

1,2-Bromochloroethane:

1-Chloro-2-fluorobenzene: Elutes close to ethylbenzene on DB-1 or Rtx-1 and close to m,p-xylene on 502.2

a,a,a-Trifluorotoluene: Good for aromatic volatiles, coelutes or very close to trichloroethene

Bromofluorobenzene: Close to 1,1,2,2-trichloroethane and 1,2,3-trichloropropane on the 502.2 column. Good on DB-1 or Rtx-1.

2-Bromo-1-chloropropane: May coelute with 1,1,2-trichloroethane

Table A-6
Concentrations for LCS and MS/MSD compounds

Standard	Components	Working Solution µg/mL	Spike amount µL (5 mL purge)	Final concentration µg/L (µg/kg)
Aromatic	Benzene	20	5	20
	Toluene	20		20
	Chlorobenzene	20		20
Halogenated	Chlorobenzene	20	5	20
	1,1-Dichloroethene	20		20
	Trichloroethene	20		20
Combination aromatic / halogenated	Benzene	20	5	20
	Toluene	20		20
	Chlorobenzene	20		20
	1,1-Dichloroethene	20		20
	Trichloroethene	20		20

1. SCOPE AND APPLICATION

This SOP Appendix describes procedures to be used when SW-846 Method 8081A is applied to the analysis of organochlorine pesticides by GC/ECD. This Appendix may also to be applied when discontinued SW-846 Method 8080A is requested, and is applicable to extracts derived from any matrix which are prepared according to the appropriate STL North Canton sample extraction SOPs. (CORP-OP-0001NC) Criteria for the analysis of wastewater by Method 608 is also included in this appendix.

Table B-1 lists compounds, which are routinely determined by this method, and gives the Reporting Limits (RL) for each matrix. RLs given are based on the low level standard and the sample preparation concentration factors. Matrix interferences may result in higher RLs than those listed.

At client request, this method may also be used for the analysis of PCBs (Arochlors) in combination with pesticides, although these are normally analyzed following method 8082, as described in Appendix C of this SOP. In any event, if samples for PCB analysis do not need the acid clean up procedure, then the same injection may be used for method 8081B and 8082, assuming all calibration and QC requirements for both methods are met. Extracts that have been acid cleaned may not be analyzed for pesticides, since several of the pesticides will be degraded.

1.1. The associated LIMS method codes are QJ (8081A) and DM (608).

2. SUMMARY OF METHOD

This method presents conditions for the analysis of prepared extracts of organochlorine pesticides. The pesticides are injected onto the column and separated and detected by electron capture detection. Quantitation may be by internal or external standard methods.

3. DEFINITIONS

Refer to the STL North Canton Laboratory Quality Manual (LQM), current version, for definitions of terms used in this document.

4. INTERFERENCES

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

4.2. Interferences in the GC analysis arise from many compounds amenable to gas chromatography that give a measurable response on the electron capture detector. Phthalate esters, which are common plasticizers, can pose a major problem in the determinations. Avoiding contact with any plastic materials minimizes interferences from phthalates.

4.3. Sulfur will interfere and can be removed using procedures described in SOP CORP-OP-0001NC.

4.4. Interferences co-extracted from samples will vary considerably from source to source. The presence of interferences may raise quantitation limits for individual samples. Specific cleanups may be performed on the sample extracts, including florisil cleanup (Method 3620), Gel Permeation Chromatography (Method 3640), and Sulfur cleanup (Method 3660). These cleanup procedures are included in SOP # CORP-OP-0001NC. Using hexane / acetone as the extraction solvent (rather than hexane / methylene chloride) will reduce the amount of interferences extracted.

5. SAFETY

5.1. Refer to section 5 of the Method 8000B SOP for general safety requirements.

5.2. Aroclors have been classified as a potential carcinogen under OSHA. Concentrated solutions of Aroclors must be handled with extreme care to avoid excess exposure. Contaminated gloves and clothing must be removed immediately. Contaminated skin surfaces must be washed thoroughly.

5.3. The following parameters covered by this method have been tentatively classified as known or suspected, human or mammalian carcinogens: 4,4'-DDT, 4,4'-DDD, and the BHCs. Primary standards of these toxic compounds should be prepared in a hood.

5.4. All ^{63}Ni sources shall be leak tested every six months, or in accordance with the manufacturer's general radioactive material license.

5.5. All ^{63}Ni sources shall be inventoried every six months. If a detector is missing, the Director, EH&S shall be immediately notified and a letter sent to the NRC or local state agency.

6. EQUIPMENT AND SUPPLIES

6.1. Refer to Section 6 of the 8000B section of this SOP. A ^{63}Ni electron capture detector is required.

6.2. Refer to Table B-2 for analytical columns.

6.3. Microsyringes, various sizes, for standards preparation, sample injection, and extract dilution.

7. REAGENTS AND STANDARDS

7.1. Refer to the method 8000B section of this SOP for general requirements for reagents and supplies.

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

7.3. Surrogate Standards

Tetrachloro-m-xylene and decachlorobiphenyl are the surrogate standards. Refer to tables B-5 and B-6 for details of surrogate standards.

7.4. Column Degradation Evaluation Mix

A mid-level standard containing 4,4'-DDT and Endrin and not containing any of their breakdown products must be prepared for evaluation of degradation of these compounds by the GC column and injection port. This mix must be replaced after one year, or whenever corrective action to columns fails to eliminate the breakdown of the compounds, whichever is shorter. This solution also contains the surrogates. Refer to Table B-4 for details of the column degradation evaluation mix.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

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

9. QUALITY CONTROL

Refer to Section 9 of the 8000B section of this SOP.

10. CALIBRATION AND STANDARDIZATION

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

10.2. Refer to Table B-2 for details of GC operating conditions. The conditions listed should result in resolution of all analytes listed in Table B-1 on both columns. Closely eluting pairs are DDE and Dieldrin on the Rtx-5 or DB-5 column and Endosulfan II and DDD on the 1701 column.

Note: Method 608 requires a minimum of three concentration levels for initial calibrations. The relative standard deviation, RSD must be less than 10%.

10.3. Column Degradation Evaluation

Before any calibration runs, either initial or 12 hour, The column evaluation mix must be injected before each initial or daily calibration. The degradation of DDT and endrin must be calculated (see equations 9 and 10) and each shown to be less than 15% before calibration can proceed. This is only necessary if the target compound list includes DDT, Endrin, or any of their degradation products.

If the breakdown of DDT and/or endrin exceeds the limits given above, corrective action must be taken. This action may include:

- Replacement of the injection port liner or the glass wool.
- Cutting off a portion of the injection end of a capillary column.
- Replacing the GC column.

10.4. Initial Calibration

Refer to Section 10 of the 8000B section of this SOP for details of calibration procedures.

10.4.1. Refer to Table B-7 for the initial calibration analytical sequence.

10.4.2. The response for each single-peak analyte will be calculated by the procedures described in the general method for GC analysis.

10.4.3. The surrogate calibration curve is calculated from the Individual AB mix. Surrogates in the other calibration standards are used only as retention time markers. If there are resolution problems, then the A and B mixes may be analyzed separately.

10.4.4. For multi-component pesticides:

Single point calibration is used for multi-component pesticides (typically toxaphene and technical chlordane). Two options are possible; the same quantitation option must be used for standards and samples. Refer to section 12.3 for guidance on which option to use.

10.4.5. For multi-component analytes, the mid level standard must be analyzed as part of the initial calibration. This single point calibration is used to quantitate multi-component analytes.

10.4.6. The analyst may include a full 5 point calibration for any of the multi-component analytes with the initial calibration.

10.5. 12 hour Calibration Verification

The 12 hour calibration verification sequence must be analyzed within 12 hours of the start of the initial calibration and at least once every 12 hours thereafter if samples are being analyzed. If more than 12 hours have elapsed since the injection of the last sample in the analytical sequence, a new analytical sequence must be started with a 12 hour calibration. A mid level calibration standard is used for the 12 hour calibration. Refer to the 8000B section of this SOP for acceptance criteria.

Note : Method 608 requires that the working calibration curve must be verified on each working day by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than ± 15%, the test must be repeated using a fresh calibration standard.

10.5.1. At a minimum, the 12 hour calibration includes analysis of the breakdown mix followed by mid level standards of any single and multi-component analytes.

10.5.2. The retention time windows for any analytes included in the 12 hour calibration are updated.

10.6. Continuing Calibration

The AB calibration mix is analyzed as the continuing calibration standard. At a minimum, this is analyzed after every 20 samples, including matrix spikes, LCS, and method blanks. If 12 hours elapse analyze the 12 hour standard sequence instead. The continuing calibration standard need not include multi-component analytes. If instrument drift is expected due to sample matrix or other factors, it may be advisable to analyze the continuing calibration standard more frequently.

10.6.1. A mid level calibration standard is used for the continuing calibration.

11. PROCEDURE

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

11.2. Extraction

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

11.3. Cleanup

Cleanup procedures are described in SOP No. CORP-OP-0001NC.

11.4. Suggested gas chromatographic conditions are given in Table B-2.

11.5. Allow extracts to warm to ambient temperature before injection.

11.6. The suggested analytical sequence is given in Table B-7.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Refer to the 8000B section of this SOP for identification and quantitation of single component analytes.

12.2. Identification of Multi-component Analytes

Retention time windows are also used for identification of multi-component analytes, but the "fingerprint" produced by major peaks of those compounds in the standard is used in tandem with the retention times to identify the compounds. The ratios of the areas of the major peaks are also taken into consideration. Identification of these compounds may be made even if the retention times of the peaks in the sample fall outside of the retention time windows of the standard, if in the analyst's judgment the fingerprint (retention time and peak ratios) resembles the standard chromatogram.

12.3. Quantitation of Multi-component Analytes

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

12.3.1. If there are no interfering peaks within the envelope of the multi-component analyte, the total area of the standards and samples may be used for quantitation. Any surrogate or extraneous peaks within the envelope must be subtracted from the total area.

12.3.1.1. Multiple peak option

This option is particularly valuable if toxaphene is identified but interferences make quantitation based on total area difficult. Select 3-10 major peaks in the analyte pattern. Calculate the response using the total area or total height of these peaks. Alternatively, find the response of each of the 3-10 peaks per multi-peak pesticide, and use these responses independently, averaging the resultant concentrations found in samples for a final concentration result. When using this option, it is appropriate to remove peaks that appear to be coeluting with contaminant peaks from the quantitation. (i.e. peaks which are significantly larger than would be expected from the rest of the pattern.)

Chlordane may be quantitated either using the multiple peak option (12.3.1.1) total area option (12.3.1.2.) or by quantitation of the major components, α-chlordane, γ-chlordane and heptachlor.

12.3.1.2. Total area option

The total area of the standards and samples may be used for quantitation of multi-component analytes. Any surrogate or extraneous peaks within the envelope must be subtracted from the total area. This option should not be used if there are significant interference peaks within the multi-component pattern in the samples. The retention time window for total area measurement must contain at least 90% of the area of the analyte.

12.4. Second column confirmation multi-component analytes will only be performed when requested by the client, because the appearance of the multiple peaks in the sample usually serves as a confirmation of analyte presence.

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

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

Equation 9

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

where:
A_{DDD}, A_{DDE}, and A_{DDT} = the response of the peaks for 4,4'-DDD, 4,4'-DDE, and 4,4'-DDT in the column degradation evaluation mix.

Equation 10

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

where:
A_{EK}, A_{EA}, and A_E = the response of endrin ketone, endrin aldehyde, and endrin in the column degradation evaluation mix.

13. METHOD PERFORMANCE

13.1. Performance limits for the four replicate initial demonstration of capability required under Section 13.1 of the main body of this SOP. Example performance limits are listed in Table B-8. The spiking level should be equivalent to a mid level calibration.

14. POLLUTION PREVENTION

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

15. WASTE MANAGEMENT

15.1. Waste generated in this procedure will be segregated and disposed according to the facility hazardous waste procedures. The Environmental Health and Safety Director should be contacted if additional information is required.

16. REFERENCES

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

16.2. CFR136A, Method 608 – Organochlorine Pesticides and PCBs

17. MISCELLANEOUS

17.1. Modifications from Reference Method

None

17.2. Modifications from Previous Revisions

17.2.1. No revisions were made to this appendix.

17.3. Tables

Table B-1
Standard Analyte list and Reporting Limits

Compound	Reporting Limit, µg/L or µg/kg		
	water	soil	waste
Aldrin	0.05	1.7	50
α-BHC	0.05	1.7	50
β-BHC	0.05	1.7	50
δ-BHC	0.05	1.7	50
γ-BHC (Lindane)	0.05	1.7	50
α-Chlordane	0.05	1.7	50
γ-Chlordane	0.05	1.7	50
Chlordane (technical)	0.5	17	500
4,4'-DDD	0.05	1.7	50
4,4'-DDE	0.05	1.7	50
4,4'-DDT	0.05	1.7	50
Dieldrin	0.05	1.7	50
Endosulfan I	0.05	1.7	50
Endosulfan II	0.05	1.7	50
Endosulfan Sulfate	0.05	1.7	50
Endrin	0.05	1.7	50
Endrin Aldehyde	0.05	1.7	50
Heptachlor	0.05	1.7	50
Heptachlor Epoxide	0.05	1.7	50
Methoxychlor	0.1	3.3	100
Toxaphene	2.0	67	2000
APPENDIX IX ADD ONs			
Diallate	1.0	33	1000
Isodrin	0.1	3.3	100
Chlorobenzilate	0.1	3.3	100
Kepone[1]	1.0	33	1000

[1] Kepone is sometimes requested for analysis by method 8081A. However kepone may produce peaks with broad tails that elute later than the standard by up to a minute (presumably due to hemi-acetal formation). As a result kepone analysis by 8081A is unreliable and not recommended. Analysis by method 8270C is a possible alternative. Note: alpha chlordane, gamma chlordane, and endrin ketone are not required for some projects.

The following concentration factors are assumed in calculating the Reporting Limits:

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

Table B-2	
Parameter	**Recommended Conditions**
Injection port temp	220°C
Detector temp	325°C
Temperature program	120°C for 1 min, 8.5°C/min to 285°C, , 6 min hold
Column 1	Rtx-CLPesticides 30m x 0.32mm id, 0.5µm
Column 2	Rtx-35 30m x 0.32 mm id, 0.5µm
Column 3	DB-608, 30m X 0.32 mm, 0.25µm
Injection	2µL
Carrier gas	Helium or Hydrogen
Make up gas	Nitrogen
Y splitter	Restek or J&W or Supelco glass tee

Table B-3

Calibration Levels ng/mL

	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6[2]
Individual Mix AB[1]						
Aldrin	5	10	25	50	100	200
g-BHC (Lindane)	5	10	25	50	100	200
Heptachlor	5	10	25	50	100	200
Methoxychlor	10	20	50	100	200	400
Dieldrin	5	10	25	50	100	200
Endosulfan I	5	10	25	50	100	200
Endosulfan II	5	10	25	50	100	200
4,4'-DDT	5	10	25	50	100	200
Endrin Aldehyde	5	10	25	50	100	200
Endrin Ketone	5	10	25	50	100	200
β-BHC	5	10	25	50	100	200
δ-BHC	5	10	25	50	100	200
α-BHC	5	10	25	50	100	200
4,4'-DDD	5	10	25	50	100	200
4,4'-DDE	5	10	25	50	100	200
Endosulfan Sulfate	5	10	25	50	100	200
Endrin	5	10	25	50	100	200
α-Chlordane[3]	5	10	25	50	100	200
γ-Chlordane[3]	5	10	25	50	100	200
Multi-component Standards						
Chlordane (Technical)			250[4]			
Toxaphene			1000[5]			
Surrogates are included with all the calibration mixes at the following levels:						
Tetrachloro-m-xylene	5	10	25	50	100	200
Decachlorobiphenyl	5	10	25	50	100	200

[1] Standards may be split into an A and B mix if resolution of all compounds on both columns is not obtained.

[2] Level 6 is optional and should only be used if linearity can be maintained on the instrument to this level.

[3] Compounds may be used in lieu of running a daily technical Chlordane standard for samples that are non-detect for technical Chlordane.

[4] This standard may be used for quantitation of technical chlordane between 50 and 1000 ng/mL. If the chlordane is more concentrated, the extract must be diluted and reanalyzed.

[5] This standard may be used for quantitation of toxaphene between 200 and 4000 ng/mL. If the toxaphene is more concentrated, the extract must be diluted and reanalyzed.

Table B-4	
Column Degradation Evaluation Mix ng/mL	
Component	Concentration
4,4'-DDT	25
Endrin	25
Tetrachloro-m-xylene (Surrogate)	20
Decachlorobiphenyl (Surrogate)	20

Table B-5			
LCS/Matrix Spike and Surrogate Spike levels µg/L or µg/kg			
	Aqueous	Soil	Waste
gamma BHC (Lindane)	0.20	33.3	200
Aldrin	0.20	33.3	200
Heptachlor	0.20	33.3	200
Dieldrin	0.50	33.3	500
Endrin	0.50	33.3	500
4,4'DDT	0.50	33.3	500
Tetrachloro-m-xylene (Surrogate)	0.20	33.3	200
Decachlorobiphenyl (Surrogate)	0.20	33.3	200

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

Table B-7
Suggested Analytical Sequence

Initial Calibration

Solvent blank (optional)	
Breakdown Mix	
Individual mix AB	All levels
Technical Chlordane	Level 3[1]
Toxaphene	Level 3[1]
Up to 20 samples unless 12 hours comes first)	
Solvent blank (optional)	
Individual mix AB	Mid level (Continuing calibration)
Samples	
After 12 hours:	
Breakdown mix	
Individual mix AB	
Any other single component analytes	

Any multi-component analytes

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

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

12 hour Calibration

At least every 12 hours, counting from the start of the initial calibration, or from the start of the last daily calibration, the retention time windows must be updated using the Individual mix AB, and the breakdown mix must be run before the continuing calibration.

Table B-8

Example Performance limits, four replicate initial demonstration of capability

Compound	Initial demonstration, mean recovery limits	Initial demonstration, RSD limits
Aldrin	46-112	21
alpha-BHC	51-122	24
beta-BHC	61-120	32
delta-BHC	49.5-118.5	36
gamma-BHC	57-116	23
Chlordane	44.8-108.6	20
4,4'-DDD	52-126	28
4,4'-DDE	46-120	27.5
4,4'-DDT	54-137	36
Dieldrin	42.5-124.5	38
Endosulfan I	43-141	24.5
Endosulfan II	78-171	61
Endosulfan Sulfate	62-132	27
Endrin	49-126	37
Heptachlor	57-100	20
Heptachlor Epoxide	43.5-131.5	25.4
Toxaphene	44.4-111.2	20

1. SCOPE AND APPLICATION

1.1. This SOP Appendix describes procedures to be used when SW-846 Method 8000B is applied to the analysis of polychlorinated biphenyls (PCB) by GC/ECD. This Appendix is to be applied when SW-846 Method 8082 is requested, and is applicable to extracts derived from any matrix which are prepared according to the appropriate STL sample extraction SOPs. (CORP-OP-0001NC). The PCBs are determined and quantitated as Arochlor mixes. Criteria for the analysis of wastewater by Method 608 is also included in this appendix.

Table C-1 lists compounds, which are routinely determined by this method, and gives the Reporting Limits (RL) for each matrix. RLs given are based on the low level standard and the sample preparation concentration factors. Matrix interferences may result in higher RLs than those listed.

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

1.2. The associated LIMS method codes are QH (8082) and DM (608).

2. SUMMARY OF METHOD

This method presents conditions for the analysis of prepared extracts of PCBs. The PCBs are injected onto the column and separated and detected by electron capture detection. Quantitation is by the external standard method.

3. DEFINITIONS

Refer to the STL North Canton Laboratory Quality Manual (LQM), current version, for definitions of terms used in this document.

4. INTERFERENCES

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

4.2. Interferences in the GC analysis arise from many compounds amenable to gas chromatography that give a measurable response on the electron capture detector. Phthalate esters, which are common plasticizers, can pose a major problem in the determinations. Avoiding contact with any plastic materials minimizes interferences from phthalates.

4.3. Sulfur will interfere and can be removed using procedures described in SOP CORP-OP-0001NC.

4.4. Interferences co-extracted from samples will vary considerably from source to source. The presence of interferences may raise quantitation limits for individual samples. Specific cleanups may be performed on the sample extracts, including florisil cleanup (Method 3620), Gel Permeation Chromatography (Method 3640), and Sulfur cleanup (Method 3660). These cleanup procedures are included in SOP # CORP-OP-0001NC.

5. SAFETY

5.1. Refer to section 5 of the Method 8000B SOP for general safety requirements.

5.2. Aroclors have been classified as a potential carcinogen under OSHA. Concentrated solutions of Aroclors must be handled with extreme care to avoid excess exposure. Contaminated gloves and clothing must be removed immediately. Contaminated skin surfaces must be washed thoroughly.

5.3. All ^{63}Ni sources shall be leak tested every six months, or in accordance with the manufacturer's general radioactive material license.

5.4. All ^{63}Ni sources shall be inventoried every six months. If a detector is missing, the Director, EH&S shall be immediately notified and a letter sent to the NRC or local state agency.

6. EQUIPMENT AND SUPPLIES

6.1. Refer to Section 6 of the 8000B section of this SOP. A ^{63}Ni electron capture detector is required.

6.2. Refer to Table C-2 for analytical columns.

6.3. Microsyringes, various sizes, for standards preparation, sample injection, and extract dilution.

7. REAGENTS AND STANDARDS

7.1. Refer to the method 8000B section of this SOP for general requirements for reagents and supplies. The standards must be replaced at least every six months or sooner if comparison with check standards indicates a problem.

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

7.3. Surrogate Standards

Tetrachloro-m-xylene and decachlorobiphenyl are the surrogate standards. Other surrogates may be used at client request. Refer to Table C-4 for details of surrogate standards.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

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

9. QUALITY CONTROL

Refer to Section 9 of the 8000B section of this SOP.

10. CALIBRATION AND STANDARDIZATION

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

10.2. Initial Calibration

10.2.1. Refer to Table C-5 for the initial calibration analytical sequence.

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

10.2.3. A five point calibration of the Arochlor 1016/1260 mix is generated with at least mid level single points for the other Aroclor mixes. The average response factor is used to quantitate Arochlors 1260 and 1016, other Arochlors are quantitated from the mid level single point.

Note: Method 608 requires a minimum of three concentration levels for initial calibrations. The relative standard deviation, RSD must be less than 10%.

10.2.4. The analyst may include a full 5 point calibration for any of the Arochlors with the initial calibration.

10.2.5. The high and low standards for the initial 5 point calibration of 1016 / 1260 define the acceptable quantitation range for the other Arochlors. If any Arochlor is determined above this concentration the extract must be diluted and reanalyzed.

10.2.6. If the analyst knows that a specific Arochlor is of interest for a particular project, that Arochlor may be used for the five point calibration rather than the 1016 / 1260 mix.

10.2.7. The surrogate calibration curve is calculated from the Aroclor 1016/1260 mix. Surrogates in the other calibration standards are used only as retention time markers.

10.2.8. Two options are possible for quantitation of Aroclors. The same quantitation option must be used for standards and samples.

10.2.8.1. Multiple peak option

Select 3-10 major peaks in the analyte pattern. Calculate the response using the total area or total height of these peaks. Alternatively, find the response of each of the 3-10 peaks per Aroclor, and use these responses independently, averaging the resultant concentrations found in samples for a final concentration result. When using this option, it is appropriate to remove peaks that appear to be coeluting with contaminant peaks from the quantitation. (i.e. peaks which are significantly larger than would be expected from the rest of the pattern.)

10.2.8.2. Total area option

The total area of the standards and samples may be used for quantitation of multi-component analytes. Any surrogate or extraneous peaks within the envelope must be subtracted from the total area. This option should not be used if there are significant interference peaks within the multi-component pattern in the samples. The retention time window for total area measurement must contain at least 90% of the area of the analyte.

10.3. 12 hour Calibration

The 12 hour calibration verification must be analyzed within 12 hours of the start of the initial calibration and at least once every 12 hours thereafter if samples are being analyzed. If there is a break in the analytical sequence of greater than 12 hours, then a new continuing calibration run must be analyzed before proceeding with the sequence. If more than 12 hours have elapsed since the injection of the last sample in the analytical sequence, a new analytical sequence must be started with a 12 hour calibration.

10.3.1. At a minimum, the 12 hour calibration includes analysis of the Arochlor 1260 / 1016 mix.

10.3.2. It is adequate to verify calibration with a mixture of Aroclors 1016 and 1260. If a specific Aroclor is expected, it may be included in the daily calibration check.

10.3.3. The retention time windows for any analytes included in the daily calibration and CCVs are updated.

10.3.4. For this method samples must be bracketed with successful calibration verification runs.

10.4. Calibration verification

The Arochlor 1260/1016 calibration mix is analyzed as the calibration verification standard. This is analyzed after every 20 samples, including matrix spikes, LCS, and method blanks. (Depending on the type of samples, it may be advisable to analyze verifications more frequently in order to minimize reruns.).

10.4.1. A mid level standard is used for the calibration verification.

Note : Method 608 requires that the working calibration curve must be verified on each working day by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than ± 15%, the test must be repeated using a fresh calibration standard.

11. PROCEDURE

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

11.2. Extraction

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

11.3. Cleanup

Cleanup procedures are described in SOP No. CORP-OP-0001NC.

11.4. Suggested gas chromatographic conditions are given in Table C-2.

11.5. Allow extracts to warm to ambient temperature before injection.

11.6. The suggested analytical sequence is given in Table C-5.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Identification of Arochlors

Retention time windows are used for identification of Arochlors, but the "fingerprint" produced by major peaks of those analytes in the standard is used in tandem with the retention times for identification. The ratios of the areas of the major peaks are also taken into consideration. Identification may be made even if the retention times of the peaks in the sample fall outside of the retention time windows of the standard, if in the analyst's judgment the fingerprint (retention time and peak ratios) resembles the standard chromatogram.

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

12.2. Quantitation of Arochlors

Use 3-10 major peaks or total area for quantitation

If the analyst believes that a combination of Aroclor 1254 and 1260, or a combination of 1242, 1248 and 1232 is present, then only the predominant Arochlor is quantitated and reported, but the suspicion of multiple Aroclors is discussed in the narrative. If well separated Aroclor patterns are present, and then both Aroclors are quantitated and reported.

12.3. If there are no interfering peaks within the envelope of the Arochlor, the total area of the standards and samples may be used for quantitation. Any surrogate or extraneous peaks within the envelope must be subtracted from the total area.

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

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

13. METHOD PERFORMANCE

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

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

14. POLLUTION PREVENTION

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

15. WASTE MANAGEMENT

15.1. Waste generated in this procedure will be segregated and disposed according to the facility hazardous waste procedures. The Environmental Health and Safety Director should be contacted if additional information is required.

16. REFERENCES

16.1. SW846, Update III, December 1996, Method 8082

16.2. CFR136A, Method 608, Organochlorine Pesticides and PCBs.

17. MISCELLANEOUS

17.1. Modifications from Reference Method

17.1.1. Method 8082 includes limited direction for congener specific quantitation. This is outside the scope of this SOP.

17.2. Modifications from Previous Revisions

No changes were made to this Appendix

17.3. Tables

Table C-1 Standard Analyte list and Reporting Limits			
	Reporting Limit, µg/L or µg/kg		
Compound	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]		
Compound	Reporting Limit	
	water (µg/L)	soil (µg/Kg)
Aroclor-1016	0.2	330
Aroclor-1221	0.2	330
Aroclor-1232	0.4	330
Aroclor 1242	0.2	330
Aroclor-1248	0.2	330
Aroclor-1254	0.2	330
Aroclor-1260	0.2	330

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

Table C-5
Suggested Analytical Sequence

Initial Calibration

Injection #		
1	Solvent blank (optional)	
2	Aroclor 1016/1260	Level 1
3	Aroclor 1016/1260	Level 2
4	Aroclor 1016/1260	Level 3
5	Aroclor 1016/1260	Level 4
6	Aroclor 1016/1260	Level 5
7	Aroclor 1232	Level 3
8	Aroclor 1242	Level 3
9	Aroclor 1248	Level 3
10	Aroclor 1221/1254	Level 3
11-30	Sample 1-20 (or as many samples as can be analyzed in 12 hours	
	Solvent blank (optional)	
32	Aroclor 1016/1260	Level 3

etc

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

12 hour Calibration

At least every 12 hours, counting from the start of the initial calibration, or from the start of the last daily calibration, the retention time windows must be updated using the Aroclor 1260 / 1016 mix. Mid level standards of any other Aroclors expected to be present in the samples are also injected.

1. SCOPE AND APPLICATION

This method is applicable to the gas chromatographic determination of Chlorinated phenoxy acid herbicides in extracts prepared by SOP CORP-OP-0001NC. The herbicides listed in Table D1 are routinely analyzed. Other chlorinated acids may be analyzed by this method if the quality control criteria in Section 9 and the initial demonstration of method performance in Section 13 are met.

1.1. The associated LIMS method code is QS.

2. SUMMARY OF METHOD

This method presents conditions for the analysis of prepared extracts of phenoxy acid herbicides by gas chromatography. The herbicides, as their methyl esters, are injected onto the column, separated, and detected by electron capture detectors. Quantitation is by the external standard method.

3. DEFINITIONS

Refer to the STL North Canton Laboratory Quality Manual (LQM), current version, for definitions of terms used in this document.

4. INTERFERENCES

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

4.2. Chlorinated acids and phenols cause the most direct interference with this method.

4.3. Sulfur may interfere and may be removed by the procedure described in SOP#CORP-OP-0001NC.

5. SAFETY

5.1. Refer to section 5 of the Method 8000B SOP for general safety requirements.

6. EQUIPMENT AND SUPPLIES

6.1. Refer to Section 6 of the 8000B section of this SOP. A Ni_{63} electron capture detector is required.

6.2. Refer to Table D2 for analytical columns.

6.3. Microsyringes, various sizes, for standards preparation, sample injection, and extract dilution.

7. REAGENTS AND STANDARDS

7.1. Refer to section 7 of the 8000B section of this SOP for general information on reagents and standards.

8. SAMPLE PREPARATION, PRESERVATION AND STORAGE

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

9. QUALITY CONTROL

9.1. Refer to Section 9 of the 8000B section of this SOP for quality control requirements, including the initial demonstration of capability, definition of a batch, surrogate limits, method blanks, laboratory control samples (LCS), and matrix spikes (MS).

9.2. Refer to Table D-3 for the components and levels of the LCS and MS mixes.

10. CALIBRATION AND STANDARDIZATION

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

10.2. Calibration standards are prepared from purchased standards in the methyl ester form.

10.3. The low level standard must be at or below the laboratory reporting limit. Other standards are chosen to bracket the expected range of concentrations found in samples, without saturating the detector or leading to excessive carryover.

10.4. Refer to Table D-2, for details of GC operating conditions.

11. PROCEDURE

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

11.2. Extraction

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

11.3. Cleanup

The alkaline hydrolysis and subsequent extraction of the basic solution described in the extraction procedure provides an effective cleanup.

11.4. Analytical Sequence

The analytical sequence starts with an initial calibration of at least five points, or a daily calibration that meets % difference criteria from an existing initial calibration.

11.4.1. The daily calibration must be analyzed at least once every 24 hours when samples are being analyzed. If there is a break in the analytical sequence of greater than 12 hours, then a new continuing calibration run must be analyzed before proceeding with the sequence. If more than 24 hours have elapsed since the injection of the last sample in the analytical sequence, a new analytical sequence must be started with a daily calibration.

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

11.4.3. After every 12 hours a continuing calibration is analyzed. The continuing calibration consists of mid level standards of all analytes of interest. Retention time windows are updated with continuing calibrations.

11.5. Gas Chromatography

Chromatographic conditions are listed in Table D-2.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Refer to the 8000B section of this SOP for identification and quantitation of single component analytes.

12.2. The herbicides are analyzed as their methyl esters, but reported as the free acid. For this reason it is necessary to correct the results for the molecular weight of the ester versus the free acid. This is achieved through the concentrations of the calibration standards. For example the 20µg/L calibration standard for 2,4-D contains 21.3 µg/L of the methyl ester. No further correction is necessary.

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

13. METHOD PERFORMANCE

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

14. POLLUTION PREVENTION

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

15. WASTE MANAGEMENT

Waste generated in this procedure will be segregated and disposed according to the facility hazardous waste procedures. The Environmental Health and Safety Director should be contacted if additional information is required.

16. REFERENCES

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

17. MISCELLANEOUS

17.1. Modifications from Reference Method

Refer to the method 8000B section of this SOP for modifications from the reference method.

17.2. Modifications from Previous Revision

The calibration procedure has been changed to require esterification of the calibration standards

17.3. Tables

Table D-1				
Standard Analyte list				
Compound	CAS Number	Reporting Limit, µg/L or µg/kg		
		Aqueous	Soil	Waste
2,4-D	94-75-7	4	80	4000
2,4-DB	94-82-6	4	80	4000
2,4,5-TP (Silvex)	93-72-1	1	20	1000
2,4,5-T	93-76-5	1	20	1000
Dalapon	75-99-0	2	40	2000
Dicamba	1918-00-9	2	40	2000
Dichloroprop	120-36-5	4	80	4000
Dinoseb	88-85-7	0.6	12	600
MCPA	94-74-6	400	8000	400,000
MCPP	93-65-2	400	8000	400,000

The following concentration factors are assumed in calculating the Reporting Limits:

	Extraction Vol.	Final Vol.	Dilution Factor
Ground water	1000 mL 10 mL	20	
Low-level Soil without GPC	50 g	10 mL	20
High-level soil / waste	1 g	10 mL	20

Specific reporting limits are highly matrix dependent. The reporting limits listed above are provided for guidance only and may not always be achievable. For special projects, the extracts may be analyzed without any dilution, resulting in reporting limits 20 times lower than those in Table D-1.

Table D-2	
Instrumental Conditions	
PARAMETER	Recommended conditions
Injection port temp	220°C
Detector temp	325°C
Temperature program	80,2/30/170,0/1/180,1
Column 1	DB-5MS or RTX 5 30x0.32, 0.5um
Column 2	DB-1701 or Rtx-1701
Injection	1-2µL
Carrier gas	Helium / Hydrogen
Make up gas	Nitrogen

Recommended conditions should result in resolution of all analytes listed in Table D-1.

The reporting limits listed in Table D-1 will be achieved with these calibration levels and a 20 fold dilution of the sample extract. Lower reporting limits can be achieved with lesser dilutions of the sample extract.

Table D-3			
LCS/Matrix Spike and Surrogate Spike levels µg/L or µg/kg[1]			
	Aqueous	Soil	Waste
2,4-D	16	800	16000
Silvex	4	200	4000
2,4,5-T	4	200	4000
2,4-DB	16	800	16000
Dalapon	8	400	8000
DCAA (surrogate)	16	800	16000

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

1. SCOPE AND APPLICATION

1.1. This SOP Appendix describes procedures to be used when SW-846 Method 8000B is applied to the analysis of polynuclear aromatic hydrocarbons (PAH) by High Performance Liquid Chromatography. This Appendix is to be applied when SW-846 Method 8310 or EPA Method 610 is requested, and is applicable to extracts derived from any matrix which are prepared according to the appropriate STL North Canton sample extraction SOPs. (CORP-OP-0001NC).

Table E-1 lists compounds, which are routinely determined by this method, and gives the Reporting Limits (RL) for each matrix. RLs given are based on the low level standard and the sample preparation concentration factors. Matrix interferences may result in higher RLs than those listed. Note: Reporting limits are subject to change due to compound sensitivity, calibration levels, MDLs, and other factors.

1.2. The associated LIMS method codes are SG (8310) and VT (610).

2. SUMMARY OF METHOD

This method presents conditions for the analysis of prepared extracts of polynuclear aromatic hydrocarbons by high performance liquid chromatography. The compounds are injected onto a column, separated, and detected by ultraviolet and fluorescence detectors. Quantitation is by the external standard method.

3. DEFINITIONS

Refer to the STL North Canton Laboratory Quality Manual (LQM), current version, for definitions of terms used in this document.

4. INTERFERENCES

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

5. SAFETY

5.1. Refer to section 5 of the Method 8000B SOP for general safety requirements.

5.2. The following parameters covered by this method have been tentatively classified as known or suspected, human or mammalian carcinogens: Benzo(a)anthracene, Benzo(a)pyrene, and Dibenzo(a,h)anthracene. Primary standards of these toxic compounds should be prepared in a hood.

6. EQUIPMENT AND SUPPLIES

6.1. Refer to Section 6 of the 8000B section of this SOP. An Ultraviolet detector and Fluorescence detector is required.

6.2. Refer to Table E2 for analytical columns.

6.3. Microsyringes, various sizes, for standards preparation, sample injection, and extract dilution.

7. REAGENTS AND STANDARDS

7.1. Refer to section 7 of the 8000B section of this SOP for general information on reagents and standards.

7.2. Refer to Table E-3 and E-4 for details of calibration and other standards.

7.3. Surrogate Standards

Terphenyl-d14 and Benzo(e)pyrene are the surrogate standards. Refer to table E-3 for details of surrogate standards.

8. SAMPLE PREPARATION, PRESERVATION AND STORAGE

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

9. QUALITY CONTROL

9.1. Refer to Section 9 of the 8000B section of this SOP for quality control requirements, including the initial demonstration of capability, definition of a batch, surrogate limits, method blanks, laboratory control samples (LCS), and matrix spikes (MS).

9.2. Refer to Table E-3 for the components and levels of the LCS and MS mixes.

10. CALIBRATION AND STANDARDIZATION

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

Note: The Initial Calibration requirement for Method 610 is as follows: If the ratio of response to amount injected (calibration factor) is a constant over the working range (<10% relative standard deviation, RSD), linearity through the origin can be assumed and the average ratio or calibration factor can be used in place of a calibration curve.

10.2. Calibration standards are prepared from purchased solutions. Table E-4 lists the calibration levels.

10.3. The low level standard must be at or below the laboratory reporting limit. Other standards are chosen to bracket the expected range of concentrations found in samples, without saturating the detector or leading to excessive carryover.

10.4. Refer to Table E-2, for details of LC operating conditions.

11. PROCEDURE

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

11.2. Extraction

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

11.3. Cleanup

11.4. Analytical Sequence

The analytical sequence starts with an initial calibration of at least five points, or a daily calibration that meets % difference criteria from an existing initial calibration.

Note: Method 610 requires that continuing calibration verifications may not vary from the predicted response for any parameter by more than ± 15%. The average response may not be used for Method 610.

11.4.1. The daily calibration must be analyzed at least once every 24 hours when samples are being analyzed. If there is a break in the analytical sequence of greater than 12 hours, then a new continuing calibration run must be analyzed before proceeding with the sequence. If more than 24 hours have elapsed since the injection of the last sample in the analytical sequence, a new analytical sequence must be started with a daily calibration.

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

11.4.3. After every 12 hours a continuing calibration is analyzed. The continuing calibration consists of mid level standards of all analytes of interest. Retention time windows are updated with continuing calibrations.

11.5. High Performance Liquid Chromatography

Chromatographic conditions are listed in Table E-2.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Refer to the 8000B section of this SOP for identification and quantitation of single component analytes.

12.2. Surrogate recovery results are calculated and reported for Terphenyl-d14 and Benzo(e)pyrene unless it is determined that sample interference has adversely affected the quantitation of one of the surrogates. One surrogate must be within QC criteria. Corrective action is only necessary if Terphenyl-d14 and Benzo(e)pyrene are both outside of acceptance limits.

13. METHOD PERFORMANCE

13.1. Performance limits for the four replicate initial demonstration of capability required as referenced under Section 13.1

14. POLLUTION PREVENTION

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

15. WASTE MANAGEMENT

15.1. Waste generated in this procedure will be segregated and disposed according to the facility hazardous waste procedures. The Environmental Health and Safety Director should be contacted if additional information is required.

16. REFERENCES

16.1. SW846, Update III, December 1996, Method 8310.

16.2. CFR136 Appendix A Method 610-Polynuclear Aromatic Hydrocarbons.

17. MISCELLANEOUS

17.1. Reporting limits

17.1.1. The lower standard reporting limits are listed in Table

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

17.2. Elution time

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

17.3. Analyte detection

17.3.1. Some compounds are detected only on the ultraviolet detector. For other compounds, the lower of the concentrations calculated from both detectors is reported, the second detector serving as confirmation of the analytes presence.

17.3.2. For any compound that is detected only on the ultraviolet detector, confirmation analysis is not possible. These detected compounds must be narrated that the quantitation is not confirmed by a second detector (Fluorescence).

17.3.3. Some compounds, due to calibration levels and detector limitations, can only be confirmed using the Fluorescence detector. The result will always be reported from the UV detector. These compounds will be narrated, when applicable. Table E-5 lists the compounds and respective detectors.

17.4. Troubleshooting guide

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

17.5. Tables

Table E-1			
Standard Analyte list			
Compound	CAS Number	Reporting Limit, µg/L or µg/kg	
		Aqueous	Soil
Acenaphthene	83-32-9	1	100
Acenaphthylene	208-96-8	1	100
Anthracene	120-12-7	2	100
Benzo(a)anthracene	56-55-3	0.1	5
Benzo(a)pyrene	50-32-8	0.1	5
Benzo(b)fluoranthene	205-99-2	0.1	5
Benzo(g,h,i)perylene	191-24-2	0.1	10
Benzo(k)fluoranthene	207-08-9	0.1	1.7
Chrysene	218-01-9	0.1	5
Dibenzo(a,h)anthracene	53-70-3	0.1	5
Fluoranthene	206-44-0	0.1	10
Fluorene	86-73-7	1	100
Indeno(1,2,3-cd)pyrene	193-39-5	0.1	5
Naphthalene	91-20-3	2	100
Phenanthrene	85-01-8	1	100
Pyrene	129-00-0	0.1	5
1-Methylnaphthalene*	90-12-0	2	100
2-Methylnaphthalene*	91-57-6	2	100

Table E-2				
Instrumental Conditions				
PARAMETER	Recommended conditions			
Injection volume	20 uL			
Detector	HP Series 1100 Fluorescence Detector			
Detector	HP Series 1100 Variable Wavelength Detector (UV)			
Solvent Program	Time	% Water	% Acetonitrile	Flow
	0 min.	50	50	1.5 mL/m
	5 min.	45	55	1.5 mL/m
	10 min.	35	65	2.0 mL/m
	15 min.	25	75	2.0 mL/m

	20 min. 25 min. 30 min.	15 5 45	85 95 55	2.0 mL/m 2.0 mL/m 2.0 mL/m
Column 1	PAH Hypersil 5 micron			
Injection	20 uL			
Solvent	Acetonitrile, HPLC grade			
Solvent	Reagent Water, HPLC grade			

Table E-3 LCS/Matrix Spike and Surrogate Spike Compounds

Compound	Concentration	Compound	Concentration
Acenaphthene	10 ug/mL	Dibenzo(a,h)anthracene	2 ug/mL
Acenaphthylene	10 ug/mL	**Fluoranthene**	2 ug/mL
Anthracene	10 ug/mL	Fluorene	2 ug/mL
Benzo(a)anthracene	2 ug/mL	**Indeno(1,2,3-cd)pyrene**	2 ug/mL
Benzo(a)pyrene	2 ug/mL	**Naphthalene**	10 ug/mL
Benzo(b)fluoranthene	2 ug/mL	**Phenanthrene**	2 ug/mL
Benzo(g,h,i)perylene	2 ug/mL	Pyrene	2 ug/mL
Benzo(k)fluoranthene	2 ug/mL	Terphenyl-d14*	1 ug/mL
Chrysene	2 ug/mL	Benzo(e)pyrene*	5 ug/mL

Bold print denotes control compounds in the LCS/LCSD and MS/MSD.
* Denotes surrogate compounds

Table E-4 Calibration Standards

Component	ST	1:2	1:5	1:10	1:20	1:50	1:100
Naphthalene	50	25	10	5	2.5	1	0.5
Acenaphthylene	50	25	10	5	2.5	1	0.5
Terphenyl d14 (surrogate)	50	25	10	5	2.5	1	0.5
Acenaphthene	10	5	2	1	0.5	0.2	0.1
Fluorene	10	5	2	1	0.5	0.2	0.1
Phenanthrene	10	5	2	1	0.5	0.2	0.1
Anthracene	10	5	2	1	0.5	0.2	0.1
Chrysene	10	5	2	1	0.5	0.2	0.1
1-Methylnaphthalene	50	25	10	5	2.5	1	0.5
Fluoranthene	10	5	2	1	0.5	0.2	0.1
Pyrene	10	5	2	1	0.5	0.2	0.1
Benzo(a)anthracene	10	5	2	1	0.5	0.2	0.1
Benzo(e)pyrene (surrogate)	50	25	10	5	2.5	1	0.5
Benzo(b)fluoranthene	10	5	2	1	0.5	0.2	0.1
Benzo(k)fluoranthene	10	5	2	1	0.5	0.2	0.1

Table E-4 Calibration Standards

Component	ST	1:2	1:5	1:10	1:20	1:50	1:100
Benzo(a)pyrene	10	5	2	1	0.5	0.2	0.1
Dibenzo(a,h)anthracene	10	5	2	1	0.5	0.2	0.1
Benzo(g,h,i)perylene	10	5	2	1	0.5	0.2	0.1
Indeno(1,2,3-cd)pyrene	10	5	2	1	0.5	0.2	0.1
2-Methylnaphthalene	50	25	10	5	2.5	1	0.5

Table E-5 Compound/Detector

Compound	Ultraviolet 254 nm	Fluorescence 280 nm
Acenaphthene	X	X
Acenaphthylene	X	
Anthracene	X	Retention Time confirmation only
Benzo(a)anthracene	X	X
Benzo(a)pyrene	X	X
Benzo(b)fluoranthene	X	X
Benzo(g,h,i)perylene	X	X
Benzo(k)fluoranthene	X	X
Chrysene	X	X
Dibenzo(a,h)anthracene	X	X
Fluoranthene	X	X
Fluorene	X	X
Indeno(1,2,3-cd)pyrene	X	X
Naphthalene	X	X
Phenanthrene	X	X
Pyrene	X	X
1-Methylnaphthalene	X	X
2-Methylnaphthalene	X	X

1. SCOPE AND APPLICATION

1.1. This method is applicable to the determination of the concentration of certain Organophosphorus Pesticides in waters, wastewaters, oils, soils, and sludges. It is based on SW846 Method 8141A. Table F1 shows reporting limits for compounds routinely analyzed by this method. The compounds include, but are not limited to, those shown in Table F1.

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

1.3. The associated LIMS method code is P2.

2. SUMMARY OF METHOD

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

3. DEFINITIONS

Refer to the STL North Canton Laboratory Quality Manual (LQM), current version, for definitions of terms used in this document.

4. INTERFERENCES

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

4.2. Analytical difficulties encountered for target analysis include:

4.2.1. The water solubility of Dichlorvos (DDVP) is 10 g/L at 20°C, and recovery is poor from aqueous solution.

4.2.2. Naled is converted to Dichlorvos (DDVP) on column by debromination. This reaction may also occur during sample workup.

4.2.3. Trichlorfon rearranges and is dehydrochlorinated in acidic, neutral, or basic media to form Dichlorvos (DDVP) and hydrochloric acid. If this method is to be used for the determination of organophosphates in the presence of Trichlorfon, the analyst should be aware of the possibility of rearrangement to Dichlorvos to prevent misidentification.

4.2.4. Merphos is a single component pesticide that is readily oxidized to Merphos oxone. Chromatographic analysis of Merphos almost always results in two peaks.

5. SAFETY

5.1. Refer to Section 5 of the Method 8000B SOP for general safety requirements.

6. EQUIPMENT AND SUPPLIES

6.1. Refer to Section 6 of the 8000B section of this SOP.

6.2. Refer to Table F2 for Instrument settings.

6.3. Microsyringes, various sizes, for standards preparation, sample injection, and extract dilution.

7. REAGENTS AND STANDARDS

7.1. Refer to Section 7 of the 8000B section of this SOP for general information on reagents and standards.

7.2. Refer to Table F-3 for details of calibration and other standards.

7.3. Surrogate Standards

Triphenyl phosphate is the surrogate standard. Refer to table F-4 for details of the surrogate standard.

8. SAMPLE PREPARATION, PRESERVATION AND STORAGE

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

9. QUALITY CONTROL

9.1. Refer to Section 9 of the 8000B section of this SOP for quality control requirements, including the initial demonstration of capability, definition of a batch, surrogate limits, method blanks, laboratory control samples (LCS), and matrix spikes (MS).

9.2. Refer to Table F-4 for the components and levels of the LCS and MS mixes.

10. CALIBRATION AND STANDARDIZATION

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

10.2. Calibration standards are made up from purchased solutions. Table F-3 lists the calibration levels.

10.3. The low level standard must be at or below the laboratory reporting limit. Other standards are chosen to bracket the expected range of concentrations found in samples, without saturating the detector or leading to excessive carryover.

11. PROCEDURE

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

11.2. Extraction

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

11.3. Cleanup

11.4. Analytical Sequence

The analytical sequence starts with an initial calibration of at least five points, or a daily calibration that meets % difference criteria from an existing initial calibration.

11.4.1. The daily calibration must be analyzed at least once every 24 hours when samples are being analyzed. If there is a break in the analytical sequence of greater than 12 hours, then a new continuing calibration run must be analyzed before proceeding with the sequence. If more than 24 hours have elapsed since the injection of the last sample in the analytical sequence, a new analytical sequence must be started with a daily calibration.

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

11.4.3. After every 12 hours a continuing calibration is analyzed. The continuing calibration consists of mid level standards of all analytes of interest. Retention time windows are updated with continuing calibrations.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Refer to the 8000B section of this SOP for identification and quantitation of single component analytes.

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

13. METHOD PERFORMANCE

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

14. POLLUTION PREVENTION

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

15. WASTE MANAGEMENT

15.1. Waste generated in this procedure will be segregated and disposed according to the facility hazardous waste procedures. The Environmental Health and Safety Director should be contacted if additional information is required.

16. REFERENCES

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

17. MISCELLANEOUS

17.1. Reporting limits

17.1.1. The lower standard reporting limits are listed in Table F-1

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

17.1.2.1. The nature of the FPD detector contributes to high dilutions for Method 8141A. There is a phenomenon known as quenching that occurs. This happens when light absorption occurs in the flame of the FPD due to hydrocarbons, sulfur, and certain light absorbing compounds.

When this happens the analytes of interest do not reach the photomultiplier tube and are not detected even though they may be present.

17.2. Elution time

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

17.3. Troubleshooting guide

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

Table F1: Organophosphorus Pesticides Routinely Analyzed and Reporting Limits

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

Table F2: Instrumental Conditions	
PARAMETER	Recommended conditions
Injection port temp	175°C
Detector temp	230°C
Initial temp	135°C
Temperature program	(A) 5°C/minute (B) 20°C/minute
Final Temp	(A) 245°C (B) 295°C
Final Hold Time	(A) 0 minutes (B) 7 minutes
Column 1	RTX-OPP, 30 meter, 0.32 mm, 0.5 µm film
Column 2	RTX-1, 30 meter, 0.32 mm, 0.5 µm film
Injection	1-2µL
Carrier gas	Helium / Hydrogen
Make up gas	Nitrogen

Table F3 Initial Calibration Concentrations (ng/uL)

COMPOUND	LEVEL1	LEVEL2	LEVEL3	LEVEL4	LEVEL5	LEVEL6	LEVEL7
o,o,o-Triethylp-hosphate	0.2	0.5	1	2	5	10	20
Dichlorvos	0.2	0.5	1	2	5	10	20
Mevinphos	0.2	0.5	1	2	5	10	20
Thionazin	0.2	0.5	1	2	5	10	20
Ethoprop	0.2	0.5	1	2	5	10	20
Naled	0.2	0.5	1	2	5	10	20
Sulfotepp	0.2	0.5	1	2	5	10	20
Phorate	0.2	0.5	1	2	5	10	20
Demeton	0.2	0.5	1	2	5	10	20
Dimethoate	0.2	0.5	1	2	5	10	20
Diazinon	0.2	0.5	1	2	5	10	20
Disulfoton	0.2	0.5	1	2	5	10	20
Methyl Parathion	0.2	0.5	1	2	5	10	20
Ronnel	0.2	0.5	1	2	5	10	20
Fenthion	0.2	0.5	1	2	5	10	20
Chlorpyrofos	0.2	0.5	1	2	5	10	20
Parathion	0.2	0.5	1	2	5	10	20
Malathion	0.2	0.5	1	2	5	10	20
Trichloronate	0.2	0.5	1	2	5	10	20
Merphos	0.2	0.5	1	2	5	10	20
Stirophos	0.2	0.5	1	2	5	10	20
Tokuthion	0.2	0.5	1	2	5	10	20
Fensulfothion	0.2	0.5	1	2	5	10	20
Bolstar	0.2	0.5	1	2	5	10	20
Famphur	0.2	0.5	1	2	5	10	20
Azinphos methyl	0.2	0.5	1	2	5	10	20
Coumaphos	0.2	0.5	1	2	5	10	20

Table F4: LCS/Matrix Spike and Surrogate Spike Compounds – 20 ug/mL

Compound	**Compound**
Thinazin	Sulfotepp
Phorate	Disulfoton
Methyl Parathion	Parathion
Famphur	O,O,O-Triethylphosphate
Dimethoate	Triphenyl Phosphate - Surrogate

1. Scope and Application

1.1. This method is applicable to the determination of the concentration and **tentative** identification of petroleum hydrocarbon mixes in waters, wastewaters, soils, and sludges.

1.2. This SOP is based on SW-846 Method 8015B, Modified, Revision 3, December 1996 and Wisconsin DNR Modified DRO method.

1.3. The associated LIMS method codes are HS (8015 MOD), KI (8015B), and C6 (Wisconsin DRO).

2. Summary of Method

2.1. This method provides gas chromatographic conditions for detection and identification of total petroleum hydrocarbons. Prior to the use of this method, appropriate sample preparation techniques are used.

2.2. Wisconsin DRO Method is designed to measure the concentration of diesel range organics in water and soil. This corresponds to a hydrocarbon range of C_{10}-C_{28} and a boiling point range between approximately 170 °C and 430 °C.

2.3. An aliquot of the prepared sample is injected into a gas chromatograph (GC) and compounds in the effluent are detected by a flame ionization detector (FID).

3. Definitions

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

3.2. Wisconsin DNR DRO Method Definition - Diesel Range Organics (DRO) – All the chromatographic response falling between the onset of the n-decane (n-C_{10}) peak and the conclusion of the n-octacosane (n-C_{28}) peak. Quantitation is based on a direct comparison of the total area within this range to the total area of the Diesel Component Standard.

3.3. Wisconsin DNR DRO Method Definition –Diesel Component Standard: A ten component blend of typical diesel compounds. This standard serves as a quantitation standard and is used to establish a retention time window for diesel range organics.

4. INTERFERENCES

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

5. SAFETY

5.1. Refer to Section 5 of the Method 8000B SOP for general safety requirements.

6. EQUIPMENT AND SUPPLIES

6.1. Refer to Section 6 of the 8000B section of this SOP.

6.2. Microsyringes, various sizes, for standards preparation, sample injection, and extract dilution.

7. REAGENTS AND STANDARDS

7.1. Refer to Section 7 of the 8000B section of this SOP.

7.2. The petroleum hydrocarbons are purchased from a chemical supplier when available. When no chemical supplier is available, the fuels are purchased from public sources.

7.3. The Diesel Component Stock Standard for the Wisconsin DRO method may be commercially prepared standards if the standards are certified by the manufacturer or by an independent source.

8. SAMPLE PREPARATION, PRESERVATION AND STORAGE

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

8.2. Wisconsin DNR DRO aqueous samples must be preserved with HCL such that the pH is < 2.

9. QUALITY CONTROL

9.1. Refer to Section 9 of the 8000B section of this SOP for quality control requirements, including the initial demonstration of capability, definition of a batch, surrogate limits, method blanks, laboratory control samples (LCS), and matrix spikes (MS).

9.2. LCS recoveries are calculated from a Diesel Calibration. The Wisconsin DNR DRO method specifies the recovery of the LCS-water spike must be between 75%-115% and the RPD <20%. LCS Soil recoveries must fall between 70%-120% of the known concentration and the RSD must be <20%.

9.2.1. The Wisconsin DNR DRO Method requires a Duplicate Laboratory Control Spike with each batch. MS/MSD samples are not required for this method. One LCS must be run at the beginning of the batch of samples and the other at the end.

9.3. MS/MSD recoveries are calculated from a Diesel calibration.

9.4. Surrogates

9.4.1. Because of the nature of the TPH analysis, whereas certain petroleum mixtures can override the C9 surrogate, the C9 surrogate recoveries are advisory. Re-extraction due to surrogate recoveries is determined by analyst judgement.

NOTE: Ohio VAP rules require reanalysis when surrogate recoveries are outside of control limits.

10. CALIBRATION AND STANDARDIZATION

10.1. Recommended Instrument Conditions

10.1.1. Hydrogen carrier gas - flow rate 5 - 6 mL/min

10.1.2. Detector gas mixture - air hydrogen mixture in a 10:1 ratio, air 80 - 120 mL/min, hydrogen 8 -12 mL/min

10.1.3. Temperature Program - refer to Appendix

10.1.4. Injection volume - 1 µL

10.2. Initial Calibration

10.2.1. Analyze a five point Diesel calibration standard and a five point DRO calibration standard referring to the recommended instrument conditions. The calibration concentrations are 100, 200, 500, 1000, and 2000 ng/uL. A 5000ng/uL standard may be analyzed if needed. The retention time window of C10-C32 shall be used for the Diesel calibration.

10.2.2. The Wisconsin DNR DRO method requires the retention time window be defined as beginning 0.1 minutes before the onset of the n-decane peak and ending 0.1 minutes after the conclusion of the n-octacosane peak in the calibration run.

10.2.3. Wisconsin DNR DRO quantitation is based on a direct comparison of the total area within the retention time window to the total area of the Diesel Component Standard.

10.2.4. Wisconsin DNR DRO integration must be "baseline to baseline" as opposed to a "valley to valley". Baseline to baseline is defined here as a flat baseline drawn parallel to the x-axis of chromatographic graph that includes all responses within the retention time window.

10.2.5. A linear regression calibration curve must be prepared for Wisconsin DNR DRO analysis. The curve must have a correlation coefficient of at least 99%.

10.3. Continuing Calibration

10.3.1. The calibration verification must bracket the LCS, MS, MSD extracts and must meet passing criteria. The Wisconsin DNR DRO method requires the calibration verification must not vary from the calibration curve by more than 20%.

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

11. PROCEDURE

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

11.2. Extraction

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

11.3. Cleanup

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

11.5. Petroleum Hydrocarbon Identification and/or Fingerprinting

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

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

11.6. Sample Quantification

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

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

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

12. DATA ANALYSIS AND CALCULATIONS

12.1. Refer to the 8000B section of this SOP for identification and quantitation of single component analytes.

12.2. Surrogate recovery results are calculated and reported for Nonane (C-9) unless it is determined that sample interference has adversely affected the quantitation of one of the surrogates. The surrogate must be within QC criteria. Corrective action is only necessary if Nonane (C-9) is outside of acceptance limits.

13. METHOD PERFORMANCE

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

14. POLLUTION PREVENTION

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

15. WASTE MANAGEMENT

15.1. Waste generated in this procedure will be segregated and disposed according to the facility hazardous waste procedures. The Environmental Health and Safety Director should be contacted if additional information is required.

16. REFERENCES

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

16.2. Method for Determining Diesel Range Organics, Modified DRO, Wisconsin DNR, Public Hearing Draft, September 1995.

16.3. Related SOP

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

Table G1: Suggested GC Temperature Program for TPH analysis

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

Table G2: Reporting Limits for TPH Analysis

Analyte	Reporting Limits		
	Water (µg/L)	Solids (mg/kg)	Waste Dilution (mg/kg)
TPH (as Diesel) or DRO	100	3.3	200
C10-C32 (Ohio VAP only)	100	3.3	200
Fingerprint Compounds[1]			
Mineral Spirits	Kerosene	Motor Oil	
Hydraulic Oil	Jet Fuel	Stoddard Solvent	
DRO Spiking Solution			
Decane	Dodecane	Tetradecane	
Hexadecane	Octobecane	Eicosane	
Docosane	Tetracosane	Hexacosane	
Octacosane			

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

1. Scope and Application

1.1. This method is applicable to the determination of the concentration of various Non-halogenated Organic Compounds in waters, wastes, sludges, and solids. It is based on SW-846 Method 8015B.

1.2. The applicable LIMs method codes are J7 (GC/FID 8015) and QU (Semivolatile Organics, 8015B). The preparation code is 88.

2. Summary of Method

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

3. Definitions

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

4. INTERFERENCES

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

5. SAFETY

5.1. Refer to section 5 of the Method 8000B SOP for general safety requirements.

6. EQUIPMENT AND SUPPLIES

6.1. Refer to Section 6 of the 8000B section of this SOP.

6.2. Recommended Columns:

6.2.1. RTX Stabilwax, fused silica, 60 m x 0.53, 0.5 µm film thickness, or equivalent column.

6.2.2. Stabilwax-DA, fused silica, 60 m x 0.32, 0.5 µm film thickness, or equivalent column.

6.3. Detectors: Flame ionization (FID)

6.4. Microsyringes, various sizes, for standards preparation, sample injection, and extract dilution.

7. REAGENTS AND STANDARDS

7.1. Refer to Section 7 of the 8000B section of this SOP.

7.1.1. Reagent water

7.2. Standards

7.2.1. Refer to Table H2.

8. SAMPLE PREPARATION, PRESERVATION AND STORAGE

8.1. Refer to section 8 of the 8000B section of this SOP.

9. QUALITY CONTROL

9.1. Refer to Section 9 of the 8000B section of this SOP for quality control requirements, including the initial demonstration of capability, definition of a batch, surrogate limits, method blanks, laboratory control samples (LCS), and matrix spikes (MS).

10. CALIBRATION AND STANDARDIZATION

10.1. Recommended Instrument Conditions

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

10.1.2. RTX- Stabilwax and Stabilwax-DA Columns:

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

10.2. Initial Calibration

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

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

11. PROCEDURE

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

11.2. Sample Preparation Summary

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

11.3. Sample Preparation Procedure

11.3.1. Waters

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

11.3.2. Sediments/soils and waste

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

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

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

11.4. Sample Analysis

11.4.1. Preliminary Evaluation

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

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

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

11.5. Analytical Documentation

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

Compound	CAS Number	Reporting Limits	
		Water, mg/L	Solid, mg/kg
Ethylene oxide	75-21-8	1.0	0.5
iso-Butanol	78-83-1	1.0	0.5

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

Table H2 Non-halogenated Organic Compounds Working Standards

COMPOUND	LEVEL1	LEVEL2	LEVEL3	LEVEL4	LEVEL5	LEVEL 6
2-Methoxyethanol	1.0	2.0	5.0	10.0	20.0	50.0
Methanol	1.0	2.0	5.0	10.0	20.0	50.0
Isopropyl alcohol	1.0	2.0	5.0	10.0	20.0	50.0
n-Propyl alcohol	1.0	2.0	5.0	10.0	20.0	50.0
Ethanol	1.0	2.0	5.0	10.0	20.0	50.0
n-Butanol	1.0	2.0	5.0	10.0	20.0	50.0
1,4-Dioxane	1.0	2.0	5.0	10.0	20.0	50.0
Ethylene oxide	1.0	2.0	5.0	10.0	20.0	50.0
iso-Butanol	1.0	2.0	5.0	10.0	20.0	50.0

1. Scope and Application

1.1. This method is applicable to the determination of the concentration of Sulfolane and N-Methyl-2-pyrrolidone in water and solid samples. It is based on SW846 Method 8015B. The working linear range is 50 to 1000 µg/L. Table I1 lists the reporting limits associated with this method.

1.2. The applicable LIMS method code is KU.

2. Summary of Method

2.1. This method provides gas chromatographic conditions for the detection of mg/L levels of Phillips 66 compounds in water. Prior to use of this method, appropriate sample extraction techniques must be used.

3. Definitions

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

4. INTERFERENCES

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

5. SAFETY

5.1. Refer to section 5 of the Method 8000B SOP for general safety requirements.

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

5.2.1. Chemicals that have been classified as **carcinogens,** or **potential carcinogens,** under OSHA include: **Methylene Chloride.**

6. EQUIPMENT AND SUPPLIES

6.1. Refer to Section 6 of the 8000B section of this SOP.

6.2. Gas Chromatograph

6.2.1. Gas Chromatograph: Modified to accept capillary columns

6.2.2. Data System: Capable of peak integration

6.2.3. Gas Chromatographic Column: 30 m x 0.32 mm ID RTX-5 fused silica capillary column

6.2.4. Autosampler: Capable of reproducible injections

6.2.5. Carrier Gas: Hydrogen

6.2.6. Detector: Flame ionization (FID)

6.3. Volumetric Flasks: 10, 50, and 100 mL

6.4. Microsyringe: 10 µL

6.5. Pipettes: Disposable µL, Pasteur

6.6. Autosampler Vials: 1 mL with 11 mm crimp cap, Teflon®/silicone septum liner.

7. REAGENTS AND STANDARDS

7.1. Refer to Section 7 of the 8000B section of this SOP.

7.2. Reagents

7.2.1. Methylene Chloride: Pesticide grade or equivalent

7.3. Standards

7.3.1. Refer to Section 7 of the 8000B section of this SOP.

8. SAMPLE PREPARATION, PRESERVATION AND STORAGE

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

9. QUALITY CONTROL

9.1. Refer to Section 9 of the 8000B section of this SOP for quality control requirements, including the initial demonstration of capability, definition of a batch, surrogate limits, method blanks, laboratory control samples (LCS), and matrix spikes (MS).

9.2. Surrogates are not used for this analysis.

10. CALIBRATION AND STANDARDIZATION

10.1. Initial Calibration

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

11. PROCEDURE

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

11.2. Sample Analysis

11.2.1. Summary

11.2.1.1. The sample extract is injected onto the GC column. The compounds are then identified and quantitated.

11.2.2. Recommended Instrument Conditions

11.2.2.1. GC Conditions

Initial Temperature:	45°C
Initial Hold Time:	4 minutes
Temperature Program:	15°C/minute
Final Temperature:	300°C, hold 2 minutes
Final Time:	23 minutes
Carrier Gas:	Hydrogen
Injection Volume:	1 µL

11.2.3. Sample Analysis Procedure

11.2.3.1. Preliminary Evaluation

The sample extracts may be screened to determine the level of analyte present. If the level of analyte exceeds the working range of the calibration curve, an appropriate dilution is performed to bring the level within the calibration range.

11.2.4. Inject 1 µL of the sample extract or diluted sample into the GC using the same conditions as those used in calibration.

11.2.5. Identification

11.2.5.1. Analytes of interest are identified by comparing retention times with known standards.

11.2.5.2. A single column is used for identification.

11.2.6. Sample Quantification

11.2.6.1. Refer to Section 11 in the 8000B Section of this SOP

11.3. Analytical Documentation

11.3.1. Record all analytical information in the analytical logbook/logsheet, including the analytical data from standards, blanks, LCSs, MS/MSDs, and any corrective actions or modifications to the method.

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

11.3.3. Documentation such as all associated instrument printouts (final runs, screens, reruns, QC samples, etc.) and daily calibration data corresponding to all final runs is available for each data file.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Refer to the 8000B section of this SOP for identification and quantitation of single component analytes.

13. METHOD PERFORMANCE

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

14. POLLUTION PREVENTION

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

15. WASTE MANAGEMENT

15.1. Waste generated in this procedure will be segregated and disposed according to the facility hazardous waste procedures. The Environmental Health and Safety Director should be contacted if additional information is required.

16. REFERENCES

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

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

17.1. Reporting limits

17.1.1. The lower reporting limits are shown in Table I1

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

TABLE I1
PHILLIPS 66 REPORTING LIMITS

Compound	Reporting Limits, µg/L
Tetramethylene sulfone (Sulfolane)	50
N-Methyl-2-pyrrolidone	50

Phillips 66 Compounds

STL NORTH CANTON STANDARD OPERATING PROCEDURE

TITLE: ACID DIGESTION OF SOILS, SW846 METHOD 3050B

(SUPERSEDES: REVISION 2.2 DATE 09/25/01)

Prepared by: _____ 1-18-02
Date

Reviewed by: Karen R. Counts 1-18-02
Technology Specialist Date

Reviewed by: _____ 2-1-02
Quality Assurance Manager Date

Reviewed by: _____ 1-24-02
Environmental Health and Safety Date

Reviewed by: _____ 1-28-02
Laboratory Director Date

Reviewed by: _____
Corporate Technology Date

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SOP No. CORP-IP-0002NC
Revision No. 2.3
Revision Date: 01/18/02
Page 1 of 26

STL NORTH CANTON STANDARD OPERATING PROCEDURE

TITLE: ACID DIGESTION OF SOILS, SW846 METHOD 3050B

(SUPERSEDES: REVISION 2.2 DATE 09/25/01)

Prepared by: _____ 1-18-02 Date

Reviewed by: Karen R. Counts 1-18-02
Technology Specialist Date

Reviewed by: _____ 2-1-02
Quality Assurance Manager Date

Reviewed by: _____ 1-24-02
Environmental Health and Safety Date

Reviewed by: _____ 1-28-02
Laboratory Director Date

Reviewed by: _____ 2/22/02
Corporate Technology Date

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SOP No. CORP-IP-0003NC
Revision No. 1.3
Revision Date: 09/25/01

STL STANDARD OPERATING PROCEDURE

TITLE: ACID DIGESTION OF AQUEOUS SAMPLES BY SW846 AND MCAWW 200 SERIES METHODS

(Supersedes: Revision 1.2 Dated 03/20/00)

Prepared by: _____ 9/26/01
Date

Reviewed by: _____ 9.26.01
Technology Specialist Date

Reviewed by: _____ 9/26/01
Quality Assurance Manager Date

Reviewed by: _____ 9-27-01
Environmental Health and Safety Date

Reviewed by: _____ 9-28-01
Laboratory Director Date

Reviewed by: _____
Corporate Technology

Date

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1. SCOPE AND APPLICATION

1.1. This procedure describes the preparation of aqueous samples for the analysis of certain metals by Graphite Furnace Atomic Absorption (GFAA), Flame Atomic Absorption (FLAA), Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP), and Inductively Coupled Plasma-Mass Spectrometry (ICP/MS) using the MCAWW 200 series methods (NPDES) and SW846 Methods 3005A, 3010A, 3020A and 7060A/7740 (RCRA).

1.2. The applicability of each of these preparation protocols to specific analytes is detailed in Tables I and II (Appendix A) and the applicable determinative methods are illustrated by Figures 6 and 7 (Section 17). Additional elements may be analyzed following digestion by these protocols provided that the method performance criteria specified in Section 13.0 of this SOP are met.

1.3. This SOP provides procedures applicable to the preparation of dissolved, suspended, total recoverable and total elements in ground water, aqueous samples, certain aqueous sludges, wastes, and biological tissues, and leachates/extracts.

1.4. SW-846 Method 3005A is used to prepare surface and groundwater samples for total recoverable and dissolved metals determination by FLAA, ICP and GFAA (antimony only).

1.5. MCAWW Method 200.7 Section 9.4 is used to prepare surface water, domestic and industrial waste samples for total recoverable and dissolved metals determination by ICP.

1.6. SW-846 Method 3010A is used to prepare aqueous samples, EP and mobility-procedure extracts, and wastes that contain suspended solids for total metals analysis by FLAA or ICP.

1.7. MCAWW Method 200.7 Section 9.3 is used to prepare surface water and wastes that contain suspended solids for total metals analysis by ICP.

1.8. SW-846 Method 3020A is used to prepare aqueous samples, EP and mobility-procedure extracts, and wastes that contain suspended solids for total metals by GFAA, or ICP/MS.

1.9. MCAWW Method 200.0 Section 4.1.3 is used to prepare surface water and wastes that contain suspended solids for total metals analysis by GFAA.

1.10. MCAWW Method 200.0 Section 4.1.4 is used to surface water, domestic and industrial waste samples for total recoverable and dissolved metals determination by GFAA.

1.11. SW-846 Methods 7060A and 7740, respectively, contain the procedure for the preparation of aqueous samples for arsenic and selenium.

1.12. MCAWW Methods 206.2 and 270.2, respectively, contain the procedure for the preparation of aqueous samples for arsenic and selenium.

1.13. All matrices require digestion prior to analysis with the exception of analyses for dissolved metals in filtered and acidified aqueous samples. Although digestion is not specifically required by the method, some clients and regulators do require digestion of dissolved samples and this must be clarified before project initiation.

2. SUMMARY OF METHOD

2.1. Method 3005A / Method 200.7 Section 9.4 - Preparation for Total Recoverable or Dissolved Metals Analysis by FLAA or ICP Spectroscopy

2.1.1. A representative aliquot of sample is heated with nitric and hydrochloric acids and substantially reduced in volume. The digestate is filtered (if necessary) and diluted to volume.

2.2. Method 3010A / Method 200.7 Section 9.3 - Preparation for Total Metals Analysis by FLAA or ICP Spectroscopy

2.2.1. A representative aliquot of sample is refluxed with nitric acid. After the digestate has been reduced to a low volume, it is refluxed with hydrochloric acid, filtered (if necessary) and brought up to volume.

2.3. Method 3020A / Method 200.0 Section 4.1.3 - Preparation for Total Metals for Analysis by GFAA Spectroscopy and ICP/MS.

2.3.1. A representative aliquot of sample is refluxed with nitric acid. After the digestate has been reduced to a low volume, it is cooled, filtered (if necessary) and brought up to volume.

2.4. Methods 7060A/206.2 and Methods 7740/270.2 - Preparation for Arsenic/Selenium Analysis by GFAA

2.4.1. A representative aliquot of sample is heated with nitric acid and peroxide until the digestate has been reduced to a low volume. The sample is cooled, filtered (if necessary) and brought up to volume.

2.5. Method 200.0 Section 4.1.4 - Total Recoverable GFAA Preparation (NPDES)

2.5.1. A representative aliquot of sample is heated with nitric acid and until the digestate has been reduced to a low volume. The sample is cooled, filtered (if necessary) and brought up to volume.

3. DEFINITIONS

Additional definitions of terms used in this SOP may be found in the glossary of the QAMP.

3.1. Dissolved Metals: Those elements which pass through a 0.45 um membrane. (Sample is acidified after filtration).

3.2. Suspended Metals: Those elements which are retained by a 0.45 um membrane.

3.3. Total Metals: The concentration determined on an unfiltered sample following digestion.

3.4. Total Recoverable Metals: The concentration determined on an unfiltered sample following treatment with hot, dilute mineral acid.

4. INTERFERENCES

4.1. There are numerous routes by which samples may become contaminated. Potential sources of trace metals contamination include: metallic or metal-containing labware (e.g., talc gloves which contain high levels of zinc), containers, impure reagents, dirty glassware, improper sample transfers, dirty work areas, atmospheric inputs such as dirt and dust, etc. Be aware of potential sources of contamination and take appropriate measures to minimize or avoid them.

4.2. The entire work area, including the bench top and fume hood, should be thoroughly cleaned on a routine schedule in order to minimize the potential for environmental contamination. Refer to Appendix D for additional contamination control guidelines.

4.3. Boron and silica from the glassware will migrate into the sample solution during and following sample processing. For critical low level determinations of boron and silica, only quartz and/or plastic labware should be used.

4.4. Physical interference effects may contribute to inaccuracies in the determinations of trace elements. Oils, solvents and other matrices may not be digested using these methods if they are not soluble with acids. If physical interferences are present, they should be documented.

4.5. Visual interferences or anomalies (such as foaming, emulsions, precipitates, etc.) must be documented.

4.6. Allowing samples to boil or go dry during digestion may result in the loss of volatile metals. If this occurs the sample must be reprepared. Antimony is easily lost by volatilization from hydrochloric acid media.

4.7. Precipitation of silver chloride (AgCl) may occur when chloride ions and high concentrations of silver (i.e., greater than 1 mg/L) are present in the sample.

4.8. Specific analytical interferences are discussed in each of the determinative methods.

5. SAFETY

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

5.2. Eye protection that satisfies ANSI Z87.1 (as per the Chemical Hygiene Plan), laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

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

5.3.1. The following materials are known to be **corrosive:**

hydrochloric acid and nitric acid.

5.3.2. The following materials are known to be **oxidizing agents**:

nitric acid and hydrogen peroxide.

5.3.3. All sample digestions, including cooling of digestates, 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. 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. Always carry bulk concentrated acid bottles in appropriate impact proof containers.

5.8. Acid/peroxide spills must be neutralized immediately, flushed with water and cleaned up using appropriate spill kits.

5.9. Discard chipped or broken beakers to prevent injury. Chipped glassware may be fire polished as an alternative to disposal.

5.10. 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 or other adjustable heating source capable of maintaining a temperature of 95°C (± 4).

6.2. Calibrated thermometer that covers a temperature range of 0-200°C.

6.3. Griffin beakers of assorted sizes or equivalent.

6.4. Watch glasses, ribbed or equivalent.

6.5. Whatman No. 4 filter paper or equivalent.

6.6. Funnels or equivalent filtration apparatus.

6.7. Centrifugation equipment (if desired method of removing particulates is centrifugation).

6.8. Graduated cylinder or equivalent capable of measuring 50 mL within 3% accuracy.

6.9. Analytical balance capable of accurately weighing to the nearest 0.01 grams.

6.10. Repipetors or suitable reagent dispensers.

6.11. Calibrated automatic pipettes with corresponding pipette tips or Class A glass volumetric pipettes.

6.12. Class A volumetric flasks.

6.13. pH indicator strips (pH range 0 - 6).

6.14. Plastic digestate storage bottles.

7. REAGENTS AND STANDARDS

7.1. Reagent water must be produced by a Millipore DI system or equivalent. Reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks as defined in the determinative SOPs.

7.2. Laboratory Control Sample (LCS) and matrix spike (MS) solutions are purchased as custom STL solutions. All standards must be stored in FEP fluorocarbon or previously unused polyethylene or polypropylene bottles. Stock standard solutions must be replaced prior to the expiration date provided by the manufacturer. If no expiration date is provided, the stock solutions may be used for up to one year and must be replaced sooner if verification from an independent source indicates a problem.

7.3. Working ICP LCS/MS spike solution: Prepare the ICP LCS/MS working spike solution from custom stock standards to the final concentration listed in Table III. The working

spike must be prepared in a matrix of 5% 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 spike solution 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 solution must be made fresh every three months.

7.5. The TCLP MS working spike solution is provided directly by the vendor, no further standard preparation is necessary.

7.6. The LCS and MS samples must contain all the elements designated for analysis in each batch of samples. If a non-routine element is required that is not contained in the custom STL solution, the individual facility must purchase a solution from the designated vendor that will cover the additional analyte(s) of interest and provide for a final spike concentration that is appropriate to the determinative method.

7.7. Aqueous laboratory control samples (LCSW) and matrix spike samples are prepared as described in Sections 9.5 and 9.6. Refer to Tables III and IV(Appendix A) for details regarding the stock, working standard and final digestate spike concentrations for ICP and GFAA LCS and matrix spike preparations.

7.8. Nitric acid (HNO_3), concentrated, trace metal grade or better.

7.9. 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.

7.10. Hydrochloric acid (HCl), concentrated, trace metal grade or better.

7.11. Hydrochloric acid, 1:1 - dilute concentrated HCl with an equal volume of reagent water.

Note: When preparing diluted acids always add acid to water. If the water is added to the acid a violent reaction may occur.

7.12. 30% Hydrogen peroxide (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. Aqueous samples are preserved with nitric acid to a pH of <2 and may be stored in either plastic or glass. If boron or silica are to be determined, plastic containers are preferred. Refrigeration is not required. Preservation must be verified prior to analysis.

8.3. For dissolved metals analysis, the samples should be filtered through a 0.45 um filter prior to preservation. Filtration must be done in the field or within 24 hours of collection.

Note: If a sample being analyzed for dissolved metals is found to contain sediment the analyst should contact their supervisor or group leader. The client should be notified of the problem to decide how to treat the sample.

9. QUALITY CONTROL

Table VI (Appendix A) provides a summary of quality control requirements including type, frequency, acceptance criteria and corrective action.

9.1. Initial Demonstration of Capability

Prior to analysis of any analyte using any method contained within this SOP the following requirements must be met:

9.1.1. Method Detection Limit (MDL) - An MDL must be determined for each analyte/matrix prior to the analysis of any samples. The MDL is determined using seven replicates of reagent water, spiked with all the analytes of interest, that have been carried through the entire analytical procedure. MDL's must be redetermined on an annual basis in accordance with 40 CFR Part 136 Appendix B requirements as detailed in STL QA Policy QA-005. The spike level must be between the calculated MDL and 10X the MDL to be valid. The result of the MDL determination must be below the STL reporting limit.

9.1.2. Initial Demonstration Study - This requires the analysis of four QC check samples. The QC check sample is a well-characterized laboratory generated sample used to monitor method performance, which should contain all the analytes of interest. The results of the initial demonstration study must be acceptable before analysis of samples may begin. The results of the initial demonstration study may be used to

extend a method for the analysis of other elements provided all acceptance criteria are met.

9.1.2.1. Four aliquots of the check sample (LCS) are prepared and analyzed using the procedures detailed in this SOP and the determinative SOPs.

9.1.2.2. Calculations and acceptance criteria for QC check samples are given in the determinative SOPs (CORP-MT-0001, CORP-MT-0003).

9.2. Preparation Batch - A group of up to 20 samples that are of the same matrix and are processed together using the same procedures and reagents. The preparation batch must contain a method blank, a LCS and a matrix spike/matrix spike duplicate. In some cases, at client request, it may be appropriate to process a matrix spike and sample duplicate in place of the MS/MSD. If clients specify specific samples for MS/MSD, the batch may contain multiple MS/MSD pairs.

9.3. Sample Count - Laboratory generated QC samples (method blanks, LCS) are not included in the sample count for determining the size of a preparation batch. MS/MSD are not included in the sample count unless there are multiple sets of MS/MSD per batch. In other words, the first MS/MSD are not counted; all additional MS and MSDs are counted as samples.

9.4. Method Blank (MB) - One method blank must be processed with each preparation batch. The method blank consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The method blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. Criteria for the acceptance of blanks are contained within the individual analytical method SOP's. If the method blank does not meet the criteria contained within the analytical method SOPs; the blank and all associated samples in the batch must be redigested.

9.4.1. Aqueous method blanks are prepared by taking 50 mL or 50 g of reagent water through the appropriate procedure as described in Section 11.

9.4.2. TCLP method blanks are prepared by taking 50 mL or 50 g of leachate fluid through the appropriate procedure as described in Section 11.

9.5. Laboratory Control Sample (LCS) - One aqueous LCS must be processed with each preparation batch. The LCS must contain all analytes of interest and must be carried

through the entire analytical procedure. The LCS is used to monitor the accuracy of the analytical process. On going monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines. Criteria for the acceptance of LCS results are contained within the individual analytical method SOP's. Corrective action when LCS results fail to meet control limits will be repreparation and reanalysis of the batch. Refer to Section 7.3 and 7.4 for instructions on preparation of the aqueous LCS spike solution.

9.5.1. The aqueous LCS is prepared by spiking a 50 mL aliquot of reagent water with 1.0 mL of the working LCS/MS spike solution (7.3 or 7.4). The LCS is then processed through the appropriate procedure as described in Section 11.

9.6. Matrix Spike/Matrix Spike Duplicate (MS/MSD) - One MS/MSD pair must be processed for each preparation batch. A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added. A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked identically as the MS) prepared and analyzed along with the sample and matrix spike. Some client specific data quality objectives (DQO's) may require the use of sample duplicates in place of or in addition to MS/MSD's. The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Samples identified as field blanks cannot be used for MS/MSD analysis. If any analyte recovery or RPD falls outside the acceptance range, the recovery of that analyte must be in control for the LCS. If the recovery of the LCS is outside limits, corrective action must be taken. Corrective action will include 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.

9.6.1. The aqueous matrix spike sample is prepared by spiking a 50 mL aliquot of a sample with 1.0 mL of the working LCS/MS spike solution (7.3 or 7.4). The matrix spike sample is then processed as described in Section 11.

9.6.2. The TCLP matrix spike sample is prepared by spiking a 50 mL aliquot of a leachate with 0.5 mL of the working TCLP spike solution (7.5). The matrix spike sample is then processed as described in Section 11.

NOTE: The TCLP matrix spike must be added prior to preservation of the leachate.

9.6.3. If insufficient sample is available to process a MS/MSD, then a second LCS must be processed. The LCS pair is then evaluated according to the MS/MSD criteria.

9.7. Quality Assurance Summaries - Certain clients may require specific project or program QC that may supersede the SOP requirements. Quality Assurance Summaries (QAS) should be developed to address these requirements.

10. CALIBRATION AND STANDARDIZATION

10.1 Hotplate temperature must be verified daily for each hotplate used and must be recorded on either the metals preparation log or in a hotplate temperature logbook. The hotplate temperature should be verified by measuring the temperature of a beaker of reagent water placed on each hotplate.

11. PROCEDURE

11.1. One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo and is approved by a Technical Specialist and QA Manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file.

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

11.3. All digestion procedures must be carried out in a properly functioning hood.

11.4. All samples are to be checked out of sample control with the chain of custody documentation filled out completely.

11.5. Proper sample identification is extremely important in any preparation procedure. Labeling of beakers and bottles must be done in a manner to ensure connection with the proper sample.

11.6. Samples are typically logged in as either waters or soils. Wastes such as organic liquids or sludges and tissues (animal/vegetable) are usually logged in with solid test codes. When initiating prep, examine the sample to see if the sample matches the matrix designation. If the sample is logged in as aqueous but it appears more like a waste (biphasic, sludge like, organic liquid, lots of sediment etc.) contact the lab supervisor or project manager for further instructions. In some cases it may be more appropriate to process these samples as solids.

11.7. If possible prepare all the samples of a project at the same time to minimize the QC required and streamline the flow of the project through the lab and reporting group.

11.8. In most cases, both AA and ICP digests are required on each sample. It is recommended that both aliquots be measured out and processed at the same time.

11.9. Guidelines are provided in the appendices on procedures to minimize contamination of samples and standards.

11.10. The following procedure must be followed for all aqueous sample preparations:

11.10.1. Measure sample pH with pH paper on a separate aliquot of sample.

Note: If the sample pH is > 2 pH units, the client must be notified of the anomaly.

Note: If sample pH has already been verified and documented in sample receipt this step may be omitted.

11.10.2. Mix sample by shaking the container.

11.10.3. Measure and transfer 50 mL or 50 g of the sample into a beaker.

Note: This SOP allows for samples to be weighed instead of measured volumetrically.

11.10.4. Measure two extra aliquots of sample selected for the MS/MSD analysis. Spike each aliquot with the appropriate spiking solutions (7.3-7.5,9.6).

11.10.5. Measure and transfer 50 mL of reagent water into a beaker for the method blank.

11.10.6. Measure and transfer 50 mL of reagent water into a beaker for the LCS and add the appropriate spiking solutions (7.3-7.5,9.6).

11.11. Proceed to the appropriate Section for the desired method as follows:

Method 3005A or Method 200.7 Section 9.4	11.12
Method 3010A or Method 200.7 Section 9.3	11.13
Method 3020A or Method 200.0 Section 4.1.3	11.14
Method 7060A/7740 or Method 206.2/270.2	11.15
Method 200.0 Section 4.1.4	11.16

11.12. **Method 3005A / Method 200.7 Section 9.4 - Preparation for Total Recoverable or Dissolved Metals Analysis by FLAA or ICP (See Figures 1, 6 and 7)**

11.12.1. To the sample beaker, add 1 mL of concentrated HNO_3 and 2.5 mL of concentrated HCl.

11.12.2. Cover with ribbed watch glass.

11.12.3. Heat at 95°C (± 4) until volume is reduced to between 15 and 20 mL.

NOTE: DO NOT ALLOW SAMPLE TO BOIL OR GO DRY. Doing so will result in the loss of analyte and the sample must be reprepared.

11.12.4. Cool the beaker in a fume hood.

11.12.5. Wash down beaker walls and watch glass with reagent water.

11.12.6. Filter sample, if insoluble materials are present, through Whatman 4 filter paper that has been pre-rinsed with dilute nitric acid.

Note: If any samples in a preparation batch are filtered, the method blank and LCS associated with that batch must also be filtered.

Note: In place of filtering, the samples, after dilution and mixing, may be centrifuged or allowed to settle by gravity overnight to remove insoluble material.

11.12.7. Rinse beaker and filter paper with reagent water to ensure complete sample transfer.

11.12.8. Adjust the final volume/mass to 50 mL or 50 g with reagent water. The sample is now ready for analysis

11.13. **Method 3010A / Method 200.7 Section 9.3 - Preparation for Total Metals Analysis by FLAA or ICP Spectroscopy (See Figures 2, 6 and 7)**

11.13.1. To the sample beaker, add 3.0mL of concentrated HNO_3.

11.13.2. Cover with ribbed watch glass.

11.13.3. Place beaker on hotplate 95°C (± 4) and evaporate for 4-5 hours or to low volume of 15-20 mL while ensuring that no portion of the bottom of the beaker is allowed to go dry.

NOTE: DO NOT ALLOW SAMPLE TO BOIL OR GO DRY. Doing so will result in the loss of analyte and the sample must be reprepared.

11.13.4. If necessary, add another 1.5 ml portion of concentrated HNO_3 and re-cover the beaker. Reflux 15 minutes.

11.13.5. Add 5 mL of 1:1 HCl.

11.13.6. Cover and reflux for an additional 15 minutes to dissolve precipitate or residue. Cool in a fume hood.

11.13.7. Wash down beaker walls and watch glass with reagent water.

11.13.8. Filter sample, if insoluble materials are present, through Whatman 4 filter paper.

Note: If any samples in the QC batch are filtered the method blank and LCS associated with that batch must also be filtered.

Note: In place of filtering, the samples, after dilution and mixing, may be centrifuged or allowed to settle by gravity overnight to remove insoluble material.

11.13.9. Rinse beaker and filter paper with reagent water to ensure complete sample transfer.

11.13.10. Adjust final volume/mass to 50 mL or 50 g with reagent water. The sample is now ready for analysis.

11.14. **Method 3020A / Method 200.0 Section 4.1.3 - Preparation for Total Metals Analysis by GFAA or Total Recoverable Metals by ICPMS (See Figures 3, 6 and 7)**

11.14.1. To the sample beaker, add 1.5 mL of concentrated HNO_3.

11.14.2. Cover with ribbed watch glass.

11.14.3. Place beaker on hotplate 95°C (± 4) and evaporate to low volume of 15-20 mL while ensuring that no portion of the bottom of the beaker is allowed to go dry.

NOTE: DO NOT ALLOW SAMPLE TO BOIL OR GO DRY. Doing so will result in the loss of analyte and the sample must be reprepared.

11.14.4. If necessary, add another 1.5 mL portion of concentrated HNO_3. Recover, and reflux 15 minutes. Cool the beaker in a fume hood.

11.14.5. Filter sample, if insoluble materials are present, through Whatman 4 filter paper.

Note: If any samples in the QC batch are filtered the method blank and LCS associated with that batch must also be filtered.

Note: In place of filtering, the samples, after dilution and mixing, may be centrifuged or allowed to settle by gravity overnight to remove insoluble material.

11.14.6. Rinse beaker and filter paper with reagent water to ensure complete sample transfer.

11.14.7. Adjust final volume to 50 mL with reagent water. The sample is now ready for analysis.

11.15. **Method 7060A/7740 and Method 206.2/270.2 - Preparation for Arsenic and Selenium Analysis by GFAA (See Figures 4, 6 and 7)**

11.15.1. To the sample beaker, add 1 mL of 30 % H_2O_2 and 1.0 mL of 1:1 HNO_3.

11.15.2. Heat, until the digestion is complete, at 95°C (± 4) or until the volume has been reduced to 15-20 mL.

11.15.3. Cool beaker.

11.15.4. Filter sample, if insoluble materials are present, through Whatman 4 filter paper that has been pre-rinsed with dilute nitric acid.

Note: If any samples in the QC batch are filtered the method blank and LCS associated with that batch must also be filtered.

Note: In place of filtering, the samples, after dilution and mixing, may be centrifuged or allowed to settle by gravity overnight to remove insoluble material.

11.15.5. Rinse beaker and filter paper with reagent water to ensure complete sample transfer.

11.15.6. Adjust final volume to 50 mL with reagent water. The sample is now ready for analysis.

11.16. **Method 200.0 Section 4.1.4 - Preparation for Total Recoverable GFAA Analyses. (See Figures 5 and 7)**

11.16.1. To the sample beaker, add 1.0 mL of 1:1 HNO_3.

11.16.2. Heat, until the digestion is complete, at 95°C (± 4) or until the volume has been reduced to 15 - 20 mL.

11.16.3. Cool beaker.

11.16.4. Filter sample, if insoluble materials are present, though Whatman 4 filter paper.

Note: If any samples in the QC batch are filtered the method blank and LCS associated with that batch must also be filtered.

Note: In place of filtering, the samples, after dilution and mixing, may be centrifuged or allowed to settle by gravity overnight to remove insoluble material.

11.16.5. Rinse beaker and filter paper with reagent water to ensure complete sample transfer.

11.16.6. Adjust final volume to 50 mL with reagent water. The sample is now ready for analysis.

12. DATA ANALYSIS AND CALCULATIONS

Not Applicable.

13. METHOD PERFORMANCE

13.1. Method performance is determined by the analysis of matrix spike and matrix spike duplicate samples as well as method blanks and laboratory control samples. In general, the matrix spike recovery should fall within +/- 20 % and the matrix spike duplicates should compare within 20% RPD. Method blanks must meet the criteria specified in determinative SOPs. The laboratory control samples should recover within 20% of the true value until in house control limits are established. Acceptance criteria are given in the determinative SOPs.

13.2. The initial demonstration study as detailed in Section 9.1.2 must be acceptable before the analysis of field samples under this SOP may begin. The results of the initial demonstration study may be used to extend a method for the analysis of other elements provided all acceptance criteria are met.

13.3. Training Qualification:

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

14. POLLUTION PREVENTION

14.1. This method allows for the proportional reduction of sample and reagent volumes to decrease waste generation.

15. WASTE MANAGEMENT

15.1. Waste generated in the procedure must be segregated and disposed according to the facility hazardous waste procedures. The facility EH & S coordinator 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 I, Revision 1, July 1992. Methods 3005A, 3010A, 3020A, 7060A and 7740A.

16.2. Methods for the Chemical Analysis of Water and Waste (MCAWW), 1983.

16.3. CORP-MT-0001, Inductively Coupled Plasma-Atomic Emission Spectroscopy, Spectrometric Method for Trace Element Analysis of Water and Wastes, Method 6010A and Method 200.7.

16.4. CORP-MT-0003, Graphite Furnace Atomic Absorption Spectroscopy, SW846 Method 7000A and MCAWW 200 Series Methods.

16.5. QA-003, STL QC Program.

16.6. QA-004, Rounding and Significant Figures.

16.7. QA-005, Method Detection Limits.

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

17.1. Modifications/Interpretations from reference methods.

17.1.1. Modifications applicable to SW-846 reference methods.

17.1.1.1. Chapter 1 of SW-846 states that the method blank should not contain any analyte of interest at or above the MDL. This SOP states that the method blank must not contain any analyte of interest at or above the reporting limit. Common lab contaminants are allowed up to two times the reporting limit in the blank following consultation with the client.

17.1.1.2. The referenced methods as well as Table 3-1 of SW-846 refer to the use of a 100 mL aliquot for digestion. This SOP requires the use of a 50 mL sample size to reduce waste generation. The use of reduced sample volumes are supported in EPA's document "Response to Public

Comments Background Document, Promulgation of the Second Update to SW-846, Third Edition" dated November 3, 1994. This document stated "flexibility to alter digestion volumes is addressed and "allowed" by the table (3-1) and is also inherently allowed by specific digestion methods. Table 3-1 is only to be used as guidance when collecting samples..." EMSL-Ci has also taken the stance that "reduction in sample size and appropriate corresponding reduction in sample volume is not considered a significant change in the methodology." Additionally, in written correspondence from the Office of Solid Waste, Olliver Fordham stated " As a "representative sample" can be assured, scaling causes no loss of precision and accuracy in the analysis."

17.1.2. Modifications Specific to Method 3010A

17.1.2.1. Section 11.13.7 of this SOP requires the sample be reduced to a volume of 15 - 20 mL. Section 7.2 of Method 3010A states the volume should be reduced to 3 mL but also states that no portion of the bottom of the beaker should go dry. The SOP required volume is a closer approximation of the volume required to provide an adequate covering of the beaker so as to prevent the loss of critical analytes through volatilization.

17.1.2.2. The scope of 3010A has been expanded to include silver based on comparison studies with 7760A. Method 3010A consistently demonstrated improved accuracy and precision over Method 7760A in the matrices tested (reagent water, surface water and TCLP leachate) up to a concentration of 1 ppm silver.

17.1.3. Modifications Specific to Method 3020A

17.1.3.1. Section 11.14.8 of this SOP requires the sample be reduced to a volume of 15 - 20 mL. Section 7.2 of Method 3010A states the volume should be reduced to 3 mL but also states that no portion of the bottom of the beaker should go dry. The SOP required volume is a closer approximation of the volume required to provide an adequate covering of the beaker so as to prevent the loss of critical analytes through volatilization.

17.1.4. Modifications Specific to Method 7060A/7740

17.1.4.1. Methods 7060A and 7740A incorporate the use of a two step dilution to accommodate the addition of a nickel nitrate modifier. This SOP performs the dilution directly in one step and omits the addition of the modifier. The modifier is added automatically at the instrument by direct injection into the furnace.

17.1.5. Modifications Specific to MCAWW Methods

It was determined by technical review that several of the MCAWW methods were equivalent to the SW-846 methods and therefore were combined under the scope of this SOP as described in Section 11.0. The nature of the differences were deemed insignificant in regards to the amount of acid added and the evaporative volume based on the flexibility allowed by the methods (i.e., add additional acid as required) and the subjective wording of the methods (i.e., evaporate to near dryness vs. an exact volume).

17.2. Modifications from previous SOP

17.2.1. Added ICP/MS to the digestion procedures.

17.3. Facility Specific SOPs

Each facility shall attach a list of facility specific SOPs or approved attachments (if applicable) which are required to implement this SOP or which are used in conjunction with this SOP. If no facility specific SOPs or amendments are to be attached, a statement must be attached specifying that there are none. Refer to the Appendices for any facility specific information required to support this SOP.

17.4. Documentation and Record Management

The preparation benchsheet should, at a minimum, include the following information:

- Preparation date, analyst name, matrix, prep type (ICP or GFAA), SOP reference.
- Sample ID; initial weight/volume and final weight/volume.
- Standards Documentation (source, lot, prep date, volume added).
- Analyst Signature.

- Reviewer's Signature and date.

Figure 1. Method 3005A / Method 200.7 Section 9.4 (Section 11.12)

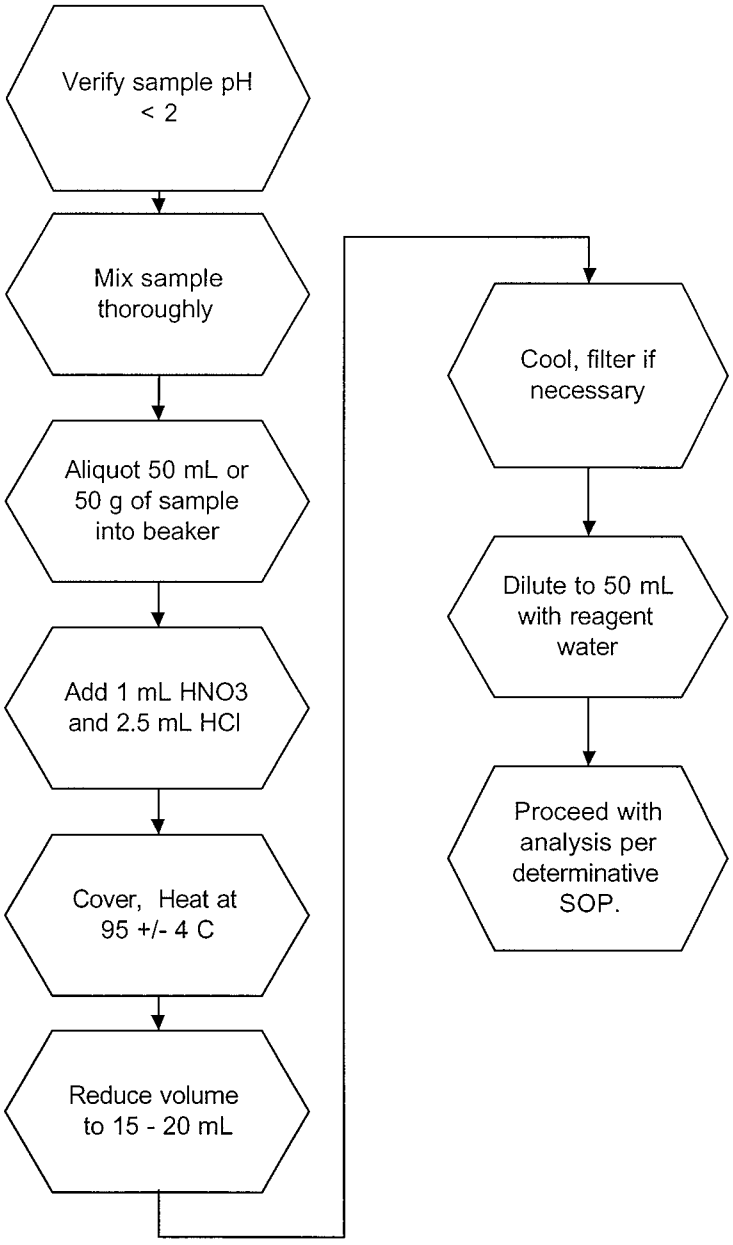


Figure 2. Method 3010A / Method 200.7 Section 9.3 (Section 11.13)

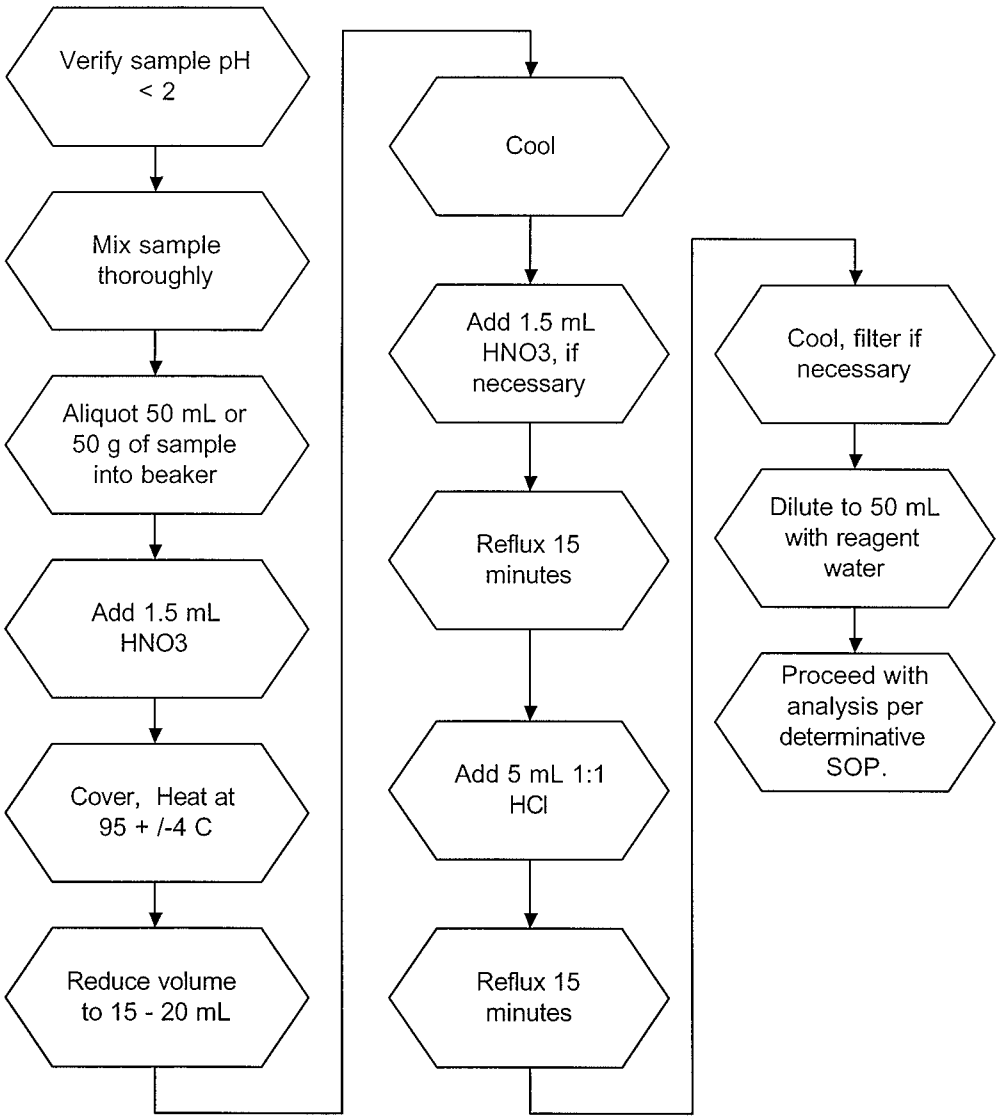


Figure 3. Method 3020A / Method 200.0 Section 4.1.3 (Section 11.14)

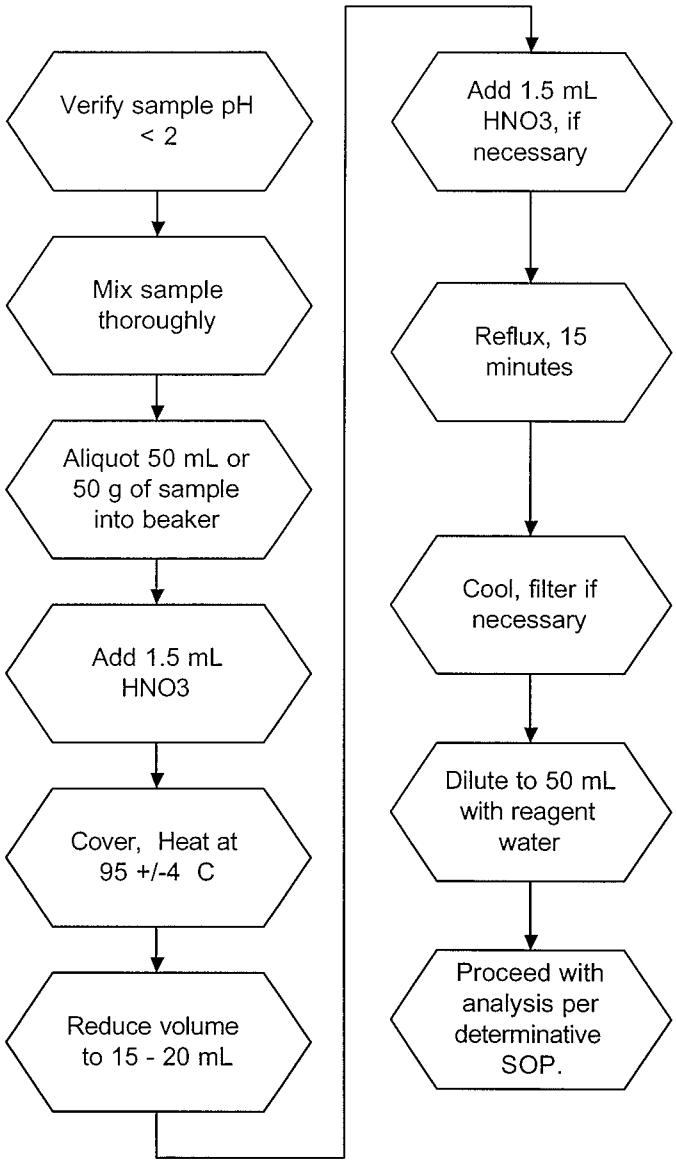


Figure 4. Method 7060A/7740A and Method 206.2/270.2 (Section 11.15)

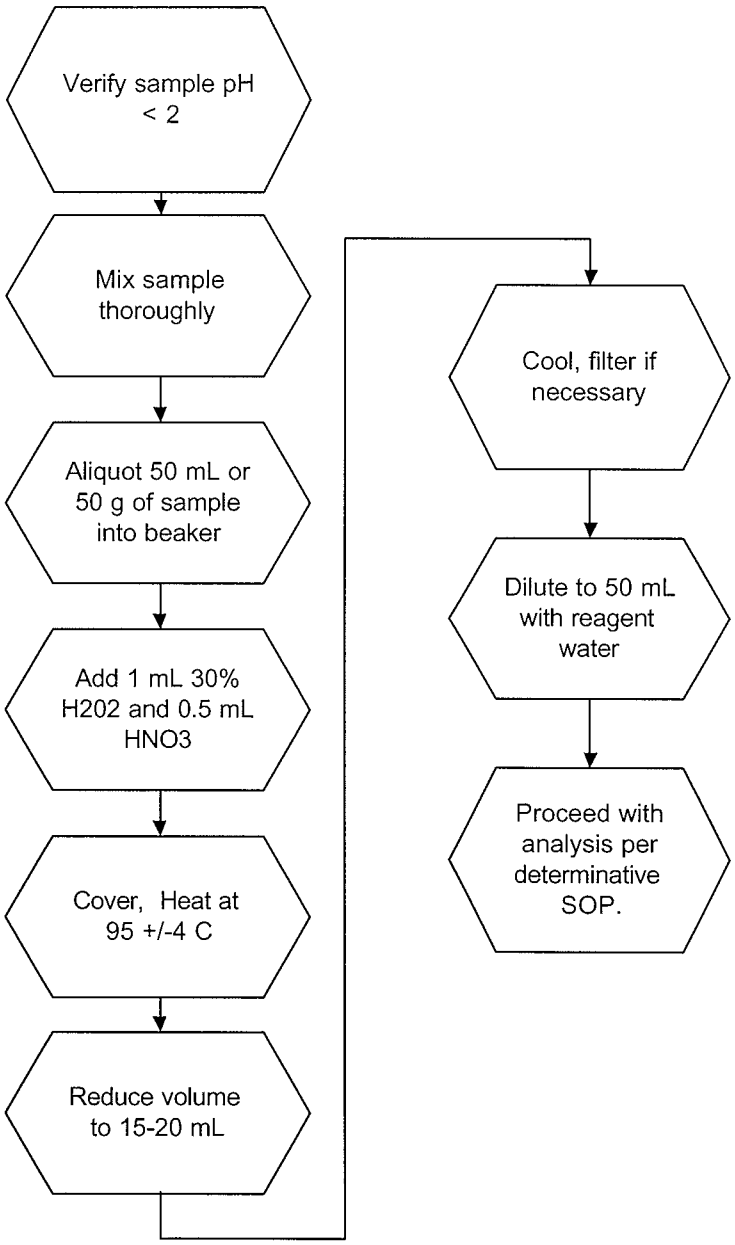


Figure 5. Method 200.0 Section 4.1.4 (Section 11.16)

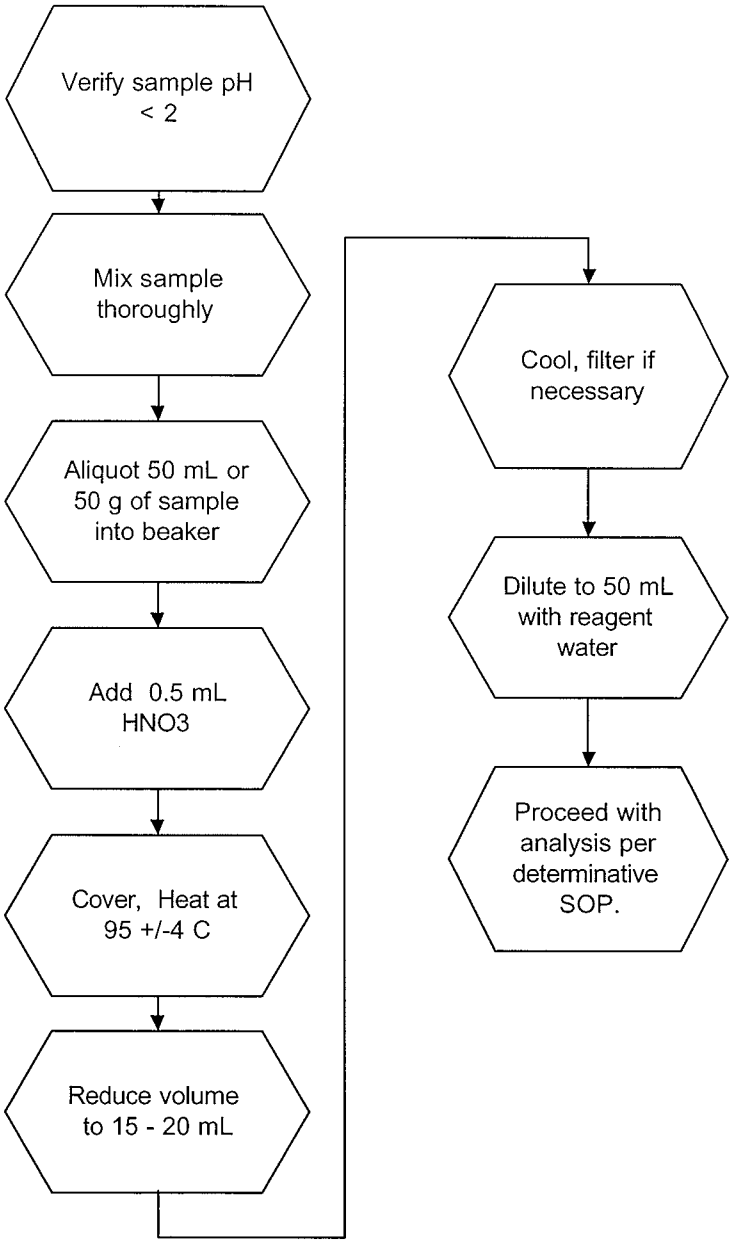
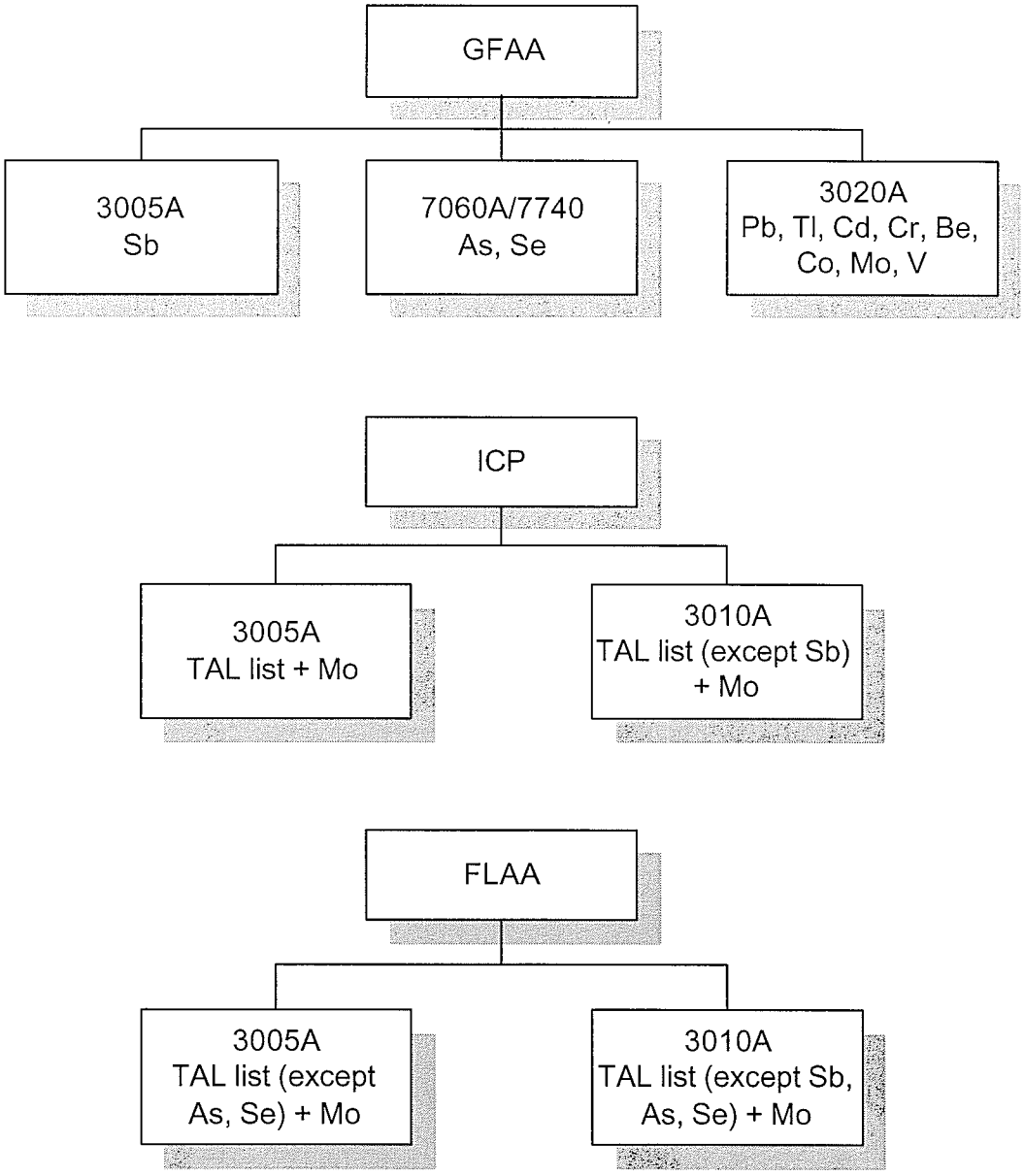
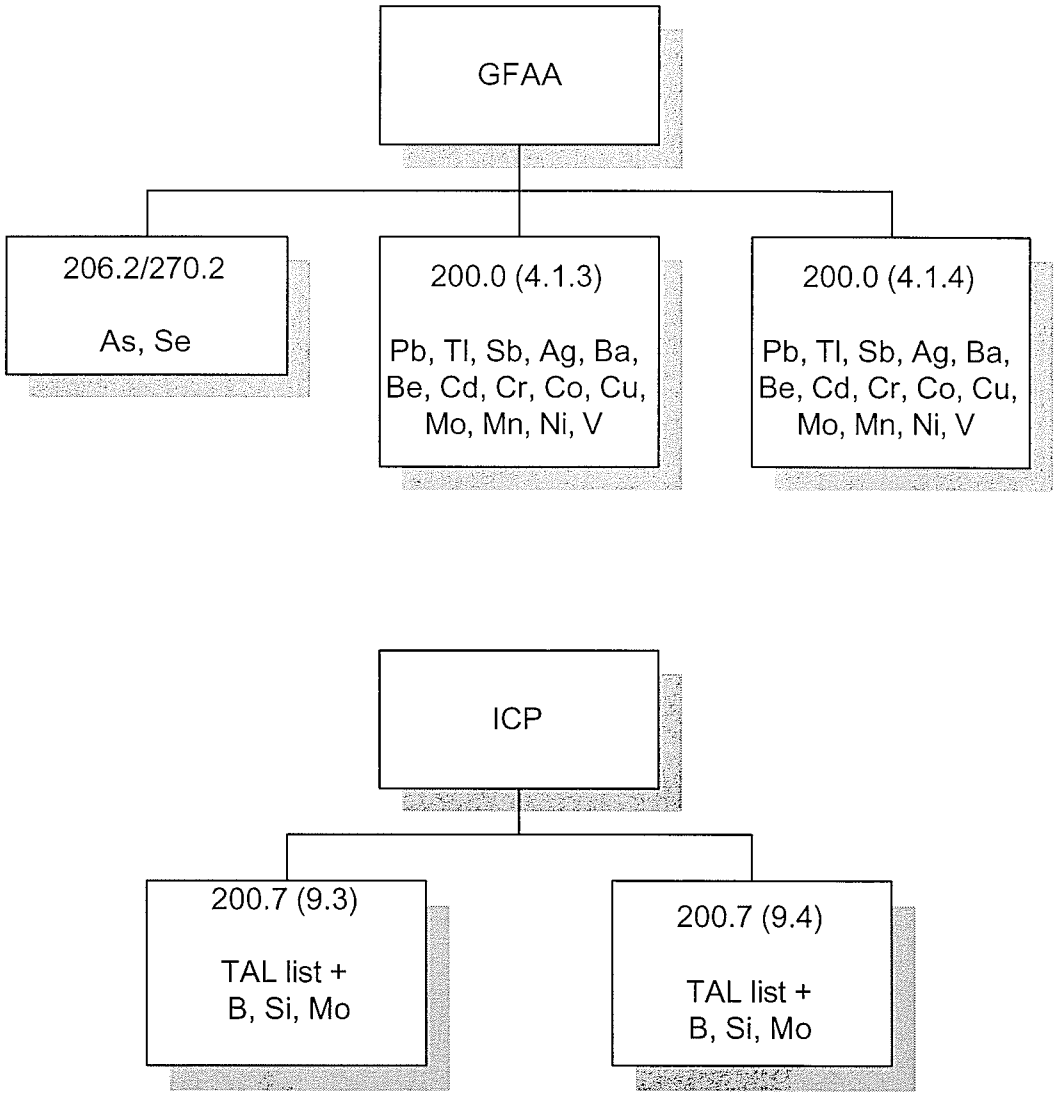


Figure 6. Overview of SW846 Aqueous Preparation Methods by Determinative Method



TAL list: Al, Sb, As, Ba, Be, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Ni, K, Se, Ag, Na, Tl, V, Zn

Figure 7. Overview of MCAWW Aqueous Preparation Methods by Determinative Technique



TAL list: Al, Sb, As, Ba, Be, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Ni, K, Se, Ag, Na, Tl, V, Zn

APPENDIX A

TABLES

TABLE I. Approved Preparation Method Analytes - SW846

ELEMENT	Symbol	CAS Number	3005A	3010A	3020A	7060A 7740
Aluminum	Al	7429-90-5	X	X		
Antimony	Sb	7440-36-0	X			
Arsenic	As	7440-38-2	X	X		X
Barium	Ba	7440-39-3	X	X		
Beryllium	Be	7440-41-7	X	X	X	
Cadmium	Cd	7440-43-9	X	X	X	
Calcium	Ca	7440-70-2	X	X		
Chromium	Cr	7440-47-3	X	X	X	
Cobalt	Co	7440-48-4	X	X	X	
Copper	Cu	7440-50-8	X	X		
Iron	Fe	7439-89-6	X	X		
Lead	Pb	7439-92-1	X	X	X	
Magnesium	Mg	7439-95-4	X	X		
Manganese	Mn	7439-96-5	X	X		
Molybdenum	Mo	7439-98-7	X	X	X	
Nickel	Ni	7440-02-0	X	X		
Potassium	K	7440-09-7	X	X		
Selenium	Se	7782-49-2	X	X		X
Silver	Ag	7440-22-4	X	X		
Sodium	Na	7440-23-5	X	X		
Thallium	Tl	7440-28-0	X	X	X	
Vanadium	V	7440-62-2	X	X	X	
Zinc	Zn	7440-66-6	X	X		

X - Designates that the preparation method is approved for an element

Note: Additional elements may be analyzed following digestion by these protocols provided the method performance criteria specified in Section 13.0 of the SOP are met.

TABLE II. Approved Preparation Method Analytes - NPDES

ELEMENT	Symbol	CAS Number	200.7 (9.4)	200.7 (9.3)	200.0 (4.1.4)	200.0 (4.1.3)	206.2 270.2
Aluminum	Al	7429-90-5	X	X			
Antimony	Sb	7440-36-0	X	X	X	X	
Arsenic	As	7440-38-2	X	X			X
Boron	B	7440-42-8	X	X			
Barium	Ba	7440-39-3	X	X	X	X	
Beryllium	Be	7440-41-7	X	X	X	X	
Cadmium	Cd	7440-43-9	X	X	X	X	
Calcium	Ca	7440-70-2	X	X			
Chromium	Cr	7440-47-3	X	X	X	X	
Cobalt	Co	7440-48-4	X	X	X	X	
Copper	Cu	7440-50-8	X	X	X	X	
Iron	Fe	7439-89-6	X	X	X	X	
Lead	Pb	7439-92-1	X	X	X	X	
Magnesium	Mg	7439-95-4	X	X			
Manganese	Mn	7439-96-5	X	X	X	X	
Molybdenum	Mo	7439-98-7	X	X	X	X	
Nickel	Ni	7440-02-0	X	X	X	X	
Potassium	K	7440-09-7	X	X			
Selenium	Se	7782-49-2	X	X			X
Silicon	Si	7631-86-9	X	X			
Silver	Ag	7440-22-4	X	X	X	X	
Sodium	Na	7440-23-5	X	X			
Thallium	Tl	7440-28-0	X	X	X	X	
Vanadium	V	7440-62-2	X	X	X	X	
Zinc	Zn	7440-66-6	X	X			

X - Designates that the preparation method is approved for an element

Note: Additional elements may be analyzed following digestion by these protocols provided the method performance criteria specified in Section 13.0 of the SOP are met.

TABLE III. ICP and FLAA Matrix Spike and Aqueous Laboratory Control Sample Levels

ELEMENT	Working LCS/MS Standard (mg/L)	Aqueous LCS/ MS Level * (ug/l)
Aluminum	100	2000
Antimony	25	500
Arsenic	100	2000
Barium	100	2000
Beryllium	2.5	50
Cadmium	2.5	50
Calcium	2500	50000
Chromium	10	200
Cobalt	25	500
Copper	12.5	250
Iron	50	1000
Lead	50	500
Magnesium	2500	50000
Manganese	25	500
Molybdenum	50	1000
Nickel	25	500
Phosphorous	500	10000
Potassium	2500	50000
Selenium	100	2000
Silver	2.5	50
Sodium	2500	50000
Thallium	100	2000
Vanadium	25	500
Zinc	25	500
Boron	50	1000
Tin	100	2000
Titanium	50	1000

* Levels shown indicate the spike concentration in the final digestate of the aqueous LCS or matrix spike based on the addition of 1.0 mL working spike (7.3) to 50 mL of sample.

TABLE IV. GFAA Matrix Spike and Aqueous LCS Spike Levels

ELEMENT	Stock LCS/MS Standard (mg/L)	Working LCS/MS Standard (ug/L)	Aqueous LCS/ MS Level * (ug/l)
Arsenic	400	2000	40
Selenium	400	2000	40
Lead	400	2000	40
Thallium	400	2000	40
Antimony	400	2000	40
Cadmium	40	200	4
Chromium	100	500	10
Silver	50	250	5

* Levels shown indicate the spike concentration in the final digestate of the aqueous LCS or matrix spike based on the addition of 1.0 mL working spike (7.4) to 50 mL of sample.

TABLE V. TCLP Reporting Limits, Regulatory Limits and Matrix Spike Levels

ELEMENT	RL (ug/L)	Regulatory Limit (ug/L)	Spike Level (ug/L)*
Arsenic	500	5000	5000
Barium	10000	100000	50000
Cadmium	100	1000	1000
Chromium	500	5000	5000
Lead	500	5000	5000
Selenium	250	1000	1000
Silver	500	5000	1000

* Levels shown indicate the spike concentration in the final digestate of the aqueous LCS or matrix spike based on the addition of 0.5 mL working spike (7.4) to 50 mL of sample.

TABLE VI. Summary of Quality Control Requirements

QC PARAMETER	FREQUENCY	ACCEPTANCE CRITERIA	CORRECTIVE ACTION
Method Blank	One per sample preparation batch of up to 20 samples.	Refer to determinative SOPs: CORP-MT-0001 CORP-MT-0003	Redigest and reanalyze samples associated with the method blank.
Laboratory Control Sample (LCS)	One per sample preparation batch of up to 20 samples.	Refer to determinative SOPs: 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.

STL STANDARD OPERATING PROCEDURE

TITLE: TOXICITY CHARACTERISTIC LEACHING PROCEDURE

AND SYNTHETIC PRECIPITATION LEACHING PROCEDURE

(SUPERSEDES: REVISION 1, REVISION DATE 02/01/00)

Prepared by: _____ 10/17/00 Date

Reviewed by: _____ 10/17/00 Date
Technology Specialist

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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 $4 \pm 2^\circ$ 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)

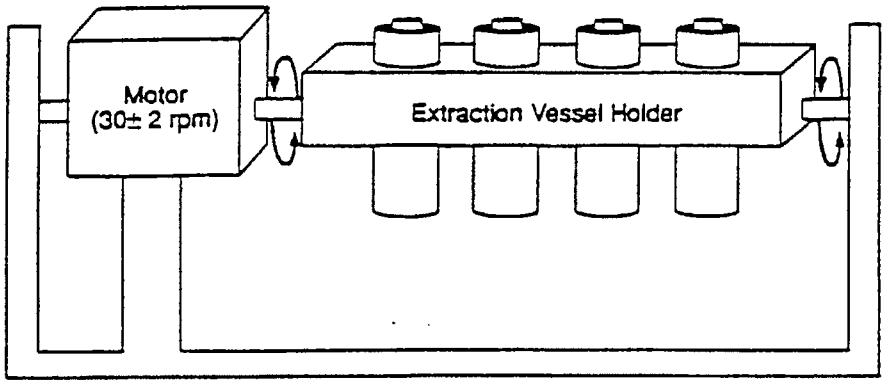


Figure 1. Rotary Agitation Apparatus

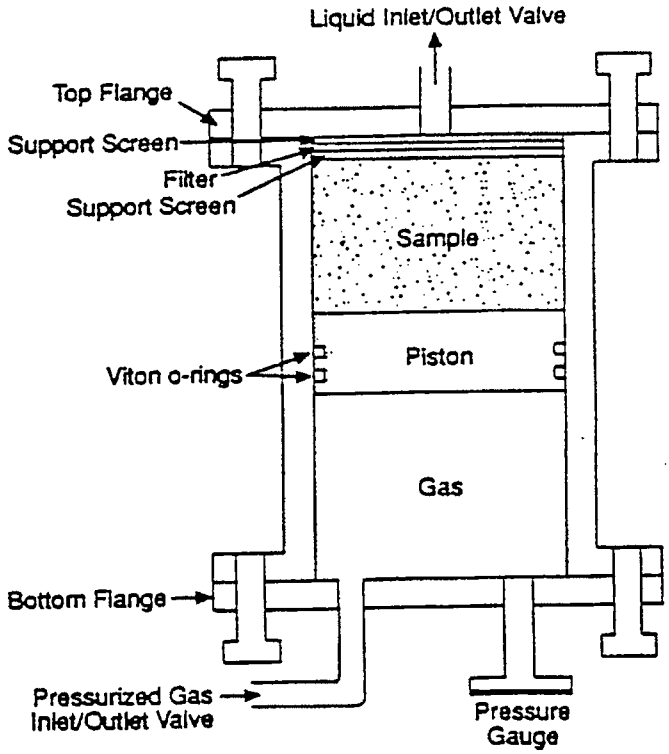


Figure 3 - US Environmental Protection Agency Memorandum #35, Page 1

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:

- o 1992 Symposium on Waste Testing and Quality Assurance
- o SW-846 Update
  - Final Rule for January 23, 1989 Proposed Rule
  - Notice, Proposed Rulemaking for the Second Update to the Third Edition
- o Chlorofluorocarbon 113 (CFC-113) Solvent Replacement Update
- o Environmental Monitoring Methods Index (EMMI)
- o Sampling Work Group Formation
- o MICE Update
- o Oily Waste Analysis
- o Electronic SW-846 Availability.

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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																			
		M B P H																			
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		M B P H																			

SOP No.: NC-IP-0005 STL NORTH CANTON TCLP LOGBOOK

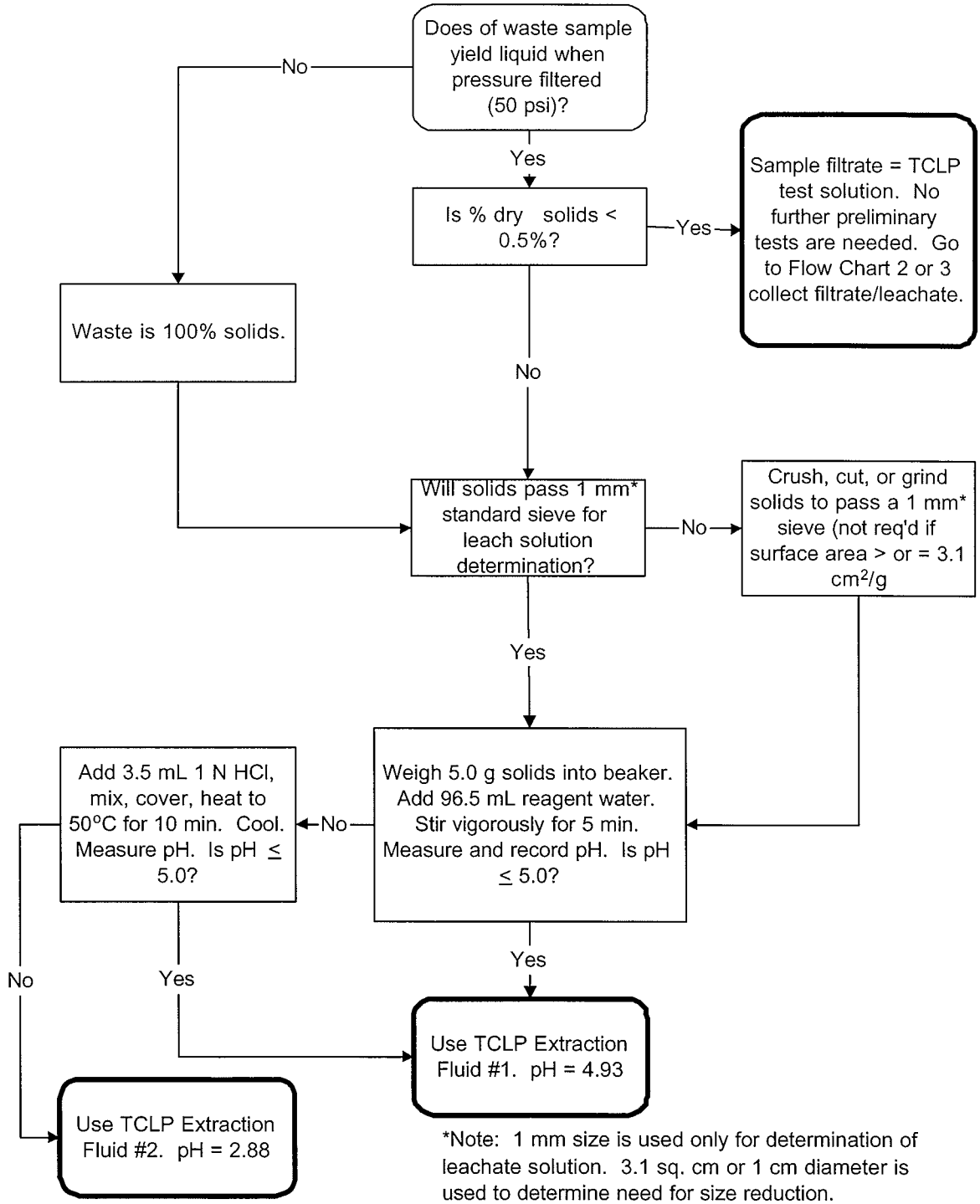
	A	B	C	D	E	F		G	H		
Sample Number	Weight of Container + Sample (g)	Weight of Container + Residue (g)	Difference (A – B) Sample Weight (g)	Weight of the Filtrate Bottle (g)	Weight of the Filtrate bottle + Filtrate(g)	Difference (E – D) Filtrate Weight (g)	Volume of Filtrate* (mL)	Difference (C – F) Wet Solids Weight (g)	G x 20 Buffer Amount (mL)	Initials	Comments

* Filtrate volume only needed when filtrate is incompatible with leachate

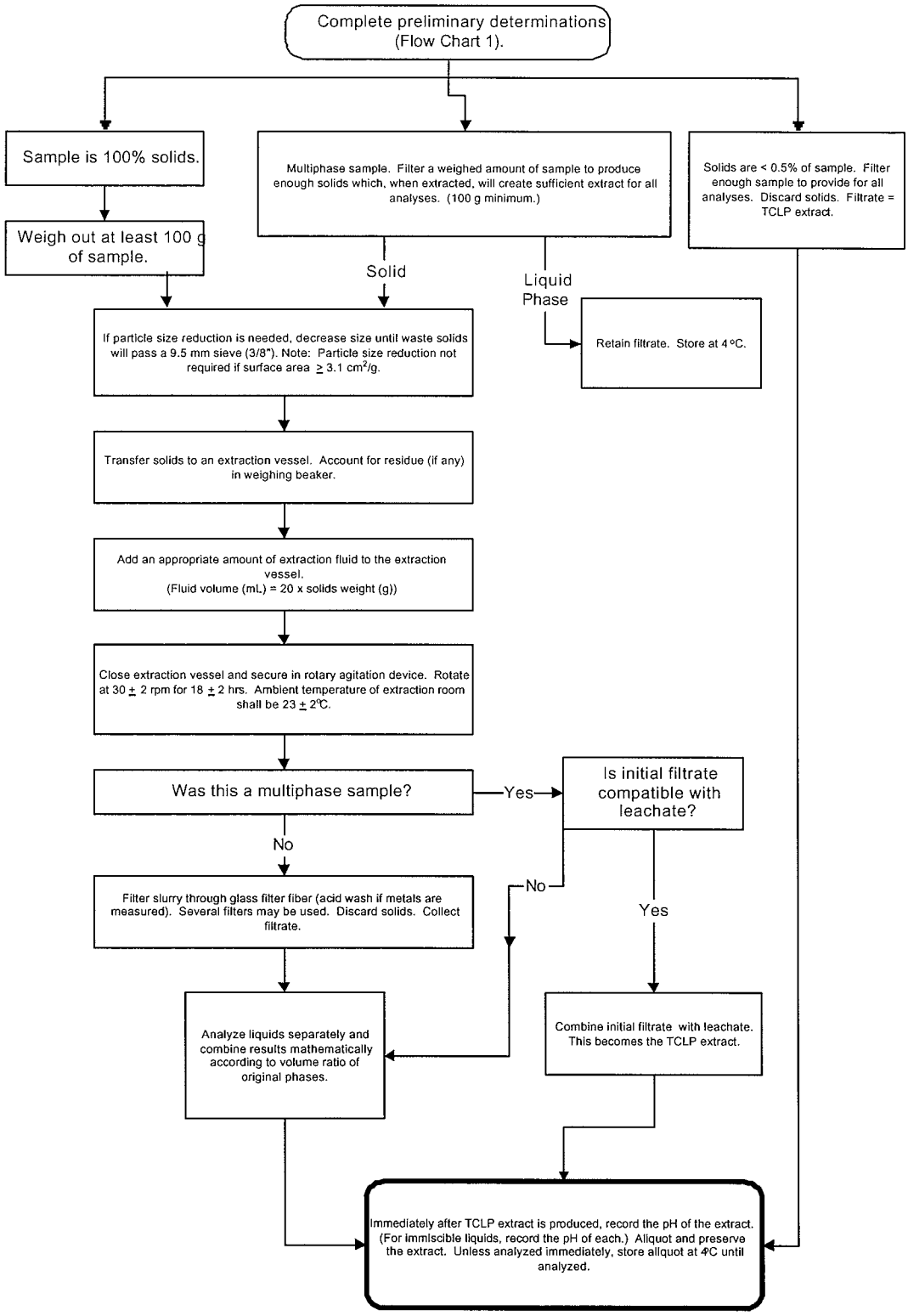
APPENDIX D

FLOW CHARTS

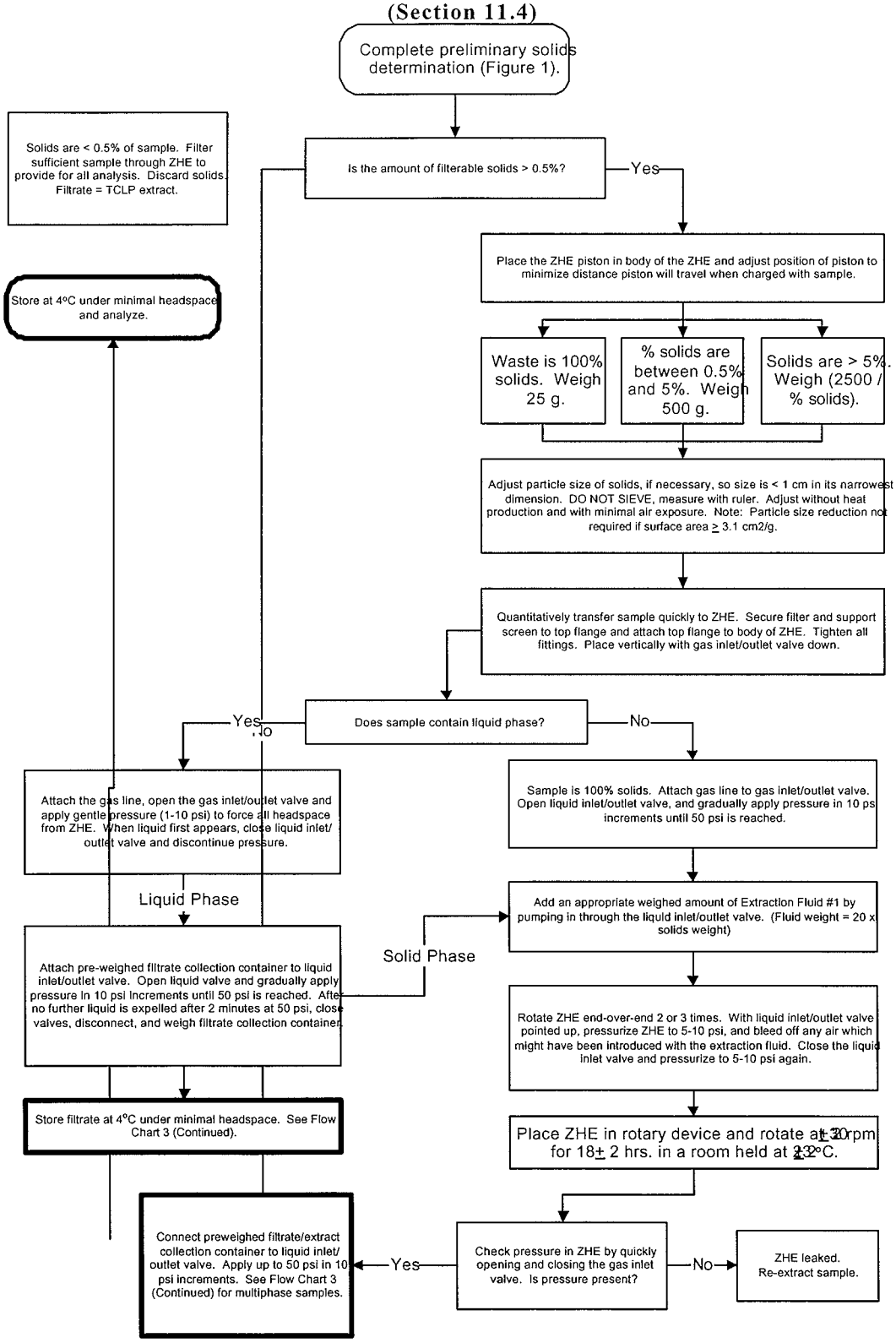
Flow Chart 1. Preliminary Sample Evaluation (Section 11.2)



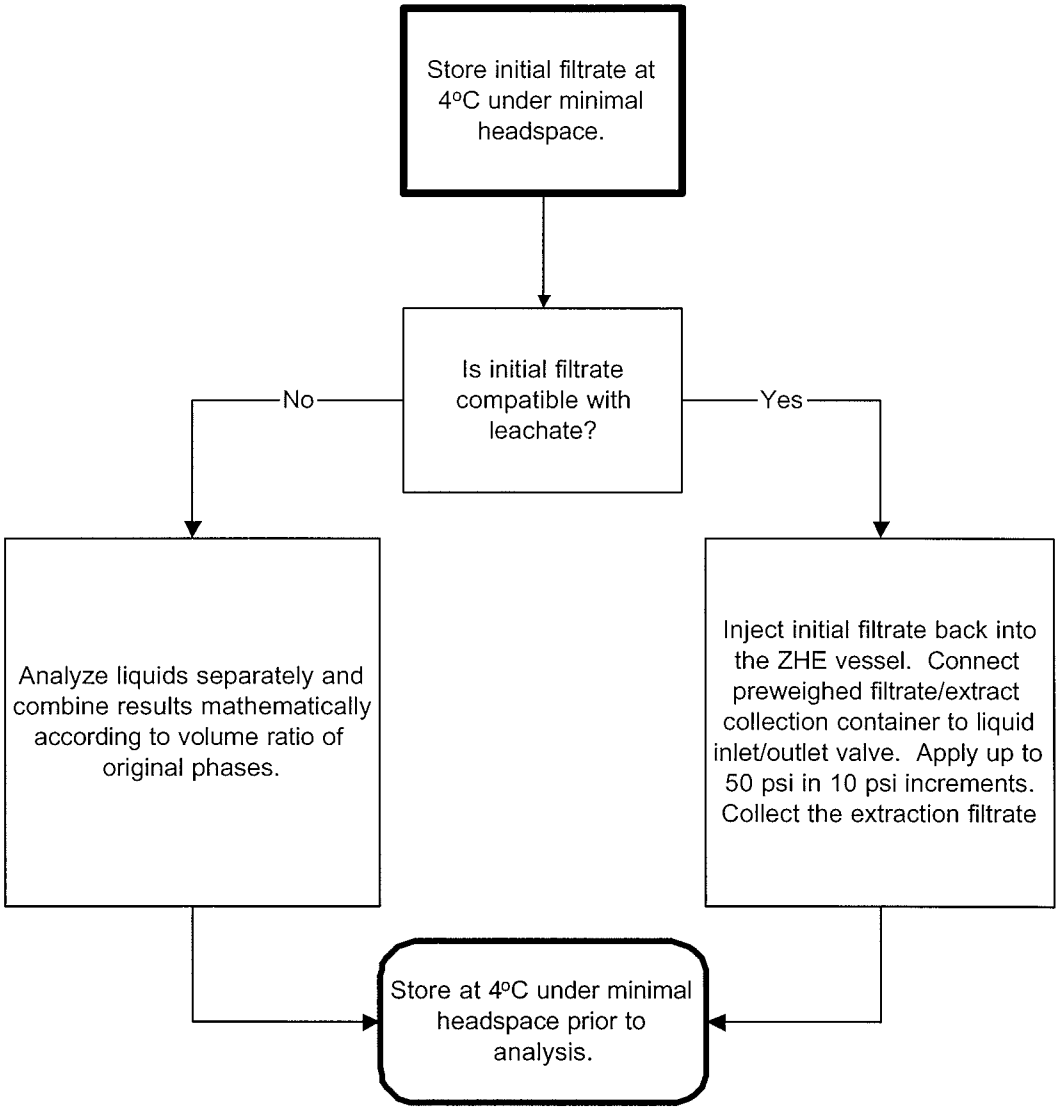
Flow Chart 2. Bottle Extraction, Non-Volatile Constituents (Section 11.3)



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-0001NC
Revision No: 2.4
Revision Date: 05/29/01
Page 1 of 59

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: _____ 5/30/01
Date

Reviewed by: _____ 5-30-01
Technology Specialist — Date

Approved by: _____ 5/29/01
Quality Assurance Manager — Date

Approved by: _____ 5-30-01
Environmental Health and Safety — Date

Approved by: _____ 5-30-01
Laboratory Director — Date

Approved by: _____
Coroporate Technology — Date

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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 decafluorotriphenyl-phosphine (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°C to -20°C may be used if it can be demonstrated that analytes do not fall out of solution at this temperature. The standards must be replaced at least once a year. The continuing calibration standard must be replaced every week and is stored at $\leq 6^{\circ}C$.

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°C, protected from light in screw cap vials equipped with unpierced Teflon lined septa.

11.5 Retention time criteria for samples

If the retention time for any internal standard changes by more than 0.5 minutes from the last continuing calibration standard, the chromatographic system must be inspected for malfunctions and corrected. Reanalysis of samples analyzed while the system was malfunctioning is required.

11.5.1 If the retention time of any internal standard in any sample varies by more than 0.1 minute from the preceding continuing calibration standard, the data must be carefully evaluated to ensure that no analytes have shifted outside their retention time windows.

11.6 Percent Moisture

Analytical results may be reported as dry or wet weight, as required by the client. Percent moisture must be determined if results will be reported as dry weight. Refer to the facility specific SOP for determination of percent moisture.

11.7 Procedural Variations

11.7.1 One-time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo and approved by a Technical Specialist and QA Manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file. Any unauthorized deviations from this procedure must also be documented as a non-conformance, with a cause and corrective action described.

11.8 Troubleshooting Guide

11.8.1 Daily Instrument Maintenance

In addition to the checks listed in the instrument maintenance schedule in the STL North Canton Quality Assurance Manual (LQM), current version, the following daily maintenance should be performed.

- Clip Column as necessary.
- Install new or cleaned injection port liner as necessary.
- Install new septum as necessary.
- Perform mass calibration as necessary.

11.8.2 Major Maintenance

A new initial calibration is necessary following major maintenance. Major maintenance includes changing the column, cleaning the ion volume or repeller, cleaning the source, and replacing the multiplier. Refer to the manufacturer's manual for specific guidance.

12 DATA ANALYSIS AND CALCULATIONS

12.1 Qualitative identification

An analyte is identified by retention time and by comparison of the sample mass spectrum with the mass spectrum of a standard of the suspected compound (standard reference spectrum). Mass spectra for standard reference may be obtained on the user's GC/MS by analysis of the calibration standards or from the NBS library. Two criteria must be satisfied

to verify identification: (1) elution of sample component at the same GC retention time as the standard component; and (2) correspondence of the sample component and the standard component characteristic ions. (Note: Care must be taken to ensure that spectral distortion due to co-elution is evaluated.)

- The sample component retention time must compare to within ± 0.2 min. of the retention time of the standard component. For reference, the standard must be run within the same twelve hours as the sample.
- All ions present in the standard mass spectra at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100%) should be present in the sample spectrum.
- The characteristic ions of a compound must maximize in the same scan or within one scan of each other.
- The relative intensities of ions should agree to within ±30% between the standard and sample spectra. (Example: For an ion with an abundance of 50% in the standard spectra, the corresponding sample abundance must be between 20% and 80%.)

12.1.1 If a compound cannot be verified by all the above criteria, but in the technical judgment of the analyst the identification is correct, the analyst shall report that identification and proceed with quantitation.

12.2 Mass chromatogram searches.

Certain compounds are unstable in the calibration standard and cannot be calibrated in the normal way. In particular, the compound hexachlorophene (CAS 70-30-4) falls into this category, and is required for Appendix IX analysis. For this analyte a mass chromatogram search is made.

12.2.1 Hexachlorophene

Display the mass chromatograms for mass 196 and mass 198 for the region of the chromatogram from at least 2 minutes before chrysene-d12 to at least 4 minutes after chrysene-d12. If peaks for both ions coincide then the analyst evaluates the spectrum for the presence of hexachlorophene. No quantitation is possible.

12.3 For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The necessity to perform this type of identification will be determined by the type of analyses being conducted. Computer generated library search routines should not use normalization routines that would

misrepresent the library or unknown spectra when compared to each other. Only after visual comparison of sample spectra with the nearest library searches shall the mass spectral interpretation specialist assign a tentative identification. Guidelines for making tentative identification are:

- Relative intensities of major ions in the reference spectrum (ions >10% of the most abundant ion) should be present in the sample spectrum.
- The relative intensities of the major ions should agree within ±20%. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance should be between 30%and 70%.)
- Molecular ions present in the reference spectrum should be present in the sample spectrum.
- Ions present in the sample spectrum, but not in the reference spectrum, should be reviewed for possible background contamination or presence of coeluting compounds.
- Ions present in the reference spectrum, but not in the sample spectrum, should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting peaks. Data system library reduction programs can sometimes create these discrepancies.
- Automatic background subtraction can severely distort spectra from samples with unresolved hydrocarbons.

12.4 Anyone evaluating data is trained to know how to handle isomers with identical mass spectra and close elution times. These include:

Dichlorobenzenes
Methylphenols
Trichlorophenols
Phenanthrene, anthracene
Fluoranthene, pyrene
Benzo(b) and (k)fluoranthene
Chrysene, benzo(a)anthracene

Extra precautions concerning these compounds are to more closely scrutinize retention time vs. the calibration standard and also to check that all isomers have distinct retention times.

A second category of problem compounds would be the poor responders or compounds that chromatograph poorly. Included in this category would be:

Benzoic acid
Chloroanilines
Nitroanilines
2,4-Dinitrophenol
4-Nitrophenol
Pentachlorophenol
3,3'-Dichlorobenzidine
Benzyl alcohol
4,6-Dinitro-2-methylphenol

Manually checking the integrations would be appropriate for these compounds.

12.5 Calculations

12.5.1 Percent Relative Standard Deviation for Initial Calibration

$$\%RSD = \frac{SD}{\overline{RF}} \times 100$$

$\overline{RF}$ = Mean of RFs from intial caibration for a compound

SD = Standard deviation of RFs from initial calibration for a compound,

$$= \sqrt{\sum_{i=1}^{N} \frac{\left(RFi - \overline{RF}\right)^2}{N-1}}$$

RFi = RF for each of the calibration levels

N = Number of RF values

12.5.2 Continuing calibration percent drift

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

C_{actual} = Known concentration in standard

C_{found} = Measured concentration using selected quantitation method

12.5.3 Concentration in the extract

The concentration of each identified analyte and surrogate in the extract is calculated from the linear or quadratic curve fitted to the initial calibration points, or from the average RF of the initial calibration. For South Carolina Certification the concentration

of each identified analyte and surrogate in the extract is calculated from the linear curve only fitted to the initial calibration points, or from the average RF of the initial calibration.

12.5.3.1 Average response factor

If the average of all the %RSDs of the response factors in the initial calibration is ≤ 15%, the average response factor from the initial calibration may be used for quantitation.

$$C_{ex} = \frac{R_x C_{is}}{R_{is} \overline{RF}}$$

12.5.3.2 Linear fit (Use only Linear fit for South Carolina Certification)

$$C_{ex} = A + B\frac{(R_x C_{is})}{R_{is}}$$

C_{ex} = Concentration in extract, µg/mL

R_x = Response for analyte

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

Table 1

STL North Canton Primary Standard[1] and Standard Reporting Limits

Analytes	CAS Number	Standard Reporting Limits	
		Aqueous µg/L	Low Soil/Sediment µg/kg
2,4-Dinitrotoluene	121-14-2	10	330
2,6-Dinitrotoluene	606-20-2	10	330
Diethylphthalate	84-66-2	10	330
4-Chlorophenyl phenyl ether	7005-72-3	10	330
Fluorene	86-73-7	10	330
4-Nitroaniline	100-01-6	50	1600
4,6-Dinitro-2-methylphenol	534-52-1	50	1600
N-Nitrosodiphenylamine	86-30-6	10	330
Azobenzene	103-33-3	10	330
4-Bromophenyl phenyl ether	101-55-3	10	330
Hexachlorobenzene	118-74-1	10	330
Pentachlorophenol	87-86-5	50	1600
Phenanthrene	85-01-8	10	330
Anthracene	120-12-7	10	330
Carbazole	86-74-8	10	330
Di-n-butyl phthalate	84-74-2	10	330
Fluoranthene	206-44-0	10	330
Benzidine	92-87-5	100	3300
Pyrene	129-00-0	10	330
Butyl benzyl phthalate	85-68-7	10	330
3,3'-Dichlorobenzidine	91-94-1	50	1600
Benzo(a)anthracene	56-55-3	10	330
Bis(2-ethylhexyl)phthalate	117-81-7	10	330
Chrysene	218-01-9	10	330
Di-n-octylphthalate	117-84-0	10	330
Benzo(b)fluoranthene	205-99-2	10	330
Benzo(k)fluoranthene	207-08-9	10	330
Benzo(a)pyrene	50-32-8	10	330
Indeno(1,2,3-cd)pyrene	193-39-5	10	330
Dibenz(a,h)anthracene	53-70-3	10	330
Benzo(g,h,i)perylene	191-24-2	10	330
Benzaldehyde	100-52-7	10	330
Caprolactam	105-60-2	10	330
1,1-Biphenyl	92-52-4	10	330
Atrazine	1912-24-9	10	330

[1] The STL North Canton primary standard is the standard normally used at F. Additional standards, such as the Appendix IX standard may be necessary to include all target analytes required for some clients.

[2] 2,2'oxybis(1-chloropropane) was 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

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
4-Nitroquinoline-1-oxide	56-57-5	100	3300
*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

Table 2A
STL North Canton Michigan Program[1]

Semivolatile	CAS Number	Michigan Reporting Limits	
		Aqueous µg/L	Low Soil/Sediment µg/kg
Hexachloroethane	67-72-1	5	330
Indeno(1,2,3-cd)pyrene	193-39-5	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

Table 3

Reportable Analytes for STL North Canton Standard Tests, Primary Standard

Analyte	CAS Number	STL North Canton Standard List	TCLP	TCL	Appendix IX
4-Methylphenol	106-44-5	X	X	X	X
N-Nitroso-di-n-propylamine	621-64-7	X		X	X
Hexachloroethane	67-72-1	X	X	X	X
Nitrobenzene	98-95-3	X	X	X	X
Isophorone	78-59-1	X		X	X
2-Nitrophenol	88-75-5	X		X	X
2,4-Dimethylphenol	105-67-9	X		X	X
Benzoic acid	65-85-0				
Bis(2-chloroethoxy)methane	111-91-1	X		X	X
2,4-Dichlorophenol	120-83-2	X		X	X
1,2,4-Trichlorobenzene	120-82-1	X		X	X
Naphthalene	91-20-3	X		X	X
4-Chloroaniline	106-47-8	X		X	X
Hexachlorobutadiene	87-68-3	X	X	X	X
4-Chloro-3-methylphenol	59-50-7	X		X	X
2-Methylnaphthalene	91-57-6	X		X	X
Hexachlorocyclopentadiene	77-47-4	X		X	X
2,4,6-Trichlorophenol	88-06-2	X	X	X	X
2,4,5-Trichlorophenol	95-95-4	X	X	X	X
2-Chloronaphthalene	91-58-7	X		X	X
2-Nitroaniline	88-74-4	X		X	X
Dimethyl phthalate	131-11-3	X		X	X
Acenaphthylene	208-96-8	X		X	X
3-Nitroaniline	99-09-2	X		X	X
Acenaphthene	83-32-9	X		X	X
2,4-Dinitrophenol	51-28-5	X		X	X
4-Nitrophenol	100-02-7	X		X	X
Dibenzofuran	132-64-9	X		X	X
2,4-Dinitrotoluene	121-14-2	X	X	X	X
2,6-Dinitrotoluene	606-20-2	X		X	X
Diethylphthalate	84-66-2	X		X	X
4-Chlorophenyl phenyl ether	7005-72-3	X		X	X
Fluorene	86-73-7	X		X	X
4-Nitroaniline	100-01-6	X		X	X
4,6-Dinitro-2-methylphenol	534-52-1	X		X	X
N-Nitrosodiphenylamine	86-30-6	X		X	X
Azobenzene[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

Table 3

Reportable Analytes for STL North Canton Standard Tests, Primary Standard

Analyte	CAS Number	STL North Canton Standard List	TCLP	TCL	Appendix IX
Fluoranthene	206-44-0	X		X	X
Benzidine	92-87-5				
Pyrene	129-00-0	X		X	X
Butyl benzyl phthalate	85-68-7	X		X	X
3,3'-Dichlorobenzidine	91-94-1	X		X	X
Benzo(a)anthracene	56-55-3	X		X	X
Bis(2-ethylhexyl)phthalate	117-81-7	X		X	X
Chrysene	218-01-9	X		X	X
Di-n-octylphthalate	117-84-0	X		X	X
Benzo(b)fluoranthene	205-99-2	X		X	X
Benzo(k)fluoranthene	207-08-9	X		X	X
Benzo(a)pyrene	50-32-8	X		X	X
Indeno(1,2,3-cd)pyrene	193-39-5	X		X	X
Dibenz(a,h)anthracene	53-70-3	X		X	X
Benzo(g,h,i)perylene	191-24-2	X		X	X
Benzaldehyde	100-52-7			X	
Caprolactam	105-60-2			X	
1,1-Biphenyl	92-52-4			X	
Atrazine	1912-24-9			X	

[1] 2,2'oxybis(1-chloropropane) was 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

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
4-Nitroquinoline-1-oxide	56-57-5				X
*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
Dimethylphthalate	163	194	164

Table 7

Analytes in Approximate Retention Time Order and Characteristic Ions, Primary Standard

Analyte	Primary	Secondary	Tertiary
Acenaphthylene	152	151	153
2,6-Dinitrotoluene	165	63	89
Acenaphthene-d10 (Internal Standard)	164	162	160
3-Nitroaniline	138	108	92
Acenaphthene	153	152	154
2,4-Dinitrophenol	184	63	154
Dibenzofuran	168	139	84
4-Nitrophenol	109	139	65
2,4-Dinitrotoluene	165	63	89
Diethylphthalate	149	177	150
Fluorene	166	165	167
4-Chlorophenylphenylether	204	206	141
4-Nitroaniline	138	92	108
4,6-Dinitro-2-methylphenol	198	182	77
N-Nitrosodiphenylamine	169	168	167
2,4,6-Tribromophenol (Surrogate Standard)	330	332	141
Azobenzene	77	182	105
4-Bromophenylphenylether	248	250	141
Hexachlorobenzene	284	142	249
Atrazine	200	173	215
Pentachlorophenol	266	264	268
Phenanthrene-d10 (Internal Standard)	188	94	80
Phenanthrene	178	179	176
Anthracene	178	179	176
Carbazole	167	166	139
Di-n-butylphthalate	149	150	104
Fluoranthene	202	101	100
Benzidine	184	92	185
Pyrene	202	101	100
Terphenyl-d14 (Surrogate Standard)	244	122	212
Butylbenzylphthalate	149	91	206
Benzo(a)Anthracene	228	229	226
Chrysene-d12 (Internal Standard)	240	120	236
3,3'-Dichlorobenzidine	252	254	126
Chrysene	228	226	229
Bis(2-ethylhexyl)phthalate	149	167	279
Di-n-octylphthalate	149	167	43
Benzo(b)fluoranthene	252	253	125
Benzo(k)fluoranthene	252	253	125
Benzo(a)pyrene	252	253	125
Perylene-d12 (Internal Standard)	264	260	265
Indeno(1,2,3-cd)pyrene	276	138	277
Dibenz(a,h)anthracene	278	139	279
Benzo(g,h,i)perylene	276	138	277

Table 8

Analytes in Approximate Retention Time Order and Characteristic Ions, Appendix IX Standard

Analyte	Primary	Secondary	Tertiary
2-Picoline	93	66	92
N-Nitrosomethylethylamine	88	42	43
Methyl methanesulfonate	80	79	65
N-Nitrosodiethylamine	102	44	57
Ethyl methanesulfonate	79	109	97
Pentachloroethane	117	119	167
Acetophenone	105	77	120
N-Nitrosopyrrolidine	100	41	42
N-Nitrosomorpholine	116	56	86
o-Toluidine	106	107	
3-Methylphenol	108	107	77
N-Nitrosopiperidine	114	42	55
o,o,o-Triethyl-Phosphorothioate	198	121	93
a,a-Dimethyl-phenethylamine	58	91	
2,6-Dichlorophenol	162	164	63
Hexachloropropene	213	215	211
p-Phenylenediamine	108	80	
n-Nitrosodi-n-butylamine	84	57	41
Safrole	162	104	77
1,2,4,5-Tetrachlorobenzene	216	214	218
Isosafrole 1	162	104	131
Isosafrole 2	162	104	131
1,4-Dinitrobenzene	168	75	122
1,4-Naphthoquinone	158	104	102
1,3-Dinitrobenzene	168	75	76
Pentachlorobenzene	250	248	252
1-Naphthylamine	143	115	
2-Naphthylamine	143	115	
2,3,4,6-Tetrachlorophenol	232	230	131
5-Nitro-o-toluidine	152	77	106
Thionazin	97	96	143
1,3,5-Trinitrobenzene	213	75	120
Sulfotepp	97	322	202
Phorate	75	97	121
Phenacetin	108	179	109
Diallate	86	234	
Dimethoate	87	93	125
4-Aminobiphenyl	169		
Pentachloronitrobenzene	237	142	214
Pronamide	173	175	255
Disulfoton	88	97	89
2-secbutyl-4,6-dinitrophenol (Dinoseb)	211	163	147
Methyl parathion	109	125	263
4-Nitroquinoline-1-oxide	190	128	160

Table 8

Analytes in Approximate Retention Time Order and Characteristic Ions, Appendix IX Standard

Analyte	Primary	Secondary	Tertiary
Parathion	109	97	291
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

Table 12[3]
Calibration Levels, Primary Standard, µg/mL

Analyte	Level 1	Level 2	Level 3	Level 4	Level 5
4,6-Dinitro-2-methylphenol	10	25	40	60	80
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

Table 13[1]

Calibration Levels, Appendix IX Standard, µg/mL

Semivolatiles	Level 1	Level 2	Level 3	Level 4	Level 5
*Isodrin	10	25	40	60	80
*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

Table 14
Initial demonstration recovery and precision limits

Compound	Spiking concentration µg/L	Limit for Relative Standard Deviation	Limit for average recovery, %
4,4'-DDE[1]	60	32.0	19.2-119.7
4,4'-DDT[1]	60	61.6	D-170.6
Dibenzo(a,h)anthracene	60	70.0	D-199.7
Di-n-butyl phthalate	60	16.7	8.4-111.0
1,2-Dichlorobenzene	60	30.9	48.6-112.0
1,3-Dichlorobenzene	60	41.7	16.7-153.9
1,4-Dichlorobenzene	60	32.1	37.3-105.7
3,3'-Dichlorobenzidine	60	71.4	8.2-212.5
Dieldrin[1]	60	30.7	44.3-119.3
Diethyl phthalate	60	26.5	D-100.0
Dimethyl phthalate	60	23.2	D-100.0
2,4-Dinitrotoluene	60	21.8	47.5-126.9
2,6-Dinitrotoluene	60	29.6	68.1-136.7
Di-n-octylphthalate	60	31.4	18.6-131.8
Endosulfan sulfate[1]	60	16.7	D-103.5
Endrin aldehyde	60	32.5	D-188.8
Fluoranthene	60	32.8	42.9-121.3
Fluorene	60	20.7	71.6-108.4
Heptachlor[1]	60	37.2	D-172.2
Heptachlor epoxide[1]	60	54.7	70.9-109.4
Hexachlorobenzene	60	24.9	7.8-141.5
Hexachlorobutadiene	60	26.3	37.8-102.2
Hexachloroethane	60	24.5	55.2-100.0
Indeno(1,2,3-cd)pyrene	60	44.6	D-150.9
Isophorone	60	63.3	46.6-180.2
Naphthalene	60	30.1	35.6-119.6
Nitrobenzene	60	39.3	54.3-157.6
N-Nitrosodi-n-propylamine	60	55.4	13.6-197.9
PCB-1260[1]	60	54.2	19.3-121.0
Phenanthrene	60	20.6	65.2-108.7
Pyrene	60	25.2	69.6-100.0
1,2,4-Trichlorobenzene	60	28.1	57.3-129.2
4-Chloro-3-methylphenol	60	37.2	40.8-127.9
2-Chlorophenol	60	28.7	36.2-120.4
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

Table 14
Initial demonstration recovery and precision limits

Compound	Spiking concentration µg/L	Limit for Relative Standard Deviation	Limit for average recovery, %
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

Analytes	CAS Number	Aqueous µg/L
Butyl benzyl phthalate	85-68-7	10
3,3'-Dichlorobenzidine	91-94-1	50
Benzo(a)anthracene	56-55-3	10
Bis(2-ethylhexyl)phthalate	117-81-7	10
Chrysene	218-01-9	10
Di-n-octylphthalate	117-84-0	10
Benzo(b)fluoranthene	205-99-2	10
Benzo(k)fluoranthene	207-08-9	10
Benzo(a)pyrene	50-32-8	10
Indeno(1,2,3-cd)pyrene	193-39-5	10
Dibenz(a,h)anthracene	53-70-3	10
Benzo(g,h,i)perylene	191-24-2	10

Table A-2. Method 625 LCS and MS compounds and spike concentrations.

LCS Compounds	Spiking Level, ng/µL in extract[1]
Phenol	100
Bis(2-chloroethyl)ether	100
2-Chlorophenol	100
1,3-Dichlorobenzene	100
1,4-Dichlorobenzene	100
1,2-Dichlorobenzene	100
2,2'-oxybis(1-chloropropane)	100
N-Nitroso-di-n-propylamine	100
Hexachloroethane	100
Nitrobenzene	100
Isophorone	100
2-Nitrophenol	100
2,4-Dimethylphenol	100
Bis(2-chloroethoxy)methane	100
2,4-Dichlorophenol	100
1,2,4-Trichlorobenzene	100
Naphthalene	100
Hexachlorobutadiene	100
4-Chloro-3-methylphenol	100
Hexachlorocyclopentadiene	100
2,4,6-Trichlorophenol	100
2-Chloronaphthalene	100
Dimethyl phthalate	100
Acenaphthylene	100
Acenaphthene	100
2,4-Dinitrophenol	100
4-Nitrophenol	100
2,4-Dinitrotoluene	100
2,6-Dinitrotoluene	100
Diethylphthalate	100
4-Chlorophenyl phenyl ether	100
Fluorene	100
4,6-Dinitro-2-methylphenol	100
N-Nitrosodiphenylamine	100
4-Bromophenyl phenyl ether	100
Hexachlorobenzene	100
Pentachlorophenol	100
Phenanthrene	100
Anthracene	100
Di-n-butyl phthalate	100
Fluoranthene	100
Benzidine	100
Pyrene	100
Butyl benzyl phthalate	100
3,3'-Dichlorobenzidine	100

LCS Compounds	Spiking Level, ng/μL in extract[1]
Benzo(a)anthracene	100
Bis(2-ethylhexyl)phthalate	100
Chrysene	100
Di-n-octylphthalate	100
Benzo(b)fluoranthene	100
Benzo(k)fluoranthene	100
Benzo(a)pyrene	100
Indeno(1,2,3-cd)pyrene	100
Dibenz(a,h)anthracene	100
Benzo(g,h,i)perylene	100

[1] **Levels are 50 and 75 ng/μL if 2 μL injection is used**

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STL STANDARD OPERATING PROCEDURE

TITLE: DETERMINATION OF VOLATILE ORGANICS BY GC/MS BASED ON METHOD 8260B, 8260A, AND 624

(SUPERSEDES: REVISION 2.2, DATED 11/28/00)

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ANALYSIS OF VOLATILE ORGANICS BY METHOD 624 55

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1.0 SCOPE AND APPLICATION

1.1. This method is applicable to the determination of Volatile Organic Compounds in waters, wastewater, soils, sludges and other solid matrices. Standard analytes are listed in Tables 5 and 6.

1.2. This SOP is applicable to method 8260B. It may also be used for analysis following method 8260A. Appendix A presents modifications to the procedures in the main SOP that are necessary for analysis of wastewater by method 624. The associated LIMS method codes are QK (8260B), DN (624), and MZ (8260A). Ohio VAP projects are distinguished by Program Code 2J. The following Prep Codes are used: 15 (5 mL purge), 25 (25 mL purge), 4B (Methanol preservation, EnCore™), 4D (Sodium Bisulfate preservation, EnCore™), 4P (Frozen, EnCore™), and 73 (5030A Methanol Prep).

1.3. This method can be used to quantify most volatile organic compounds that have boiling points below 200°C and are insoluble or slightly soluble in water. Volatile water soluble compounds can be included in this analytical technique; however, for more soluble compounds, quantitation limits are approximately ten times higher because of poor purging efficiency.

1.4. The method is based upon a purge and trap, gas chromatograph/mass spectrometric (GC/MS) procedure. The approximate working range is 5 to 200 µg/L for 5 mL waters, 1 to 40 µg/L for 25 mL purge waters, 5 to 200 µg/kg for low-level soils, and 250 to 25,000 µg/kg for medium-level soils. Reporting limits are listed in Tables 1 and 3.

1.5. Method performance is monitored through the use of surrogate compounds, matrix spike/matrix spike duplicates, and laboratory control spike samples.

2. SUMMARY OF METHOD

2.1. Volatile compounds are introduced into the gas chromatograph by the purge and trap method. The components are separated via the chromatograph and detected using a mass spectrometer, which is used to provide both qualitative and quantitative information.

2.2. Aqueous samples are purged directly. Generally, soils are preserved by extracting the volatile analytes into methanol. If especially low detection limits are required, soil samples may be preserved with sodium bisulfate and purged directly.

2.3. In the purge and trap process, an inert gas is bubbled through the solution at ambient temperature or at 40°C (40°C required for low level soils) and the volatile components are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbant

column where the volatile components are trapped. After purging is completed, the sorbant column (trap) is heated and backflushed with inert gas to desorb the components onto a gas chromatographic column. The gas chromatographic column is then heated to elute the components which are detected with a mass spectrometer.

2.4. Qualitative identifications are confirmed by analyzing standards under the same conditions used for samples and comparing the resultant mass spectra and GC retention times. Each identified component is quantified by relating the MS response for an appropriate selected ion produced by that compound to the MS response for another ion produced by an internal standard.

3. DEFINITIONS

3.1. Batch

The batch is a set of up to 20 samples of the same matrix processed using the same procedures and reagents within the same time period. Using this method, each BFB analysis will normally start a new batch. Batches for medium level soils are defined at the sample preparation stage and may be analyzed on multiple instruments over multiple days, although reasonable effort should be made to keep the samples together.

3.1.1. The Quality Control batch must contain a matrix spike/spike duplicate (MS/MSD), a Laboratory Control Sample (LCS), and a method blank. In some cases, at client request, the MS/MSD may be replaced with a matrix spike and sample duplicate. Refer to the STL QC Program document (QA-003) for further details of the batch definition.

3.2. Method Blank

3.2.1. A method blank consisting of all reagents added to the samples must be analyzed with each batch of samples. The method blank is used to identify any background interference or contamination of the analytical system which may lead to the reporting of elevated concentration levels or false positive data.

3.3. Laboratory Control Sample (LCS)

3.3.1. Laboratory Control Samples are well characterized, laboratory generated samples used to monitor the laboratory's day-to-day performance of routine analytical methods. The LCS, spiked with a group of target compounds representative of the method analytes, is used to monitor the accuracy of the analytical process, independent of matrix effects. Ongoing monitoring of the LCS results provides evidence that the laboratory is performing the method within accepted QC guidelines for accuracy and precision.

3.4. Surrogates

3.4.1. Surrogates are organic compounds which are similar to the target analyte(s) in chemical composition and behavior in the analytical process, but which are not normally found in environmental samples. Each sample, blank, LCS, and MS/MSD is spiked with surrogate standards. Surrogate spike recoveries must be evaluated by determining whether the concentration (measured as percent recovery) falls within the required recovery limits.

3.5. Matrix Spike/Matrix Spike Duplicate (MS/MSD)

3.5.1. A matrix spike is an environmental sample to which known concentrations of target analytes have been added. A matrix spike duplicate is a second aliquot of the same sample which is prepared and analyzed along with the sample and matrix spike. Matrix spikes and duplicates are used to evaluate accuracy and precision in the actual sample matrix.

3.6. Calibration Check Compound (CCC)

3.6.1. CCCs are a representative group of compounds which are used to evaluate initial calibrations and continuing calibrations. Relative percent difference for the initial calibration and % drift for the continuing calibration response factors are calculated and compared to the specified method criteria.

3.7. System Performance Check Compounds (SPCC)

SPCCs are compounds which are sensitive to system performance problems and are used to evaluate system performance and sensitivity. A response factor from the continuing calibration is calculated for the SPCC compounds and compared to the specified method criteria.

4. INTERFERENCES

4.1. Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus that lead to discrete artifacts. All of these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. The use of ultra high purity gases, pre-purged purified reagent water, and approved lots of purge and trap grade methanol will greatly reduce introduction of contaminants. In extreme cases the purging vessels may be pre-purged to isolate the instrument from laboratory air contaminated by solvents used in other parts of the laboratory.

4.2. Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride and fluorocarbons) into the sample through the septum seal during shipment and storage. A field blank prepared from reagent water and carried through the sampling and handling protocol can serve as a check on such contamination.

4.3. Matrix interferences may be caused by non-target contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from source to source depending upon the nature and diversity of the site being sampled.

4.4. Cross-contamination can occur whenever high-level and low-level samples are analyzed sequentially or in the same purge position on an autosampler. Whenever an unusually concentrated sample is analyzed, it should be followed by one or more blanks to check for cross-contamination. The purge and trap system may require extensive bake-out and cleaning after a high-level sample.

4.5. Some samples may foam when purged due to surfactants present in the sample. When this kind of sample is encountered an antifoaming agent (e.g., J.T. Baker's Antifoam B silicone emulsion) can be used. A blank spiked with this agent must be analyzed with the sample because of the non-target interferences associated with the agent.

5. SAFETY

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

5.2. The Chemical Hygiene Plan (CHP) gives details about the specific health and safety practices which are to be followed in the laboratory area. Personnel must receive training in the CHP, including the written Hazard Communication plan, prior to working in the laboratory. Consult the CHP, the STL Health and Safety Policies and Procedures Manual, and available Material Safety Data Sheets (MSDS) prior to using the chemicals in the method.

5.3. Consult the STL Health and Safety Policies and Procedures Manual for information on Personal Protective Equipment. Eye protection that protects against splash and a laboratory coat must be worn in the lab. Appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately. Disposable gloves shall not be reused.

5.4. The health and safety hazards of many of the chemicals used in this procedure have not been fully defined, therefore each chemical compound should be treated as a potential health hazard. Additional health and safety information can be obtained from the MSDS files maintained in the laboratory. The following specific hazards are known:

5.4.1. Chemicals that have been classified as carcinogens, or potential carcinogens, under OSHA include: Acrylonitrile, benzene, carbon tetrachloride, chloroform, 1,2-dibromo-3-chloropropane, 1,4-dichlorobenzene, and vinyl chloride.

5.4.2. Chemicals known to be flammable are: **Methanol**.

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

5.6. The preparation of standards and reagents will be conducted in a fume hood with the sash closed as far as the operations will permit.

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

5.8. Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices outlined in the STL Health and Safety Manual. These employees must have training on the hazardous waste disposal practices initially upon assignment of these tasks, followed by an annual refresher training.

6. EQUIPMENT AND SUPPLIES

6.1. Microsyringes: 10 µL and larger, 0.006 inch ID needle.

6.2. Syringe: 5 or 25 mL glass with luerlok tip, if applicable to the purging device.

6.3. Balance: Analytical, capable of accurately weighing 0.0001 g, and a top-loading balance capable of weighing 0.1 g

6.4. Glassware:

6.4.1. Vials: 20 mL with screw caps and Teflon liners.

6.4.2. Volumetric flasks: 10 mL and 100 mL, class A with ground-glass stoppers.

6.5. Spatula: Stainless steel.

6.6. Disposable pipets: Pasteur.

6.7. pH paper: Wide range.

6.8. Gases:

6.8.1. Helium: Ultra high purity, gr. 5, 99.999%.

6.8.2. Nitrogen: Ultra high purity, from cylinders of gas generators, may be used as an alternative to helium for purge gas.

6.8.3. Compressed air: Used for instrument pneumatics.

6.8.4. Liquid nitrogen: Used for cryogenic cooling if necessary.

6.9. Purge and Trap Device: The purge and trap device consists of the sample purger, the trap, and the desorber.

6.9.1. Sample Purger: The recommended purging chamber is designed to accept 5 mL samples with a water column at least 3 cm deep. The purge gas must pass through the water column as finely divided bubbles, each with a diameter of less than 3 mm at the origin. The purge gas must be introduced no more than 5 mm from the base of the water column. Alternative sample purge devices may be used provided equivalent performance is demonstrated. Low level soils are purged directly from a VOA vial.

6.9.2. Trap: A variety of traps may be used, depending on the target analytes required. For most purposes the Vocarb 3000 trap is suitable. Other traps, such as Vocarb 4000, or Tenax / Silica gel / Charcoal may be used if the Quality Control criteria are met.

6.9.3. Desorber: The desorber should be capable of rapidly heating the trap to 180°C. Many such devices are commercially available.

6.9.4. Sample Heater: A heater capable of maintaining the purge device at 40°C is necessary for low level soil analysis.

6.10. Gas Chromatograph/Mass Spectrometer System:

6.10.1. Gas Chromatograph: The gas chromatograph (GC) system must be capable of temperature programming.

6.10.2. Gas Chromatographic Columns: Capillary columns are used. Some typical columns are listed below:

6.10.2.1. Column 1: 105m x 0.53 ID Rtx-624 with 3 µm film thickness.

6.10.2.2. Column 2: 75 m x 0.53 ID DB-624 widebore with 3 µm film thickness.

6.10.2.3. Mass Spectrometer: The mass spectrometer must be capable of scanning 35-300 AMU every two seconds or less, using 70 volts electron energy in the electron impact mode and capable of producing a mass spectrum that meets the required criteria when 50 ng of 4-Bromofluorobenzene (BFB) are injected onto the gas chromatograph column inlet.

6.10.3. GC/MS interface: In general glass jet separators are used but any interface (including direct introduction to the mass spectrometer) that achieves all acceptance criteria may be used.

6.10.4. Data System: A computer system that allows the continuous acquisition and storage on machine readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that allows searching any GC/MS data file for ions of a specified mass and plotting such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundances in any EICP between the specified time or scan-number limits. Also, for the non-target compounds, software must be available that allows for the comparison of sample spectra against reference library spectra. The most recent release of the NIST/EPA mass spectral library should be used as

the reference library. The computer system must also be capable of backing up data for long-term off-line storage.

6.10.5. Cryogenic Cooling: Some columns require the use of liquid nitrogen to achieve the subambient temperature required for the proper separation of the gases.

7. REAGENTS AND STANDARDS

7.1. Reagents

7.1.1. Methanol: Purge and Trap Grade, High Purity

7.1.2. Reagent Water: High purity water that meets the requirements for a method blank when analyzed. (See section 9.4) Reagent water may be purchased as commercial distilled water and prepared by purging with an inert gas overnight. Other methods of preparing reagent water are acceptable.

7.2. Standards

7.2.1. Calibration Standard

7.2.1.1. Stock Solutions: Stock solutions may be purchased as certified solutions from commercial sources or prepared from pure standard materials as appropriate. These standards are prepared in methanol and stored in Teflon-sealed screw-cap bottles with minimal headspace at -10° to -20°C.

7.2.1.2. Working standards: A working solution containing the compounds of interest prepared from the stock solution(s) in methanol. These standards are stored in the freezer or as recommended by the manufacturer. Working standards are monitored by comparison to the initial calibration curve. If any of the calibration check compounds drift in response from the initial calibration by more than 20% then corrective action is necessary. This may include steps such as instrument maintenance, preparing a new calibration verification standard or tuning the instrument. If the corrective actions do not correct the problem then a new initial calibration must be performed.

7.2.1.3. Aqueous Calibration Standards are prepared in reagent water using the secondary dilution standards. These aqueous standards must be prepared daily.

7.2.1.4. If stock or secondary dilution standards are purchased in sealed ampoules they may be used up to the manufacturers expiration date.

7.2.2. Internal Standards: Internal standards are added to all samples, standards, and blank analyses. Refer to Table 7 for internal standard components.

7.2.3. Surrogate Standards: Refer to Table 8 for surrogate standard components and spiking levels.

7.2.4. Laboratory Control Sample Spiking Solutions: Refer to Table 9 for LCS components and spiking levels.

7.2.5. Matrix Spiking Solutions: The matrix spike contains the same components as the LCS. Refer to Table 9.

7.2.6. Tuning Standard: A standard is made up that will deliver 50 ng on column upon injection. A recommended concentration of 25 ng/µL of 4-Bromofluorobenzene in methanol is prepared as described in Sections 7.2.1.1 and 7.2.1.2.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Holding times for all volatile analysis are 14 days from sample collection.

8.2. Water samples are normally preserved at pH $\leq$ 2 with 1:1 hydrochloric acid. If residual chlorine is present, 2 drops of 10% sodium thiosulfate are added.

8.3. Solid samples are field preserved with sodium bisulfate solution for low level analysis, or with methanol for medium level analysis. Soil samples can also be taken using the EnCore™ sampler and preserved in the lab within 48 hours of sampling. At specific client request, unpreserved soil samples may be accepted.

8.4. There are several methods of sampling soil. The recommended method, which provides the minimum of field difficulties, is to take an EnCore™ sample. (The 5 g or 25 g sampler can be used, depending on client preference). Following shipment back to the lab the soil is preserved in methanol. This is the medium level procedure. If very low detection limits are needed (< 50 µg/kg for most analytes) then it will be necessary to use two additional 5 g EnCore™ samplers or to use field preservation.

8.5. Sample collection for medium level analysis using EnCore™ samplers.

8.5.1. Ship one 5 g (or 25 g) EnCore™ sampler per field sample position.

8.5.2. An additional bottle must be shipped for percent moisture determination.

8.5.3. When the samples are returned to the lab, extrude the (nominal) 5g (or 25 g) sample into a tared VOA vial containing 5 mL methanol (25 mL methanol for the 25 g sampler). Obtain the weight of the soil added to the vial and note on the label.

8.5.4. Add the correct amount of surrogate spiking mixture. (Add 25 µL of 2500 µg/mL solution for a nominal 25 g sample, 5 µL for a nominal 5 g sample.) Refer to Section 17.8 for Michigan project criteria.

8.5.5. Add the correct amount of matrix spiking solution to the matrix spike and matrix spike duplicate samples. (Add 500 µL of 50 µg/mL solution for a nominal 25 g sample, 100 µL for a nominal 5 g sample.) Reduce the volume of methanol added to ensure the final volume is 25 mL for nominal 25 g sample or 5 mL methanol for a nominal 5 g sample. Refer to Section 17.8 for Michigan project criteria.

8.5.6. Prepare an LCS for each batch by adding the correct amount of matrix spiking solution to clean methanol. (50 µL of spike to 25 mL methanol or 10 µL spike to 5 mL methanol). Refer to Section 17.8 for Michigan project criteria.

8.5.7. Shake the samples for two minutes to distribute the methanol throughout the soil.

8.5.8. Allow to settle, then remove a portion of methanol and store in a clean Teflon capped vial at 4 ±2°C until analysis.

8.6. Sample collection for medium level analysis using field methanol preservation

8.6.1. Prepare a 2 oz sample container by adding 25 mL purge and trap grade methanol. (If a 5 g sample is to be used, add 5 mL methanol to a 2 oz container or VOA vial).

8.6.2. Seal the bottle and attach a label.

8.6.3. Weigh the bottle to the nearest 0.01g and note the weight on the label.

8.6.4. Ship with appropriate sampling instructions.

8.6.5. Each sample will require an additional bottle with no preservative for percent moisture determination.

8.6.6. At client request, the methanol addition and weighing may also be performed in the field.

8.6.7. When the samples are returned to the lab, obtain the weight of the soil added to the vial and note on the label.

8.6.8. Add the correct amount of surrogate spiking mixture. (Add 25 µL of 2500 µg/mL solution for a nominal 25 g sample, 5 µL for a nominal 5 g sample.) Refer to Section 17.8 for Michigan project criteria.

8.6.9. Add the correct amount of matrix spiking solution to the matrix spike and matrix spike duplicate samples. (Add 25 µL of 50 µg/mL solution for a nominal 25 g sample, 100 µL for a nominal 5 g sample.) Reduce the volume of methanol added to ensure the final volume is 25 mL for nominal 25 g sample or 5 mL methanol for a nominal 5 g sample. Refer to Section 17.8 for Michigan project criteria.

8.6.10. Prepare an LCS for each batch by adding the correct amount of matrix spiking solution to clean methanol. (500 µL of spike to 25 mL methanol or 100 µL spike to 5 mL methanol). Refer to Section 17.8 for Michigan project criteria.

8.6.11. Shake the samples for two minutes to distribute the methanol throughout the soil.

8.6.12. Allow to settle, then remove a portion of methanol and store in a clean Teflon capped vial at 4+2°C until analysis.

8.7. Low level procedure

8.7.1. If low detection limits are required (typically < 50 µg/kg) sodium bisulfate preservation must be used. However, it is also necessary to take a sample for the medium level (field methanol preserved or using the EnCore™ sampler) procedure, in case the concentration of analytes in the soil is above the calibration range of the low level procedure.

8.7.2. A purge and trap autosampler capable of sampling from a sealed vial is required for analysis of samples collected using this method. (Varian Archon or O.I. 4552).

8.7.3. The soil sample is taken using a 5g EnCore™ sampling device and returned to the lab. It is recommended that two EnCore™ samplers be used for each field sample position, to allow for any reruns than may be necessary. A separate sample for % moisture determination is also necessary.

8.7.4. Prepare VOA vials by adding a magnetic stir bar, approximately 1 g of sodium bisulfate and 5 mL of reagent water.

8.7.5. Seal and label the vial. It is strongly recommended that the vial is labeled with an indelible marker rather than a paper label, since paper labels may cause the autosampler to bind and malfunction. The label absolutely must not cover the neck of the vial or the autosampler will malfunction.

8.7.6. Weigh the vial to the nearest 0.1g and note the weight on the label.

8.7.7. Extrude the soil sample from the EnCore™ sampler into the prepared VOA vial. Reweigh the vial to obtain the weight of soil and note on the label.

Note: Soils containing carbonates may effervesce when added to the sodium bisulfate solution. If this is the case at a specific site, add 5 mL of water instead, and freeze at <-10°C within 48 hours, analyzed within 12 days after preserving with water, and stored at a 45 degree angle in the freezer.

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

8.7.9. Alternatively the sodium bisulfate preservation may be performed in the field. This is not recommended because of the many problems that can occur in the field setting. Ship at least two vials per sample. The field samplers must determine the weight of soil sampled. Each sample will require an additional bottle with no preservative for percent moisture determination, and an additional bottle preserved with methanol for the medium level procedure. Depending on the type of soil it may also be necessary to ship vials with no or extra preservative.

8.8. Unpreserved soils

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

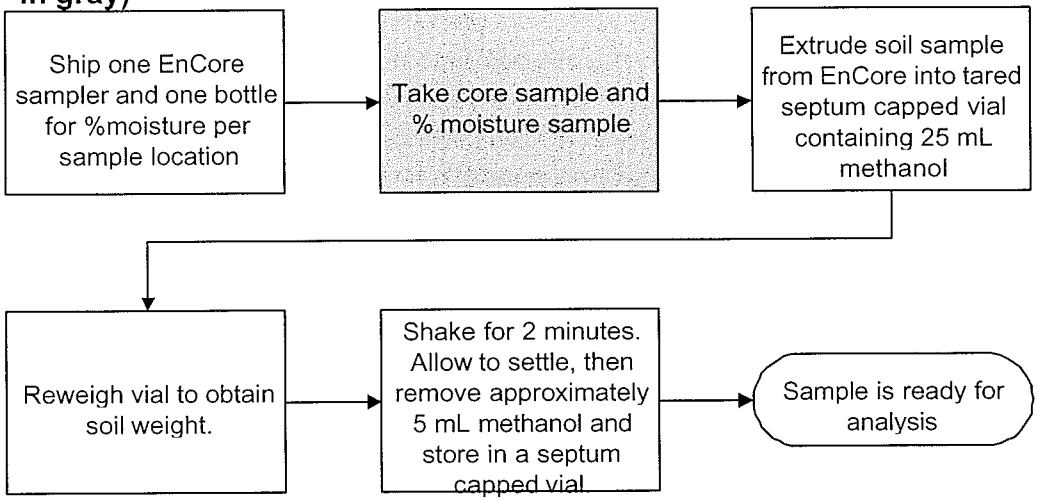
8.9. Aqueous samples are stored in glass containers with Teflon lined septa at 4°C +/- 2°C, with minimum headspace.

8.10. Medium level solid extracts are aliquoted into 2 - 5 mL glass vials with Teflon lined caps and stored at 4°C +/- 2°C. The extracts are stored with minimum headspace.

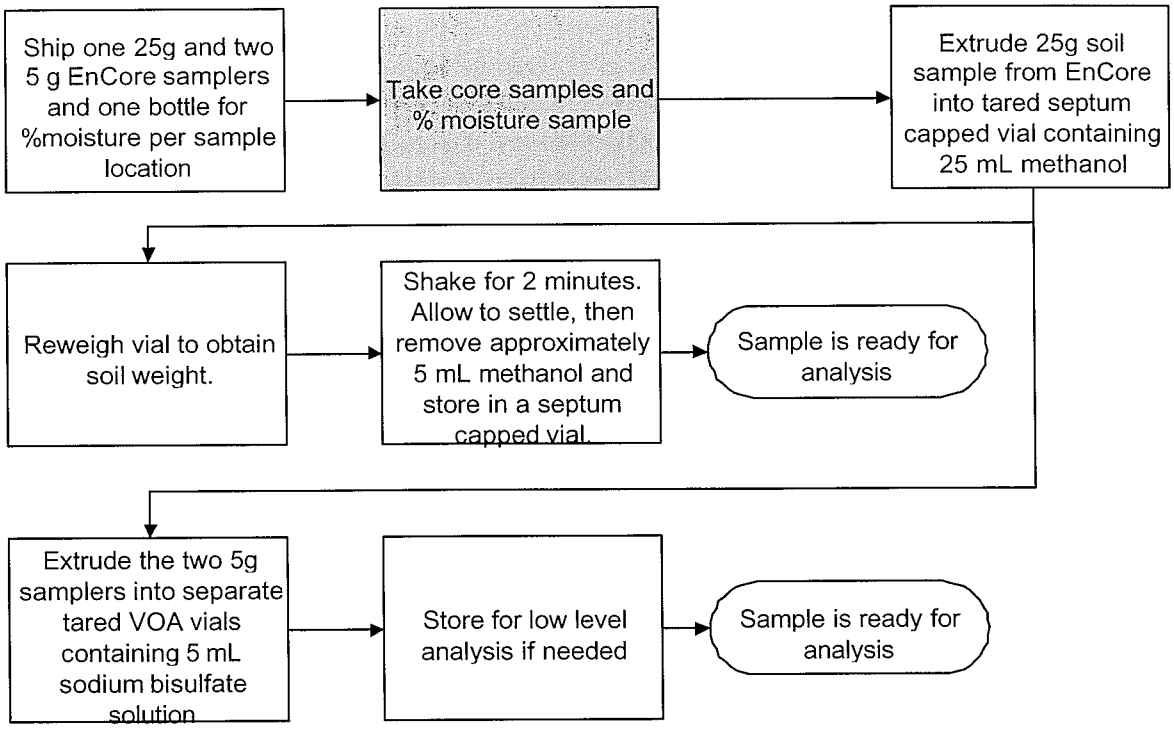
8.11. The maximum holding time is 14 days from sampling until the sample is analyzed. (Samples that are found to be unpreserved still have a 14 day holding time. However they should be analyzed as soon as possible. The lack of preservation should be addressed in the case narrative). Maximum holding time for the EnCore™ sampler (before the sample is added to methanol or sodium bisulfate) is 48 hours.

8.12. A holding blank is stored with the samples. This is analyzed and replaced if any of the trip blanks show any contamination. Otherwise it is replaced every 14 days.

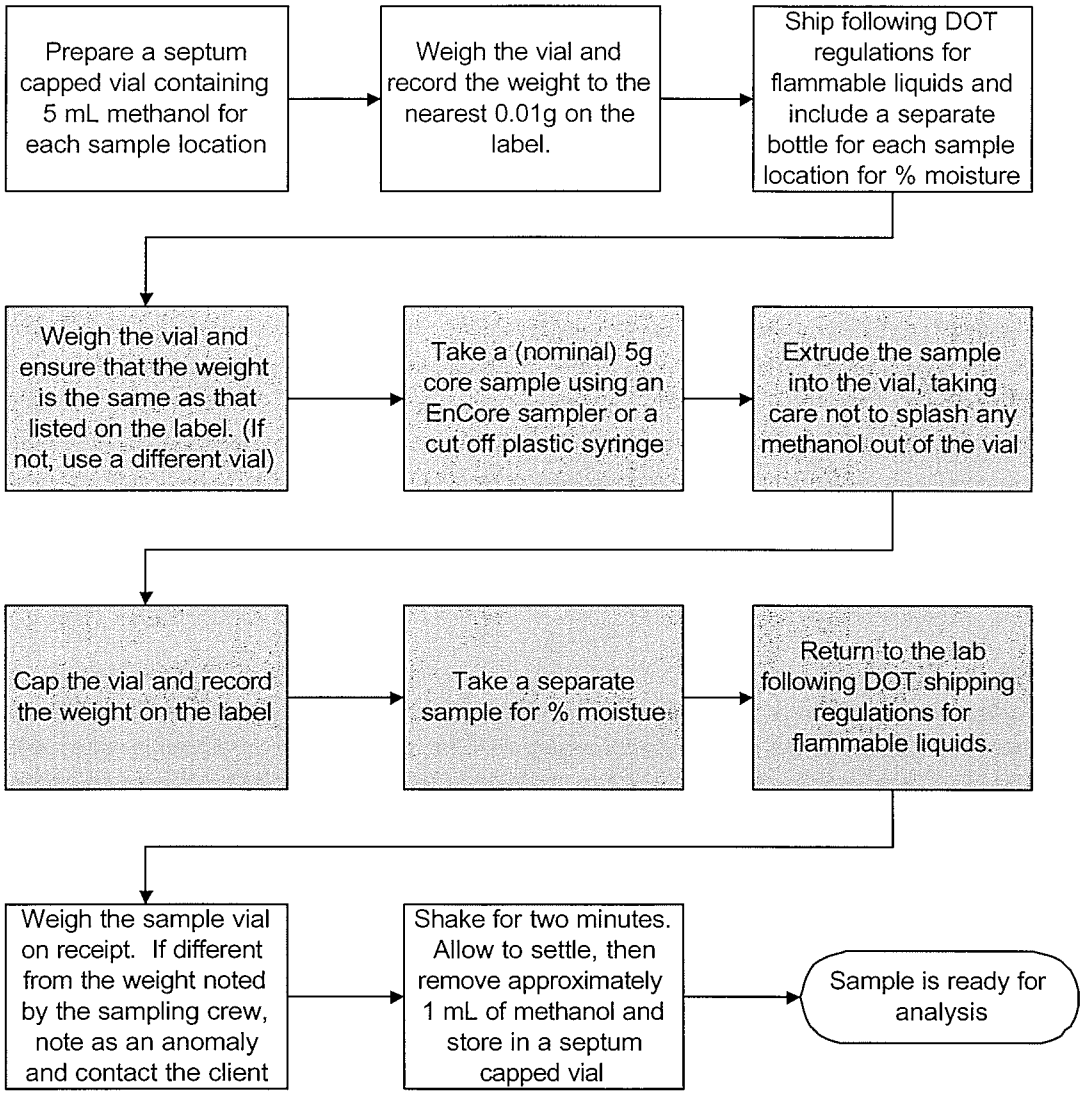
EnCore procedure when low level is not required (field steps in gray)



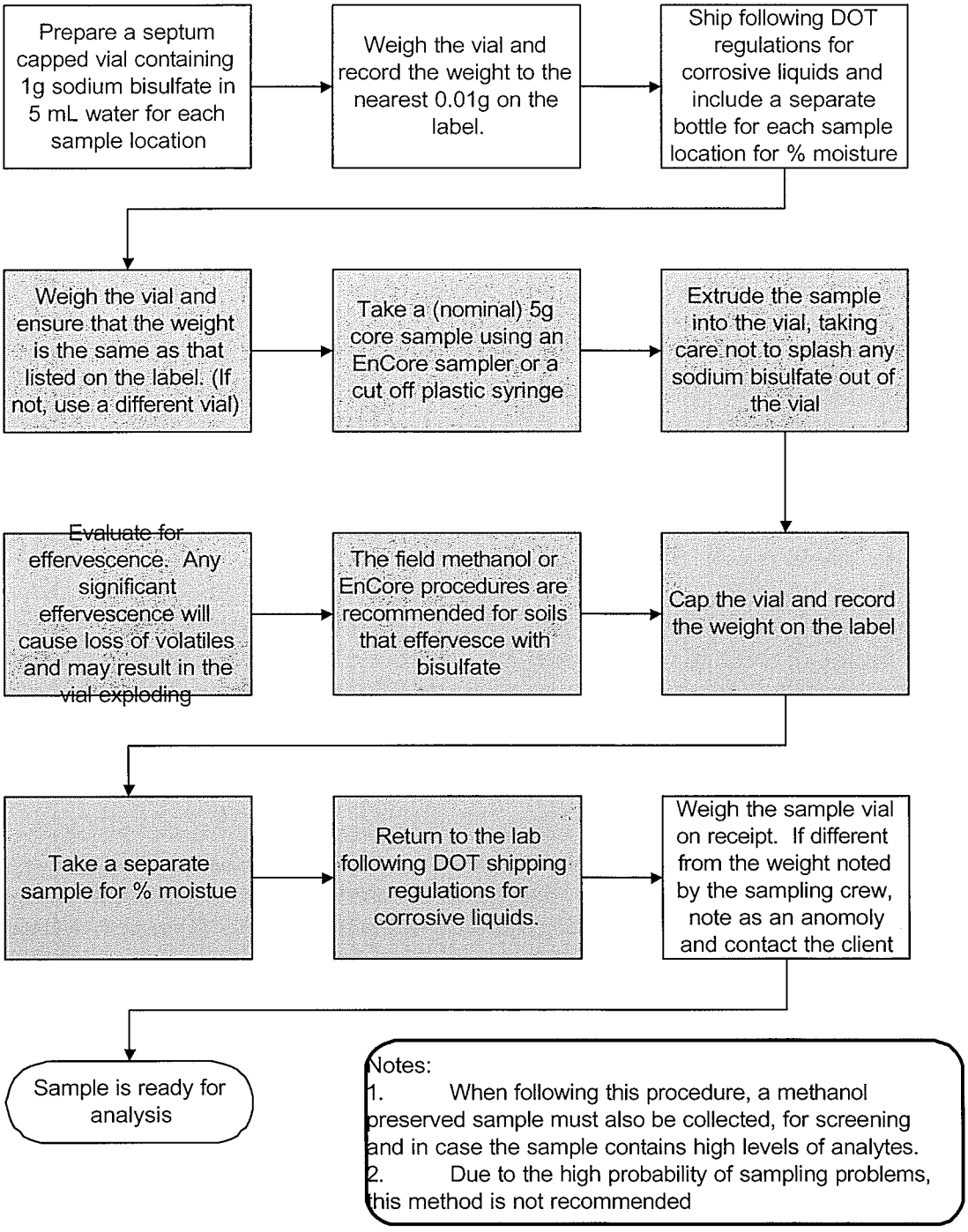
EnCore procedure when low level is required



Field methanol extraction procedure (field steps in gray)



Field bisulfate preservation procedure (field steps in gray)



9. QUALITY CONTROL

9.1. Initial Demonstration of Capability

9.1.1. For the standard analyte list, the initial demonstration described in Section 13 and method detection limit (MDL) studies must be acceptable before analysis of samples may begin. MDLs should be analyzed for low and medium soils and aqueous samples.

9.1.2. For non-standard analytes, a MDL study must be performed and calibration curve generated before analyzing any samples, unless lesser requirements are previously agreed to with the client. In any event, the minimum initial demonstration required is analysis of a standard at the reporting limit and a single point calibration.

9.2. Control Limits

In-house historical control limits must be determined for surrogates, matrix spikes, and laboratory control samples (LCS). These limits must be determined at least annually. The recovery limits are mean recovery +/- 3 standard deviations for surrogates, matrix spikes and LCS. Precision limits for matrix spikes / matrix spike duplicates are 0 to mean relative percent difference + 3 standard deviations.

9.2.1. All surrogate, LCS, and MS recoveries (except for dilutions) must be entered into QuantIMS (when available) or other database so that accurate historical control limits can be generated. For tests without a separate extraction, surrogates and matrix spikes will be reported for all dilutions.

9.2.2. Refer to the QC Program document (QA-003) for further details of control limits.

9.3. Surrogates

Every sample, blank, and QC sample is spiked with surrogates. Surrogate recoveries in samples, blanks, and QC samples must be assessed to ensure that recoveries are within established limits. The compounds included in the surrogate spiking solutions are listed in Table 8. If any surrogates are outside limits, the following corrective actions must take place (except for dilutions):

- Check all calculations for error.
- Ensure that instrument performance is acceptable.

- Recalculate the data and/or reanalyze if either of the above checks reveal a problem.

- Reprepare and reanalyze the sample or flag the data as "Estimated Concentration" if neither of the above resolves the problem.

The decision to reanalyze or flag the data should be made in consultation with the client. It is only necessary to reprepare/reanalyze a sample once to demonstrate that poor surrogate recovery is due to matrix effect, unless the analyst believes that the repeated out of control results are not due to matrix effect.

9.3.1. If the surrogates are out of control for the sample, matrix spike, and matrix spike duplicate, then matrix effect has been demonstrated for that sample and repreparation is not necessary. If the sample is out of control and the MS and/or MSD is in control, then reanalysis or flagging of the data is required.

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

9.4. Method Blanks

9.4.1. For each batch of samples, analyze a method blank. The method blank is analyzed after the calibration standards, normally before any samples. For low-level volatiles, the method blank consists of reagent water. For medium-level volatiles, the method blank consists of 25.0 mL of methanol. Surrogates are added and the method blank is carried through the entire analytical procedure. The method blank must not contain any analyte of interest at or above the reporting limit (except common laboratory contaminants, see below) or at or above 5% of the measured concentration of that analyte in the associated samples, whichever is higher.

- If the analyte is a common laboratory contaminant (methylene chloride, acetone, 2-butanone) the data may be reported with qualifiers if the concentration of the analyte is less than five times the reporting limit. Such action must be taken in consultation with the client.

- Reanalysis of samples associated with an unacceptable method blank is required when reportable concentrations are determined in the samples.

- If there is no target analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. Such action should be done in consultation with the client.

9.4.2. The method blank must have acceptable surrogate recoveries. If surrogate recoveries are not acceptable, the data must be evaluated to determine if the method blank has served the

purpose of demonstrating that the analysis is free of contamination. If surrogate recoveries are low and there are reportable analytes in the associated samples re-extraction of the blank and affected samples will normally be required. Consultation with the client should take place.

9.4.3. If reanalysis of the batch is not possible due to limited sample volume or other constraints, the method blank is reported, all associated samples are flagged with a "B," and appropriate comments may be made in a narrative to provide further documentation.

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

9.5. Laboratory Control Samples (LCS)

9.5.1. For each batch of samples, analyze a LCS. The LCS is analyzed after the calibration standard, and normally before any samples. The LCS contains a representative subset of the analytes of interest (See Table 9), and must contain the same analytes as the matrix spike. If any analyte or surrogate is outside established control limits, the system is out of control and corrective action must occur. Corrective action will normally be repreparation and reanalysis of the batch.

- If the batch is not re-extracted and reanalyzed, the reasons for accepting the batch must be clearly presented in the project records and the report. (Examples of acceptable reasons for not reanalyzing might be that the matrix spike and matrix spike duplicate are acceptable, and sample surrogate recoveries are good, demonstrating that the problem was confined to the LCS.)

- If re-extraction and reanalysis of the batch is not possible due to limited sample volume or other constraints, the LCS is reported, all associated samples are flagged, and appropriate comments are made in a narrative to provide further documentation.

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

9.5.3. If full analyte spike lists are used at client request, it will be necessary to allow a percentage of the components to be outside control limits as this would be expected statistically. These requirements should be negotiated with the client. Refer to Section 17.5 for Ohio VAP specific analytes.

9.6. Matrix Spikes

9.6.1. For each QC batch, analyze a matrix spike and matrix spike duplicate. Spiking compounds and levels are given in Table 9. Compare the percent recovery and relative percent difference

(RPD) to that in the laboratory specific historically generated limits. See Section 17.5 for Ohio VAP specific analytes.

- If any individual recovery or RPD falls outside the acceptable range, corrective action must occur. The initial corrective action will be to check the recovery of that analyte in the Laboratory Control Sample (LCS). Generally, if the recovery of the analyte in the LCS is within limits, then the laboratory operation is in control and analysis may proceed. The reasons for accepting the batch must be documented.

- If the recovery for any component is outside QC limits for both the matrix spike/ spike duplicate and the LCS, the laboratory is out of control and corrective action must be taken. Corrective action will normally include reanalysis of the batch.

- If a MS/MSD is not possible due to limited sample, then a LCS duplicate should be analyzed. RPD of the LCS and LCSD are compared to the matrix spike limits.

- The matrix spike/duplicate must be analyzed at the same dilution as the unspiked sample, even if the matrix spike compounds will be diluted out.

9.7. Nonconformance and Corrective Action

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

9.8. Quality Assurance Summaries

Certain clients may require specific project or program QC which may supersede these method requirements. Quality Assurance Summaries should be developed to address these requirements.

9.9. STL QC Program

Further details of QC and corrective action guidelines are presented in the STL QC Program document (QA-003). Refer to this document if in doubt regarding corrective actions.

10. CALIBRATION AND STANDARDIZATION

10.1. Summary

10.1.1. Prior to the analysis of samples and blanks, each GC/MS system must be tuned and calibrated. Hardware tuning is checked through the analysis of the 4-Bromofluorobenzene (BFB) to establish that a given GC/MS system meets the standard mass spectral abundance criteria. The

GC/MS system must be calibrated initially at a minimum of five concentrations (analyzed under the same BFB tune), to determine the linearity of the response utilizing target calibration standards. Once the system has been calibrated, the calibration must be verified each twelve hour time period for each GC/MS system.

10.2.1. General

Electron Energy:	70 volts (nominal)
Mass Range:	35–300 AMU
Scan Time:	to give at least 5 scans/peak, but not to exceed 2 second/scan
Injector Temperature:	200–250°C
Source Temperature:	According to manufacturer's specifications
Transfer Line	Temperature: 250–300°C
Purge Flow:	40 mL/minute
Carrier Gas	Flow: 15 mL/minute
Make-up Gas Flow:	25–30 mL/minute

10.2.2. Gas chromatograph suggested temperature program

10.2.2.1. BFB Analysis

Isothermal:	170°C

10.2.2.2. Sample Analysis

Initial Temperature:	40°C
Initial Hold Time:	4 minutes
Temperature Program:	8°C/minute
Final Temperature:	184°C
Second Temperature	Program: 40°C/minute
Final Temperature:	240°C
Final Hold Time:	2.6 minutes

10.3. Instrument Tuning

10.3.1. Each GC/MS system must be hardware-tuned to meet the abundance criteria listed in Table 10 for a maximum of a 50 ng injection or purging of BFB. Analysis must not begin until these criteria are met. These criteria must be met for each twelve-hour time period. The twelve-hour time period begins at the moment of injection of BFB.

10.4. Initial Calibration

10.4.1. A series of five initial calibration standards is prepared and analyzed for the target compounds and each surrogate compound. Six standards must be used for a quadratic least squares calibration. Suggested calibration levels for a 5 mL purge are: 5, 20, 50, 100, and 200 µg/L. Certain analytes are prepared at higher concentrations due to poor purge performance. Suggested calibration levels for a 25 mL purge are 1, 5, 10, 20, and 40 µg/L. Again, some analytes are prepared at higher levels. Tables 2 and 4 list the calibration levels for each analyte. Other calibration levels and purge volumes may be used depending on the capabilities of the specific instrument. (For example, adequate sensitivity can be obtained on the Agilent 5973 instruments to use a 5 mL purge volume to reach the same reporting limits that once required a 25 mL purge. The calibration levels will still be the same 1, 5, 10, 20, 40µg/L.) However, the same purge volume must be used for calibration and sample analysis, and the low level standard must be at or below the reporting limit.

10.4.2. It may be necessary to analyze more than one set of calibration standards to encompass all of the analytes required for same tests. For example, the Appendix IX list requires the Primary standard (Table 5) and the Appendix IX standard (Table 6). If acceptable analytical performance can be obtained the primary and appendix IX standards may be analyzed together.

10.4.3. Internal standard calibration is used. The internal standards are listed in Table 7. Target compounds should reference the nearest internal standard. Each calibration standard is analyzed and the response factor (RF) for each compound is calculated using the area response of the characteristic ions against the concentration for each compound and internal standard. See equation 1, Section 12, for calculation of response factor.

10.4.4. The % RSD of the calibration check compounds (CCC) must be less than 30%. Refer to Table 12 for the CCCs.

10.4.4.1. If none of the CCCs are required analytes, project specific calibration specifications must be agreed with the client.

10.4.5. The average RF must be calculated for each compound. A system performance check is made prior to using the calibration curve. The five system performance check compounds (SPCC) are checked for a minimum average response factor. Refer to Table 11 for the SPCC compounds and required minimum response factors.

10.4.6. If the average of all the %RSDs in the calibration is $\leq$ 15%, then all analytes may use average response factor for calibration.

10.4.6.1. If the software in use is capable of routinely reporting curve coefficients for data validation purposes, and the necessary calibration reports can be generated, then the analyst should evaluate analytes with %RSD > 15% for calibration on a curve. If it appears that substantially better accuracy would be obtained using quantitation from a curve then the appropriate curve should be used for quantitation. If Relative Standard Error (RSE) is used to evaluate the curve it must be better than 15%. Otherwise the correlation coefficient (coefficient of determination for non-linear curves) must be $\geq$ 0.990.

10.4.6.2. If the average of all the %RSDs in the calibration is > 15% then calibration on a curve must be used for all analytes with %RSD > 15%. 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 $\geq$ 0.990. If the correlation coefficient is < 0.990, then any hit for these compounds must be flagged as estimated.

10.4.6.3. Refer to Section 17.5 for specific Ohio VAP criteria.

10.4.7. Weighting of data points

In a linear or quadratic calibration fit, the points at the lower end of the calibration curve have less weight in determining the curve generated than points at the high concentration end of the curve. However, in environmental analysis, accuracy at the low end of the curve is very important. For this reason it is preferable to increase the weighting of the lower concentration points. 1/Concentration^2 weighting (often called 1/X^2 weighting) will improve accuracy at the low end of the curve and should be used if the data system has this capability.

10.4.8. If time remains in the 12-hour period initiated by the BFB injection before the initial calibration, samples may be analyzed. Otherwise, proceed to continuing calibration.

10.4.9. The calibration standards for the initial 5-point calibration for low level soils that are not preserved in sodium bisulfate (i.e. are preserved by freezing, or not preserved) must be heated to 40°C for purging. Using this calibration curve for water samples is acceptable as long as all calibration, QC, and samples are also heated to 40°C. A separate five point calibration must be prepared for analysis of low level soils that are preserved with sodium bisulfate. Low level soils analysis requires the use of a closed vial autosampler such as the Varian Archon, O.I. 4552 or Tekmar Precept. Each standard for analysis of sodium

bisulfate preserved samples is prepared by spiking the methanolic standard solution through the septum of a VOA vial containing 5 mL of water and 1 g sodium bisulfate. The standards are heated to 40°C for purging. All low-level soil samples, standards, and blanks must also be heated to 40°C for purging. Medium soil extracts should be analyzed using the water (unheated or optionally heated) calibration curve as long as all calibration standards, samples, and QC samples are purged at the same temperature.

10.4.10. Non-standard analytes are sometimes requested. For these analytes, it is acceptable to analyze a single standard at the reporting limit with each continuing calibration rather than a five point initial calibration. If the analyte is detected in any of the samples, a five point initial calibration must be generated and the sample(s) reanalyzed for quantitation. However, if the analyte is not detected, the non-detect may be reported and no further action is necessary.

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

10.5. Continuing Calibration: The initial calibration must be verified every twelve hours.

10.5.1. Continuing calibration begins with analysis of BFB as described in Section 10.3. If the system tune is acceptable, the continuing calibration standard(s) are analyzed. The level 3 calibration standard is used as the continuing calibration.

10.5.2. The RF data from the standards are compared with the average RF from the initial five-point calibration to determine the percent drift of the CCC compounds. The calculation is given in equation 4, Section 12.3.4.

10.5.3. The % drift of the CCCs must be $\leq$ 20% for the continuing calibration to be valid. The SPCCs are also monitored. The SPCCs must meet the criteria described in Table 11. In addition, the % drift of all analytes must be $\leq$ 50% with allowance for up to six target analytes to have % drift > 50%.

10.5.3.1. If none of the CCCs are required analytes, project specific calibration specifications must be agreed with the client.

10.5.3.2. Cyclohexanone, one of the components of the Appendix IX standard, is unstable in the calibration solution, forming 1,1-dimethoxycyclohexane. No calibration criteria are applied to cyclohexanone and quantitation is tentative. Cyclohexanone is included on the Universal Treatment Standard and FO-39 regulatory lists (but not on Appendix IX).

10.5.3.3. Refer to Table 12 for specific Ohio VAP analytes.

10.5.4. If the CCCs and or the SPCCs do not meet the criteria in Sections 10.5.3 and 10.5.4, the system must be evaluated and corrective action must be taken. The BFB tune and continuing calibration must be acceptable before analysis begins. Extensive corrective action such as a different type of column will require a new initial calibration.

10.5.5. Once the above criteria have been met, sample analysis may begin. **Initial calibration average RFs (or the calibration curve) will be used for sample quantitation, not the continuing calibration RFs.** Analysis may proceed until 12 hours from the injection of the BFB have passed. (A sample *desorbed* less than or equal to 12 hours after the BFB is acceptable.)

11. PROCEDURE

11.1. Procedural Variations

11.1.1. One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation shall be completely documented using a Nonconformance Memo and approved by a Supervisor or group leader and QA Manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file.

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

11.2. Preliminary Evaluation

11.2.1. Where possible, samples are screened by headspace or GC/MS off-tune analysis to determine the correct aliquot for analysis. Alternatively, an appropriate aliquot can be determined from sample histories.

11.2.2. Dilutions should be done just prior to the GC/MS analysis of the sample. Dilutions are made in volumetric flasks or in a Luerlok syringe. Calculate the volume of reagent water required for the dilution. Fill the syringe with reagent water, compress the water to vent any residual air and adjust the water volume to the desired amount. Adjust the plunger to the mark and inject the proper aliquot of sample into the syringe. If the dilution required would use less than 1 µL of sample then serial dilutions must be made in volumetric flasks.

11.2.2.1. The diluted concentration is to be estimated to be in the upper half of the calibration range.

11.3. Sample Analysis Procedure

11.3.1. All analysis conditions for samples must be the same as for the continuing calibration standards (including purge time and flow, desorb time and temperature, column temperatures, multiplier setting etc.).

11.3.2. All samples must be analyzed as part of a batch. The batch is a set of up to 20 samples of the same matrix processed using the same procedures and reagents within the same time period. The batch also must contain a MS/MSD, a LCS, and a method blank.

11.3.2.1. If there is insufficient time in the 12-hour tune period to analyze 20 samples, the batch may be continued into the next tune period. However, if any re-tuning of the instrument is necessary, or if a period of greater than 24 hours from the preceding BFB tune has passed, a new batch must be started. For medium level soils the batch is defined at the sample preparation stage.

11.3.2.2. Laboratory generated QC samples (Blank, LCS, MS/MSD) do not count towards the maximum 20 samples in a batch. Field QC samples are included in the batch count.

11.3.2.3. It is not necessary to reanalyze batch QC with reanalyses of samples. However, any reruns must be as part of a valid batch.

11.4. Water Samples

11.4.1. All samples and standard solutions must be at ambient temperature before analysis.

11.4.2. Fill a syringe with the sample. If a dilution is necessary it may be made in the syringe if the sample aliquot is $\geq$ 5 µL. Check and document the pH of the remaining sample.

11.4.3. Add 250 ng of each internal and surrogate standard (10 µL of a 25 µg/mL solution, refer to Tables 7, 8 and 16). The internal standards and the surrogate standards may be mixed and added as one spiking solution (this results in a 50 µg/L solution for a 5 mL sample, and a 10 µg/L solution for a 25 mL sample). Inject the sample into the purging chamber.

11.4.3.1. For TCLP samples use 0.5 mL of TCLP leachate with 4.5 mL reagent water and spike with 10 µL of the 25 µg/mL TCLP spiking solution. (Note that TCLP reporting limits will be 10 times higher than the corresponding aqueous limits).

11.4.4. Purge the sample for eleven minutes (the trap must be below 35°C).

11.4.5. After purging is complete, desorb the sample, start the GC temperature program, and begin data acquisition. After desorption, bake the trap for approximately 3-10 minutes to condition it for the next analysis. When the trap is cool, it is ready for the next sample.

11.4.6. Desorb and bake time and temperature are optimized for the type of trap in use. The same conditions must be used for samples and standards.

11.5. Methanol Extract Soils

11.5.1. Rinse a gas-tight syringe with organic free water. Fill the syringe with the same volume of organic free water as used in the calibrations. Add no more than 2% (v/v) (100 µL for a 5 mL purge) methanolic extract (from Section 8.5 or 8.6) to the syringe. Add internal standard (if used). Load the sample onto the purge and trap device and analyze as for aqueous samples. If less than 5µL of methanolic extract is to be added to the water, dilute the methanolic extract such that a volume greater than 5µL will be added to the water in the syringe. Refer to Section 17.8 for Michigan project requirements.

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

11.6.1. Pipet 2 mL of the sample into a tared vial. Use a top-loading balance. Record the weight to the nearest 0.1 gram.

11.6.2. Quickly add 7 mL of methanol, then add 1 mL of surrogate spiking solution to bring the final volume to 10 mL. Cap the vial and shake for 2 minutes to mix thoroughly. For a MS/MSD or LCS, 6 mL of methanol, 1 mL of surrogate solution, and 1 mL of matrix spike solution is used.

11.6.3. Rinse a gas-tight syringe with organic free water. Fill the syringe with the same volume of organic free water as used in the calibrations. Add no more than 2% (v/v) (100 µL for a 5 mL purge) methanolic extract (from Section 8.5 or 8.6) to the syringe. Add internal standard (if used). Load the sample onto the purge and trap device and analyze as for aqueous samples. If less than 5µL of methanolic extract is to be added to the water, dilute the methanolic extract such that a volume greater than 5µL will be added to the water in the syringe.

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

11.7.1. Units which sample from the VOA vial should be equipped with a module which automatically adds surrogate and internal standard solution to the sample prior to purging the sample.

11.7.2. If the autosampler uses automatic IS/SS injection, no further preparation of the VOA vial is needed. Otherwise the internal and surrogate standards must be added to the vial. *Note:* Aqueous samples with high amounts of sediment present in the vial may not be suitable for analysis on this instrumentation, or they may need to analyzed as soils.

11.7.3. Soil samples must be quantitated against a curve prepared with standards containing about the same amount of sodium bisulfate as the samples (1 g in 5 mL).

11.7.4. Sample remaining in the vial after sampling with one of these mechanisms is no longer valid for further analysis. A fresh VOA vial must be used for further sample analysis.

11.7.5. For aqueous samples, check the pH of the sample remaining in the VOA vial after analysis is completed.

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

Note: This technique may seriously underestimate analyte concentration and must not be used except at specific client request for the purpose of comparability with previous data. It is no longer part of SW-846.

This method is based on purging a heated soil/sediment sample mixed with reagent water containing the surrogates and internal standards. Analyze all reagent blanks and standards under the same conditions as the samples (e.g., heated). The calibration curve is also heated during analysis. Purge temperature is 40°C.

11.8.1. Do not discard any supernatant liquids. Mix the contents of the container with a narrow metal spatula.

11.8.2. Weigh out 5 g (or other appropriate aliquot) of sample into a disposable culture tube or other purge vessel. Record the weight to the nearest 0.1 g. If method sensitivity is demonstrated, a smaller aliquot may be used. Do not use aliquots less than 1.0 g. If the sample is contaminated with analytes such that a purge amount less than 1.0 g is appropriate, use the medium level method. For the medium level method, add 4g soil to 10 mL methanol containing the surrogates, mix for two minutes, allow to settle then remove a portion of the methanol and store in a clean Teflon capped vial at 4°C until analysis. Analyze as described in section 11.5.

11.8.3. Connect the purge vessel to the purge and trap device.

11.8.4. Rinse a 5 mL gas-tight syringe with organic free water, and fill. Compress to 5 mL. Add surrogate/internal standard (and matrix spike solutions if required.). Add directly to the sample from 11.5.2.

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

11.8.6. Add the heater jacket or other heating device and start the purge and trap unit.

11.8.7. Soil samples that have low IS recovery when analyzed (<50%) should be reanalyzed once to confirm matrix effect.

11.9. Medium-Level Soil/Sediment and Waste Samples

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

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

11.9.5.1.1. Gently mix the contents of the sample container with a narrow metal or wood spatula. Weigh 4 g (wet weight) into a tared vial. Use a top-loading balance. Record the weight to 0.1 gram. Do not discard any supernatant liquids.

11.9.5.1.2. Quickly add 9 mL of methanol, and 1 mL of surrogate spiking solution to bring the final volume of methanol to 10 mL. For an LCS or MS/MSD sample add 8 mL of methanol, 1 mL of surrogate spike solution, and 1 mL of matrix spike solution. Cap the vial and vortex to mix thoroughly.

NOTE: Sections 11.9.5.1.1 and 11.9.5.1.2 must be performed rapidly and without interruption to avoid the loss of volatile organics.

11.10. Initial review and corrective actions

11.10.1. If the retention time for any internal standard in the continuing calibration changes by more than 0.5 minutes from the mid-level initial calibration standard, the chromatographic system must be inspected for malfunctions and corrected. Reanalysis of samples analyzed while the system was malfunctioning is required.

11.10.2. If the internal standard response in the continuing calibration is more than 200% or less than 50% of the response in the mid-level of the initial calibration standard, the chromatographic system must be inspected for malfunctions and corrected. Reanalysis of samples analyzed while the system was malfunctioning is required.

11.10.2.1. Any samples that do not meet the internal standard criteria for the continuing calibration must be evaluated for validity. If the change in sensitivity is a matrix effect confined to an individual sample reanalysis is not necessary. If the change in sensitivity is

due to instrumental problems all affected samples must be reanalyzed after the problem is corrected.

11.10.3. The surrogate standard recoveries are evaluated to ensure that they are within limits. Corrective action for surrogates out of control will normally be to reanalyze the affected samples. However, if the surrogate standard response is out high and there are no target analytes or tentatively identified compounds, reanalysis may not be necessary. Out of control surrogate standard response may be a matrix effect. It is only necessary to reanalyze a sample once to demonstrate matrix effect, but reanalysis at a dilution should be considered.

11.11. Dilutions

If the response for any compound exceeds the working range of the GC/MS system, a dilution of the extract is prepared and analyzed. An appropriate dilution should be in the upper half of the calibration range. Samples may be screened to determine the appropriate dilution for the initial run. If the initial diluted run has no hits or hits below 20% of the calibration range and the matrix allows for analysis at a lesser dilution, then the sample must be reanalyzed at a dilution targeted to bring the largest hit above 50% of the calibration range.

11.10.1. Guidance for Dilutions Due to Matrix

If the sample is initially run at a dilution and the baseline rise is less than half the height of the internal standards, or if individual non target peaks are less than twice the height of the internal standards, then the sample should be reanalyzed at a more concentrated dilution. This requirement is approximate and subject to analyst judgement.

11.10.2. Reporting Dilutions

The most concentrated dilution with no target compounds above the calibration range will be reported. Other dilutions will only be reported at client request.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Qualitative identification

An analyte is identified by retention time and by comparison of the sample mass spectrum with the mass spectrum of a standard of the suspected compound (standard reference spectrum). Mass spectra for standard reference may be obtained on the user's GC/MS by analysis of the calibration standards or from the NIST Library. Two criteria must be satisfied to verify identification: (1) elution of sample component at the same GC retention time as the standard component; and (2) correspondence of the sample component and the standard component

characteristic ions. (Note: Care must be taken to ensure that spectral distortion due to co-elution is evaluated.)

- The sample component retention time must compare to within ± 0.2 min. of the retention time of the standard component. For reference, the standard must be run within the same twelve hours as the sample.

- All ions present in the standard mass spectra at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100%) should be present in the sample spectrum.

- The relative intensities of ions should agree to within ±30% between the standard and sample spectra. (Example: For an ion with an abundance of 50% in the standard spectra, the corresponding sample abundance must be between 20 and 80 percent.)

12.1.1. If a compound cannot be verified by all the above criteria, but in the technical judgment of the analyst, the identification is correct, then the analyst shall report that identification and proceed with quantitation.

12.2. Tentatively Identified Compounds (TICs)

12.2.1. If the client requests components not associated with the calibration standards, a search of the NIST library may be made for the purpose of tentative identification. Guidelines are:

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

12.2.1.2. The relative intensities of the major ions should agree to within 20%. (Example: If an ion shows an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30% and 70%).

12.2.1.3. Molecular ions present in the reference spectrum should be present in the sample spectrum.

12.2.1.4. Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.

12.2.1.5. Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the spectrum because of background contamination or coeluting peaks. (Data system reduction programs can sometimes create these discrepancies.)

12.2.1.6. Computer-generated library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other. Only after visual inspection of the sample with the nearest library searches should the analyst assign a tentative identification.

12.3. Calculations.

12.3.1. Response factor (RF):

Equation 1

$$RF = \frac{A_x C_{is}}{A_{is} C_x}$$

Where:

A_x = Area of the characteristic ion for the compound to be measured

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

C_{is} = Concentration of the specific internal standard, ng

C_x = Concentration of the compound being measured, ng

12.3.2. Standard deviation (SD):

Equation 2

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

X_i = Value of X at i through N

N = Number of points

X = Average value of X_i

12.3.3. Percent relative standard deviation (%RSD):

Equation 3

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

$\overline{RF_i}$ = Mean of RF values in the curve

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

Equation 4

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

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:

$\mathbf{A_x}$ = Area of characteristic ion for the compound being measured (secondary ion quantitation is allowed only when there are sample interferences with the primary ion)

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

$\mathbf{I_s}$ = Amount of internal standard added in ng

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

$\mathbf{V_o}$ = Volume of water purged, mL

12.3.5.5. Calculation of x for Medium level soils:

Equation 9

$$x = \frac{(A_x)(I_s)(V_t)(1000)(D_f)}{(A_{is})(V_a)(W_s)(D)}$$

Where:

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

$\mathbf{V_t}$ = Volume of total extract, mL (Typically 25 mL)

$\mathbf{V_a}$ = Volume of extract added for purging, µL

$\mathbf{W_s}$ = Weight of sample extracted, g

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

12.3.5.6. Calculation of x for Low level soils:

Equation 10

$$x = \frac{(A_x)(I_s)}{(A_{is})(W_s)(D)}$$

Where:

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

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

Where:

RPD = Relative percent difference

MSR = Matrix spike result

MSDR = Matrix spike duplicate result

13. METHOD PERFORMANCE

13.1. Method Detection Limit

13.2. Generally, each laboratory must generate a valid method detection limit for each analyte of interest. The MDL must be below the reporting limit for each analyte. The procedure for determination of the method detection limit is given in 40 CFR Part 136, Appendix B, and further defined in QA Policy #: QA-005. When non-standard compounds are analyzed at client request, lesser requirements are possible with client agreement. At a minimum, a standard at the reporting limit must be analyzed to demonstrate the capability of the method.

13.3. Initial Demonstration

13.4. Each laboratory must make a one time initial demonstration of capability for each individual method. Demonstration of capability for both soil and water matrices is required. This requires analysis of QC check samples containing all of the standard analytes for the method. For some tests it may be necessary to use more than one QC check mix to cover all analytes of interest. The QC check sample is made up at 20 µg/L. (Some compounds will be at higher levels, refer to the calibration standard levels for guidance.)

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

13.4.2. Calculate the average recovery and standard deviation of the recovery for each analyte of interest. The %RSD should be $\leq$ 15% for each analyte, and the % recovery should be within 80-120%.

13.4.3. If any analyte does not meet the acceptance criteria, check the acceptance limits in the reference methods (Table 6 of method 8240B, paragraph 8.3.5 of method 8260A). If the recovery or precision is outside the limits in the reference methods, the test must be repeated. Only those analytes that did not meet criteria in the first test need to be evaluated. Repeated failure for any analyte indicates the need for the laboratory to evaluate the analytical procedure and take corrective action.

13.4.4. Training Qualification

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

14. POLLUTION PREVENTION

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

15. WASTE MANAGEMENT

15.1. Waste generated in the procedure must be segregated and disposed according to the facility hazardous waste procedures. The Health and Safety Director should be contacted if additional information is required.

16. REFERENCES

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

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

17. MISCELLANEOUS

17.1. Modifications from the reference method

17.1.1. Ion 119 is used as the quantitation ion for chlorobenzene-d5 for 25 mL purge tests.

17.1.2. A retention time window of 0.2 minutes is used for all components, since some data systems do not have the capability of using the relative retention time units specified in the reference method.

17.1.3. The quantitation and qualifier ions for some compounds have been changed from those recommended in SW-846 in order to improve the reliability of qualitative identification.

17.1.4. Method 8260A recommends that the purge vessel is run through an additional purge cycle after 25 mL sample analysis to remove carryover. Instead, purge vessels are oven baked between analyses or disposable vessels are used one time only.

17.1.5. SW-846 recommends that a curve be used for any analytes with %RSD of the response factors > 15%. However, some industry standard data systems and forms generation software cannot report this data with the necessary information for data validation. In

addition most software available does not allow weighting of the curve. Unweighted curves may exhibit serious errors in quantitation at the low end, resulting in possible false positives or false negatives. Therefore, this SOP allows used of average response factors if the average %RSD for all compounds is $\leq$ 15%.

17.2. Modifications from previous revision

This SOP has been substantially revised to reflect the changes included in Update III to SW-846. Directions for method 524.2 and method 624 have also been added.

17.3. Facility specific SOPs

Each facility shall attach a list of facility-specific SOPs or approved attachments (if applicable) which are required to implement this SOP or which are used in conjunction with this SOP. If no facility specific SOPs or amendments are to be attached, a statement must be attached specifying that there are none.

17.4. Flow diagrams

17.4.1. Initial Demonstration and MDL

17.5. The following are protocols that must be followed when analyzing OhioVAP samples:

- Sections 9.5 and 9.6: n-Hexane must be spiked and reported for both the LCS and MS/MSD.
- Sections 10.4.6: All analytes must have a %RSDs $\leq$ 15%. Corrective action must be completed for any compounds failing the <15% requirement.
- Section 11.1 and 17.1.5 (Method deviations) are not to be performed.
- Section 11.9.2: For OhioVAP projects, the laboratory will reanalyze any sample where the internal standard fails and there is no evidence of matrix interference.

17.6. The following are protocols that must be followed when analyzing BP Oil – Lima Refinery RFI work plan.

- Section 8.1 STL will continue to follow the 14 day holding time specified in the Corporate SOP.
- Delete for this project Section 8.3 At specific client request, unpreserved soil samples may be accepted.

- Delete for this project Section 8.8.1 At specific client request unpreserved soils packed into glass jars or brass tubes may be accepted and subsampled in the lab. This is the old procedure based on method 5030A. It is no longer included and is likely to generate results that are biased low, possibly by more than an order of magnitude.

- Modify Section 8.5.8 For the purpose of this project, the soil/methanol mixture may be stored for two days prior to analysis.

- Modify Section 8.6.12 For the purpose of this project, the soil/methanol mixture may be stored for two days prior to analysis.

- Modify (per discussion with Region V representative) to Section 10.4.6.2 Compounds with %RSD >15% are to be calibrated using an alternate calibration technique (e.g. linear or quadratic calibration curve). For poor responders, the alternate calibration technique requirements may not be met either. This sentence is added for those cases.If the correlation coefficient is < 0.990, then any hit for these compounds must be flagged as estimated.

- Modify Section 10.4.2 It is necessary to analyze the Appendix IX standard separately from the primary standard due to the presence of xylene solvent in the Appendix IX standard. Alternatively, STL will purchase the Appendix IX standard in a solvent other than xylene.

- Modify Section 10.4.9 For this project, this section will be modified to comply with the requirement of adding methanol to the calibration standards so that those standards contain the same amount of methanol as the diluted soil extracts.

- Modify Table 6

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

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

- **Delete** from Section 10.4.7 In a linear *or quadratic* calibration fit, the points at the lower end of the calibration curve have less weight in determining the curve generated than points at the high concentration end of the curve.

- **Delete** from Section 12.3.5 Concentrations in the sample may be determined from linear *or second order (quadratic)* curve fitted to the initial calibration points, or from the average response factor of the initial calibration points.

- **Delete** from Section 12.3.5.1

- Calculation of concentration using Quadratic fit

Equation 13

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

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

- **Change** Section 9.3 The compounds included in the surrogate spiking solutions are listed in Tables 8 *and 9*.

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

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

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

17.8.3. Modify Section 8.5.6 and 8.6.10 (add 100 uL of 50 ug/mL spike solution for a nominal 25g sample).

17.8.4. Michigan reporting limits for methanol preserved soils are achieved by injecting 100 uL of the methanol extract in a 5 mL purge. The instrument is calibrated using the recommended calibration levels in water of 1 ug/L, 2 ug/L (if a quadratic calibration is to be used), 5 ug/L, 10 ug/L, 20 ug/L and 40 ug/L. Some analytes are prepared at higher concentrations.

17.8.5. Samples for Michigan projects frequently require calibration for 2-Methylnaphthalene. Recommended calibration levels for this compounds are 2 ug/L, 10 ug/L, 20 ug/L, 40 ug/L and 80 ug/L.

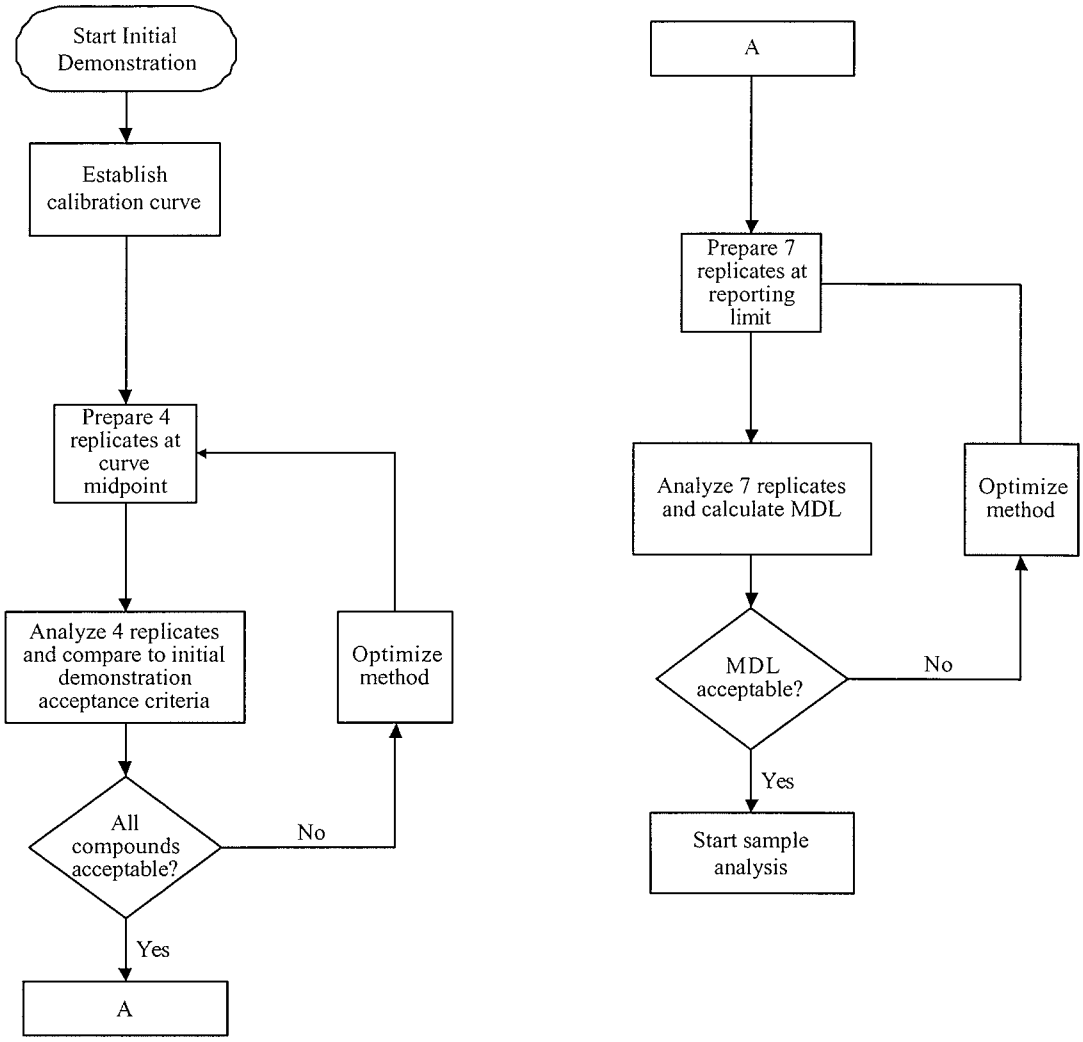

Start Initial Demonstration
Establish calibration curve
Prepare 4 replicates at curve midpoint
Analyze 4 replicates and compare to initial demonstration acceptance criteria
Optimize method
All compounds acceptable?
No
Yes
A
A
Prepare 7 replicates at reporting limit
Analyze 7 replicates and calculate MDL
Optimize method
MDL acceptable?
No
Yes
Start sample analysis

Table 1

STL Primary Standard and Reporting Limits

Compound	CAS Number	Reporting Limits[1]				
		5 mL Water µg/L	25 mL[3] water µg/L	Low soil µg/kg	8260B/ 5035 Soil ug/kg	8260A 5030A Med Level Soil µg/kg
Dichlorodifluoromethane	75-71-8	10	2	10	250	1200
Chloromethane	74-87-3	10	2	10	250	1200
Bromomethane	74-83-9	10	2	10	250	1200
Vinyl chloride	75-01-4	10	2	10	250	1200
Chloroethane	75-00-3	10	2	10	250	1200
Trichlorofluoromethane	75-69-4	10	2	10	250	1200
Acrolein	107-02-8	100	20	100	5000	12000
Acetone	67-64-1	20	10	20	1000	2500
Trichlorotrifluoroethane	76-13-1	5	1	5	250	620
Iodomethane	74-88-4	5	1	5	250	620
Carbon disulfide	75-15-0	5	1	5	250	620
Methylene chloride	75-09-2	5	1	5	250	620
tert-Butyl alcohol	75-65-0	200	50	200	10,000	25000
1,1-Dichloroethene	75-35-4	5	1	5	250	620
1,1-Dichloroethane	75-34-3	5	1	5	250	620
trans-1,2-Dichloroethene	156-60-5	5.0	1.0	5.0	250	310
Acrylonitrile	107-13-1	100	20	100	5000	12000
Methyl *tert*-butyl ether (MTBE)	1634-04-4	20	5	20	1000	2500
Hexane	110-54-3	5	1	5	250	620
cis-1,2-Dichloroethene	156-59-2	5.0	1.0	5.0	250	310
1,2-Dichloroethene (Total)	540-59-0	5	1	5	250	620
Tetrahydrofuran	109-99-9	20	5	20	1000	2500
Chloroform	67-66-3	5	1	5	250	620
1,2-Dichloroethane	107-06-2	5	1	5	250	620
Dibromomethane	74-95-3	5	1	5	250	620
2-Butanone	78-93-3	20	5	20	1000	2500
1,4-Dioxane	123-91-1	500	200	500	25000	62000
1,1,1-Trichloroethane	71-55-6	5	1	5	250	620
Carbon tetrachloride	56-23-5	5	1	5	250	620
Bromodichloromethane	75-27-4	5	1	5	250	620
1,2-Dichloropropane	78-87-5	5	1	5	250	620
cis-1,3-Dichloropropene	10061-01-5	5	1	5	250	620

Table 1

STL Primary Standard and Reporting Limits

Compound	CAS Number	Reporting Limits[1]				
		5 mL Water µg/L	25 mL[3] water µg/L	Low soil µg/kg	8260B/ 5035 Soil ug/kg	8260A 5030A Med Level Soil µg/kg
Trichloroethene	79-01-6	5	1	5	250	620
Dibromochloromethane	124-48-1	5	1	5	250	620
1,2-Dibromoethane	106-93-4	5	1	5	250	620
1,2,3-Trichloropropane	96-18-4	5	1	5	250	620
1,1,2-Trichloroethane	79-00-5	5	1	5	250	620
Benzene	71-43-2	5	1	5	250	620
Ethylmethacrylate	97-63-2	5	1	5	250	620
trans-1,3-Dichloropropene	10061-02-6	5	1	5	250	620
Bromoform	75-25-2	5	1	5	250	620
4-Methyl-2-pentanone	108-10-1	20	5	20	1000	2500
2-Hexanone	591-78-6	20	5	20	1000	2500
Tetrachloroethene	127-18-4	5	1	5	250	620
Toluene	108-88-3	5	1	5	250	620
1,1,2,2-Tetrachloroethane	79-34-5	5	1	5	250	620
2-Chloroethyl vinyl ether	110-75-8	N/A[2]	N/A	50	1000	6200
Vinyl acetate	108-05-4	10	2	10	500	1200
Chlorobenzene	108-90-7	5	1	5	250	620
Ethylbenzene	100-41-4	5	1	5	250	620
Styrene	100-42-5	5	1	5	250	620
t-1,4-Dichloro-2-butene	110-57-6	5	1	5	250	620
m and p Xylenes		5.0	0.5	2.5	125	310
o-xylene	95-47-6	5.0	0.5	2.5	125	310
Total xylenes	1330-20-7	5	1	5	250	620
1,3-Dichlorobenzene	541-73-1	5	1	5	250	620
1,4-Dichlorobenzene	106-46-7	5	1	5	250	620
1,2-Dichlorobenzene	95-50-1	5	1	5	250	620
2,2-Dichloropropane	590-20-7	5	1	5	250	
Bromochloromethane	74-97-5	5	1	5	250	
1,1-Dichloropropene	563-58-6	5	1	5	250	
Bromodichloromethane	75-27-4	5	1	5	250	
1,2-Dichloropropane	78-87-5	5	1	5	250	
1,3-Dichloropropane	142-28-9	5	1	5	250	

Table 1

STL Primary Standard and Reporting Limits

Compound	CAS Number	Reporting Limits[1]				
		5 mL Water µg/L	25 mL[3] water µg/L	Low soil µg/kg	8260B/ 5035 Soil ug/kg	8260A 5030A Med Level Soil µg/kg
Isopropylbenzene	98-82-8	5	1	5	250	
Bromobenzene	108-86-1	5	1	5	250	
n-Propylbenzene	103-65-1	5	1	5	250	
2-Chlorotoluene	95-49-8	5	1	5	250	
4-Chlorotoluene	106-43-4	5	1	5	250	
1,3,5-Trimethylbenzene	108-67-8	5	1	5	250	
tert-Butylbenzene	98-06-6	5	1	5	250	
1,2,4-Trimethylbenzene	95-63-6	5	1	5	250	
sec-butylbenzene	135-98-8	5	1	5	250	
4-Isopropyltoluene	99-87-6	5	1	5	250	
n-Butylbenzene	104-51-8	5	1	5	250	
1,2,4-Trichlorobenzene	120-82-1	5	1	5	250	
Napthalene	91-20-3	5	1	5	250	
Hexachlorobutadiene	87-68-3	5	1	5	250	
1,2,3-Trichlorobenzene	87-61-6	5	1	5	250	
Acetonitrile	75-05-8	100	20	100	5000	

[1] Reporting limits listed for soil/sediment are based on wet weight. The reporting limits calculated by the laboratory for soil/sediment, calculated on dry weight basis, will be higher.

[2] 2-Chloroethyl vinyl ether cannot be reliably recovered from acid preserved samples

[3] Optionally, 5 mL purge volume if adequate sensitivity is obtained.

Table 2

STL Primary Standard Calibration Levels, 5 mL purge[1]

Compound	Calibration Level ug/L				
	Level 1	Level 2	Level 3	Level 4	Level 5
1,2-Dichloroethane-d4 (Surrogate)	5	20	50	100	200
Toluene-d8 (Surrogate)	5	20	50	100	200
4-Bromofluorobenzene (Surrogate)	5	20	50	100	200
Dichlorodifluoromethane	5	20	50	100	200
Chloromethane	5	20	50	100	200
Bromomethane	5	20	50	100	200
Vinyl chloride	5	20	50	100	200
Chloroethane	5	20	50	100	200
Trichlorofluoromethane	5	20	50	100	200
Acrolein	50	200	500	1000	2000
Acetone	5	20	50	100	200
Trichlorotrifluoroethane	5	20	50	100	200
Iodomethane	5	20	50	100	200
Carbon disulfide	5	20	50	100	200
Methylene chloride	5	20	50	100	200
tert-Butyl alcohol	100	400	1,000	2,000	4,000
1,1-Dichloroethene	5	20	50	100	200
1,1-Dichloroethane	5	20	50	100	200
trans-1,2-Dichloroethene	5	20	50	100	200
Acrylonitrile	50	200	500	1,000	2,000
Methyl *tert*-butyl ether (MTBE)	5	20	50	100	200
Hexane	5	20	50	100	200
cis-1,2-Dichloroethene	5	20	50	100	200
Tetrahydrofuran	5	20	50	100	200
Chloroform	5	20	50	100	200
1,2-Dichloroethane	5	20	50	100	200
Dibromomethane	5	20	50	100	200
2-Butanone	5	20	50	100	200
1,4-Dioxane	250	1000	2,500	5,000	10,000
1,1,1-Trichloroethane	5	20	50	100	200
Carbon tetrachloride	5	20	50	100	200
Bromodichloromethane	5	20	50	100	200
1,2-Dichloropropane	5	20	50	100	200
cis-1,3-Dichloropropene	5	20	50	100	200
Trichloroethene	5	20	50	100	200
Dibromochloromethane	5	20	50	100	200

Table 2

STL Primary Standard Calibration Levels, 5 mL purge[1]

Compound	Calibration Level ug/L				
	Level 1	Level 2	Level 3	Level 4	Level 5
1,2-Dibromoethane	5	20	50	100	200
1,2,3-Trichloropropane	5	20	50	100	200
Acetonitrile	50	200	500	1000	2000
1,1,2-Trichloroethane	5	20	50	100	200
Benzene	5	20	50	100	200
Ethylmethacrylate	5	20	50	100	200
trans-1,3-Dichloropropene	5	20	50	100	200
Bromoform	5	20	50	100	200
4-Methyl-2-pentanone	5	20	50	100	200
2-Hexanone	5	20	50	100	200
Tetrachloroethene	5	20	50	100	200
Toluene	5	20	50	100	200
1,1,2,2-Tetrachloroethane	5	20	50	100	200
2-Chloroethyl vinyl ether	10	40	100	200	400
Vinyl acetate	5	20	50	100	200
Chlorobenzene	5	20	50	100	200
Ethylbenzene	5	20	50	100	200
Styrene	5	20	50	100	200
t-1,4-Dichloro-2-butene	5	20	50	100	200
m and p Xylenes	10	40	100	200	400
o-xylene	5	20	50	100	200
1,3-Dichlorobenzene	5	20	50	100	200
1,4-Dichlorobenzene	5	20	50	100	200
1,2-Dichlorobenzene	5	20	50	100	200
2,2-Dichloropropane	5	20	50	100	200
Bromochloromethane	5	20	50	100	200
1,1-Dichloropropene	5	20	50	100	200
Bromodichloromethane	5	20	50	100	200
1,2-Dichloropropane	5	20	50	100	200
1,3-Dichloropropane	5	20	50	100	200
Isopropylbenzene	5	20	50	100	200
Bromobenzene	5	20	50	100	200
n-Propylbenzene	5	20	50	100	200
2-Chlorotoluene	5	20	50	100	200
4-Chlorotoluene	5	20	50	100	200
1,3,5-Trimethylbenzene	5	20	50	100	200
tert-Butylbenzene	5	20	50	100	200

Table 2

STL Primary Standard Calibration Levels, 5 mL purge[1]

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

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

Table 2A

STL Primary Standard Calibration Levels, Low Level [1]

Compound	Calibration Level ug/L				
	Level 1	Level 2	Level 3	Level 4	Level 5
Dibromofluoromethane (Surrogate)	1	5	10	20	40
1,2-Dichloroethane-d4 (Surrogate)	1	5	10	20	40
Toluene-d8 (Surrogate)	1	5	10	20	40
Bromofluorobenzene (Surrogate)	1	5	10	20	40
Dichlorodifluoromethane	1	5	10	20	40
Chloromethane	1	5	10	20	40
Vinyl Chloride	1	5	10	20	40
Bromomethane	1	5	10	20	40
Chloroethane	1	5	10	20	40
Trichlorofluoromethane	1	5	10	20	40
Acrolein	10	50	100	200	400
Acetone	2	10	20	40	80
1,1-Dichloroethene	1	5	10	20	40
Trichlorotrifluoroethane	1	5	10	20	40
Iodomethane	1	5	10	20	40
Carbon Disulfide	1	5	10	20	40
Methylene Chloride	1	5	10	20	40
Acetonitrile	10	50	100	200	400
Acrylonitrile	10	50	100	200	400
Methyl tert-butyl ether	1	5	10	20	40
trans-1,2-Dichloroethene	1	5	10	20	40
Hexane	1	5	10	20	40
Vinyl acetate	1	5	10	20	40
1,1-Dichloroethane	1	5	10	20	40
tert-Butyl Alcohol	20	100	200	400	800
2-Butanone	2	10	20	40	80
cis-1,2-dichloroethene	1	5	10	20	40
2,2-Dichloropropane	1	5	10	20	40
Bromochloromethane	1	5	10	20	40
Chloroform	1	5	10	20	40
Tetrahydrofuran	1	5	10	20	40
1,1,1-Trichloroethane	1	5	10	20	40
1,1-Dichloropropene	1	5	10	20	40
Carbon Tetrachloride	1	5	10	20	40
1,2-Dichloroethane	1	5	10	20	40
Benzene	1	5	10	20	40
Trichloroethene	1	5	10	20	40
1,2-Dichloropropane	1	5	10	20	40
1,4-Dioxane	50	250	500	1000	2000
Dibromomethane	1	5	10	20	40

Table 2A

STL Primary Standard Calibration Levels, Low Level [1]

Compound	Calibration Level ug/L				
	Level 1	Level 2	Level 3	Level 4	Level 5
Bromodichloromethane	1	5	10	20	40
2-Chloroethyl vinyl ether	2	10	20	40	80
cis-1,3-Dichloropropene	1	5	10	20	40
4-Methyl-2-pentanone	2	10	20	40	80
Toluene	1	5	10	20	40
trans-1,3-Dichloropropene	1	5	10	20	40
Ethyl Methacrylate	1	5	10	20	40
1,1,2-Trichloroethane	1	5	10	20	40
1,3-Dichloropropane	1	5	10	20	40
Tetrachloroethene	1	5	10	20	40
2-Hexanone	2	10	20	40	80
Dibromochloromethane	1	5	10	20	40
1,2-Dibromoethane	1	5	10	20	40
Chlorobenzene	1	5	10	20	40
1,1,1,2-Tetrachloroethane	1	5	10	20	40
Ethylbenzene	1	5	10	20	40
m + p-Xylene	2	10	20	40	80
Xylene-o	1	5	10	20	40
Styrene	1	5	10	20	40
Bromoform	1	5	10	20	40
Isopropylbenzene	1	5	10	20	40
1,1,2,2-Tetrachloroethane	1	5	10	20	40
1,4-Dichloro-2-butene	1	5	10	20	40
1,2,3-Trichloropropane	1	5	10	20	40
Bromobenzene	1	5	10	20	40
n-Propylbenzene	1	5	10	20	40
2-Chlorotoluene	1	5	10	20	40
1,3,5-Trimethylbenzene	1	5	10	20	40
4-Chlorotoluene	1	5	10	20	40
tert-Butylbenzene	1	5	10	20	40
1,2,4-Trimethylbenzene	1	5	10	20	40
sec-Butylbenzene	1	5	10	20	40
4-Isopropyltoluene	1	5	10	20	40
1,3-Dichlorobenzene	1	5	10	20	40
1,4-Dichlorobenzene	1	5	10	20	40
n-Butylbenzene	1	5	10	20	40
1,2-Dichlorobenzene	1	5	10	20	40
1,2-Dibromo-3-chloropropane	1	5	10	20	40

Table 2A

STL Primary Standard Calibration Levels, Low Level [1]

Compound	Calibration Level ug/L				
	Level 1	Level 2	Level 3	Level 4	Level 5
1,2,4-Trichlorobenzene	1	5	10	20	40
Hexachlorobutadiene	1	5	10	20	40
Naphthalene	1	5	10	20	40
1,2,3-Trichlorobenzene	1	5	10	20	40
Cyclohexane	1	5	10	20	40
Methyl Acetate	2	10	20	40	80
Methylcyclohexane	1	5	10	20	40
1,3,5-Trichlorobenzene	1	5	10	20	40

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

Table 3

STL Appendix IX Standard and Reporting Limits, 5 mL purge

Compound	CAS Number	Reporting Limits			
		5 mL Water µg/L	25mL[2] water µg/L	Low Soil µg/kg	Medium Soil µg/mL
Allyl Chloride	107-05-1	10	2	10	500
Acetonitrile	75-05-8	100	20	100	5000
Dichlorofluoromethane		10	2	10	500
Isopropyl ether	108-20-3	10	2	10	500
Chloroprene	126-99-8	5	2	5	250
n-Butanol	71-36-3	200	50	200	10,000
Propionitrile	107-12-0	20	4	20	1000
Methacrylonitrile	126-98-7	5	2	5	250
Isobutanol	78-83-1	200	50	200	10,000
Methyl methacrylate	80-62-6	5	2	5	250
1,1,1,2-Tetrachloroethane	630-20-6	5	1	5	250
1,2-Dibromo-3-chloropropane	96-12-8	10	2	10	500
Ethyl ether	60-29-7	10	2	10	500
Ethyl Acetate	141-78-6	20	4	20	1,000
2-Nitropropane	79-46-9	10	4	10	500
Cyclohexanone	108-94-1	N/A[1]	N/A[1]	N/A[1]	N/A[1]
Isopropylbenzene	98-82-8	5	1	5	250
2-Methylnaphthalene (Michigan only)	91-57-6	NA	5	NA	330

[1] Cyclohexanone decomposes to 1,1-dimethoxycyclohexane in methanolic solution. Reporting limits cannot be accurately determined.

[2] Optionally, 5 mL purge volume if adequate sensitivity is obtained.

Table 4

Recommended/STL Appendix IX Standard Calibration Levels, µg/L

Compound	Level 1	Level 2	Level 3	Level 4	Level 5
Allyl Chloride	5	20	50	100	200
Acetonitrile	50	200	500	1,000	2,000
Dichlorofluoromethane	5	20	50	100	200
Isopropyl ether	5	20	50	100	200
Chloroprene	5	20	50	100	200
n-Butanol	100	400	1,000	2,000	4,000
Propionitrile	10	40	100	200	400
Methacrylonitrile	5	20	50	100	200
Isobutanol	100	400	1,000	2,000	4,000
Methyl methacrylate	5	20	50	100	200
1,1,1,2-Tetrachloroethane	5	20	50	100	200
1,2-Dibromo-3-chloropropane	10	40	100	200	400
Ethyl ether	5	20	50	100	200
Ethyl Acetate	10	40	100	200	400
2-Nitropropane	10	40	100	200	400
Cyclohexanone	50	200	500	1,000	2,000
2-Methylnaphthalene (Michigan only)	2	10	20	40	80

Table 5

Reportable Analytes for STL Standard Tests, Primary Standard

Compound	CAS Number	STL Standard List	TCLP	TCL	Appendix IX	UTS
Dichlorodifluoromethane	75-71-8				X	X
Chloromethane	74-87-3	X		X	X	X
Bromomethane	74-83-9	X		X	X	X
Vinyl chloride	75-01-4	X	X	X	X	X
Chloroethane	75-00-3	X		X	X	X
Trichlorofluoromethane	75-69-4				X	X
Acrolein	107-02-8				X	X
Acetone	67-64-1	X		X	X	X
Trichlorotrifluoroethane	76-13-1					X
Ethanol	64-17-5					
Iodomethane	74-88-4				X	X
Carbon disulfide	75-15-0	X		X	X	X
Methylene chloride	75-09-2	X		X	X	X
tert-Butly alcohol	75-65-0					
1,1-Dichloroethene	75-35-4	X	X	X	X	X
1,1-Dichloroethane	75-34-3	X		X	X	X
trans-1,2-Dichloroethene	156-60-5	X		X	X	X
Total dichloroethene		X		X	X	X
Acrylonitrile	107-13-1				X	X
Methyl *tert*-butyl ether (MTBE)	1634-04-4					
Hexane	110-54-3					
cis-1,2-Dichloroethene	156-59-2	X		X		
Tetrahydrofuran	109-99-9					
Chloroform	67-66-3	X	X	X	X	X
1,2-Dichloroethane	107-06-2	X	X	X	X	X
Dibromomethane	74-95-3				X	X
2-Butanone	78-93-3	X	X	X	X	X
1,4-Dioxane	123-91-1				X	X
1,1,1-Trichloroethane	71-55-6	X		X	X	X
Carbon tetrachloride	56-23-5	X	X	X	X	X
Bromodichloromethane	75-27-4	X		X	X	X
1,2-Dichloropropane	78-87-5	X		X	X	X
cis-1,3-Dichloropropene	10061-01-5	X		X	X	X
Trichloroethene	79-01-6	X	X	X	X	X

Table 5

Reportable Analytes for STL Standard Tests, Primary Standard

Compound	CAS Number	STL Standard List	TCLP	TCL	Appendix IX	UTS
Dibromochloromethane	124-48-1	X		X	X	X
1,2-Dibromoethane	106-93-4				X	X
1,2,3-Trichloropropane	96-18-4				X	X
1,1,2-Trichloroethane	79-00-5	X		X	X	X
Benzene	71-43-2	X	X	X	X	X
Ethylmethacrylate	97-63-2				X	X
trans-1,3-Dichloropropene	10061-02-6	X		X	X	X
Bromoform	75-25-2	X		X	X	X
4-Methyl-2-pentanone	108-10-1	X		X	X	X
2-Hexanone	591-78-6	X		X	X	
Tetrachloroethene	127-18-4	X	X	X	X	X
Toluene	108-88-3	X		X	X	X
1,1,2,2-Tetrachloroethane	79-34-5	X		X	X	X
2-Chloroethyl vinyl ether	110-75-8					
Vinyl acetate	108-05-4				X	
Chlorobenzene	108-90-7	X	X	X	X	X
Ethylbenzene	100-41-4	X		X	X	X
Styrene	100-42-5	X		X	X	
t-1,4-Dichloro-2-butene	110-57-6				X	
m and p Xylenes		X		X	X	X
o-xylene	95-47-6	X		X	X	X
Total xylenes	1330-20-7	X		X	X	X
1,3-Dichlorobenzene	541-73-1					
1,4-Dichlorobenzene	106-46-7					
1,2-Dichlorobenzene	95-50-1					

Table 6

Reportable Analytes for STL Standard Tests, Appendix IX standard

Compound	Number	STL Standard List	TCLP	TCL	Appendix IX	UTS
Allyl Chloride	107-05-1				X	
Acetonitrile	75-05-8				X	X
Dichlorofluoromethane	75-43-4					
Isopropyl ether	108-20-3					
Chloroprene	126-99-8				X	
n-Butanol	71-36-3					
Propionitrile	107-12-0				X	
Methacrylonitrile	126-98-7				X	X
Isobutanol	78-83-1				X	X
Methyl methacrylate	80-62-6				X	X
1,1,1,2-Tetrachloroethane	630-20-6				X	X
1,2-Dibromo-3-chloropropane	96-12-8				X	X
Ethyl ether	60-29-7					X
Ethyl Acetate	141-78-6					X
2-Nitropropane	79-46-9					
Cyclohexanone	108-94-1					X
Isopropylbenzene	98-82-8					

Table 7

Internal Standards

	Standard Concentration µg/mL	Quantitation ion (5 mL purge)	Quantitation ion (25 mL purge)
Fluorobenzene	50	96	96
Chlorobenzene-d5	50	117	119
1,4-Dichlorobenzene-d4	50	152	152

Notes:

1) 5 µL of the internal standard is added to the sample. This results in a concentration of each internal in the sample of 50µg/L for a 5 mL purge or 10 µg/L for a 25 mL purge.

2) Except for medium level soils, the surrogate and internal standards may be combined in one solution.

Table 8

Surrogate Standards

Surrogate Compounds	Standard Concentration µg/mL
1,2-Dichloroethane-d_4	50
Dibromofluoromethane	50
Toluene-d_8	50
4-Bromofluorobenzene	50

Notes:

1) 5 µL of the surrogate standard is added to the sample. This results in a concentration of each surrogate in the sample of 50µg/L for a 5 mL purge or 10 µg/L for a 25 mL purge.

2) Except for medium level soils, the surrogate and internal standards may be combined in one solution.

3) Recovery limits for surrogates are generated from historical data and are maintained by the QA department.

Table 9

Matrix Spike / LCS Control Compounds

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

Notes:

1) 5 µL of the standard is added to the LCS or matrix spiked sample. This results in a concentration of each spike analyte in the sample of 50µg/L for a 5 mL purge or 10 µg/L for a 25 mL purge.

2) Recovery and precision limits for LCS and MS/MSD are generated 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

Table 13

Characteristic ions

Compound	Primary*	Secondary	Tertiary
1,1-Dichloroethene	96	61	98
Acrolein	56	55	58
Iodomethane	142	127	141
Carbon disulfide	76	78	
Trichlorotrifluoroethane	151	101	153
Ethanol	45	46	
Acetone	43	58	
Methylene chloride	84	49	51, 86
tert-Butyl alcohol	59	74	
trans-1,2-Dichloroethene	96	61	98
Acrylonitrile	53	52	51
Methyl *tert* butyl ether	73		
Hexane	57	43	
1,1-Dichloroethane	63	65	83
cis-1,2-Dichloroethene	96	61	98
2-Butanone	43	72**	
Tetrahydrofuran	42	71	
Chloroform	83	85	47
1,2-Dichloroethane	62	64	98
Dibromomethane	93	174	95, 172, 176
1,4-Dioxane	88	58	
Vinyl acetate	43	86	
1,1,1-Trichloroethane	97	99	117
Carbon tetrachloride	117	119	121
Benzene	78	52	77
Trichloroethene	130	95	97, 132
1,2-Dichloropropane	63	65	41
Bromodichloromethane	83	85	129
2-Chloroethyl vinyl ether	63	65	106
cis-1,3-Dichloropropene	75	77	39
trans-1,3-Dichloropropene	75	77	39
1,1,2-Trichloroethane	97	83	85, 99
Chlorodibromomethane	129	127	131
Bromoform	173	171	175, 252
1,2,3-Trichloropropane	75	110	77, 112, 97
Toluene-d_8 (Surrogate)	98	70	100
4-Bromofluorobenzene (Surrogate)	95	174	176
Toluene	91	92	65
4-Methyl-2-pentanone	43	58	57, 100

Table 13

Characteristic ions

Compound	Primary*	Secondary	Tertiary
Tetrachloroethene	164	166	131
Ethyl methacrylate	69	41	99, 86, 114
2-Hexanone	43	58	57, 100
Chlorobenzene	112	114	77
Ethylbenzene	106	91	
Xylenes	106	91	
Styrene	104	103	78, 51, 77
Dichlorobenzene (all isomers)	146	148	111
trans 1,4-Dichloro-2-butene	53	75	89, 77, 124
1,1,2,2-Tetrachloroethane	83	85	131, 133
Allyl Chloride	76	41	78
Acetonitrile	40	41	
Dichlorofluoromethane	67	69	
Isopropyl ether	87	59	45
Chloroprene	53	88	90
n-Butanol	56	41	42
Propionitrile	54	52	55
Methacrylonitrile	41	67	52
Isobutanol	41	43	74
Methyl methacrylate	41	69	100
1,1,1,2-Tetrachloroethane	131	133	119
1,2-Dibromo-3-chloropropane	157	155	75
Ethyl ether	59	74	
Ethyl Acetate	43	88	61
2-Nitropropane	41	43	46
Cyclohexanone	55	42	98
Isopropylbenzene	105	120	

* The primary ion should be used for quantitation unless interferences are present, in which case a secondary ion may be used.

** m/z 43 may be used for quantitation of 2-Butanone, but m/z 72 must be present for positive identification.

1. REQUIREMENTS FOR EPA 624

1.1. Method 624 is required for demonstration of compliance with NPDES wastewater discharge permits. This method can be applied only to aqueous matrices. The standard analyte list and reporting limits are listed in Table B-1.

1.2. The tune period for this method is defined as 24 hours.

1.3. The initial calibration curve for this method requires at least three points.

1.4. Sample concentrations are calculated using the average RRF from the initial calibration curve.

1.5. Each target analyte is assigned to the closest eluting internal standard.

1.6. Initial demonstration of Proficiency

1.6.1. The spiking level for the four replicate initial demonstration of proficiency is 20 µg/L. The acceptance criteria are listed in Table B-2

1.7. Initial calibration curve requirements:

1.7.1. Target compounds must have RSD ≤ 35%.

1.7.2. If this requirement can not be met, a regression curve must be constructed for the non-compliant compounds. There is no correlation coefficient requirement for the regression curve.

1.8. Continuing calibration verification requirements:

1.8.1. The continuing calibration standard is from a different source than the initial calibration standard. The acceptance criteria are listed in Table B-2.

1.9. Matrix Spike and LCS requirements

1.9.1. The matrix spike and LCS are spiked at 20 µg/L. A matrix spike duplicate is not necessary for this method. The recovery limits for matrix spike and LCS recovery are listed in Table C-2.

1.10. Method clarifications, modifications and additions

1.10.1. Section 5.2.2 of the source method describes the trap packing materials as Tenax GC, Methyl silicone, silica gel and coconut charcoal. STL routinely employs the Supelco VOCARB 3000, which consists of Carbopack B and Carboxen 1000 and 1001.

1.10.2. Section 5.3.2 of the source method describes a packed analytical column. STL routinely employs capillary columns when performing this method.

1.10.3. The source method provides a suggested list of compounds for internal and surrogate standards. STL uses the following two compounds which are not on the table: Chlorobenzene-d_5 (internal standard) and 1,2-Difluorobenzene-d_4 (surrogate).

Table A-1.

Method 624 Analytes and Reporting Limits

Analytes	µg/L
Benzene	5
Bromodichloromethane	5
Bromoform	5
Bromomethane	5
Carbon tetrachloride	5
Chlorobenzene	5
Chloroethane	5
2-Chloroethyl vinyl ether	5
Chloroform	5
Chloromethane	5
Dibromochloromethane	5
1,2-Dichlorobenzene	5
1,3-Dichlorobenzene	5
1,4-Dichlorobenzene	5
1,1-Dichloroethane	5
1,2-Dichloroethane	5
1,1-Dichloroethene	5
trans-1,2-Dichloroethene	5
1,2-Dichloropropane	5
cis-1,3-Dichloropropene	5
trans-1,3-Dichloropropene	5
Ethylbenzene	5
Methylene chloride	5
1,1,2,2-Tetrachloroethane	5
Tetrachloroethene	5
Toluene	5
1,1,1-Trichloroethane	5
1,1,2-Trichloroethane	5
Trichloroethene	5
Trichlorofluoromethane	5
Vinyl chloride	5

Table A-2.

Method 624 QC Acceptance Criteria

Analytes	Daily QC check acceptance criteria (20µg/L spike)	Mean recovery, 4 replicate initial demonstration acceptance criteria (20µg/L spike)	Standard deviation, 4 replicate initial demonstration acceptance criteria (20µg/L spike)	Matrix spike and LCS acceptance criteria (% recovery)
Benzene	12.8-27.2	15.2-26.0	6.9	37-151
Bromodichloromethane	13.1-26.9	10.1-28.0	6.4	35-155
Bromoform	14.2-25.8	11.4-31.1	5.4	45-169
Bromomethane	2.8-37.2	D-41.2	17.9	D-242
Carbon tetrachloride	14.6-25.4	17.2-23.5	5.2	70-140
Chlorobenzene	13.2-26.8	16.4-27.4	6.3	37-160
Chloroethane	7.6-32.4	8.4-40.4	11.4	14-230
2-Chloroethyl vinyl ether	D-44.8	D-50.4	25.9	D-305
Chloroform	13.5-26.5	13.7-24.2	6.1	51-138
Chloromethane	D-40.8	D-45.9	19.8	D-273
Dibromochloromethane	13.5-26.5	13.8-26.6	6.1	53-149
1,2-Dichlorobenzene	12.6-27.4	11.8-34.7	7.1	18-190
1,3-Dichlorobenzene	14.6-25.4	17.0-28.8	5.5	59-156
1,4-Dichlorobenzene	12.6-27.4	11.8-34.7	7.1	18-190
1,1-Dichloroethane	14.5-25.5	14.2-28.5	5.1	59-155
1,2-Dichloroethane	13.6-26.4	14.3-27.4	6.0	49-155
1,1-Dichloroethene	10.1-29.9	3.7-42.3	9.1	D-234
trans-1,2-Dichloroethene	13.9-26.1	13.6-28.5	5.7	54-156
1,2-Dichloropropane	6.8-33.2	3.8-36.2	13.8	D-210
cis-1,3-Dichloropropene	4.8-35.2	1.0-39.0	15.8	D-227
trans-1,3-Dichloropropene	10.0-30.0	7.6-32.4	10.4	17-183
Ethylbenzene	11.8-28.2	17.4-26.7	7.5	37-162
Methylene chloride	12.1-27.9	D-41.0	7.4	D-221
1,1,2,2-Tetrachloroethane	12.1-27.9	13.5-27.2	7.4	46-157
Tetrachloroethene	14.7-25.3	17.0-26.6	5.0	64-148
Toluene	14.9-25.1	16.6-26.7	4.8	47-150
1,1,1-Trichloroethane	15.0-25.0	13.7-30.1	4.6	52-162
1,1,2-Trichloroethane	14.2-25.8	14.3-27.1	5.5	52-150
Trichloroethene	13.3-26.7	18.6-27.6	6.6	71-157
Trichlorofluoromethane	9.6-30.4	8.9-31.5	10.0	17-181
Vinyl chloride	0.8-39.2	D-43.5	20.0	D-251

STL NORTH CANTON STANDARD OPERATING PROCEDURE

TITLE: INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROSCOPY, SPECTROMETRIC METHOD FOR TRACE ELEMENT ANALYSES, SW-846 METHOD 6010B AND EPA METHOD 200.7

(SUPERSEDES: REVISION 3.2, REVISION DATE 01/19/01)

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1. SCOPE AND APPLICATION

1.1. This procedure describes the analysis of trace elements including metals in solution by Inductively Coupled Plasma -Atomic Emission Spectroscopy (ICP-AES) using SW-846 Method 6010B and EPA Method 200.7 . Table I of Appendix A lists the elements appropriate for analysis by Methods 6010B and 200.7. Additional elements may be analyzed under Methods 6010B and 200.7 provided that the method performance criteria presented in Section 13.0 are met.

1.2. ICP analysis provides for the determination of metal concentrations over several orders of magnitude. Detection limits, sensitivity and optimum concentration ranges of the metals will vary with the matrices and instrumentation used. For instance, in comparison to conventional ICP technique, ICP-Trace can achieve detection levels comparable to those determined using the graphite furnace atomic absorption spectroscopy (GFAAS) technique.

1.3. Method 6010B is applicable to the determination of dissolved, suspended, total recoverable and total elements in ground water, aqueous samples, soils, sludges, wastes, sediments, and TCLP, EP and other leachates/extracts. All matrices require digestion prior to analysis with the exception of analyses for dissolved metals in filtered and acidified aqueous samples. Although digestion is not specifically required by the method, some clients and regulators may require digestion of **dissolved samples** and this must be clarified and documented before project initiation. Silver concentrations must be below 2.0 mg/L in aqueous samples and 100 mg/kg in solid matrix samples. Precipitation may occur in samples where silver concentrations exceed these levels and lead to the generation of erroneous data.

1.4. Method 200.7 is applicable to the determination of dissolved, suspended, total recoverable, and total elements in water, waste water, and solid wastes. All matrices require digestion prior to analysis with the exception of analyses for dissolved metals in filtered and acidified aqueous samples if the criteria in Section 11.1 are met. Silver concentrations must be below 0.1 mg/L in aqueous samples and 50 mg/kg in solid matrix samples.

1.5. State-specific requirements may take precedence over this SOP for drinking water sample analyses.

1.6. The applicable LIMS method codes are QO (6010B), QM (6010B Trace), AS (200.7), JI (200.7 Trace).

2. SUMMARY OF METHOD

2.1. This method describes a technique for the determination of multi elements in solution using sequential or simultaneous optical systems and axial or radial viewing of the plasma. The basis of the method is the measurement of atomic emission by an optical spectroscopic technique. Samples are nebulized and the aerosol that is produced is transported to the plasma torch where excitation occurs. Characteristic atomic-line emission spectra are produced by a radio frequency inductively coupled plasma (ICP). The spectra are dispersed by a grating spectrometer and the intensities of the emission lines are monitored by photomultiplier tubes. The photocurrents from the photomultiplier tubes are processed and controlled by a computer system. A background correction technique is required to compensate for variable background contribution to the determination of trace elements. Background must be measured adjacent to analyte lines during analysis. The position selected for the background intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used must be free of spectral interferences and reflect the same change in background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result. The possibility of additional interferences should also be recognized and appropriate actions taken. Alternatively, multivariate calibration methods may be chosen for which point selection for background correction is superfluous since whole spectral regions are processed.

2.2. Refer to the appropriate SOPs for details on sample preparation methods.

3. DEFINITIONS

3.1. Dissolved Metals: Those elements which pass through a 0.45 um membrane. (Sample is acidified after filtration).

3.2. Suspended Metals: Those elements which are retained by a 0.45 um membrane.

3.3. Total Metals: The concentration determined on an unfiltered sample following vigorous digestion.

3.4. Total Recoverable Metals: The concentration determined on an unfiltered sample following treatment with hot, dilute mineral acid.

4. INTERFERENCES

4.1. Spectral, physical and chemical interference effects may contribute to inaccuracies in the determinations of trace elements by ICP. Spectral interferences are caused by:

- Overlap of a spectral line from another element.
- Unresolved overlap of molecular band spectra.
- Background contribution from continuous or recombination phenomena.
- Stray light from the line emission of high concentration elements.

4.1.1. A background correction technique is required to compensate for variable background contribution to the determination of trace elements. Background correction is not required in cases where a background corrective measurement would actually degrade the analytical result.

4.1.2. Inter-element correction factors (IECs) are necessary to compensate for spectral overlap. Inter-element interferences occur when elements in the sample emit radiation at wavelengths so close to that of the analyte that they contribute significant intensity to the analyte channel. If such conditions exist, the intensity contributed by the matrix elements will cause an excessively high (or sometimes low) concentration to be reported for the analyte. Inter-element corrections IECs must be applied to the analyte to remove the effects of these unwanted emissions.

4.1.3. Physical interferences are generally considered to be effects associated with sample transport, nebulization and conversion within the plasma. These interferences may result in differences between instrument responses for the sample and the calibration standards. Physical interferences may occur in the transfer of solution to the nebulizer (e.g., viscosity effects), at the point of aerosol formation and transport to the plasma (e.g., surface tension) or during excitation and ionization processes within the plasma itself. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples containing high dissolved solids or high acid concentrations. If physical interferences are present, dilution of the sample, use of a peristaltic pump, mass flow controller, use of an internal standard and/or use of a high solids nebulizer can reduce the effect.

4.1.4. Chemical interferences are characterized by molecular compound formation, ionization effects and solute vaporization effects. Normally these effects are not significant with the ICP technique but if observed can be minimized by buffering the sample, matrix matching or standard addition procedures.

5. SAFETY

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

5.2. Eye protection that satisfies ANSI Z87.1 (as per the Chemical Hygiene Plan), laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.3. The health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the Material Safety Data Sheets (MSDS) maintained in the laboratory.

5.3.1. The following materials are known to be **corrosive**:

sulfuric acid, hydrochloric acid, nitric acid and hydrofluoric acid. (NOTE: sulfuric and hydrofluoric acids are used in cleaning the ICP torch and hydrofluoric acid is also commonly used in air toxics preparations.)

5.3.2. The following materials are known to be **oxidizing agents**:

nitric acid and hydrogen peroxide.

5.3.3. The plasma emits strong UV light and is harmful to vision. **NOTE: AVOID looking directly at the plasma**.

5.3.4. The RF generator produces strong radio frequency waves, most of which are unshielded. People with pacemakers should not go near the instrument while in operation.

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

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

5.6. The use of hydrofluoric acid requires special safety precautions. Consult the facility EH&S Manager and laboratory supervisor for guidance.

6. EQUIPMENT AND SUPPLIES

6.1. Inductively Coupled Plasma Atomic Emission Spectrometer equipped with autosampler and background correction.

6.2. Radio Frequency Generator.

6.3. Argon gas supply, welding grade or equivalent.

6.4. Coolflow or appropriate water cooling device.

6.5. Peristaltic Pump.

6.6. Calibrated automatic pipettes or Class A glass volumetric pipettes.

6.7. Class A volumetric flasks.

6.8. Autosampler tubes.

7. REAGENTS AND STANDARDS

7.1. Intermediate standards are purchased as custom STL North Canton multi-element mixes or as single-element solutions. All standards must be stored in FEP

fluorocarbon or unused polyethylene or polypropylene bottles. Intermediate standard solutions must be replaced prior to the expiration date provided by the manufacturer. If no expiration date is provided, the intermediate solutions may be used for up to one year and must be replaced sooner if verification from an independent source indicates a problem. Expiration dates can be extended provided that the acceptance criteria described in laboratory-specific SOPs are met.

7.2. Working calibration and calibration verification solutions may be used for up to 3 months and must be replaced sooner if verification from an independent source indicates a problem. Standards should be prepared in a matrix of 5% hydrochloric and 5% nitric acids. An exception to this is in the event the Trace ICP is utilized without the internal standard. In this case, the standard acid matrix must be matched to the final preparation matrix as listed in Section 11.9.

7.3. Refer to Tables III, IV, IVA, V and VI (Appendix A) for details regarding the working standard concentrations for calibration, calibration verification, interference correction and spiking solutions.

7.4. Concentrated nitric acid (HNO_3), trace metal grade or better.

7.5. Concentrated hydrochloric acid (HCl), trace metal grade or better.

7.6. Reagent water must be produced by a Millipore DI system or equivalent. Reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Sample holding times for metals are six months from time of collection to the time of analysis.

8.2. Aqueous samples are preserved with nitric acid to a pH of <2 and may be stored in either plastic or glass. If boron or silica are to be determined, plastic containers are preferred. Refrigeration is not required. Preservation must be verified prior to analysis.

8.3. Soil samples do not require preservation but must be stored at 4°C ± 2° until the time of preparation .

9. QUALITY CONTROL

Table VII (Appendix A) provides a summary of quality control requirements including type, frequency, acceptance criteria and corrective action.

9.1. Initial Demonstration of Capability

Prior to analysis of any analyte using either Method 200.7 or Method 6010B, the following requirements must be met.

Instrument Detection Limit (IDL) - The IDL for each analyte must be determined for each analyte wavelength used least each instrument. The IDL must be determined annually. If the instrument is adjusted in anyway that may affect the IDL, the IDL for that instrument must be redetermined. The IDL shall be determined by multiplying by 3, the standard deviation obtained from the analysis of a standard solution (each analyte in reagent water) at a concentration 3x - 5x the previously determined IDL, with seven consecutive measurements. Each measurement must be performed as though it were a separate analytical sample (i.e., each measurement must be followed by a rinse and/or any other procedure performed between the analysis of separate samples). The result of the IDL determination must be below the STL North Canton reporting limit. The CLP IDL procedure can be used for this method.

9.1.1. Method Detection Limit (MDL) - An MDL must be determined for each analyte prior to the analysis of any client samples. Refer to STL North Canton SOP NC-QA-0021 for details on MDL analysis and criteria.

9.1.2. Linear Range Verification (LR) - The linear range must be determined on at least an annual basis for each analyte wavelength used on each instrument. The linear range is the concentration above which results cannot be reported without dilution of the sample. The standards used to verify the linear range limit must be analyzed during a routine analytical run and must read within 5% of the expected value.

For the **initial** determination of the upper limit of the linear dynamic range (LDR) for each wavelength, determine the signal responses from a minimum of three to five different concentration standards across the estimated range. One standard should be near the upper limit of the estimated range. The concentration measured at the LDR must be no more than 10% less than the expected level extrapolated from lower standards. If the instrument is adjusted in any way that may affect the LRs, new dynamic ranges must be determined. The LR data must be documented and kept on file.

9.1.3. Background Correction Points - To determine the appropriate location for off-line background correction when establishing methods, the user must scan the area on either side adjacent to the wavelength and record the apparent emission intensity from all other method analytes. This spectral information must be documented and kept on file. The location selected for background correction must be either free of off-line interelement spectral interference or a computer routine must be used for automatic correction on all determinations. Tests to determine spectral interference must be done using analyte concentrations that will adequately describe the interference. Background correction points must be set prior to determining IECs. Refer to the facility-specific instrument

operation SOP and ICP instrument manual for specific procedures to be used in setting background correction points.

9.1.4. Inter-element Corrections (IECs) - ICP interelement correction factors must be determined prior to the analysis of samples and every six months thereafter. If the instrument is adjusted in any way that may affect the IECs, the IECs must be redetermined. When initially determining IECs for an instrument, wavelength scans must be performed to ensure that solutions in use are free from contaminants. If an IEC varies significantly from the previously determined IEC then the possibility of contamination should be investigated. The purity of the IEC check solution can be verified by using a standard from a second source or an alternate method (i.e., GFAA or ICP-MS). Published wavelength tables (e.g. MIT tables, Inductively Coupled Plasma-Atomic Spectroscopy: Prominent Lines) can also be consulted to evaluate the validity of the IECs. Refer to the facility specific instrument operation SOP and instrument manufacturer's recommendations for specific procedures to be used in setting IECs. An IEC must be established to compensate for any interelement interference which results in a false analyte signal greater than $\pm$ 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:

Original Run: Instrument Calibration

ICV

ICB

CRI

ICSA

ICSAB

7 samples

CCV1

CCB1

10 samples

CCV2

CCB2

10 samples **

CCV3 * * Failure occurs at CCV3/CCB3

CCB3 * **Samples requiring rerun for affected analytes

10 samples **

CCV4

CCB4

10 samples

CCV5

CCB5

Reanalysis: Recalibrate

ICV

ICB

CRI

ICSA

ICSAB

CCV2

CCB2

10 samples

CCV3

CCB3

10 samples

CCV4

CCB4

Notes:

Samples between CCV4 and CCV5 do not require reanalysis as they were bracketed by compliant QC samples.

See CORP-MT-0002NC for the appropriate reanalysis sequence if CLP requirements must also be met.

11.14 The instrument may be reprofiled between CCV/CCB pairs to correct for environment induced drift.

11.15 Guidelines are provided in the appendices on procedures to minimize contamination of samples and standards, preventive maintenance and troubleshooting.

11.16 All measurements must fall within the defined linear range where spectral interference correction factors are valid. Dilute and reanalyze all samples for required analytes that exceed the linear range or use an alternate wavelength for which QC data are established. If an interelement correction exists for an analyte which exceeds the linear range, the IEC may be inaccurately applied. Therefore, even if an overrange analyte may not be required to be reported for a sample, if that analyte is a interferent for any requested analyte in that sample, the sample must be diluted. Acid strength must be maintained in the dilution of samples.

11.17 For TCLP samples, full four-point MSA will be required if all of the following conditions are met:

1) recovery of the analyte in the matrix spike is not at least 50%,

2) the concentration of the analyte does not exceed the regulatory level, and,

3) the concentration of the analyte is within 20% of the regulatory level.

The reporting and regulatory limits for TCLP analyses as well as matrix spike levels are detailed in Table VI (Appendix A). Appendix E provides guidance on performing MSA analyses.

11.18 Any variation in procedure shall be completely documented using instrument run logs, maintenance logs, report narratives, a Nonconformance Memo, or an anomaly report and is approved by a Supervisor/Group Leader and QA Manager. If contractually required, the client shall be notified by the Project Manager.

11.19 Nonconformance documentation shall be filed in the project file.

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

12 DATA ANALYSIS AND CALCULATIONS

12.1 ICV percent recoveries are calculated according to the equation:

$$\%R = 100\left(\frac{Found(ICV)}{True(ICV)}\right)$$

12.2 CCV percent recoveries are calculated according to the equation:

$$\%R = 100\left(\frac{Found(CCV)}{True(CCV)}\right)$$

12.3 Matrix Spike Recoveries are calculated according to the following equation:

$$\%R = 100\left(\frac{SSR - SR}{SA}\right)$$

Where:
SSR = Spike Sample Result
SR = Sample Result
SA = Spike Added

12.4 The relative percent difference (RPD) of matrix spike/matrix spike duplicates are calculated according to the following equations:

$$RPD = 100\left[\frac{|MSD - MS|}{\left(\frac{MSD + MS}{2}\right)}\right]$$

Where:
MS = determined spiked sample concentration
MSD = determined matrix spike duplicate concentration

12.5 The final concentration for a digested aqueous sample is calculated as follows:

$$mg/L = \frac{C \times V1 \times D}{V2}$$

Where:
C = Concentration (mg/L) from instrument readout
D = Instrument dilution factor
V1 = Final volume in liters after sample preparation
V2 = Initial volume of sample digested in liters

12.6 The final concentration determined in digested solid samples when reported on a dry weight basis is calculated as follows:

$$mg / Kg, dry\,weight = \frac{C \times V \times D}{W \times S}$$

Where:

C = Concentration (mg/L) from instrument readout
D = Instrument dilution factor
V = Final volume in liters after sample preparation
W = Weight in Kg of wet sample digested
S = Percent solids/100

Note: A Percent Solids determination must be performed on a separate aliquot when dry weight concentrations are to be reported. If the results are to be reported on wet weight basis the "S" factor should be omitted from the above equation.

12.7 The LCS percent recovery is calculated according to the following equation:

$$\%R = 100\left(\frac{Found(LCS)}{True(LCS)}\right)$$

12.8 The dilution test percent difference for each component is calculated as follows:

$$\%Difference = \frac{|I - S|}{I} \times 100$$

Where:

I = Sample result (Instrument reading)
S = Dilution test result (Instrument reading × 5)

12.9 Appropriate factors must be applied to sample values if dilutions are performed.

12.10 Sample results should be reported with up to three significant figures in accordance with the STL North Canton significant figure policy.

13 METHOD PERFORMANCE

13.1 Each laboratory must have initial demonstration of performance data on file for each analyte of interest as described in Section 9.0.

13.2 Refer to Tables I, IA & II in Appendix A for the list of Method 6010B and 200.7 analytes as well as additional analytes that may be analyzed using this SOP.

13.3 Method performance is determined by the analysis of MS and MSD samples as well as method blanks and laboratory control samples. The MS or MSD recovery should fall within +/- 25 % and the MS/MSD should compare within 20% RPD or within the laboratory's historical acceptance limits. These criteria apply to analyte concentrations greater than or equal to 10xIDL. Method blanks must meet the criteria specified in Section 9.2. The laboratory control samples should recover within 20% of the true value or within the laboratory's historical acceptance limits.

13.4 Training Qualification:

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

14 POLLUTION PREVENTION

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

15 WASTE MANAGEMENT

15.1 Waste generated in the procedure must be segregated and disposed of according to the facility hazardous waste procedures and per the local, state, and federal regulations. The Environmental Health and Safety Director should be contacted, if additional information is required.

15.2 Standards should be purchased and prepared in volumes consistent with laboratory use to minimize the volume of expired standards to be disposed.

16 REFERENCES

16.1 40 CFR Part 136, Appendix B, 7-5-95, Determination of Method Detection Limits.

16.2 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition, Final Update III, Revision 2, December 1996. Method 6010B.

16.3 Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma-Atomic Emission Spectrometry, Revision 4.4, May 1994. Method 200.7.

16.4 CORP-MT-0002NC, Inductively Coupled Plasma-Atomic Emission Spectroscopy, Method 200.7 & CLP-M, SOW ILMO3.0 and ILMO4.0).

16.5 QA-003, STL North Canton QC Program.

16.6 QA-004, Rounding and Significant Figures.

16.7 QA-005, Method Detection Limits.

17 MISCELLANEOUS (TABLES, APPENDICES, ETC.)

17.1 Modifications/Interpretations from reference method

17.1.1 Modifications/interpretations from both Methods 6010B and 200.7.

17.1.1.1 STL North Canton laboratories use mixed calibration standard solutions purchased from approved vendors instead of using individual mixes prepared in house as recommended by the subject methods.

17.1.1.2 Methods 200.7 and 6010B state that if the correction routine is operating properly, the determined apparent analyte(s) concentration from analysis of each interference solution should fall within a specific concentration range around the calibration blank. In determining IECs, because of lack of definition clarification for "concentration range around the calibration blank," STL North Canton has adopted the procedure in EPA CLP ILMO4.0.

17.1.1.3 Section 8.5 of Method 6010B and Section 9.5 of Method 200.7 recommend that whenever a new or unusual matrix is encountered, a series of tests be performed prior to reporting concentration data for that analyte. The dilution test helps determine if a chemical or physical interference exists. Because STL North Canton laboratories receive no prior information from clients regarding when to expect a new or unusual matrix, STL North Canton may select to perform a dilution test on one sample in each prep batch. According to the method, the post digestion spike (PDS) determines any potential matrix interferences. At STL North Canton LABS, matrix interference is determined by evaluating data for the LCS and MS/MSD. STL North Canton REQUIRES documented, clear guidance when a new or unusual matrix will be received for a project and a request to perform the dilution test or PDS on a client-identified sample.

17.1.2 Modifications from Method 200.7.

17.1.2.1 Method 200.7 defines the IDL as the concentration equivalent to a signal, due to the analyte, which is equal to three times the standard deviation of a series of ten replicate measurements of the calibration blank signal at the same wavelength. STL North Canton labs utilize the CLP IDL definition as defined in Section 9.1.1 of this SOP.

17.1.2.2 The calibration blank is prepared in an acid matrix of 5% HNO_3/5% HCl instead of the specified 2% HNO_3/10% HCl matrix as the former matrix provides for improved performance relative to the wide variety of digestate acid matrices which result from the various EPA preparation protocols applied.

17.1.2.3 Method section 9.3.4 specifies that "Analysis of the IPC (ICSA/AB) solution immediately following calibration must verify that the instrument is within ± 5% of calibration with a relative standard deviation <3% from replicate integrations ≥ 4." STL North Canton uses a minimum of two exposures.

17.1.2.4 Section 7.12 of 200.7 indicates that the QCS (ICV) should be prepared at a concentration near 1 ppm. The ICV specified in this SOP accommodates the 1 ppm criteria for the majority of analytes. For the remaining analytes, this SOP specifies ICV concentrations which are appropriate to the range of calibration. The intent of the ICV, verification of calibration standard accuracy, is independent of the ICV concentration used.

17.1.2.5 The ICS criteria applied by this SOP differ from those stated in the method. Method 200.7 section 10.4 states that results should fall within the established control limits of 3 times the standard deviation of the calibration blank for that analyte. The control limits listed in this SOP are those applicable to the EPA designed solution.

17.1.2.6 Method 200.7 section 9.3.4 states the CCB should be less than the IDL, but > the lower 3-sigma control limit of the calibration blank. The intent of this requirement is to ensure that the calibration is not drifting at the low end. STL North Canton has adopted an absolute control limit of +/- RL from zero for calibration blank criteria. SOP section 9.7 provides the detailed corrective action criteria that must be followed.

17.1.3 Modifications from Method 6010B.

17.1.3.1 Chapter 1 of SW-846 states that the method blank should not contain any analyte of interest at or above the MDL. This SOP states that the method blank must not contain any analyte of interest at or above the reporting limit. Common lab contaminants are allowed up to two times the reporting limit in the blank following consultation with the client.

17.1.3.2 Method 6010B section 8.6.1.3 states that the results of the calibration blank are to agree within 3x the IDL. If not, repeat the analysis two or more times and average the results. If the average is not within three standard deviations of the background mean, terminate the analysis, correct the problem, recalibrate, and reanalyze the previous 10 samples. The intent of this requirement is to ensure that the calibration is not drifting at the low end. STL North Canton has adopted an absolute control limit of +/- RL from zero for calibration blank criteria. See SOP Section 9.7 for a detailed description of the required corrective action procedures.

17.2 Modifications from previous SOP

Refer to revision 2 of this SOP.

17.3 Facility-Specific SOPs

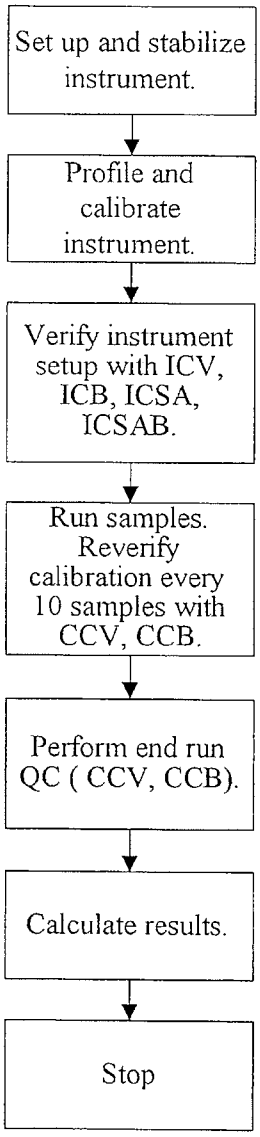
Each facility shall review and revise as appropriate this SOP to reflect any facility-specific requirements. If no facility-specific amendments are required, the SOP can be adopted as is.

17.4 Documentation and Record Management

The following documentation comprises a complete ICP raw data package:

- Raw data (direct instrument printout).
- Relevant sample preparation benchsheets.
- Run log printout from instrument software where this option is available (TJA) or manually generated run log (i.e., Ward WSL printout).
- Data review checklist - See Appendix B.
- Standards documentation (including prep and expiration dates, source, and lot #).
- Nonconformance/anomaly documentation (if applicable).

17.5 Flow Diagram



APPENDIX A

TABLES

TABLE I. Method 200.7 and 6010B Target Analyte List

ELEMENT	Symbol	CAS #	6010B analyte	200.7 analyte	Reporting Limit (ug/L) Water	Reporting Limit (mg/kg) Soil
Aluminum	Al	7429-90-5	X	X	200	20
Antimony	Sb	7440-36-0	X	X	60	6
Arsenic	As	7440-38-2	X	X	300	30
Barium	Ba	7440-39-3	X	X	200	20
Beryllium	Be	7440-41-7	X	X	5.0	0.5
Boron	B	7440-42-8		X	200	20
Cadmium	Cd	7440-43-9	X	X	5.0	0.5
Calcium	Ca	7440-70-2	X	X	5000	500
Chromium	Cr	7440-47-3	X	X	10	1
Cobalt	Co	7440-48-4	X	X	50	5
Copper	Cu	7440-50-8	X	X	25	2.5
Iron	Fe	7439-89-6	X	X	100	10
Lead	Pb	7439-92-1	X	X	100	10
Magnesium	Mg	7439-95-4	X	X	5000	500
Manganese	Mn	7439-96-5	X	X	15	1.5
Molybdenum	Mo	7439-98-7	X	X	40	4
Nickel	Ni	7440-02-0	X	X	40	4
Potassium	K	7440-09-7	X	X	5000	500
Selenium	Se	7782-49-2	X	X	250	25
Silver	Ag	7440-22-4	X	X	10	1
Sodium	Na	7440-23-5	X	X	5000	500
Thallium	Tl	7440-28-0	X	X	2000	200
Vanadium	V	7440-62-2	X	X	50	5
Zinc	Zn	7440-66-6	X	X	20	2

TABLE IA. Method 200.7 and 6010B Trace ICP Target Analyte List

ELEMENT	Symbol	CAS #	Reporting Limit (ug/L) Water	Reporting Limit (mg/kg) Soil
Arsenic	As	7440-38-2	10	1.0
Lead	Pb	7439-92-1	3.0	0.3
Selenium	Se	7782-49-2	5.0	0.5
Thallium	Tl	7440-28-0	10	1.0
Antimony	Sb	7440-36-0	10	1.0
Cadmium	Cd	7440-43-9	2.0	0.2
Silver	Ag	7440-22-4	5.0	0.5
Chromium	Cr	7440-47-3	5.0	0.5

TABLE II. Non-Routine Analyte List

ELEMENT	Symbol	CAS #	Reporting Limit (ug/L) Water	Reporting Limit (mg/kg) Soil
Tin	Sn	7440-31-5	100	10
Titanium	Ti	7440-32-6	50	5

TABLE III. Matrix Spike and Aqueous Laboratory Control Sample Levels

ELEMENT	LCS Level (ug/L)	Matrix Spike Level (ug/L)
Aluminum	2000	2000
Antimony	500	500
Arsenic	2000	2000
Barium	2000	2000
Beryllium	50	50
Cadmium	50	50
Calcium	50000	50000
Chromium	200	200
Cobalt	500	500
Copper	250	250
Iron	1000	1000
Lead	500	500
Magnesium	50000	50000
Manganese	500	500
Molybdenum	1000	1000
Nickel	500	500
Potassium	50000	50000
Selenium	2000	2000
Silver	50	50
Sodium	50000	50000
Thallium	2000	2000
Vanadium	500	500
Zinc	500	500
Boron	1000	1000
Tin	2000	2000
Titanium	1000	1000

TABLE IV. ICP Calibration and Calibration Verification Standards

Element	Calibration Level	RL (ug/L)	ICV (ug/L)	CCV (ug/L)
Aluminum	100000	200	25000	50000
Antimony	10000	60	1000	5000
Arsenic	10000	300	1000	5000
Barium	10000	200	1000	5000
Beryllium	10000	5	1000	5000
Cadmium	10000	5	1000	5000
Calcium	100000	5000	25000	50000
Chromium	10000	10	1000	5000
Cobalt	10000	50	1000	5000
Copper	10000	25	1000	5000
Iron	100000	100	25000	50000
Lead	10000	100	1000	5000
Magnesium	100000	5000	25000	50000
Manganese	10000	15	1000	5000
Molybdenum	10000	40	1000	5000
Nickel	10000	40	1000	5000
Potassium	100000	5000	25000	50000
Selenium	10000	250	1000	5000
Silver	2000	10	500	1000
Sodium	100000	5000	25000	50000
Thallium	20000	2000	5000	10000
Vanadium	10000	50	1000	5000
Zinc	10000	20	1000	5000
Boron	10000	200	1000	5000
Tin	10000	100	1000	5000
Titanium	10000	50	1000	5000

TABLE IVA. Trace ICP Calibration and Calibration Verification Standards

Element	Calibration Level	RL (ug/L)	ICV (ug/L)	CCV (ug/L)
Aluminum	50000	200	12500	25000
Antimony	1000	10	250	500
Arsenic	1000	10	250	500
Barium	4000	10	1000	2000
Beryllium	4000	5	1000	2000
Cadmium	1000	2	250	500
Calcium	100000	5000	25000	50000
Chromium	4000	5	1000	2000
Cobalt	4000	50	1000	2000
Copper	4000	25	1000	2000
Iron	50000	100	12500	25000
Lead	1000	3	250	500
Magnesium	100000	5000	25000	50000
Manganese	4000	15	1000	2000
Molybdenum	4000	40	1000	2000
Nickel	4000	40	1000	2000
Potassium	100000	5000	25000	50000
Selenium	1000	5	250	500
Silver	2000	5	500	1000
Sodium	100000	5000	25000	50000
Thallium	2000	10	500	1000
Vanadium	4000	50	1000	2000
Zinc	4000	20	1000	2000

TABLE V. Interference Check Sample Concentrations*

Element	ICSA (ug/L)	ICSAB (ug/L)
Aluminum	500000	500000
Antimony	-	1000
Arsenic	-	1000
Barium	-	500
Beryllium	-	500
Cadmium	-	1000
Calcium	500000	500000
Chromium	-	500
Cobalt	-	500
Copper	-	500
Iron	200000	200000
Lead	-	1000
Magnesium	500000	500000
Manganese	-	500
Molybdenum	-	1000
Nickel	-	1000
Potassium	-	10000
Selenium	-	1000
Silver	-	1000
Sodium	-	10000
Thallium	-	10000**
Vanadium	-	500
Zinc	-	1000
Tin	-	1000
Boron		1000
Titanium		1000

* Custom STL North Canton solutions contain analytes common to all STL North Canton facilities. Non-routine elements not listed above should be spiked into the ICSAB at 1000 ug/L.

** Thallium level for Trace ICP should be at 1000 ug/L.

TABLE VI. TCLP Reporting Limits, Regulatory Limits and Matrix Spike Levels

ELEMENT	Reporting Level (ug/L)	Regulatory Limit (ug/L)	Spike Level (ug/L)
Arsenic	500	5000	5000
Barium	10000	100000	50000
Cadmium	100	1000	1000
Chromium	500	5000	5000
Lead	500	5000	5000
Selenium	250	1000	1000
Silver	500	5000	1000

TABLE VII. Summary Of Quality Control Requirements

QC PARAMETER	FREQUENCY *	ACCEPTANCE CRITERIA	CORRECTIVE ACTION
Two-point Initial Calibration	Beginning of every analytical run, every 24 hours, whenever instrument is modified, or CCV criterion is not met		Terminate analysis; Correct the problem; Prepare new standards; Recalibrate following system performance.
ICV	Beginning of every analytical run.	Method 200.7: 95 - 105 % recovery. RSD dupl. exp < 3% Method 6010B: 90 - 110 % recovery. RSD dupl. exp < 5%	Terminate analysis; Correct the problem; Recalibrate.
ICB	Beginning of every analytical run, immediately following the ICV.	The result must be within +/- RL from zero.	Terminate analysis; Correct the problem; Recalibrate.
CCV	Every 10 samples and at the end of the run.	Method 200.7 & 6010B: 90 - 110 % recovery. RSD dupl. exp < 5%	Terminate analysis; Correct the problem; Recalibrate and rerun all samples not bracketed by acceptable CCV.
CCB	Immediately following each CCV.	The result must be within +/- RL from zero.	Terminate analysis; Correct the problem; Recalibrate and rerun all samples not bracketed by acceptable CCB.
CRI	Beginning of every run	50-150% recovery (advisory)	Evaluate associated samples.
ICSA	Beginning of every run	See Section 9.8.3	See Section 9.8.3
ICSAB	Immediately following each ICSA.	Results must be within 80 - 120% recovery.	See Section 9.8.2.

* See Sections 11.10 and 11.13 for exact run sequence to be followed.

TABLE VII. Summary of Quality Control Requirements (Continued)

QC PARAMETER	FREQUENCY	ACCEPTANCE CRITERIA	CORRECTIVE ACTION
Dilution Test	One per prep batch.	For samples > 50x IDL, dilutions must agree within 10%.	Narrate the possibility of physical or chemical interference per client request.
Method Blank	One per sample preparation batch of up to 20 samples.	The result must be less than or equal to the RL. Common lab contaminants may be accepted up to 2x the RL after consultation with the client (See 9.2). Sample results greater than 10x the blank concentration are acceptable. Samples for which the contaminant is < RL may not require redigestion or reanalysis (see Section 9.2).	Redigest and reanalyze samples. Note exceptions under criteria section. See Section 9.2 for additional requirements.
Laboratory Control Sample (LCS)	One per sample preparation batch of up to 20 samples.	Aqueous LCS must be within 80 - 120% recovery or in-house control limits. Samples for which the contaminant is < RL and the LCS results are > 120% may not require redigestion or reanalysis (see Section 9.3)	Terminate analysis; Correct the problem; Redigest and reanalyze all samples associated with the LCS.

TABLE VII. Summary of Quality Control Requirements (Continued)

QC PARAMETER	FREQUENCY	ACCEPTANCE CRITERIA	CORRECTIVE ACTION
Matrix Spike	One per sample preparation batch of up to 20 samples.	75 - 125 % recovery or in-house control limits. For TCLP See Section 11.17.	In the absence of client specific requirements, flag the data; no flag required if the sample level is > 4x the spike added. For TCLP see Section 11.17.
Matrix Spike Duplicate	See Matrix Spike	75 - 125 % recovery; RPD ≤ 20% .	See Corrective Action for Matrix Spike.

APPENDIX B

STL NORTH CANTON ICP DATA REVIEW CHECKLIST

(EXAMPLE)

SCAL STD_____ ICSA STD_____ SCAL2 STD_____ ICSAB STD_____

CRI STD_____ ICV STD_____ CLP CRI STD_____ CCV STD_____

(Example)

STL North Canton ICP Data Review Checklist

Run/Project Information:

Run Date: _____ **Analyst:**_____ **Instrument:**_____

Prep Batches Run:_____

Cu/MnRatio:_____

Circle Methods used: **6010B / 200.7: CORP-MT-0001 Rev 2 CLP ILM03.0: CORP-MT-0002 Rev 1**

6010A/200.7: CORP-MT-0001NC, Rev 2

Review Items

A. Calibration/Instrument Run QC	Yes	No	N/A	2nd Level
1. Instrument calibrated per manufacturer's instructions and at SOP specified levels ?				
2. ICV/CCV analyzed at appropriate frequency and within control limits ? (*ICV*: 6010B, CLP = 90 - 110%, 200.7 = 95 -105%) *(CCV: 90 - 110%)*				
3. ICB/CCB analyzed at appropriate frequency and within +/- RL or +/- CRDL (CLP) ?				
4. High Std. (HCAL) reanalyzed before samples and recovered within QC limits ? (6010A/200.7 95-105%, CLP- N/A)				
5. CRI run and recovered within QC limits ? (+/- 50% for non-CLP - 6010A only)				
6. ICSA/ICSAB run at required frequency and within SOP limits ?				
B. Sample Results				
1. Were samples with concentrations > the linear range for any parameter diluted and reanalyzed ?				
2. All reported results bracketed by in control QC ?				
3. Sample analyses done within holding time ?				
C. Preparation/Matrix QC				
1. LCS done per prep batch and within QC limits ?				
2. Method blank done per prep batch and < RL or CRDL (CLP) ?				

3. MS/MSD run at required frequency and within limits ?				
4. MSD or DU run at required frequency and RPD within SOP limits ?				
5. Serial dilution done per prep batch (or per SDG for CLP) ?				
6. Post digest spike analyzed if required (CLP only) ?				
D. Other				
1. Are all nonconformances documented appropriately ?				
2. Current IDL/LR/IEC data on file ?				
3. Calculations checked for error ?				
4. Transcriptions checked for error ?				
5. All client/project specific requirements met ?				
6. Date/time of analysis verified as correct ?				

Level I Analyst:_____ **Date:**_____ **Time:**_____

Comments:_____

Level II Reviewer:_____ **Date:**_____ **Time:**_____

APPENDIX C

CROSS REFERENCE OF TERMS USED IN METHODS 6010B, 200.7, AND BY STL NORTH CANTON

CROSS REFERENCE OF TERMS COMMONLY USED IN METHODS EPA 200.7, SW6010B, AND STL NORTH CANTON INC. SOP

EPA 200.7	SW6010B	STL North Canton Inc. SOP
Calibration blank (CB)	Calibration blank	Initial and continuing calibration blanks (ICB/CCB)
Dilution test	Dilution test	Dilution Test
Instrument detection limit (IDL)	Instrument detection limit (IDL)	Instrument detection limit (IDL)
Instrument performance check (IPC)	Continuing calibration verification (CCV)	Continuing calibration verification (CCV)
Internal standard	Internal standard	Internal standard (IS)
Laboratory duplicates	n/a	n/a
Laboratory fortified blank (LFB)	n/a	Laboratory control sample (LCS)
Laboratory fortified sample matrix (LFM)	Matrix spike and matrix spike duplicate (MS/MSD)	Matrix spike and matrix spike duplicate (MS/MSD)
Laboratory reagent blank (LRB)	Method blank	Method or Prep blank (MB)
Linear dynamic range (LDR)	Linear dynamic range (LDR)	Linear dynamic range (LDR)
Method detection limit (MDL)	Method detection limit (MDL)	Method detection limit (MDL)
Quality control sample (QCS)	Check standard or Initial calibration verification (ICV)	Initial calibration verification (ICV)
Spectral interference check solution (SIC)	Interference check solution (ICS)	Interference check solution (ICSA/ICSAB)

APPENDIX D

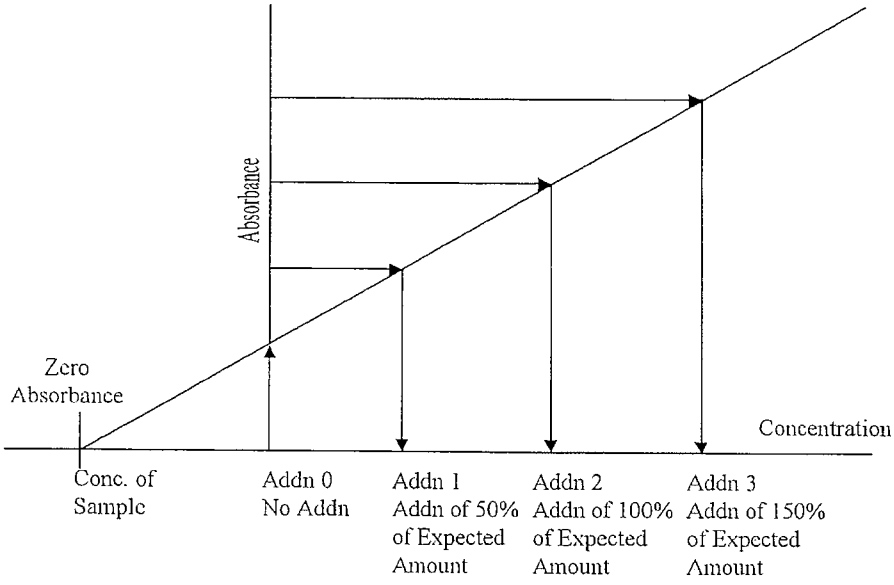
MSA GUIDANCE

Appendix D. MSA Guidance

Method of Standard Addition

Four equal volume aliquots of sample are measured and known amounts of standards are added to three aliquots. The fourth aliquot is the unknown and no standard is added to it. The concentration of standard added to the first aliquot should be 50% of the expected concentration. The concentration of standard added to the second aliquot should be 100% of the expected concentration and the concentration of standard added to the third aliquot should be 150% of the expected concentration. The volume of the unspiked and spiked standard should be the same.

In order to determine the concentration of analyte in the sample, the analytical value of each solution is determined and a plot or linear regression performed. On the vertical axis the analytical value is plotted versus the concentrations of the standards on the horizontal axis. An example plot is shown in Figure 1. When the resulting line is extrapolated back to zero absorbance, the point of interception of the horizontal axis is the concentration of the unknown.



For the method of standard additions to be correctly applied, the following limitations must be taken into consideration:

- The plot of the sample and standards must be linear over the concentration range of concern. For best results, the slope of the curve should be similar to that of a plot of the aqueous standard curve.

- The effect of the interference should not vary as the ratio of the standard added to the sample matrix changes.

APPENDIX E

TROUBLESHOOTING GUIDE

APPENDIX E. TROUBLESHOOTING GUIDE

Problem	Possible Cause/ Solution
High Blanks	Increase rinse time Clean or replace tip Clean or replace torch Clean or replace sample tubing Clean or replace nebulizer Clean or replace mixing chamber Lower Torch
Instrument Drift	RF not cooling properly Vacuum level is too low Replace torch (Crack) Clean or replace nebulizer (blockage) Check room temperature (changing) Replace pump tubing Room humidity too high Clean torch tip (salt buildup) Check for argon leaks Adjust sample carrier gas Reprofile Horizontal Mirror Replace PA tube
Erratic Readings, Flickering Torch or High RSD	Check for argon leaks Adjust sample carrier gas Replace tubing (clogged) Check drainage(back pressure changing) Increase uptake time (too short) Increase flush time (too short) Clean nebulizer, torch or spray chamber Increase sample volume introduced Check that autosampler tubes are full Sample or dilution of sample not mixed Increase integration time (too short) Realign torch Reduce amount of tubing connectors
Cu/Mn Ratio Outside Limits or Low Sensitivity	Plasma conditions changed Clean nebulizer, torch or spray chamber Replace tubing (clogged) Realign torch Check IECs
Standards reading twice normal absorbance or concentration	Incorrect standard used Incorrect dilution performed

APPENDIX F

CONTAMINATION CONTROL GUIDELINES

APPENDIX F. CONTAMINATION CONTROL GUIDELINES

The following procedures are strongly recommended to prevent contamination:

All work areas used to prepare standards and spikes should be cleaned before and after each use.

All glassware should be washed with detergent and tap water and rinsed with 1:1 nitric acid followed by deionized water.

Proper laboratory housekeeping is essential in the reduction of contamination in the metals laboratory. All work areas must be kept scrupulously clean.

Powdered or Latex Gloves must not be used in the metals laboratory since the powder contains silica and zinc as well as other metallic analytes. Only vinyl or nitrile gloves should be used in the metals laboratory.

Glassware should be periodically checked for cracks and etches and discarded if found. Etched glassware can cause cross contamination of any metallic analytes.

Autosampler trays should be covered to reduce the possibility of contamination. Trace levels of elements being analyzed in the samples can be easily contaminated by dust particles in the laboratory.

The following are helpful hints in the identification of the source of contaminants:

Yellow pipet tips and volumetric caps can sometimes contain cadmium.

Some sample cups have been found to contain lead.

The markings on glass beakers have been found to contain lead. If acid baths are in use for glassware cleaning, they should be periodically checked for contaminants since contaminant concentrations will increase over time.

New glassware especially beakers can be a source of silica and boron.

Reagents or standards can contain contaminants or be contaminated with the improper use of a pipette.

Improper cleaning of glassware can cause contamination.

Latex gloves contain over 500 ppb of zinc.

APPENDIX G

PREVENTIVE MAINTENANCE

APPENDIX G. PREVENTIVE MAINTENANCE

A maintenance log is used to record when maintenance is performed on instruments. When an instrument problem occurs indicate the date, time and instrument number, then identify the problem and corrective action in the maintenance log.

The following procedures are required to ensure that that the instrument is fully operational.

Daily	Change sample pump tubing and pump windings Check argon gas supply level Check rinse solution and fill if needed Check waste containers and empty if needed Check sample capillary tubing is clean and in good condition Check droplet size to verify nebulizer is not clogged. Check sample flow for cross flow nebulizer Check Cu/Mn ratio-should be 30% of value at date that IECs were performed Check pressure for vacuum systems
As Needed	Clean plasma torch assembly to remove accumulated deposits Clean nebulizer and drain chamber; keep free-flowing to maintain optimum performance Replace peristaltic pump tubing, sample capillary tubing and autosampler sipper probe
Weekly	Apply silicon spray on autosampler tracks Check water level in coolflow
Monthly	Clean air filters on back of power unit to remove dust Check D mirror for air instruments
Bi-yearly	Change oil for vacuum systems Replace coolant water filter (may require more or less frequently depending on quality of cooling water)

APPENDIX H

ICP OPERATING INSTRUCTIONS

ICP Analysis (TJA 61E)

(Example)

1. SETUP

a. Plasma Control Panel (enter)

b. (F1)-Startup

c. (F9)-Continue

d. (F2)-Levels

1. Change auxiliary gas to low – use space bar to toggle
2. Change nebulizer gas flow to 0.5 L/min.
3. Change pump rate to 130
4. Esc
5. Allow instrument to warm up approximately 30 minutes.

2. DEVELOPMENT

a. Methods (enter)

b. Enter method name

c. (F3)-Method Info.

d. Change file name

e. (F9)-Done

f. (F9)-Done/Keep

18 OPERATION

a. Analysis (enter)

b. (F5)-Profile

1. (F3)-Automatic

2. (F1)-Run

3. If peak position is greater than +/- .05 units from the center peak position, you must adjust the profile. If it is within +/- .05 units, press (F9)-done.

4. To adjust select (F1)-CalcSS and enter current vernier position. (enter)

5. Adjust to new vernier position(F9)-done

6. Rerun profile until peak position is +/- .05 units.

7. (F9)-Done

c. Autosampler (F9)

1. Enter method name (enter)

2. Enter autosampler table name (enter)

3. (F1)-Run

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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Intranet Controlled

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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

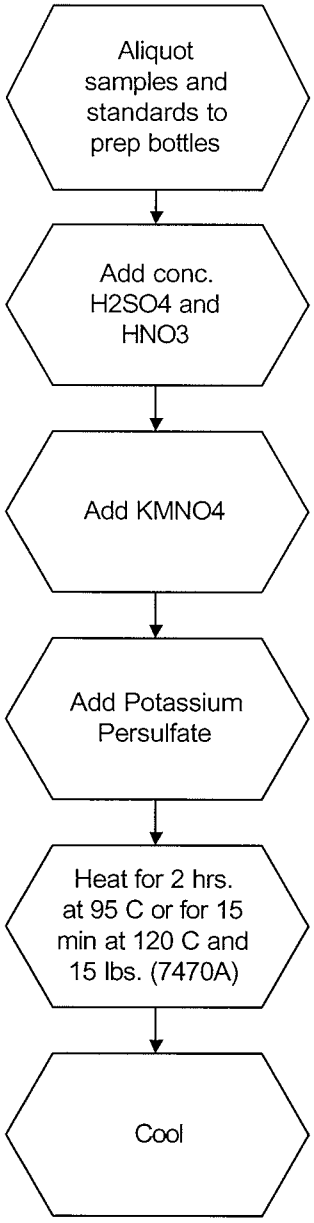
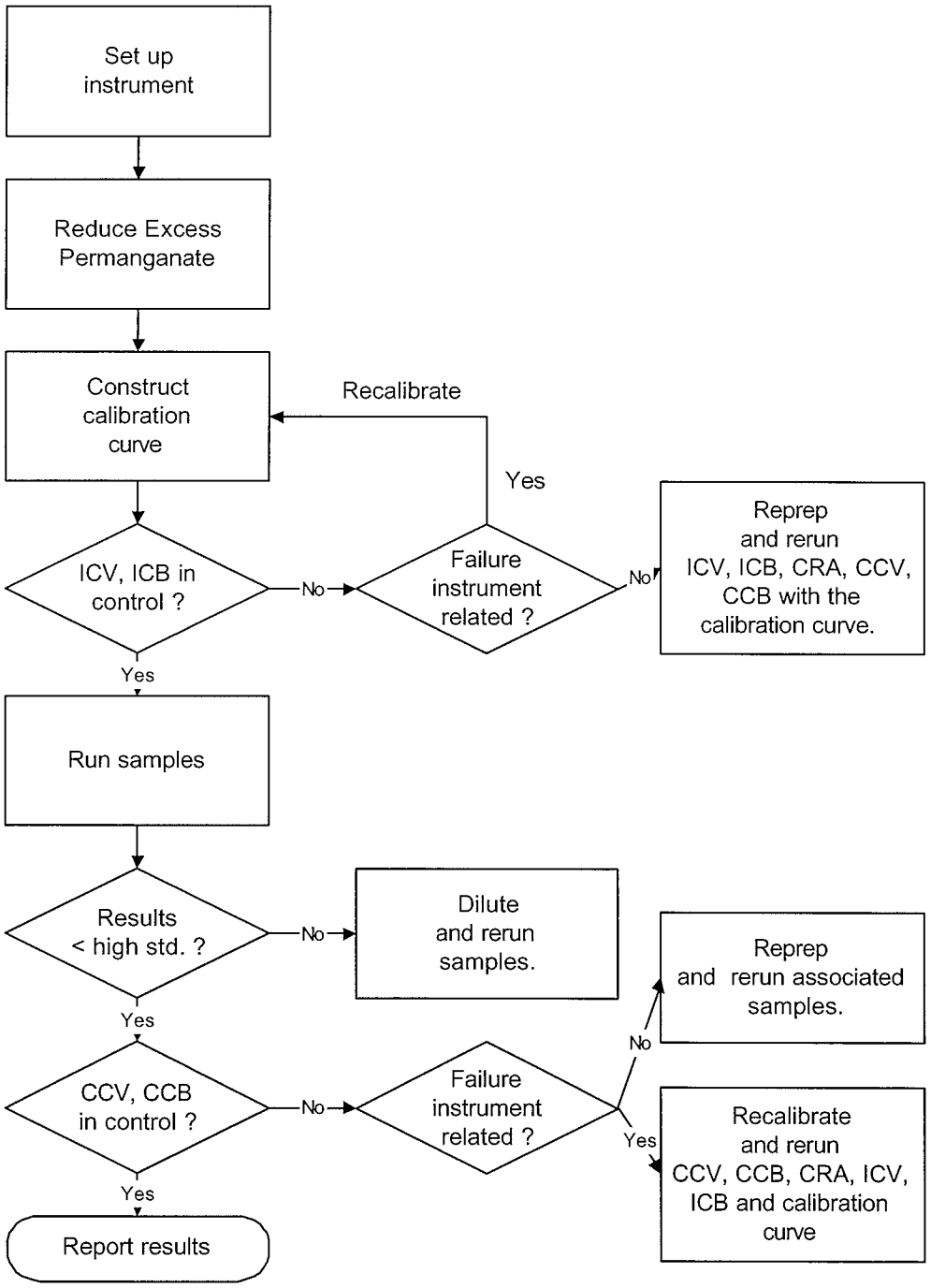


Figure 2. CVAA Mercury Analysis



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

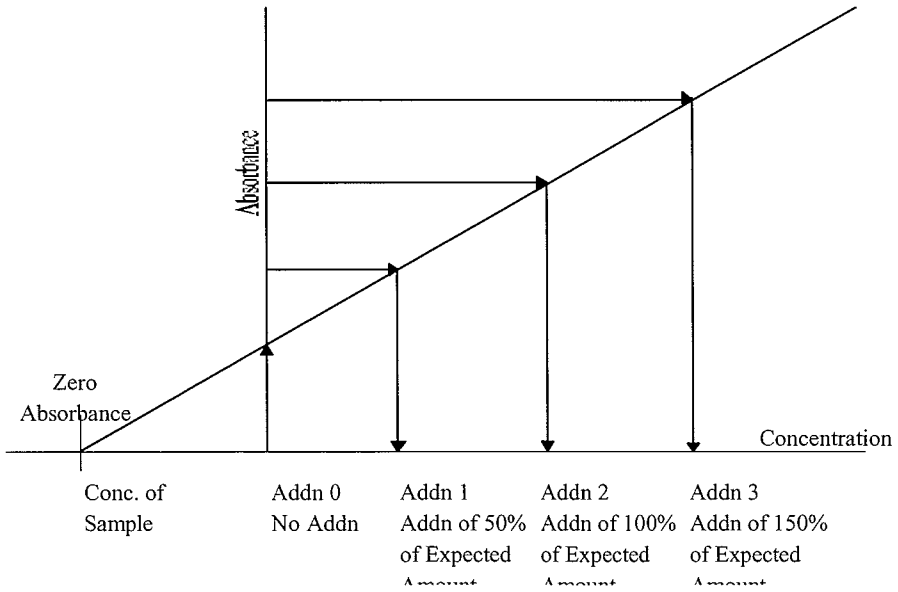
APPENDIX C. MSA GUIDANCE

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.

Controlled Copy
Copy No. _____

Implementation Date: 06/05/01

SOP No. CORP-MT-0007NC
Revision No. 2.3
Revision Date: 05/15/01
Page 1 of 42

STL NORTH CANTON STANDARD OPERATING PROCEDURE

TITLE: PREPARATION AND ANALYSIS OF MERCURY IN SOLID SAMPLES BY COLD VAPOR ATOMIC ABSORPTION SPECTROSCOPY, SW846 7471A AND MCAWW 245.5
(SUPERSEDES: REVISION 2.2, DATED 02/06/01)

Prepared by:		5/21/01 Date
Approved by:	Technical Specialist	5-21-01 Date
Approved by:	Quality Assurance Manager	5/23/01 Date
Approved by:	Environmental Health and Safety Coordinator	5-23-01 Date
Approved by:	Laboratory Director	5-23-01 Date
Approved by:	Corporate Technology	5/17/01 Date

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1. SCOPE AND APPLICATION

1.1. This procedure describes the preparation and analysis of mercury (Hg, CAS # 7439-97-6) by Cold Vapor Atomic Absorption Spectroscopy (CVAA) using SW-846 Method 7471A and MCAWW Method 245.5.

1.2. The associated LIMs method code is O9.

1.3. CVAA analysis provides for the determination of total mercury (organic and inorganic). The combination of the oxidants, potassium permanganate and potassium persulfate, has been found to give 100% recovery with both types of compounds. Detection limits, sensitivity and optimum concentration ranges for mercury analysis will vary with the matrices, instrumentation and volume of sample used.

1.4. Methods 7471A and 245.5 are applicable to the preparation and analysis of mercury in soils, sediments, bottom deposits, wastes, wipes and sludge-type materials. All matrices require sample preparation prior to analysis.

1.5. The STL North Canton reporting limit for mercury in solid matrices is 0.033 mg/kg based on a 0.6 g sample aliquot (wet weight).

2. SUMMARY OF METHOD

2.1. This SOP describes a technique for the determination of mercury in solution. The procedure is a physical method based on the absorption of radiation at 253.7 nm by mercury vapor. A representative portion of the sample is digested in hydrochloric and nitric acids. Organic mercury compounds are oxidized with potassium permanganate and potassium persulfate and the mercury reduced to its elemental state with stannous chloride and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance is measured as a function of mercury concentration. Concentration of the analyte in the sample is determined by comparison of the sample absorbance to the calibration curve (absorbance vs. concentration).

3. DEFINITIONS

3.1. Total Metals: The concentration determined on an unfiltered sample following digestion.

4. INTERFERENCES

Chemical and physical interferences may be encountered when analyzing samples using this method.

4.1. Potassium permanganate which is used to breakdown organic mercury compounds also eliminates possible interferences from sulfide. Concentrations as high as 20 mg/L of sulfide as sodium sulfide do not interfere with the recovery of inorganic mercury from reagent water.

4.2. Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/L had no effect on the recovery of mercury from spiked samples.

4.3. Chlorides can cause a positive interference. Samples high in chlorides require additional permanganate (as much as 25 mL) because, during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation at 253.7 nm. Care must be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell. This is accomplished by adding excess hydroxylamine reagent (25 mL) and purging the sample headspace before stannous chloride is added. Both inorganic and organic mercury spikes have been quantitatively recovered from seawater using this technique.

Note: Sufficient addition of permanganate is apparent when the purple color persists at least 15 minutes. Some samples may require dilution prior to digestion due to extremely high concentrations of chloride.

4.4. Interference from certain volatile organic materials that absorb at this wavelength may also occur. If suspected, a preliminary run without stannous chloride can determine if this type of interference is present. While the possibility of absorption from certain organic substances present in the sample does exist, this problem is not routinely encountered. This is mentioned only to caution the analyst of the possibility. If this condition is found to exist, the mercury concentration in the sample can be determined by subtracting the result of the sample run without the reducing reagent (stannous chloride) from that obtained with the reducing reagent.

4.5. Samples containing high concentrations of oxidizable organic materials, as evidenced by high COD levels, may not be completely oxidized by this procedure. When this occurs the recovery of mercury will be low. The problem can be eliminated by reducing the volume of original sample used.

4.6. The most common interference is laboratory contamination which may arise from impure reagents, dirty glassware, improper sample transfers, dirty work areas, etc. Be aware of potential sources of contamination and take appropriate measures to minimize or avoid them.

5. SAFETY

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

5.2. Eye protection that satisfies ANSI Z87.1 (as per the Chemical Hygiene Plan), laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

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

5.3.1. The following materials are known to be **corrosive:**

hydrochloric acid, nitric acid and sulfuric acid.

5.3.2. The following materials are known to be **oxidizing agents**:

nitric acid, potassium permanganate, potassium persulfate and magnesium perchlorate.

5.3.3. Mercury is a highly toxic element that must be handled with care. The analyst must be aware of the handling and clean-up techniques before working with mercury. Since mercury vapor is toxic, precaution must be taken to avoid its inhalation, ingestion or absorption through skin. All lines should be checked for leakage and the mercury vapor must be vented into a hood or passed through a mercury absorbing media such as:

5.3.3.1. Equal volumes of 0.1 M $KMnO_4$ and 10% H_2SO_4, or

5.3.3.2. Iodine, 0.25%, in a 3% KI solution.

5.3.4. Magnesium sulfate is known to be a reproductive toxin (mutagen).

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

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

5.6. Do not look directly into the beam of the Hg lamp. The UV light that these lamps radiate is harmful to the eyes.

5.7. Cylinders of compressed gas must be handled with caution, in accordance with local regulations. It is recommended that, wherever possible, cylinders be located outside the laboratory and the gas led to the instrument through approved lines.

5.8. The CVAA apparatus must be properly vented to remove potentially harmful fumes generated during sample analysis.

6. EQUIPMENT AND SUPPLIES

6.1. Temperature controlled water bath (capable of maintaining temperature of 90- 95 °C).

6.2. Atomic Absorption Spectrophotometer equipped with:

6.2.1. Absorption Cell with quartz end windows perpendicular to the longitudinal axis. Dimensions of the cell must result in sufficient sensitivity to meet the SOP defined reporting limit. The quartz windows must be maintained to provide accurate measurements. Any scratches or fingerprints can alter the absorption of UV radiation.

6.2.2. Mercury specific hollow cathode lamp (HCL) or electrodeless discharge lamp (EDL).

6.2.3. Peristaltic pump which can deliver 1 L/min air.

6.2.4. Flowmeter capable of measuring an airflow of 1 L/min.

6.2.5. Recorder or Printer.

6.2.6. Aeration Tubing: A straight glass frit having a course porosity and Tygon tubing is used for the transfer of mercury vapor from the sample bottle to the absorption cell and return.

6.2.7. Drying device (a drying tube containing magnesium perchlorate or magnesium sulfate and/or a lamp with a 60 W bulb) to prevent condensation in cell. The lamp is positioned to shine on the absorption cell maintaining the air temperature in the cell about 10 °C above room temperature. Other drying devices that acheive the same purpose are also acceptable (i.e., Gortex filter).

Note: Instruments designed specifically for the measurement of mercury using the cold vapor technique may be substituted for the atomic absorption spectrophotometer.

6.3. BOD bottles or equivalent.

6.4. Nitrogen or argon gas supply, welding grade or equivalent.

6.5. Calibrated automatic pipettes or Class A glass volumetric pipettes.

6.6. Class A volumetric flasks.

6.7. Top-loading balance, capable of reading up to two decimal places.

6.8. Thermometer (capable of accurate readings at 95 °C).

6.9. Disposable cups or tubes.

7. REAGENTS AND STANDARDS

7.1. Reagent water must be produced by a Millipore DI system or equivalent. Reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks.

7.2. Stock (10 ppm) mercury standards (in 10% HNO_3) are purchased as custom STL North Canton solutions. All standards must be stored in FEP fluorocarbon or previously unused

polyethylene or polypropylene bottles. Stock standard solutions must be replaced prior to the expiration date provided by the manufacturer. If no expiration date is provided, the stock solutions may be used for up to one year and must be replaced sooner if verification from an independent source indicates a problem.

7.3. Working mercury standard (0.1 ppm): Take 1 mL of the stock mercury standard (7.2) and dilute to 100 mL with reagent water. The working mercury standard must be made daily and must be prepared in a matrix of 0.15% HNO_3. This acid (150 uL of concentrated HNO_3) must be added to the flask/bottle before the addition of the stock standard aliquot.

7.4. The calibration standards must be prepared fresh daily from the working standard (7.3) by transferring 0, 0.2, 0.5, 1.0, 5.0 and 10.0 mL aliquots of the working mercury standard into sample preparation bottles and proceeding as specified in Section 11.1

Note: Alternate approaches to standard preparation may be taken and alternate volumes of standard may be prepared as long as the accuracy and final standard concentrations as detailed in Table I are maintained. For example, automated mercury systems do not require 100 mL of standard and therefore smaller volumes may be generated to reduce waste generation.

7.5. The initial calibration verification standard must be made from a different stock solution than that of the calibration standards.

7.6. Refer to Table I (Appendix A) for details regarding the working standard concentrations for calibration, calibration verification and spiking solutions. All standards must be processed through the entire analytical procedure including sample preparation.

7.7. Nitric acid (HNO_3), concentrated, trace metal grade or better.

Note: If a high reagent blank is obtained, it may be necessary to distill the nitric acid.

7.8. Sulfuric acid (H_2SO_4), concentrated, trace metal grade or better.

7.9. Hydrochloric acid (HCl), concentrated, trace metal grade or better.

7.10. Aqua Regia: Prepare immediately before use by carefully adding three volumes of concentrated HCl to one volume of concentrated HNO_3.

7.11. Stannous sulfate solution: Add 25 g of stannous sulfate to 250 mL of 0.5 N sulfuric acid. This mixture is a suspension and should appear cloudy. This solution should be made daily and should be stirred continuously during use.

Note: Stannous chloride may be used in place of stannous sulfate. Prepare the stannous chloride solution according to the recommendations provided by the instrument manufacturer.

7.12. Sodium chloride-hydroxylamine hydrochloride solution: Add 12 g of sodium chloride and 12 g of hydroxylamine hydrochloride to every 100 mL of reagent water.

Note: Hydroxylamine sulfate may be used in place of hydroxylamine hydrochloride.

7.13. Potassium permanganate, 5% solution (w/v): Dissolve 5 g of potassium permanganate for every 100 mL of reagent water.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Sample holding time for mercury is 28 days from time of collection to the time of sample analysis.

8.2. Soil samples do not require preservation but must be stored at 4° C ± 2° C until the time of analysis.

9. QUALITY CONTROL

Table II (Appendix A) provides a summary of quality control requirements including type, frequency, acceptance criteria and corrective action.

9.1. Initial Demonstration of Capability

Prior to the analysis of any analyte using 7471A or the 245.5, the following requirements must be met.

9.1.1. Method Detection Limit (MDL) - An MDL must be determined for each analyte/matrix prior to the analysis of any samples. The MDL is determined using seven replicates of reagent water, spiked with all the analytes of interest, that have been carried through the entire analytical procedure. MDLs must be redetermined on an annual basis in accordance with 40 CFR Part 136 Appendix B requirements. The spike level must be between the calculated MDL and 10X the MDL to be valid. The result of the MDL determination must be below the STL North Canton reporting limit.

9.1.2. Initial Demonstration Study - This requires the analysis of four QC check samples. The QC check sample is a well characterized laboratory generated sample used to

monitor method performance. The results of the initial demonstration study must be acceptable before analysis of samples may begin.

9.1.2.1. Four aliquots of the check sample (LCS) are prepared and analyzed using the procedures detailed in this SOP and the determinative SOPs.

9.2. Preparation Batch - A group of up to 20 samples that are of the same matrix and are processed together using the same procedures and reagents. The preparation batch must contain a method blank, a LCS and a matrix spike/matrix spike duplicate. In some cases, at client request, it may be appropriate to process a matrix spike and sample duplicate in place of the MS/MSD. If clients specify specific samples for MS/MSD, the batch may contain multiple MS/MSD pairs.

9.3. Sample Count - Laboratory generated QC samples (method blanks, LCS, MS/MSD) are not included in the sample count for determining the size of a preparation batch.

9.4. Method Blank (MB) - One method blank must be processed with each preparation batch. The method blank consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The method blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. The method blank should not contain any analyte of interest at or above the reporting or at or above 5% of the measured concentration of that analyte in associated samples, whichever is higher (sample result must be a minimum of 20 times higher than the blank contamination level).

- Repreparation and reanalysis of all samples associated with an unacceptable method blank is required when reportable concentrations are determined in the samples (see exception noted above).
- If there is no analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. **Such action must be taken in consultation with the client and must be addressed in the project narrative.**
- If the above criteria are not met and reanalysis is not possible, then the sample data must be qualified. **This anomaly must be addressed in the project narrative and the client must be notified.**

9.5. Laboratory Control Sample (LCS) - One aqueous LCS must be processed with each preparation batch. The LCS is used to monitor the accuracy of the analytical process. On-going monitoring of the LCS results provides evidence that the laboratory is performing the

method within acceptable accuracy and precision guidelines. The LCS must be carried through the entire analytical procedure. If the LCS is outside established control limits the system is out of control and corrective action must occur. Until in-house control limits are established, a control limit of 70-130% recovery must be applied.

- In the instance where the LCS recovery is > 130% and the sample results are < RL, the data may be reported with qualifiers. Such action must be taken in consultation with the client and must be addressed in the case narrative."

- In the event that an MS/MSD analysis is not possible, a Laboratory Control Sample Duplicate (LCSD) must be analyzed. The RPD of the LCS and LCSD must be compared to the matrix spike RPD limits.

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

9.6. Matrix Spike/Matrix Spike Duplicate (MS/MSD) - One MS/MSD pair must be processed for each preparation batch. A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added. A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked identically as the MS) prepared and analyzed along with the sample and matrix spike. Some client specific data quality objectives (DQO's) may require the use of sample duplicates in place of or in addition to MS/MSD's. The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Due to the potential variability of the matrix of each sample, these results may have immediate bearing only on the specific sample spiked. Samples identified as field blanks cannot be used for MS/MSD analysis. Spiking levels are provided in Table I (Appendix A).

- If analyte recovery or RPD falls outside the acceptance range, the recovery of that analyte must be in control for the LCS. Until in-house control limits are established, a control limit of 70 - 130 % recovery and 20% RPD must be applied to the MS/MSD. If the LCS recovery is within limits, then the laboratory operation is in control and the results may be accepted. If the recovery of the LCS is outside limits, corrective action must be taken. Corrective action will include repreparation and reanalysis of the batch. MS/MSD results which fall outside the control limits must be addressed in the narrative.

- If the native analyte concentration in the MS/MSD exceeds 4 times the spike level for that analyte, the recovery data are reported as NC (i.e., not calculated). If the reporting software does not have the ability to report NC then the actual recovery must be reported and narrated as follows: "Results outside of limits do not

necessarily reflect poor method performance in the matrix due to high analyte concentrations in the sample relative to the spike level."

- If an MS/MSD is not possible due to limited sample volume, then a laboratory control sample duplicate (LCSD) should be analyzed. The RPD of the LCS and LCSD must be compared to the matrix spike RPD limits.

9.7. Initial Calibration Verification (ICV/ICB) - Calibration accuracy is verified by analyzing a second source standard (ICV). The ICV result must fall within 10% of the true value for that solution . An ICB is analyzed immediately following the ICV to monitor low level accuracy and system cleanliness. The ICB result must fall within +/- the reporting limit (RL) from zero. If either the ICV or ICB fail to meet criteria, the analysis should be terminated, the problem corrected and the instrument recalibrated. (See Section 11.2.10 and Section 11.2.11 for required run sequence). If the cause of the ICV or ICB failure was not directly instrument related the corrective action will include repreparation of the ICV, ICB, CRA, CCV and CCB with the calibration curve.

9.8. Continuing Calibration Verification (CCV/CCB) - Calibration accuracy is monitored throughout the analytical run through the analysis of a known standard after every 10 samples. The CCV must be a mid-range standard at a concentration other than that of the ICV. The CCV result must fall within 20% of the true value for that solution. A CCB is analyzed immediately following each CCV. (See Section 11.2.10 and 11.2.11 for required run sequence.) The CCB result must fall within +/- RL from zero. Each CCV and CCB analyzed must reflect the conditions of analysis of all associated samples. Sample results may only be reported when bracketed by valid ICV/CCV and ICB/CCB pairs.

9.9. Method of Standard Addition (MSA) -This technique involves adding known amounts of standard to one or more aliquots of the sample prior to preparation. This technique compensates for a sample interferent that may enhance or depress the analyte signal, thus producing a different slope from that of the calibration standards. It will not correct for additive interferences which cause a baseline shift. Refer to Section 11.2.12 for additional information on when full 4 point MSA is required as well as Appendix C for specific MSA requirements.

10. CALIBRATION AND STANDARDIZATION

10.1. Calibration standards must be processed through the preparation procedure as described in Section 11.1.

10.2. Due to the differences in preparation protocols separate calibration and calibration verification standards must be prepared for aqueous and solid matrices.

10.3. Calibration must be performed daily (every 24 hours) and each time the instrument is set up. The instrument calibration date and time must be included in the raw data.

10.4. Set up the instrument with the operating parameters recommended by the manufacturer. Allow the instrument to become thermally stable before beginning calibration (approximately 30 minutes of warm-up is required). Refer to the facility specific instrument SOP and CVAA instrument manual for detailed setup and operation protocols.

10.5. Calibrate the instrument according to instrument manufacturer's instructions, using a minimum of five standards and a blank. One standard must be at the STL North Canton reporting limit. Analyze standards in ascending order beginning with the blank. Refer to Section 7.5 and Table I for additional information on preparing calibration standards and calibration levels.

10.6. The calibration curve must have a correlation coefficient of ≥0.995 or the instrument shall be stopped and recalibrated prior to running samples. Sample results can not be reported from a curve with an unacceptable correlation coefficient.

10.7. Refer to Section 9.0 for calibration verification procedures, acceptance criteria and corrective actions.

11. PROCEDURE

11.1. Standard and Sample Preparation:

11.1.1. All calibration and calibration verification standards (ICV, ICB, CCV, CCB) are processed through the digestion procedure as well as the field samples.

11.1.2. Transfer 0, 0.2, 0.5, 1.0, 5.0 and 10.0 mL aliquots of the working standard (7.3) into a series of sample digestion bottles. For the ICV, transfer a 2.5 ml aliquot of the working standard. The ICV working standard must be made from a source other than that used for the calibration standards.

Note: Alternate volumes of standard may be prepared as long as the accuracy and final standard concentrations as detailed in Table I are maintained.

11.1.3. Add reagent water to each standard bottle to make a total volume of 10 mL. Continue preparation as described under 11.1.5 below.

11.1.4. Transfer triplicate 0.2 g portions of a well mixed sample into a clean sample digestion bottle. Add 10mL of reagent water to each standard bottle. Continue

preparation as described under 11.1.5.

11.1.5. Water Bath protocol:

11.1.5.1. To each **standard** bottle: Add 5 mL of aqua regia.
To each **sample** bottle: Add *10* mL of reagent water and 5 mL of aqua regia.

11.1.5.2. Heat for 2 minutes in a water bath at 90 - 95 ° C.

11.1.5.3. Add *40* mL of distilled water.

11.1.5.4. Add 15 mL of potassium permanganate solution.

11.1.5.5. Heat for 30 minutes in the water bath at 90 - 95 °C.

11.1.5.6. Cool.

11.1.5.7. Add 6 mL of sodium chloride-hydroxylamine sulfate solution to reduce the excess permanganate.

11.1.5.8. To each **standard** bottle: Add 50 mL of reagent water.
To each **sample** bottle: Add *50* mL of reagent water.

11.1.5.9. Continue as described under Section 11.2.

11.2. Sample Analysis:

11.2.1. Because of differences between various makes and models of CVAA instrumentation, no detailed operating instructions can be provided. Refer to the facility specific instrument operating SOP and the CVAA instrument manual for detailed setup and operation protocols.

11.2.2. All labs are required to detail the conditions/programs utilized for each instrument within the facility specific instrument operation SOP.

11.2.3. Manual determination:

11.2.3.1. Treating each sample individually, purge the head space of the sample bottle for at least one minute.

11.2.3.2. Add 5 mL of stannous chloride solution and immediately attach the bottle to the aeration apparatus.

11.2.3.3. Allow the sample to stand quietly without manual agitation while the sample is aerated (1 L/min flow). Monitor the sample absorbance during aeration. When the absorbance reaches a maximum and the signal levels off, open the bypass valve and continue aeration until the absorbance returns to its baseline level. Close the bypass valve and remove the aeration device.

11.2.3.4. Place the aeration device into 100 mLs of 1% HNO_3 and allow to bubble rinse until the next sample is analyzed.

11.2.4. Automated determination: Follow instructions provided by instrument manufacturer.

11.2.5. Perform a linear regression analysis of the calibration standards by plotting maximum response of the standards vs. ug of mercury. Determine the mercury concentration in the samples from the linear regression fit of the calibration curve. Calibration using computer or calculation based regression curve fitting techniques on concentration/response data is acceptable.

11.2.6. All measurements must fall within the defined calibration range to be valid. Dilute and reanalyze all samples for analytes that exceed the highest calibration standard.

11.2.7. If the sample results are negative and the absolute value of the negative result is greater than the reporting limit, the sample must be diluted and reanalyzed.

11.2.8. The samples must be allowed to cool to room temperature prior to analysis or a decrease in the response signal can occur.

11.2.9. Baseline correction is acceptable as long as it is performed after every sample or after the CCV and CCB; resloping is acceptable as long as it is immediately preceded and followed by a compliant CCV and CCB.

11.2.10. The following analytical sequence must be used with 7471A and 245.5:

Instrument Calibration
ICV
ICB

Maximum 10 samples
CCV
CCB
Repeat sequence of 10 samples between CCV/CCB pairs as required to complete run
CCV
CCB

Refer to Quality Control Section 9.0 and Table II (Appendix A) for quality control criteria to apply to Methods 7471A and 245.5.

Note: Samples include the method blank, LCS, MS, MSD, duplicate, field samples and sample dilutions.

11.2.11. The following run sequence is consistent with 7471A, CLP and 245.5 and may be used as an alternate to the sequence in 11.2.10. This run sequence is recommended if multiple method requirements must be accommodated in one analytical run:

Instrument Calibration
ICV
ICB
CRA*
CCV
CCB
10 samples
CCV
CCB
Repeat sequence of 10 samples between CCV/CCB pairs as required to complete run.
CCV
CCB

Refer to the appropriate CLP SOP (CORP-MT-0008) for quality control requirements for QC samples.

* Refer to the CLP SOP for information on the CRA.

11.2.12. For TCLP samples, full four point MSA will be required if all of the following conditions are met:

1) recovery of the analyte in the matrix spike is not at least 50%,

2) the concentration of the analyte does not exceed the regulatory level, and,

3) the concentration of the analyte is within 20% of the regulatory level.

Appendix E provides guidance on performing MSA analyses. For TCLP mercury determinations, MSA spikes must be added prior to sample preparation.

11.3. To facilitate the early identification of QC failures and samples requiring rerun it is strongly recommended that sample data be reviewed periodically throughout the run.

11.4. Guidelines are provided in the appendices on procedures to minimize contamination of samples and standards, preventive maintenance and troubleshooting.

11.5. One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo and is approved by a Technical Specialist and QA Manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file.

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

12. DATA ANALYSIS AND CALCULATIONS

12.1. ICV percent recoveries are calculated according to the equation:

$$\%R = 100\left(\frac{Found(ICV)}{True(ICV)}\right)$$

12.2. CCV percent recoveries are calculated according to the equation:

$$\%R = 100\left(\frac{Found(CCV)}{True(CCV)}\right)$$

12.3. Matrix spike recoveries are calculated according to the following equation:

$$\%\ R\ =\ 100\left(\frac{SSR-SR}{SA}\right)$$

Where:

SSR = Spike Sample Result
SR = Sample Result
SA = Spike Added

12.4. The relative percent difference (RPD) of matrix spike/matrix spike duplicates or sample duplicates are calculated according to the following equations:

$$RPD = 100\left[\frac{|MSD-MS|}{\left(\frac{MSD+MS}{2}\right)}\right]$$

Where:

MS = determined spiked sample concentration
MSD = determined matrix spike duplicate concentration

$$RPD = 100\left[\frac{|DU1-DU2|}{\left(\frac{DU1+DU2}{2}\right)}\right]$$

Where:

DU1 = Sample result
DU2 = Sample duplicate result

12.5. For automated determinations, the final concentration determined in solid samples when reported on a dry weight basis is calculated as follows:

$$mg/kg,\ dry\ weight = \ (C \times V \times D)/(W \times S)$$

Where:

C = Concentration (ug/L) from instrument readout
V = Volume of digestate (L)
D = Instrument dilution factor
W = Weight in g of wet sample digested
S = Percent solids/100

Note: A Percent Solids determination must be performed on a separate aliquot when dry weight concentrations are to be reported. If the results are to be reported on a wet weight basis, the "S" factor should be omitted from the above equation.

12.6. For manual (total) determinations, the final concentration determined in solid samples when reported on a dry weight basis is calculated as follows:

$$mg/kg,\ dry\ weight = \quad (C)/(W \times S)$$

Where:
C = Concentration (ug) from instrument readout
W = Weight in g of wet sample digested
S = Percent solids/100

Note: A Percent Solids determination must be performed on a separate aliquot when dry weight concentrations are to be reported. If the results are to be reported on a wet weight basis, the "S" factor should be omitted from the above equation.

12.7. The LCS percent recovery is calculated according to the following equation:

$$\%R = 100\left(\frac{Found(LCS)}{True(LCS)}\right)$$

12.8. Sample results should be reported with up to three significant figures in accordance with the STL North Canton significant figure policy.

13. METHOD PERFORMANCE

13.1. Each laboratory must have initial demonstration of performance data on file for each analyte of interest as described in Section 9.1.

13.2. Method performance is determined by the analysis of method blank, laboratory control sample, matrix spike and matrix spike duplicate samples. The matrix spike recovery should fall within +/- 30 % and the matrix spike duplicates should compare within 20% RPD. The method blanks must meet the criteria in Section 9.4. The laboratory control sample should recover within 20% of the true value until in house limits are established.

13.3. Training Qualification:

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

14. POLLUTION PREVENTION

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

15. WASTE MANAGEMENT

15.1. Waste generated in the procedure must be segregated and disposed according to the facility hazardous waste procedures. The Environmental Health and Safety Director should be contacted if additional information is required.

16. REFERENCES

16.1. Test Methods for Evaluating Solid Waste , Physical/Chemical Methods, SW-846, 3rd Edition, Final Update II, Revision I, September 1994, Method 7471A (Mercury).

16.2. "Methods for the Chemical Analysis of Water and Wastes", EPA-600/4-79-020, U.S.EPA, August 1983, Method 245.5.

16.3. U.S.EPA Statement of Work for Inorganics Analysis, ILMO3.0.

16.4. QA-003, STL 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 7471A and 245.5.

17.1.1.1. A potassium persulfate oxidation step has been included to facilitate the breakdown of organic mercurials which are not completely oxidized by potassium permanganate. Use of potassium persulfate in combination with the permanganate improves the recovery of mercury from organo-mercury compounds. The use of persulfate has been incorporated in several recent EPA mercury protocols.

17.1.1.2. The alternate run sequence presented in Section 11.2.11 is consistent with method requirements. An additional QC analysis (CRA) was added to accommodate the CLP protocol requirements.

17.1.2. Modifications from Method 7471A

17.1.2.1. Chapter 1 of SW846 specify the use of reagent water with a purity equivalent to ASTM Type II water. This SOP specifies the use of a Millipore DI system or equivalent to produce reagent water. This SOP requires that reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks.

17.1.2.2. Chapter 1 of SW-846 states that the method blank should not contain any analyte of interest at or above the MDL. This SOP states that the method blank must not contain any analyte of interest at or above the reporting limit.

17.1.3. Modifications from 245.5

17.1.3.1. Method 245.5 Section 9.3 states concentrations should be reported as follows: Between 0.1 and 1 ug/g, to the nearest 0.01 ug; between 1 and 10 ug/g, to the nearest 0.1ug; above 10 ug/g, to the nearest ug. STL North Canton reports all Hg results under this SOP to two significant figures.

17.2. Modifications from previous SOP

17.2.1. Section 1.4 reporting limit changed form 0.1 mg/kg based on a 0.2 g to 0.3 mg/kg based on a 0.6 g sample aliquot

17.2.2. Section 9.3 added MS and MSDs as not counted in determination of preparation batches.

17.3. Facility Specific SOPs

Each facility shall attach a list of facility specific SOPs or approved attachments (if applicable) which are required to implement this SOP or which are used in conjunction with this SOP. If no facility specific SOPs or amendments are to be attached, a statement must be attached specifying that there are none. Refer to the Appendices for any facility specific information required to support this SOP.

17.4. Documentation and Record Management

The following documentation comprises a complete CVAA raw data package:

- Raw data (direct instrument printout)
- Run log printout from instrument software where this option is available or manually generated run log. (A bench sheet may be substituted for the run log as long as it contains an accurate representation of the analytical sequence).
- Data review checklist - See Appendix B
- Standards Documentation (source, lot, date).
- Copy of digestion log.

Non-conformance summary (if applicable).

Figure 1. Solid Sample Preparation for Mercury - Water Bath Procedure

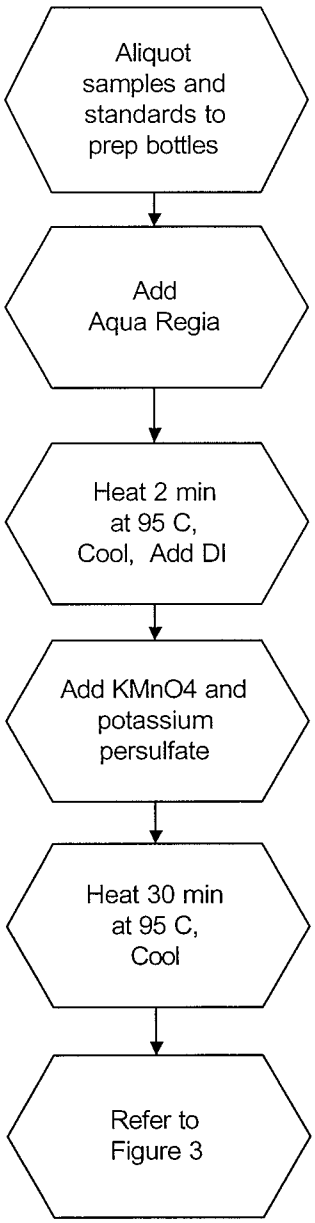
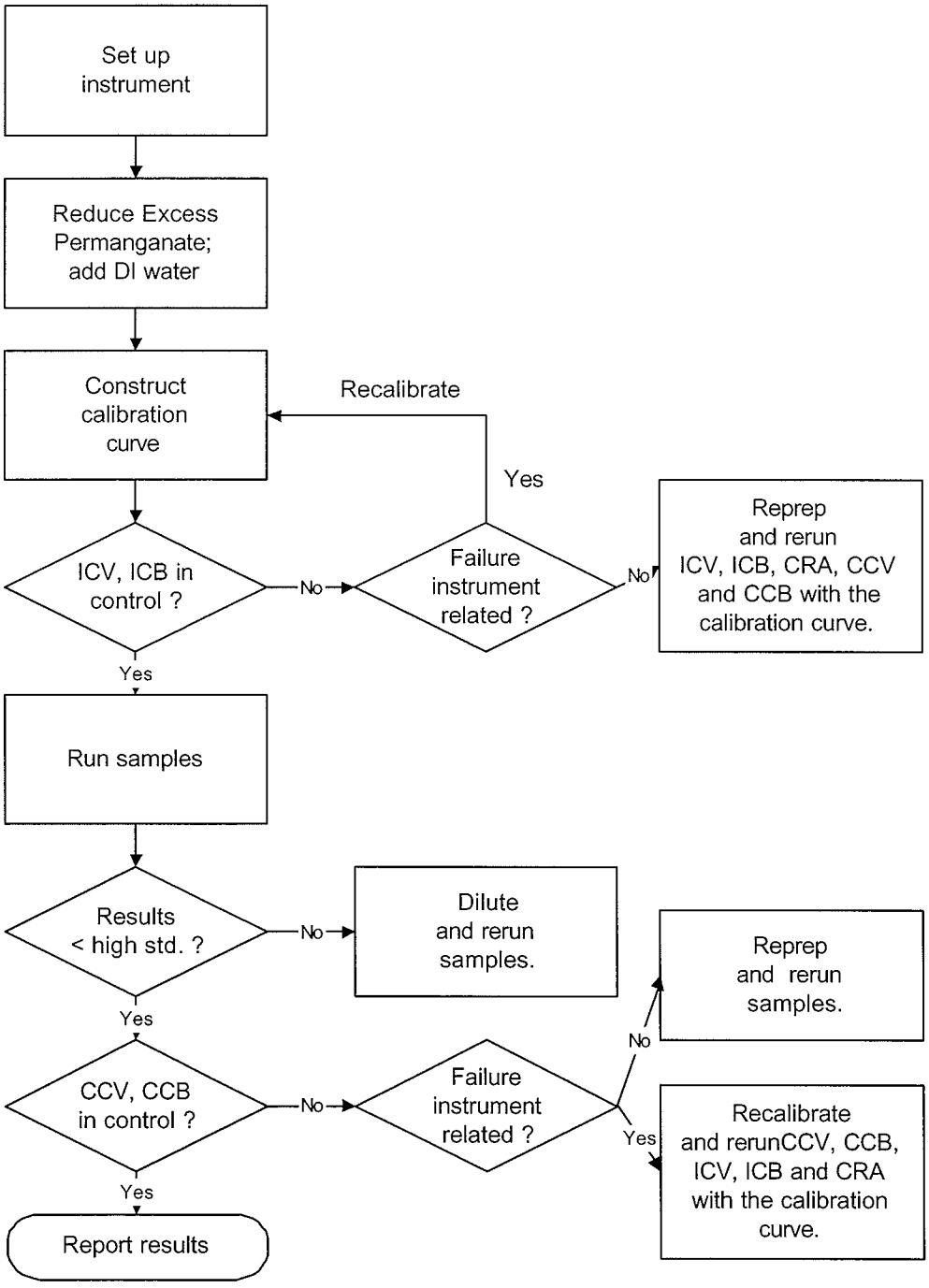


Figure 2. CVAA Mercury Analysis



APPENDIX A

TABLES

TABLE I . MERCURY REPORTING LIMITS, CALIBRATION STANDARD*, QC STANDARD AND SPIKING LEVELS

Soil RL (mg/kg)	0.1
Std 0 (mg/L)	0
Std 1 (mg/L)	0.0002
Std 2 (mg/L)	0.0005
Std 3 (mg/L)	0.001
Std 4 (mg/L)	0.005
Std 5 (mg/L) **	0.010
ICV (mg/L)	0.001 or 0.0025 ***
CCV/LCS (mg/L)	0.0025 or 0.005 ***
MS (mg/L)	0.001

* **SOP specified calibration levels must be used unless prevented by the instrument configuration or client specific requirements. Deviations from specified calibration levels must be documented in the facility specific instrument operation SOP and must be approved by the facility technical manager and Quality Assurance Manager.**

** **Optional standard which may be used to extend the calibration range as allowed by the instrument configuration. If the instrument configuration prevents the use of 6 standards, the 2 ppb standard may be eliminated in favor of the 10 ppb standard.**

*** **Concentration level dependent on high calibration standard used. CCV must be 50% of the high standard concentration and the ICV must be 20-25% of the high standard concentration.**

TABLE II. Summary Of Quality Control Requirements

QC PARAMETER	FREQUENCY *	ACCEPTANCE CRITERIA	CORRECTIVE ACTION
ICV	Beginning of every analytical run.	90-110 % recovery.	Terminate analysis; Correct the problem; Recalibrate or reprep with calibration curve (see Section 9.7).
ICB	Beginning of every analytical run, immediately following the ICV.	The result must be within +/- RL from zero.	Terminate analysis; Correct the problem; Recalibrate or reprep with calibration curve (see Section 9.7).
CCV	Every 10 samples and at the end of the run.	80 - 120 % recovery.	Terminate analysis; Correct the problem; Recalibrate and rerun all samples not bracketed by acceptable CCV or reprep with calibration curve (see Section 9.8).
CCB	Immediately following each CCV.	The result must be within +/- RL from zero.	Terminate analysis; Correct the problem; Recalibrate and rerun all samples not bracketed by acceptable CCB or reprep with calibration curve (see Section 9.8).
Method Blank	One per sample preparation batch of up to 20 samples.	The result must be less than or equal to the RL. Sample results greater than 20x the blank concentration are acceptable. Samples for which the contaminant is < RL do not require redigestion (See Section 9.4)	Redigest and reanalyze samples. Note exceptions under criteria section. See Section 9.4 for additional requirements.

*See Sections 11.2.10 and 11.2.11 for exact run sequence to be followed.

TABLE II. Summary of Quality Control Requirements (Continued)

QC PARAMETER	FREQUENCY	ACCEPTANCE CRITERIA	CORRECTIVE ACTION
Laboratory Control Sample (LCS)	One per sample preparation batch of up to 20 samples.	Aqueous LCS must be within 80 - 120% recovery or in-house control limits.	Terminate analysis; Correct the problem; Redigest and reanalyze all samples associated with the LCS (see Section 9.5).
Matrix Spike	One per sample preparation batch of up to 20 samples.	75 - 125 % recovery or in-house control limits. If the MS/MSD is out for an analyte, it must be in control in the LCS.	In the absence of client specific requirements, flag the data; no flag required if the sample level is > 4x the spike added. (see Section 9.6) For TCLP see Section 11.3.12
Matrix Spike Duplicate	See Matrix Spike	75 - 125 % recovery or in-house control limits; RPD ≤ 20%. (See MS)	See Corrective Action for Matrix Spike.

APPENDIX B

EXAMPLE
STL NORTH CANTON Hg DATA REVIEW CHECKLIST

Example
STL North Canton Hg Data Review Checklist

Run/Project Information

Run Date: _____ **Analyst:**_____ **Instrument:**_____
Prep Batches Run:_____

Circle Methods used: **7470A / 245.1 :** CORP-MT-0005 Rev 1 **7471 / 245.5 :** CORP-MT-0007 Rev 1
CLP - AQ : CORP-MT-0006 Rev 0 **CLP - SOL :** CORP-MT-0008 Rev 0

Review Items

A. Calibration/Instrument Run QC	Yes	No	N/A	2ndLevel
1. Instrument calibrated per manufacturer's instructions and at SOP specified levels ?				
2. ICV/CCV analyzed at appropriate frequency and within control limits?				
3. ICB/CCB analyzed at appropriate frequency and within +/- RL or +/- CRDL (CLP)?				
4. CRA run (CLP only)?				
B. Sample Results				
1. Were samples with concentrations > the high calibration standard diluted and reanalyzed?				
2. All reported results bracketed by in control QC ?				
3. Sample analyses done within holding time?				
C. Preparation/Matrix QC				
1. LCS done per prep batch and within QC limits ?				
2. Method blank done per prep batch and < RL or CRDL (CLP) ?				
3. MS run at required frequency and within limits ?				
4. MSD or DU run at required frequency and RPD within SOP limits?				
D. Other				
1. Are all nonconformances documented appropriately ?				
2. Current IDL/MDL data on file?				
3. Calculations and Transcriptions checked for error ?				
4. All client/ project specific requirements met?				
5. Date of analysis verified as correct ?				

Analyst: _____ **Date:**_____
Comments:
_____
_____
_____

2nd Level Reviewer : _____ **Date:**_____
_____
_____
_____

APPENDIX C

MSA GUIDANCE

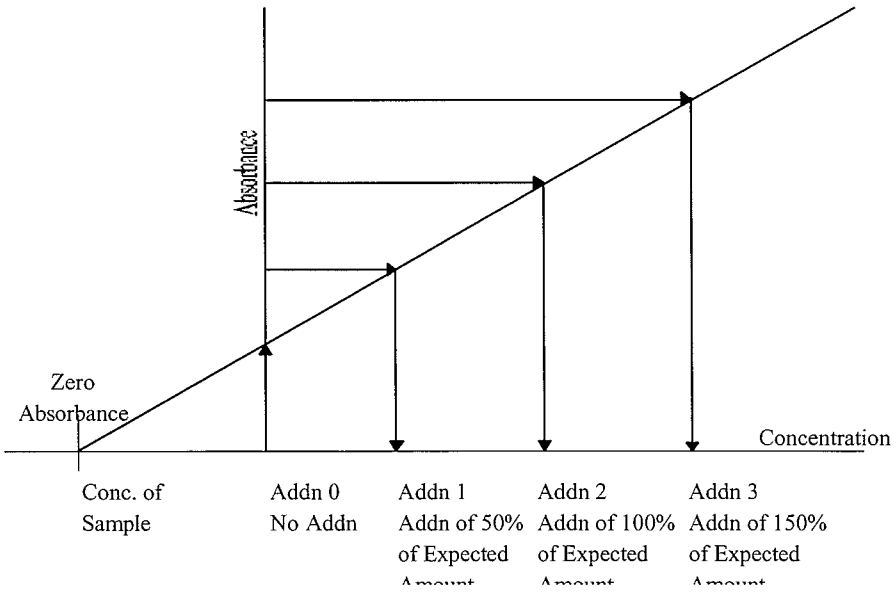
APPENDIX C. MSA GUIDANCE

Method of Standard Addition

Four equal volume aliquots of sample are measured and known amounts of standards are added to three aliquots. The fourth aliquot is the unknown and no standard is added to it. The concentration of standard added to the first aliquot should be 50% of the expected concentration. The concentration of standard added to the second aliquot should be 100% of the expected concentration and the concentration of standard added to the third aliquot should be 150% of the expected concentration. The volume of the unspiked and spiked aliquots should be the same (i.e., the volume of the spike added should be negligible in relation to the volume of sample).

To determine the concentration of analyte in the sample, the absorbance (or response) of each solution is determined and a linear regression performed. On the vertical axis the absorbance (or response) is plotted versus the concentrations of the standards on the horizontal axis using 0 as the concentration of the unspiked aliquot. An example plot is shown in Figure 1. When the resulting line is extrapolated back to zero absorbance, the point of interception of the horizontal axis is the concentration of the unknown. Calculate the correlation coefficient (r) and the x-intercept (where y=0) of the curve. The concentration in the digestate is equal to the negative x-intercept.

Figure 1



- For the method of standard additions to be correctly applied, the following limitations must be taken into consideration.
- The plot of the sample and standards must be linear over the concentration range of concern. For best results, the slope of the curve should be similar to that of a plot of the aqueous standard curve.
- The effect of the interference should not vary as the ratio of the standard added to the sample matrix changes.

APPENDIX D

TROUBLESHOOTING GUIDE

APPENDIX D. TROUBLESHOOTING GUIDE

Problem	Possible Cause
Poor or No Absorbance or Sensitivity Check failed	Incorrect wavelength Dirty windows Window loose Etched or dirty optics Wrong lamp Bad lamp Not enough or no sample introduced Empty sample cup Incorrectly made standards Gas leak EDL power supply set on "Continuous"
Erratic Readings	Source lamp not aligned properly Lamp not prewarmed Injection tip partially clogged Contaminated reagents Contaminated glassware Drying tube saturated Bad lamp Injection tip hitting outside of tube Injection tip coated or not set properly Leak in sample tubing Power fluctuations Air bubbles in tubing
EDL Won't Light	Lamp cable not plugged in Lamp power set at 0 Lamp is dead Power supply fuse is blown Short in cord
Standards reading twice or half normal absorbance or concentration	Incorrect standard used Incorrect dilution performed Dirty cell
Background Correction Light Blinking	Background screen or attenuator faulty

APPENDIX E

CONTAMINATION CONTROL GUIDELINES

APPENDIX E. CONTAMINATION CONTROL GUIDELINES

The following procedures are strongly recommended to prevent contamination:

All work areas used to prepare standards and spikes should be cleaned before and after each use.

All glassware should be washed with detergent and tap water and rinsed with 1:1 nitric acid followed by deionized water.

Proper laboratory housekeeping is essential in the reduction of contamination in the metals laboratory. All work areas must be kept scrupulously clean.

Powdered or Latex Gloves must not be used in the metals laboratory since the powder contains silica and zinc, as well as other metallic analytes. Only vinyl or nitrile gloves should be used in the metals laboratory.

Glassware should be periodically checked for cracks and etches and discarded if found. Etched glassware can cause cross contamination of any metallic analytes.

Autosampler trays should be covered to reduce the possibility of contamination. Trace levels of elements being analyzed in the samples can be easily contaminated by dust particles in the laboratory.

The following are helpful hints in the identification of the source of contaminants:

Reagents or standards can contain contaminants or be contaminated with the improper use of a pipette.

Improper cleaning of glassware can cause contamination.

Separate glassware if an unusually high sample is analyzed and soak with sulfuric acid prior to routine cleaning.

APPENDIX F

PREVENTIVE MAINTENANCE

APPENDIX F. PREVENTIVE MAINTENANCE

A maintenance log is used to record when maintenance is performed on instruments. When an instrument problem occurs indicate the date, time and instrument number, then identify the problem and corrective action in the maintenance log.

The following procedures are required to ensure that that the instrument is fully operational.

Cold Vapor Atomic Absorption (Leeman PS 200) [1]

Daily	Semi-annually	Annually
Clean lens.	Check Hg lamp intensity.	Change Hg lamp.
Check aperture.		Check liquid/gas separator.
Check argon flow.		
Check tubing.		
Check drain.		
Replace drying tube.		

Cold Vapor Atomic Absorption (PE 5000) [1]

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

APPENDIX G

INSTRUMENT SET UP

Hg Analysis (Leeman PS200II)

SYSTEM INITIALIZATION AND WARM UP

1. F1 Menu
2. Instrument

a. Taskmaster

b. #4 Wake System Up Enter

The warming up period takes approximately 10 minutes.

TO SET UP INSTRUMENT FOR ANALYSIS

1. F1 Menu
2. Autosampler
    A. Rack Entry
    B. Edit (ex. Rack 1), Enter
    C. Cup ID - Enter (clears sample #'s)
    D. Extended ID- type in matrix of sample (water or solid), Enter.
    E. Press Insert Key and move cursor with arrows to cup ID and begin typing labels.
    F. F3 Print Screen
3. Press F2 Macro key and type in analyst's first name - Enter
    A. Enter folder name - ex. HG0306, Enter. If folder does not exist, type Y - Enter.
    B. Type in - "Rack 1", "Rack 2" etc. , Enter.

D. Type in : FROM CUP TO CUP

Ex. = 1 30

Do the same for position 2 if needed. If not needed, you must press Enter 3 times to begin analysis.

STL NORTH CANTON STANDARD OPERATING PROCEDURE

TITLE: EXTRACTION AND CLEANUP OF ORGANIC COMPOUNDS FROM WATERS AND SOILS, BASED ON SW-846 3500 SERIES, 3600 SERIES, 8151A AND 600 SERIES METHODS.

(SUPERSEDES: Revision 3.8 (Dated 05/23/01)

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Laboratory Director Date

Approved by: _____
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Table A4 Herbicide matrix spike and LCS components

1. SCOPE AND APPLICATION

This SOP describes procedures for preparation (extraction and cleanup) of semivolatile organic analytes in aqueous, TCLP leachate, and soil matrices for analysis by Gas Chromatography (GC) and Gas Chromatography / Mass Spectrometry (GC/MS). The procedures are based on SW-846 and 600 series methodology and are applicable for measurements made to comply with the Resource Conservation and Recovery Act (RCRA) and for wastewater testing.

1.1. Extraction procedures for the following determinative methods are covered:
8081A, 8082, 8141A, 8151B, 8270C, 8310, 8015B, 8100, 608, 610, and 625

1.2. The extraction procedures here may be appropriate for other determinative methods when appropriate spiking mixtures are used.

1.3. Other extraction procedures (PFE, SPE, accelerated Soxhlet, etc.) may be used but are not currently covered in this SOP.

1.4. The applicable LIMS method codes are: P2 (8141A), QJ (8081A), QS (8151A), QL (8270C), SG (8310), DM (608), VT (610), DP (625), A1 (8100), HS (8015B)

2. SUMMARY OF METHOD

2.1. Separatory Funnel Extraction

A measured volume of sample, typically 1 liter, is adjusted, if necessary, to a specified pH and serially extracted with methylene chloride using a separatory funnel.

2.2. Continuous Liquid/Liquid Extraction

A measured volume of sample, typically 1 liter, is placed into a continuous liquid/liquid extractor, adjusted, if necessary, to a specific pH and extracted with methylene chloride for 18-24 hours.

2.3. Sonication Extraction

A measured weight of sample, typically 30 g, is mixed with anhydrous sodium sulfate to form a free flowing powder. This is solvent extracted three times using an ultrasonic horn.

2.4. Soxhlet Extraction

A 30 g sample is mixed with anhydrous sodium sulfate to form a free flowing powder. This is extracted with refluxing solvent.

2.5. Cleanup and Concentration

Procedures are presented for removing interferents from sample extracts, and for drying and concentration of the extract to final volume for analysis.

2.6. Phenoxy acid herbicide extractions

Procedures for the extraction and cleanup of phenoxy acid herbicides are presented in Appendix A.

3. DEFINITIONS

Definitions of terms used in this SOP may be found in the glossary of the STL North Canton Laboratory Quality Manual (LQM), current version .

4. INTERFERENCES

4.1. Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus. All these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. Specific selection of reagents may be required to avoid introduction of contaminants.

4.2. Visual interferences or anomalies (such as foaming, emulsions, odor, etc.) must be documented.

5. SAFETY

5.1. Procedures shall be carried out in a manner that protects the health and safety of all STL North Canton associates. The following requirements must be met:

5.2. Eye protection that satisfies ANSI Z87.1 (as per the Chemical Hygiene Plan), laboratory coat and appropriate gloves must be worn while samples, standards, solvents and reagents are being handled. Disposable gloves that have become contaminated will be removed and discarded, other gloves will be cleaned immediately. Viton gloves may be worn when halogenated solvents are used for extractions or sample preparation. Nitrile gloves may be used when other solvents are handled. [Note: VITON is readily degraded by acetone]. When good manual dexterity is needed, for example, when handling small quantities/containers, disposable gloves (such as latex or N-DEX®) shall be used. While these gloves protect against splashes, they give little or no protection against contact with large quantities of solvent, and no protection against spills or immersion.

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

Chemicals that have been classified as **carcinogens** or **potential carcinogens** under OSHA include methylene chloride, PCBs, certain pesticides.

The following materials are known to be **corrosive**: Concentrated sulfuric acid, sodium hydroxide, 1N nitric acid.
Sulfuric acid cleanup must not be performed on any matrix that may have water present as a violent reaction between the acid and water may result in acid exploding out of the vessel.

Chemicals known to be **flammable** are: Diethyl ether, acetone, hexane, 2-propanol.
Mercury is a highly toxic compound that must be handled with care. The analyst must be aware of the appropriate handling and clean-up techniques before handling this material.

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

5.5. The preparation of standards and reagents and glassware cleaning procedures that involve solvents such as methylene chloride will be conducted in a fume hood with the sash closed as far as the operations will permit. Use of methylene chloride for glassware cleaning should be avoided as far as possible. If more than 500 mL of Methylene chloride is spilled, evacuate the area until the area has been cleaned by a Hazardous Material Team.

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

6. EQUIPMENT AND SUPPLIES

6.1. Glassware should be cleaned with soap and water, rinsed with water and dried in an oven at 400°C for at least 2 hours. Alternatively the glassware can be solvent rinsed with acetone or methanol followed by methylene chloride after the water rinse.

6.2. Equipment and supplies for extraction procedures

EQUIPMENT AND SUPPLIES	Sep fun.	CLLE	Soni	Sox	Conc
Separatory Funnel: 2 L	√				
Separatory Funnel Rack	√				
Balance: >1400 g capacity, accurate ±1 g	√	√			
pH indicator paper, wide-range: covers extraction pH	√	√			
Graduated cylinder: 1 liter. (other sizes may be used)	√	√			
Erlenmeyer Flask or Fleaker: 125 & 300 mL (other sizes optional)	√		√		
Centrifuge	√				
Auto-Shaker	√				
Methylene Chloride Collection Tank	√	√			
Solvent Dispenser Pump or 100 mL Graduated Cylinder	√		√		
Continuous Liquid/Liquid Extractor		√			
Round or flat Bottom: 250, 500 mL or 1 L		√			
Boiling Chips: Contaminant free, approximately 10/40 mesh		√		√	√

EQUIPMENT AND SUPPLIES	Sep fun.	CLLE	Soni	Sox	Conc
(Teflon® PTFE, carbide or equivalent).					
Cooling Condensers		√		√	
Heating Mantle: Rheostat controlled		√		√	
Auto-timer for heating mantle		√		√	
Beakers: 250 & 400 mL, graduated			√		
Balance: >100 g capacity, accurate ±0.1 g			√	√	
Soxhlet Extractor				√	
Sonicator (at least 300 watts)			√		
Sonicator horn, 3/4 inch			√		
Kuderna-Danish (K-D) Apparatus: 500 mL					√
Concentrator Tube: 10 mL, attached to K-D with clips					√
Supply Manifold: Heated, capable of temperature control (± 5°C) up to 95°C.					√
MegaCT: 150 ml					√
Snyder Column: Three-ball macro					√
Water Bath: Heated, with concentric ring cover, capable of temperature control (± 5°C) up to 95°C. The bath must be used in a hood or with a solvent recovery system.					√
Vials: Glass, 2 mL, 4 mL, and 10 mL capacity with Teflon®-lined screw-cap					√
Nitrogen Blowdown Apparatus					√
Nitrogen: reagent grade.					√
Culture tubes: 10 mL, 16 mmx100 mm					√
Syringe: 1 mL	√	√	√	√	
Phase Separation Paper	√	√	√	√	
Glass Wool	√	√	√	√	
Glass Funnel: 75 X 75 mm	√	√	√	√	√
Disposable Pipets	√	√	√	√	√
Aluminum foil	√	√	√	√	√
Paper Towels	√	√	√	√	√
Wrist Shaker					

6.3. Equipment and Supplies for Cleanup Procedures

EQUIPMENT AND SUPPLIES	GPC	Florisil	Sulfur	Acid	A/B	*FC*
Gel permeation chromatography system (GPC Autoprep Model 1002A or 1002B Analytical Biochemical Laboratories, Inc. or Zymark Benchmate or equivalent).	√					
Bio Beads: (S-X3) -200-400 mesh, 70 gm (Bio-Rad Laboratories, Richmond, CA, Catalog 152-2750 or equivalent).	√					
Chromatographic column: 700 mm x 25 mm ID glass column. Flow is upward.	√					
Ultraviolet detector: Fixed wavelength (254 nm) and a semi-prep	√					

EQUIPMENT AND SUPPLIES	GPC	Florisil	Sulfur	Acid	A/B	*FC*
flow-through cell.						
Strip chart recorder, recording integrator, or laboratory data system.	√					
Syringe: 10 mL with Luerlok fitting.	√					
Syringe filter assembly, with disposable 5 um filter discs, Millipore No. LSWP 01300 or equivalent.	√					
Chromatographic column: 250 mm long x 10 mm ID; with Pyrex glass wool at the bottom and a Teflon stopcock (for silica gel cleanup).	√					
Vacuum system for eluting multiple cleanup cartridges. Vac Elute Manifold - Analytichem International, J.T. Baker, or Supelco (or equivalent). The manifold design must ensure that there is no contact between plastics containing phthalates and sample extracts.		√				
Vacuum trap made from a 500 mL sidearm flask fitted with a one-hole stopper and glass tubing.		√				
Vacuum pressure gauge.		√				
Rack for holding 10 mL volumetric flasks in the manifold.		√				
Mechanical shaker or mixer: Vortex Genie or equivalent.			√	√		
Separatory Funnels with Ground-Glass Stoppers: 250 mL					√	
Erlenmeyer Flasks: 125 mL					√	
Disposable Pipets		√	√	√	√	√
Culture tubes: 10 mL, 16 mmx100 mm	√	√	√	√	√	√

7. REAGENTS AND STANDARDS

7.1. Reagents for Extraction Procedures

All reagents must be ACS reagent grade or better unless otherwise specified.

REAGENTS	Sep fun.	CLLE	Soni	Sox	Conc
Sodium hydroxide (NaOH), Pellets: Reagent Grade	√	√			
Sodium hydroxide solution, 10 N: Dissolve 40 g of NaOH in reagent water and dilute to 100 mL.	√	√			
Sulfuric acid (H_2SO_4), Concentrated: Reagent Grade	√	√			
Sulfuric acid (1:1): Carefully add 500 mL of H_2SO_4 to 500 mL of reagent water. Mix well.	√	√			
Hydrochloric Acid (HCl)					
Organic free reagent water.	√	√			
Sodium sulfate (Na_2SO_4), Granular, Anhydrous: Purify by heating at 400°C a minimum of two hours.	√	√	√	√	√
Extraction/Exchange Solvents: Methylene chloride, hexane, acetonitrile, acetone, pesticide quality or equivalent	√	√	√	√	√

REAGENTS	Sep fun.	CLLE	Soni	Sox	Conc
Acetone: Used for cleaning	√	√	√	√	√

7.2. Reagents for Cleanup Procedures

REAGENTS	GPC	Florisil	Sulfur	Acid	A/B	*FC*
Florisil: 500 mg or 1 g cartridges with stainless steel or Teflon frits (calalog 694-313, Analytichem, 24201 Frampton Ave., Harbor City, CA, or equivalent.)		√				
Mercury: triple distilled			√			
Tetrabutylammonium hydrogen sulfate			√			
Sodium sulfite			√			
Tetrabutylammonium (TBA) sulfite reagent: Prepare reagent by dissolving 3.39 g of Tetrabutylammonium hydrogen sulfate in 100 mL organic-free reagent water. Extract this solution 3 times with 20 mL portions of hexane. Discard the hexane extracts. Add 25 g sodium sulfite to the water solution.			√			
2-Propanol			√			
Nitric acid: 1N			√			
Copper powder: remove oxides (if powder is dark) by treating with 1N nitric acid, rinse with organic-free reagent water to remove all traces of acid, rinse with acetone, and dry under a stream of nitrogen.			√			
Sulfuric acid, Concentrated				√		
Sodium hydroxide, Pellets					√	
Sodium hydroxide, 10N: Dissolve 40 g of NaOH in 100 mL of reagent water					√	
Sulfuric acid (H_2SO_4), Concentrated: Reagent Grade					√	
Sulfuric acid (1:1): Carefully add 500 mL of H_2SO_4 to 500 mL of reagent water. Mix well.					√	
Fluorocarbon: PF-5080, 3M						√

7.3. Standards

7.3.1. Stock Standards

Stock standards are purchased as certified solutions or prepared from neats. Semivolatile stock standards are stored at $\leq 6^{\circ}C$. All stock standards must be protected from light. Stock standard solutions must be replaced after one year (from the time of preparation, if prepared in house, or from the time the ampoule is opened if purchased.) Standards must be allowed to come to room temperature before use.

7.3.2. Surrogate Spiking Standards

Prepare or purchase surrogate spiking standards at the concentrations listed in Table 5. Surrogate spiking standards are purchased or prepared as dilutions of the stock standards. Surrogate spiking solutions must be refrigerated and protected from light.

The standards must be replaced at least every six months or sooner if there is reason to believe that the standard has degraded or concentrated.

7.3.3. Matrix Spiking and Laboratory Control Spiking Standards.

The same spiking solution is used for the matrix spike and the Laboratory Control Sample. Prepare MS/LCS spiking standards at the concentrations listed in Table 6. Spiking standards are purchased or prepared as dilutions of the stock standards. Spiking solutions must be refrigerated and protected from light. The standards must be replaced at least every six months or sooner if there is reason to believe that the standard has degraded or concentrated.

7.3.4. GPC calibration solution - prepare or purchase a solution in methylene chloride that contains the following analytes in the concentrations listed below:

Analyte	mg/mL
Corn Oil	25.0
Bis (2-ethylhexyl) phthalate	1.0
Methoxychlor	0.2
Perylene	0.02
Sulfur	0.08

NOTE: Sulfur is not very soluble in methylene chloride, however, it is soluble in warm corn oil. Therefore, one approach is to weigh out the corn oil, warm it, and transfer the weighed amount of sulfur into the warm corn oil. Mix it and then transfer into a volumetric flask with methylene chloride, along with the other calibration compounds. This standard has a lifetime of 6 months.

8. SAMPLE COLLECTION PRESERVATION AND STORAGE

8.1. Samples are not chemically preserved.

8.2. Samples are stored at 4°C ± 2°C in glass containers with Teflon®-lined caps.

8.3. Holding Times

8.3.1 Extraction is initiated within 7 days of the sampling date for aqueous samples, 14 days for solid and waste samples.

8.3.2 For TCLP leachates, extraction is initiated within seven days from when the TCLP Leach tumbling has been completed, excluding the filtration step. If the filtration step requires extended times, this time counts as part of the seven day holding time.

8.3.3. Analysis of the extracts is completed within forty days of extraction.

9. QUALITY CONTROL

9.1. Quality Control Batch

The batch is a set of up to 20 samples that are of the same matrix and are processed together using the same procedures and reagents. The batch must contain a method blank, an LCS and a matrix spike / matrix spike duplicate. (In some cases, at client request, it may be appropriate to process a matrix spike and sample duplicate in place of the MS / MSD). If clients specify specific samples for MS/MSD, the batch may contain multiple MS/MSD. See policy QA-003 for further definition of the batch.

9.2. Definition of matrix

The possible matrix types are aqueous, soil, waste and TCLP leachate.

9.3. Insufficient Sample

If insufficient sample is available to process a MS/MSD, then a second LCS must be processed. The LCS pair is then evaluated according to the MS/MSD criteria. Use of a LCS pair in place of a MS/MSD must be documented.

9.4. Sample count

Laboratory generated QC samples (method blanks, LCS, MS/MSD) are not included in the sample count. Field samples are included.

9.5. Method Blank

A method blank consisting of all reagents added to the samples must be prepared and analyzed with each batch of samples. Surrogates are spiked into the method blank at the same level as the samples. The method blank is used to identify any background interference or contamination of the analytical system which may lead to the reporting of elevated concentration levels or false positive data.

9.5.1. Aqueous Method Blanks use 1000 mL of reagent water spiked with the surrogates. The method blank goes through the entire analytical procedure, including any cleanup steps.

9.5.2. Solid method blanks use 30 g of sodium sulfate spiked with the surrogates. The method blank goes through the entire analytical procedure, including any cleanup steps.

9.5.3. TCLP method blanks use 250 mL of leachate fluid (100 mL for herbicides) spiked with the surrogates. The leachate may optionally be diluted to 1000 mL with reagent water. The method blank goes through the entire analytical procedure, including any cleanup steps.

9.6. Laboratory Control Sample (LCS)

Laboratory Control Samples are well-characterized, laboratory generated samples used to monitor the laboratory's day to day performance of routine analytical methods. The LCS, spiked with a group of target compounds representative of the method analytes, is used to monitor the accuracy of the analytical process, independent of matrix effects. On-going

monitoring of the LCS results provides evidence that the laboratory is performing the method within accepted QC guidelines for accuracy and precision. The LCS goes through the entire analytical procedure, including any cleanup steps.

9.6.1. The LCS is made up in the same way as the method blank (See sections 9.5.1 - 9.5.3) but spiked with the LCS standard and the surrogates.

9.7. Surrogates

9.7.1. Surrogates are organic compounds which are similar to the target analyte(s) in chemical composition and behavior in the analytical process, but which are not normally found in environmental samples.

9.7.2. Each applicable sample, blank, LCS and MS/MSD is spiked with surrogate standards. Surrogate spike recoveries must be evaluated by determining whether the concentration (measured as percent recovery) falls within the required recovery limits.

9.8. Matrix Spike/Matrix Spike Duplicate (MS/MSD)

A matrix spike is an environmental sample to which known concentrations of target analytes have been added. A matrix spike duplicate is a second spiked aliquot of the same sample which is prepared and analyzed along with the sample and matrix spike.

9.9. Initial Demonstration of Capability

The initial demonstration and method detection limit studies described in section 13 must be acceptable before analysis of samples may begin.

9.10. Quality Assurance Summaries

Certain clients may require specific project or program QC which may supersede these method requirements. Quality Assurance Summaries (QAS) should be developed to address these requirements.

9.11. STL North Canton QC Program

Further details of QC and corrective action guidelines are presented in the STL North Canton QC Program document (QA-003). Refer to this document if in doubt regarding corrective actions.

10. CALIBRATION AND STANDARDIZATION

10.1. On a weekly basis, measure 1.0 mL of solvent into an autovial using a gastight syringe that is manufactured to a certified volume delivery tolerance of ±0.01 mL (1mL total volume). The "standard" autovial is sealed and the top and bottom of the meniscus are marked. The autovials containing the sample extracts are then compared against the "standard" vial to ensure that the final volume is consistently 1.0 ± 0.01mL. If a new box of autovials are used, then the steps are repeated to further ensure that variations due to vial size and shape are minimized. A log is kept of the lot number of the vials and the day the vials were prepared.

10.2. Refer to section 11.8.1.2. for calibration of the GPC. Otherwise this section is not applicable.

11. PROCEDURE

Procedures for separatory funnel liquid/liquid extraction (11.2), continuous liquid/liquid extraction (11.3), sonication extraction (11.4), soxhlet extraction (11.5), waste dilution (11.6), extract concentration (11.7), and extract cleanup (11.8) are presented in this section.

11.1. Procedural Variations

Procedural variations are allowed only if deemed necessary in the professional judgment of the supervisor to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance memo and approved by a supervisor and QA/QC manager. If contractually required, the client will be notified. The Nonconformance memo will be filed in the project file. Any deviations from this procedure identified after the work has been completed must be documented as a nonconformance, with a cause and corrective action described. A Nonconformance memo shall be used for this documentation.

11.2. Separatory Funnel Liquid/Liquid Extraction of Water Samples.

A flow chart for this procedure is included in Section 17.

11.2.1. Measure the initial sample pH with wide-range pH paper and record on the extraction benchsheet. If sample is a leachate (e.g. TCLP), compare the current pH against leachate log, note on the benchsheet if there is any discrepancy.

11.2.2. The normal sample volume is 1 liter. Other sample volumes may be used to obtain specific reporting limits, and reduced sample volumes, diluted to 1 liter with reagent water, may be used for very dirty samples.

11.2.3. Weigh the sample container on a balance (± 1 g), taring the sample and container. Transfer the sample to the separatory funnel. . Add the appropriate volume of surrogate spiking solution (see Table 3). Also add appropriate volume of matrix spiking solution to any matrix spike / matrix spike duplicate samples (see.Table 4) Mix well. If the sample is a 600 series analysis or BP GCLN sample rinse the sample bottle with 60 mL methylene chloride and transfer to the separatory funnel. Reweigh the container. Assume a density of 1 g/mL and record the difference as the sample volume on the benchsheet to the nearest milliliter.

Note: Aqueous samples must be determined volumetrically for Ohio VAP samples.

Warning: Dichloromethane creates excessive pressure very rapidly! Therefore, initial venting should be done immediately after the sample container has been sealed and inverted. Vent into hood away from analysts and other samples.

11.2.3.1. If the entire sample bottle will not be used, transfer the aliquot to the separatory funnel, then add the spiking solutions to the sample in the separatory funnel.

Note: Alternative methods of measurement of sample volume include a) transferring the sample to a measuring cylinder and b) marking a meniscus on the sample bottle and then measuring the volume of water required to fill the bottle to the meniscus after the sample is transferred. The former method is not recommended because of the risk of cross contamination while the latter is not recommended because of poor accuracy. However, either method may be necessary for specific client programs.

11.2.4. Prepare a method blank, LCS and MS/MSD for each batch as specified in section 9 of this SOP. Use 1 L of reagent water for method blanks and LCS. The LCS is spiked with the surrogate and matrix spike solutions, the method blank only with the surrogates.

11.2.5. Use 250 mL of leachate for TCLP pesticides and TCLP semivolatiles, measured in a graduated cylinder. An alternative method would be to tare 400ml beaker on the balance and then add 250g to the beaker. Assume a density of 1g/mL and record the volume on the benchsheet. The leachate may be made up to 1 L in volume with reagent water.

11.2.6. For a TCLP method blank,LCS and LCS Dup measure 250 mL of the buffer solution used in the leaching procedure and transfer to the separatory funnel. Add 60 mL of methylene chloride to the separatory funnel. The TCLP leachate may be diluted to approximately 1 liter before extraction if desired.

11.2.7. Adjust sample pH as indicated in Table 1 for the initial extraction. Use the minimum amount of 1:1 H_2SO_4 or 10 N NaOH necessary. Recheck the sample with pH paper by dipping a disposable pipette into the sample and wetting the pH paper. Record adjusted pH, spiking volumes and standard numbers on the benchsheet. Return spiking solutions to the refrigerator as soon as possible.

11.2.8. Seal and shake or rotate the separatory funnel vigorously for 2 minutes with periodic venting to release excess pressure. An autoshaker may be used to shake and rotate the separatory funnel.

Warning: Dichloromethane creates excessive pressure very rapidly! Therefore, initial venting should be done immediately after the separatory funnel has been sealed and inverted. Vent into hood away from analysts and other samples.

11.2.9. Allow the organic layer to separate from the water phase until complete visible separation has been achieved (approximately 10 minutes). If the emulsion interface between layers is more than one-third the size of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample and may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods. If the emulsion cannot be broken (recovery of <80% of the methylene chloride*), transfer the sample, solvent, and emulsion into the extraction chamber of a continuous extractor and proceed as

described in continuous liquid-liquid extraction (Section 11.2.). If this is done, the sample must be extracted as part of a valid CLLE batch.

*Note: 15 - 20 mL of methylene chloride is expected to dissolve in 1 L of water. Thus, solvent recovery could be as low as 35 mL from the first shake and still be acceptable. Subsequent shakes should recover at least 50 mL of solvent.

11.2.10. Fill a funnel with 10-20 g of anhydrous sodium sulfate. The funnel can be plugged with glass wool or filter paper may be used to hold the sodium sulfate. Drain the solvent extract from the separatory funnel through the prepared filtration funnel into a clean glass container. The extract may be drained directly into the KD flask. Close the stopcock just before the water level begins draining out of the separatory funnel. If the sodium sulfate becomes saturated with water add more to the funnel or replace the existing sodium sulfate with fresh drying agent.

11.2.11. Repeat the extraction process two more times using fresh 60 mL portions of solvent, combining the three solvent extracts in the collection container.

11.2.12. If extraction at a secondary pH is required, adjust the pH of the sample in the separatory funnel to the pH indicated in Table 1 with a minimum amount of 10 N NaOH or 1:1 H_2SO_4. Measure with pH paper and record the adjusted pH on the benchsheet. Serially extract with three 60 mL portions of methylene chloride, as outlined in Steps 11.1.7 to 11.1.9. Collect these three extracts in the same container used for the previous fraction.

11.2.13. Rinse the extract residue from the sodium sulfate by pouring 20-30 mL of clean methylene chloride through the funnel and into the collection container.

11.2.14. Dispose of solvent and water remaining in the extractor into the appropriate waste container.

11.2.15. Cover with aluminum foil if the extract is not concentrated immediately. Refer to Section 11.8 for concentration and Section 11.9 for cleanup.

11.3 Short-Term Continuous Liquid-Liquid Extraction

11.3.1 Extraction personnel must first determine if one liter of sample exists in the sample bottle.

11.3.2 Mark the meniscus on the side of the sample bottle for later determination of sample volume.

11.3.3 Add 225 mL methylene chloride to the extractor, turn stopcock to the open position. Connect extractor to a 250 ml boiling flask with boiling chips.

11.3.4 Check the pH of the sample and adjust, if necessary, using 1:1 H2SO4 or 10N sodium

hydroxide. Quantitatively transfer the sample from the sample bottle to the extractor. *Rinse the sample bottle with 25-ml of methylene chloride for BP samples. Pour the rinsate from the sample bottle into the continuous extractor.

11.3.5 Adjust the volume of solvent in the boiling flask by adding reagent water to the extractor, if necessary.

11.3.6 Next, fill the sample bottle to the mark with reagent water. Pour the reagent water into a graduated cylinder. Measure the reagent water to ± 10 ml and document this sample volume on the extraction benchsheet.

11.3.7 Add the appropriate volume of surrogate to each sample and spiking solutions to the MS, MSD, LCS, and/or LCSD in the extractor and mix well.

11.3.8 Extract samples for 12 hours. 8270 extractions will still be performed in two pH extraction steps. Each step will run 6 hours, however, where timing is a factor the samples may be left to extract for longer than 12 hours.

11.3.9 Turn stopcocks to the closed position.

11.3.10 Allow the extractors to run another 5 minutes, then turn off the rheostats and mantles.

11.3.11 The samples will macro concentrate in the CLLE. After the flasks have cooled, continue to concentrate the extracts by KD or QES methodology.

11.3.12 This method of extraction **cannot** be used for method 625, 610 or 608.

11.4 Continuous Liquid/Liquid Extraction from Water Samples.

A flow chart for this procedure is included in Section 17.

11.4.1. Assemble the apparatus. Add 250-400mL of methylene chloride to the extractor body. Add 3 to 5 boiling chips to the round-bottom distilling flask.

11.4.2. Measure the initial sample pH with wide-range pH paper and record on the extraction benchsheet. If sample is a leachate (e.g. TCLP), compare the current pH against leachate log, note on the benchsheet if there is any discrepancy.

11.4.3. Weigh the sample container on a balance (± 1 g), taring the sample and container. Transfer the sample to the continuous liquid/liquid extractor . Add the appropriate volume of surrogate spiking solution (see Table 3). Also add appropriate volume of matrix spiking solution to any matrix spike / matrix spike duplicate samples (see.Table 4) Mix well. If the sample is a 600 series analysis or BP GCLN sample rinse the sample bottle with 60 mL methylene chloride and transfer to the continuous liquid/liquid extractor. Reweigh the container. Assume

a density of 1 g/mL and record the difference as the sample volume on the benchsheet to the nearest milliliter.

Note: Aqueous samples must be determined volumetrically for Ohio VAP samples.

Warning: Dichloromethane creates excessive pressure very rapidly! Therefore, during the rinse for 600 series methodology venting should be done immediately after the sample container has been sealed and inverted. Vent into hood away from analysts and other samples.

11.4.3.1. If the entire sample bottle will not be used, transfer the aliquot to the extractor, then add the spiking solutions to the sample in the extractor.

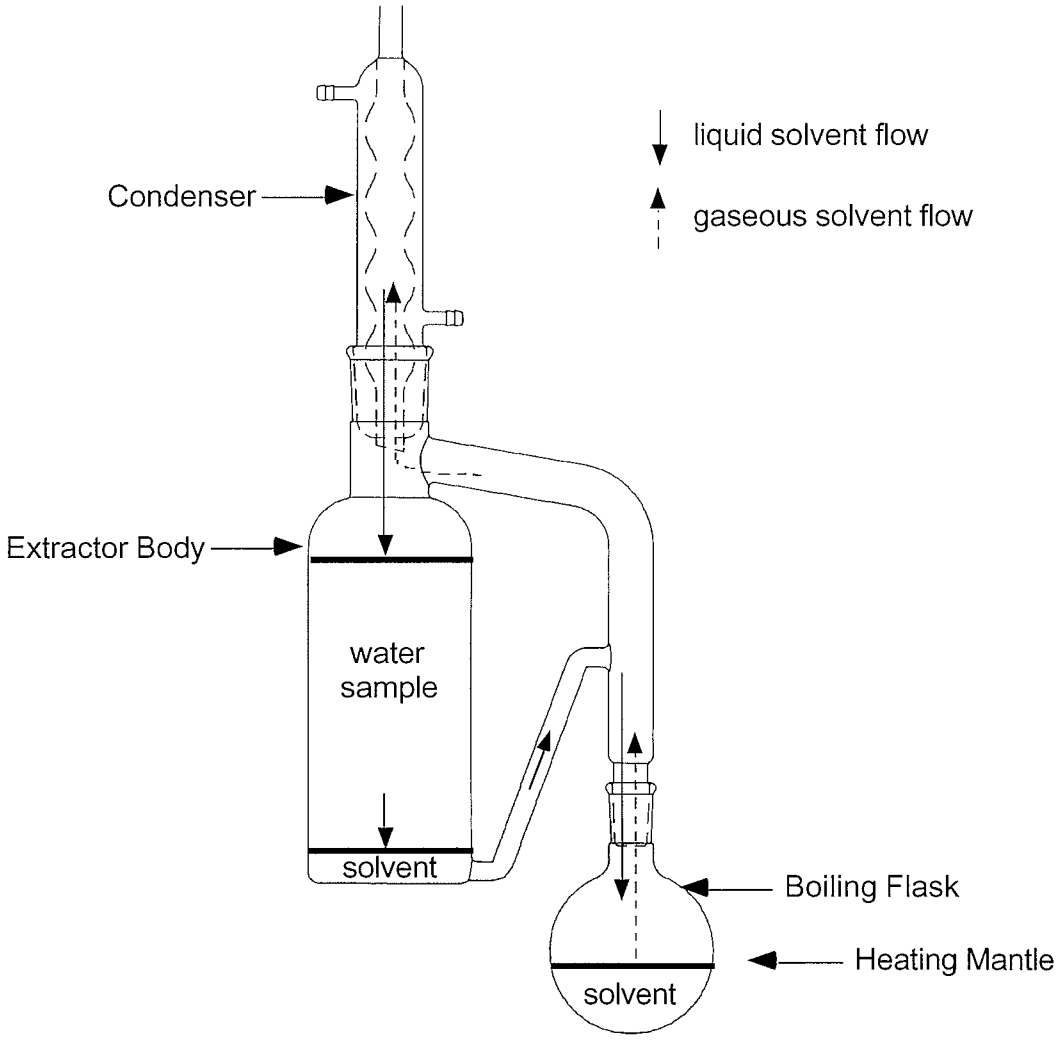
Note: Alternative methods of measurement of sample volume include: a.) transferring the sample to a measuring cylinder and b.) marking a meniscus on the sample bottle and then measuring the volume of water required to fill the bottle to the meniscus after the sample is transferred. The former method is not recommended because of the risk of cross contamination while the latter is not recommended because of poor accuracy. However, either method may be necessary for specific client programs.

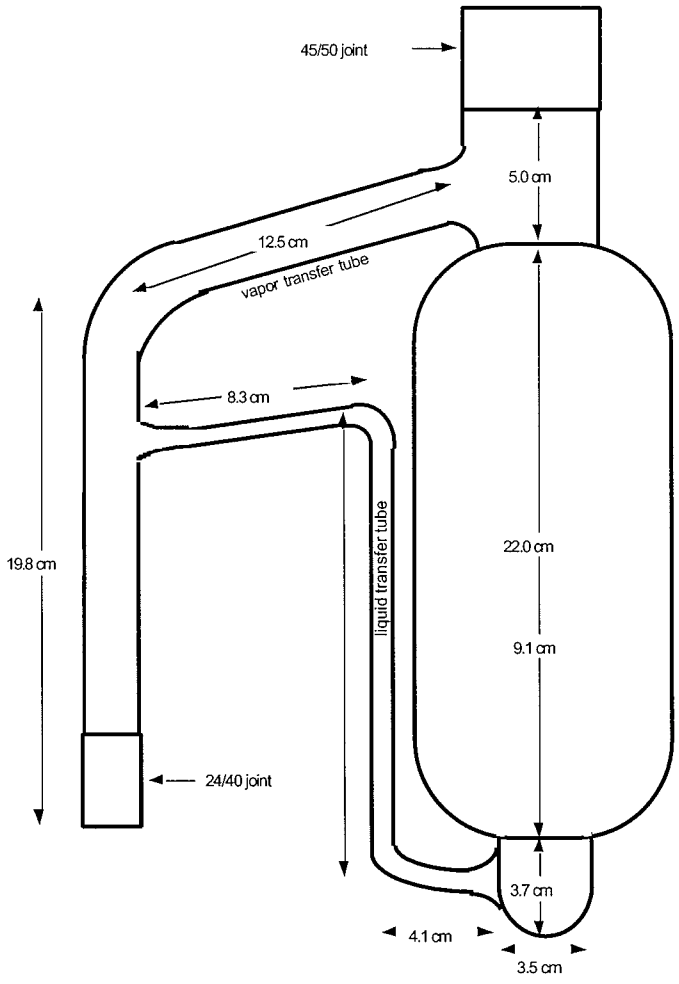
11.4.3.2. Prepare a method blank, LCS and MS/MSD for each batch as specified in section 9 of this SOP. Use 1 L of reagent water for method blanks and LCS. The method blank is spiked with the surrogates, the LCS and matrix spikes with the surrogates and matrix spiking solutions.

11.4.3.3. Use 250mL of leachate for TCLP for TCLP semivolatiles and TCLP pesticides measured in a graduated cylinder. An alternative method would be to tare 400ml beaker on the balance and then add 250g to the beaker. Assume a density of 1g/mL and record the volume on the benchsheet. Dilute to about 1 liter with reagent water.

11.4.3.4. For a TCLP method blank, LCS and LCS Dup measure 250 mL of the buffer solution used in the leaching procedure and transfer to the separatory funnel. Dilute to about 1 liter with reagent water.

11.4.3.5. Less than one liter of sample may be used, for highly contaminated samples, or if the reporting limit can be achieved with less than one liter of sample. In this event dilute the sample to about 1 liter with reagent water.


liquid solvent flow
gaseous solvent flow
Condenser
Extractor Body
water
sample
solvent
Boiling Flask
Heating Mantle
solvent



11.4.4. Adjust sample pH as indicated in Table 1 for the initial extraction. Use the minimum amount of 1:1 H_2SO_4 or 10 N NaOH necessary. Recheck the sample with pH paper. Record adjusted pH, spiking volumes and standard numbers on the benchsheet. Return spiking solutions to the refrigerator as soon as possible.

11.4.5. Add reagent water to the extractor body until approximately 250 mL of methylene chloride is pushed over into the round-bottomed flask to ensure proper operation and solvent cycling. Attach cold condenser (about 10°C). Turn on heating mantle. Inspect joints for leaks once solvent has begun cycling. Extract for 18-24 hours. (24 hours required for 600 series)

11.4.6. If extraction at a secondary pH is required, (see Table 1) turn off the heating mantle and allow the extractor to cool. Detach the condenser and adjust the pH of the sample in the extractor body to the pH indicated in Table 1 with a minimum amount of 10 N NaOH or 1:1 H_2SO_4. Measure with pH paper and record the adjusted pH on the benchsheet. Reattach the condenser and turn on heating mantle. Extract for 18-24 hours.

11.4.7. Turn off the heating mantle and allow the extractor to cool.

11.4.8. Place a funnel containing 10-20 g of anhydrous sodium sulfate on the Kuderna-Danish (K-D) apparatus or other glass container. The funnel can be plugged with glass wool enabling it to hold the granular anhydrous sodium sulfate or phase separation filter paper may be used.

11.4.9. Dry the extract in the round bottom flask by filtering it through the sodium sulfate filled funnel. Note that it is not necessary or advisable to attempt to add the solvent remaining in the continuous extractor body to the extract.

11.4.10. Collect the dried extract in a K-D or other glass container. Rinse the flask which contained the solvent extract with 20-30 mL of methylene chloride and add it to the funnel to complete the quantitative transfer. Dispose of solvent and water remaining in the extractor in the appropriate waste container.

Note: Some types of CLLE apparatus have built in drying columns. If this type of apparatus is used then a drying step subsequent to the extraction may not be necessary.

11.4.11. Cover with aluminum foil if the extract is not concentrated immediately. Refer to Section 11.8 for concentration and Section 11.9 for cleanup.

11.5. Sonication

A flow chart for this procedure is included in Section 17.

11.5.1. Determination of percent moisture (Optional - if a different group performs this test, refer to the facility SOP.)

In some cases, sample results are needed on a dry weight basis. If this is the case, weigh 5-10 g of sample into a suitable tared container (typically an aluminum weigh pan. Determine the % moisture by drying overnight (at least 12 hours) at 105°C. Allow to cool in a desiccator before weighing.

$$\% \text{ Moisture} = \frac{(\text{weight of wet sample} - \text{weight of dry sample})}{\text{weight of wet sample}} \times 100$$

11.5.2. Determination of pH (Optional - if a different group performs this test, refer to the facility SOP.)

If pH determination is required, transfer 10 g of soil to a beaker. Add 10 mL of water. Stir for five minutes then let stand for 1 hour. Determine the pH of the sample with a glass electrode and pH meter.

11.5.3. Decant and discard any water layer on a sediment/soil sample. Record and document if a water layer was discarded on the benchsheet. Homogenize the sample by mixing it thoroughly in the container. If this is not possible place the sample in clean beaker and homogenize. Upon completion of homogenization in beaker return sample to original container. Discard foreign objects such as sticks, leaves and rocks, unless extraction of this material is required by client. If the sample consists primarily of foreign materials consult with the client (via the Project Manager or Administrator).

11.5.4. Remove surrogate and matrix spiking solutions from refrigerator and allow to warm to room temperature.

11.5.5. Weigh 30 g of sample ± 0.2g into a 250 or 400 mL beaker. Record the weight to the nearest 0.01 g in the appropriate column on the benchsheet. Use 30 g of sodium sulfate for the method blank and 30 g of sodium sulfate with 30 g of reagent sand for the LCS.

11.5.6. Mix weighed sample with a spatula adding enough anhydrous sodium sulfate (approximately 30 g) to be free flowing. (If the sample is not free flowing extraction efficiency may be reduced)

11.5.7. Prepare a method blank, LCS and MS/MSD for each batch as specified in section 9 of this SOP.

11.5.8. Add the appropriate volume of surrogate spiking solution (see Table 3). Also add appropriate volume of matrix spiking solution to any matrix spike / matrix spike duplicate samples (see.Table 4) Add 1 mL of the surrogate spiking solution to each sample, method blank, Laboratory Control Sample (LCS), and matrix spikes. Refer to Table 6 for details of the surrogate spiking solutions. Add 1 mL of the appropriate matrix spiking solution to each Matrix Spike/Matrix Spike Duplicate (MS/MSD) and LCS. Refer to Tables 3 and 5 for details of the spiking solutions. Record spiking volumes and standard numbers on the benchsheet. Return spiking solutions promptly to refrigerator.

Note: The same volume of surrogate and matrix spiking solution is used if GPC is indicated since the final volume would be reduced to compensate for loss of extract during the GPC procedure.

11.5.9. Immediately add a minimum of 100 mL of solvent to the beaker.

Solvents:

Semivolatile GC/MS, TPH, Organochlorine pesticides and PCBs	1:1 Methylene Chloride / Acetone

Note: Steps 11.5.5 - 11.5.9 should be performed rapidly to avoid loss of the more volatile extractables.

11.5.10. Place the bottom surface of the appropriate disrupter horn tip approximately ½ inch below the surface of the solvent, but above the sediment layer.

11.5.11. Sonicate for 3 minutes, making sure the entire sample is agitated. If the W-380 or W-385 sonicator is used the output should be set at 6 for the 3/4 inch high gain (Q) horn or 10 for the 3/4 inch standard horn. with mode switch on pulse, and percent-duty cycle knob set at 50%.

Note: Do ***not*** use ***Microtip*** probe.

11.5.12. Loosely plug the stem of a 75 mm x 75 mm glass funnel with glass wool and/or line the funnel with filter paper. Add 10-20 g of anhydrous sodium sulfate to the funnel cup.

11.5.13. Place the prepared funnel on a collection apparatus (beaker or K-D Apparatus.

11.5.14. Decant and filter extracts through the prepared funnel into a clean beaker or K-D Apparatus.

11.5.15. Repeat the extraction two more times with additional 100 mL minimum portions of solvent each time. Decant off extraction solvent after each sonication. On the final sonication pour the entire sample (sediment and solvent) into the funnel and rinse with an additional 10 mL-20 mL of the methylene chloride/acetone appropriate solvent (Refer to Table in 11.5.9).

Note: Alternatively, the three extracts may be collected together and then filtered through the sodium sulfate.

11.5.16. Cover with aluminum foil if the extract is not concentrated immediately. Refer to Section 11.8 for concentration and Section 11.9 for cleanup.

11.5.17. Sonicator Tuning.

11.5.17.1. Tune the sonicator according to manufacturer's instructions. The sonicator must be tuned at least every time a new horn is installed.

11.6. Soxhlet

11.6.1. Determination of % moisture

In some cases, sample results are needed on a dry weight basis. If this is the case, weigh 5-10 g of sample into a suitable tared container (typically an aluminum weigh pan. Determine the % moisture by drying overnight at 105°C. Allow to cool in a desiccator before weighing.

$$\% \text{ Moisture} = \frac{(\text{weight of wet sample} - \text{weight of dry sample})}{\text{weight of wet sample}} \times 100$$

11.6.2. Determination of pH

If pH determination is required, transfer 10 g of soil to a beaker. Add 10 mL of water. Stir for 1 hour. Determine the pH of the sample with a glass electrode and pH meter.

11.6.3. Decant and discard any water layer on a sediment/soil sample. Record and document if a water layer was discarded on the benchsheet. Homogenize the sample by mixing it thoroughly in the container. If this is not possible place the sample in clean beaker and homogenize. Upon completion of homogenization in beaker return sample to original container. Discard foreign objects such as sticks, leaves and rocks, unless extraction of this material is required by client. If the sample consists primarily of foreign materials consult with the client (via the Project Manager or Administrator).

11.6.4. Remove surrogate and matrix spiking solutions from refrigerator and allow to warm to room temperature.

11.6.5. Weigh 30 g of sample ± 0.2g into a beaker, recording the weight to the nearest 0.01 g on the benchsheet.. Use 30 g of sodium sulfate for the method blank and LCS. Add 30 g of anhydrous sodium sulfate and mix well. The mixture should have a free flowing texture. If not, add more sodium sulfate. Add the sample/sodium sulfate mixture to a soxhlet thimble, but do not pack the thimble tightly. The extraction thimble must drain freely for the duration of the extraction period. A glass wool plug above and below the sample in the soxhlet extractor is an acceptable alternative for the thimble.

11.6.6. Add the appropriate amount of surrogate and matrix spiking solution as indicated in Tables 3, 4, 5, and 6.

Sample weights less than 30 g but over 5 g may be used if the appropriate reporting limits can be met.

11.6.7. Prepare a method blank, LCS and MS/MSD for each batch as specified in section 9 of this SOP, using sodium sulfate as the matrix. The weight of sodium sulfate used should be approximately the weight of soil used in each sample.

11.6.8. Place approximately 200mL of solvent into a 250 mL flat bottom flask containing one or two clean boiling chips. Attach the flask to the extractor and extract the sample for 16-24 hours at 4-6 cycles per hour. Check the system for leaks at the ground glass joints after it has warmed up.

NOTE: If a reduced quantity of sample is extracted, it is usually necessary to increase the amount of sodium sulfate added or increase the solvent boiling rate to properly set the cycling rate.

Solvents:

Semivolatile GC/MS, OPP, PAH, TPH Organochlorine pesticides and PCBs	1:1 Methylene Chloride / Acetone

11.6.9. Allow the extract to cool after the extraction is complete, then disassemble by gently twisting the soxhlet from the flask. Dry the extract in the flask by filtering it through a sodium sulfate filled funnel.

11.6.10. Collect the dried extract in a K-D or other glass container. Rinse the flask which contained the solvent extract with 20-30 mL of methylene chloride and add it to the funnel to complete the quantitative transfer.

11.6.11. Cover with aluminum foil if the extract is not concentrated immediately. Refer to Section 11.8 for concentration and Section 11.9 for cleanup.

11.7. Waste Dilution

11.7.1. This method is used for materials that are soluble in an organic solvent.

11.7.2. Transfer 10 mL of the solvent to be used for dilution into a Teflon capped vial. Mark the meniscus on the vial, then discard the solvent.

11.7.3. Tare the vial, then transfer approximately 1g of sample to the vial. Record the weight to the nearest 0.01 g.

11.7.4. Add appropriate volume of surrogate and spike solutions (Table 3).

11.7.5. Dilute to 10 mL with the appropriate solvent. (Methylene Chloride for GC/MS-BNA and GCS-TPH. Add 10 mL of appropriate solvent (Hexane) for GCS-pesticide and/or PCB analysis.

11.7.6. Add 2 g + 0.1 g sodium sulfate to the sample. Cap and shake or vortex each extract for 2 minutes.

11.7.7. If H2O is still present, add 4-5 g sodium sulfate to a small pipette funnel. The funnel can be plugged with glass wool or phase separation filter paper may be used to hold the sodium sulfate.

11.7.8. Pour the sample through the funnel, collecting as much as possible in a clean vial. Do NOT rinse the funnel with additional solvent, and do NOT concentrate the sample. The final volume is defined as 10 mL.

11.7.9. Label the sample, which is now ready for cleanup or analysis.

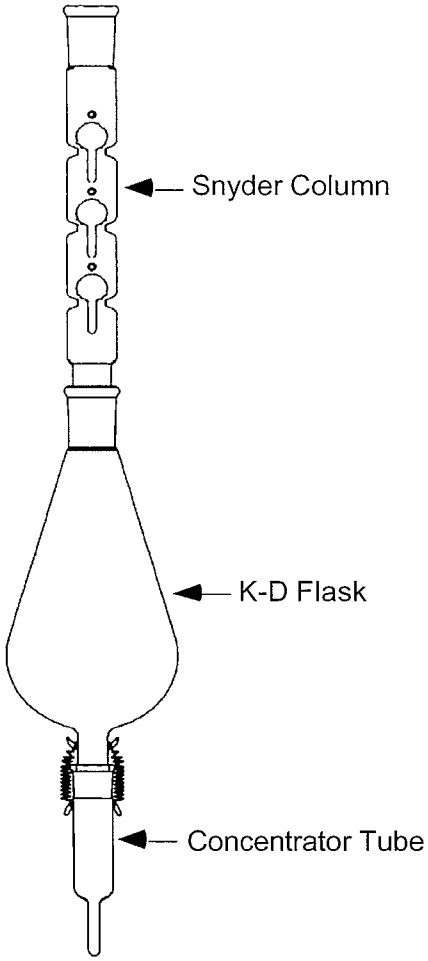
11.8. Concentration

According to the type of sample and any cleanup procedures needed, different final solvents and volumes will be required. Refer to Table 2 for the appropriate final volumes and concentrations.

11.8.1. Kuderna-Danish (KD) Method:

11.8.1.1. Assemble a Kuderna-Danish concentrator by attaching a 10 mL concentrator tube to the 500 mL KD flask. Transfer the sample to the K-D flask.

11.8.1.2. Add one or two clean boiling chips and the extract to be concentrated to the KD flask and attach a three ball Snyder Column. Add approximately 1 mL of clean methylene chloride to the top of the Snyder column (this is important to ensure that the balls are not stuck and that the column will work properly).



11.8.1.3. Place the KD apparatus on a water bath (90-98°C) so that the tip of the concentrator tube is submerged. The water level should not reach the joint between the concentrator and the KD flask. At the proper rate of distillation, the balls will actively chatter but the chambers should not flood.

11.8.1.4. Concentrate to 5-15 mL. If the determinative method requires a solvent exchange add the appropriate exchange solvent (50 mL hexane, 20 ml hexane/acetone, or 4 mL acetonitrile,4mL toluene (Herbicide TCLP), or 10 mL toluene) to the top of the Snyder Column, and then continue the water bath concentration back down to 1-4 mL. Refer to Table 2 for details of exchange solvents and final volumes.

The Snyder column may be insulated if necessary to maintain the correct rate of distillation.

Note: Add an additional boiling chip with the addition of exchange solvent. An alternative technique for solvent exchange is to replace the macro Snyder column and KD flask with a micro Snyder column, concentrate to approximately 1 mL, add the appropriate solvent, and concentrate back down to 1 mL. The extract must be cool before the macro Snyder assembly is removed.

Note: It is very important not to concentrate to dryness as analytes will be lost.

11.8.1.5. Remove the KD apparatus from the water bath and allow to cool for a minimum of 10 minutes. If the level of the extract is above the level of the concentrator tube joint, continue to distill the solvent as necessary. Again, allow the KD flask to cool for a minimum of 10 minutes.

11.8.1.6. If the final volume is 5 or 10 mL the extract may be made up to volume in the graduated KD tube or transferred to a 12 mL vial previously marked at the appropriate volume level. Document the final volume. Otherwise proceed to section 11.8.2

11.8.2. Nitrogen Evaporation to Final Concentration

11.8.2.1. Transfer the entire extract to a calibrated evaporation tube. Rinse the concentrator tube with 1-2 mL of the appropriate solvent and transfer the solvent rinsate to the evaporation tube.

11.8.2.2. Place the tube in a warm water bath that is at least 5°C below the boiling temperature of the solvent being evaporated and evaporate the solvent using a gentle stream of nitrogen. The nitrogen flow will form a slight depression on the surface of the solvent, but should not create splattering of the extract.

Boiling points of commonly used solvents are:

Methylene chloride	40°C
Acetone	56°C
Hexane	69°C
Acetonitrile	82°C
Toluene	111°C

11.8.2.3. During the course of the evaporation rinse the sides of the evaporation tube twice with approximately 1 mL of clean solvent. The first rinse should be about half way through he process, with the second rinse when the solvent volume gets close to 1 mL. Concentrate the solvent accurately to the calibrated volume line and transfer the extract to the appropriate storage vial.

Note: It is very important not to concentrate to dryness as analytes will be lost.

An alternative technique is to follow the previous steps concentrating the solvent to slightly below the required final volume and then drawing the extract into a syringe. Rinse the evaporation tube with a small amount of solvent and draw additional solvent into the syringe to make up the accurate final volume.

Note: It is very important not to concentrate to dryness as analytes will be lost.

Note: The final concentration and volume measurement steps are critical. Use care when concentrating and make certain that the final volume measurement is accurate.

Alternative QES Concentration Method:

This concentration method uses a hot water jacketed concentrator tube (CT) instead of the hot water bath and concentrator tube used in Section 11.8.1.1. The construction of the jacketed concentrator tube reduces the tendency of the extract to evaporate to dryness. Thus, low boiling analytes are retained in the extract better with less analyst monitoring of the concentration process.

Assemble the jacketed concentrator tube, KD body and hot water hoses. Add 1mL of exchange solvent (if needed) and one large, clean boiling chip.

***NOTE**: The boiling chips used in the jacketed concentrator tube must be large enough to prevent them falling down into the tip of the CT. If the boiling chip is not in the proper position, the extract may superheat and bump vigorously if the extract solvent warms up slowly.*

Pour the extract to be concentrated into the KD flask, and attach a three-ball Snyder column.

Turn on the hot (95°C) water flow to the jacketed concentrator tube.

Concentrate to 1 mL. If the determinative method requires a solvent exchange, add the appropriate exchange solvent (5-10 mL hexane, 1 mL acetonitrile, 4 mL acetone/hexane) to the top of the Snyder column. Continue to concentrate until the Snyder column balls stop chattering.

Cool the jacketed concentrator tube until it is cold to the touch.

Quantitatively transfer the extract and dilute to final volume, or continue concentration with nitrogen evaporation (section 11.8.2).

11.8.3. Turbovap Method

11.8.3.1. Turn on the Turbovap and adjust the water temperature to 5-10°C less than the boiling point of the solvent to be evaporated.

11.8.3.2. Switch all endpoint sensors to the "NO" position.

11.8.3.3. Adjust the water bath level

11.8.3.4. Adjust the nitrogen gas pressure to approximately 12 psi.

11.8.3.5. Transfer the extract into the Turbovap tube and load into the Turbovap. Do not fill the Turbovap tubes over approximately 3/4 full.

11.8.3.6. Reset the sensor and close the lid.

Note: If the extract splashes when the nitrogen flow starts, reduce the nitrogen flow or transfer a portion of the extract back into the original extract container.

11.8.3.7. As the extract concentrates, transfer the remainder of the extract into the appropriate Turbovap tube. After all of the extract has been transferred, rinse the flask with a few mL of methylene chloride and add to the Turbovap tube.

11.8.3.8. During the concentration rinse the Turbovap tube walls with a few mL of solvent 1 or 2 times.

11.8.3.9. Concentrate the extract to slightly less than the required final volume.

11.8.3.10. If solvent exchange is required, concentrate to 1-4 mL and add 50 mL of the exchange solvent. Concentrate back down to the appropriate volume. Refer to Table 2 for details of exchange solvents and final volumes.

11.8.3.11. Transfer the concentrated extract to volumetric glassware for adjustment of final volume, using a small amount of solvent to rinse the tube and complete the transfer.

Note: Water contamination from condensation during concentration is not acceptable. If water is present, remove the Turbovap tube and filter the extract through sodium sulfate. Transfer to a clean Turbovap tube and continue the concentration.

Note 2: Dark, opaque or turbid samples may not concentrate. If this occurs, set the concentrator sensor to dryness and supervise the entire concentration procedure.

11.9. Cleanup Techniques

The following techniques may be used to remove interfering peaks, and /or to remove materials that may cause column deterioration and/ or loss of detector sensitivity.
Gel Permeation Chromatography (Section 11.9.1) is a generally applicable technique which can be used to prepare extracts for Semivolatiles (8270), and pesticides (8081) analysis. It is capable of separating high molecular weight material from the sample analytes, and so is particularly useful if tissue or vegetable matter is part of the sample, and for many soil samples.
Note: GPC used only for CLP Projects

Florisil column cleanup (Section 11.9.2) is particularly useful for cleanup of pesticides for analysis by method 8081 and should normally be applied to these samples unless the matrix is clean. It separates compounds with a different polarity from the target analytes.
Note: GPC used only for CLP Projects
Gel Permeation Chromatography and Florisil column cleanup may both be applied to samples for analysis by method 8081/8082. In this case the GPC should be performed first.

Sulfur cleanup (Section 11.9.3) is generally applied to samples for analysis by method 8081/8082, since the Electron Capture Detector responds strongly to sulfur. It is performed after GPC and Florisil cleanup.

Sulfuric acid cleanup (Section 11.9.4) is applied to samples requiring analysis for Polychlorinated Biphenyls (PCBs) only. Most organic matter is destroyed by the sulfuric acid. WARNING: Sulfuric acid cleanup must not be performed on any matrix that may have water present as a violent reaction between the acid and water may result in acid exploding out of the vessel.

Acid Base Partition Cleanup (Section 11.9.5) is useful for separating organic acids and phenols from basic and neutral organics.

Fluorocarbon cleanup (Section 11.9.7) is used to remove hydrocarbons from water samples to be analyzed for water soluble alcohols.

11.9.1. Gel Permeation Chromatography (GPC)

Note: GPC systems include the GPC Autoprep Model 1002A or 1002B Analytical Biochemical Laboratories, Inc., Zymark Benchmate, or equivalent.

11.9.1.1. GPC Column Preparation

11.9.1.1.1. Weigh out 70 g of Bio Beads (SX-3) into a 400-mL beaker.

11.9.1.1.2. Add approximately 300 mL of methylene chloride and stir gently.

11.9.1.1.3. Cover with aluminum foil and allow the beads to swell for a minimum of two hours. Maintain enough solvent to sufficiently cover the beads at all times.

11.9.1.1.4. Position and tighten the outlet bed support (top) plunger assembly in the tube by inserting the plunger and turning it clockwise until snug. Install the plunger near the column end but no closer than 5 cm (measured from the gel packing to the collar).

11.9.1.1.5. Turn the column upside down from its normal position with the open end up. Place the tubing from the top plunger assembly into a waste beaker below the column.

11.9.1.1.6. Swirl the bead/solvent slurry to get a homogeneous mixture and pour the mixture into the open end of the column. Transfer as much as possible with one continuous pour trying to minimize bubble formation. Pour enough to fill the column. Wait for the excess solvent to drain out before pouring in the rest. Add additional methylene chloride to transfer the remaining beads and to rinse the beaker and the sides of the column. If the top of the gel begins to look dry, add more methylene chloride to rewet the beads.

11.9.1.1.7. Wipe any remaining beads and solvent from the inner walls of the column with a laboratory tissue. Loosen the seal slightly on the other plunger assembly (long plunger) and insert it into the column. Make the seal just tight enough so that any beads on the glass surface will be pushed forward, but loose enough so that the plunger can be pushed forward.

CAUTION: Do not tighten the seal if beads are between the seal and the glass surface because this can damage the seal and cause leakage.

11.9.1.1.8. Push the plunger until it meets the gel, then compress the column bed about 4 cm.

11.9.1.1.9. Connect the column inlet to the solvent reservoir and place the column outlet tube in a waste container. Pump methylene chloride through the column at a rate of 5 mL/min. for one hour.

11.9.1.1.10. After washing the column for at least one hour, connect the column outlet tube to the inlet side of the UV detector. Connect the system outlet to the outlet side of the UV detector. Placing a restrictor (made from a piece of capillary tubing of 1/16"OD x 10/1000"ID x 2") in the outlet tube from the UV detector will prevent bubble formation which causes a noisy UV baseline. The restrictor will not effect the flow rate. After pumping methylene chloride through the column for an additional 1-2 hours, adjust the inlet bed support plunger until approximately 6-10 psi back-pressure is achieved. Push the plunger in to increase pressure or slowly pull outward to reduce pressure.

11.9.1.1.11. When the GPC column is not to be used for several days, connect the column inlet and outlet lines to prevent column drying and/or channeling. If channeling occurs, the gel must be removed from the column, re-swelled, and re-poured as described above. If drying occurs, pump methylene chloride through the column until the observed column pressure is constant and the column appears wet. Always recalibrate after column drying has occurred to verify that retention volumes have not changed.

11.9.1.2. Initial Calibration of the GPC Column

11.9.1.2.1. Before use, the GPC must be calibrated based on monitoring the elution of standards with a UV detector connected to the GPC column.

11.9.1.2.2. Pump solvent through the GPC column for 2 hours. Verify that the flow rate is 4.5-5.5 mL/min. Corrective action must be taken if the flow rate is outside this range. Record the column pressure (should be 6-10 psi) and room temperature (22°C is ideal).

Note: Changes in pressure, solvent flow rate, and temperature conditions can affect analyte retention times and must be monitored. If the flow rate and/or column pressure do not fall within the above ranges, a new column should be prepared.

11.9.1.2.3. Inject the calibration solution and retain a UV trace that meets the following requirements (See resolution calculation in section 11.9.1.6):

- Peaks must be observed and should be symmetrical for all compounds in the calibration solution.
- Corn oil and phthalate peaks must exhibit >85% resolution.
- Phthalate and methoxychlor peaks must exhibit >85% resolution.
- Methoxychlor and perylene peaks must exhibit >85% resolution.
- Perylene and sulfur peaks must not be saturated and must exhibit >90% baseline resolution.

11.9.1.2.4. A UV trace that does not meet the criteria in paragraph 11.9.1.2.3 indicates the need for system maintenance and/or the need for a new column.

11.9.1.2.5. Determine appropriate collect and dump cycles.

11.9.1.2.6. The calibrated GPC program for pesticides/PCB should dump >85% of the phthalate and should collect >95% of the methoxychlor and perylene. Use a wash time of 10 minutes.

11.9.1.2.7. For semivolatile extracts, initiate a column eluate collection just before the elution of bis (2-ethylhexyl) phthalate and after the elution of the corn oil.

Stop eluate collection shortly after the elution of perylene. Stop collection before sulfur elutes. Use a wash time of 10 minutes after the elution of sulfur.

11.9.1.2.8. Reinject the calibration solution after appropriate dump and collect cycles have been set.

11.9.1.2.9. Measure and record the volume of collected GPC eluate in a graduated cylinder.

11.9.1.2.10. The retention times for both bis(2-ethylhexyl) phthalate and perylene must not vary more than +/- 5% between calibrations.

11.9.1.3. GPC calibration check

Check the calibration of the GPC immediately after the initial calibration and at least every 7 days thereafter, while the column is in use.

11.9.1.3.1. Inject the calibration solution, and obtain a UV trace. If the retention times of bis(2-ethylhexyl)phthalate or perylene have changed by more than $\pm$ 5% use this run as the start of a new initial calibration. Otherwise, proceed with the recovery check. Excessive retention time shifts may be caused by poor laboratory temperature control or system leaks, an unstabilized column, or high laboratory temperature causing outgassing of methylene chloride. Pump methylene chloride through the system and check the retention times each day until stabilized.

11.9.1.4. GPC Recovery Check for Pesticides/ PCBs

11.9.1.4.1. The recovery from the GPC must be verified immediately after the initial calibration and at least every 7 days, when the instrument is in use. Two recovery check solutions are used. The first mixture is prepared by diluting 1.0 2.0 mL of the pesticide matrix spiking solution (Table 6) to 10 mL in methylene chloride. The second mixture is prepared by diluting 12.0 mL of the PCB only matrix spiking solution (Table 6) to 10 mL with methylene chloride.

11.9.1.4.2. Load the pesticide matrix spike mixture, the PCB mixture, and a methylene chloride blank onto the GPC using the GC dump and collect values.

Note: If the analysis is for PCBs only, then the pesticide recovery check is not necessary.

11.9.1.4.3. After collecting the GPC calibration check fraction, concentrate, solvent exchanging to hexane. Adjust the final volume to 5.0 mL, and analyze by GC/EC. Refer to concentration, section 11.8.

11.9.1.4.4. The methylene chloride blank may not exceed more than one half the reporting limit of any analyte. And if the recovery of each of the single component analytes is 80-10120% and if the Aroclor pattern is the same as previously run standards, then the analyst may use the column. If the above criteria are not met, there may be a need for system maintenance.

11.9.1.5. GPC Blank for Semivolatiles

11.9.1.5.1. The recovery from the GPC must be verified immediately after the initial calibration and at least every 7 days, when the instrument is in use.

11.9.1.5.2. Load a methylene chloride blank onto the GPC using the semivolatiles dump and collect values.

11.9.1.5.3. After collecting the GPC recovery check fraction, concentrate, and analyze by GC/MS. Refer to the concentration section 11.8.

The blank should not contain any analytes at or above the reporting limit. If these conditions are met the column may be used for sample analysis. Otherwise correct the contamination problem, or extend the collect time to improve recovery of target analytes.

11.9.1.6. Sample Extract Cleanup

11.9.1.6.1. Reduce the sample extract volume to 1-2 mL, then adjust to 10 mL with methylene chloride prior to cleanup. This reduces the amount of acetone in the extract. Refer to section 11.8.

11.9.1.6.2. Start the pump and let the flow stabilize for 2 hours. The solvent flow rate should be 4.5-5.5 mL/min. The ideal laboratory temperature to prevent outgassing of the methylene chloride is 22°C. The normal backpressure is 6-10 psi.

11.9.1.6.3. In order to prevent overloading of the GPC column, highly viscous sample extracts must be diluted prior to cleanup. Any sample extract with a viscosity greater than that of a 1:1 glycerol:water solution (by visual comparison) must be diluted and loaded into several loops.

11.9.1.6.4. Samples being loaded onto the GPC should be filtered with a 5 micron (or less) filter disk. Attach a filter to a 10 mL Luerlok syringe and filter the 10 mL sample extract into the sample tube.

Note: The Zymark Benchmate automatically filters the sample extracts, but manual prefiltration of very dirty extracts may be necessary.

11.9.1.6.5. Load the filtered (or unfiltered if using the Benchmate) samples into the proper sample tubes and place on the GPC.

Note: For the GPC Autoprep Model 1002A, wash the loading port with methylene chloride after loading each sample loop in order to minimize cross contamination. This step is automated on the GPC Autoprep 1002B and on the Benchmate.

11.9.1.6.6. Set the collect, dump, and wash times determined by the calibration procedure.

11.9.1.6.7. Switch to the run mode and start the automated sequence. Process each sample using the collect and dump cycle times established by the calibration procedure.

11.9.1.6.8. Collect each sample in a suitable glass container. Monitor sample volumes collected.

11.9.1.6.9. Any samples that were loaded into 2 or more positions must be recombined.

11.9.1.6.10. Concentrate semivolatile sample extracts to 0.5 mL in methylene chloride. Refer to the concentration section 11.8.

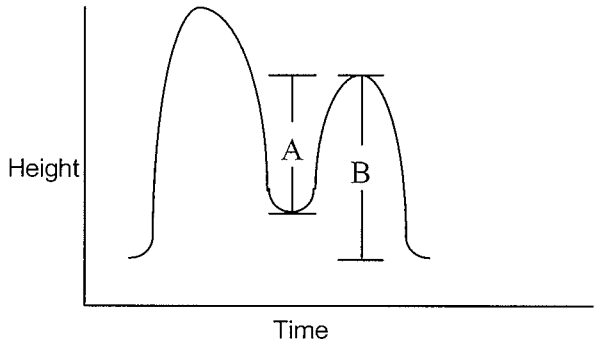
11.9.1.6.11. Solvent exchange pesticide/PCB sample extracts into hexane and concentrate to 5.0 mL. Refer to the concentration section 11.8.

11.9.1.7. Calculations

11.9.1.7.1. Resolution

To calculate the resolution between two peaks on a chromatograph, divide the depth of the valley between the peaks by the peak height of the smaller peak being resolved and multiply by 100.

Resolution Calculation



$$\% \text{ Resolution} = \frac{A}{B} \times 100$$

Where: A = depth of valley to height of smaller peak
B = peak height of smaller peak

11.9.1.7.2. Dump Time

Mark on the chromatograph the point where collection is to begin. Measure the distance from the injection point. Divide the distance by the chart speed. Alternatively the collect and dump times may be measured by means of an integrator or data system.

$$\text{Dump time (min)} = \frac{\text{Distance (cm) from injection to collection start}}{\text{Chart speed (cm / min)}}$$

11.9.1.7.3. Collection Time

$$\text{Collection time (min)} = \frac{\text{Distance (cm) between collection start and stop}}{\text{Chart speed (cm / min)}}$$

11.9.2. Florisil Cartridge Cleanup

Florisil cleanup is generally used for organochlorine pesticides, although it may be applied to other analytes. Sections 11.9.8.2.1 through 11.9.8.2.8 outline the procedure for organochlorine pesticides, while section 11.9.2.9 outlines modifications required for other analytes.

Note 1: Systems for eluting multiple cleanup cartridges include the Supelco, Inc. Solid Phase Extraction (SPE) assemblyor equivalent.

Note 2: Follow the lab specific procedure when using ABC Model 1002B.

11.9.2.1. Before Florisil cleanup sample volume must be reduced to 10 mL (5 mL if GPC cleanup was used) and the solvent must be hexane. Refer to Section 11.8 for details of concentration.

11.9.2.2. Attach a vacuum manifold to a vacuum pump or water aspirator with a trap installed between the manifold and the vacuum. Adjust the vacuum in the manifold to 5-10 psi.

11.9.2.3. Place one Florisil cartridge into the vacuum manifold for each sample extract. Prior to cleanup of samples, pre-elute each cartridge with 5 mL of hexane/acetone (9:1). Adjust the vacuum applied to each cartridge so that the flow through each cartridge is approximately 2 mL/min. Do not allow the cartridges to go dry.

11.9.2.4. Just before the cartridges go dry, release the vacuum to the manifold and remove the manifold top.

11.9.2.5. Place a rack of clean labeled 12 mL concentrator tubes into the manifold and replace the manifold top. Make sure that the solvent line from each cartridge is placed inside the appropriate tube.

11.9.2.6. After the clean tubes are in place, vacuum to the manifold is restored and 2.0 mL of the extract is added to the appropriate Florisil cartridge.

11.9.2.7. The pesticides/aroclors in the extract concentrates are then eluted through the column with 8 mL of hexane/acetone (90:10) and are collected into the 10 mL culture tube or concentrator tube held in the rack inside the vacuum manifold.

11.9.2.8. Transfer the extract to a graduated concentrator tube and concentrate the extract to 2 mL. Refer to the concentration section. (11.8)

Note 1: A cartridge performance standard must be run with each lot of Florisil cartridges.

Note 2: Florisil cartridge performance check--every lot number of Florisil must be tested before use. Add 0.5 ug/mL of 2,4,5-trichlorophenol solution and 0.5 mL of GC Standard Mix A (midpoint concentration) to 4 mL hexane. Reduce volume to 0.5 mL. Add the concentrate to a pre-washed Florisil cartridge and elute with 9 mL hexane/acetone [(90:10)(v/v)]. Rinse cartridge with 1.0 mL hexane two additional times. Concentrate eluate to 1.0 mL final volume and transfer to vial. Analyze the solution by GC/EC. The test sample must show 80 to 120% recovery of all pesticide analytes with <5% trichlorophenol recovery, and no peaks

interfering with target compounds can be detected. This standard has a lifetime of six months. Alternatively, this standard may be purchased as a stock solution.

11.9.2.9. Modifications for other analyte classes

11.9.2.9.1. PCBs

Pre-elute the cartridge with 4 mL hexane. Add 2 mL of the sample extract and elute with 3 mL hexane. The eluant will contain the PCBs together with any heptachlor, aldrin, 4,4'DDE and part of any 4,4'DDT. Any BHC isomers, heptachlor epoxide, chlordane, endosulfan I and II, endrin aldehyde and endrin sulfate and methoxychlor will be retained on the column and can be eluted in a separate fraction with 8 mL 90:10 hexane:acetone if required.

11.9.3. Sulfur Removal

11.9.3.1. Sulfur can be removed by one of three methods: mercury, copper, or tetrabutylammonium sulfite (TBA) according to laboratory preference. If the sulfur concentration is such that crystallization occurs in the concentrated extract, centrifuge the extract to settle the crystals, and carefully draw off the sample extract with a disposable pipet, leaving the excess sulfur in the centrifuge tube. Transfer the extract to a clean concentrator tube before proceeding with further sulfur cleanup.

11.9.3.2. Sulfur Removal with Elemental Mercury

Note: Use Mercury sparingly in order to minimize exposure and disposal costs.

11.9.3.2.1. Transfer 2 mL of sample extract into a clean concentrator tube or Teflon sealed vial.

11.9.3.2.2. Add one to three drops of mercury to the extract vial and seal.

11.9.3.2.3. Shake well for 15-30 seconds. If prolonged shaking is required, use a mechanical shaker.

11.9.3.2.4. Remove the extract from the mercury using a disposable pipette and transfer to a clean vial.

11.9.3.2.5. If black precipitate forms, sulfur was present. Shake again, then centrifuge. After centrifugation, transfer the supernate to a clean test tube and repeat. Do this until relatively little precipitate remains, or the screens indicate that cleanup is complete.

11.9.3.2.6. Properly dispose of the mercury waste.

11.9.3.3. Sulfur Removal with Copper

11.9.3.3.1. Transfer 1.0 mL of sample extract into a centrifuge or concentrator tube.

11.9.3.3.2. Add approximately 2 g of cleaned copper powder (see 8.2 for copper cleaning procedure) to the sample extract tube.

11.9.3.3.3. Mix for one minute on a mechanical shaker.

11.9.3.3.4. If the copper changes color, sulfur was present. Repeat the sulfur removal procedure until the copper remains shiny.

11.9.3.3.5. Transfer the supernate to a clean vial.

11.9.3.4. Sulfur Removal with Tetrabutylammonium (TBA) Sulfite Reagent

11.9.3.4.1. Transfer 1.0 mL of sample extract into a culture tube.

11.9.3.4.2. Add 1.0 mL TBA sulfite reagent and 2 mL 2-propanol to the sample extract. Cap and shake for 1 minute. If clear crystals (precipitated sodium sulfite) form, sufficient sodium sulfite is present.

11.9.3.4.3. If a precipitate does not form, add sodium sulfite in approximately 0.1 g portions until a solid residue remains after repeated shaking.

11.9.3.4.4. Add 5 mL organic free reagent water and shake for 1 minute. Allow sample to stand for 5-10 minutes. (Centrifuge if necessary to separate the layers). Transfer the sample extract (top layer) to a vial. The final volume is defined as 1.0 mL in section 11.9.3.4.1.

11.9.4. Sulfuric Acid Cleanup

11.9.4.1. Add approximately 2-5 mL of concentrated sulfuric acid to 2 mL of sample extract in a Teflon capped vial.

Caution: There must be no water present in the extract or the reaction may shatter the sample container.

11.9.4.2. Shake or vortex for about thirty seconds and allow to settle. (Centrifuge if necessary)

11.9.4.3. Remove the sample extract (top layer) from the acid using a Pasteur pipette and transfer to a clean vial. ***CAUTION:*** It is not necessary to remove all the extract since the final volume is already determined. Transfer of small amounts of sulfuric acid along with the extract will result in extremely rapid degradation of the chromatographic column.

11.9.4.4. If the sulfuric acid layer becomes highly colored after shaking with the sample extract, transfer the hexane extract to a clean vial and repeat the cleanup procedure until color is no longer being removed by the acid, or a maximum of 5 acid cleanups.

11.9.4.5. Properly dispose of the acid waste.

11.9.5. Acid/Base Partition Cleanup

11.9.5.1. Place 10 mL of the solvent extract from a prior extraction procedure into a 125 mL separatory funnel.

11.9.5.2. Add 20 mL of methylene chloride to the separatory funnel.

11.9.5.3. Slowly add 20 mL of DI water which has been previously adjusted to a pH of 12 to 13 with 10 N sodium hydroxide.

11.9.5.4. Seal and shake the separatory funnel for at least two minutes with periodic venting to release excess pressure.

CAUTION: Methylene chloride creates excessive pressure very rapidly. Initial venting should be done immediately after the separatory funnel has been sealed.

11.9.5.5. Allow the organic layer to separate from the aqueous phase for a minimum of ten minutes.

11.9.5.6. If an emulsion interface between layers is more than one-third the size of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, and may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods.

11.9.5.7. Separate the aqueous phase and transfer it to a 125 mL Erlenmeyer flask. Repeat the extraction two more times using fresh 20 mL aliquots of dilute sodium hydroxide (pH 12-13) . Combine the aqueous extracts.

11.9.5.8. Water-soluble organic acids and phenols will be primarily in the aqueous phase. Base/neutral analytes will be in the methylene chloride. If the analytes of interest are only in the aqueous phase discard the methylene chloride and proceed to Section 11.9.5.9. If the analytes of interest are only in the methylene chloride, discard the aqueous phase and proceed to Section 11.9.5.11.

11.9.5.9. Externally cool the flask with ice while adjusting the aqueous phase to a pH of 1-2 with sulfuric acid (1:1). Transfer the cool aqueous phase to a clean 125 mL separatory funnel.

11.9.5.10. Add 20 mL of methylene chloride to the separatory funnel and shake for at least two minutes. Allow the methylene chloride to separate from the aqueous phase and collect the methylene chloride in an Erlenmeyer flask. Repeat the extraction two more times using fresh methylene chloride and extracting at pH 1-2. Combine the three extracts.

11.9.5.11. Dry the extract by passing through a funnel containing 10-20 g anhydrous sodium sulfate. Rinse the funnel with an additional 20-30 mL of clean methylene chloride

11.9.5.12. Cover with aluminum foil if the extract is not concentrated immediately. Refer to section 11.9 for concentration.

11.9.5.13. Dispose of solvent and water remaining in the separatory funnel into the appropriate waste container.

11.9.6. Fluorocarbon Cleanup

This procedure is appropriate for the removal hydrocarbons from water samples prior to analysis for water soluble alcohols

11.9.6.1. Transfer 1-2 mL of water sample to a 10 mL culture tube.

11.9.6.2. Add 1-2 mL of fluorocarbon solvent (PF-5080) to the culture and cap.

11.9.6.3. Shake for 30-60 seconds.

11.9.6.4. After the two phases have separated, pipette about 1 mL of water sample (top layer) into an autosampler vial for analysis. If necessary, centrifuge to enhance the phase separation.

12. DATA ANALYSIS AND CALCULATIONS

Not applicable

13. METHOD PERFORMANCE

13.1. Method detection limit

Each laboratory must generate a valid method detection limit for each analyte of interest. The procedure for the determination of the method detection limit is given in STL North Canton QA Policy #: QA-005

13.2. Initial demonstration

Each laboratory must make an initial demonstration of capability for each individual method. This requires analysis of four QC Check samples. The QC check sample is a well-characterized laboratory generated sample used to monitor method performance, which should

contain all the analytes of interest. The spiking level should be equivalent to a mid-level calibration. (For certain tests more than one set of QC check samples may be necessary in order to demonstrate capability for the full analyte list.)

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

13.2.2. Calculations and acceptance criteria for the QC check samples are given in the determinative SOPs. (CORP-GC-0001, CORP-MS-0001, 0002)

13.3. Training Qualification

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

14. POLLUTION PREVENTION

Within the constraints of following the methodology in this SOP, use of organic solvents should be minimized.

15. WASTE MANAGEMENT

Waste generated in this procedure will be segregated, and disposed according to the facility hazardous waste procedures. The Laboratory Environmental, Health and Safety Coordinator should be contacted if additional information is required.

15.1. Solvent waste must be disposed of in the clearly labeled waste cans.

15.2. Acid waste must be collected in the clearly labeled acid waste containers.

15.3. Solid materials (soil, gloves, soiled paper products) are placed in the solid debris container. Do not put liquids in the solid waste container.

15.4. Methylene chloride saturated water and remaining sample after the extraction is dumped into Methylene chloride waste cans.

16. REFERENCES

Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW846, 3rd Edition, Final Update III (December 1996). Sections 3500B, 3510C, 3520C, 3540C, 3550B, 3600C, 3610B, 3620B, 3640A, 3650B, 3660B, AND 3665A.

17. MISCELLANEOUS

17.1. Modifications from Reference method

17.1.1. Some surrogate spiking concentrations are modified from those recommended in SW-846, in order to make the concentrations more consistent with the calibration levels in the determinative methods.

17.1.2. Aqueous sample volumes may be determined by weight.

17.1.3. Spiking levels for method 608 have been reduced by a factor of ten to bring the levels within the normal calibration range of the instrument.

17.1.4. 10 g of soil is used for pH determination, rather than the 50 g suggested in the reference method. The volume of water is also adjusted to maintain the sample / water ratio specified in the method.

17.2. Modifications from previous revision

17.2.1. SOP change forms are on record in the Quality Assurance Department.

17.3. Facility Specific SOPs

Each facility shall attach a list of facility specific SOPs or approved attachments (if applicable) which are required to implement this SOP or which are used in conjunction with this SOP. If no facility specific SOPs or amendments are to be attached, a statement must be attached specifying that there are none.

17.4. Tables

Table 1
Liquid /Liquid Extraction Conditions

Determinative Method	Initial Ext. pH	Secondary Ext. pH
BNA: 8270C[1]	1-2	11-12
625	11-12	1-2
Pest/PCB: 8081A, 8082 & 608	5-9	None
Wisconsin DRO	2	
OPP: 8141A	as received	None
Hydrocarbons: 8015B	as received	None
PAH: 8310, & 610	as received	None

[1] If the laboratory has validated acid only 8270 extraction for the target compound list required then the base extraction step may be omitted. The required validation consists of a 4 replicate initial demonstration of capability and a method detection limit study. (See section 13). Additionally, either of the base or acid fractions of Method 8270 can be run first.

Table 2
Exchange Solvents and Final Volumes

Final Volumes and Exchange Solvents if no cleanup is used		

Type	Exchange Solvent for Analysis	Final Volume for Analysis in mL
Semivolatiles	N/A	5.0*- Solids, 2.0 for H2O
PCB	Hexane	10.0 for solids 5.0 for H2O 2.0 for H2O**
Pesticides	Hexane	10.0 for solids 5.0 for H2O
Pesticides/TCLP	Hexane	3.0 mL
PAH by HPLC	Acetonitrile	1.0 mL
BNA – SIM	N/A	2.0 mL - Solids & H2O
TPH	N/A	1.0
OPP	Hexane/Acetone	2.0

*Requires high sensitivity mass spec tune (refer to NC-MS-0015 PAH by SIM)
** Michigan work requires a final volume of 2 mL.

Final Volumes and exchange solvents if GPC cleanup is used CLP ONLY – SOLIDS ONLY			
Type	Exchange Solvent for GPC	Final Volume for GPC	Final Volume and solvent for Analysis
Semivolatiles Semivolatiles	CH_2Cl_2 CH_2Cl_2	10 mL[1] 10 mL[1]	0.5 mL CH_2Cl_2 -OLM03.1 2.5 mL CH_2Cl_2 -OLM04.2
Pesticides	CH_2Cl_2	10 mL[1]	5 mL, Hexane

[1] Final volume for GPC may be 4 mL if a 2 mL sample loop is used

Final volumes and exchange solvents if Florisil cleanup is used CLP ONLY			
Type	Exchange Solvent for Florisil	Final Volume for Florisil	Final Volume and solvent for Analysis
Pesticides	Hexane	10 mL (2 mL aliquot used)	2 mL, hexane

Final volumes and exchange solvents if both GPC and Florisil cleanup are used CLP ONLY					
Type	Exchange Solvent for GPC	Final Volume for GPC	Exchange Solvent for Florisil	Final Volume for Florisil	Final volume for analysis
Pesticides	Methylene Chloride	10 mL	Hexane	5 mL (2 mL aliquot used)	2 mL, hexane

Note: Different final volumes may be necessary to meet special client reporting limit requirements.

.

Table 3		
Surrogate Spiking Solutions		
Analyte Group	Surrogate Spike Solution ID	Volume (mL)
BNA-SOLIDS	100/150 ppm BNA	0.5

BNA / SIM	100/150 ppm BNA	.2 / 0.02
BNA-H2O	100/150 ppm BNA	0.2
Pest	0.2 ppm DCB/TCX	1.0
TPH	40ng C9	1.0
PCB	0.2 ppm DCB/TCX	1.0
PAH	1.0 ug/mL p-Terphenyl-d14 5.0 ug/mL Benzo(e)pyrene	1.0
OPP	10 ug/mL Triphenyl Phosphate	1.0

Table 4

Matrix Spike and LCS Solutions

Analyte Group	Matrix Spike Solution ID	Volume (mL)
BNA-H2O, BNA-TCLP	100 ppm BNA All-Analyte Spike & Restek Spike	0.2
BNA- SOLIDS	100 ppm BNA All-Analyte Spike & Restek Spike	0.5
BNA / SIM	100 ppm BNA All-Analyte Spike & Restek Spike	0.2 / 0.02
PEST – SOLIDS & H2O	Pest NPDES Spike	1.0
PEST TCLP	Pest TCLP Spike	1.0
PCB	10 ppm PCB Spike	1.0
PAH	See Spike List – Table 6	1.0
TPH	See Spike List – Table 6	1.0
OPP	See Spike List – Table 6	1.0

Table 5
Surrogate Spike Components

Type	Compounds	Solvent	Conc. (µg/mL)
BNA	2-Fluorobiphenyl	Methanol	100
	Nitrobenzene-d5		100
	p-Terphenyl-d14		100
	2-Fluorophenol		150
	Phenol-d6		150
	2,4,6-Tribromophenol		150
	1,2-Dichlorobenzene-d4		100
	2-Chlorophenol-d4		150
Pest/PCB	Decachlorobiphenyl	MethanolAcetone	0.2
	Tetrachloro-m-xylene		0.2
TPH	Nonane (C9)	Methanol	40.0
PAH	p-Terphenyl-d-14	CH3CN	1.0
	Benzo(e)pyrene		5.0
OPP	Triphenylphosphate	Acetone	10.0

Table 6

Matrix Spike Components

Type	Compounds	Solvent	Conc. (µg/mL)
TCL BNA	Acenaphthene	Methanol	100
	4-Chloro-3-Methylphenol		150
	2-Chlorophenol		150
	1,4-Dichlorobenzene		100
	2,4-Dinitrotoluene		100
	4-Nitrophenol		150
	N-Nitroso-Di-n-Propylamine		100
	Pentachlorophenol		150
	Phenol		150
	Pyrene		100
	1,2,4-Trichlorobenzene		100
BNA TCLP	1,4-Dichlorobenzene	Methanol	100
	2,4-Dinitrotoluene		100
	Hexachlorobenzene		100
	Hexachlorobutadiene		100
	Hexachloroethane		100
	2-Methylphenol		100
	3-Methylphenol		100
	4-Methylphenol		100
	Nitrobenzene		100
	Pentachlorophenol		100
	Pyridine		100
	2,4,5-Trichlorophenol		100
	2,4,6-Trichlorophenol		100
BNA		Methanol	

Table 6

Matrix Spike Components

Type	Compounds	Solvent	Conc. (µg/mL)
NPDES			
	Acenaphthene		100
	Acenaphthylene		100
	Anthracene		100
	Benzo(a)anthracene		100
	Benzo(b)fluoranthene	Methanol	100
	Benzo(k)fluoranthene		100
	Benzo(a)pyrene		100
	Benzo(ghi)perylene		100
	Benzyl butyl phthalate		100
	Bis(2-chloroethyl)ether		100
	Bis(2-chloroethoxy)methane		100
	Bis(2-ethylhexyl)phthalate		100
	Bis(2-chloroisopropyl)ether		100
	4-Bromophenyl phenyl ether		100
	2-Chloronaphthalene		100
	4-Chlorophenyl phenyl ether		100
	Chrysene		100
	Dibenzo(a,h)anthracene		100
	Di-n-butylphthalate		100
	1,3-Dichlorobenzene		100
	1,2-Dichlorobenzene		100
	1,4-Dichlorobenzene		100
	3,3'-Dichlorobenzidine		100
	Diethyl phthalate		100

Table 6

Matrix Spike Components

Type	Compounds	Solvent	Conc. (µg/mL)
	Dimethyl phthalate		100
	2,4-Dinitrotoluene		100
	2,6-Dinitrotoluene		100
	Di-n-octylphthalate		100
	Fluoranthene		100
	Fluorene		100
	Hexachlorobenzene		100
	Hexachlorobutadiene		100
	Hexachloroethane		100
	Indeno(1,2,3-cd)pyrene		100
	Isophorone		100
	Naphthalene		100
	Nitrobenzene		100
	N-Nitrosodi-n-propylamine		100
	Phenanthrene		100
	Pyrene		100
	1,2,4-Trichlorobenzene		100
	4-Chloro-3-methylphenol		100
	2-Chlorophenol		100
	2,4-Dichlorophenol		100
	2,4-Dimethylphenol		100
	2,4-Dinitrophenol		100
	2-Methyl-4,6-dinitrophenol		100
	2-Nitrophenol		100
	4-Nitrophenol		100

Table 6

Matrix Spike Components

Type	Compounds	Solvent	Conc. (µg/mL)
	Pentachlorophenol		100
	Phenol		100
	2,4,6-Trichlorophenol		100
	Acetophenone		100
	Atrazine		100
	Caprolactum		100
	Benzaldehyde		100
	1,1′-Biphenyl		100
	Safrole		100
	1,4-Dioxane		100
	Pronamide		100
	p-Chlorobenzilate		100
	Phenacetin		100
	Ethyl methanesulfonate		100
	2-Picoline		100
	Phorate		100
	Quinoline		100
Pest TCLP	Heptachlor	Methanol Acetone	0.5
	Heptachlor epoxide		0.5
	Lindane		0.5
	Endrin		0.5
	Methoxychlor		1.0
Pest NPDES /Pest	Aldrin	MethanolAcetone	1.0

Table 6			
Matrix Spike Components			
Type	Compounds	Solvent	Conc. (µg/mL)
	alpha-BHC		1.0
	beta-BHC		1.0
	delta-BHC		1.0
	gamma-BHC (Lindane)		1.0
	4,4'-DDD		1.0
	4,4'-DDE		1.0
	4,4'-DDT		1.0
	Dieldrin		1.0
	alpha-Endosulfan		1.0
	beta-Endosulfan		1.0
	Endosulfan Sulfate		1.0
	Endrin		1.0
	Heptachlor		1.0
	Heptachlor Epoxide		1.0

Diesel Range Organics (8015B) Spike	
Compound	**Final Concentration**
n-decane	50 µg/ml
n-dodecane	50 µg/ml
n-tetradecane	50 µg/ml
n-hexadecane	50 µg/ml
n-octadecane	50 µg/ml
n-eicosane	50 µg/ml
n-docosane	50 µg/ml
n-tetracosane	50 µg/ml
n-hexacosane	50 µg/ml
n-octacosane	50 µg/ml

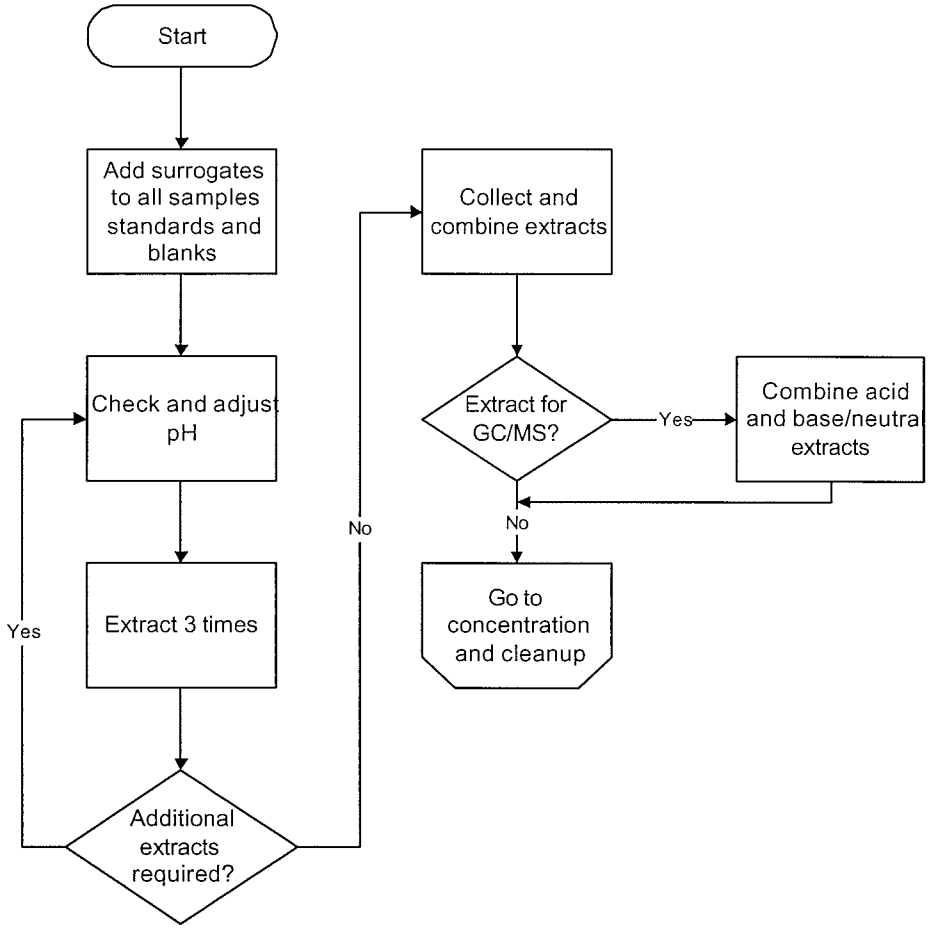
Organophorphorous Pesticides (8141A)

Compound	Final Concentration
dimethoate	20 µg/mL
disulfoton	20 µg/mL
famphur	20 µg/mL
methyl parathion	20 µg/mL
parathion (ethyl)	20 µg/mL
phorate	20 µg/mL
sulfotepp	20 µg/mL
thionazin	20 µg/mL
o,o,o-triethyl phosphorothioate	20 µg/mL
triphenylphosphate (surrogate)	20 µg/mL

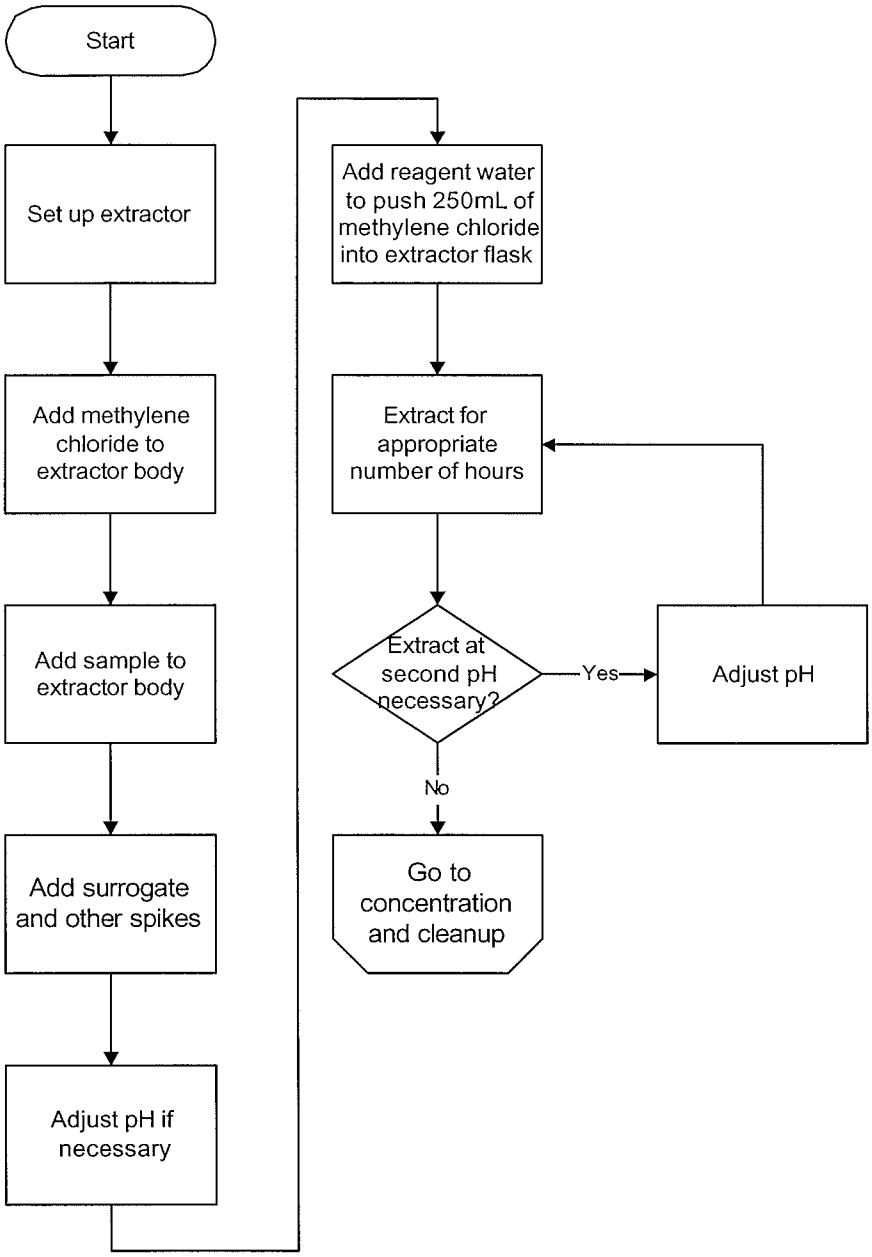
Polynuclear Aromatic Hydrocarbons (8310)	
Compound	**Final Concentration**
Acenaphthylene	10 µg/mL
Carbazole	10 µg/mL
Naphthalene	10 µg/mL
1-Methylnaphthalene	10 µg/mL
2-Methylnaphthalene	10 µg/mL
Acenaphthene	10 µg/mL
Fluorene	2 µg/mL
Phenanthrene	2 µg/mL
Anthracene	2 µg/mL
Fluoranthene	2 µg/mL
Pyrene	2 µg/mL
Benzo(a)anthracene	2 µg/mL
Chrysene	2 µg/mL
Benzo(a)pyrene	2 µg/mL
Benzo(k)fluoranthene	2 µg/mL
Benzo(a)pyrenek)fluoranthene	2 µg/mL
Dibenzo(a,h)anthracene	2 µg/mL
Benzo(g,h,I)perylene	2 µg/mL
Indeno(1,2,3-cd)pyrene	2 µg/mL

17.5. Flow diagrams

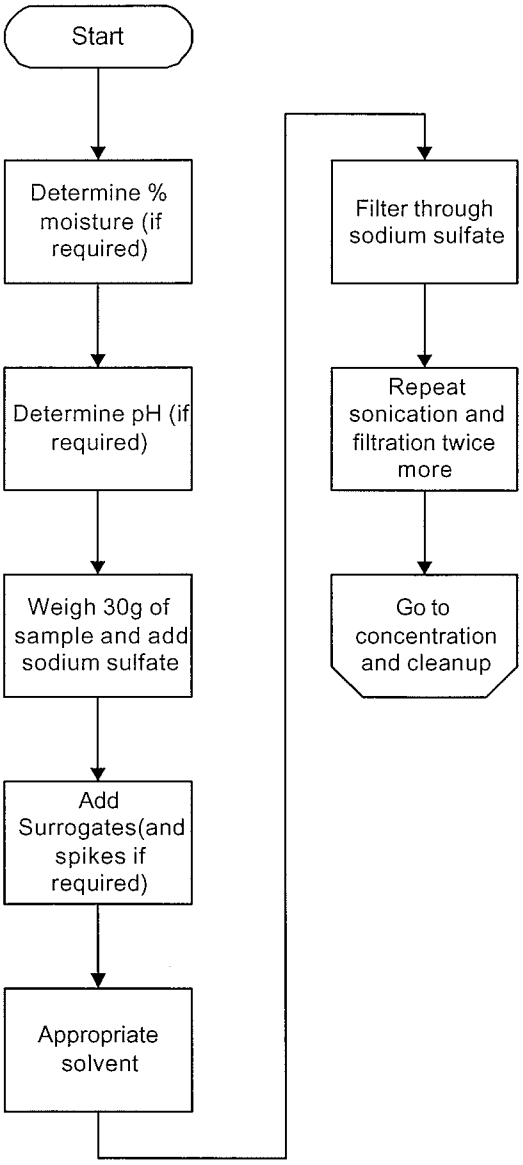
17.5.1. Separatory funnel extraction



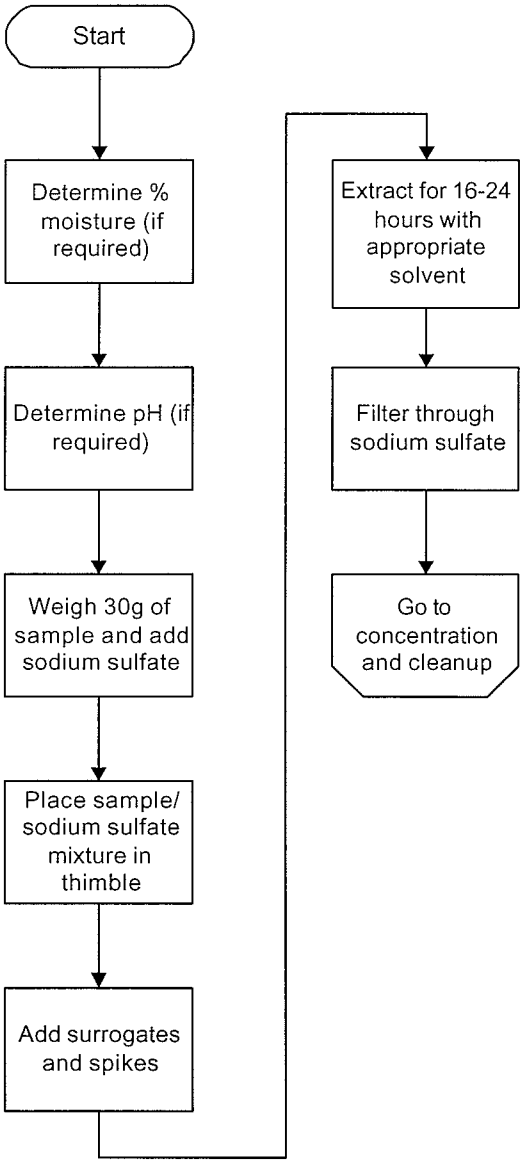
17.5.2. Continuous liquid/liquid extraction



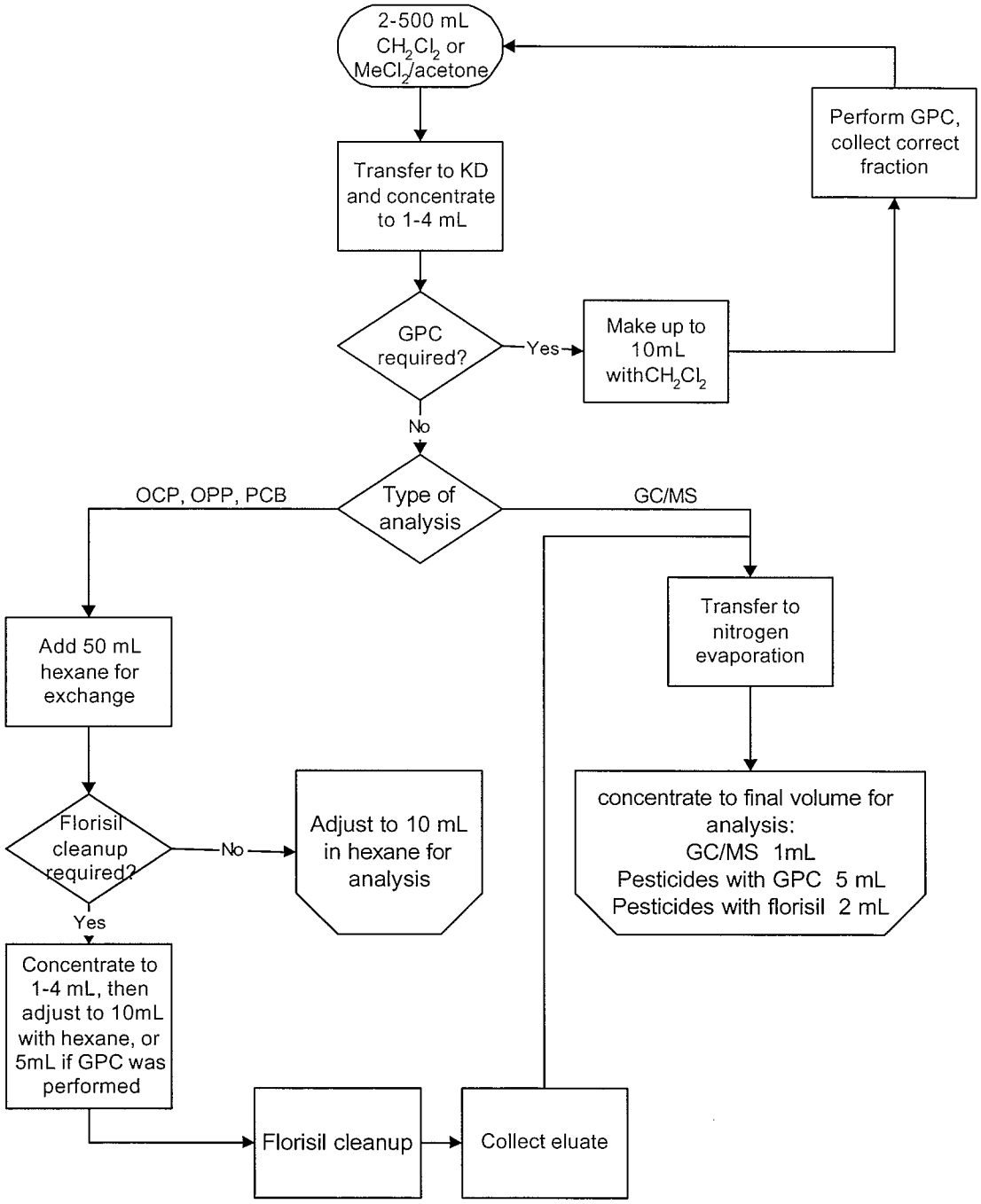
17.5.3. Sonication Extraction



17.5.4. Soxhlet extraction



17.5.5. Concentration and cleanup



18. SCOPE AND APPLICATION

This method is applicable to the extraction of chlorinated herbicides in waters, solids, oils, and TCLP extracts. Appropriate compounds for extraction by this method are listed in CORP-GC-0001, Appendix D, Gas Chromatography of Phenoxy Acid Herbicides based on Method 8151A.

19. SUMMARY OF METHOD

This method is based on SW846 method 8151A. Aqueous samples are hydrolyzed if esters and acids are to be determined, then washed with methylene chloride by a separatory funnel extraction. After acidifying the sample the free acids are extracted into diethyl ether. Solids are extracted into methylene chloride/ acetone by sonication. If esters and acids are to be determined, the extract is hydrolyzed and extracted into diethyl ether. For both soils and aqueous samples, the free acid herbicides in the ether extract are esterified. The final volume is adjusted to prepare the extract for gas chromatography.

20. DEFINITIONS

Refer to section 3 of the main body of this SOP.

21. INTERFERENCES

Refer to section 4 of the main body of this SOP.

22. SAFETY

22.1. Refer to section 5 of the main body this SOP for basic safety information.

22.2. DIAZOMETHANE is an extremely toxic gas with an explosion potential. Since the explosion potential is catalyzed by imperfections in glass, generation of diazomethane must be carried out in glassware free of scratches, cracks, chips and which does not have ground glass joints. Solutions of diazomethane will be kept at temperatures below 90°C. Diazomethane must be generated and handled in a fume hood.

22.3. Diethyl ether is extremely flammable. It also tends to form peroxides when exposed to air. The peroxides can present an explosion hazard, especially when the ether is concentrated.

22.4. Diethyl ether must be free of peroxides as demonstrated by EM (or equivalent) Quant test strips. This test can be done every time the ether is used or once per week if the bottle is marked with the test date(s).

22.5. Concentrated potassium hydroxide solution is highly caustic.

23. EQUIPMENT AND SUPPLIES

23.1. Refer to Section 6 of the main body of this SOP for basic extraction equipment and supplies. Additional equipment and supplies needed for this procedure are listed below.

23.2. Diazomethane generation apparatus

24. REAGENTS AND STANDARDS

24.1. Reagents are listed in Section 7 of the main body of this SOP. Additional reagents and standards needed for this procedure are listed below.

24.2. Reagents

24.2.1. Potassium hydroxide solution, 37% aqueous solution, (w/v): Dissolve 37 g of potassium hydroxide pellets in reagent water and dilute to 100 mL. **Caution:** Considerable heat will be generated. Other volumes of solution may be made up as convenient.

24.2.2. Toluene, reagent grade

24.2.3. 2-(2-Ethoxyethoxy)ethanol, trade name Carbitol, 98%+purity

24.2.4. Diazald, 99% purity

24.2.5. Sodium sulfate, Na_2SO_4, Anhydrous, granular, acidified: Heat sodium sulfate in a shallow tray at 400°C for a minimum of 4 hours to remove phthalates and other interfering organic substances. In a large beaker, acidify by slurrying 500 g sodium sulfate with just enough diethyl ether to cover. Add 20 mL of concentrated sulfuric acid and mix thoroughly. Place the mixture on a steam bath in a hood to evaporate the ether, or allow the ether to evaporate overnight. Larger or smaller batches of acidified sodium sulfate may be prepared using the reagents in the same proportions.

24.2.6. Sodium Chloride, NaCl

24.2.7. BF3-Methanol, Boron trifluoride-MeOH, lab use only

24.2.8. Diethyl ether, reagent grade.

24.2.9. Methanol, reagent grade.

24.2.10. Silica gel

24.2.11. 2% methanolic KOH, semi-conductor grade

24.3. Standards

24.3.1. Surrogate Standard
See Table A3.

24.3.2. Matrix Spike and LCS standard
See Table A4.

25. SAMPLE COLLECTION PRESERVATION AND STORAGE

25.1. Sample collection and storage is described in Section 8 of the main body of this SOP.

26. QUALITY CONTROL

26.1. Refer to Section 9 of the main body of this SOP for Quality control procedures.

27. CALIBRATION AND STANDARDIZATION

Not applicable

28. PROCEDURE

28.1. Preparation of Aqueous Samples

28.1.1. Weigh the sample bottle and pour approximately 500 ml (100 mL for TCLP leachates) into a 1 liter wide-mouth amber jar. Reweigh the bottle and record the sample volume on the benchsheet, assuming a density of 1.0. Alternatively, measure 500 ml in a graduated cylinder. If less than 500 mL was used, reagent water may be added to make the volume up to 500 mL.

Note: Aqueous samples must be determined volumetrically for Ohio VAP samples.

28.1.2. Spike each sample blank, LCS and MS with 1.0 mL of DCAA surrogate solution. Spike matrix spikes and LCS with 1 mL of herbicide matrix spiking solution. (Refer to tables A1 and A2)

28.1.3. Add 60-80 g of NaCl to the sample and shake to dissolve the salt.

28.1.4. Hydrolysis

Use this step only if herbicide esters in addition to herbicide acids are to be determined. This is normally the case. If the herbicide esters are not to be determined, omit this step and go to 28.1.10.

Add 3 mL of 10N NaOH to the sample, seal and shake. Check the pH of the sample with pH paper. If the pH of the sample is not $\geq$12 adjust to $\geq$12 by adding more NaOH. Let the sample sit at room temperature for 2 hours to complete the hydrolysis.

28.1.6. Add 300 mL of methylene chloride to the amber jar.

28.1.7. Prior to placing samples in tumbler, the samples should be shaken or rotated vigorously for 2 minutes, venting as necessary. Place the samples in tumbler and allow them to tumble for one (1) hour. Allow the organic layer to separate from the aqueous layer. If an emulsion layer greater than one third of the solvent layer forms, use mechanical techniques to complete the phase separation. Suggested techniques are stirring, filtration through glass wool and centrifugation.

28.1.8. Pour contents of amber jar into a pre-rinsed teflon sep funnel.

28.1.9. Discard the **methylene chloride** phase.

28.1.10. Add 6 mL of cold (4°C) 1:1 sulfuric acid to the sample. Seal, and shake to mix. Check the pH of the sample with pH paper. If the pH is not $\leq$ 2, and more acid to adjust the pH to $\leq$ 2.

Caution: Addition of acid may cause heat and / or pressure build up.

28.1.11. Add 100 mL diethyl ether to the sample and extract by shaking or rotating vigorously for 10 minutes, venting as necessary. Allow the organic layer to separate from the aqueous layer. If an emulsion layer greater than one third of the solvent layer forms, use mechanical techniques to complete the phase separation. Suggested techniques are stirring, filtration through glass wool and centrifugation.

28.1.12. Drain the aqueous layer into a clean flask or beaker. Collect the ether phase in a clean flask or bottle containing approximately 10g of acidified anhydrous sodium sulfate.

28.1.13. Return the aqueous phase to the separatory funnel, add 100 mL diethyl ether and repeat the extraction procedure a second time, combining the ether extracts. Repeat the extraction a third time with 100 mL diethyl ether. Discard the aqueous phase after the third extraction.

28.1.14. Allow the extract to remain in contact with the sodium sulfate for at least 2 hours, shaking periodically. (May be left overnight). The drying step is critical: if the sodium sulfate solidifies in a cake, add a few additional grams of acidified sodium sulfate. The amount of sodium sulfate is sufficient if some free flowing crystals are visible when the flask or bottle is swirled or shaken.

28.1.15. Proceed to section 28.5, concentration.

28.2. Extraction of soil and sediment samples

28.2.1. Decant and discard any water layer on a sediment/soil sample. Record and document if a water layer was discarded on the benchsheet. Homogenize the sample by mixing it thoroughly in the container. If this is not possible place the sample in clean beaker and homogenize. Upon completion of homogenization in beaker return sample to original container. Discard foreign objects such as sticks, leaves and rocks, unless extraction of this material is required by client. If the sample consists primarily of foreign materials consult with the client (via the Project Manager or Administrator).

28.2.2. Weigh 50.0 g of moist solid sample into a clean glass jar. Use 50 g of sodium sulfate for the Method Blank and the LCS. Acidify the sample with 5 mL of concentrated HCl.

28.2.3. There should be a small amount of liquid phase. If not, add reagent water until there is. Stir well with a spatula. (Note: This is not necessary for the method blank or LCS)

28.2.4. After 15 minutes, stir with a spatula and check the pH of the liquid phase. Add more acid if necessary to bring the pH to <2, repeating the stirring and standing time after each acid addition. (Note: The pH of the method blank and LCS are not determined.)

28.2.5. Add 60 g of acidified sodium sulfate and mix well. The sample should be free flowing. If not, add more sodium sulfate.

28.2.6. Spike each sample blank, LCS and MS with 1.0 mL of DCAA surrogate solution. Spike matrix spikes and LCS with 1 mL of herbicide matrix spiking solution. (Refer to tables A1 and A2)

28.2.7. Add a minimum of 100 mL of 1:1 methylene chloride:acetone to the beaker or 100 mL of methylene chloride for long list (dinoseb).

28.2.8. Place the bottom surface of the appropriate disrupter horn tip approximately ½ inch below the surface of the solvent, but above the sediment layer.

28.2.9. Sonicate for 3 minutes, making sure the entire sample is agitated.

28.2.10. Loosely plug the stem of a 75 mm x 75 mm glass funnel with glass wool and/or line the funnel with filter paper. Add 10-20 g of anhydrous sodium sulfate to the funnel cup.

28.2.11. Place the prepared funnel on a collection apparatus. If the herbicide esters are *not* to be determined, the collection apparatus is a bottle or flask containing approximately 10g of anhydrous acidified sodium sulfate. If the herbicide esters *are* to be determined, (normally the case) the collection apparatus is glassware suitable for the hydrolysis step, typically a KD flask or Turbovap tube.

28.2.12. Decant and filter extracts through the prepared funnel into the collection apparatus.

28.2.13. Repeat the extraction two more times with additional 100 mL minimum portions of the appropriate solvent each time. Decant off extraction solvent after each sonication. On the final sonication pour the entire sample (sediment and solvent) into the funnel and rinse with an additional 10 mL-20 mL of the methylene chloride/acetone.

Note: Alternatively, the three extracts may be collected together and then filtered through the sodium sulfate.

28.2.14. If the herbicide esters are not to be determined, dry the extract as described in 28.4 or go to cleanup, section 28.3. If the herbicide esters are to be determined (normally the case) proceed to section 28.2.15

28.2.15. Add 5 mL of 37% aqueous potassium hydroxide and 30 mL of water to the extract. Check the pH with pH paper. If the pH is not $\geq$12, adjust with additional KOH.

28.2.16. Heat on a water bath at 60-65°C for 2 hours. Allow to cool. Higher temperatures, up to 90°C, may be used if needed to remove the ether layer within 2 hours.

28.2.17. Transfer the solution to a separatory funnel and extract three times with 100 mL portions of methylene chloride. **Discard the methylene chloride phase.** The aqueous solution contains the herbicides.

28.2.18. Adjust the pH of the solution to ≤2 with 1:1 sulfuric acid.

28.2.19. Extract three times with 60 mL diethyl ether.

28.2.20. Proceed to section 28.3, Cleanup, if required, or Section 28.4, Extract drying.

28.3. Cleanup

This cleanup step may be necessary if the procedure for determining the herbicide acids only is being followed. (See section 28.2.14) It is not normally required if the acids and esters are being determined. (The usual case.) If cleanup is not required, proceed to section 28.4, Extract drying.

28.3.1. Prepare 45 mL of basic extraction fluid by mixing 30 mL of reagent water with 15 mL of 37% KOH. Use three 15 mL portions of this fluid to partition the extract from section 28.2.12 or 28.2.20, using a small separatory funnel. **Discard the organic phase.**

28.3.2. Adjust the pH of the solution to ≤2 with cold (4°C) sulfuric acid. (1:1). Extract once with 40 mL diethyl ether and twice with 20 mL diethyl ether.

Caution: Addition of acid may cause heat and / or pressure build up.

28.4. Extract drying

28.4.1. Pour the extracts through a funnel containing acidified sodium sulfate into a flask or bottle containing approximately 10 g acidified sodium sulfate. Rinse the funnel with a little extra diethyl ether.

28.4.2. Allow the extract to remain in contact with the sodium sulfate for at least 2 hours, shaking periodically. (May be left overnight). The drying step is critical: if the sodium sulfate solidifies in a cake, add a few additional grams of acidified sodium sulfate. The amount of sodium sulfate is sufficient if some free flowing crystals are visible when the flask or bottle is swirled or shaken. Proceed to section 28.5, concentration.

28.5. Concentration

28.5.1. Transfer the ether extract into a Turbovap concentrator tube or a 500 mL K-D flask equipped with a 10 mL concentrator tube. Use a stirring rod to crush the caked sodium sulfate during transfer. Rinse the flask or bottle with 20-30 mL ether to complete transfer.

28.5.2. Attach a three ball Snyder column to the K-D apparatus, prewet the column with a few mL of ether from the top, and place the apparatus on a water bath at approximately 60°C. At the proper rate of distillation, the balls of the column will chatter, but the chambers will not flood. When the apparent volume reaches 2 mL, remove from the water bath and allow to completely cool.

28.5.3. For TCLP extracts only, add 4 mL of toluene to the K-D (buffer reacts with diazald solution used in esterification).

28.5.4. Remove TCLP extracts at approximately 2 mL when boiling slows and only toluene is remaining. Cool and cap in CT.

28.5.5. Carefully disassemble the concentrator tube and rinse the lower glass joint with a small amount of diethyl ether.

28.5.6. The extract is now ready for esterification by the Diazomethane Bubbler Method (28.7) or the TCLP esterification by Boron Triflouride Method (28.8).

28.6. Esterification (Bubbler Method)

28.6.1. Assemble the diazomethane apparatus (see figure below) in a hood. Add 25-30 mL of diethyl ether to tube 1. Add 1.5 mL 37% KOH, 1 mL Carbitol, and 1 mL of ether and 3-4 g of diazald to tube 2.

28.6.2. Place the tip of the disposable pipette into the vial containing the first sample extract. Apply nitrogen flow (approx. 10 mL/min) to bubble diazomethane through the sample extract for about 4-5 minutes. Replace the disposable pipette and place the tip into the vial containing the second extract. Replace Tube 2 solution after second extract.

28.6.3. Allow the extracts to stand for 20 minutes, then add approximately 0.2 g of silica gel to each extract. Allow to stand for an additional 20 minutes.

28.6.4. Adjust the volume to 10 mL with hexane. The sample is now ready for gas chromatography.

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

laboratory bench sheet will be recorded as 100mL to avoid using the dilution factor field in QuantIMS.

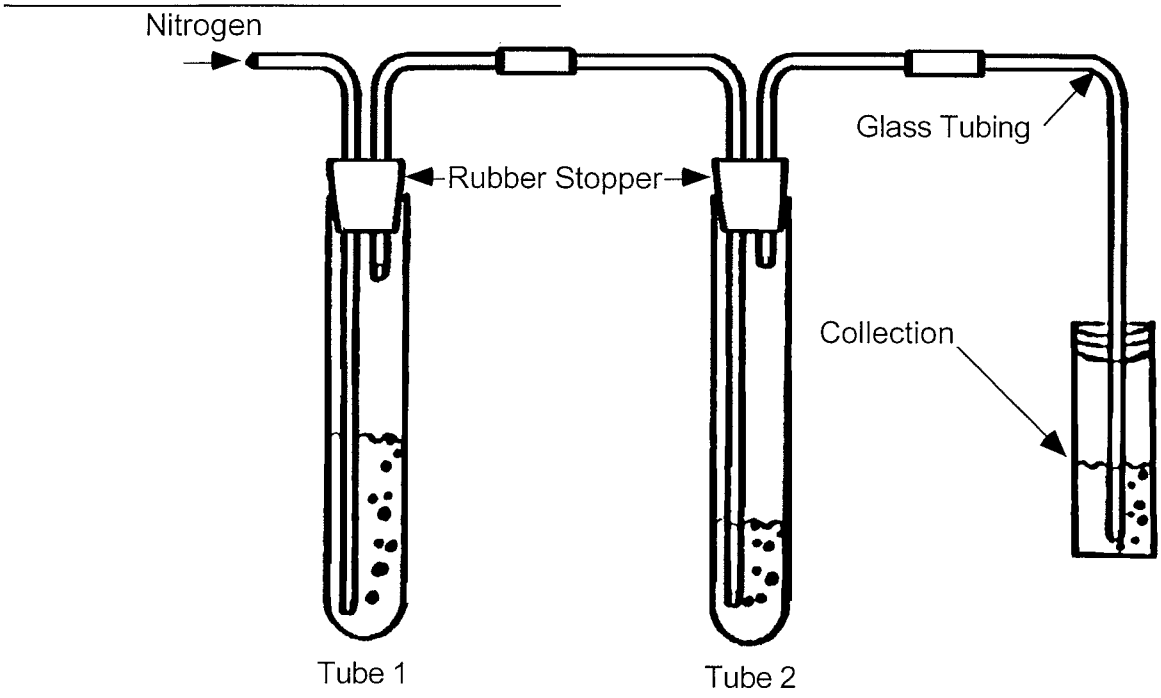
28.7. Exterification by Boron trifluoride (TCLP extracts only).

28.7.1. To the concentrator tube with the extract, add 2 mL of Boron trifluoride. Place a two-ball micro-Snyder column on the concentrator tube and place in the Hot-Blok water bath adjusted to 35-40°C for 60 minutes. Remove and let cool for approximately ten minutes.

28.7.2 With a 10 mL graduated disposable 5-3/4" pipette 4.5 mL of 5% neutral sodium sulfate and place it in the concentrator tube. Seal with a tight fitting ground glass stopper. Vortex the mixture for one minute. Let stand for ten minutes to settle. With a 5-3/4" disposable pipette, withdraw the bottom aqueous layer into a 16 x 100 culture tube for proper disposal.

28.7.3 Prepare a clean up column in a 5-3/4" disposable pipette by placing a small amount of glass wool in the narrow end of the pipette and add about ½ inch – 1 inch of florisil and sodium sulfate each. Leave about a 1 inch gap at the top. Place the extract in the clean-up column and gently force it through by using a pipette bulb into a small test tube. **Care should be taken to avoid channeling.** Rinse the concentrator tube with 1-2 mL of toluene. Transfer the column rinsate into the test tube. Rinse the column with additional toluene. There should be approximately 4 mL collected in the test tube. Bring the final volume to 10 mL with toluene by visually comparing it to a calibrated collection tube.

Note: It is critical that all toluene is retained and no water should enter the column.



29. DATA ANALYSIS AND CALCULATIONS

Not applicable

30. METHOD PERFORMANCE

Refer to CORP-GC-0001 for details of method performance.

31. POLLUTION PREVENTION

Refer to section 14 of the main body of this SOP.

32. WASTE MANAGEMENT

Refer to section 15 of the main body of this SOP.

33. REFERENCES

33.1. SW846, Test Methods for Evaluating Solid Waste, Third Edition, Update III, December 1996, Chlorinated Herbicides, Method 8151A.

34. MISCELLANEOUS

34.1. Modifications from Reference Method

34.1.1. Directions to add sufficient reagent water to the soil sample so that the pH can be measured have been added (Section 11.1.2)

34.1.2. The bubbler esterification method uses methanolic KOH in place of the aqueous KOH / carbitol mixture recommended in method 8150B. This has been found to provide a more effective and reliable esterification.

34.2. Modifications from previous revisions

References have been updated

34.3. Tables

Table A1
Herbicide Surrogate Spiking Solutions

Analyte Group	Surrogate Spike Solution ID	Volume (mL)
Herbicides	Herbicides Water	1.0
Herbicides	Herbicides Soil	1.0

Table A2
Herbicide Matrix Spike and LCS Solutions

Analyte Group	Matrix Spike Solution ID	Volume (mL)
Herbicides	Herbicides MS-Soil	1.0
Herbicides	Herbicides MS-Water	1.0

Table A3
Herbicide Surrogate Spike Components

Type	Compounds[1]	Solvent	Conc. (ug/mL)
Herbicides WS	2,4-DCAA	Acetone	2

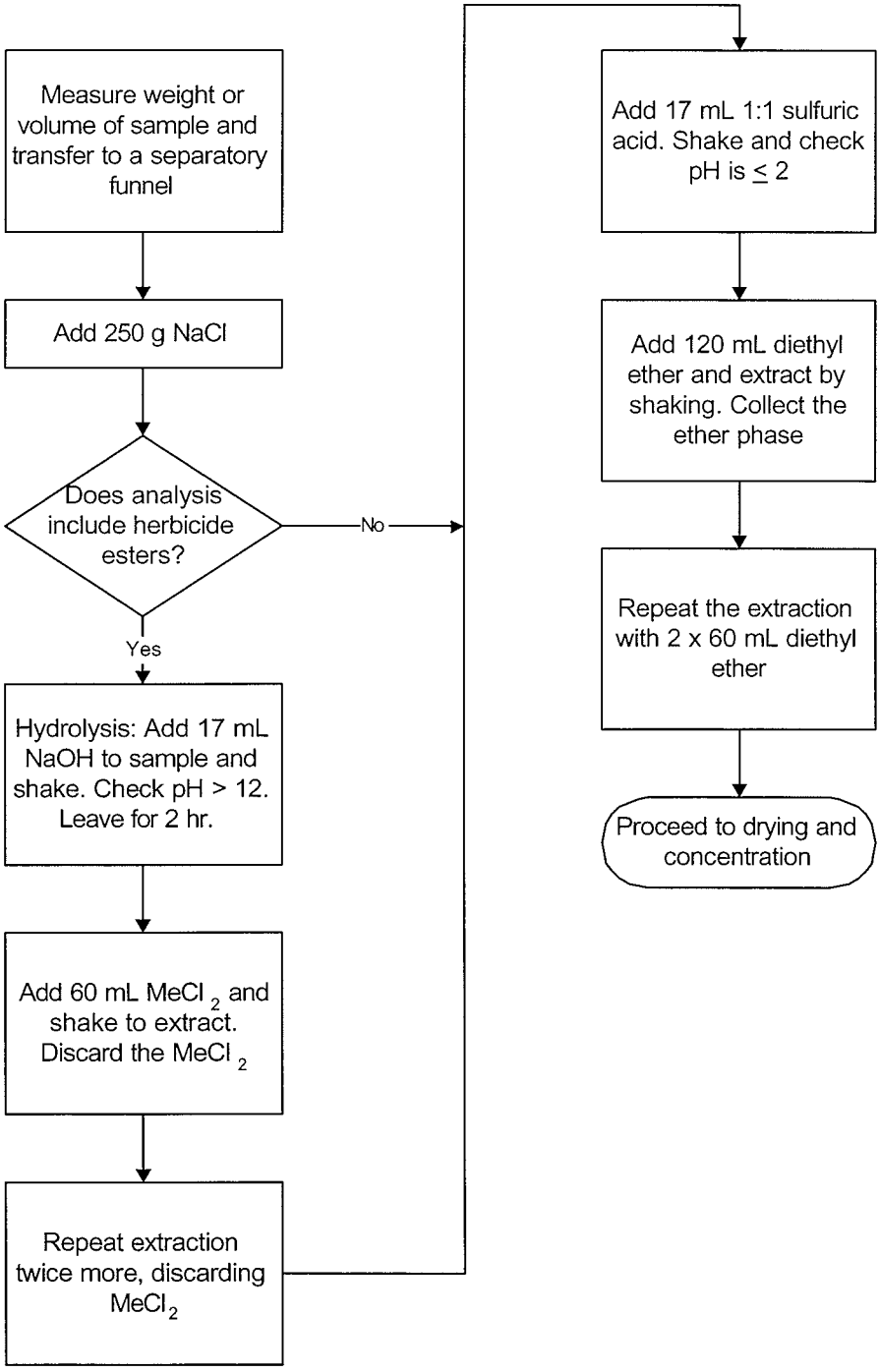
Table A3 Herbicide Surrogate Spike Components			
Type	Compounds[1]	Solvent	Conc. (ug/mL)
Herbicides SS	2,4-DCAA	Acetone Methanol	20

[1]The surrogate is spiked as the free acid

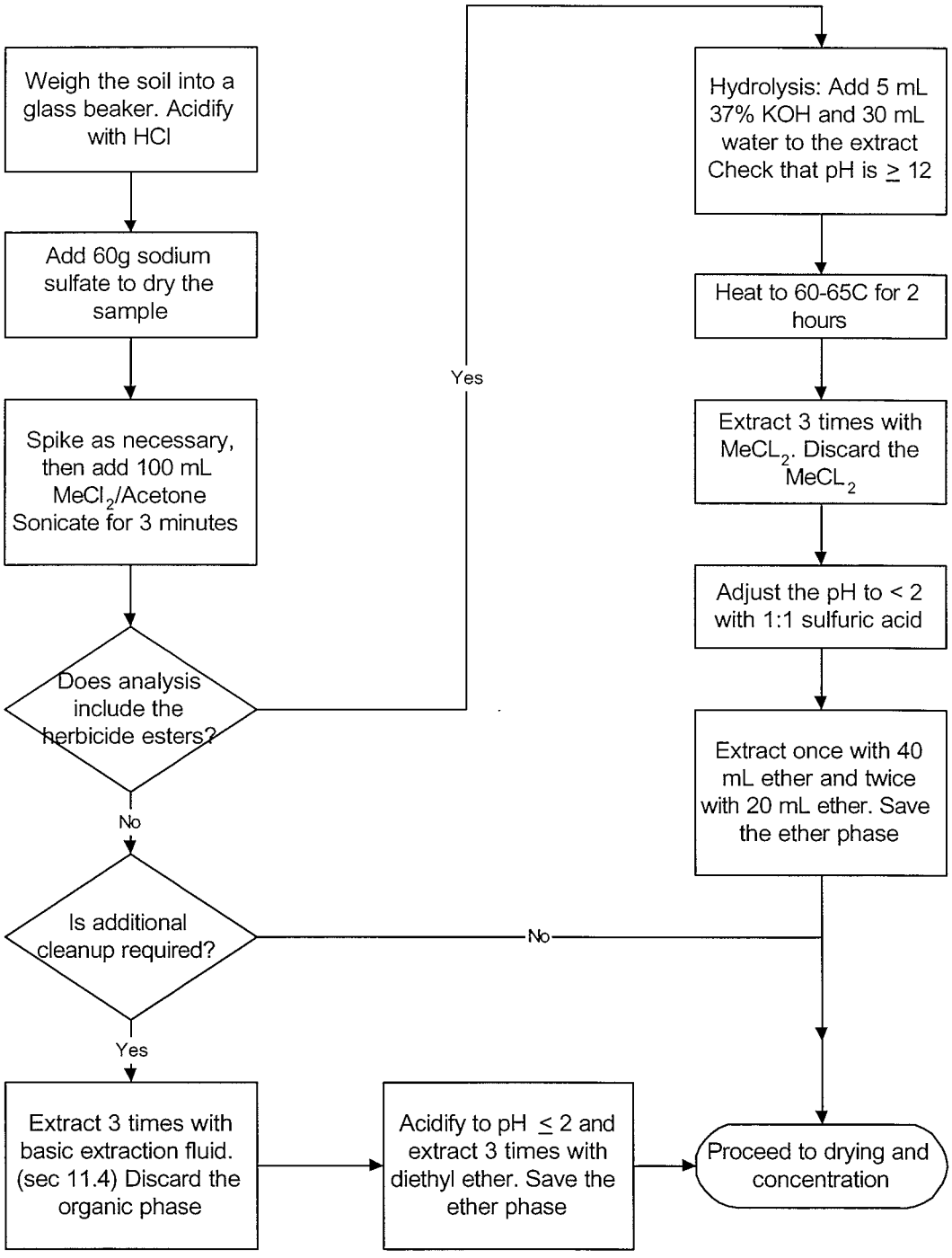
Table A4 Herbicide Matrix Spike Components				
Type	Compounds[1]	Compounds[1] Solvent	Soil Conc. (ug/mL) Solvent	Water Conc. (ug/mL)
Herbicides MS	2,4-D	Acetone	20 Methanol	2
	2,4-DB		20	2
	2,4,5-TP (Silvex)		5	0.5
	Dalapon		10	1
	Dicamba		10	1
	Dichloroprop		10	1
	Dinoseb		3	.3
	2,4,5-T		5	0.5

[1]The herbicide spiking solution contains the herbicides as the free acids.

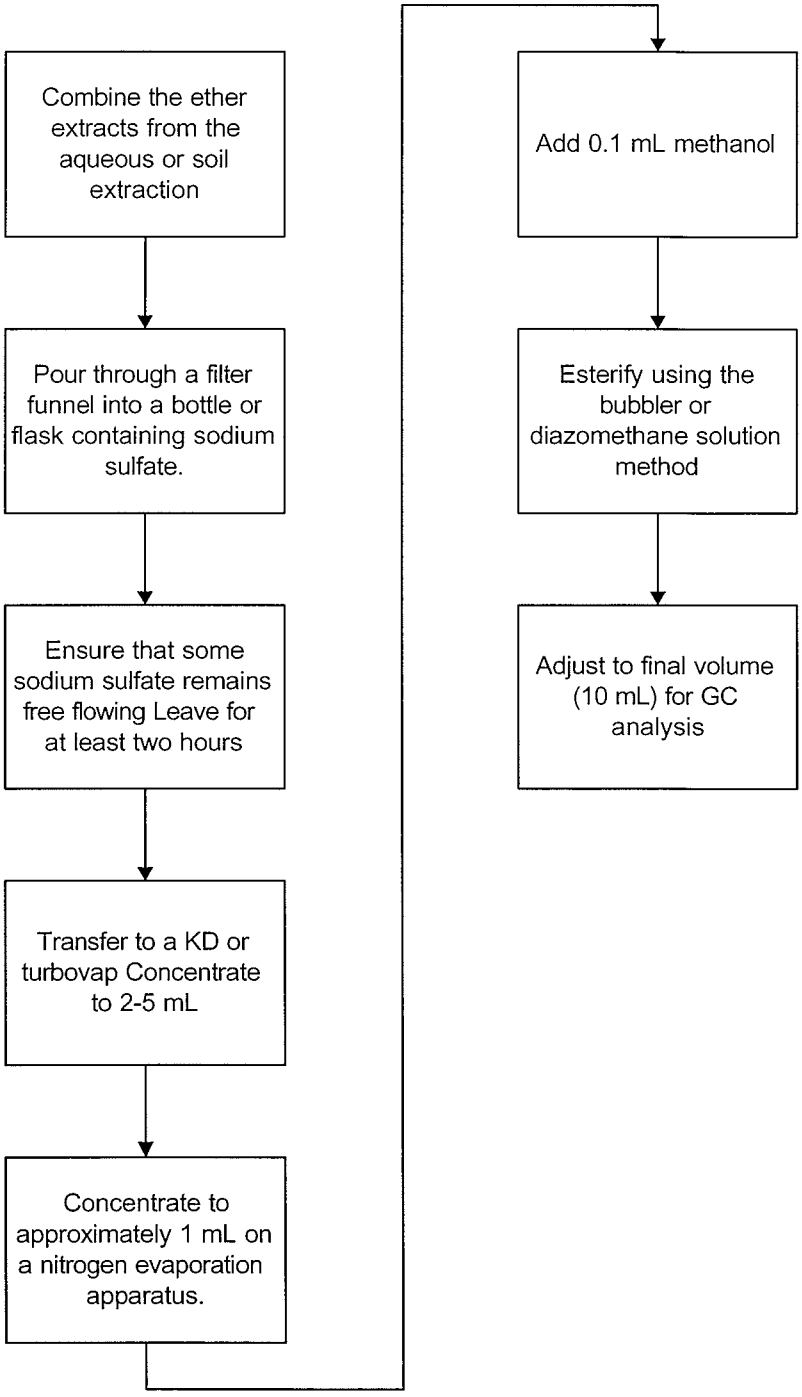
Extraction of Aqueous Samples



Extraction of Soils and Sediments



Drying, Concentration and Esterification



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Implementation Date: 6/5/01

SOP No. NC-GC-0025
Revision No. 4
Revision Date: 05/23/01
Page 1 of 20

STL NORTH CANTON STANDARD OPERATING PROCEDURE

TITLE: VOLATILE PETROLEUM HYDROCARBONS AS GASOLINE BY PURGE AND TRAP GAS CHROMATOGRAPHY

(SUPERSEDES: REVISION 3 (DATED 03/30/01))

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1. SCOPE AND APPLICATION

1.1. This method encompasses the analysis of Volatile Total Petroleum Hydrocarbons as gasoline in water and solid samples using purge and trap gas chromatography with flame ionization detectors (FID) or photoionization detectors (PID)/FID in series. This standard operating procedure (SOP) is based on SW-846 Methods 8015A and 8015B. The approximate working range is 50 to 1000 µg/L for waters, 50 to 1000 µg/kg for low-level solids, and 500 to 5000 µg/kg for medium-level solids.

1.2. The associated QuantIMs method codes are KJ and WU.

1.3. This document accurately reflects current laboratory SOPs 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. Volatile petroleum hydrocarbons are extracted from an aqueous or solid sample by purging with an inert gas. The extracted compounds are trapped on an absorbent material and then heated and back-flushed with helium in order to release the volatile petroleum hydrocarbons. At this point they are carried onto a capillary gas chromatography column for analysis by an FID or PID/FID in series.

3. DEFINITIONS

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

4. INTERFERENCES

4.1. Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus that lead to discrete artifacts. All of these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. Specific selection of reagents may be required to avoid introduction of contaminants.

4.2. When analyzing for volatile organics, samples can be contaminated by diffusion of volatile organics (particularly chlorofluorocarbons and methylene chloride) through the sample container septum during shipment and storage. A trip blank prepared from organic-free reagent water and carried through sampling and subsequent storage and handling must serve as a check on such contamination.

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 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: Benzene

5.3.2. Chemicals known to be **flammable** are: Methanol (MeOH)

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

5.5. The preparation of standards and reagents will be conducted in a fume hood with the sash closed as far as the operation will permit.

5.6. It is recommended that neat standards be purchased only as a last resort. The preparation of standards from neat materials and reagents {as well as glassware cleaning procedures that involved solvents such as methylene chloride} should be conducted in a fume hood with the sash closed as far as the operations will permit.

5.7. Standards in solution may be diluted in the open laboratory when syringes and the like are utilized.

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

6. EQUIPMENT AND SUPPLIES

6.1. Gas chromatographic system set-up with purge and trap capabilities, FID or PID/FID in series, helium gas, integrators and columns

6.1.1. Recommended GC Columns

6.1.1.1.Restek RTx502.2, 60 m × 0.53 mm ID, 3.0 µm film thickness

6.1.1.2.Restek RTx1, 105 m × 0.53 mm ID, 3.0 µm film thickness

6.1.2. Helium Carrier Gas: 22 cm/sec linear velocity

6.1.3. Recommended Instrument Conditions

6.1.3.1.Oven Temperature

6.1.3.1.1. 50°C, hold for two (2) minutes

6.1.3.1.2. 5°C per minute to 180°C, hold for 2.5 minutes

6.1.3.2.Detector Temperatures

6.1.3.2.1.FID - 250°C

6.1.3.2.2.PID - 250°C

6.1.3.3.Inlet Temperature

6.1.3.3.1.Right inlet at 230°C

6.1.3.4.Purge Parameters

6.1.3.4.1.Purge at 40 mL/minute for eleven (11) minutes

6.1.3.4.2.Dry purge for four (4) minutes

6.1.3.4.3.Desorb for one (1) minute at 250°C

6.1.3.4.4.Bake for twelve (12) minutes at 260°C

6.1.3.4.5.Preheat for three (3) minutes at 40°C

6.2. Syringes: 500 µL, 5 mL, and 10 mL luerlok with needles

6.3. Volumetric Flasks: 50 mL and 100 mL with ground-glass stoppers

6.4. Microsyringes: 10 µL and 50 µL with needles

6.5. Test Tubes and Caps: 10 mL or 20 mL

6.6. Vials: 40 mL sampling vials

6.7. Aluminum Foil

6.8. Tongue Blades

6.9. Top-Loading Balance: capable of accurately weighing ± 0.01 g

6.10. Vortex

7. REAGENTS AND STANDARDS

7.1. Reagents

7.1.1. Methanol: Purge and Trap grade

7.2. Standards

7.2.1. Stock solutions may be prepared from pure materials or purchased as certified solutions. It is acceptable to use either a commercial fuel or GRO (Gasoline Range Organics) component standard for the stock solution.

7.2.2. Secondary dilution standards are prepared at 100 µg/mL for a commercial fuel standard and at 10 µg/mL for a GRO standard.

7.2.3. Standards must be replaced after 6 months or sooner if comparison with check standards prepared from an independent source indicates a problem.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Solid, sludge, and water samples are stored in glass containers with Teflon®-lined caps at 4°C ± 2°C until the time of analysis.

8.1.1. Soil can be collected using an EnCore sampler or other appropriate device. A methanol trip blank must accompany each batch of samples (for each site and each day that samples are collected).

8.2. Holding Times

8.2.1. The holding time is fourteen (14) days from sampling to the completion of analysis.

9. QUALITY CONTROL

9.1. Batch Definition

9.1.1. A batch is a group of no greater than 20 samples, excluding QC samples (LCS, Method Blank, MS, MSD), which are processed similarly with respect to the procedure. All sample setups must be initiated within a 24 hour period from the initial preparation or extraction and without interruption of the process. All samples within the batch must be treated with the same lots of reagents and the same processes.

9.2. Method Blank

9.2.1. One method blank (MB) must be processed with each preparation batch. The method blank consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The method blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. The method blank should not contain any analyte of interest at or above the reporting limit.

9.2.2. Corrective Action for Blanks

9.2.2.1. If the analyte level in the method blank exceeds the reporting limit for the analytes of interest in the sample, all associated samples are reprepared and reanalyzed. If this is not possible due to limited sample quantity or other considerations, the corresponding sample data **must be addressed in the project narrative.**

9.2.2.2. If there is no analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers.

Such action must be taken in consultation with the client and must be addressed in the project narrative.

9.3. Laboratory Control Sample (LCS)

9.3.1. One LCS 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. Corrective Action for LCS

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

9.3.2.1.1. The only exception is, if the LCS is biased high and the analyte is not detected (ND) in the associated sample, the batch is acceptable. **This must be addressed in the project narrative.**

9.3.2.1.2. 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. Corrective action for MS/MSDs

9.4.2.1. If the analyte recovery or RPD falls outside the acceptance range, the recovery of that analyte must be in control for the LCS. If the LCS recovery is within limits, then the laboratory operation is in control and

the results may be accepted. If the recovery of the LCS is outside limits, corrective action must be taken. Corrective action will include repreparation and reanalysis of the batch.

9.4.2.2. If the native analyte concentration in the MS/MSD exceeds 4x the spike level for that analyte, the recovery data is reported as DIL (diluted out).

9.4.2.3. If an MS/MSD is not possible due to limited sample volume then a laboratory control sample duplicate (LCSD) should be analyzed. The RPD of the LCS and LCSD must be compared to the matrix spike RPD limits.

9.4.2.4. If client program requirements specify to confirm matrix interference's, repreparation and reanalysis of the MS/MSD may be necessary.

9.5. Surrogates

9.5.1. 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.

9.5.2. Refer to corporate SOP #CORP-GC-0001 when running TPH/BTEX in tandem.

9.5.3. All associated samples, blank and QC, will be spiked with a Trifluorotoluene surrogate standard. Control limits are 50-150 until sufficient data points are available to generate historical limits as described in SOP #NC-QA-0018. Surrogate recoveries outside of control limits due to hydrocarbon interference in samples, will be narrated in the final report. All Ohio VAP samples will be reanalyzed if surrogate recoveries are outside of control limits.

9.5.4. Corrective action is required if the surrogate compound(s) in the blank or samples fall outside the recovery limits. The following corrective action should be taken:

9.5.4.1. Check all calculations to ensure that no errors were made; check internal standard (if applicable) and surrogate spiking solution for degradation, contamination, etc.; also check instrument performance.

9.5.4.2. If the above step fails to reveal a problem, reanalyze the blanks and/or samples. If reanalysis does not confirm original results and is within QC acceptance criteria, then the problem was within the analyst's control and only the reanalyzed data should be reported.

9.5.4.3. If the sample with surrogate recoveries outside the recovery limits was a sample used for a MS/MSD and the surrogate recoveries in the MS/MSD are also outside the control limits, then the sample, the MS, and the MSD do not require reanalysis as this phenomenon would indicate a possible matrix problem.

9.5.4.4. If the reanalysis does confirm the original results, then the following steps should be taken.

9.5.4.4.1. For a blank, the analytical system must be considered out of control. The problem must be corrected before continuing. This may include recalibration of the instrument.

9.5.4.4.2. For a sample, the results from the original analyses must be reported and the data flagged as surrogates out due to matrix effect.

9.5.5. Surrogate spiking and calculations

9.5.5.1. Water and low-level soil samples are spiked with a 50 ng standard.

9.5.5.2. Medium-level soils are spiked with a 50ng standard for a 5g prep.

9.5.5.3. The surrogate area and hydrocarbon areas are measured separately or subtracted from each other, and the results are calculated according to the following equations.

9.5.5.3.1. $$\textit{TPH, ng} = \frac{\textit{Total TPH area - Surrogate area}}{\textit{Average Response Factor}}$$

9.5.5.3.2. $$\textit{Surrogate, ng} = \frac{\textit{Surrogate Area}}{\textit{Average Response Factor}}$$

9.6. Control Limits

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

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

9.7. Method Detection Limits (MDLs) and MDL Checks

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

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

9.8. Nonconformance and Corrective Action

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

10. CALIBRATION AND STANDARDIZATION

10.1. External calibration is recommended. Prepare and analyze standards at a minimum of five concentration levels. The low level standard should be at the reporting limit. The other standards define the working range of the detector. 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.

10.1.1. The gasoline standard calibration range is 250-8000 ng. The gasoline standard is analyzed when samples are listed as TPH (as Gasoline). Ohio VAP rules require the carbon range to be listed as C6-C10.

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

Note: 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. Use of peak area or height must be consistent. It is not permitted to switch between using peak area and height for quantitation within an analytical sequence.

10.1.3. 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 and any changes in instrument operating parameters, including gas flows, detector temperatures, oven temperatures, etc.

10.1.4. The standards used for medium-level analysis must contain a constant amount of methanol (100µL) to compensate for the effects of methanol on purge efficiency and detector response.

10.2. Average response factor, linear regression, or quadratic curves may be used to fit the data.

10.2.1. The average response factor may be used if the percent relative standard deviation (%RSD) of the response factors or calibration factors is <20%.

10.2.1.1. $$\textit{Average Response Factor} = \frac{\sum RF_{1-n}}{n}$$

Where:

n = Number of calibration levels

$\Sigma RF_{1\text{-}n}$ = *Sum of response factors for each calibration level*

10.2.2. Linear regression is a special case of the quadratic fit and may be used if the calibration range is sufficiently narrow so that a straight line will fit the calibration points.

10.2.2.1. $\boldsymbol{Amount\ (ng) = A + BR}$

Where:

A = Intercept

B = Slope

R = Response

10.2.3. Quadratic Curve

10.2.3.1. $\boldsymbol{Amount\ (ng) = A + BR + CR^2}$

Where:

A = Intercept

B = Slope

C = Curvature

R = Response

10.3. Evaluation of Calibration Curves

10.3.1. The percent relative standard deviation (%RSD) 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.

10.3.2. The least squares regression line is calculated and used to calculate the predicted concentration for each level. The percent relative standard deviation is calculated as follows:

10.3.2.1. $$\%\ RSD = 100\% \times \sqrt{\frac{\sum_{i=1}^{N}\left[\frac{C_i - PC_i}{C_i}\right]^2}{(N-P)}}$$

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: When average response factors are used, this equation gives the same value as the %RSD of the response factors.

10.4. The following requirements must be met for any calibration to be used:

10.4.1. Response must increase with increasing concentration.

10.4.2. If a curve is used, the intercept of the curve at zero response must be less than the reporting limit for the analyte.

10.4.3. Relative standard deviation of the calibration points from the curve used must be <20%.

10.4.4. Some data systems will not measure the %RSD from a linear or quadratic fit. In this case, the correlation coefficient may be used as an alternative to the %RSD and must be greater than 0.995.

Note: In a linear or quadratic calibration fit, the points at the lower end of the calibration curve have less weight in determining the curve generated than points at the high concentration end of the curve. However, in environmental analysis, accuracy at the low end of the curve is very important. For this reason it is preferable to increase the weighting of the lower concentration points. 1/Concentration^2 weighting (often called 1/X^2 weighting) will improve accuracy at the low end of the curve and should be used if the data system has this capability.

10.5. Calibration verification

10.5.1. Continuing Calibration

10.5.1.1. The working calibration curve or RF must be verified by the analysis of a mid point continuing calibration standard at the beginning, after every 10 samples, and at the end of the analysis sequence.

10.5.2. Daily Calibration

10.5.2.1. At least every 24 hours, a daily calibration must be analyzed. The requirements of the daily calibration are the same as the continuing calibration with the addition that retention times are updated.

10.5.3. Any analyte that is reportable as found must have a % difference of ≤ 15% in the preceding continuing calibration, on the column used for quantitation.

Note: "Reportable as found" is defined as any analyte that would be reported as anything other than a non-detect.

10.5.4. It is not necessary to run a continuing calibration standard at the beginning of the sequence if the first 10 samples are analyzed immediately after the completion of the initial calibration.

10.5.5. The last sample in the sequence must be followed by an ending calibration. The ending calibration serves the analyst in judging the validity of the sequence.

10.5.6. Percent Difference Calculation

10.5.6.1. $$\textit{\% Difference} = \frac{\textit{Expected value - Calculated value}}{\textit{Expected value}} \times 100\%$$

10.5.7. Corrective Actions for Continuing Calibration

10.5.7.1. If the % difference for any analyte is > -15% to +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 response for any analyte still varies by more than 15%, a new calibration curve must be prepared.

10.5.8. Corrective Action for Samples

10.5.8.1. Any samples injected *after* the standard exceeding the continuing calibration criteria must be reinjected.

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. Summary

11.3.1.1. Samples fall into three general categories: water, low-level soil, and medium-level soil or waste. For water and low-level soil samples, no preparation is necessary. For those soils which contain greater than 1 mg/kg of individual purgeable compounds, a medium-level preparation is necessary.

11.3.2. Medium-Level Sample Preparation

11.3.2.1. Mix the contents of the sample container with a narrow metal or wood spatula. Using a top-loading balance, weigh 5 g of sample (wet weight) into a tared vial. Record the weight to 0.1 g.

11.3.2.2. Quickly add MeOH and bring the final volume to 5 mL. Cap the vial and vortex to mix for two (2) minutes. Inject 100 µL or less into 5 mL reagent water in luerlok syringe.

Note: Sections 11.3.2.1 and 11.3.2.2 must be performed rapidly and without interruption to avoid the loss of volatile organics.

11.4. Sample Analysis

11.4.1. Summary

11.4.1.1. Samples are analyzed upon successful completion of the initial QC and calibration activities. Where possible, samples are screened to determine the correct aliquot for analysis. Alternatively, an appropriate aliquot can be determined from sample histories.

11.4.2. Sample Analysis - Water

11.4.2.1. Fill a 5 mL syringe with the proper aliquot (as determined in Section 11.4.1.1) of sample. Adjust the final volume to 5 mL before the sample is purged.

11.4.2.2. Purge the sample for eight (8) minutes, ensuring that the trap is cooled (below 30°C).

11.4.2.3. After purging is complete, desorb the sample onto the column, start the temperature program, and begin data acquisition. After desorption, bake the trap to condition it for the next analysis. When the trap is cool, it is ready for the next sample.

11.4.2.4. If the initial analysis of a sample or a dilution of the sample has a concentration of analytes that exceed the initial calibration range, the sample must be reanalyzed at a higher dilution. If the analysis has very high concentrations of analytes, then this analysis must be followed by the analysis of a blank to ensure that the system is free of contamination.

11.4.3. Sample Analysis - Medium-Level Soil/Sediment and Waste

11.4.3.1. Fill a 5 mL syringe with 5 mL of reagent water. Add 100 µL of methanol extract from the sample preparation. If less than 100 µL of methanol extract is to be added to the water, dilute the extract, or add methanol, such that a volume equal to 100 µL will be added to the water in the syringe. Inject the sample into the purging chamber and proceed with the analysis as described in Sections 11.4.2.3 through 11.4.2.4.

11.4.4. Sample Analysis - Low-Level Soil

Note: This analysis applies to samples containing individual purgeable compounds of < 1 mg/kg. It is limited to soil/sediment and waste samples of a similar (granular and porous) consistency.

11.4.4.1. Weigh 5 g of sample (or less, if a dilution is required) into a tared purge vessel. Add 5 mL of reagent water. Proceed with the analysis as described

in Sections 11.4.2.3 through 11.4.2.4, with the exception that the sample is heated to 40° C during the purge cycle.

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.

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

12. DATA ANALYSIS AND CALCULATIONS

12.1. Water and Water-Miscible Waste

12.1.1. $$\textit{Concentration, } \mu g/L = \frac{\textit{ng from calibration curve (Sec. 10.2.2.1 or 10.2.3.1)}}{\textit{Sample Volume (mL)}}$$

12.2. Medium-Level Soil

12.2.1.

$$\textit{Concentration, } mg/kg = \frac{\textit{ng from calibration curve (Sec. 10.2.2.1 or 10.2.3.1)} \times 10\ mL}{\textit{amt injected (mL)} \times \textit{amt extracted (g)} \times 1000}$$

12.3. Low-Level Soil

12.3.1. $$\textit{Concentration, } \mu g/kg = \frac{\textit{ng from calibration curve (Sec. 10.2.2.1 or 10.2.3.1)}}{\textit{amt purged (g)}}$$

13. METHOD PERFORMANCE

13.1. Each laboratory must have initial demonstration of performance data on file and corresponding method detection limit files.

13.2. Training Qualifications:

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

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

14. POLLUTION PREVENTION

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

15. WASTE MANAGEMENT

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

15.2. Solid materials (gloves, soiled paper products, etc.) are placed in the solid debris container. Do not put liquids in the solid waste container.

15.3. Refer to the Laboratory Sample and Waste Disposal plan.

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

16. REFERENCES

16.1. References

16.1.1. SW-846 Method 8015B, Revision 2, December 1996.

16.1.2. SW-846 Method 8015A, Revision 1, July 1992.

16.1.3. SW-846 Method 5030A, Revision 1, July 1992.

16.1.4. STL North Canton Laboratory Quality Manual (LQM), current revision

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

16.2. Associated SOPs

16.2.1. CORP-GC-0001, current revision.

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

16.2.3. QA Policy, QA-003

16.2.4. Glassware Washing, NC-QA-0014

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

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

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

17.1. Reporting limits

17.1.1. The lower reporting limit (RL) for undiluted samples are 100 µg/L for water, 100 µg/kg for low-level soils, and 10 mg/kg for medium-level soils.

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

STL North Canton
STANDARD OPERATING PROCEDURE

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

(SUPERSEDES: None)

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1. SCOPE AND APPLICATION

1.1 This document describes a procedure for the determination of dissolved gases in groundwater. The method is applicable to the preparation of water samples for the analysis of the headspace to quantify part-per-billion levels of dissolved gases in water samples.

1.2 The associated QuantIMs method code is MM.

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

2. SUMMARY OF METHOD

2.1. A water sample is collected in the field in a 43-mL VOA vial with no headspace. Prior to analysis the sample is transferred into a 22-mL serum vial with a crimp cap. Headspace is generated using UHP helium. The sample is loaded onto the headspace autosampler and analyzed by a Gas Chromatograph (GC) equipped with an FID detector.

3. DEFINITIONS

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

4. INTERFERENCES

4.1. Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus that lead to discrete artifacts. All of these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. Specific selection of reagents may be required to avoid introduction of contaminants.

5. SAFETY

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

5.2.1. 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. 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.

5.4. The preparation of standards and reagents will be conducted in a fume hood with the sash closed as far as the operation will permit.

5.5. It is recommended that neat standards be purchased only as a last resort. The preparation of standards from neat materials and reagents {as well as glassware cleaning procedures that involved solvents such as methylene chloride} should be conducted in a fume hood with the sash closed as far as the operations will permit.

5.6. Standards in solution may be diluted in the open laboratory when syringes and the like are utilized.

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.

6. EQUIPMENT AND SUPPLIES

6.1 Sample Containers: 44mLVOA vials, 22mL crimp cap vials.

6.2 Instrumentation

6.2.1 Column(FID) - Restek Rt-UPLOT; 30m, 0.53mm ID

6.2.2 Autosampler - Tekmar 7000 Headspace Autosampler

6.3 Syringes - 10µL - 5.0-mL gas tight syringes.

6.3 Data System – Chemstation for acquisition and Target™ for data processing.

7. REAGENTS AND STANDARDS

7.1. Gas cylinders of ultrahigh purity helium, hydrogen, and nitrogen.

7.2 Calibration Standards: The primary standard is purchased through Scott Specialty Gases. The FID calibration standard is composed of nominally 1% (mole basis) methane, ethane, ethene, acetylene, and propane.

7.3 The calibration levels are achieved by injecting different amounts of the standard into a 22-mL vial that contains 18 mL of deionized water and 4 mL of headspace.

7.4 Laboratory Control and Initial Calibration Verification Samples: The LCS and ICV are fortified to the concentration of the middle calibration standard.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

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

9. QUALITY CONTROL

9.1. Batch Definition

9.1.1. A batch is a group of no greater than 20 samples excluding QC samples (LCS, Method Blank, MS, MSD) which are processed similarly, with respect to the procedure. All sample setups must be initiated within a 24 hour period from the initial preparation or extraction and without interruption of the process. All samples within the batch must be treated with the same lots of reagents and the same processes.

9.2. Method Blank

9.2.1. One method blank (MB) must be processed with each preparation batch. The method blank consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The method blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. The method blank should not contain any analyte of interest at or above the reporting limit, with the exception of common laboratory contaminants.

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

9.2.2. Corrective Action for Blanks

9.2.2.1. If the analyte level in the method blank exceeds the reporting limit for the analytes of interest in the sample, all associated samples are reprepared and reanalyzed. If this is not possible due to limited sample quantity or other considerations, the corresponding sample data **must be addressed in the project narrative.**

9.2.2.2. If there is no analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. **Such action must be taken in consultation with the client and must be addressed in the project narrative.**

9.3. Laboratory Control Sample (LCS)

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

procedure. The LCS is used to monitor the accuracy of the analytical process. On-going monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines.

9.3.2. Corrective Action for LCS

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

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

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

9.4. Control Limits

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

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

9.5. Method Detection Limits (MDLs) and MDL Checks

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

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

9.6. Nonconformance and Corrective Action

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

10. CALIBRATION AND STANDARDIZATION

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

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

Concentrations are in µg/L unless noted otherwise.

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

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

10.1.3. The %RSD average of all analytes must be ≤ 30%.

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

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

include, but is not limited to, instrument maintenance and/or re-preparation of standards.

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

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

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

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

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

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

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

11. PROCEDURE

11.1. One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo and is approved by a Technical Specialist and QA Manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file.

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

11.3. Sample Analysis

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

GC Conditions

Gas Flows:

Carrier (Helium):	20 mL/min
Oven Program:	50°C for 2.1 minutes

FID Conditions

FID Temp.:	200°C
Hydrogen Flow:	40 mL/min
Air Flow:	450 mL/min

11.4. Analytical Documentation

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

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

11.4.3. Documentation such as all associated instrument printouts (final runs, screens, reruns, QC samples, etc.) and daily calibration data corresponding to all final runs is available for each data file.

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

12. DATA ANALYSIS AND CALCULATIONS

12.1 Calibration Factor for GC-FID

$$\mathbf{CF_\chi = A_\chi / C_\chi}$$

where:

CF_χ = Calibration factor of compound χ

A_x = Peak height or area

C_x = Calibration amount

12.2 Percent Difference for Calibration Factors

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

where:

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

CF_c = CF for an analyte from current check standard

12.3 Relative Standard Deviation

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

where:

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

SD = Standard Deviation of average CFs for a compound

12.4 Sample Concentration in water

$$C_\chi = (A_\chi / CF_{ave}) \times DF$$

where:

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

A_χ = Peak area of analyte χ

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

DF = Dilution factor

13. METHOD PERFORMANCE

13.1. Each laboratory must have initial demonstration of performance data on file and corresponding method detection limit files.

13.2. Training Qualifications:

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

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

14. POLLUTION PREVENTION

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

15. WASTE MANAGEMENT

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

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

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

16.2. Associated SOPs and Policies, latest version

16.2.1. QA Policy, QA-003

16.2.2. Glassware Washing, NC-QA-0014

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

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

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

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

17.1. Reporting limits

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

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

17.1.3. Compound Constants

Table 1: Compound Constants

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

APPENDIX I – EXAMPLE CALCULATION

(Calculations Based on 22°C at 754 mmHg – Molar Equivalent .04099)

(Level 5) 1000 ul of 10,000 ppmv – 18 mL H_20

$$\frac{10{,}000\,ulCH_4}{LN_2}\times\frac{1LCH_4}{1{,}000{,}000\,ulCH_4}\times\frac{.04099\ molesCH_4}{1LCH_4}\times\frac{16\,gCH_4}{1moleCH_4}\times\frac{.001\,LN_2}{.018\,LH_20}\times$$

$$\frac{1{,}000{,}000\,ugCH_4}{1gCH_4}=\frac{6.5584}{.018}=\frac{364\,ugCH_4}{LH_20}$$

SEVERN TRENT SERVICES

STL Los Angeles

SOP No. COI-MS-0007
Revision No. 1
Revision Date: 03/15/01
Effective Date: 04/01/01

STANDARD OPERATING PROCEDURE

TITLE: DETERMINATION OF LOW-LEVEL VOLATILE ORGANICS (VOCS) IN AMBIENT AIR BY GC/MS - SCAN MODE USING EPA METHODS TO-14A & TO-15

(SUPERSEDES: COI-MS-0007 REV. 0)

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1. SCOPE AND APPLICATION

1.1. This method is applicable to the GC/MS determination of low-level volatile organic compounds (VOCs) in ambient air samples collected in SUMMA canisters or Tedlar Bags. This method is based on EPA methods TO14A and TO15.

1.2. Target analytes and reporting limits are listed in Table 1.

1.3. Applicable matrices - air, vapor

2. SUMMARY OF METHOD

2.1. An air sample and internal standards are metered through a mass flow controller and concentrated onto a cryogenically cooled glass bead trap. The trap is heated and the contents are transferred to a Tenax trap to remove water. The Tenax trap is heated and the analytes are transferred to a cryofocusing module. The cryofocuser is heated to transfer the analytes to the CG column for separation and detection by a mass spectrometer operated in the SCAN mode.

3. DEFINITIONS

3.1. Batch

An analytical batch is defined as a set of 20 or fewer samples of the same matrix processed using the same procedures and reagents within the same time period. A batch must contain a Laboratory Control Sample (LCS), a laboratory control sample duplicate (LCSD), and a method blank. Refer to the STL LQM for further details of the batch definition.

3.2. Method Blank

A method blank consisting of all reagents added to the samples must be analyzed with each batch of samples. The method blank is used to identify any background interference or contamination of the analytical system that may lead to the reporting of elevated concentration levels or false positive data.

3.3. Laboratory Control Samples (LCS/LCSD)

Laboratory control samples are laboratory-generated samples used to monitor the laboratory's day-to-day performance. 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. LCS is prepared from a source independent of the calibration standards. LCS spiking compounds are listed in Table 1.

3.4. Surrogates

Surrogates are organic compounds which are similar to the target analytes in chemical composition and behavior in the analytical process, but which are not normally found in environmental samples. Each sample, blank, and LCS is spiked with surrogate standards. Surrogate spike recoveries may be evaluated against project specific requirements by determining whether the concentration (measured as percent recovery) falls within the required limits. Surrogate compounds are listed in Table 1.

3.5. Reporting Units

Routinely, calibration and sample results are calculated in part-per-billion volume/volume [ppb (v/v)] units. Client-specific requirements may require conversion to mass/volume units.

4. INTERFERENCES

4.1. Gas regulators are cleaned by the manufacturer using Freon 113, which is one of the target compounds. Before using ultra high purity (UHP) Nitrogen (N_2), Hydrocarbon (HC) free air, Internal Standard (IS), or a target compound standard mix, each regulator should be purged a minimum of three times with the appropriate gas.

4.2. Contamination may occur in the sampling system if canisters are not properly cleaned prior to use. Canisters should not be used for the collection of samples until a batch blank analysis indicates that no target compounds are present above the reporting limit, or a level previously agreed upon by STL and the Client. (Further information regarding the cleaning and certification of canisters can be found in the SOP COI-QA-0005) All other sampling equipment including pumps, flow controllers and filters must be thoroughly cleaned to ensure that the filling apparatus will not contaminate samples.

4.3. Carry over may occur when samples with high levels of contaminants are analyzed. The sample immediately following a high level sample should be reanalyzed if carryover is suspected.

4.4. Tedlar bags may contain low levels of target analytes.

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 should 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. 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. 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. At no time should SUMMA canisters be pressurized over 30 psig.

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

6. EQUIPMENT AND SUPPLIES

6.1. Gas chromatograph - capable of subambient temperature programming and electronic pressure control.

6.2. Mass-selective detector - equipped with computer and appropriate software (Hewlett Packard 5972/5973)

6.3. Sample concentrator – equipped with a cryogenic trap and appropriate systems for the control of moisture (Entech 7000 or equivalent)

6.4. Electronic mass flow controller – device used to accurately meter gas flow in sample concentrators.

6.5. Chromatographic grade stainless steel or nickel tubing and stainless steel plumbing fittings.

6.6. Chromatographic column – Rtx-Volatiles, 0.32 mm ID, 1.5um df, 60 meter length, methyl polysilicate liquid phase (Restek Corporation) or equivalent.

6.7. Stainless steel vacuum/pressure gauge capable of measuring from 30" of mercury (Hg) to 40 psig (Span Instruments) or equivalent.

6.8. High precision vacuum gauge - for making daily standards. (Wallace & Tiernan Pennwalt)

6.9. Pressure regulators for carrier gas and standards - 2 stage, stainless steel diaphragm (single stage acceptable for standards).

6.10. SUMMA passivated canisters 6 L or 15 L (Scientific Instrumentation Specialists, Anderson Instruments) or equivalent.

6.11. 7 micron filters (Nupro), or equivalent.

6.12. Variable Flow Regulator (VFR) – used during composite air sampling with SUMMA canisters.

6.13. Tedlar Bag – an inert plastic like bag used as an alternative to SUMMA canisters for sample collection.

6.14. Diaphragm type vacuum pump to draw sample through mass flow controller.

7. REAGENTS AND STANDARDS

7.1. Reagents

7.1.1. High purity (UHP) Nitrogen. UHP Nitrogen is used for method blanks and making dilutions of samples and standards. All method blanks are humidified with 50ul of distilled water.

7.1.2. UHP Helium used as the GC carrier gas.

7.1.3. Pressurized air source for Entech 7000 heater gas.

7.2. Standards

7.2.1. Gas calibration stock standards containing the target compounds are purchased from commercial sources or prepared from neat in SUMMA canisters. Suppliers are required to provide certification of the analyte concentrations.

7.2.2. Internal/surrogate stock standard mix at 250 ppbv. See tables 1 and 7 for surrogates and internal standard compound list.

7.2.3. Expiration dates for standards and reagents are based on vendor specification. Expiration dates must be documented on the gas cylinders.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Samples should be collected in precleaned and batch analyzed SUMMA passivated canisters. A 7-micron filter should be placed on the inlet of the can to protect the valve from particulates. Canisters should never be pressurized over 40 psig.

8.2. The absolute pressure of the canister should be recorded before and after sample collection. See Section 11.3.1 for sample preparation.

8.3. Samples must be kept within the temperature range of 20 to 30 °C.

8.4. Tedlar bag samples should be protected from sunlight.

8.5. Canister samples should be analyzed within 30 days of collection.

8.6. Tedlar Bag samples should be analyzed within 3 days of collection.

9. QUALITY CONTROL

9.1. Demonstration of Capability

9.1.1. STL Los Angeles will 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 specified in 40 CFR part 136, Appendix B, and further defined in QA Policy #QA-005.

9.1.2. In addition to the MDL study, the laboratory must complete the analysis of four LCSs (or 2 sets of LCSD) with acceptable accuracy and precision for each analyte.

9.1.3. For non-standard analytes, an MDL study can be performed and calibration curve generated prior to sample analysis, unless lesser requirements are acceptable to the client. The minimum initial demonstration required is analysis of a single point calibration.

9.2. Control Limits

If the reference methods do not specify accuracy and precision limits, in-house historical control limits must be generated for surrogates and the LCS results. These limits should be updated at least annually. The recovery limits are determined as the mean recovery plus or minus three standard deviations for surrogates and LCS.

9.3. Surrogates

Surrogate recoveries in samples, blanks and QC samples may be assessed to ensure that recoveries are within established limits. If any surrogates are outside limits and if surrogates are a project-specific requirement, the following corrective actions must take place:

- 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.
- 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 reanalyze a sample once to demonstrate that poor surrogate recovery is due to matrix effect, unless the analyst has reason to believe that the repeated out of control results are due to problems other than matrix effect.

9.4. Method Blanks

For each batch of samples an acceptable method blank must be analyzed. The method blank is analyzed after the calibration standards and LCS prior to sample analysis. 6-liter blank cans are humidified with 50ul of water and carried through the entire analytical sequence.

9.4.1. The method blank must not contain any analyte of interest above the reporting limit. A method blank that does not meet this criterion must be reanalyzed unless no reportable concentrations of target analytes are present in the associated samples.

9.4.2. If surrogates are a project-specific requirement then 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, reanalysis of the blank and affected samples will normally be required. Consultation with the client should take place.

9.5. Laboratory Control Samples (LCS/LCSD)

For each batch of samples an LCS/LCSD pair must be analyzed. The LCS/LCSD is analyzed after the calibration standard and before the method blank and samples. The LCS should contain a representative subset of the analytes of interest (See Table 1) although client specific requirements may require additional compounds. If any analyte is outside the established control limits, the analysis is out of control and corrective action must be taken. Corrective action will normally be reanalysis of the batch. LCS compounds and acceptance criteria are given in Table 1.

- If the batch is not reanalyzed the reasons for accepting the batch must be clearly stated in the case narrative.

- If the analytes in the LCS exceed the upper control limit and no analytes are detected in any of the samples; they may be reported without qualification. Positive bias is not expected to impact ND results.

9.6 Internal standard

The internal standard (IS) areas are monitored for each shift by comparing the IS areas in each sample with those of the associated Continuing Calibration Verification Standard (CCV). Sample IS areas are considered acceptable if they fall between ±40% of the CCV IS areas for TO-15 and –50% to +100% for TO-14A low level. Any sample exceeding this criterion must be reanalyzed. If the IS area(s) fails upon reanalysis, it is documented in a Non-Conformance Memo (NCM) and discussed in the report narrative. Internal standards are listed in Table 7.

10. CALIBRATION AND STANDARDIZATION

10.1. Prior to the analysis of samples and blanks, each GC/MS system must be tuned and calibrated. Hardware tuning is checked to establish that the system meets the standard mass spectral abundance criteria. This is done through the analysis of 50ng of BFB and must meet the acceptance criteria listed in tables 3 or 4.

10.2. Standard Preparation

Static dilutions of the stock standard gas mixtures is made in 6 or 15 liter summa canisters to create working standards. A high precision vacuum gauge is flushed with UHP Nitrogen and attached to the top valve of a clean, evacuated canister, and the absolute pressure is recorded. Depending on the concentration of each stock standard gas mixture, a particular pressure of each is added to the canister to achieve the desired concentration in the working standard. Care should be taken to flush each regulator and transfer line with standard prior to transfer to the canister. After all the stock standard mixes are added the standard canister is pressurized with UHP nitrogen to achieve the appropriate concentration.

Currently the daily standard has a nominal concentration of 25ppbv and is created by adding 1 psia each of the two 1 ppmv stock standard mixes and adding UHP nitrogen to the canister to achieve a final pressure of 40 psia.

10.3. Initial Calibration and Continuing Calibration Verification

10.3.1. An initial calibration curve consisting of a minimum of 5 points (ICAL) is analyzed to determine the linear working range of the system for each compound. An average response factor (RF) and per-cent relative standard deviation (%RSD) are calculated for each target analyte using the calculation in section 12. The ICAL is considered acceptable if less than 90% of the target analytes have a %RSD less than or equal to 30% and the average of the %RSD for all target compounds is less than 30%. All compounds must have a relative response factor greater than or equal to 0.05.

10.3.2. The nominal concentrations of the standards are typically 0.2, 0.4, 1.25, 5.0, 10 and 50 ppbv. The standards are run by varying the trapped volume of the two working standards from the "default" volume of 250 ml. For example, the 0.2, 0.5, and 1.25 ppbv standards are analyzed by trapping 40, 100 and 250 ml of a 1.25 ppbv-working standard.

10.3.3. Each new five-point ICAL must be verified using a second source standard, if available. Since the regulatory agencies have not provided guidance on second source verification, the following acceptance criterion is typically used: ± 35% for target analytes with warning limits of ± 35 - 55% for poor performers. These limits are provided as guidance. If this criterion is not met: (1) rerun the second source check standard, (2) reprepare or acquire new standard, (3) evaluate instrument conditions, and (4) regenerate a new ICAL.

10.3.4. Analyte quantitation must be performed off the initial calibration and not from daily continuing calibration standard analysis. Test results must be qualified in reports when analyte quantitation is based on the CCV at the client's request.

10.3.5. For each QC batch or every 24 hours of operation, a Continuing Calibration Verification Standard (CCV) is analyzed to verify the ICAL average RF. The percent difference (%D) of the CCV RF from the ICAL average RF is calculated for each compound. The CCV is considered acceptable if less than 90% of the target analytes have a %D less than or equal to 30% and the average of the %D for all target compounds is less than 30%. If the criteria are not met the CCV or the ICAL must be reanalyzed prior to sample analysis.

10.3.5.1. For projects requiring NELAC accreditation, the concentration for the CCV standard must be varied within the working range of the initial instrument calibration. This will be done at least once per year.

11. PROCEDURE

11.1. Procedural Variations

Any variation must be completely documented using the nonconformance database (Clouseau) and shall be approved by the Supervisor, PM, and QA Manager.

11.2. Sample Analysis Procedure

All analysis conditions for samples must be the same for the CCV, including flow rates, desorb time and temperature, column temperatures, multiplier setting etc.

11.3. Sample Preparation

11.3.1. The initial pressure of the sample canister is checked and recorded by attaching a vacuum/pressure gauge to the canister. The gauge should be rinsed before use with zero grade nitrogen by physically holding against the air outlet and flushing for a few seconds. If the pressure is less than approximately 6 psig, pressurize the canister to 10 psig with zero grade nitrogen and record the final pressure. Pressures should be recorded in the sample pressurizing log and on the individual canister field sheets.

11.3.2. If the canister pressure is increased, a dilution factor (DF) is calculated and applied to results:

$$DF = \frac{Y_a}{X_a}$$

Where:

X_a = *absolute canister pressure before dilution (initial pressure)*
Y_a = *absolute canister pressure after dilution (final pressure)*

The pressure dilution factor (pDF) must be compensated for by trapping more sample. For example a sample received at 12.0 psia and pressurized to 24.6 psia has a pDF of 2.05. If the default volume is 250 ml, then 513ml should be trapped (the volume is rounded up to three significant figures).

11.3.3. If it is suspected that a sample may contain significant contamination, the canister is screened using GC/FID analysis or other screening method to determine a proper dilution. A sample that requires only a small dilution can be analyzed by trapping a volume less than the standard volume. The minimum volume that can be trapped is 40ml. Larger dilutions will require the transfer of an aliquot of sample to a Tedlar bag and diluting with UHP nitrogen. Bag dilutions should be analyzed within 24 hours. Dilution to Tedlar bag can be used for reporting the analytes that exceed calibration range in the original analysis but not as a single reportable analysis due to low level contamination in Tedlar bag.

11.3.4. If non-standard reporting limits are required, the standard sample volume can be adjusted. The maximum trapped volume is 1500ml.

11.4. Initial/Daily GC/MS Tuning

11.4.1. At the beginning of each 24-hour shift, prior to any analytical runs, the GC/MS system must be verified that acceptable tune performance criteria are achieved. If any of the key ions fail the abundance criteria listed in tables 5 or

6, the system is considered out of tune and any subsequent sample/standard analysis should be considered unacceptable.

11.4.2. Using the BFB method in the cryotrap software trap the internal standard mixture volume required to put 50ng of BFB on column (currently 28ml of 250 ppbv standard). The MS software will evaluate the average of the spectra of the peak apex and the scans immediately before and after.

11.5. Analysis

11.5.1. Each canister is attached to the autosampler (A/S) and recorded in the instrument logbook. A sequence is created in the GC/MS software to prepare the instrument for data acquisition. The sequence information controls the GC/MS method, data file creation, sample parameters, and report output. A second sequence must be created in the A/S control software to control the sampling process, such as, line position, sample volume, trap temperatures, flow rates, and times.

11.5.2. The valves are opened on all canisters and the A/S and GC/MS sequences are started.

11.5.3. For routine analysis the A/S will follow this sequence of events:

- Glass bead trap (Module 1) cooled to –150C.
- Trap internal standard.
- Trap sample.
- The Tenax trap (Module 2) is cooled to –10 C and the glass bead trap is heated. The sample is transferred to Module 2 by passing helium through Module 1. This step is designed to remove water from the sample.
- When GC is ready, the cryofocuser (Module 3) is cooled to –150 C. Module 2 is heated. The sample is transferred to Module 3
- Module 3 is heated and the GC/MS column flow is routed through Module 3 to inject the sample and begin the run.
- The system is pre-flushed with the next sample and the system is baked to limit carryover.

11.5.4. Upon completion of the analytical sequence, the concentrator generates a QA/QC report that records data from the sampling event (i.e. actual volume trapped, temperature at the time of trapping, sample pressure, etc.)

12. DATA INTERPRETATION

12.1. Qualitative Analyses

12.1.1. Two criteria must be satisfied to verify positive identification: (1) Elution of sample component at the same GC relative or absolute retention time as those of the standard component and (2) correspondence of the sample component and the standard component mass spectra.

12.1.1.1. The sample component relative retention time (RRT) must compare within ± 0.06 RRT units of the RRT of the standard component. As an option, RT must compare within 0.33 minutes of the standard component absolute retention time (RT). For reference, the RT standard must be run within the same 24-hour shift as the sample.

12.1.1.2. (1) All ions present in the standard mass spectra at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100%) must be present in the sample spectrum. (2) The relative intensities of ions specified in (1) must agree within plus or minus 30% between the standard reference and sample spectra. (Example: For an ion with an abundance of 50% in the reference spectra, the corresponding sample abundance must be between 20 and 80 percent.

12.1.1.3. If a compound cannot be verified by all of the criteria in the above paragraphs but in the technical judgment of the analytical chemist the identification is correct, then the compound may be reported.

12.1.2. Tentatively Identified Compounds (TICs)

12.1.2.1. 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 analysis being conducted. 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 ± 30%. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 20 and 80%).

- 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 co-eluting 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.

- Only peaks having a total ion current greater than 10% of the nearest eluting Internal Standard total ion current will be evaluated for reporting.

12.1.2.2. Semi-quantitative results will be calculated for tentatively identified compounds using total ion current areas and assuming a relative response factor of 1.0.

12.1.2.3. 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 with the nearest library searches will the mass spectral interpretation specialist assign a tentative identification.

12.2. Quantitative Analysis:

12.2.1. When a compound has been identified, the quantification of that compound will be based on the integrated abundance from the EICP of the primary characteristic ion. Quantification will take place using the internal standard technique. A summary table of primary and secondary ions for target

compounds and internal standards is listed in Table 4. The calculation for quantitation of sample is found in section 12.3.

12.3. Calculations

12.3.1. The HP data system automatically quantitates the sample results based on a "standard" sample size of 250 ml. The default result units are in ppbv. If a sample size other than 250 ml was used and/or a canister sample was pressurized, the result must be adjusted as shown below:

$$Final\ result\ ppbv = raw\ result ppbv X \frac{250mL}{sample volum injected} X \frac{final psia}{initial psia}$$

12.3.2. Calculation for Relative Response Factor (RRF):

$$RRF = \frac{Area\ cpd\ in\ Std.}{Area\ I.S.} X \frac{Conc.I.S.}{Conc.cpd\ in\ Std.}$$

The area of the primary quantitation ion is used in the calculation.
I.S.: Internal Standard

12.3.3. Calculation for Percent Relative Standard Deviation (%RSD):

$$\%RSD = \frac{Std.Dev.of\ RRFs}{Mean of\ RRFs} X 100$$

12.3.4. Calculation for Percent Difference (%D):

$$\%D = \frac{Average\ RRF\ from\ initial\ curve\ RRF\ cpd.}{Average\ RRF\ from\ initial\ curve} X 100$$

12.3.5. Calculation for Determining Concentration of Compounds:

$$Conc.Cpd(ppbv) = \frac{Areacpdinsample}{AreaI.S.insample} X \frac{Conc.I.S.}{RRFICAL.} X Dil.Factor$$

The area of the primary quantitation ion is used in the calculation.
I.S.: Internal Standard

12.3.6. Calculation for Percent Recovery (%Rec):

$$\%\,Rec = \frac{Amount\ cpd.\ recovered}{Amount\ cpd.\ spiked} X 100\%$$

12.3.7. Calculation for Relative Percent Difference (RPD):

$$RPD = \frac{Value\ A - Value\ B}{Average\ of\ Values} X 100$$

13. REPORTING

13.1. Standard reporting units are ppb v/v. If results are to be reported in ng/L or ug/m^3 use the following equation:

$$result\ ppbv\ X \frac{Molecular\ weight\ of\ compound}{24.5} = results\ ng/L\ or\ ug/m^3$$

Note: 24.5 is the molar volume of ideal gas at 25° Centigrade and 1 atm.

13.2. Reporting limits

13.2.1. See Table 1. All reporting limits and MDLs must be derived on GC/MS systems at the STL laboratory and are updated annually.

13.2.2. "J" values (results below the normal reporting limit but above the MDL) are reported on request only.

13.3. Significant figures

13.3.1. All results should be reported to two significant figures.

13.4. No conversion of the analytical results to standard conditions is made.

14. METHOD PERFORMANCE

14.1. Method performance is controlled through the measurement of accuracy and precision. Analysis of a LCS and LCSD are preformed to measure both accuracy and precision. The control limits established for the LCS and LCSD are used to maintain method performance within a well-defined set of criteria.

14.2. Monitoring of background contamination by the analysis of method blanks, trip blanks, and system blanks is also critical to method performance.

15. POLLUTION PREVENTION & WASTE MANAGEMENT

15.1. Ambient air analysis does not generate any solid or liquid hazardous waste.

16. REFERENCES

16.1. Method Source

16.1.1. "EPA Compendium Method TO-14A. Determination of Volatile Organic Compounds (VOCs) in Ambient Air using Specially Prepared Canisters With Subsequent Analysis Gas Chromatographic Analysis." January 1999.

16.1.2. "EPA Compendium Method TO-15. The Determination of Volatile Organic Compounds (VOCs) in Air Collected in Specially-Prepared Canisters and Analyzed by Gas Chromatography/Mass Spectrometry (GC/MS)." January 1999.

16.2. Laboratory Quality Manual (LQM), current revision.

16.3. Deviations from Method

16.3.1. Nitrogen is used for dilution/pressurization purposes.

16.3.2. TO-14A describes the use of a Nafion dryer to remove excess moisture from air matrices. STL does not use a Nafion dryer since polar compounds may be lost during this removal step.

16.3.3. TO-14A and TO-15 describe the use of SUMMA passivated steel canisters for sampling and analysis. No mention is made of Tedlar sampling bags. STL analyzes samples in Tedlar bags for VOCs using the same procedures described herein. A modification to the method is noted in the narrative of the final report.

16.3.4. TO-15 describes a shelf life of thirty days for Primary working standards. STL maintains these standards for longer periods of time as determined by the manufacturer's recommendation and the results of stability monitoring.

16.3.5. The methods indicate that for initial and continuing calibrations all samples must have a %RSD and %D less than or equal to 30%. STL Los Angeles uses criteria of 90% of compounds and the average less than or equal to 30% for the ICAL and the 90% of compounds and the average %D less than or equal to 30% for the CCV. This is to account for analytical issues that arise for poor performing analytes.

16.3.6. TO-15 sets method performance criteria of accuracy of plus or minus 30% and precision less than or equal to 25%. STL uses project-specific QC criteria or control limits bases on historical data.

17. MISCELLANEOUS (TABLES, APPENDICES, ETC.)

Table 1. VOC Target Compounds and Reporting Limits

Compound	RL ppb v/v	QC Limits (%R)	Precision (RPD)
Acetone	0.8		20
Benzene	0.2		20
Benzyl chloride	0.4		20
Bromodichloromethane	0.2		20
Bromoform	0.2		20
Bromomethane	0.2		20
2-Butanone (MEK)	1		20
Carbon disulfide	1		20
Carbon tetrachloride	0.2		20
Chlorobenzene	0.2		20
Dibromochloromethane	0.2		20
Chloroethane	0.4		20
Chloroform	0.2		20
Chloromethane	0.4		20
1,2-Dibromoethane (EDB)	0.2		20
1,2-Dichlorobenzene	0.2		20
1,3-Dichlorobenzene	0.2		20
1,4-Dichlorobenzene	0.2		20
Dichlorodifluoromethane	0.2		20
1,1-Dichloroethane	0.2		20
1,2-Dichloroethane	0.2		20
cis-1,2-Dichloroethene	0.2		20
trans-1,2-Dichloroethene	0.2		20
1,1-Dichloroethene*	0.2	80 - 130	20
1,2-Dichloropropane	0.2		20
cis-1,3-Dichloropropene	0.2		20
trans-1,3-Dichloropropene	0.2		20
1,2-Dichloro-1,1,2,2-tetrafluoroethane	0.2		20
Ethylbenzene	0.2		20

Compound	RL ppb v/v	QC Limits (%R)	Precision (RPD)
4-Ethyltoluene	0.4		20
Hexachlorobutadiene	0.4		20
2-Hexanone	0.4		20
Methylene chloride*	0.2	80 - 125	20
4-Methyl-2-pentanone (MIBK)	0.4		20
Styrene	0.2		20
1,1,2,2-Tetrachloroethane*	0.2	60 - 130	20
Tetrachloroethene	0.2		20
Toluene*	0.3	80 - 125	20
1,2,4-Trichlorobenzene	0.8		20
1,1,1-Trichloroethane	0.2		20
1,1,2-Trichloroethane	0.2		20
Trichloroethene*	0.2	80 - 135	20
Trichlorofluoromethane	0.4		20
1,1,2-Trichloro-1,2,2-trifluoroethane	0.4		20
1,2,4-Trimethylbenzene	0.4		20
1,3,5-Trimethylbenzene	0.4		20
Vinyl acetate	1		20
Vinyl chloride	0.2		20
m-Xylene & p-Xylene	0.5		20
o-Xylene	0.2		20
Xylenes (total)	0.5		20
4-Bromofluorobenzene**	--	70 - 130	--
1,2-Dichloroethane-d4**	--	70 - 130	--
Toluene-d8**	--	70 - 130	--

* LCS/LCSD Spiking compound

** Surrogate compound

TABLE 2. BFB GC Operating Conditions

Method file: TO14BFB

METHOD FILE LIST

Method file:	GC Type: 5890 Column: Cap	Run type: SCAN,GC,E1 Splitless: Yes	

Temperature:	Inj.P	Intfc	Source
	150	280	NA

GC/DIP		LEVEL A	LEVEL B	POST RUN
Temp 1	150	150	0.0	
Time 1	1.0	0.0	0.0	
Rate		11	0.0	
Temp 2		210	0.0	
Time		2.5	0.0	

Oven equilibration Time. 0 min

Run time: ~9 mins
Scan Start time 8 mins

Scan Parameters:				
	Mass Range:	34 to 300		
	Multiplier voltage:	varies	Number of samples:	2
	Threshold:	150 counts		

TABLE 3. GC Analytical Method

Method file: LOWTO14

METHOD FILE LIST

Method file:	GC Type: 5890 Column: Cap	Run type: SCAN,GC,E1 Splitless: Yes	

Temperature:	Inj.P	Intfc	Source
	150	280	NA

GC/DIP		LEVEL A	LEVEL B	POST RUN
Temp 1	35	35		
Time 1	5.5	0.0		
Rate		11		
Temp 2		210		
Time		7.6		

Oven equilibration Time. 0 min

Run time: ~29 mins
Scan Start time 3.8 mins

Scan Parameters:				
	Mass Range:	34 to 300		
	Multiplier voltage:	varies	Number of samples:	2
	Threshold:	150 counts		

TABLE 4. VOC Key Ions

Compound	Primary	Secondary		
Bromochloromethane I.S. #1	49	130	128	
Dichlorodifluoromethane (Freon 12)	85	87,	50	
Chloromethane	50	52		
1,2-Dichloro-1,1,2,2-tetrafluoroethane (Freon 114)	85	135	87	
Vinyl Chloride	62	64		
Bromomethane	94	96,	79	
Chloroethane	64	66,	49	
Trichlorofluoromethane (11)	101	103	66	
1,1-Dichloroethene	61	96,	63,	
Carbon Disulfide	76	78,		
1,1,2-Trichloro-1,2,2-trifluoroethane (Freon 113)	151	101	103	
Acetone	43	58		
Methylene Chloride	49	84	86	
trans-1,2-Dichloroethene	96	61,	98,	
1,1-Dichloroethane	63	65,	83	
Vinyl Acetate	43	42	86,	
cis-1,2-Dichloroethene	96	61,	98,	
2-Butanone	72 *	57,	43	
Chloroform	83	85,	47	
1,1,1-Trichloroethane	97	99,	61	
Carbon Tetrachloride	117	119	121	
1,4-Difluorobenzene I.S. #2	114	63,	88	
Benzene	78	50,	52,	
1,2-Dichloroethane	62	64,	49,	
Trichloroethene	130	95,	132	
1,2-Dichloropropane	63	62,	39	
Bromodichloromethane	83	85,	129	
cis-1,3-Dichloropropene	75	77,	39	
4-Methyl-2-pentanone	43	58,	100	
Toluene	91	65,	92	
Chlorobenzene-d5 I.S. #3	117	54	82	
trans-1,3-Dichloropropene	75	77,	39	
1,1,2-Trichloroethane	97	83,	61	
Tetrachloroethene	166	164	131	
2-Hexanone	58	43	100	
Dibromochloromethane	129	127	131	
1,2-Dibromoethane	107	109	188	
Chlorobenzene	112	77,	114	

TABLE 4. VOC Key Ions

Compound	Primary	Secondary		
Ethylbenzene	91	106		
1,4-and 1,3-(p,m)Xylene	91	106		
1,2-(ortho)Xylene	91	106		
Styrene	104	78	103	
Bromoform	173	171	175	
1,1,2,2-Tetrachloroethane	83	85	60	
Benzyl Chloride	91	126	63	
4-Ethyltoluene	105	120	77	
1,3,5-Trimethylbenzene	105	120	77	
1,2,4-Trimethylbenzene	105	120	77	
1,3-Dichlorobenzene	146	148	111	
1,4-Dichlorobenzene	146	148	111	
1,2-Dichlorobenzene	146	148	111	
1,2,4-Trichlorobenzene	180	182	145	
Hexachlorobutadiene	225	227	223	

* Quant ion for 2-Butanone is different from those listed in Method TO-15. STL Los Angeles expects this ion to be subject to less interference.

Table 5. TO14A BFB 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	5.0 to 9.0% of mass 95
173	<2.0% of mass 174
174	>50% of mass 95
175	5.0 to 9.0% of mass 174
176	>95% but <101% of mass 174
177	5.0 to 9.0% of mass 176

Table 6. TO15 BFB Criteria

Mass	Ion Abundance Criteria
50	8.0 to 40% of mass 95
75	30 to 66% of mass 95
95	Base Peak, 100% Relative Abundance
96	5.0 to 9.0% of mass 95
173	<2% of mass 174
174	50 to 120% of mass 95
175	4.0 to 9.0% of mass 174
176	93% to 101% of mass 174
177	5.0 to 9.0% of mass 176

Table 7. Internal Standards

Bromochloromethane
1,4-Difluorobenzene
Chlorobenzene-d5

Controlled Copy
Copy No. _____

Implementation Date_____

SOP No. NC-MT-0002
Revision No. 3.0
Revision Date: 03/26/02
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STL North Canton
STANDARD OPERATING PROCEDURE

TITLE: **INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETRY, EPA METHODS 6020 AND 200.8**

(SUPERSEDES: 2.0)

Prepared by: _____ 4-26-02
Date

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1. SCOPE AND APPLICATION

1.1. This procedure describes multi-elemental analysis by inductively coupled plasma-mass spectrometry (ICP-MS) based on SW-846 protocol as described in EPA Method 6020 and 200.8. The source method lists fifteen elements approved for analysis by ICP/MS (Al, Sb, As, Ba, Be, Cd, Cr, Co, Cu, Pb, Mn, Ni, Ag, Tl, and Zn). Additional elements may be included provided that the method performance criteria presented in Section 9 is met. However, project approval may be required from the controlling agencies for compliance testing beyond the fifteen elements included in the promulgated method.

1.2. This procedure also describes the requirements for performing analysis of ground waters, surface waters and drinking water.

1.3. The procedure is applicable to the analysis of waters, soils, and wastes. No digestion is required prior to analysis for dissolved elements in water samples, but the samples must be filtered and preserved prior to analysis. Preliminary acid digestion is required for groundwater, aqueous samples, sludges, sediments, and other solid wastes for which total (acid-leachable) elements are requested. See SOP # CORP-IP-0002NC and SOP #CORP-IP-0003NC for preparation details.

1.4. The associated QuantIMs method codes are MH (6020) and QV (200.8).

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

2. SUMMARY OF METHOD

2.1. Aqueous samples, digestates or leachates are nebulized into a spray chamber where a stream of argon carries the sample aerosol through the quartz torch and injects it into an R.F. plasma. There the sample is decomposed and desolvated. The ions produced are entrained in the plasma gas and by means of a water-cooled, differentially pumped interface, introduced into a high-vacuum chamber that houses a quadrapole mass spectrometer capable of providing a resolution better than or equal to 0.9 AMU peak width at 10% of the peak height. For analysis by methods 200.8 the resolution requirement is 1.0 amu at 5% peak height. The ions are sorted according to their mass-to-charge ratio and measured with a channel electron multiplier. Interference must be assessed and valid corrections applied, or the data flagged to indicate problems. Interference correction must include compensation for background ions contributed by the plasma gas, reagents and the constituents of the sample matrix. Recommended elemental equations which correct for many of these interferences are listed in Table I. Use of the internal standard technique is required to compensate for suppressions and enhancements caused by sample matrices.

3. DEFINITIONS

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

3.2. *Dissolved Metals* - Those elements which pass through a 0.45 µm membrane filter (sample is acidified after filtration).

3.3. *Suspended Metals* - Those elements which are retained by a 0.45 µm membrane filter.

3.4. *Total Metals* - The concentration determined on an unfiltered sample following vigorous acid digestion.

3.5. *Total Recoverable Metals* - The concentration determined on an unfiltered sample following treatment with hot, dilute mineral acids.

3.6. *Instrument Detection Limit (IDL)* - See Section 9.1.1.

3.7. *Sensitivity* - The slope of the analytical curve (i.e. the functional relationship between raw instrument signal and the concentration).

3.8. *Tuning Solution* - This is a multi-element solution containing analytes which are representative of the entire mass range capable of being scanned by the instrument. It is used to optimize the sensitivity of the instrument and to verify the mass resolution meets method criteria.

3.9. *Initial Calibration Verification/Quality Control Standard (ICV/QCS)* - A multi-element standard of known concentrations prepared to verify instrument calibration. This solution must be an independent standard prepared near the mid-point of the calibration curve, and at a concentration other than that used for instrument calibration.

3.10. *Continuing Calibration Verification (CCV).* - A multi-element standard of known concentrations prepared to monitor and verify the instrument daily continuing performance.

3.11. *Interference Check Standard (ICS)* - A solution containing both interfering and analyte elements of know concentration that is used to verify background and interelement correction factors.

3.12. *Laboratory Control Sample / Laboratory Fortified Blank (LCS/LFB)* - A multi-element standard of known concentrations which is carried through the entire sample preparation and analysis procedure. This solution is used to verify the accuracy of the sample preparation.

3.13. *Reagent Blank* - High purity (> 18 megohm-cm)water carried through the entire digestion process.

3.14. *Calibration Blank* - High purity (> 18 megohm- cm) water acidified with the same acid concentrations present in the standards and samples Also referred to as the Initial Calibration Blank (ICB) and Continuing Calibration Blank (CCB).

3.15. *Method Detection Limit (MDL)*. See section 9.1.3

4. INTERFERENCES

4.1. Isobaric Interferences - Isobaric interferences in the ICPMS are caused by isotopes of different elements forming ions with the same nominal mass-to-charge ratio (m/z). Most interferences of this type are corrected for by the instrument software.

4.2. Isobaric Molecular and Doubly Charged Ion Interferences - Isobaric molecular interferences are caused by ions consisting of more than one atom or charge. Table II lists isobaric interferences which might possibly affect required analytes. When these interferences cannot be avoided by the use of another isotope with sufficient natural abundance, corrections must be applied and the data flagged to indicate the presence of interferences.

4.3. Physical Interferences - Physical interferences are associated with the transport and nebulization process. Internal standards are used to compensate for these types of interferences.

4.3.1. Internal standards should be added at a level to give approximately 50,000 - 800,000 counts of raw signal intensity. The mass of the internal standard should ideally be within 20 amu of the mass of the measured analyte.

4.3.2. Matrix effects will be monitored by comparing the internal standard intensity in the sample to the internal standard intensity of the calibration blank. When performing method 6020 the internal standard intensities must be between 30% and 120% of the intensities in the calibration blank. If they fall outside this window, a five fold dilution (1:4) is performed on the sample to correct for matrix effects and the sample reanalyzed. When performing method 200.8 the internal standards must be between 60% and 125% of the calibration blank. If they are outside this window the calibration blank is reanalyzed to verify internal standard intensities. If the intensities are within limits the sample is diluted by a factor of 2 (1:1) and reanalyzed.

4.3.3. Memory effects are dependent on the relative concentration differences between samples and/or standards which are analyzed sequentially. The rinse period between samples must be long enough to eliminate significant memory interference.

4.3.4. Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus that lead to discrete artifacts. All of these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. Specific selection of reagents may be required to avoid introduction of contaminants.

5. SAFETY

5.1. 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. 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 **oxidizing agents** are: Nitric acid and hydrogen peroxide

5.3.2. The following materials are known to be **corrosive:** Sulfuric acid, hydrochloric acid, nitric acid, and hydrofluoric acid.

Note: Sulfuric and hydrochloric acids are used in cleaning the ICP/MS torch and hydrofluoric acid is also commonly used in air toxics preparations

5.4. The **RF Generator** produces strong radio frequency waves, most of which are unshielded. People with pacemakers should not go near the instrument while in operation.

5.5. Exposure to chemicals must be maintained **as low as reasonably achievable**, therefore, unless they are known to be non-hazardous, all samples must be opened, transferred and

prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

5.6. It is recommended that neat standards be purchased only as a last resort. The preparation of standards from neat materials and reagents {as well as glassware cleaning procedures that involved solvents such as methylene chloride} should be conducted in a fume hood with the sash closed as far as the operations will permit.

5.7. Standards in solution may be diluted in the open laboratory when syringes and the like are utilized.

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

6. EQUIPMENT AND SUPPLIES

6.1. Argon gas: High purity grade (99.99%).

6.2. Inductively Coupled Plasma Mass Spectrometer capable of providing resolution, less than or equal to 0.9 AMU at 10% peak height from 6-253 AMU and 1.0AMU at 5% peak height from 6-253 AMU with a data system that allows corrections for isobaric interferences and the application of the internal standard technique.

6.3. A four channel peristaltic pump.

6.4. Appropriate water cooling device.

6.5. Calibrated automatic pipettes or Class A glass volumetric pipettes.

6.6. Autosampler with autosampler tubes.

7. REAGENTS AND STANDARDS

7.1. Calibration standards are purchased as custom STL multielement mixes or as single element solutions. All standards must be stored in FEP fluorocarbon or previously unused polyethylene or polypropylene bottles. Intermediate standard solutions must be replaced prior to the expiration date provided by the manufacturer. If no expiration date is provided, the intermediate solutions may be used for up to one year and must be replaced sooner if verification from an independent source indicates a problem. See Table XI.

7.2. Check Calibration Standard (ICV)

A quality control standard similar to the calibration standards and prepared in the same acid matrix. This solution must be made at a concentration near the midpoint of the calibration curve. This standard is composed of analytes from a different source from those used in the calibration of the instrument. See Table XI.

7.3. The tuning solution is purchased as custom STL multielement mixes or as single element solutions. All standards must be stored in FEP fluorocarbon or previously unused polyethylene or polypropylene bottles. The solution must be replaced prior to the expiration date provided by the manufacturer. If no expiration date is provided, the intermediate solutions may be used for up to one year.

7.4. The use of hydrochloric and sulfuric acids should be minimized due to higher incidence of molecular-ion interferences with the presence of these acids. Excessive amounts of nitric acid can also lead to molecular interferences.

7.5. Reagent water:

ASTM Type I or equivalent for the elements of interest, generated using an ion-exchange water polishing system capable of achieving 18.0 megohm-cm.

7.6. Nitric acid, 5% HNO_3:

Carefully dilute 100 mL of concentrated HNO_3 to 2.0 L with reagent water.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Aqueous samples are preserved with nitric acid to a pH of 2, and may be stored in plastic or glass. Preservation must be verified prior to analysis.

8.2. Soil samples do not require preservation, but must be stored at 4° ± 2°C until the time of preparation.

8.3. The analytical holding times for metals are six months from the time of collection.

8.4. Solid and aqueous samples must be digested prior to analysis by the appropriate method.

9. QUALITY CONTROL

9.1. Initial Demonstration of Capability

Table X provides a summary of quality control requirements including type, frequency, acceptance criteria and corrective action. Prior to analysis of any analyte the following requirements must be met.

9.1.1. Instrument Detection Limit (IDL) - IDLs can be determined by calculating the average of the standard deviations of the three runs on three non-consecutive days from the analysis of a reagent blank solution with seven consecutive measurements per day. Each measurement must be performed as a separate analytical sample. The IDL should be performed every three months.

9.1.2. Linear Calibration Ranges - Linear calibration ranges are primarily detector limited. The linear range must be determined at instrument setup, and the upper limit must be verified annually or whenever a change in instrument hardware or operating conditions, in the judgement of the analyst, may lower expected ranges. Standards used to determine or verify linear ranges must be analyzed during a routine analytical run. The linear range is the concentration above which sample results cannot be reported.

9.1.3. For initial determination of the upper limit of the linear range, determine the signal responses from three different concentration standards across the estimated range. One standard must be at the upper limit of the estimated range. Results must recover within 10% of the expected value for the three standards. The Linear Range is then set at the concentration of the high standard.

9.1.4. For verification of the upper limit of the linear range, the high standard must recover within 10% of its expected value.

9.1.5. Method Detection Limit (MDL) - The laboratory shall determine a method detection limit for all analytes of interest initially and annually thereafter. The MDL study is performed and calculated according to STL Policy number CORP-QA-005, which is based on 40CFR Part 136 Appendix B.

9.2. Batch Definition

9.2.1. A batch is a group of no greater than 20 samples excluding QC samples (LCS, Method Blank, MS, MSD) which are processed similarly, with respect to the procedure. All sample setups must be initiated within a 24 hour period from the initial preparation or extraction and without interruption of the process. All samples within the batch must be treated with the same lots of reagents and the same processes.

9.3. Method Blank

9.3.1. One method blank (MB) must be processed with each preparation batch. The method blank consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The method blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. The method blank should not contain any analyte of interest at or above the reporting limit (exception: common laboratory contaminants, see below) or at or above 5% of the measured concentration of that analyte in associated samples, whichever is higher (sample result must be a minimum of 20x higher than the blank contamination level).

- If the analyte is a common laboratory contaminant (copper, iron, lead, calcium, magnesium, potassium, sodium or zinc) the data may be reported with qualifiers if the concentration of the analyte in the method blank is less than two times the RL. **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.**

9.3.2. For dissolved metals samples which have not been digested, a CCB result is reported as the method blank. The CCB run immediately prior to the start of the dissolved sample analyses must be used for this purpose. No more than 20 samples can be associated with one CCB

9.4. Laboratory Control Sample (LCS)

9.4.1. One LCS from an independent source must be processed with each preparation batch. The LCS must be carried through the entire analytical procedure. The LCS is used to monitor the accuracy of the analytical process. On-going monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines. The historical limits for the LCS for each analyte are in the LIMS system. Initial limits shall be set at 80-120% for method 6020 and 85-115% for method 200.8. If the LCS exceeds these limits for any analyte, that analyte is judged to be out of control and must be corrected before the analysis can be reported

9.4.2. Corrective Action for LCS

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

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

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

9.5. Matrix Spike/Matrix Spike Duplicate (MS/MSD)

9.5.1. One MS/MSD pair must be processed for each batch. A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added. A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked identically as the MS) prepared and analyzed along with the sample and matrix spike. Some client specific data quality objectives (DQO's) may require the use of sample duplicates in place of or in addition to MS/MSD's. The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Due to the potential variability of the matrix of each sample, these results may have immediate bearing only on the specific sample spiked. Samples identified as field blanks cannot be used for MS/MSD analysis. The historical spike recovery acceptance limits for each analyte are in the LIMS

system. Initial limits shall be 70-130% for methods 6020 and 200.8. and the spike concentration must be the same level as the LFB. If they are not in control and all other quality control criteria have been met then a matrix interference is suspected.

9.5.2. Corrective action for MS/MSDs

9.5.2.1. If the analyte recovery or RPD falls outside the acceptance range, the recovery of that analyte must be in control for the LCS. If the LCS recovery is within limits, then the laboratory operation is in control and the results may be accepted. If the recovery of the LCS is outside limits, corrective action must be taken. Corrective action will include repreparation and reanalysis of the batch.

9.5.2.2. If the native analyte concentration in the MS/MSD exceeds 4x the spike level for that analyte, the recovery data is reported as NC (not calculated).

9.5.2.3. If an MS/MSD is not possible due to limited sample volume then a laboratory control sample duplicate (LCSD) should be analyzed. The RPD of the LCS and LCSD must be compared to the laboratory limits.

9.5.2.4. If client program requirements specify to confirm matrix interference's, repreparation and reanalysis of the MS/MSD may be necessary.

9.6. Sample Duplicate

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

9.6.2. Sample duplicates may be performed in lieu of or in addition to MSD's.

9.7. Control Limits

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

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

9.8. Method Detection Limits (MDLs) and MDL Checks

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

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

9.9. ICV/CCV/QCS - Calibration accuracy is verified at the beginning of each analytical run by analyzing a second-source initial calibration verification (ICV) standard. A continuing calibration verification (CCV) standard is analyzed at a 10% frequency throughout the run. The ICV must be within 10% of the expected value, or the analysis is terminated. The CCV must be within 10% of the expected value for method 6020 or 15% of the expected value for method 200.8, or the analysis is terminated and all samples since the last successful ICV/CCV reanalyzed.

9.10. RL Verification Standard –An independent standard is analyzed after the ICV to monitor the lab's ability to produce reliable results at RL-level concentrations. There is no set acceptance criteria established for this standard, but generally results should be within 50% of the expected value.

9.11. ICB/CCB/CB - The initial calibration blank must be analyzed immediately following the ICV. The continuing calibration blank must be analyzed at a frequency of 10% throughout the remainder of the analytical run. The ICB/CCB must be less than the reporting limit to be accepted.

9.12. Interference Check Solutions (ICSA/ICSAB) ***method 6020 only***- The interference check solution is prepared with known concentrations of interfering elements so a determination may be made as to the magnitude of the interference on analytes of interest as well as a test of any software corrections. The required elements and their concentrations are listed in Table V. The interference check solutions must be analyzed at the beginning of every analytical run and every 12 hours thereafter. The results of solution "A" and solution "AB" should be monitored for possible interferences. See Table VI for analyte concentrations.

Note: It may not be possible to obtain absolutely clean ICSA/ICSAB standards. If

contamination can be confirmed by another method (ICP/GFAA), acceptance criteria will be applied at that level and the data accepted.

9.13. Internal Standards:

The intensities of all internal standards must be monitored throughout the run. The internal standard in the samples must be between 30% and 125% of the intensity of the calibration blank. If the sample falls outside of this criteria, perform the following procedures. First, evaluate nearby CCV's and CCB's. If sample internal standard recoveries appear to be related to instrument drift, then rerun affected samples. If sample internal standard recoveries appear to be primarily sample related, then perform serial fivefold (1+4) dilutions until the internal standard recoveries are within the 30-125% criteria. Alternately, the run may be reprocessed with an alternative internal standard that is not in the samples and at an appropriate mass for the masses being reported.

9.14. Serial Dilution ***method 6020 only*** - One serial five-fold dilution should be analyzed per batch for each matrix. If the analyte concentration is within linear range of the instrument and sufficiently high (generally, a factor of 100 times above the reporting limit), the serial dilution must agree within 10% of the original analysis. If not, an interference effect must be suspected, the result is flagged and included in the final report narrative. Samples identified as blanks cannot be used for serial dilution.

9.15. Post-Digestion Spike Addition (PDS) ***method 6020 only*** - If the serial dilution fails to meet the acceptance criteria, a PDS must be performed as follows. An analytical spike added to a portion of a prepared sample, or its dilution, should be recovered within 75 - 125% of the known value. If the PDS fails to meet this criterion, matrix interference should be suspected.

9.16. General Corrective Action Requirements - The general requirements for evaluation of QC results and corrective action for failures is described in STL Policy # QA-003

9.17. Nonconformance and Corrective Action

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

10. CALIBRATION AND STANDARDIZATION

10.1. Instrument Start Up

Set up the instrument according to manufacturers operating instructions. Allow the instrument to become thermally stable for at least 30 minutes before tuning.

10.2. Instrument Tuning / Mass Calibration / Daily Performance

10.2.1. Daily Performance - Refer to the facility specific instrument SOP and ICP/MS instrument manual for detailed set up and operation protocols. Verify instrument performance daily with a solution containing elements representing all of the mass regions of interest. The relative standard deviations must be less than 5% after running the tuning solution a minimum of 4 times. For method 200.8, the tuning solution must be analyzed 5 times with a relative standard deviation less than 5%.

10.2.2. Check mass calibration and resolution as needed.

10.2.2.1. Mass Calibration Check – The mass calibration results must be within 0.1 amu from the true value. If this criterion is not met, the mass calibration must be adjusted before running samples.

10.2.2.2. Mass Resolution Check - The resolution must be verified to be less than 0.9 amu full width at 10% peak height. Due to a limitation of the instrument software, the resolution requirement for method 200.8 of 1.0 amu full width at 5% peak height cannot be verified automatically. If the mass resolution requirement of 0.9AMU at 10% peak height is met the 200.8 requirement is also satisfied.

10.3. Calibrate the instrument for the analytes of interest according to manufacturer's instructions. Routine calibration and calibration verification levels are shown in Table XI. The calibration should include a blank and a three standards. For a linear, multi-point calibration curve, the correlation coefficient must be >/= 0.995. Report the average of at least three integrations for both calibration and sample analysis. A calibration must be performed daily and each time the instrument is set up.

11. PROCEDURE

11.1. One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo and is approved by a Technical Specialist and QA Manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file.

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

11.3. Sample Preparation

11.3.1. Preliminary acid digestion is required for groundwater, aqueous samples, sludges, sediments, and other solid wastes for which total (acid-leachable) elements are requested. See SOP # CORP-IP-0002NC and SOP #CORP-IP-0003NC for preparation details.

11.4. Sample Analysis

11.4.1. Flush the system with the rinse blank for at least 30 seconds between samples and standards during the analytical run.

11.4.2. Masses which would affect the data quality must be monitored during the analytical run to determine the potential effects of matrix on a given element.

11.4.3. Dilute and reanalyze samples that are more concentrated than the linear range for an analyte or specific isotope of interest . No analyte may be reported from an analysis of a diluted sample in which the analyte concentration is less than 5 times the IDL. (The sample should be diluted to the approximate midrange of the analytical curve.)

11.4.4. The analytical run sequence should be performed as follows to meet all quality control criteria:

Warm-up

Verify instrument performance

Calibration blank

Calibration standards

ICV

ICB

RL verification standard

ICSA (6020 Only)

ICSAB (6020 Only)

CCV

CCB

10 Samples

CCV

CCB

11.5. Analytical Documentation

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

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

11.5.3. Documentation such as all associated instrument printouts (final runs, screens, reruns, QC samples, etc.) and daily calibration data corresponding to all final runs is available for each data file.

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

12. DATA ANALYSIS AND CALCULATIONS

12.1. ICV percent recoveries are calculated according to the equation:

$$\%R = 100 \times \left(\frac{\textbf{Found (ICV)}}{\textbf{True (ICV)}} \right)$$

12.2. CCV percent recoveries are calculated according to the equation:

$$\%R = 100 \times \left(\frac{\textbf{Found (CCV)}}{\textbf{True (CCV)}} \right)$$

12.3. Matrix Spike Recoveries are calculated according to the following equation:

$$\%R = 100 \times \left(\frac{SSR - SR}{SA} \right)$$

Where:
SSR = Spike Sample Result
SR = Sample Result
SA = Spike Added

Note: When sample concentration is less than the method detection limit, use SR = 0 for purposes of calculating % Recovery.

12.4. The relative percent difference (RPD) of sample duplicates are calculated according to the following equation:

$$RPD = 100 \times \left[\frac{(DU1 - DU2)}{(DU1 + DU2)/2} \right]$$

Where:
DU1 = Sample result
DU2 = Sample duplicate result

12.5. The final concentration for an aqueous sample is calculated as follows:

$$\text{Result (ug/L)} = \frac{\mathbf{(C \times V1 \times D)}}{\mathbf{V2}}$$

Where:
C = Concentration from instrument readout, ppb
D = Instrument dilution factor
V1 = Final volume in liters after sample preparation
V2 = Initial volume of sample digested in liters

12.6. The concentration determined in digested solid samples when reported on a wet weight basis is as follows:

$$\text{Result (ug/kg)} = \frac{\mathbf{(C \times V \times D)}}{\mathbf{W}}$$

Where:

C = Concentration from instrument readout, ppb
D = Instrument dilution factor
V = Final volume in liters after sample preparation
W = Weight, in g, of wet sample digested

12.7. Sample results should be reported according to the following significant figure rules:

12.7.1. All uncorrected values less than the detection limit are reported as "less than" the detection limit.

12.7.2. Positive results for target analytes are reported to three significant figures if the method is used without dilution.

12.8. Positive results obtained after dilution and results for non-certified analytes are reported to two significant figures

13. METHOD PERFORMANCE

13.1. Each laboratory must have initial demonstration of performance data on file and corresponding method detection limit files.

13.2. Refer to Table I for the list of analytes that may be analyzed using this SOP for methods 6020 and 200.8.

13.3. Method performance is determined by the analysis of matrix spike and matrix spike duplicate samples as well as method blanks and laboratory control samples. The matrix spike recovery should fall within historical laboratory control limits and the matrix spike duplicates should compare within 20% RPD. Method blanks must meet the criteria specified in Section 9.3. The laboratory control samples should recover within 20% of the true value until in house control limits are established.

13.4. Training Qualifications:

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

14. POLLUTION PREVENTION

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

15. WASTE MANAGEMENT

15.1. 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. Test Methods For Evaluating Solid Waste, EPA SW-846, 3rd Edition, Final Update II, Method 6020: "Inductively Coupled Argon Plasma - Mass Spectrometry", Revision 0, September 1994.

16.1.2. Environmental Monitoring Systems Laboratory, EPA Method 200.8, "Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma - Mass Spectrometry", Revision 5.4, EMMC Version

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

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

16.2. Associated SOPs and Policies, latest version

16.2.1. QA Policy, QA-003

16.2.2. Glassware Washing, NC-QA-0014

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

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

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

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

17.1. Reporting limits

17.1.1. Refer to Appendix for associated reporting limits

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

17.2. Method deviations

17.2.1. Deviations from method 6020

17.2.1.1. Commercially available standards are purchased and verified at the laboratory rather than being prepared from the solid material. These verification records are kept on file with QA.

17.2.1.2. The results of the calibration blank as well as all other blanks must be less than the reporting limit, not 3 times the instrument IDL.

17.2.1.3. Milli-Q or Nanopure water is substituted when reagent water is called for. This water is tested to be free of contaminants by conductivity (18megOhm) and by the analysis of blanks.

17.2.2. Deviations from method 200.8

17.2.2.1. Commercially available standards are purchased and verified at the laboratory rather than being prepared from the solid material. These verification records are kept on file with QA.

17.2.2.2. The results of the calibration blank as well as all other blanks must be less than the reporting limit, not 3 times the instrument IDL.

17.2.2.3. Milli-Q or Nanopure water is substituted when reagent water is called for. This water is tested to be free of contaminants by conductivity (18 megOhm) and by the analysis of blanks.

17.2.2.4. Resolution criteria of the mass calibration is met if the resolution criteria for method 6020 is satisfied.

17.2.2.5. The concentration of most analytes in the LCS is 100 µg/L. This is made from a commercially available stock solution and has all analytes at the same level. Verification records for this solution are on file with QA.

17.2.2.6. Internal standards are evaluated based upon a recovery criteria of 30% - 125%.

17.2.2.7. Results are reported up to the verified linear range, not up to only 90% of the linear range.

TABLE I: Recommended Elemental Interference Equations

Element	Isobaric Correction	Mathematical Equation
Al	none	(1.0000)(27M)
Sb	none	(1.0000)(121M)
As	ArCl, Se	(1.0000)(75M) - (3.1278)(77M) + (1.0177)(78M)
Ba	none	(1.0000)(135M)
Be	none	(1.0000)(9M)
Cd	MoO, Sn	(1.0000)(114M) - (0.0268)(118M) - (1.0000)(135M)
Ca	none	(1.0000)(44M)
Cr	none	(1.0000)(52M)
Co	none	(1.0000)(59M)
Cu	none	(1.0000)(65M)
Fe	none	(1.0000)(57M)
Pb	none	(1.0000)(208M) + (1.0000)(207M) + (1.0000)(206M)
Mg	none	(1.0000)(25M)
Mn	none	(1.0000)(55M)
Ni	none	(1.0000)(60M)
K	none	(1.0000)(39M)
Se	Ar2	(1.0000)(78M) - (1.1869)(76M)
Ag	none	(1.0000)(107M)
Na	none	(1.0000)(23M)
Tl	none	(1.0000)(205M)
V	ClO, Cr	(1.0000)(51M) - (3.1081)(53M) + (0.3524)(52M)
Zn	none	(1.0000)(66M)
6Li	Li (natural)	(1.0000)(6M) - (0.0813)(7M)
Sc	none	(1.0000)(45M)
Y	none	(1.0000)(89M)
Rh	none	(1.0000)(103M)
In	Sn	(1.0000)(115M) - (0.0149)(118M)
Tb	none	(1.0000)(159M)
Ho	none	(1.0000)(165M)
Bi	none	(1.0000)(209M)

M = Total ion count rate at the specified mass

TABLE II: Isobaric Molecular-Ion Interferences Which Could Affect the Analytes

Analyte	Interferences						
	Oxygen	Hydroxyl	Nitrogen	Chlorine	Sulfur	Carbon	Other
^{121}Sb	PdO		AgN			AgC	
^{123}Sb	AgO		AgN	SrCl	ZrS	CdC	
^{75}As	CoO	NiOH	NiN	ArCl	CaS	CuC	
^{138}Ba	SnO	SbOH					
^{137}Ba	SbO	SnOH		MoCl			
^{136}Ba	SnO	SnOH				SnC	
^{135}Ba	SnO	SnOH		MoCl			
^{134}Ba	SnO	SnOH	SnN	MoCl		SnC	
^{132}Ba	SnO, CdO	InOH	SnN	MoCl	MoS	SnC	
^{130}Ba	CdO	CdOH	SnN, CdN	MoCl	MoS	SnC	
^{9}Be							
^{114}Cd	MoO	MoOH	MoN	SeCl	SeS		
^{112}Cd	MoO, ZrO	MoOH	MoN	AsCl, SeCl	SeS	MoC	
^{111}Cd	MoO	MoOH	MoN	GeCl			
^{110}Cd	MoO, ZrO		MoN, ZrN	GeCl, AsCl	SeS	MoC	
^{113}Cd	MoO	MoOH		SeCl, AsCl			
^{116}Cd	MoO						
^{106}Cd	ZrO		MoN, ZrN		GeS	MoC, ZrC	
^{108}Cd	MoO, ZrO	ZrOH	MoN, ZrN	GeCl	SeS, GeS	MoC, ZrC	
^{52}Cr	ArO	ClOH				ArC	
^{53}Cr	ClO	ArOH	KN	NCl, OCl		KC	
^{50}Cr	SO		ArN		SO	ArC	Mo^{++}
^{54}Cr		ClOH	ArN, CaN			CaC	
^{59}Cr	CaO	CaOH	ScN	MgCl	AlS	TiC	Sn^{++}
^{63}Cu	TiO, PO_2	TiOH	TiN	SiCl, MgCl	PS	VC	ArNa
^{65}Cu	TiO	TiOH	VN	SiCl	SS,SO_2H	CrC	
^{208}Pb							
^{206}Pb							
^{207}Pb							
^{204}Pb							
^{55}Mn	KO	ArOH	KN		NaS	CaC	Cd^{++}

TABLE II: (cont.) Isobaric Molecular-Ion Interferences Which Could Affect the Analytes

Analyte	Interferences						
	Oxygen	Hydroxyl	Nitrogen	Chlorine	Sulfur	Carbon	Other
^{202}Hg	WO						
^{200}Hg	WO	WOH	WN				
^{199}Hg	WO	WOH					
^{201}Hg		WOH					
^{198}Hg	WO	TaOH	WN			WC	
^{204}Hg							
^{196}Hg			WN				
^{58}Ni	CaO	KOH	CaN	NaCl	MgS	TiC	Cd^{++}, Sn^{++}
^{60}Ni	CaO	CaOH	TiN	MgCl, NaCl	SiS	TiC	Sn^{++}
^{62}Ni	TiO	ScOH	TiN	AlCl, MgCl	SiS	TiC, CrC	Sn^{++}
^{61}Ni	SeO	CaOH	TiN	MgCl	SiS	TiC	
^{64}Ni	TiO	TiOH	TiN, CrN	SiCl, AlCl	SS	CrC	
^{80}Se	ZnO	CuOH	ZnN	ScCl, CaCl	TiS	ZnC	
^{78}Se	NiO	NiOH	ZnN	CaCl, KCl	TiS	ZnC	
^{82}Se	ZnO	CuOH	ZnN	TiCl, ScCl	TiS, CrS		
^{76}Se	NiO	CoOH	NiN	KCl	CaS	ZnC	
^{77}Se	NiO	CuN	CuN	CaCl, ArCl	ScS	CuC	
^{74}Se	NiO	NiN	NiN	ClCl, KCl	CaS	NiC	
^{107}Ag	ZrO	ZrOH		GeCl	AsS	MoC	
^{109}Ag		MoOH	MoN	GeCl	SeS	MoC	
^{205}Tl							
^{203}Tl		WOH					
^{51}V	ClO	SOH	ClN	ClO, ClN	FS	KC	
^{50}V	SO		ArN			ArC	Mo
^{64}Zn	TiO	TiOH	TiN, CrN	SiCl, AlCl	SS	CrC	
^{66}Zn	TiO	TiOH	CrN	PCl, SiCl	SS	FeC	
^{68}Zn	CrO	VOH	FeN	PCl	ArS	FeC	Ba^{++}
^{67}Zn	VO	TiOH, Cr	CrN	SCl	ClS	MnC	Ba^{++}
^{70}Zn	FeO	CrOH	GeN	ClCl	ArS	NiC	

Note: The information provided in this table does not indicate that all of the described interferences need to be tested. However, the table can be consulted for informational purposes if unusual samples are encountered.

Table III: Changes in Isobaric Molecular-Ion Interferences with Changing Plasma Conditions**

	Molecular Interference	Nebulizer Flow Rate		
		High	Average	Low
Oxides:	ScO/Sc	0.00326	0.00055	0.00116
	YO/Y	0.00568	0.00395	0.00353
	TbO/Tb	0.0156	0.00648	0.00614
	ClO, Cl	0.00725	0.00227	0.00233
Hydroxides:	ScOH/Sc	0.00040	0.00011	0.00000
	YOH/Y	0.00078	0.00044	0.00048
	TbOH/Tb	0.00034	0.00008	0.00011
	ClOH/Cl	0.00048	0.00031	0.00029
Chlorine:	ClO/Cl	0.00725	0.00227	0.00233
	ClOH/Cl	0.00048	0.00031	0.00029
	ArCl/Cl	0.00605	0.00091	0.00477

** Information for this table is being determined by the EPA.

Table IV: Recommended Internal Standards

Method 6020	Method 200.8
Li	Sc
Sc	Y
Y	In
Rh	Tb
In	Bi
Tb	
Ho	
Bi	
Ge	

Table V: Interference Check Sample Components and Concentrations

(ICSAB minors are suggested spike levels)

Interference Component	Solution A Concentration (mg/L)	Solution AB Concentration (mg/L)
Al	50	50
Ca	50	50
Fe	50	50
Mg	50	50
Na	50	50
P	50	50
K	50	50
S	50	50
C	100	100
Cl	500	500
Mo	1.0	1.0
Ti	1.0	1.0
As	0.0	0.1
Cd	0.0	0.1
Cr	0.0	0.1
Co	0.0	0.1
Cu	0.0	0.1
Mn	0.0	0.1
Ni	0.0	0.1
Se	0.0	0.1
Ag	0.0	0.1
V	0.0	0.1
Zn	0.0	0.1

Table VI: Sample Preservation and Holding Times

Measurement Parameter	Container (1)	Preservative (2)	Maximum Holding Time (3)
Waters:			
Metals (4)	P,G	HNO_3 to pH < 2	6 months
Soils/Sediments/Wastes:			
The preservation required for soil/sediment/waste samples is maintenance at 4°C (± 2°C) until digestion.			

Footnotes: (1) Polyethylene (P) or glass (G).

(2) Sample preservation is performed by the sampler immediately upon sample collection.

(3) Samples must be analyzed as soon as possible after collection. The times listed are the maximum times that sample may be held before analysis and still considered valid. Holding times are calculated from the date when the sample was collected.

(4) Samples are filtered immediately on-site by the sampler before adding preservative for dissolved elements.

Table VII: Suggested Mass Choices

Boldface masses indicate the masses which must have the most impact on data quality and the elemental equations used to collect the data. Suggested masses for method 200.8 are in "quotes".

Mass	Element of Interest
"**27**"	Aluminum
121, "**123**"	Antimony
"75"	Arsenic
138, "137", 136, **135**, 134, 132, 130	Barium
"9"	Beryllium
114, 112, "111", 110, 113, 116, 106	Cadmium
42, 43, **44**, 46, 48	Calcium
"**52**", **53**, **50**, 54	Chromium
"**59**"	Cobalt
"**63**", **65**	Copper
56, **54**, **57**, 58	Iron
"**208**", "**207**", "**206**", 204	Lead
24, **25**, **26**	Magnesium
"**55**"	Manganese
58, "**60**", 62, **61**, 64	Nickel
39	Potassium
80, **78**, "**82**", **76**, **77**, 74	Selenium
"**107**", **109**	Silver
23	Sodium
"**205**", 203	Thallium
"**51**", **50**	Vanadium
64, "**66**", **68**, **67**, 70	Zinc
72	Germanium
139	Lanthanum
118	Tin
35, 37	Chlorine
"98", 96, 92, **97**, 94	Molybdenum

Note: It is strongly recommended that elements other than those of interest be monitored to indicate other potential molecular interferences which could affect the data quality.

Table VIII: Tuning Solution

A tuning solution containing elements representing all of the mass regions of interest must be analyzed. Below are two groups of suggested solutions which cover a typical mass calibration range.

Method 6020

Element	Concentration (µg/L)
Solution A	
Mg	10.
Rh	10.
Pb	10.
Solution B	
Li	10.
Co	10.
In	10.
Tl	10.

Method 200.8

Element	Concentration (µg/L)
Be	10.
Mg	10.
Co	10.
In	10.
Pb	10.

Table IX: Suggested Tuning and Response Factor Criteria

Minimum Response from Tuning Solution:

Be	>1,000
Mg	>20,000
Rh	>200,000
Pb	>100,000
Li	>2,000
Co	>20,000
In	>1,000
Tl	>1,000

Suggested Mass Calibration:

Be	9.0122
Mg	23.98
Rh	102.91
Pb	207.98
Li	7.016
Co	58.9332
In	114.904
Tl	204.9744

Table X: Summary of Quality Control Requirements

QC Parameter	Frequency*	Acceptance Criteria	Corrective Action
ICV/QCS	Beginning of every analytical run.	90 - 110% recovery.	Terminate analysis; correct the problem; recalibrate.
ICB/CB	Immediately after each ICV	The result must be < RL.	Terminate analysis; correct the problem; recalibrate.
CCV	Beginning and end of run and every 10 samples.	**6020-** 90 - 110% recovery. **200.8-** 85-115% recovery.	Reanalyze once. If acceptable, continue. If unacceptable, terminate analysis; correct the problem recalibrate the instrument, reverify calibration and rerun all samples since the last acceptable CCV.
CCB	Immediately following each CCV.	The result must be < RL.	Reanalyze once. If acceptable, continue. If unacceptable, terminate analysis; correct the problem recalibrate the instrument, reverify calibration and rerun all samples since the last acceptable CCB.
ICSA (6020 Only)	Beginning and every 12 hours.	Monitor for possible interferences.	See Section 9.12
ICSAB (6020 Only)	Immediately following each ICSA.	Monitor for possible interferences.	See Section 9.12

Table X (cont.) Summary of Quality Control Requirements

QC Parameter	Frequency*	Acceptance Criteria	Corrective Action
Method Blank/Laboratory Reagent Blank	One per lot of 20 field samples or fewer.	The result must be < RL. Sample results greater than 20x the blank concentration or samples for which the contaminant is < RL, do not require redigestion or reanalysis.	Redigest and reanalyze samples. Note exceptions under criteria section. See Section 9.3 for additional requirements.
Laboratory Control Sample/Laboratory Fortified Blank	One per lot of 20 field samples or fewer.	80-120%, or in-house limits (6020), 85-115% (200.8)	Redigest and reanalyze samples. See Section 9.4.
Serial Dilution (6020 Only)	One per lot of 20 field samples or fewer.	90 – 110% recovery	See section 9.14 for additional requirements.
Post-Digestion Spike (6020 Only)	See section 9.15	75-125% recovery	See section 9.15.
Matrix Spike/Matrix Spike Duplicate	One per lot of 20 field samples or fewer.	Must be within laboratory control limits	See section 9.5 for additional requirements.

Table XI: ICP/MS Calibration and Calibration Verification Checklist

Suggested Levels in µg/L

Element	Calibration			ICV	CCV
	1	2	3		
Aluminum	**10**	**50**	**100**	25	50
Antimony	10	50	100	25	50
Arsenic	10	50	100	25	50
Barium	10	50	100	25	50
Beryllium	10	50	100	25	50
Cadmium	10	50	100	25	50
Chromium	10	50	100	25	50
Cobalt	10	50	100	25	50
Copper	10	50	100	25	50
Lead	10	50	100	25	50
Manganese	10	50	100	25	50
Nickel	10	50	100	25	50
Silver	10	50	100	25	50
Thallium	10	50	100	25	50
Zinc	10	50	100	25	50

This procedure has been developed for additional elements. Additional elements may be included in the calibration solution at the appropriate levels. Levels may be adjusted to meet specific regulatory or client programs.

Table XII: Suggested ICP/MS Reporting Limits

Water 6020 and 200.8

Solid 6020 (only)

#	Compound	RL	Units	RL	Units
128	Antimony	2	ug/L	200	ug/kg
140	Arsenic	5	ug/L	500	ug/kg
194	Barium	5	ug/L	500	ug/kg
222	Beryllium	1	ug/L	100	ug/kg
411	Cadmium	1	ug/L	100	ug/kg
2952	Chromium	2	ug/L	200	ug/kg
637	Cobalt	1	ug/L	100	ug/kg
643	Copper	5	ug/L	500	ug/kg
1605	Lead	1	ug/L	100	ug/kg
1659	Manganese	5	ug/L	500	ug/kg
1906	Molybdenum	2	ug/L	200	ug/kg
1956	Nickel	2	ug/L	100	ug/kg
2281	Selenium	5	ug/L	500	ug/kg
2285	Silver	1	ug/L	100	ug/kg
2477	Thallium	1	ug/L	100	ug/kg
2479	Tin	10	ug/L	1000	ug/kg
2607	Vanadium	5	ug/L	500	ug/kg
2649	Zinc	10	ug/L	1000	ug/kg

APPENDIX A: DATA REVIEW CHECKLIST

STD1/CRI/QCSTD3	STD_____	ICSA/QCSTD4	STD_____
STD2/CCV/QCSTD6	STD_____	ICSAB/QCSTD5	STD_____
STD3	STD_____	ICV/QCSTD1	STD_____

QCSTD2= ICB QCSTD7 = CCB

STL North Canton ICP/MS Data Review Checklist

Run/Project Information:

Run Date: _____ Analyst:_____ Instrument:_____

Prep Batches Run:_____

Circle Methods used: 6020/ 200.8: CORP-MT-0001NC

Review Items

A. Tune/Daily Performance	Yes	No	N/A	2nd Level
1. Resolution </= 0.9 AMU full width at 10% peak height, and within +/- 0.1 AMU of true mass?				
2. Performance check within recommended specfications? (Mg>10,000cps) (Rh >75,000 cps) (Pb >50,000 cps) (CeO/Ce ≤ 0.03) (Ba++/Ba+ ≤ 0.03) (Background < 30cps @ Mass 220)				
B. Calibration/Instrument Run QC				
1. Instrument calibrated per manufacturer's instructions and at SOP specified levels ? Correlation coefficient ≥ .995 ?				
2. ICV/CCV analyzed at appropriate frequency and within control limits? *(ICV:* = 90 – 110%) *(CCV: 90 – 110%,* 200.8 = 85 –115%*)*				

3. ICB/CCB analyzed at appropriate frequency and within +/- RL?				
4. CRI run and recovered within QC limits (+/-50%)?				
5. ICSA/ICSAB run at required frequency and within SOP control limits?				
C. 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 ?				
D. Preparation/Matrix QC				
1. LCS done per prep batch and within QC limits ?				
2. Method blank done per prep batch and < RL?				
3. MS 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?				
6. Post digest spike analyzed if required?				
D. Other				
1. Are all nonconformances documented appropriately ?				
2. Current IDL/LR 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:_____

Comments:_____

APPENDIX B – OPERATION INSTRUCTIONS – P.E. 6100

ICP/MS INSTRUCTIONS

A. Light the plasma and start the peristaltic pump.

1. Allow the instrument to warm up approximately 10-15 minutes.

B. Daily Performance

1. Open Daily2_asx workplace.
2. Open the sampling tab in the method screen.
3. Select and initialize the autosampler. Click O.K.
4. Click on probe. Click go to rinse. Send probe to tube #8.
5. Allow solution to reach plasma and then click on analyze sample.
6. When analysis is complete, send probe back to rinse.

C. Analysis Setup

1. Open Analysis workspace.
2. Under the method window, open the report tab and type in your report filename. Save the method.
3. Highlight the dataset window. Go to file and select new. Type in the dataset name (normally the same as the filename).
4. Highlight autosampler window. Type in your autosampler locations and samples. Right click under measurement action and select what needs to be analyzed. Right click under method description and select method. Verify that all times and rpms on table are correct. Go to file and click save as. Type autosampler table name (normally the same as the filename).

D. Analyze samples

1. Highlight samples to be analyzed.
2. Left click on analyze batch.

APPENDIX C – OPTIMIZATIONS – P.E. 6100

X-Y ADJUSTMENT – Adjusts torch to achieve best intensities. This should be done whenever anything is done to the torch or the cones.

1. Open X-Y_asx.wrk.
2. Under the method window, go to the sampling tab and send the probe to tube #8.
3. Allow solution to reach plasma and hit analyze sample.
4. Adjust x and y while watching the signal on the realtime window. Adjust only until signal is at its highest.

NEB LENS – This also is done to get best intensities. It effects the shape and the depth of the plasma. This should be done if your oxides or doubly charged are >3%.

1. Open neb lens power oxides.wrk
2. Under the method window, go to the sampling tab and send the probe to tube #8.
3. Click on the Autooptimize tab. Select nebulizer gas flow.
4. Click get analyte list.
5. Make sure solution has reached the plasma and click optimize.
6. When done, save the optimization file.

AUTOLENS – Each element done represents a section of the mass spectrum. Be is on the low end, CO is in the middle and IN is on the higher end. If there is a problem with any particular section of the spectrum, it may be an indication that this needs done. This should probably be performed on a weekly basis.

1. Open Autolens_asx.wrk.
2. Under the method window, go to the sampling tab and send the probe to tube #8.
3. Click on the autolens tab.
4. Click on clear calibration.
5. Click on get analyte list.

6. Make sure the solution has reached the plasma and click on calibrate.
7. Save the optimization file.
8. In the interactive window, the optimization curve can be printed.

DUAL DETECTOR CALIBRATION – This extends the dynamic range of the detector. This should be done on a weekly basis. All analytes of interest must be included in the solution.

1. Open dual detector2.wrk
2. Under the method window, go to the sampling tab and send the probe to tube #8.
3. Click on dual detector cal tab.
4. Click on clear calibration.
5. Click on get analyte list.
6. Make sure the solution has reached the plasma and click on calibrate.
7. When complete, check to make sure that all r values are at least .999.
8. Save the optimization file.
9. In the interactive window, the plots can be displayed.

TUNING – This adjusts the electronics to assure the accuracy of the mass spec. The resolution adjustment assures that the resolution of each mass of interest is within range. This should be done monthly.

1. Open tuning_asx.wrk.
2. Under the method window, go to the sampling tab and send the probe to tube #8.
3. Allow sample to reach the plasma and click on tune mass spec.
4. Make sure measured mass and peak width is within range. If its not, resolution will need adjusted. Adding 30 units will decrease the amu by about 0.1. Subtracting 30 units will increase the amu about 0.1.

GENERAL NOTES –

1. All optimizations can be done with the tuning solution, except the dual detector cal needs the cross cal standard with all the elements of interest.
2. All optimizations can be run at 12 rpm, except the dual detector calibration should be done at 24 rpm.

Appendix D – ICPMS Maintenance Schedule

Daily	Change sample and internal standard pump tubing and pump windings
	Check argon gas supply level
	Check rinse solution and fill if needed
	Check waste containers and empty if needed
	Check sample capillary tubing is clean and in good condition
	Check sample flow for cross flow nebulizer
	Check pressure for vacuum systems
	Check daily performance
As Needed	Clean Sampler and skimmer cones
	Clean plasma torch assembly to remove accumulated deposits
	Clean nebulizer
	Replace sample and internal standard capillary tubing and autosampler sipper probe
	Replace drain tubing
	Perform necessary optimizations
	Clean autolens
Monthly	Inspect air filters; clean or replace as needed
Bi-Yearly	Change oil in vacuum pumps
	Check water in coolflow

STL NORTH CANTON STANDARD OPERATING PROCEDURE

TITLE: CARBONATE, BICARBONATE, AND HYDROXIDE ALKALINITY

(SUPERSEDES: REVISION 1, REVISION DATE 05/16/95)

Prepared by:	Angela Sessa	02/08/01 Date
Reviewed by:	Kurt C. Lee Technology Specialist	02/08/01 Date
Approved by:	Gail Ann Cahn Quality Assurance Manager	2/15/01 Date
Approved by:	 Environmental Health and Safety Coordinator	2-19-01 Date
Approved by:	Cindy M Grandi Laboratory Director	2-20-01 Date

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1. SCOPE AND APPLICATION

1.1. This method is applicable to the determination of Carbonate, Bicarbonate, and Hydroxide Alkalinity in waters and wastewaters. It is based on EPA Method 310.1 and Standard Methods 2320B. The approximate working range is 5 to 1000 mg/L $CaCO_3$.

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. QuantIMs references are UX (Bicarbonate – 310.1), AU (Bicarbonate – SM 2320B), H1 (Carbonate – SM 2320B), CB (Carbonate – 310.1), B6 (Hydroxide – SM 2320B)

2. SUMMARY OF METHOD

2.1. An unaltered sample is tested for Alkalinity and calculations are performed to determine Carbonate (CO_3-2), Bicarbonate (HCO_3-), and/or Hydroxide (OH-).

3. DEFINITIONS

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

4. INTERFERENCES

4.1. Samples with salts of weak organic and inorganic acids and greases or oils will interfere with pH measurements.

4.2. Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus that lead to discrete artifacts. All of these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. Specific selection of reagents may be required to avoid introduction of contaminants.

5. SAFETY

5.1. 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:

5.4. 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. Not Applicable

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 plastic or glass containers at 4°C ± 2°C.

9. QUALITY CONTROL

9.1. Batch Definition

9.1.1. A batch is a group of no greater than 20 samples excluding QC samples (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. Corrective Action for Blanks

9.2.2.1. If the analyte level in the method blank exceeds the reporting limit for the analytes of interest in the sample, all associated samples are reprepared and reanalyzed. If this is not possible due to limited sample quantity or other considerations, the corresponding sample data **must be addressed in the project narrative.**

9.2.2.2. If there is no analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. **Such action must be taken in consultation with the client and must be addressed in the project narrative.**

9.2.3. QC Acceptance Criteria

9.2.3.1. Control limits are established by the laboratory as described in NC-QA-0018.

9.3. Duplicates

9.3.1. Sample duplicates are performed at a minimum frequency of one per analytical batch and must meet laboratory-specific limits for precision.

10. CALIBRATION AND STANDARDIZATION

10.1. Follow SOP NC-WC-0006, Total Alkalinity, for calibration

11. PROCEDURE

11.1. One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo and is approved by a Technical Specialist and QA Manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file.

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

11.3. Sample Preparation

11.3.1. For solids preparation, see SOP NC-WC-0073.

11.4. Sample Analysis

11.4.1. Follow the Total Alkalinity SOP (NC-WC-0006). Record the initial pH prior to analysis.

11.5. Analytical Documentation

11.5.1. Record all analytical information in the analytical logbook/logsheet, including the analytical data from standards, Blank, Sample duplicate, and any corrective actions or modifications to the method.

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

11.5.3. Documentation such as all associated instrument printouts (final runs, screens, reruns, QC samples, etc.) and daily calibration data corresponding to all final runs is available for each data file.

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

12. DATA ANALYSIS AND CALCULATIONS

12.1. Calculations

12.1.1. Calculate the Alkalinity according to the Total Alkalinity Method.

12.1.2. Calculate the following Alkalinities using the Total Alkalinity value.

ALKALINITY RELATIONSHIPS

Result of Titration	Hydroxide Alkalinity as $CaCO_3$	Carbonate Alkalinity as $CaCO_3$	Bicarbonate Concentration as $CaCO_3$
P = 0	0	0	T
P < ½ T	0	2P	T – 2P
P = ½ T	0	2P	0
P > ½ T	2P – T	2(T – P)	0
P = T	T	0	0

P – phenolphthalein alkalinity

T – total alkalinity

12.2. Calculation of Alkalinity Relationships: See the referenced methods for these calculations

13. METHOD PERFORMANCE

13.1. Each laboratory must have initial demonstration of performance data on file and corresponding method detection limit files.

13.2. Training Qualifications:

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

14. POLLUTION PREVENTION

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

15. WASTE MANAGEMENT

15.1. Solid materials (gloves, soiled paper products, etc.) are placed in the solid debris container. Do not put liquids in the solid waste container.

15.2. Refer to the Laboratory Sample and Waste Disposal plan.

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

16. REFERENCES

16.1. References

16.1.1. Standard Methods, Eighteenth Edition, Alkalinity Methods, Method 2320B

16.1.2. Methods for Chemical Analysis of Water and Wastes, EPA 310.1

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

16.1.4. STL North Canton SOP NC-WC-0012 Alkalinity, Phenolphthalein.

16.2. Associated SOPs

16.2.1. Alkalinity (Total), NC-WC-0006.

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

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

17.1. Reporting limits

17.1.1. The lower reporting limit (RL) is 10 mg/L $CaCO_3$.

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

LABORATORY-SPECIFIC

STL NORTH CANTON STANDARD OPERATING PROCEDURE

TITLE: PH ELECTROMETRIC METHOD

(SUPERSEDES: REVISION 4.0; DATED 01/04/99)

Prepared by: _____ 11/28/00 Date

Reviewed by: _____ Technology Specialist 11/28/00 Date

Approved by: _____ Quality Assurance Manager 11/29/00 Date

Approved by: _____ Environmental Health and Safety Coordinator 12-4-00 Date

Approved by: _____ Laboratory Director 11/28/00 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.

10.1.3 The pH meter should be calibrated daily. The calibration is recorded on the analytical logsheet.

10.1.4 If the pH meter has been turned off, it must be calibrated prior to use.

10.2. Continuing Calibration

10.2.1. A pH 7 buffer is analyzed before analysis and every ten samples to ensure the calibration remains linear.

10.2.2. The pH meter must be recalibrated if the buffer deviates by more than ± 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.

LABORATORY-SPECIFIC

QUANTERRA® STANDARD OPERATING PROCEDURE

TITLE: TOTAL ORGANIC CARBON (TOC) AND TOTAL INORGANIC CARBON (TIC)

(SUPERSEDES: REVISION 1, DATED 11/20/96)

Prepared by: Laurel E. Wood 6/1/99
Date

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1. SCOPE AND APPLICATION

1.1. This method is applicable to the determination of Total Organic Carbon (TOC) or Total Inorganic Carbon (TIC) in waters and similar matrices. It is based on SW846 Method 9060 and EPA Method 415.1. The working linear range is instrument dependent at 1 mg/L to 50 mg/L with a reporting limit of 1 mg/L.

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

1.3. QuantIMS method codes are I8 (415.1 TIC), AY (9060 TIC), DA (415.1 – TOC) FM (9060 – TOC).

2. SUMMARY OF METHOD

2.1. Organic carbon is converted to carbon dioxide (CO_2) using chemical oxidation. The CO_2 is then measured by an infrared detector.

3. DEFINITIONS

3.1. Refer to the glossary in the Quality Assurance Management Plan (QAMP), current version.

4. INTERFERENCES

4.1. Contaminants in solvents, reagents, glassware, and other processing apparatus that lead to discrete artifacts may cause Method interferences. All of these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. Specific selection of reagents may be required to avoid introduction of contaminants.

4.2. Carbonate and bicarbonate interfere but are eliminated by the acidification and purging step of the instrument.

5. SAFETY

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

5.2. Eye protection that satisfies ANSI Z87.1 (per the Chemical Hygiene Plan), Laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.3. The health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the Material Safety Data Sheets (MSDS) maintained in the laboratory. The following specific hazard is known:

5.3.1. The following materials are known to be **corrosive:** Phosphoric **Acid, Sulfuric Acid**.

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

5.5. The preparation of standards and reagents will be conducted in/a fume hood with the sash closed as far as the operation will permit.

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

6. EQUIPMENT AND SUPPLIES

6.1. O•I Corporation Model 1010 TOC Analyzer with 1051 vial multisampler and Printer

6.2. Nitrogen Gas and Regulator

6.3. Volumetric flasks: Various sizes

6.4. Volumetric pipettes: Various sizes

6.5. Vials: 40 mL glass

6.6. Graduated cylinders: Various sizes

6.7. pH Strips

6.8. Whatman filter #4

6.9. Top loading balance: capable of accurately weighing ± 0.01 g

7. REAGENTS AND STANDARDS

7.1. Reagents

7.1.1. Sodium Persulfate: Reagent Grade

7.1.2. Sodium Persulfate Solution: Add 200 g sodium persulfate ($Na_2S_2O_8$) to a 1 liter volumetric flask and dilute to volume with reagent water.

7.1.3. Phosphoric Acid, concentrated: Reagent Grade

7.1.4. Phosphoric Acid Solution: Carefully add 59 mL concentrated phosphoric acid (H_2PO_4) to 900 mL of reagent water in a 1 liter volumetric flask. Dilute to volume with reagent water.

7.1.5. Sulfuric Acid, concentrated: Reagent Grade

7.2. Standards

7.2.1. All standards should be prepared in volumetric flasks, using volumetric pipettes, and diluted to volume with reagent water.

7.2.2. TOC Stock Standard

7.2.2.1. Primary and secondary sources are needed.

7.2.2.2. TOC 1000 mg/L

7.2.2.2.1. Dilute 1.06 g KHP (potassium acid phthalate) to volume in a 500 mL volumetric flask.

7.2.2.3. Prepare every six months.

7.2.3. TOC Calibration Standards

7.2.3.1. Prepare the following standards from the primary stock standard described in Section 7.2.2.2.1.

Concentration (mg/L)	Volume (mL)	Stock Concentration (mg/L)	Final Volume (mL)
50	5	1000	100
25	2.5	1000	100
10	1	1000	100
1	0.1	1000	100

7.2.4. TOC Verification Standard (LCS, MS/MSD and CCV)

7.2.4.1. Prepare the following standard from the secondary stock standard described in Section 7.2.2.2.1.

Concentration (mg/L)	Volume (mL)	Stock Concentration (mg/L)	Final Volume (mL)
25	12.5	1000	500

7.2.4.2. Prepare when setting up run.

7.2.5. TIC Stock Standard 1000 mg/L

7.2.5.1. Add 3.5 g Na_2HCO_3 (sodium bicarbonate) and 4.418 g Na_2CO_3 (sodium carbonate) to a 1000 mL flask. Dilute to volume with reagent water.

7.2.5.2. Prepare every 3 months.

7.2.6. TIC Calibration Standard

7.2.6.1. Prepare in the same manner as the TOC calibration standard (Section 7.2.3.1), using the TIC stock standard described in Section 7.2.5.1.

7.2.6.2. Prepare weekly.

7.2.7. TIC Verification Standard (LCS, MS/MSD and CCV)

7.2.7.1. Prepare in the same manner as the TOC verification standard (Section 7.2.4.1), using the TIC stock standard described in Section 7.2.5.1.

7.2.7.2. Prepare daily.

8. SAMPLE PRESERVATION AND STORAGE

8.1. Samples are preserved to a pH < 2 with sulfuric acid (H_2SO_4) or hydrochloric acid (HCl) and stored in plastic or glass containers at 4°C ± 2° C.

8.2. The holding time is twenty-eight days from sampling to analysis.

9. QUALITY CONTROL

9.1. Batch Definition

9.1.1. A batch is a group of no greater than 20 samples, excluding QC samples (LCS, MS, MSD, and Method Blanks), which are processed similarly with respect to the procedure. All samples within the batch must be treated with the same lots of reagents and the same processes. All samples within the batch must be treated with the same processes.

9.2. Method Blank (MB)

9.2.1. One method blank (MB) must be processed with each preparation batch. The method blank consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The method blank is used to identify any system and process interferences or contamination

of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. The method blank should not contain any analyte of interest at or above the reporting limit.

9.2.2. A method blank consisting of 40 mL of reagent water and all reagents added to the samples must be prepared and analyzed with each batch of samples. The method blank is used to identify any background interference or contamination of the analytical system, which may lead to the reporting of elevated concentration levels or false positive data.

9.2.3. Corrective Action for Blanks

9.2.3.1. If the analyte level in the method blank exceeds the reporting limit for the analytes of interest in the sample, all associated samples are reprepared and reanalyzed. If this is not possible due to limited sample quantity or other considerations, the corresponding sample data **must be taken in consultation with the client and must be addressed in the project narrative.**

9.2.3.2. If there is no analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. **Such action must be taken in consultation with the client and must be addressed in the project narrative.**

9.3. Laboratory Control Sample

9.3.1. Laboratory Control Samples are well characterized; laboratory generated samples used to monitor the laboratory's day to day performance of routine analytical methods. The LCS is used to monitor the accuracy of the analytical process, independent of matrix effects. Ongoing monitoring of the LCS results provides evidence that the laboratory is performing the method within accepted QC guidelines for accuracy and precision.

9.3.2. A 25 mg/L LCS (TOC or TIC) must be analyzed with each batch of samples.

9.3.3. Corrective Action for LCS

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

9.3.3.1.1. The only exception to the requirement established in section 9.3.3.1 occurs if the LCS recovery is biased high and the associated sample(s) are ND (non detect). Under this condition, the batch is acceptable.

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

9.4. Matrix Spike/Matrix Spike Duplicate (MS/MSD)

9.4.1. One MS/MSD pair must be processed for each batch. A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added. A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked identically as the MS) prepared and analyzed along with the sample and matrix spike. Some client specific data quality objectives (DQO's) may require the use of sample duplicates in place of or in addition to MS/MSD's. The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Due to the potential variability of the matrix of each sample, these results may have immediate bearing only on the specific sample spiked. Samples identified as field blanks cannot be used for MS/MSD analysis.

9.4.2. An MS/MSD consisting of 20 mL of sample and 20 mL of the 25 mg/L standard will be analyzed with each analytical batch of samples.

9.4.3. Corrective action for MS/MSDs

9.4.3.1. If the analyte recovery or RPD falls outside the acceptance range, the recovery of that analyte must be in control for the LCS. If the LCS recovery is within limits, then the laboratory operation is in control and the results may be accepted. If the recovery of the LCS is outside limits, corrective action must be taken. Corrective action will include repreparation and reanalysis of the batch.

9.4.3.2. If the native analyte concentration in the MS/MSD exceeds 4x the spike level for that analyte, the recovery data is reported as DIL (diluted out).

9.4.3.3. If an MS/MSD is not possible due to limited sample volume then a laboratory control sample duplicate (LCSD) should be analyzed. The RPD of the LCS and LCSD must be compared to the matrix spike RPD limits.

9.5. QC Acceptance Criteria

9.5.1. Control limits are established by the laboratory as described in NC-QA-0018.

10. CALIBRATION AND BLANKING

10.1. Recommended Initial Setup

Contant Settings		
STD Mass	=	6.76 ug C
Sample Vol	=	2.0 mL
Acid Vol	=	4 x 100 uL
Oxidant Vol	=	10 x 100 uL

10.1.1. Adjust the nitrogen to 30 psi using the flow valve on the tank. The gauge should always be set at 30 psi when the instrument is not in use.

10.1.1.1. If the main valve reads < 200 psi, the tank should be changed. **Do not** allow the tank to go empty.

10.1.2. Remove the reagent bottles and fill with appropriate reagents (phosphoric acid solution and sodium persulfate). Do not fill bottles completely full; leave a small amount of air space. Loosely reconnect caps (and tubing), and replace the bottles into the instrument.

10.1.3. Blank and calibrate the instrument when CCVs and/or CCBs fail to meet acceptance criteria or when other problems are encountered.

10.1.3.1. Choose "sequences" from the "databases" menu option, open up the calibration template.

10.1.3.2. Confirm all information. If blanking is required, it is best if done at this step. Enter the desired number of blanks (no less than five) in the "reagent blanks before" field.

10.1.3.3. Analyze an ICV/ICB

10.1.3.4. Save the file using the current date as the filename.

10.1.3.5. Update data file information:

10.1.3.5.1. Choose the setup menu option, go into win TOC output, change the log fill name and prefix counter.

10.1.3.6. When analysis is complete, print the run from "/utilities/view run log"

10.1.3.7. Evaluate the data. The correlation coefficient of the original curve must be ≥0.995 or recalibration is required.

10.2. Continuing Calibration

10.2.1. The run is checked at the beginning, after every ten samples, and at the end of the run of the same species (TOC or TIC) using a midrange CCV made from a secondary source (Section 7.2.4 or 7.2.7) to verify continued linearity. A CCV cannot vary from the original curve by more than ± 10%, or recalibration is required.

10.2.2. System cleanliness is checked every ten samples and at the end of the run using a Continuing Calibration Blank (CCB). A CCB cannot contain the analyte of interest above the reporting limit, or recalibration is required.

10.3. Analytical Documentation

10.3.1. Record all analytical information in the analytical logbook/logsheet, including the analytical data from standards, blanks, LCSs, MS/MSDs, and any corrective actions or modifications to the method.

10.3.2. All standards are logged into a department standard logbook. All standards are assigned a unique number for identification. The supervisor or designee reviews logbooks.

10.3.3. Documentation, such as all associated instrument printouts (final runs, screens, reruns, QC samples, etc.) and daily calibration data corresponding to all final runs, is available for each data file.

10.3.4. Sample results and associated QC are entered into the Laboratory Information Management System (LIMS) after final technical review.

11. PROCEDURE

11.1. Sample Preparation Procedure

11.1.1. Check the pH of the sample. If the pH > 2, add concentrated H_2SO_4 drop by drop to the sample (in the TOC vial) until the pH is < 2.

11.1.2. If excess particulate matter exists, filter an aliquot of sample through a Whatman #4 filter into a TOC vial.

11.2. Preparation Documentation

11.2.1. Record any sample preparation on the analytical logsheet.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Sample Analysis Procedure

12.1.1. Type a run protocol sequence into the computer using the run template, if desired. Update the data file information in the setup/winTOC output.

12.1.1.1. For method 9060, quadruplicate analysis is required. If quadruplicate reporting is requested each of four results are reported. Replicate analysis should be taken from separate vials, if available. If only one reportable result is requested per sample, the four results should be taken from one vial, and the average of the four results are reported.

12.1.1.2. For method 415.1 only one analysis is required. The single analysis result is reported directly from the instrument printout.

12.1.2. All samples and standards should be poured into 40 mL vials. Samples received in vials can be run in those containers, provided there is not an excess of solids.

12.1.3. Be sure the samples are loaded on the sampler, the first one positioned under the needle.

12.1.4. Click on the "Start" button.

12.1.5. Samples that fall outside the linear range (> 100 mg/L) of the instrument must be diluted and reanalyzed.

12.1.5.1. Samples following a high sample should be re-analyzed if carryover is a concern.

12.1.6. Print the run from "utilities/view run log."

12.1.7. When analysis is complete, properly dispose of or put away samples and standards.

12.2. Calculations

12.2.1. ***Total Organic Carbon, mg/L = Average Instrument Value x Dilution***

Where:

TOC, mg/L = average of the 4 instrument values x dilution, calculated (without dilution) by the instrument.*

12.2.2. ***LCS % Recovery =*** $\dfrac{\dfrac{\textit{Average of 4 instrument values*}}{25} \textit{ x 100}}{}$

12.2.3. ***MS/MSD % recovery***

$$\frac{\dfrac{\textit{(Avg of 4 instrument values* MS or MSD) - (Avg sample instrument value* ÷ 2)}}{12.5}}{100} \text{ x}$$

**One of the values may be judged erroneous and disregarded if three of the four are consistent. If no consistency can be found in the four values, the sample must be rerun.*

13. METHOD PERFORMANCE

13.1. Each laboratory must have initial demonstration of performance data on file and corresponding method detection limit files.

13.2. Training Qualifications:

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

14. POLLUTION PREVENTION

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

15. WASTE MANAGEMENT

15.1. Acid waste must be collected in clearly labeled acid water containers.

15.2. Solid materials (gloves, soiled paper products) are placed in the solid debris container. Do not put liquids in the solid waste container.

15.3. Refer to the Laboratory Sample and Waste Disposal plan.

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

16. REFERENCES

16.1. References

16.1.1. SW846, Test Methods for Evaluating Solid Waste, Third Edition, Total Organic Carbon, Method 9060

16.1.2. EPA 600, Methods for Chemical Analysis of Water and Wastes, Organic Carbon, Method 415.1

16.1.3. Quanterra® Quality Assurance Management Plan (QAMP), current version.

16.2. Associated SOP

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

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

17.1. Reporting limits

17.1.1. The lower reporting limit is 1 mg/L.

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

17.2. Troubleshooting guide

17.2.1. See the manufacturer's instructions for an instrument troubleshooting guide and maintenance requirements.

17.3. Deviations from the Method

17.3.1. A blender is not used to homogenize samples.

STL NORTH CANTON STANDARD OPERATING PROCEDURE

TITLE: REACTIVE CYANIDE

(SUPERSEDES: REVISION 2,10/11/00)

Prepared by: _____ 5/15/02
Date

Approved by: _____ 5/15/02
Technology Specialist Date

Approved by: _____ 5/16/02
Quality Assurance Manager Date

Approved by: _____ 5-16-02
Environmental Health and Safety Coordinator Date

Approved by: _____ 5-15-02
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 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: 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. Addition 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.

6.12. Lead Acetate test strips.

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. A commercially prepared solution may also be used.

7.1.7. 0.0192 N Silver Nitrate Solution: reagent grade

7.1.8. Rhodanine Indicator: Dimethylaminobenzalrhodanine, reagent grade

7.1.9. Kaolin: reagent grade

7.1.10. Cadmium Carbonate: ($CdCO_3$), reagent grade

7.1.11. Spiking Solution (LCS, MS/MSD): Add 1.25g KCN to a 250mL volumetric flask. Bring to volume with 0.01N NaOH.

7.1.12. 0.01N NaOH: Add 0.4g NaOH to a 1 L volumetric flask. Bring to volume with reagent water.

8. SAMPLE PRESERVATION AND STORAGE

8.1. Samples are stored in plastic or glass containers at 4° ± 2°C.

8.2. Solid and water samples are not chemically preserved.

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 (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. Laboratory Control Sample (LCS)

9.3.1. One LCS from an independent source must be processed with each preparation batch. The LCS must be carried through the entire analytical procedure. The LCS is used to monitor the accuracy of the analytical process. On-going monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines.

9.3.2. Corrective Action for LCS

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

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

9.3.2.3. Corrective action will be 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. Corrective action for MS/MSDs

9.4.2.1. If the analyte recovery or RPD falls outside the acceptance range, the recovery of that analyte must be in control for the LCS. If the LCS recovery is within limits, then the laboratory operation is in control and the results may be accepted. If the recovery of the LCS is outside limits, corrective action must be taken. Corrective action will include repreparation and reanalysis of the batch.

9.4.2.2. If the native analyte concentration in the MS/MSD exceeds 4x the spike level for that analyte, the recovery data is reported as "amount" MSB. The Exception Code is

changed to NC. The following two footnotes will appear on the report page "NC The recovery and/or RPD were not calculated." "MSB The recovery and RPD were not calculated because the sample amount was greater than four times the spike amount."

9.4.2.3. If an MS/MSD is not possible due to limited sample volume then a laboratory control sample duplicate (LCSD) should be analyzed. The RPD of the LCS and LCSD must be compared to the laboratory limits.

9.4.2.4. If client program requirements specify to confirm matrix interference's, repreparation and reanalysis of the MS/MSD may be necessary.

9.5. QC Acceptance Criteria

9.5.1. Control limits are established by the laboratory as described in NC-QA-0018.

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. Add 1.25 mL of spiking solution to LCS, MS, and MSD samples.

11.2.5. Close the entire system and begin the flow of nitrogen. The flow should be 3-5 bubbles per second.

11.2.6. 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.

11.2.7. Allow the sample to react (while mixing) for thirty minutes. Document mixing time.

11.2.8. After the thirty minute reacting period, disconnect the system and shut off the nitrogen.

11.2.9. 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, check the scrubber solution with lead acetate test paper for the presence of sulfide. If negative for sulfide, go to Section 11.4.2. If positive for sulfide,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. All QC and field samples must be treated for sulfide prior to cyanide analysis.

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. Filter 100 mLs of treated scrubber solution through a #4 Whatman filter paper into an Erlenmeyer flask.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Calculations

$$HCN(mg/kg) = (X * L) \div W$$

Where:

X= concentration CN (mg/L) = {[mL titrant (sample) – mL titrant (blank)]/mL sample titrated}X 100

L = volume of solution in scrubber

W = weight of sample used

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.

17.2.3. Note that bottles may be received with headspace or multiple tests may be analyzed from the same container resulting in headspace at the time of 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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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

QUANTERRA® STANDARD OPERATING PROCEDURE

TITLE: TOTAL HARDNESS (MG/L $CACO_3$), TITRIMETRIC

(SUPERSEDES: REVISION 2, DATED 12/23/98)

Intranet Controlled

Prepared by: _____ Date

Reviewed by: _____
Technology Specialist Date

Approved by: _____
Quality Assurance Manager Date

Approved by: _____
Environmental Health and Safety Coordinator Date

Approved by: _____
Laboratory Director Date

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1. SCOPE AND APPLICATION

1.1. This method is applicable to the determination of Hardness in waters and wastewaters. It is based on EPA Method 130.2. The approximate working range is 2 to 400 mg/L.

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

1.3. The applicable LIMs method code is AD. The preparation code for aqueous samples is 88.

2. SUMMARY OF METHOD

2.1. Calcium and magnesium ions in the sample are sequestered upon the addition of magnesium ethylenediamine tetraacetate (MgEDTA). The end point of the reaction is detected using Eriochrome Black T indicator, which has a red color in the presence of calcium and magnesium and a blue color when the cations are sequestered.

3. DEFINITIONS

3.1. Refer to the glossary in the Quality Assurance Management Plan (QAMP), 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. Excessive amounts of heavy metals can interfere. This can be overcome by complexing the metals with cyanide. Sodium cyanide solution (**Caution: deadly poision)** may be added to prevent metallic interference.

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.

5.3.1. The following materials are known to be **corrosive: Ammonium 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 Quanterra associate. The situation must be reported **immediately** to a laboratory supervisor.

6. EQUIPMENT AND SUPPLIES

6.1. Stir plate and stir bars

6.2. Erlenmeyer flasks: various

6.3. Graduated cylinders: various

6.4. Autopipettor and disposable tips

6.5. Class A Microburet: 10 mL

6.6. Volumetric flasks: various

6.7. Plastic bottles: various

6.8. Analytical balance: Capable of accurately weighing ± 0.0001 g

7. REAGENTS AND STANDARDS

7.1. Reagents

7.1.1. Ammonium Chloride (NH_4Cl): reagent grade

7.1.2. Ammonium Hydroxide (NH_4OH): reagent grade

7.1.3. Magnesium EDTA: reagent grade

7.1.4. EDTA Buffer Solution: Dissolve 16.9 g of NH_4Cl in 143 mL of NH_4OH. Add 1.25 g of magnesium salt of EDTA and dilute to 250 mL with reagent water. Mix well and store in a plastic bottle. This solution is stable for one month. Alternatively, use purchased hardness buffer.

7.1.5. Eriochrome Black T Indicator: reagent grade

7.1.6. Sodium Chloride (NaCl): reagent grade

7.1.7. Indicator: Mix together 0.5 g of Eriochrome Black T and 100 g of NaCl. Alternatively, use purchased indicator (such as Calamagite).

7.1.8. 1 N Ammonium Hydroxide: Dilute 7 mL of NH_4OH to 100 mL with reagent water and mix well.

7.1.9. Disodium EDTA Dihydrate: Primary standard grade

7.1.10. 0.02 N EDTA Titrant: Purchased. Alternatively, prepare titrant by dissolving 3.723 g of disodium EDTA dihydrate in about 400 mL of reagent water in a 1000 mL volumetric flash. Dilute to 1 liter with reagent water and mix well. This solution is stable for six months. Calibrate weekly against standard calcium solution by titration. Store in polyethylene bottle.

7.1.10.1. Standardization Titration Procedure: Place 5.0 mL of 1000 ppm standard calcium solution in a vessel containing about 50 mL of reagent water. Add 1 mL of buffer solution. Add about 0.5 - 1 g of dry indicator. Titrate slowly with continuous stirring until the last reddish tinge disappears, adding the last few drops at 3 - 5 second intervals. At the end point, the color is blue. Repeat the standardization procedure two more times and average the values.

$$\textbf{N of EDTA} = \frac{\textbf{0.1}}{\textbf{mL of EDTA}}$$

7.2. Standards

7.2.1. Calcium Carbonate Standard Solution, 1000 mg/L: Purchased standard (Hach or other supplier). Alternately, a standard may be made: Place 1.0 g of anhydrous calcium carbonate (primary standard grade) in a 500 mL Erlenmeyer flask. Slowly add 6 N HC1 until all the $CaCO_3$ has dissolved. Add 200 mL of reagent water and boil for five minutes. Cool the solution and add several drops of methyl red indicator. Adjust the solution to an intermediate orange color with 3 N NH_4 OH or 6 N HCl as required. Quantitatively transfer the solution to a 1 liter volumetric flask and dilute to volume with reagent water. This solution is stable for six months.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Samples are preserved to a pH < 2 with concentrated nitric acid.

8.2. Samples are stored in plastic or glass containers at 4°C ± 2°C.

8.3. The holding time is six months from sampling to the completion of analysis.

9. QUALITY CONTROL

9.1. Batch Definition

9.1.1. A batch is a group of no greater than 20 samples excluding QC samples (LCS, Method Blank, MS, MSD) which are processed similarly, with respect to the procedure. All sample setups must be initiated within a 24 hour period from the initial preparation or extraction and without interruption of the process. All samples within the batch must be treated with the same lots of reagents and the same processes.

9.2. Method Blank

9.2.1. One method blank (MB) must be processed with each preparation batch. The method blank consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The method blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. The method blank should not contain any analyte of interest at or above the reporting limit.

9.2.2. A reagent water blank consisting of 50 mL of reagent water and all other reagents added to samples must be analyzed with each analytical batch of samples.

9.2.3. Corrective Action for Blanks

9.2.3.1. If the analyte level in the method blank exceeds the reporting limit for the analytes of interest in the sample, all associated samples are reprepared and reanalyzed. If this is not possible due to limited sample quantity or holding time considerations, the corresponding sample data **must be addressed in the project narrative.**

9.2.3.2. If there is no analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. **Such action must be 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 must be analyzed with each analytical batch of samples. The LCS is made of 45 mL reagent water and 5.0 mL 1000 ppm $CaCO_3$ standard.

9.3.3. Corrective Active for LCS

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

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

9.4. Matrix Spike/Matrix Spike Duplicate (MS/MSD)

9.4.1. One MS/MSD pair must be processed for each batch. A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added. A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked identically as the MS) prepared and analyzed along with the sample and matrix spike. Some client specific data quality objectives (DQO's) may require the use

of sample duplicates in place of or in addition to MS/MSD's. The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Due to the potential variability of the matrix of each sample, these results may have immediate bearing only on the specific sample spiked. Samples identified as field blanks cannot be used for MS/MSD analysis.

9.4.2. An MS/MSD must be analyzed per analytical batch. The MS/MSD is composed of 25 mL reagent water, 25 mL sample, and 0.5 mL 10,000 ppm $CaCO_3$.

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. In an MS/MSD is not possible due to limited sample volume then a laboratory control sample duplicate (LCSD) should be analyzed. The RPD of the LCS and LCSD must be compared to the matrix spike RPD limits.

9.5. Duplicates

9.5.1. If samples are analyzed for NPDES work or drinking waters, a duplicate sample is prepared and analyzed per batch of 10 samples processed.

9.6. QC Acceptance Criteria

9.6.1. 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 - Not Applicable

11.4. Sample Analysis Procedure

11.4.1. Rinse the burette with reagent water once and with EDTA titrant once. Fill with EDTA titrant and be sure all air bubbles are removed.

11.4.2. Place 25 mL of sample and 25 mL of reagent water in an Erlenmeyer flask. Add approximately 1 to 2 mL of 1N NH_4OH, approximately 1 to 2 mL of EDTA buffer, and approximately 0.5 to 1 g of Indicator. Titration should be completed within 5 minutes of the addition of the buffer.

11.4.3. While stirring, slowly titrate with EDTA titrant until the last reddish tint disappears. The end point is blue. Record the volume of titrant used and its true normality on the analytical logsheet.

NOTE: Samples requiring more than 10 mL of titrant must be diluted. An aliquot is diluted to a final volume of 50 mL with reagent water.

All reagents and samples must be at ambient temperature prior to analysis.

11.5. Report Documentation

11.5.1. Record all analytical information on the analytical logsheet, including the analytical data from Standards, blanks, LCSs, MS/MSDs, and sample duplicate.

11.5.2. All standards are logged into the departmental standard logbook.

12. DATA ANALYSIS AND CALCULATIONS

12.1.1. **Hardness, mg/L $CaCO_3$** $= \dfrac{(A - B) \times N \times 50{,}000}{C} \times D$

Where:

A = Volume of EDTA titrant used for sample, mL

B = Volume of EDTA titrant used for blank, mL

C = Volume of sample used, mL (not total volume after addition of DI water)

D = *Dilution Factor* $= \dfrac{\textit{Final Dilution Volume, mL}}{\textit{Initial Sample Volume Used For Dilution, mL}}$

N = Normality of EDTA titrant

50,000 = 50 (Equivalent weight of Calcium) x 1000 mg/g

12.1.2. **LCS Recovery:**

$$\textbf{LCS \% Recovery} = \frac{\textbf{mL titrant x N x 50,000}}{\textbf{(25)(200)}} \times \textbf{100}$$

Where:

N = Normality of EDTA titrant

12.1.3. **MS/MSD Calculation:**

$$\textbf{MS / MSD \% Recovery} = \frac{\textbf{(A – B)}}{\textbf{200}} \times \textbf{100}$$

Where:

A = MS/MSD concentration (from 12.1.1)

B = Sample concentration (from 12.1.1)

13. METHOD PERFORMANCE

13.1. Each laboratory must have initial demonstration of performance data on file and corresponding method detection limit files.

13.2. Training Qualifications.

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

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 containers.

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. EPA 600, Methods for Chemical Analysis of Water and Wastes, Hardness, Total (Mg/L as $CaCO_3$, Titrimetric, EDTA), Method 130.2

16.1.2. Quanterra® Quality Assurance Management Plan (QAMP), current version.

16.2. Associated SOPs

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

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

17.1. Reporting Limits

17.1.1. The lower reporting limit (RL) for undiluted samples is 2 mg/L $CaCO_3$.

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

17.2. Deviation from EPA Method 130.2

17.2.1. Wastewater samples are not digested.

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

$$Normality\ Iodine = \frac{(Normality\ Na_2S_2O_3)(mL\ of\ titrant\ Na_2S_2O_3)}{20\ mL\ Iodine}$$

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

$$\textit{Sulfide, mg / L or mg / kg} = \frac{\textit{[(A x B) - (C x D)] x 16,000}}{\textit{mL or g of sample used}}$$

Where:

A = ***mL of iodine solution***

B = ***Normality of iodine solution***

C = ***mL of sodium thiosulfate titrant***

D = ***Normality of sodium thiosulfate titrant***

$$\textit{Sulfide, mg / L or mg / kg} = \frac{\textit{(20 - mL titrant) x 400}}{\textit{mL or g of sample used}}$$

12.1.1.

$$LCS\,\%\ \text{Recovery} = \frac{\text{mg/L (from 12.1.1)}}{\text{20 (true)}} \text{ x } 100$$

12.1.2.

$$\text{MS/MSD \% Recovery} = \frac{\text{A - B}}{\text{20 (waters) or 1000 (solids)}} \text{ x } 100$$

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-S^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.

STL NORTH CANTON

STANDARD OPERATING PROCEDURE

TITLE: REACTIVE SULFIDE

(SUPERSEDES: (REVISION 1.1, DATED 04/23/01))

Prepared by: _____ 5/15/02
Date

Reviewed by: _____ 5/15/02
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Approved by: _____ 5/16/02
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Approved by: _____ 5-16-02
Environmental Health and Safety Coordinator Date

Approved by: _____ 5-15-02
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 500 mg/kg. The EPA guidance level is 500 mg H_2S/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 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, 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. Addition 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, 0.028 N: Manufactured., or 0.025 N prepared. 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. A commercially prepared solution may also be used.

7.1.5.1. Standardization 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. A commercially prepared solution may also be used.

7.1.6.1. Standardization of 0.025 N Sodium Thiosulfate Solution: To make 0.025N Biiodate 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. Alternatively, a commercially prepared solution may be used.

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. Alternatively, a commercially prepared solution may be used.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Samples are unpreserved.

8.2. Samples are stored in glass containers at 4°C ± 2°C.

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. Laboratory Control Sample (LCS)

9.3.1. One LCS from an independent source must be processed with each preparation batch. The LCS must be carried through the entire analytical procedure. The LCS is used to monitor the accuracy of the analytical process. On-going monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines.

9.3.1.1. The LCS solution is prepared by adding 3.5 g Na_2S to a 250mL volumetric flask and bringing to volume with 0.01N NaOH. 1.25mL of this solution is added to the LCS sample.

9.3.2. Corrective Action for LCS

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

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

9.3.2.3. Corrective action will be 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.

9.4.1.1. The MS/MSD solution is prepared by adding 3.5 g Na_2S to a 250mL volumetric flask and bringing to volume with 0.01N NaOH. 1.25mL of this solution is added to the MS/MSD samples.

9.4.2. Corrective action for MS/MSDs

9.4.2.1. If the analyte recovery or RPD falls outside the acceptance range, the recovery of that analyte must be in control for the LCS. If the LCS recovery is within limits, then the laboratory operation is in control and the results may be accepted. If the recovery of the LCS is outside limits, corrective action must be taken. Corrective action will include repreparation and reanalysis of the batch.

9.4.2.2. If the native analyte concentration in the MS/MSD exceeds 4x the spike level for that analyte, the recovery data is reported as "amount" MSB. The Exception Code is changed to NC. The following two footnotes will appear on the report page "NC The recovery and/or RPD

were not calculated." "MSB The recovery and RPD were not calculated because the sample amount was greater than four times the spike amount."

9.4.2.3. If an MS/MSD is not possible due to limited sample volume then a laboratory control sample duplicate (LCSD) should be analyzed. The RPD of the LCS and LCSD must be compared to the laboratory limits.

9.4.2.4. If client program requirements specify to confirm matrix interference's, repreparation and reanalysis of the MS/MSD may be necessary.

9.5. QC Acceptance Criteria

9.5.1. Control limits are established by the laboratory as described in NC-QA-0018.

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. Add spike solutions to LCS, MS, and MSD samples.

11.3.2.5. Close the entire system and begin the flow of nitrogen. The flow should be 3-5 bubbles per second.

11.3.2.6. 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.

11.3.2.7. Begin timing for thirty minutes. Document mixing time.

11.3.2.8. After the thirty minute reacting period, disconnect the system and shut off the nitrogen.

11.3.2.9. 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 (for the addition of the iodide solution, make sure the tip of the pipette is below the surface of the sample), 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, additional Iodine solution is needed to keep the color consistent. The additional amount of Iodine then needs to be taken into account in the calculation.

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. $$mg/L\ Sulfide\ in\ scrubber\ solution = \frac{[(A \bullet a) - (B \bullet b)]16{,}000}{C} = X$$

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. $$Reactive\ Sulfide\ (mg/kg) = \frac{(X)(L)}{(W)}$$

Where:

X = *Concentrated Sulfide from 12.1*

L = *Total volume of scrubber solution in liters (0.05 L)*

W = *Weight of original sample used in kg (0.01 kg)*

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 9030B for Sulfide Distillation, Method 9034 for Sulfide Titration.

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 500 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.

17.2.3. Note that bottles may be received with headspace. In addition, multiple tests may be analyzed from the same container resulting in headspace at the time of analysis.

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Implementation Date: 10/16/00

SOP No: NC-WC-0084
Revision No: 3
Revision Date: 10/03/00

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: [signature] 10/5/00
Technology Specialist Date

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Quality Assurance Manager Date

Approved by: [signature] 10-10-00
Environmental Health and Safety Coordinator Date

Approved by: [signature] 10/11/00
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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

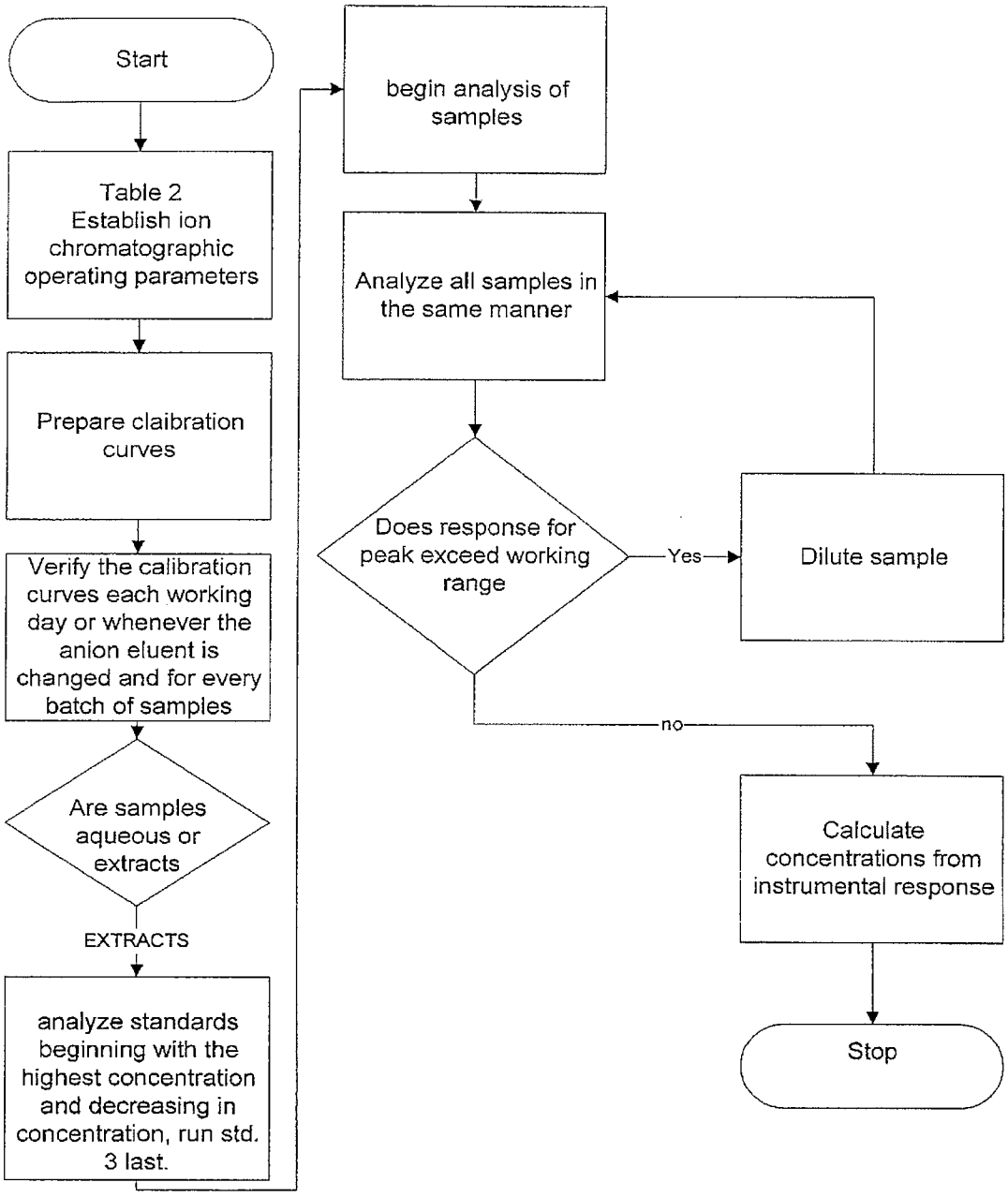
17.2. Table 1, Quality Control Samples

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)*

Analyte	Concentration (mg/L) 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

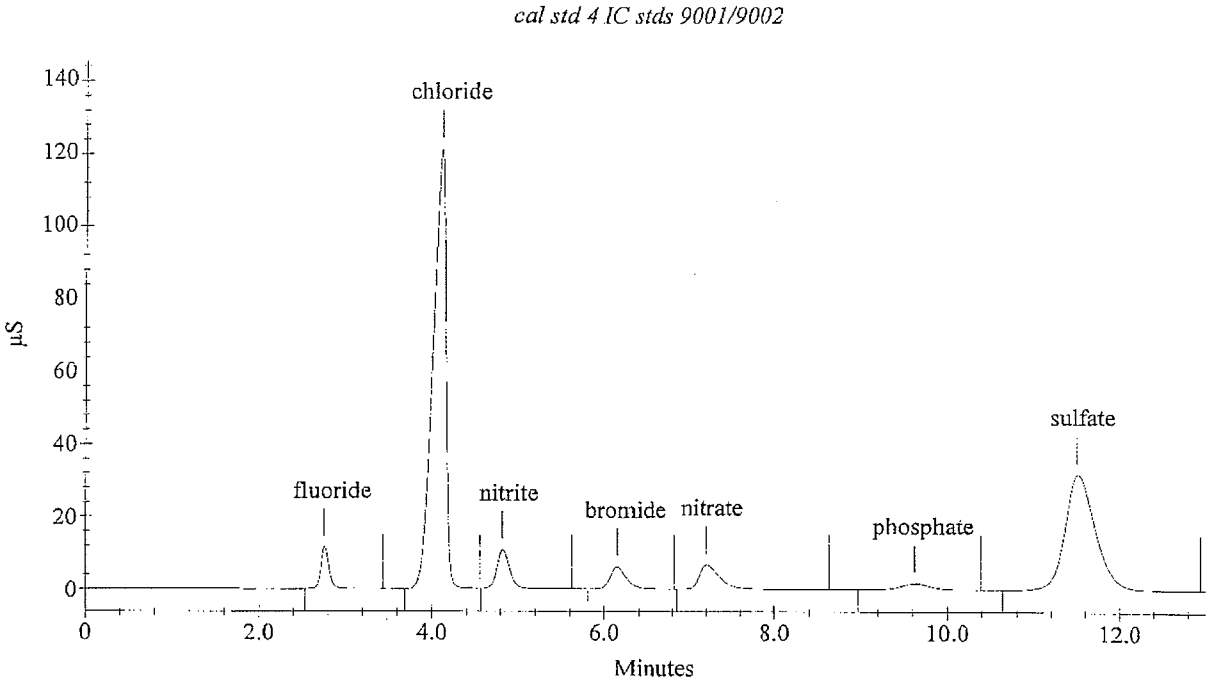


Figure #1

ATTACHMENT 3

LABORATORY REFERENCE DATA

STL Reference Data Summary

Structured Analysis Code: I-25-QK-72-01

Target Analyte List: NC: OLM03.1/4.2 Volatile List

Matrix: WATER
Extraction: PURGE AND TRAP - 25 mL purge (Waters)
Method: Volatile Organics, GC/MS (8260B)
QC Program: MICHIGAN CRA
Location: STL North Canton

Target List 4121			Detection Limits				Check List 1630							Spike List 1631						
Syn	Compound	RL	Units	MDL	Units	Run Date	T	A	Amt	Units	LCL	UCL	RPD	T	A	Amt	Units	LCL	UCL	RPD
11	Acetone	25	ug/L	1.1	ug/L	20020313		Y	20	ug/L	22	200	95		Y	20	ug/L	45	128	30
196	Benzene	1	ug/L	0.37	ug/L	20020313	C	Y	20	ug/L	80	116	20	C	Y	20	ug/L	78	118	20
323	Bromodichloromethane	1	ug/L	0.32	ug/L	20020313		Y	20	ug/L	87	130	30		Y	20	ug/L	80	146	30
340	Bromoform	1	ug/L	0.37	ug/L	20020205		Y	20	ug/L	76	150	30		Y	20	ug/L	58	176	30
343	Bromomethane	1	ug/L	0.3	ug/L	20020211		Y	20	ug/L	64	129	30		Y	20	ug/L	55	145	30
372	2-Butanone	25	ug/L	0.59	ug/L	20020313		Y	20	ug/L	28	237	65		Y	20	ug/L	71	123	30
459	Carbon disulfide	5	ug/L	0.24	ug/L	20020313		Y	20	ug/L	73	139	30		Y	20	ug/L	69	138	41
463	Carbon tetrachloride	1	ug/L	0.37	ug/L	20020313		Y	20	ug/L	75	149	30		Y	20	ug/L	63	176	30
521	Chlorobenzene	1	ug/L	0.38	ug/L	20020313	C	Y	20	ug/L	76	117	20	C	Y	20	ug/L	76	117	20
535	Dibromochloromethane	1	ug/L	0.37	ug/L	20020313		Y	20	ug/L	81	138	30		Y	20	ug/L	71	158	30
550	Chloroethane	1	ug/L	0.29	ug/L	20020205		Y	20	ug/L	66	126	30		Y	20	ug/L	59	142	30
569	Chloroform	1	ug/L	0.35	ug/L	20020313		Y	20	ug/L	84	128	30		Y	20	ug/L	83	141	30
574	Chloromethane	1	ug/L	0.49	ug/L	20020313		Y	20	ug/L	48	123	30		Y	20	ug/L	40	137	39
669	Cyclohexane	1	ug/L	0.33	ug/L	20020205														
539	1,2-Dibromo-3-chloropropane	1	ug/L	0.82	ug/L	20020313														
870	1,2-Dibromoethane	1	ug/L	0.34	ug/L	20020313														
904	1,2-Dichlorobenzene	1	ug/L	0.38	ug/L	20020313														
907	1,3-Dichlorobenzene	1	ug/L	0.38	ug/L	20020313														
910	1,4-Dichlorobenzene	1	ug/L	0.38	ug/L	20020313														
924	Dichlorodifluoromethane	1	ug/L	0.49	ug/L	20020205														
933	1,1-Dichloroethane	1	ug/L	0.3	ug/L	20020313		Y	20	ug/L	86	123	30		Y	20	ug/L	88	127	30
936	1,2-Dichloroethane	1	ug/L	0.28	ug/L	20020313		Y	20	ug/L	79	136	30		Y	20	ug/L	71	160	30
948	cis-1,2-Dichloroethene	1	ug/L	0.35	ug/L	20020313		Y	20	ug/L	85	113	30		Y	20	ug/L	87	114	30
950	trans-1,2-Dichloroethene	1	ug/L	0.33	ug/L	20020313		Y	20	ug/L	79	120	30		Y	20	ug/L	85	116	30
943	1,1-Dichloroethene	1	ug/L	0.31	ug/L	20020313	C	Y	20	ug/L	63	130	20	C	Y	20	ug/L	62	130	20
986	1,2-Dichloropropane	1	ug/L	0.41	ug/L	20020313		Y	20	ug/L	82	115	30		Y	20	ug/L	87	114	30
998	cis-1,3-Dichloropropene	1	ug/L	0.35	ug/L	20020313		Y	20	ug/L	84	130	30		Y	20	ug/L	82	130	30
1000	trans-1,3-Dichloropropene	1	ug/L	0.35	ug/L	20020313		Y	20	ug/L	84	130	30		Y	20	ug/L	73	147	30
1332	Ethylbenzene	1	ug/L	0.41	ug/L	20020313		Y	20	ug/L	86	116	30		Y	20	ug/L	86	132	30
1515	2-Hexanone	50	ug/L	0.58	ug/L	20020313		Y	20	ug/L	35	200	52		Y	20	ug/L	81	128	30
1578	Isopropylbenzene	5	ug/L	0.39	ug/L	20020313														
1774	Methyl acetate	10	ug/L	0.54	ug/L	20020313														
1799	Methylcyclohexane	1	ug/L	0.42	ug/L	20020313														
1811	Methylene chloride	5	ug/L	0.29	ug/L	20020313		Y	20	ug/L	78	118	30		Y	20	ug/L	82	115	30
1845	4-Methyl-2-pentanone	50	ug/L	0.26	ug/L	20020104		Y	20	ug/L	78	141	32		Y	20	ug/L	82	135	30
2772	Methyl tert-butyl ether	5	ug/L	0.27	ug/L	20020313														

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Structured Analysis Code: I-25-QK-72-01

Target Analyte List: NC: OLM03.1/4.2 Volatile List

Matrix: WATER
Extraction: PURGE AND TRAP - 25 mL purge (Waters)
Method: Volatile Organics, GC/MS (8260B)
QC Program: MICHIGAN CRA
Location: STL North Canton

	Target List 4121		Detection Limits				Check List 1630							Spike List 1631						
Syn	Compound	RL	Units	MDL	Units	Run Date	T	A	Amt	Units	LCL	UCL	RPD	T	A	Amt	Units	LCL	UCL	RPD
2355	Styrene	1	ug/L	0.35	ug/L	20020313		Y	20	ug/L	85	117	30		Y	20	ug/L	83	120	30
2439	1,1,2,2-Tetrachloroethane	1	ug/L	0.36	ug/L	20020313		Y	20	ug/L	85	118	30		Y	20	ug/L	88	116	30
2445	Tetrachloroethene	1	ug/L	0.42	ug/L	20020313		Y	20	ug/L	88	113	30		Y	20	ug/L	85	121	30
2489	Toluene	1	ug/L	0.39	ug/L	20020313	C	Y	20	ug/L	74	119	20	C	Y	20	ug/L	70	119	20
2515	1,2,4-Trichlorobenzene	5	ug/L	0.4	ug/L	20020313														
2518	1,1,1-Trichloroethane	1	ug/L	0.39	ug/L	20020313		Y	20	ug/L	78	140	30		Y	20	ug/L	71	162	30
2522	1,1,2-Trichloroethane	1	ug/L	0.36	ug/L	20020313		Y	20	ug/L	83	122	30		Y	20	ug/L	86	129	30
2525	Trichloroethene	1	ug/L	0.42	ug/L	20020313	C	Y	20	ug/L	75	122	20	C	Y	20	ug/L	62	130	20
1428	Trichlorofluoromethane	1	ug/L	0.54	ug/L	20020313														
2566	1,1,2-Trichloro-1,2,2-trifluoroethane	1	ug/L	0.32	ug/L	20020313														
2613	Vinyl chloride	1	ug/L	0.36	ug/L	20020313		Y	20	ug/L	61	120	30		Y	20	ug/L	88	126	30
2627	Xylenes (total)	3	ug/L	0.44	ug/L	20020205		Y	60	ug/L	87	116	30		Y	60	ug/L	89	121	30
337	4-Bromofluorobenzene						X	Y	10	ug/L	74	116	0	X	Y	20	ug/L	74	116	0
2735	1,2-Dichloroethane-d4						X	Y	10	ug/L	61	128	0	X	Y	10	ug/L	61	128	0
2740	Toluene-d8						X	Y	10	ug/L	76	110	0	X	Y	10	ug/L	76	110	0
2863	Dibromofluoromethane						X	Y	10	ug/L	73	122	0	X	Y	10	ug/L	73	122	0

STL Reference Data Summary

Structured Analysis Code: I-88-DA-01-01

Target Analyte List: All Analytes

Matrix: WATER
Extraction: NO SAMPLE PREPARATION PERFORMED / DIRECT INJE
Method: Carbon, Total Organic "TOC" (415.1)
QC Program: STANDARD TEST SET
Location: STL North Canton

Analyte List			Detection Limits				Check List 1215							Spike List 1216						
Syn	Compound	RL	Units	MDL	Units	Run Date	T	A	Amt	Units	LCL	UCL	RPD	T	A	Amt	Units	LCL	UCL	RPD
470	Total Organic Carbon	1.0	mg/L	0.68	mg/L	20020204	C	Y			88	115	20	C	Y	25	mg/L	72	136	20

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STL Reference Data Summary

Structured Analysis Code: I-04-QO-01-01

Target Analyte List: Q: CLP ICP Metals TAL Standard List

Matrix: WATER
Extraction: METALS, TOTAL RECOVERABLE
Method: Inductively Coupled Plasma (6010B)
QC Program: STANDARD TEST SET
Location: STL North Canton

Target List 2600		Detection Limits					Check List 906							Spike List 907						
Syn	Compound	RL	Units	MDL	Units	Run Date	T	A	Amt	Units	LCL	UCL	RPD	T	A	Amt	Units	LCL	UCL	RPD
88	Aluminum	0.2	mg/L	0.057	mg/L	20020213		Y	2000	ug/L	80	120	20		Y	2000	ug/L	75	125	20
128	Antimony	0.06	mg/L	0.0034	mg/L	20020213		Y	500	ug/L	80	120	20		Y	500	ug/L	75	125	20
194	Barium	0.20	mg/L	0.00094	mg/L	20020209		Y	2000	ug/L	80	120	20		Y	2000	ug/L	75	125	20
222	Beryllium	0.005	mg/L	0.0006	mg/L	20020209		Y	50	ug/L	80	120	20		Y	50	ug/L	75	125	20
411	Cadmium	0.005	mg/L	0.00028	mg/L	20020213		Y	50	ug/L	80	120	20		Y	50	ug/L	75	125	20
413	Calcium	5.0	mg/L	0.059	mg/L	20020209		Y	50000	ug/L	80	120	20		Y	50000	ug/L	75	125	20
2952	Chromium	0.01	mg/L	0.0015	mg/L	20020213		Y	200	ug/L	80	120	20		Y	200	ug/L	75	125	20
637	Cobalt	0.05	mg/L	0.00074	mg/L	20020209		Y	500	ug/L	80	120	20		Y	500	ug/L	75	125	20
643	Copper	0.025	mg/L	0.0017	mg/L	20020209		Y	250	ug/L	80	120	20		Y	250	ug/L	75	125	20
1539	Iron	0.1	mg/L	0.042	mg/L	20020209		Y	1000	ug/L	77	127	20		Y	1000	ug/L	75	125	20
1618	Magnesium	5.0	mg/L	0.035	mg/L	20020209		Y	50000	ug/L	80	120	20		Y	50000	ug/L	75	125	20
1659	Manganese	0.015	mg/L	0.00068	mg/L	20020209		Y	500	ug/L	80	120	20		Y	500	ug/L	75	125	20
1956	Nickel	0.04	mg/L	0.0029	mg/L	20020213		Y	500	ug/L	80	120	20		Y	500	ug/L	75	125	20
2214	Potassium	5	mg/L	0.023	mg/L	20020209		Y	50000	ug/L	80	120	20		Y	50000	ug/L	75	125	20
2285	Silver	0.01	mg/L	0.00098	mg/L	20020209		Y	50	ug/L	80	120	20		Y	50	ug/L	75	125	20
2315	Sodium	5	mg/L	0.360	mg/L	20020213		Y	50000	ug/L	80	120	20		Y	50000	ug/L	75	125	20
2607	Vanadium	0.05	mg/L	0.00067	mg/L	20020209		Y	500	ug/L	80	120	20		Y	500	ug/L	75	125	20
2649	Zinc	0.02	mg/L	0.014	mg/L	20020209		Y	500	ug/L	80	120	20		Y	500	ug/L	75	125	20

STL Reference Data Summary

Structured Analysis Code: I-88-VC-01-01

Target Analyte List: All Analytes

Matrix: WATER
Extraction: NO SAMPLE PREPARATION PERFORMED / DIRECT INJE
Method: Alkalinity, Total (310.1)
QC Program: STANDARD TEST SET
Location: STL North Canton

Analyte List			Detection Limits				Check List 1306							Spike List 1307						
Syn	Compound	RL	Units	MDL	Units	Run Date	T	A	Amt	Units	LCL	UCL	RPD	T	A	Amt	Units	LCL	UCL	RPD
3041	Total Alkalinity	5	mg/L	1.3	mg/L	20020102	C	Y			90	127	20	C	Y	500	mg/L	10	160	24

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STL Reference Data Summary

Structured Analysis Code: I-88-AD-01-01

Target Analyte List: All Analytes

Matrix: WATER
Extraction: NO SAMPLE PREPARATION PERFORMED / DIRECT INJE
Method: Hardness, Total (130.2, titrimetric)
QC Program: STANDARD TEST SET
Location: STL North Canton

Analyte List		Detection Limits					Check List 1145							Spike List 1146						
Syn	Compound	RL	Units	MDL	Units	Run Date	T	A	Amt	Units	LCL	UCL	RPD	T	A	Amt	Units	LCL	UCL	RPD
1469	Hardness, as CaCO3	5	mg/L	2.1	mg/L	20020305	C	Y			84	116	20	C	Y	500	mg/L	10	176	23

STL Reference Data Summary

Structured Analysis Code: I-88-CX-01-01

Target Analyte List: All Analytes

Matrix: WATER
Extraction: NO SAMPLE PREPARATION PERFORMED / DIRECT INJE
Method: Chloride (300.0, Ion Chromatography)
QC Program: STANDARD TEST SET
Location: STL North Canton

Analyte List		Detection Limits					Check List 1045							Spike List 1046						
Syn	Compound	RL	Units	MDL	Units	Run Date	T	A	Amt	Units	LCL	UCL	RPD	T	A	Amt	Units	LCL	UCL	RPD
512	Chloride	1	mg/L	0.094	mg/L	20020124	C	Y	50	mg/L	90	110	20	C	Y	50	mg/L	90	110	20

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STL Reference Data Summary

Structured Analysis Code: I-88-C9-01-01

Target Analyte List: All Analytes

Matrix: WATER
Extraction: NO SAMPLE PREPARATION PERFORMED / DIRECT INJE
Method: Nitrate as N (300.0, Ion Chromatography)
QC Program: STANDARD TEST SET
Location: STL North Canton

Analyte List		Detection Limits					Check List 1045							Spike List 1046						
Syn	Compound	RL	Units	MDL	Units	Run Date	T	A	Amt	Units	LCL	UCL	RPD	T	A	Amt	Units	LCL	UCL	RPD
3744	Nitrate as N	0.1	mg/L	0.0076	mg/L	20020124	C	Y	2.5	mg/L	90	110	20	C	Y	2.5	mg/L	90	110	20

STL Reference Data Summary

Structured Analysis Code: I-88-GO-01-01

Target Analyte List: All Analytes

Matrix: WATER
Extraction: NO SAMPLE PREPARATION PERFORMED / DIRECT INJE
Method: Nitrite as N (300.0, Ion Chromatography)
QC Program: STANDARD TEST SET
Location: STL North Canton

Analyte List		Detection Limits					Check List 1045							Spike List 1046						
Syn	Compound	RL	Units	MDL	Units	Run Date	T	A	Amt	Units	LCL	UCL	RPD	T	A	Amt	Units	LCL	UCL	RPD
3746	Nitrite as N	0.1	mg/L	0.02	mg/L	20020124	C	Y	2.5	mg/L	88	110	20	C	Y	2.5	mg/L	90	110	20

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STL Reference Data Summary

Structured Analysis Code: I-88-CY-01-01

Target Analyte List: All Analytes

Matrix: WATER
Extraction: NO SAMPLE PREPARATION PERFORMED / DIRECT INJE
Method: Sulfate (300.0, Ion Chromatography)
QC Program: STANDARD TEST SET
Location: STL North Canton

Analyte List		Detection Limits					Check List 1045							Spike List 1046						
Syn	Compound	RL	Units	MDL	Units	Run Date	T	A	Amt	Units	LCL	UCL	RPD	T	A	Amt	Units	LCL	UCL	RPD
2363	Sulfate	1	mg/L	0.11	mg/L	20020124	C	Y	50	mg/L	90	110	20	C	Y	50	mg/L	90	110	20

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STL Reference Data Summary

Structured Analysis Code: I-88-CT-01-01

Target Analyte List: All Analytes

Matrix: WATER
Extraction: NO SAMPLE PREPARATION PERFORMED / DIRECT INJE
Method: Sulfide (376.1)
QC Program: STANDARD TEST SET
Location: STL North Canton

Analyte List			Detection Limits				Check List 1204							Spike List 1205						
Syn	Compound	RL	Units	MDL	Units	Run Date	T	A	Amt	Units	LCL	UCL	RPD	T	A	Amt	Units	LCL	UCL	RPD
2366	Total Sulfide	1	mg/L	0.25	mg/L	20020322	C	Y			79	104	20	C	Y	20	mg/L	75	107	20

STL Reference Data Summary

Structured Analysis Code: I-2X-MM-01-01

Target Analyte List: All Analytes

Matrix: WATER
Extraction: EXTRACTION, WATER/GAS (MANUAL) -> EQUILIBRATIO
Method: Dissolved Gases in Water - preserved
QC Program: STANDARD TEST SET
Location: STL North Canton

Analyte List		Detection Limits					Check List 961							Spike List 961						
Syn	Compound	RL	Units	MDL	Units	Run Date	T	A	Amt	Units	LCL	UCL	RPD	T	A	Amt	Units	LCL	UCL	RPD
3443	Acetylene	1	ug/L	0.39	ug/L	20020506	C	Y			70	130	30	C	Y			70	130	30
3377	Ethane	0.5	ug/L	0.3	ug/L	20020506	C	Y			70	130	30	C	Y			70	130	30
3386	Ethene	0.5	ug/L	0.29	ug/L	20020506	C	Y			70	130	30	C	Y			70	130	30
2841	Methane	0.5	ug/L	0.39	ug/L	20020506	C	Y			70	130	30	C	Y			70	130	30

STL Reference Data Summary

Structured Analysis Code: I-51-QL-72-01

Target Analyte List: NC: PAH (W/ METHYL NAPHTHALENENS) Standard List

Matrix: WATER
Extraction: LIQ/LIQ, CONT (Acids,Phenols) - Acid
Method: Base/Neutrals and Acids (8270C)
QC Program: MICHIGAN CRA
Location: STL North Canton

	Target List 4112		Detection Limits				Check List 1114							Spike List 1115						
Syn	Compound	RL	Units	MDL	Units	Run Date	T	A	Amt	Units	LCL	UCL	RPD	T	A	Amt	Units	LCL	UCL	RPD
1	Acenaphthene	5	ug/L	0.8	ug/L	20010424	C	Y	50	ug/L	39	118	35	C	Y	50	ug/L	26	118	35
5	Acenaphthylene	5	ug/L	0.71	ug/L	20010424		Y	50	ug/L	51	110	30		Y	50	ug/L	49	111	51
122	Anthracene	5	ug/L	0.68	ug/L	20010424		Y	50	ug/L	54	116	33		Y	50	ug/L	49	118	51
202	Benzo(a)anthracene	4	ug/L	0.7	ug/L	20010424		Y	50	ug/L	49	112	34		Y	50	ug/L	48	115	51
205	Benzo(b)fluoranthene	4	ug/L	0.94	ug/L	20010424		Y	50	ug/L	51	115	38		Y	50	ug/L	44	123	54
208	Benzo(k)fluoranthene	5	ug/L	0.84	ug/L	20010424		Y	50	ug/L	52	116	34		Y	50	ug/L	46	123	53
210	Benzo(ghi)perylene	5	ug/L	0.85	ug/L	20010424		Y	50	ug/L	47	118	35		Y	50	ug/L	44	122	55
211	Benzo(a)pyrene	4	ug/L	0.73	ug/L	20010424		Y	50	ug/L	50	116	34		Y	50	ug/L	44	122	51
633	Chrysene	5	ug/L	0.75	ug/L	20010424		Y	50	ug/L	49	118	34		Y	50	ug/L	49	118	52
860	Dibenz(a,h)anthracene	4	ug/L	0.79	ug/L	20010205		Y	50	ug/L	48	124	36		Y	50	ug/L	45	127	57
1414	Fluoranthene	5	ug/L	0.81	ug/L	20010424		Y	50	ug/L	54	118	33		Y	50	ug/L	49	122	53
1417	Fluorene	5	ug/L	1	ug/L	20010215		Y	50	ug/L	53	114	31		Y	50	ug/L	51	119	51
1535	Indeno(1,2,3-cd)pyrene	4	ug/L	0.63	ug/L	20010219		Y	50	ug/L	45	120	43		Y	50	ug/L	39	126	59
1829	2-Methylnaphthalene	5	ug/L	0.64	ug/L	20010424		Y	50	ug/L	52	110	32		Y	50	ug/L	45	119	51
2770	1-Methylnaphthalene	10	ug/L	0.71	ug/L	20010424														
1932	Naphthalene	5	ug/L	0.75	ug/L	20010424		Y	50	ug/L	49	112	35		Y	50	ug/L	50	176	52
2154	Phenanthrene	5	ug/L	0.82	ug/L	20010424		Y	50	ug/L	53	112	32		Y	50	ug/L	52	117	51
2252	Pyrene	5	ug/L	1.1	ug/L	20010424	C	Y	50	ug/L	46	130	31	C	Y	50	ug/L	27	138	31
1425	2-Fluorobiphenyl						X	Y	50	ug/L	30	110	0	X	Y	50	ug/L	30	110	0
1426	2-Fluorophenol						X	Y	75	ug/L	13	110	0	X	Y	75	ug/L	13	110	0
2512	2,4,6-Tribromophenol						X	Y	75	ug/L	21	122	0	X	Y	75	ug/L	21	122	0
2736	Nitrobenzene-d5						X	Y	50	ug/L	32	112	0	X	Y	50	ug/L	32	112	0
2737	Phenol-d5						X	Y	75	ug/L	10	113	0	X	Y	75	ug/L	10	113	0
2738	Terphenyl-d14						X	Y	50	ug/L	10	144	0	X	Y	50	ug/L	10	144	0

STL Reference Data Summary

Structured Analysis Code: A-4B-QK-72-01

Target Analyte List: NC: OLM03.1/4.2 Volatile List

Matrix: SOLID
Extraction: PURGE AND TRAP - Lab MEOH Ext. (Solids or Wastes)
Method: Volatile Organics, GC/MS (8260B)
QC Program: MICHIGAN CRA
Location: STL North Canton

	Target List 4121		Detection Limits				Check List 924							Spike List 925						
Syn	Compound	RL	Units	MDL	Units	Run Date	T	A	Amt	Units	LCL	UCL	RPD	T	A	Amt	Units	LCL	UCL	RPD
11	Acetone	750	ug/kg	48	ug/kg	20020213		Y	20	ug/kg	58	130	30		Y	50	ug/kg	10	200	66
196	Benzene	50	ug/kg	6.9	ug/kg	20020213	C	Y	20	ug/kg	75	129	20	C	Y	50	ug/kg	55	138	20
323	Bromodichloromethane	100	ug/kg	8.2	ug/kg	20020213		Y	20	ug/kg	72	125	30		Y	50	ug/kg	47	131	51
340	Bromoform	100	ug/kg	11	ug/kg	20020213		Y	20	ug/kg	43	149	30		Y	50	ug/kg	26	141	64
343	Bromomethane	250	ug/kg	42	ug/kg	20020213		Y	20	ug/kg	24	152	30		Y	50	ug/kg	15	152	72
372	2-Butanone	750	ug/kg	52	ug/kg	20020213		Y	20	ug/kg	27	200	46		Y	50	ug/kg	21	195	60
459	Carbon disulfide	250	ug/kg	4.5	ug/kg	20020213		Y	20	ug/kg	50	137	30		Y	50	ug/kg	27	149	73
463	Carbon tetrachloride	50	ug/kg	14	ug/kg	20020213		Y	20	ug/kg	57	137	30		Y	50	ug/kg	32	143	68
521	Chlorobenzene	50	ug/kg	5.8	ug/kg	20020213	C	Y	20	ug/kg	75	127	22	C	Y	50	ug/kg	49	139	22
535	Dibromochloromethane	50	ug/kg	11	ug/kg	20020213		Y	20	ug/kg	49	135	30		Y	50	ug/kg	44	135	61
550	Chloroethane	250	ug/kg	47	ug/kg	20020213		Y	20	ug/kg	31	144	30		Y	50	ug/kg	32	140	66
569	Chloroform	50	ug/kg	12	ug/kg	20020213		Y	40	ug/kg	73	115	30		Y	50	ug/kg	59	128	46
574	Chloromethane	250	ug/kg	14	ug/kg	20020213		Y	20	ug/kg	15	136	30		Y	50	ug/kg	28	130	81
669	Cyclohexane	1200	ug/kg	6.2	ug/kg	20020213														
539	1,2-Dibromo-3-chloropropane	250	ug/kg	23	ug/kg	20020214														
870	1,2-Dibromoethane	250	ug/kg	7.6	ug/kg	20020213														
904	1,2-Dichlorobenzene	100	ug/kg	6.9	ug/kg	20020213														
907	1,3-Dichlorobenzene	100	ug/kg	8.3	ug/kg	20020213														
910	1,4-Dichlorobenzene	100	ug/kg	8.6	ug/kg	20020213														
924	Dichlorodifluoromethane	100	ug/kg	23	ug/kg	20020213														
933	1,1-Dichloroethane	50	ug/kg	11	ug/kg	20020213		Y	20	ug/kg	77	119	30		Y	50	ug/kg	56	130	54
936	1,2-Dichloroethane	50	ug/kg	13	ug/kg	20020213		Y	20	ug/kg	78	121	30		Y	50	ug/kg	56	126	38
948	cis-1,2-Dichloroethene	50	ug/kg	7.8	ug/kg	20020213		Y	20	ug/kg	77	114	30		Y	50	ug/kg	48	127	52
950	trans-1,2-Dichloroethene	50	ug/kg	10	ug/kg	20020213		Y	20	ug/kg	68	117	30		Y	50	ug/kg	47	127	58
943	1,1-Dichloroethene	50	ug/kg	7.9	ug/kg	20020213	C	Y	20	ug/kg	55	142	27	C	Y	50	ug/kg	43	147	27
986	1,2-Dichloropropane	50	ug/kg	9.4	ug/kg	20020213		Y	20	ug/kg	78	116	30		Y	50	ug/kg	54	125	43
998	cis-1,3-Dichloropropene	50	ug/kg	7.7	ug/kg	20020213		Y	20	ug/kg	71	125	30		Y	50	ug/kg	30	138	49
1000	trans-1,3-Dichloropropene	50	ug/kg	5.3	ug/kg	20020213		Y	20	ug/kg	67	125	30		Y	50	ug/kg	34	134	57
1332	Ethylbenzene	50	ug/kg	6.5	ug/kg	20020213		Y	20	ug/kg	79	114	30		Y	50	ug/kg	36	133	72
1515	2-Hexanone	2500	ug/kg	16	ug/kg	20020213		Y	20	ug/kg	29	200	41		Y	50	ug/kg	20	190	70
1578	Isopropylbenzene	250	ug/kg	8.5	ug/kg	20020213														
1774	Methyl acetate	1200	ug/kg	24	ug/kg	20020213														
1799	Methylcyclohexane	1200	ug/kg	8.9	ug/kg	20020213														
1811	Methylene chloride	250	ug/kg	16	ug/kg	20020213		Y	20	ug/kg	58	130	30		Y	50	ug/kg	45	129	49
1845	4-Methyl-2-pentanone	2500	ug/kg	24	ug/kg	20020213		Y	20	ug/kg	68	142	60		Y	50	ug/kg	42	143	60
2772	Methyl tert-butyl ether	250	ug/kg	8.2	ug/kg	20020213														

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Structured Analysis Code: A-4B-QK-72-01

Target Analyte List: NC: OLM03.1/4.2 Volatile List

Matrix: SOLID
Extraction: PURGE AND TRAP - Lab MEOH Ext. (Solids or Wastes)
Method: Volatile Organics, GC/MS (8260B)
QC Program: MICHIGAN CRA
Location: STL North Canton

Target List 4121			Detection Limits				Check List 924							Spike List 925							
Syn	Compound	RL	Units	MDL	Units	Run Date	T	A	Amt	Units	LCL	UCL	RPD	T	A	Amt	Units	LCL	UCL	RPD
2355	Styrene	50	ug/kg	7.2	ug/kg	20020213		Y	20	ug/kg	80	114	30		Y	50	ug/kg	23	136	65
2439	1,1,2,2-Tetrachloroethane	100	ug/kg	10	ug/kg	20020213		Y	20	ug/kg	70	133	30		Y	50	ug/kg	33	162	90
2445	Tetrachloroethene	50	ug/kg	11	ug/kg	20020213		Y	20	ug/kg	72	120	30		Y	50	ug/kg	31	137	81
2489	Toluene	100	ug/kg	5.6	ug/kg	20020213	C	Y	20	ug/kg	71	130	24	C	Y	50	ug/kg	46	147	24
2515	1,2,4-Trichlorobenzene	250	ug/kg	11	ug/kg	20020213														
2518	1,1,1-Trichloroethane	50	ug/kg	8.9	ug/kg	20020213		Y	20	ug/kg	67	123	30		Y	50	ug/kg	48	132	57
2522	1,1,2-Trichloroethane	50	ug/kg	7.9	ug/kg	20020213		Y	20	ug/kg	82	116	30		Y	50	ug/kg	58	128	52
2525	Trichloroethene	50	ug/kg	8.7	ug/kg	20020213	C	Y	20	ug/kg	70	131	23	C	Y	50	ug/kg	46	143	23
1428	Trichlorofluoromethane	100	ug/kg	8.8	ug/kg	20020213														
2566	1,1,2-Trichloro-1,2,2-trifluoroethane	250	ug/kg	29	ug/kg	20020213														
2613	Vinyl chloride	100	ug/kg	11	ug/kg	20020213		Y	20	ug/kg	24	152	30		Y	50	ug/kg	30	136	80
2627	Xylenes (total)	150	ug/kg	19	ug/kg	20010223		Y	60	ug/kg	80	114	30		Y	150	ug/kg	33	135	78
337	4-Bromofluorobenzene						X	Y	50	ug/kg	47	158	0	X	Y	50	ug/kg	47	158	0
2735	1,2-Dichloroethane-d4						X	Y	50	ug/kg	61	130	0	X	Y	50	ug/kg	61	130	0
2740	Toluene-d8						X	Y	50	ug/kg	60	143	0	X	Y	50	ug/kg	60	143	0
2863	Dibromofluoromethane						X	Y	50	ug/kg	59	138	0	X	Y	50	ug/kg	59	138	0

STL Reference Data Summary

Structured Analysis Code: I-25-QK-72-01

Target Analyte List: NC: OLM03.1/4.2 Volatile List

Matrix: WATER
Extraction: PURGE AND TRAP - 25 mL purge (Waters)
Method: Volatile Organics, GC/MS (8260B)
QC Program: MICHIGAN CRA
Location: STL North Canton

	Target List 4121		Detection Limits				Check List 1630							Spike List 1631						
Syn	Compound	RL	Units	MDL	Units	Run Date	T	A	Amt	Units	LCL	UCL	RPD	T	A	Amt	Units	LCL	UCL	RPD
11	Acetone	25	ug/L	1.1	ug/L	20020313		Y	20	ug/L	22	200	95		Y	20	ug/L	45	128	30
196	Benzene	1	ug/L	0.37	ug/L	20020313	C	Y	20	ug/L	80	116	20	C	Y	20	ug/L	78	118	20
323	Bromodichloromethane	1	ug/L	0.32	ug/L	20020313		Y	20	ug/L	87	130	30		Y	20	ug/L	80	146	30
340	Bromoform	1	ug/L	0.37	ug/L	20020205		Y	20	ug/L	76	150	30		Y	20	ug/L	58	176	30
343	Bromomethane	1	ug/L	0.3	ug/L	20020211		Y	20	ug/L	64	129	30		Y	20	ug/L	55	145	30
372	2-Butanone	25	ug/L	0.59	ug/L	20020313		Y	20	ug/L	28	237	65		Y	20	ug/L	71	123	30
459	Carbon disulfide	5	ug/L	0.24	ug/L	20020313		Y	20	ug/L	73	139	30		Y	20	ug/L	69	138	41
463	Carbon tetrachloride	1	ug/L	0.37	ug/L	20020313		Y	20	ug/L	75	149	30		Y	20	ug/L	63	176	30
521	Chlorobenzene	1	ug/L	0.38	ug/L	20020313	C	Y	20	ug/L	76	117	20	C	Y	20	ug/L	76	117	20
535	Dibromochloromethane	1	ug/L	0.37	ug/L	20020313		Y	20	ug/L	81	138	30		Y	20	ug/L	71	158	30
550	Chloroethane	1	ug/L	0.29	ug/L	20020205		Y	20	ug/L	66	126	30		Y	20	ug/L	59	142	30
569	Chloroform	1	ug/L	0.35	ug/L	20020313		Y	20	ug/L	84	128	30		Y	20	ug/L	83	141	30
574	Chloromethane	1	ug/L	0.49	ug/L	20020313		Y	20	ug/L	48	123	30		Y	20	ug/L	40	137	39
669	Cyclohexane	1	ug/L	0.33	ug/L	20020205														
539	1,2-Dibromo-3-chloropropane	1	ug/L	0.82	ug/L	20020313														
870	1,2-Dibromoethane	1	ug/L	0.34	ug/L	20020313														
904	1,2-Dichlorobenzene	1	ug/L	0.38	ug/L	20020313														
907	1,3-Dichlorobenzene	1	ug/L	0.38	ug/L	20020313														
910	1,4-Dichlorobenzene	1	ug/L	0.38	ug/L	20020313														
924	Dichlorodifluoromethane	1	ug/L	0.49	ug/L	20020205														
933	1,1-Dichloroethane	1	ug/L	0.3	ug/L	20020313		Y	20	ug/L	86	123	30		Y	20	ug/L	88	127	30
936	1,2-Dichloroethane	1	ug/L	0.28	ug/L	20020313		Y	20	ug/L	79	136	30		Y	20	ug/L	71	160	30
948	cis-1,2-Dichloroethene	1	ug/L	0.35	ug/L	20020313		Y	20	ug/L	85	113	30		Y	20	ug/L	87	114	30
950	trans-1,2-Dichloroethene	1	ug/L	0.33	ug/L	20020313		Y	20	ug/L	79	120	30		Y	20	ug/L	85	116	30
943	1,1-Dichloroethene	1	ug/L	0.31	ug/L	20020313	C	Y	20	ug/L	63	130	20	C	Y	20	ug/L	62	130	20
986	1,2-Dichloropropane	1	ug/L	0.41	ug/L	20020313		Y	20	ug/L	82	115	30		Y	20	ug/L	87	114	30
998	cis-1,3-Dichloropropene	1	ug/L	0.35	ug/L	20020313		Y	20	ug/L	84	130	30		Y	20	ug/L	82	130	30
1000	trans-1,3-Dichloropropene	1	ug/L	0.35	ug/L	20020313		Y	20	ug/L	84	130	30		Y	20	ug/L	73	147	30
1332	Ethylbenzene	1	ug/L	0.41	ug/L	20020313		Y	20	ug/L	86	116	30		Y	20	ug/L	86	132	30
1515	2-Hexanone	50	ug/L	0.58	ug/L	20020313		Y	20	ug/L	35	200	52		Y	20	ug/L	81	128	30
1578	Isopropylbenzene	5	ug/L	0.39	ug/L	20020313														
1774	Methyl acetate	10	ug/L	0.54	ug/L	20020313														
1799	Methylcyclohexane	1	ug/L	0.42	ug/L	20020313														
1811	Methylene chloride	5	ug/L	0.29	ug/L	20020313		Y	20	ug/L	78	118	30		Y	20	ug/L	82	115	30
1845	4-Methyl-2-pentanone	50	ug/L	0.26	ug/L	20020104		Y	20	ug/L	78	141	32		Y	20	ug/L	82	135	30
2772	Methyl tert-butyl ether	5	ug/L	0.27	ug/L	20020313														

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Structured Analysis Code: I-25-QK-72-01

Target Analyte List: NC: OLM03.1/4.2 Volatile List

Matrix: WATER
Extraction: PURGE AND TRAP - 25 mL purge (Waters)
Method: Volatile Organics, GC/MS (8260B)
QC Program: MICHIGAN CRA
Location: STL North Canton

Target List 4121			Detection Limits			Check List 1630							Spike List 1631						
Syn	Compound	RL	Units	MDL	Units	Run Date	T	A	Amt	Units	LCL	UCL	RPD	T	A	Amt	Units	LCL	UCL	RPD
2355	Styrene	1	ug/L	0.35	ug/L	20020313		Y	20	ug/L	85	117	30		Y	20	ug/L	83	120	30
2439	1,1,2,2-Tetrachloroethane	1	ug/L	0.36	ug/L	20020313		Y	20	ug/L	85	118	30		Y	20	ug/L	88	116	30
2445	Tetrachloroethene	1	ug/L	0.42	ug/L	20020313		Y	20	ug/L	88	113	30		Y	20	ug/L	85	121	30
2489	Toluene	1	ug/L	0.39	ug/L	20020313	C	Y	20	ug/L	74	119	20	C	Y	20	ug/L	70	119	20
2515	1,2,4-Trichlorobenzene	5	ug/L	0.4	ug/L	20020313														
2518	1,1,1-Trichloroethane	1	ug/L	0.39	ug/L	20020313		Y	20	ug/L	78	140	30		Y	20	ug/L	71	162	30
2522	1,1,2-Trichloroethane	1	ug/L	0.36	ug/L	20020313		Y	20	ug/L	83	122	30		Y	20	ug/L	86	129	30
2525	Trichloroethene	1	ug/L	0.42	ug/L	20020313	C	Y	20	ug/L	75	122	20	C	Y	20	ug/L	62	130	20
1428	Trichlorofluoromethane	1	ug/L	0.54	ug/L	20020313														
2566	1,1,2-Trichloro-1,2,2-trifluoroethane	1	ug/L	0.32	ug/L	20020313														
2613	Vinyl chloride	1	ug/L	0.36	ug/L	20020313		Y	20	ug/L	61	120	30		Y	20	ug/L	88	126	30
2627	Xylenes (total)	3	ug/L	0.44	ug/L	20020205		Y	60	ug/L	87	116	30		Y	60	ug/L	89	121	30
337	4-Bromofluorobenzene						X	Y	10	ug/L	74	116	0	X	Y	20	ug/L	74	116	0
2735	1,2-Dichloroethane-d4						X	Y	10	ug/L	61	128	0	X	Y	10	ug/L	61	128	0
2740	Toluene-d8						X	Y	10	ug/L	76	110	0	X	Y	10	ug/L	76	110	0
2863	Dibromofluoromethane						X	Y	10	ug/L	73	122	0	X	Y	10	ug/L	73	122	0

STL Reference Data Summary

Structured Analysis Code: S-88-YN-01-13

Target Analyte List: All Analytes

Matrix: AIR
Extraction: NO SAMPLE PREPARATION PERFORMED / DIRECT INJE
Method: Volatile Organics by GC/MS (TO-14A Std.) ppb(v/v)
QC Program: STANDARD TEST SET
Location: STL City of Industry

Analyte List			Detection Limits				Check List 5700							Spike List 0						
Syn	Compound	RL	Units	MDL	Units	Run Date	T	A	Amt	Units	LCL	UCL	RPD	T	A	Amt	Units	LCL	UCL	RPD
3036	Acetaldehyde	4.0	ppb(v/v)	1.7	ppb(v/v)	20011108														
11	Acetone	10	ppb(v/v)	2.0	ppb(v/v)	20011108		Y			0	0	20							
20	Acetonitrile	4.0	ppb(v/v)	0.8	ppb(v/v)	20011108		Y			0	0	20							
39	Acrolein	4.0	ppb(v/v)	0.8	ppb(v/v)	20011108														
46	Acrylonitrile	10	ppb(v/v)	1.0	ppb(v/v)	20011108														
196	Benzene	2.0	ppb(v/v)	0.8	ppb(v/v)	20011108		Y			0	0	20							
220	Benzyl chloride	10	ppb(v/v)	0.8	ppb(v/v)	20011108		Y			0	0	20							
318	Bromobenzene	10	ppb(v/v)	3.0	ppb(v/v)	20011108														
3357	1-Bromo-2-chloroethane	2.0	ppb(v/v)	--	ppb(v/v)	20011108														
323	Bromodichloromethane	2.0	ppb(v/v)	0.8	ppb(v/v)	20011108		Y			0	0	20							
340	Bromoform	2.0	ppb(v/v)	0.5	ppb(v/v)	20011108		Y			0	0	20							
343	Bromomethane	2.0	ppb(v/v)	1.0	ppb(v/v)	20011108		Y			0	0	20							
355	1,3-Butadiene	4.0	ppb(v/v)	0.9	ppb(v/v)	20011108														
3271	2-Butanone (MEK)	10	ppb(v/v)	2.0	ppb(v/v)	20011108		Y			0	0	20							
1772	tert-Butyl alcohol	10	ppb(v/v)	0.5	ppb(v/v)	20011108														
393	n-Butylbenzene	2.0	ppb(v/v)	0.6	ppb(v/v)	20011108														
395	sec-Butylbenzene	2.0	ppb(v/v)	0.6	ppb(v/v)	20011108														
398	tert-Butylbenzene	2.0	ppb(v/v)	0.6	ppb(v/v)	20011108														
459	Carbon disulfide	10	ppb(v/v)	2.0	ppb(v/v)	20011108		Y			0	0	20							
463	Carbon tetrachloride	2.0	ppb(v/v)	0.5	ppb(v/v)	20011108		Y			0	0	20							
1323	Cellosolve acetate	20	ppb(v/v)	5.0	ppb(v/v)	20011108														
521	Chlorobenzene	2.0	ppb(v/v)	0.5	ppb(v/v)	20011108		Y			0	0	20							
535	Dibromochloromethane	2.0	ppb(v/v)	0.5	ppb(v/v)	20011108		Y			0	0	20							
2922	Chlorodifluoromethane	10	ppb(v/v)	--	ppb(v/v)	20011108														
550	Chloroethane	4.0	ppb(v/v)	0.8	ppb(v/v)	20011108		Y			0	0	20							
568	2-Chloroethyl vinyl ether	50	ppb(v/v)			0														
569	Chloroform	2.0	ppb(v/v)	0.8	ppb(v/v)	20011108		Y			0	0	20							
574	Chloromethane	4.0	ppb(v/v)	1.0	ppb(v/v)	20011108		Y			0	0	20							
606	Allyl chloride	4.0	ppb(v/v)	0.5	ppb(v/v)	20020214														
669	Cyclohexane	2.0	ppb(v/v)	0.5	ppb(v/v)	20011108														
676	Cyclohexanone	10	ppb(v/v)	2.0	ppb(v/v)	20011108														
539	1,2-Dibromo-3-chloropropane	5.0	ppb(v/v)	0.5	ppb(v/v)	20011108														
3261	1,2-Dibromoethane (EDB)	2.0	ppb(v/v)	0.5	ppb(v/v)	20011108		Y			0	0	20							
888	Dibromomethane	2.0	ppb(v/v)	0.5	ppb(v/v)	20011108														
904	1,2-Dichlorobenzene	2.0	ppb(v/v)	0.8	ppb(v/v)	20011108		Y			0	0	20							
907	1,3-Dichlorobenzene	2.0	ppb(v/v)	0.6	ppb(v/v)	20011108		Y			0	0	20							

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Structured Analysis Code: S-88-YN-01-13

Target Analyte List: All Analytes

Matrix: AIR
Extraction: NO SAMPLE PREPARATION PERFORMED / DIRECT INJE
Method: Volatile Organics by GC/MS (TO-14A Std.) ppb(v/v)
QC Program: STANDARD TEST SET
Location: STL City of Industry

Analyte List			Detection Limits				Check List 5700							Spike List 0						
Syn	Compound	RL	Units	MDL	Units	Run Date	T	A	Amt	Units	LCL	UCL	RPD	T	A	Amt	Units	LCL	UCL	RPD
910	1,4-Dichlorobenzene	2.0	ppb(v/v)	0.8	ppb(v/v)	20011108		Y			0	0	20							
924	Dichlorodifluoromethane	2.0	ppb(v/v)	0.5	ppb(v/v)	20011108		Y			0	0	20							
933	1,1-Dichloroethane	2.0	ppb(v/v)	0.5	ppb(v/v)	20011108		Y			0	0	20							
936	1,2-Dichloroethane	2.0	ppb(v/v)	0.8	ppb(v/v)	20011108		Y			0	0	20							
948	cis-1,2-Dichloroethene	2.0	ppb(v/v)	0.8	ppb(v/v)	20011108		Y			0	0	20							
950	trans-1,2-Dichloroethene	2.0	ppb(v/v)	0.5	ppb(v/v)	20011108		Y			0	0	20							
943	1,1-Dichloroethene	2.0	ppb(v/v)	0.5	ppb(v/v)	20011108	C	Y			70	125	20							
958	Dichlorofluoromethane	10	ppb(v/v)	--	ppb(v/v)	20011108														
986	1,2-Dichloropropane	2.0	ppb(v/v)	0.8	ppb(v/v)	20011108		Y			0	0	20							
989	1,3-Dichloropropane	10	ppb(v/v)	1.0	ppb(v/v)	20011108														
998	cis-1,3-Dichloropropene	2.0	ppb(v/v)	0.5	ppb(v/v)	20011108		Y			0	0	20							
1000	trans-1,3-Dichloropropene	2.0	ppb(v/v)	0.8	ppb(v/v)	20011108		Y			0	0	20							
1015	1,2-Dichloro-1,1,2,2-tetrafluoroethane	2.0	ppb(v/v)	0.8	ppb(v/v)	20011108		Y			0	0	20							
1585	Diisopropyl ether	2.0	ppb(v/v)	0.2	ppb(v/v)	20011108														
1199	1,4-Dioxane	10	ppb(v/v)	2.0	ppb(v/v)	20011108														
1290	Ethanol	25	ppb(v/v)	2.2	ppb(v/v)	20011108														
4370	Tert-amyl methyl ether	2.0	ppb(v/v)	0.2	ppb(v/v)	20011108														
4372	Tert-butyl ethyl ether	2.0	ppb(v/v)	0.2	ppb(v/v)	20011108														
1325	Ethyl acetate	4.0	ppb(v/v)	0.8	ppb(v/v)	20011108														
1332	Ethylbenzene	2.0	ppb(v/v)	0.5	ppb(v/v)	20011108		Y			0	0	20							
3790	4-Ethyltoluene	2.0	ppb(v/v)	0.7	ppb(v/v)	20011108		Y			0	0	20							
5098	1-Heptene	10	ppb(v/v)	2.0	ppb(v/v)	20011108														
1481	n-Heptane	2.0	ppb(v/v)	0.5	ppb(v/v)	20011108														
1489	Hexachlorobutadiene	4.0	ppb(v/v)	1.0	ppb(v/v)	20011108		Y			0	0	20							
1514	n-Hexane	2.0	ppb(v/v)	0.5	ppb(v/v)	20011108														
1515	2-Hexanone	10	ppb(v/v)	1.0	ppb(v/v)	20011108		Y			0	0	20							
4966	Isobutylene	20	ppb(v/v)	2.0	ppb(v/v)	20011108														
4969	Cumene	10	ppb(v/v)	--	ppb(v/v)	20011108														
1571	Isopropanol	10	ppb(v/v)	1.0	ppb(v/v)	20011108														
1719	Methanol	25	ppb(v/v)	2.9	ppb(v/v)	20011108														
1799	Methylcyclohexane	10	ppb(v/v)	--	ppb(v/v)	20011108														
1811	Methylene chloride	2.0	ppb(v/v)	0.8	ppb(v/v)	20011108	C	Y			75	120	20							
1823	Methyl methacrylate	2.0	ppb(v/v)	0.4	ppb(v/v)	20011108														
3283	4-Methyl-2-pentanone (MIBK)	10	ppb(v/v)	2.0	ppb(v/v)	20011108		Y			0	0	20							
3794	Methyl tert-butyl ether (MTBE)	2.0	ppb(v/v)	0.5	ppb(v/v)	20011108		Y			0	0	20							
1932	Naphthalene	50	ppb(v/v)	--	ppb(v/v)	20011108														
2748	n-Nonane	10	ppb(v/v)	--	ppb(v/v)	20011108														
2047	n-Octane	10	ppb(v/v)	--	ppb(v/v)	20011108														
2247	n-Propylbenzene	2.0	ppb(v/v)	0.6	ppb(v/v)	20011108														

Structured Analysis Code: S-88-YN-01-13

Target Analyte List: All Analytes

Matrix: AIR
Extraction: NO SAMPLE PREPARATION PERFORMED / DIRECT INJE
Method: Volatile Organics by GC/MS (TO-14A Std.) ppb(v/v)
QC Program: STANDARD TEST SET
Location: STL City of Industry

Analyte List			Detection Limits				Check List 5700							Spike List 0						
Syn	Compound	RL	Units	MDL	Units	Run Date	T	A	Amt	Units	LCL	UCL	RPD	T	A	Amt	Units	LCL	UCL	RPD
3448	Propylene	5.0	ppb(v/v)	0.8	ppb(v/v)	20011108														
2355	Styrene	2.0	ppb(v/v)	0.5	ppb(v/v)	20011108		Y			0	0	20							
4968	1,1,1,2-Tetrachloroethane	2.0	ppb(v/v)	0.5	ppb(v/v)	20011108														
2439	1,1,2,2-Tetrachloroethane	2.0	ppb(v/v)	0.5	ppb(v/v)	20011108	C	Y			70	130	20							
2445	Tetrachloroethene	2.0	ppb(v/v)	0.6	ppb(v/v)	20011108		Y			0	0	20							
2469	Tetrahydrofuran	5.0	ppb(v/v)	0.5	ppb(v/v)	20011108														
2489	Toluene	2.0	ppb(v/v)	0.5	ppb(v/v)	20011108	C	Y			70	120	20							
2909	TPH (as Gasoline)	100	ppb(v/v)	20	ppb(v/v)	20020612														
4734	Total Non-Methane Hydrocarbons as H	500	ppb(v/v)	100	ppb(v/v)	20011108														
2514	1,2,3-Trichlorobenzene	2.0	ppb(v/v)	0.5	ppb(v/v)	20020612														
2515	1,2,4-Trichlorobenzene	5.0	ppb(v/v)	0.6	ppb(v/v)	20011108		Y			0	0	20							
2518	1,1,1-Trichloroethane	2.0	ppb(v/v)	0.5	ppb(v/v)	20011108		Y			0	0	20							
2522	1,1,2-Trichloroethane	2.0	ppb(v/v)	0.6	ppb(v/v)	20011108		Y			0	0	20							
2525	Trichloroethene	2.0	ppb(v/v)	0.5	ppb(v/v)	20011108	C	Y			80	125	20							
1428	Trichlorofluoromethane	2.0	ppb(v/v)	0.5	ppb(v/v)	20011108		Y			0	0	20							
2563	1,2,3-Trichloropropane	2.0	ppb(v/v)	0.5	ppb(v/v)	20011108														
2566	1,1,2-Trichloro-1,2,2-trifluoroethane	2.0	ppb(v/v)	0.5	ppb(v/v)	20011108		Y			0	0	20							
5331	1,2,3-Trimethylbenzene	2.0	ppb(v/v)	0.5	ppb(v/v)	20011108														
2587	1,2,4-Trimethylbenzene	2.0	ppb(v/v)	0.5	ppb(v/v)	20011108		Y			0	0	20							
2592	1,3,5-Trimethylbenzene	2.0	ppb(v/v)	0.8	ppb(v/v)	20011108		Y			0	0	20							
1564	2,2,4-Trimethylpentane	2.0	ppb(v/v)	0.5	ppb(v/v)	20011108														
2610	Vinyl acetate	10	ppb(v/v)	2.0	ppb(v/v)	20011108		Y			0	0	20							
2613	Vinyl chloride	2.0	ppb(v/v)	0.8	ppb(v/v)	20011108		Y			0	0	20							
2940	m-Xylene & p-Xylene	2.0	ppb(v/v)	0.8	ppb(v/v)	20011108		Y			0	0	20							
2623	o-Xylene	2.0	ppb(v/v)	0.6	ppb(v/v)	20011108		Y			0	0	20							
2627	Xylenes (total)	2.0	ppb(v/v)	0.8	ppb(v/v)	20011108		Y			0	0	20							
337	4-Bromofluorobenzene						X	Y			70	130	0							
2735	1,2-Dichloroethane-d4						X	Y			70	130	0							
2740	Toluene-d8						X	Y			70	130	0							

STL Reference Data Summary

Structured Analysis Code: N-73-KJ-01-01

Target Analyte List: All Analytes

Matrix: WASTE
Extraction: PURGE AND TRAP, MeOH EXTRACTION (Solids or Waste
Method: Hydrocarbons, Volatile Petroleum (8015B)
QC Program: STANDARD TEST SET
Location: STL North Canton

Analyte List		Detection Limits					Check List 1600							Spike List 1601						
Syn	Compound	RL	Units	MDL	Units	Run Date	T	A	Amt	Units	LCL	UCL	RPD	T	A	Amt	Units	LCL	UCL	RPD
2909	TPH (as Gasoline)	10	mg/kg	17	ug/kg	20000209	C	Y			74	133	23	C	Y			10	114	49

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STL Reference Data Summary

Structured Analysis Code: N-14-KI-01-01

Target Analyte List: All Analytes

Matrix: WASTE
Extraction: WASTE DILUTION
Method: Hydrocarbons, Extractable Petroleum (8015B)
QC Program: STANDARD TEST SET
Location: STL North Canton

Analyte List		Detection Limits					Check List 1801							Spike List 1802						
Syn	Compound	RL	Units	MDL	Units	Run Date	T	A	Amt	Units	LCL	UCL	RPD	T	A	Amt	Units	LCL	UCL	RPD
3052	TPH (as Diesel)	3	mg/kg	1.3	mg/kg	19980213	C	Y	16.7	mg/kg	37	153	98	C	Y	16.7	mg/kg	70	130	50
2976	C9 (nonane)						X	Y	1.33	mg/kg	10	110	0	X	Y	1.33	mg/kg	10	110	0

STL Reference Data Summary

Structured Analysis Code: N-73-QK-01-01

Target Analyte List: NC: OLM03.1/4.2 Volatile List

Matrix: WASTE
Extraction: PURGE AND TRAP, MeOH EXTRACTION (Solids or Waste
Method: Volatile Organics, GC/MS (8260B)
QC Program: STANDARD TEST SET
Location: STL North Canton

Target List 4121			Detection Limits				Check List 924							Spike List 925						
Syn	Compound	RL	Units	MDL	Units	Run Date	T	A	Amt	Units	LCL	UCL	RPD	T	A	Amt	Units	LCL	UCL	RPD
11	Acetone	2500	ug/kg	48	ug/kg	20020213		Y			10	200	40		Y			10	200	66
196	Benzene	620	ug/kg	6.9	ug/kg	20020213	C	Y			75	129	20	C	Y			55	138	20
323	Bromodichloromethane	620	ug/kg	8.2	ug/kg	20020213		Y			79	128	30		Y			47	131	51
340	Bromoform	620	ug/kg	11	ug/kg	20020213		Y			64	135	30		Y			26	141	64
343	Bromomethane	1200	ug/kg	42	ug/kg	20020213		Y			10	167	30		Y			15	152	72
372	2-Butanone	2500	ug/kg	52	ug/kg	20020213		Y			29	190	43		Y			21	195	60
459	Carbon disulfide	620	ug/kg	4.5	ug/kg	20020213		Y			51	139	30		Y			27	149	73
463	Carbon tetrachloride	620	ug/kg	14	ug/kg	20020213		Y			69	127	30		Y			32	143	68
521	Chlorobenzene	620	ug/kg	5.8	ug/kg	20020213	C	Y			75	127	22	C	Y			49	139	22
535	Dibromochloromethane	620	ug/kg	11	ug/kg	20020213		Y			76	120	30		Y			44	135	61
550	Chloroethane	1200	ug/kg	47	ug/kg	20020213		Y			10	158	30		Y			32	140	66
569	Chloroform	620	ug/kg	12	ug/kg	20020213		Y			81	123	30		Y			59	128	46
574	Chloromethane	1200	ug/kg	14	ug/kg	20020213		Y			12	127	30		Y			28	130	81
669	Cyclohexane	2500	ug/kg	6.2	ug/kg	20020213														
539	1,2-Dibromo-3-chloropropane	1200	ug/kg	23	ug/kg	20020214														
870	1,2-Dibromoethane	620	ug/kg	7.6	ug/kg	20020213														
904	1,2-Dichlorobenzene	1200	ug/kg	6.9	ug/kg	20020213														
907	1,3-Dichlorobenzene	1200	ug/kg	8.3	ug/kg	20020213														
910	1,4-Dichlorobenzene	1200	ug/kg	8.6	ug/kg	20020213														
924	Dichlorodifluoromethane	1200	ug/kg	23	ug/kg	20020213														
933	1,1-Dichloroethane	620	ug/kg	11	ug/kg	20020213		Y			77	126	30		Y			56	130	54
936	1,2-Dichloroethane	620	ug/kg	13	ug/kg	20020213		Y			79	127	30		Y			56	126	38
948	cis-1,2-Dichloroethene	310	ug/kg	7.8	ug/kg	20020213		Y			78	121	30		Y			48	127	52
950	trans-1,2-Dichloroethene	310	ug/kg	10	ug/kg	20020213		Y			69	123	30		Y			47	127	58
943	1,1-Dichloroethene	620	ug/kg	7.9	ug/kg	20020213	C	Y			55	142	27	C	Y			43	147	27
986	1,2-Dichloropropane	620	ug/kg	13	ug/kg	20020213		Y			79	122	30		Y			54	125	43
998	cis-1,3-Dichloropropene	620	ug/kg	7.7	ug/kg	20020213		Y			79	126	30		Y			30	138	49
1000	trans-1,3-Dichloropropene	620	ug/kg	5.3	ug/kg	20020213		Y			78	118	30		Y			34	134	57
1332	Ethylbenzene	620	ug/kg	6.5	ug/kg	20020213		Y			86	110	30		Y			36	133	72
1515	2-Hexanone	2500	ug/kg	16	ug/kg	20020213		Y			56	155	31		Y			20	190	70
1578	Isopropylbenzene	1200	ug/kg	8.5	ug/kg	20020213														
1774	Methyl acetate	1200	ug/kg	24	ug/kg	20020213														
1799	Methylcyclohexane	620	ug/kg	8.92	ug/kg	20020213														
1811	Methylene chloride	620	ug/kg	16	ug/kg	20020213		Y			70	119	30		Y			45	129	49
1845	4-Methyl-2-pentanone	2500	ug/kg	24	ug/kg	20020213		Y			70	144	30		Y			42	143	60
2772	Methyl tert-butyl ether	2500	ug/kg	8.2	ug/kg	20020213														

Structured Analysis Code: N-73-QK-01-01

Target Analyte List: NC: OLM03.1/4.2 Volatile List

Matrix: WASTE
Extraction: PURGE AND TRAP, MeOH EXTRACTION (Solids or Waste
Method: Volatile Organics, GC/MS (8260B)
QC Program: STANDARD TEST SET
Location: STL North Canton

Target List 4121			Detection Limits				Check List 924							Spike List 925						
Syn	Compound	RL	Units	MDL	Units	Run Date	T	A	Amt	Units	LCL	UCL	RPD	T	A	Amt	Units	LCL	UCL	RPD
2355	Styrene	620	ug/kg	7.2	ug/kg	20020213		Y			86	113	30		Y			23	136	65
2439	1,1,2,2-Tetrachloroethane	620	ug/kg	10	ug/kg	20020213		Y			75	126	30		Y			33	162	90
2445	Tetrachloroethene	620	ug/kg	11	ug/kg	20020213		Y			76	113	30		Y			31	137	81
2489	Toluene	620	ug/kg	5.6	ug/kg	20020213	C	Y			71	130	24	C	Y			46	147	24
2515	1,2,4-Trichlorobenzene	1200	ug/kg	11	ug/kg	20020213														
2518	1,1,1-Trichloroethane	620	ug/kg	8.9	ug/kg	20020213		Y			73	125	30		Y			48	132	57
2522	1,1,2-Trichloroethane	620	ug/kg	7.9	ug/kg	20020213		Y			86	111	30		Y			58	128	52
2525	Trichloroethene	620	ug/kg	8.7	ug/kg	20020213	C	Y			70	131	23	C	Y			46	143	23
1428	Trichlorofluoromethane	1200	ug/kg	8.8	ug/kg	20020213														
2566	1,1,2-Trichloro-1,2,2-trifluoroethane	2500	ug/kg	29	ug/kg	20020213														
2613	Vinyl chloride	1200	ug/kg	18	ug/kg	20020213		Y			24	131	30		Y			30	136	80
2627	Xylenes (total)	620	ug/kg	49	ug/kg	20010223		Y			88	110	30		Y			33	135	78
337	4-Bromofluorobenzene						X	Y			47	158	0	X	Y	50	ug/kg	47	158	0
2735	1,2-Dichloroethane-d4						X	Y			61	130	0	X	Y			61	130	0
2740	Toluene-d8						X	Y			60	143	0	X	Y			60	143	0
2863	Dibromofluoromethane						X	Y			59	138	0	X	Y			59	138	0

STL Reference Data Summary

Structured Analysis Code: N-14-QL-01-01

Target Analyte List: NC: OLM03.1/4.2 Semivolatile List

Matrix: WASTE
Extraction: WASTE DILUTION
Method: Base/Neutrals and Acids (8270C)
QC Program: STANDARD TEST SET
Location: STL North Canton

Target List 4122			Detection Limits				Check List 1114							Spike List 1115						
Syn	Compound	RL	Units	MDL	Units	Run Date	T	A	Amt	Units	LCL	UCL	RPD	T	A	Amt	Units	LCL	UCL	RPD
1	Acenaphthene	330	ug/kg	14	ug/kg	20011231	C	Y	1700	ug/kg	44	108	44	C	Y	1700	ug/kg	13	133	44
5	Acenaphthylene	330	ug/kg	19	ug/kg	20011231		Y	1700	ug/kg	55	110	30		Y	1700	ug/kg	43	120	75
24	Acetophenone	330	ug/kg	20	ug/kg	20011231														
122	Anthracene	330	ug/kg	17	ug/kg	20011231		Y	1700	ug/kg	57	116	30		Y	1700	ug/kg	34	137	83
158	Atrazine	330	ug/kg	22	ug/kg	20011231														
3398	Benzaldehyde	330	ug/kg	14	ug/kg	20011231														
202	Benzo(a)anthracene	330	ug/kg	23	ug/kg	20011231		Y	1700	ug/kg	56	110	30		Y	1700	ug/kg	30	136	63
205	Benzo(b)fluoranthene	330	ug/kg	20	ug/kg	20011231		Y	1700	ug/kg	54	116	30		Y	1700	ug/kg	31	139	67
208	Benzo(k)fluoranthene	330	ug/kg	16	ug/kg	20011231		Y	1700	ug/kg	54	110	36		Y	1700	ug/kg	30	133	84
210	Benzo(ghi)perylene	330	ug/kg	16	ug/kg	20011231		Y	1700	ug/kg	48	124	31		Y	1700	ug/kg	23	142	89
211	Benzo(a)pyrene	330	ug/kg	15	ug/kg	20011231		Y	1700	ug/kg	56	115	30		Y	1700	ug/kg	28	142	86
3474	1,1'-Biphenyl	330	ug/kg	18	ug/kg	20011231														
289	bis(2-Chloroethoxy)methane	330	ug/kg	26	ug/kg	20011231		Y	1700	ug/kg	59	110	30		Y	1700	ug/kg	46	116	97
293	bis(2-Chloroethyl) ether	330	ug/kg	18	ug/kg	20011231		Y	1700	ug/kg	62	111	30		Y	1700	ug/kg	49	123	93
302	bis(2-Ethylhexyl) phthalate	330	ug/kg	13	ug/kg	20020115		Y	1700	ug/kg	53	115	30		Y	1700	ug/kg	36	131	54
348	4-Bromophenyl phenyl ether	330	ug/kg	15	ug/kg	20011231		Y	1700	ug/kg	58	110	30		Y	1700	ug/kg	47	121	95
403	Butyl benzyl phthalate	330	ug/kg	21	ug/kg	20011231		Y	1700	ug/kg	54	113	30		Y	1700	ug/kg	34	136	94
5101	Caprolactam	330	ug/kg	28	ug/kg	20011231														
2751	Carbazole	330	ug/kg	19	ug/kg	20011231		Y	1700	ug/kg	56	117	31		Y	1700	ug/kg	40	130	85
518	4-Chloroaniline	330	ug/kg	20	ug/kg	20011231		Y	1700	ug/kg	28	110	33		Y	1700	ug/kg	10	110	99
578	4-Chloro-3-methylphenol	330	ug/kg	19	ug/kg	20011231	C	Y	1700	ug/kg	43	110	55	C	Y	1700	ug/kg	17	128	55
589	2-Chloronaphthalene	330	ug/kg	17	ug/kg	20011231		Y	1700	ug/kg	52	116	30		Y	1700	ug/kg	43	125	75
600	2-Chlorophenol	330	ug/kg	18	ug/kg	20011231	C	Y	1700	ug/kg	43	110	54	C	Y	1700	ug/kg	17	116	54
602	4-Chlorophenyl phenyl ether	330	ug/kg	17	ug/kg	20011231		Y	1700	ug/kg	59	110	30		Y	1700	ug/kg	47	119	74
633	Chrysene	330	ug/kg	22	ug/kg	20011231		Y	1700	ug/kg	56	110	30		Y	1700	ug/kg	28	139	63
860	Dibenz(a,h)anthracene	330	ug/kg	18	ug/kg	20011231		Y	1700	ug/kg	50	129	33		Y	1700	ug/kg	31	142	99
863	Dibenzofuran	330	ug/kg	17	ug/kg	20011231		Y	1700	ug/kg	57	110	30		Y	1700	ug/kg	35	132	58
891	Di-n-butyl phthalate	330	ug/kg	23	ug/kg	20011231		Y	1700	ug/kg	58	114	30		Y	1700	ug/kg	44	128	74
918	3,3'-Dichlorobenzidine	1600	ug/kg	18	ug/kg	20011231		Y	1700	ug/kg	22	110	33		Y	1700	ug/kg	10	110	99
971	2,4-Dichlorophenol	330	ug/kg	16	ug/kg	20011231		Y	1700	ug/kg	60	111	30		Y	1700	ug/kg	45	122	85
1082	Diethyl phthalate	330	ug/kg	19	ug/kg	20011231		Y	1700	ug/kg	57	112	30		Y	1700	ug/kg	45	122	76
1145	2,4-Dimethylphenol	330	ug/kg	18	ug/kg	20011231		Y	1700	ug/kg	41	110	35		Y	1700	ug/kg	31	119	99
1149	Dimethyl phthalate	330	ug/kg	17	ug/kg	20011231		Y	1700	ug/kg	60	111	30		Y	1700	ug/kg	48	124	75
1167	4,6-Dinitro-2-methylphenol	1600	ug/kg	48	ug/kg	20020109		Y	1700	ug/kg	37	126	37		Y	1700	ug/kg	10	142	99
1187	2,4-Dinitrophenol	1600	ug/kg	47	ug/kg	20020109		Y	1700	ug/kg	15	131	53		Y	1700	ug/kg	10	149	99
1191	2,4-Dinitrotoluene	330	ug/kg	22	ug/kg	20011231	C	Y	1700	ug/kg	48	111	45	C	Y	1700	ug/kg	10	171	45

Structured Analysis Code: N-14-QL-01-01

Target Analyte List: NC: OLM03.1/4.2 Semivolatile List

Matrix: WASTE
Extraction: WASTE DILUTION
Method: Base/Neutrals and Acids (8270C)
QC Program: STANDARD TEST SET
Location: STL North Canton

Target List 4122			Detection Limits				Check List 1114							Spike List 1115						
Syn	Compound	RL	Units	MDL	Units	Run Date	T	A	Amt	Units	LCL	UCL	RPD	T	A	Amt	Units	LCL	UCL	RPD
1193	2,6-Dinitrotoluene	330	ug/kg	15	ug/kg	20011231		Y	1700	ug/kg	61	121	30		Y	1700	ug/kg	45	124	99
1162	Di-n-octyl phthalate	330	ug/kg	64	ug/kg	20011231		Y	1700	ug/kg	47	129	33		Y	1700	ug/kg	34	143	99
1414	Fluoranthene	330	ug/kg	16	ug/kg	20011231		Y	1700	ug/kg	57	118	30		Y	1700	ug/kg	25	150	92
1417	Fluorene	330	ug/kg	15	ug/kg	20011231		Y	1700	ug/kg	57	110	30		Y	1700	ug/kg	35	133	80
1482	Hexachlorobenzene	330	ug/kg	22	ug/kg	20011231		Y	1700	ug/kg	57	111	30		Y	1700	ug/kg	45	123	74
1489	Hexachlorobutadiene	330	ug/kg	16	ug/kg	20011231		Y	1700	ug/kg	56	113	30		Y	1700	ug/kg	43	126	86
1492	Hexachlorocyclopentadiene	1600	ug/kg	10	ug/kg	20011231		Y	1700	ug/kg	10	113	57		Y	1700	ug/kg	10	110	99
1497	Hexachloroethane	330	ug/kg	17	ug/kg	20011231		Y	1700	ug/kg	61	110	30		Y	1700	ug/kg	36	134	97
1535	Indeno(1,2,3-cd)pyrene	330	ug/kg	19	ug/kg	20011231		Y	1700	ug/kg	44	128	54		Y	1700	ug/kg	20	147	73
1566	Isophorone	330	ug/kg	22	ug/kg	20011231		Y	1700	ug/kg	58	110	30		Y	1700	ug/kg	45	116	95
1829	2-Methylnaphthalene	330	ug/kg	17	ug/kg	20011231		Y	1700	ug/kg	58	110	30		Y	1700	ug/kg	30	137	79
1851	2-Methylphenol	330	ug/kg	21	ug/kg	20011231		Y	1700	ug/kg	41	102	39		Y	1700	ug/kg	33	113	39
1857	4-Methylphenol	330	ug/kg	20	ug/kg	20011231		Y	1700	ug/kg	56	110	30		Y	1700	ug/kg	36	123	86
1932	Naphthalene	330	ug/kg	17	ug/kg	20011231		Y	1700	ug/kg	59	110	30		Y	1700	ug/kg	31	138	65
1960	2-Nitroaniline	1600	ug/kg	13	ug/kg	20011231		Y	1700	ug/kg	58	113	30		Y	1700	ug/kg	42	126	99
1964	3-Nitroaniline	1600	ug/kg	22	ug/kg	20011231		Y	1700	ug/kg	42	110	37		Y	1700	ug/kg	17	113	99
1968	4-Nitroaniline	1600	ug/kg	17	ug/kg	20020115		Y	1700	ug/kg	42	116	40		Y	1700	ug/kg	14	125	99
1972	Nitrobenzene	330	ug/kg	24	ug/kg	20011231		Y	1700	ug/kg	62	110	30		Y	1700	ug/kg	49	120	99
1998	2-Nitrophenol	330	ug/kg	21	ug/kg	20011231		Y	1700	ug/kg	55	118	30		Y	1700	ug/kg	44	125	99
2001	4-Nitrophenol	1600	ug/kg	53	ug/kg	20020109	C	Y	1700	ug/kg	22	128	64	C	Y	1700	ug/kg	10	148	64
2028	N-Nitrosodiphenylamine	330	ug/kg	19	ug/kg	20011231		Y	1700	ug/kg	58	113	30		Y	1700	ug/kg	37	135	94
2024	N-Nitrosodi-n-propylamine	330	ug/kg	15	ug/kg	20011231	C	Y	1700	ug/kg	38	110	50	C	Y	1700	ug/kg	12	128	50
3597	2,2'-oxybis(1-Chloropropane)			27	ug/kg	20011231														
2118	Pentachlorophenol	330	ug/kg	60	ug/kg	20020109	C	Y	1700	ug/kg	10	123	87	C	Y	1700	ug/kg	10	144	87
2154	Phenanthrene	330	ug/kg	21	ug/kg	20011231		Y	1700	ug/kg	56	110	30		Y	1700	ug/kg	24	145	81
2155	Phenol	330	ug/kg	18	ug/kg	20011231	C	Y	1700	ug/kg	35	110	50	C	Y	1700	ug/kg	10	148	50
2252	Pyrene	330	ug/kg	21	ug/kg	20011231	C	Y	1700	ug/kg	42	122	66	C	Y	1700	ug/kg	10	218	66
2555	2,4,5-Trichlorophenol	330	ug/kg	15	ug/kg	20011231		Y	1700	ug/kg	52	115	37		Y	1700	ug/kg	39	123	99
2559	2,4,6-Trichlorophenol	330	ug/kg	19	ug/kg	20011231		Y	1700	ug/kg	51	112	30		Y	1700	ug/kg	43	123	99
1425	2-Fluorobiphenyl						X	Y	1700	ug/kg	43	110	0	X	Y	1700	ug/kg	43	110	0
1426	2-Fluorophenol						X	Y	2500	ug/kg	11	116	0	X	Y	2500	ug/kg	11	116	0
2512	2,4,6-Tribromophenol						X	Y	2500	ug/kg	35	116	0	X	Y	2500	ug/kg	35	116	0
2736	Nitrobenzene-d5						X	Y	1700	ug/kg	42	110	0	X	Y	1700	ug/kg	42	110	0
2737	Phenol-d5						X	Y	2500	ug/kg	25	115	0	X	Y	2500	ug/kg	25	115	0
2738	Terphenyl-d14						X	Y	1700	ug/kg	37	137	0	X	Y	1700	ug/kg	37	137	0

STL Reference Data Summary

Structured Analysis Code: N-46-QO-01-01

Target Analyte List: Q: CLP ICP Metals TAL Standard List

Matrix: WASTE
Extraction: METALS, TOTAL - Soils
Method: Inductively Coupled Plasma (6010B)
QC Program: STANDARD TEST SET
Location: STL North Canton

Target List 2600			Detection Limits				Check List 906							Spike List 907						
Syn	Compound	RL	Units	MDL	Units	Run Date	T	A	Amt	Units	LCL	UCL	RPD	T	A	Amt	Units	LCL	UCL	RPD
88	Aluminum	20	mg/kg	4.8	mg/kg	20020213		Y	200	mg/kg	80	120	20		Y	200	mg/kg	75	125	20
128	Antimony	6	mg/kg	0.23	mg/kg	20020213		Y	50	mg/kg	80	120	20		Y	50	mg/kg	75	125	20
194	Barium	20	mg/kg	0.066	mg/kg	20020213		Y	200	mg/kg	80	120	20		Y	200	mg/kg	75	125	20
222	Beryllium	0.5	mg/kg	0.068	mg/kg	20020213		Y	5	mg/kg	80	120	20		Y	5	mg/kg	75	125	20
411	Cadmium	0.5	mg/kg	0.016	mg/kg	20020209		Y	5	mg/kg	80	120	20		Y	5	mg/kg	75	125	20
413	Calcium	500	mg/kg	11	mg/kg	20020213		Y	5000	mg/kg	80	120	20		Y	5000	mg/kg	75	125	20
2952	Chromium	1	mg/kg	0.13	mg/kg	20020209		Y	20	mg/kg	80	120	20		Y	20	mg/kg	75	125	20
637	Cobalt	5	mg/kg	0.053	mg/kg	20020213		Y	50	mg/kg	80	120	20		Y	50	mg/kg	75	125	20
643	Copper	2.5	mg/kg	0.14	mg/kg	20020209		Y	25	mg/kg	80	120	20		Y	25	mg/kg	75	125	20
1539	Iron	10	mg/kg	3.6	mg/kg	20020209		Y	100	mg/kg	73	137	20		Y	100	mg/kg	75	125	20
1618	Magnesium	500	mg/kg	2.2	mg/kg	20020213		Y	5000	mg/kg	80	120	20		Y	5000	mg/kg	75	125	20
1659	Manganese	1.5	mg/kg	0.071	mg/kg	20020213		Y	50	mg/kg	80	120	20		Y	50	mg/kg	75	125	20
1956	Nickel	4	mg/kg	0.15	mg/kg	20020213		Y	50	mg/kg	80	120	20		Y	50	mg/kg	75	125	20
2214	Potassium	500	mg/kg	2.1	mg/kg	20020209		Y	5000	mg/kg	80	120	20		Y	5000	mg/kg	75	125	20
2285	Silver	1	mg/kg	0.1	mg/kg	20020209		Y	5	mg/kg	80	120	20		Y	5	mg/kg	75	125	20
2315	Sodium	500	mg/kg	40	mg/kg	20020213		Y	5000	mg/kg	80	120	20		Y	5000	mg/kg	75	125	20
2607	Vanadium	5	mg/kg	0.069	mg/kg	20020213		Y	50	mg/kg	80	120	20		Y	50	mg/kg	75	125	20
2649	Zinc	2	mg/kg	1.5	mg/kg	20020213		Y	50	mg/kg	80	120	20		Y	50	mg/kg	75	125	20

STL Reference Data Summary

Structured Analysis Code: N-46-QM-01-01

Target Analyte List: Q: CLP Trace ICP Metals TAL Standard List

Matrix: WASTE
Extraction: METALS, TOTAL - Soils
Method: Inductively Coupled Plasma (6010B Trace)
QC Program: STANDARD TEST SET
Location: STL North Canton

Target List 2610		Detection Limits				Check List 906							Spike List 907						
Syn	Compound	RL	Units	MDL	Units	Run Date	T	A	Amt	Units	LCL	UCL	RPD	T	A	Amt	Units	LCL	UCL	RPD
140	Arsenic	1.0	mg/kg	0.28	mg/kg	20020213		Y	200	mg/kg	80	120	20		Y	200	mg/kg	75	125	20
1605	Lead	0.3	mg/kg	0.19	mg/kg	20020209		Y	50	mg/kg	80	120	20		Y	50	mg/kg	75	125	20
2281	Selenium	0.5	mg/kg	0.43	mg/kg	20020209		Y	200	mg/kg	80	120	20		Y	200	mg/kg	75	125	20
2477	Thallium	1.0	mg/kg	0.58	mg/kg	20020209		Y	200	mg/kg	80	120	20		Y	200	mg/kg	75	125	20

STL Reference Data Summary

Structured Analysis Code: N-70-O9-01-01

Target Analyte List: All Analytes

Matrix: WASTE
Extraction: METALS, TOTAL (Method Exclusive) - Solids
Method: Mercury (7471A, Cold Vapor) - Solids
QC Program: STANDARD TEST SET
Location: STL North Canton

Analyte List			Detection Limits				Check List 1021							Spike List 1026						
Syn	Compound	RL	Units	MDL	Units	Run Date	T	A	Amt	Units	LCL	UCL	RPD	T	A	Amt	Units	LCL	UCL	RPD
1701	Mercury	0.1	mg/kg	0.016	mg/kg	20020227		Y	.833333	mg/kg	52	127	20		Y	0.1666	mg/kg	10	209	20

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STL Reference Data Summary

Structured Analysis Code: A-4B-QK-72-01

Target Analyte List: NC: OLM03.1/4.2 Volatile List

Matrix: SOLID
Extraction: PURGE AND TRAP - Lab MEOH Ext. (Solids or Wastes)
Method: Volatile Organics, GC/MS (8260B)
QC Program: MICHIGAN CRA
Location: STL North Canton

Target List 4121			Detection Limits				Check List 924							Spike List 925						
Syn	Compound	RL	Units	MDL	Units	Run Date	T	A	Amt	Units	LCL	UCL	RPD	T	A	Amt	Units	LCL	UCL	RPD
11	Acetone	750	ug/kg	48	ug/kg	20020213		Y	20	ug/kg	58	130	30		Y	50	ug/kg	10	200	66
196	Benzene	50	ug/kg	6.9	ug/kg	20020213	C	Y	20	ug/kg	75	129	20	C	Y	50	ug/kg	55	138	20
323	Bromodichloromethane	100	ug/kg	8.2	ug/kg	20020213		Y	20	ug/kg	72	125	30		Y	50	ug/kg	47	131	51
340	Bromoform	100	ug/kg	11	ug/kg	20020213		Y	20	ug/kg	43	149	30		Y	50	ug/kg	26	141	64
343	Bromomethane	250	ug/kg	42	ug/kg	20020213		Y	20	ug/kg	24	152	30		Y	50	ug/kg	15	152	72
372	2-Butanone	750	ug/kg	52	ug/kg	20020213		Y	20	ug/kg	27	200	46		Y	50	ug/kg	21	195	60
459	Carbon disulfide	250	ug/kg	4.5	ug/kg	20020213		Y	20	ug/kg	50	137	30		Y	50	ug/kg	27	149	73
463	Carbon tetrachloride	50	ug/kg	14	ug/kg	20020213		Y	20	ug/kg	57	137	30		Y	50	ug/kg	32	143	68
521	Chlorobenzene	50	ug/kg	5.8	ug/kg	20020213	C	Y	20	ug/kg	75	127	22	C	Y	50	ug/kg	49	139	22
535	Dibromochloromethane	50	ug/kg	11	ug/kg	20020213		Y	20	ug/kg	49	135	30		Y	50	ug/kg	44	135	61
550	Chloroethane	250	ug/kg	47	ug/kg	20020213		Y	20	ug/kg	31	144	30		Y	50	ug/kg	32	140	66
569	Chloroform	50	ug/kg	12	ug/kg	20020213		Y	40	ug/kg	73	115	30		Y	50	ug/kg	59	128	46
574	Chloromethane	250	ug/kg	14	ug/kg	20020213		Y	20	ug/kg	15	136	30		Y	50	ug/kg	28	130	81
669	Cyclohexane	1200	ug/kg	6.2	ug/kg	20020213														
539	1,2-Dibromo-3-chloropropane	250	ug/kg	23	ug/kg	20020214														
870	1,2-Dibromoethane	250	ug/kg	7.6	ug/kg	20020213														
904	1,2-Dichlorobenzene	100	ug/kg	6.9	ug/kg	20020213														
907	1,3-Dichlorobenzene	100	ug/kg	8.3	ug/kg	20020213														
910	1,4-Dichlorobenzene	100	ug/kg	8.6	ug/kg	20020213														
924	Dichlorodifluoromethane	100	ug/kg	23	ug/kg	20020213														
933	1,1-Dichloroethane	50	ug/kg	11	ug/kg	20020213		Y	20	ug/kg	77	119	30		Y	50	ug/kg	56	130	54
936	1,2-Dichloroethane	50	ug/kg	13	ug/kg	20020213		Y	20	ug/kg	78	121	30		Y	50	ug/kg	56	126	38
948	cis-1,2-Dichloroethene	50	ug/kg	7.8	ug/kg	20020213		Y	20	ug/kg	77	114	30		Y	50	ug/kg	48	127	52
950	trans-1,2-Dichloroethene	50	ug/kg	10	ug/kg	20020213		Y	20	ug/kg	68	117	30		Y	50	ug/kg	47	127	58
943	1,1-Dichloroethene	50	ug/kg	7.9	ug/kg	20020213	C	Y	20	ug/kg	55	142	27	C	Y	50	ug/kg	43	147	27
986	1,2-Dichloropropane	50	ug/kg	9.4	ug/kg	20020213		Y	20	ug/kg	78	116	30		Y	50	ug/kg	54	125	43
998	cis-1,3-Dichloropropene	50	ug/kg	7.7	ug/kg	20020213		Y	20	ug/kg	71	125	30		Y	50	ug/kg	30	138	49
1000	trans-1,3-Dichloropropene	50	ug/kg	5.3	ug/kg	20020213		Y	20	ug/kg	67	125	30		Y	50	ug/kg	34	134	57
1332	Ethylbenzene	50	ug/kg	6.5	ug/kg	20020213		Y	20	ug/kg	79	114	30		Y	50	ug/kg	36	133	72
1515	2-Hexanone	2500	ug/kg	16	ug/kg	20020213		Y	20	ug/kg	29	200	41		Y	50	ug/kg	20	190	70
1578	Isopropylbenzene	250	ug/kg	8.5	ug/kg	20020213														
1774	Methyl acetate	1200	ug/kg	24	ug/kg	20020213														
1799	Methylcyclohexane	1200	ug/kg	8.9	ug/kg	20020213														
1811	Methylene chloride	250	ug/kg	16	ug/kg	20020213		Y	20	ug/kg	58	130	30		Y	50	ug/kg	45	129	49
1845	4-Methyl-2-pentanone	2500	ug/kg	24	ug/kg	20020213		Y	20	ug/kg	68	142	60		Y	50	ug/kg	42	143	60
2772	Methyl tert-butyl ether	250	ug/kg	8.2	ug/kg	20020213														

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Structured Analysis Code: A-4B-QK-72-01

Target Analyte List: NC: OLM03.1/4.2 Volatile List

Matrix: SOLID
Extraction: PURGE AND TRAP - Lab MEOH Ext. (Solids or Wastes)
Method: Volatile Organics, GC/MS (8260B)
QC Program: MICHIGAN CRA
Location: STL North Canton

Target List 4121			Detection Limits				Check List 924							Spike List 925						
Syn	Compound	RL	Units	MDL	Units	Run Date	T	A	Amt	Units	LCL	UCL	RPD	T	A	Amt	Units	LCL	UCL	RPD
2355	Styrene	50	ug/kg	7.2	ug/kg	20020213		Y	20	ug/kg	80	114	30		Y	50	ug/kg	23	136	65
2439	1,1,2,2-Tetrachloroethane	100	ug/kg	10	ug/kg	20020213		Y	20	ug/kg	70	133	30		Y	50	ug/kg	33	162	90
2445	Tetrachloroethene	50	ug/kg	11	ug/kg	20020213		Y	20	ug/kg	72	120	30		Y	50	ug/kg	31	137	81
2489	Toluene	100	ug/kg	5.6	ug/kg	20020213	C	Y	20	ug/kg	71	130	24	C	Y	50	ug/kg	46	147	24
2515	1,2,4-Trichlorobenzene	250	ug/kg	11	ug/kg	20020213														
2518	1,1,1-Trichloroethane	50	ug/kg	8.9	ug/kg	20020213		Y	20	ug/kg	67	123	30		Y	50	ug/kg	48	132	57
2522	1,1,2-Trichloroethane	50	ug/kg	7.9	ug/kg	20020213		Y	20	ug/kg	82	116	30		Y	50	ug/kg	58	128	52
2525	Trichloroethene	50	ug/kg	8.7	ug/kg	20020213	C	Y	20	ug/kg	70	131	23	C	Y	50	ug/kg	46	143	23
1428	Trichlorofluoromethane	100	ug/kg	8.8	ug/kg	20020213														
2566	1,1,2-Trichloro-1,2,2-trifluoroethane	250	ug/kg	29	ug/kg	20020213														
2613	Vinyl chloride	100	ug/kg	11	ug/kg	20020213		Y	20	ug/kg	24	152	30		Y	50	ug/kg	30	136	80
2627	Xylenes (total)	150	ug/kg	19	ug/kg	20010223		Y	60	ug/kg	80	114	30		Y	150	ug/kg	33	135	78
337	4-Bromofluorobenzene						X	Y	50	ug/kg	47	158	0	X	Y	50	ug/kg	47	158	0
2735	1,2-Dichloroethane-d4						X	Y	50	ug/kg	61	130	0	X	Y	50	ug/kg	61	130	0
2740	Toluene-d8						X	Y	50	ug/kg	60	143	0	X	Y	50	ug/kg	60	143	0
2863	Dibromofluoromethane						X	Y	50	ug/kg	59	138	0	X	Y	50	ug/kg	59	138	0

STL Reference Data Summary

Structured Analysis Code: A-58-QK-01-01

Target Analyte List: Q: TCLP MSVOA Standard List

Matrix: SOLID
Extraction: TCLP(1311-ZHE/filter) -> PURGE-AND-TRAP (Low Level)
Method: Volatile Organics, GC/MS (8260B)
QC Program: STANDARD TEST SET
Location: STL North Canton

Target List 2006		Detection Limits					Check List 924							Spike List 925						
Syn	Compound	RL	Units	MDL	Units	Run Date	T	A	Amt	Units	LCL	UCL	RPD	T	A	Amt	Units	LCL	UCL	RPD
196	Benzene	0.025	mg/L	0.25	ug/L	20020207	C	Y	20	ug/kg	75	129	20	C	Y	50	ug/kg	55	138	20
373	Methyl ethyl ketone	0.05	mg/L	1.4	ug/L	20020207														
463	Carbon tetrachloride	0.025	mg/L	0.47	ug/L	20020212		Y	20	ug/kg	57	137	30		Y	50	ug/kg	32	143	68
521	Chlorobenzene	0.025	mg/L	0.38	ug/L	20020207	C	Y	20	ug/kg	75	127	22	C	Y	50	ug/kg	49	139	22
569	Chloroform	0.025	mg/L	0.37	ug/L	20020207		Y	40	ug/kg	73	115	30		Y	50	ug/kg	59	128	46
936	1,2-Dichloroethane	0.025	mg/L	0.42	ug/L	20020207		Y	20	ug/kg	78	121	30		Y	50	ug/kg	56	126	38
946	1,1-Dichloroethylene	0.07	mg/L	0.52	ug/L	20020207														
2446	Tetrachloroethylene	0.07	mg/L	0.51	ug/L	20020207														
2526	Trichloroethylene	0.05	mg/L	0.63	ug/L	20020207														
2613	Vinyl chloride	0.050	mg/L	0.45	ug/L	20020207		Y	20	ug/kg	24	152	30		Y	50	ug/kg	30	136	80
337	4-Bromofluorobenzene						X	Y	50	ug/kg	47	158	0	X	Y	50	ug/kg	47	158	0
2735	1,2-Dichloroethane-d4						X	Y	50	ug/kg	61	130	0	X	Y	50	ug/kg	61	130	0
2740	Toluene-d8						X	Y	50	ug/kg	60	143	0	X	Y	50	ug/kg	60	143	0
2863	Dibromofluoromethane						X	Y	50	ug/kg	59	138	0	X	Y	50	ug/kg	59	138	0

STL Reference Data Summary

Structured Analysis Code: A-59-QL-01-01

Target Analyte List: Q: TCLP MSSemi Standard List

Matrix: SOLID
Extraction: TCLP(1311) -> LIQ/LIQ, CONT - Acid->Base
Method: Base/Neutrals and Acids (8270C)
QC Program: STANDARD TEST SET
Location: STL North Canton

Target List 2105			Detection Limits			Check List 1116							Spike List 1117						
Syn	Compound	RL	Units	MDL	Units	Run Date	T	A	Amt	Units	LCL	UCL	RPD	T	A	Amt	Units	LCL	UCL	RPD
2778	m-Cresol & p-Cresol	0.1	mg/L	0.02	mg/L	19991202	C	Y	0.4000	mg/L	46	109	32	C	Y	0.4000	mg/L	46	109	32
910	1,4-Dichlorobenzene	0.05	mg/L	0.00077	mg/L	20010424	C	Y	0.2000	mg/L	28	110	36	C	Y	0.2000	mg/L	18	110	36
1191	2,4-Dinitrotoluene	0.05	mg/L	0.00079	mg/L	20010424	C	Y	0.2000	mg/L	47	131	32	C	Y	0.2000	mg/L	31	131	32
1482	Hexachlorobenzene	0.05	mg/L	0.00074	mg/L	20010205	C	Y	0.2000	mg/L	57	128	22	C	Y	0.2000	mg/L	36	132	22
1489	Hexachlorobutadiene	0.05	mg/L	0.00073	mg/L	20010220	C	Y	0.2000	mg/L	36	116	32	C	Y	0.2000	mg/L	18	116	32
1497	Hexachloroethane	0.05	mg/L	0.00074	mg/L	20010424	C	Y	0.2000	mg/L	30	110	33	C	Y	0.2000	mg/L	18	110	33
1853	o-Cresol	0.05	mg/L	0.0011	mg/L	20010219	C	Y	0.2000	mg/L	33	115	31	C	Y	0.2000	mg/L	33	115	31
1972	Nitrobenzene	0.05	mg/L	0.00081	mg/L	20010424	C	Y	0.2000	mg/L	45	130	50	C	Y	0.2000	mg/L	19	211	59
2118	Pentachlorophenol	0.10	mg/L	0.0024	mg/L	20010329	C	Y	0.2000	mg/L	10	140	56	C	Y	0.2000	mg/L	10	140	56
2256	Pyridine	0.10	mg/L	0.0015	mg/L	20010219	C	Y	0.2000	mg/L	10	148	65	C	Y	0.2000	mg/L	10	148	65
2555	2,4,5-Trichlorophenol	0.25	mg/L	0.0012	mg/L	20010219	C	Y	0.2000	mg/L	41	125	22	C	Y	0.2000	mg/L	24	143	22
2559	2,4,6-Trichlorophenol	0.05	mg/L	0.0017	mg/L	20010219	C	Y	0.2000	mg/L	46	135	27	C	Y	0.2000	mg/L	36	135	27
1425	2-Fluorobiphenyl						X	Y			30	110	0	X	Y			30	110	0
1426	2-Fluorophenol						X	Y			13	110	0	X	Y			13	110	0
2512	2,4,6-Tribromophenol						X	Y			21	122	0	X	Y			21	122	0
2736	Nitrobenzene-d5						X	Y			32	112	0	X	Y			32	112	0
2737	Phenol-d5						X	Y			10	113	0	X	Y			10	113	0
2738	Terphenyl-d14						X	Y			10	144	0	X	Y			10	144	0

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STL Reference Data Summary

Structured Analysis Code: A-34-QO-01-01

Target Analyte List: Q: TCLP Metals ICP Standard List

Matrix: SOLID
Extraction: TCLP(1311) -> METALS, TOTAL
Method: Inductively Coupled Plasma (6010B)
QC Program: STANDARD TEST SET
Location: STL North Canton

Target List 2804		Detection Limits				Check List 1900							Spike List 1901						
Syn	Compound	RL	Units	MDL	Units	Run Date	T	A	Amt	Units	LCL	UCL	RPD	T	A	Amt	Units	LCL	UCL	RPD
140	Arsenic	0.5	mg/L	0.0021	mg/L	20020213		Y	2	mg/L	50	150	20		Y	5	mg/L	50	150	20
194	Barium	10	mg/L	0.00094	mg/L	20020209		Y	2	mg/L	50	150	20		Y	50	mg/L	50	150	20
411	Cadmium	0.1	mg/L	0.00028	mg/L	20020213		Y	.05	mg/L	50	150	20		Y	1	mg/L	50	150	20
2952	Chromium	0.5	mg/L	0.0015	mg/L	20020213		Y	.2	mg/L	50	150	20		Y	5	mg/L	50	150	20
1605	Lead	0.5	mg/L	0.0016	mg/L	20020209		Y	.5	mg/L	50	150	20		Y	5	mg/L	50	150	20
2281	Selenium	0.25	mg/L	0.0047	mg/L	20020209		Y	2	mg/L	50	150	20		Y	1	mg/L	50	150	20
2285	Silver	0.5	mg/L	0.00098	mg/L	20020209		Y	.05	mg/L	50	150	20		Y	1	mg/L	50	150	20

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STL Reference Data Summary

Structured Analysis Code: A-0M-O8-01-01

Target Analyte List: All Analytes

Matrix: SOLID
Extraction: TCLP(1311) -> METALS, TOTAL (Method exclusive)
Method: Mercury (7470A, Cold Vapor) - Liquid
QC Program: STANDARD TEST SET
Location: STL North Canton

Analyte List		Detection Limits					Check List 1900							Spike List 1901						
Syn	Compound	RL	Units	MDL	Units	Run Date	T	A	Amt	Units	LCL	UCL	RPD	T	A	Amt	Units	LCL	UCL	RPD
1701	Mercury	0.002	mg/L	0.087	ug/L	20020211		Y	5	ug/L	50	150	20		Y	5	ug/L	50	150	20

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STL Reference Data Summary

Structured Analysis Code: A-88-DZ-01-01

Target Analyte List: All Analytes

Matrix: SOLID
Extraction: NO SAMPLE PREPARATION PERFORMED / DIRECT INJE
Method: Corrosivity
QC Program: STANDARD TEST SET
Location: STL North Canton

Analyte List		Detection Limits					Check List 1111							Spike List 1111						
Syn	Compound	RL	Units	MDL	Units	Run Date	T	A	Amt	Units	LCL	UCL	RPD	T	A	Amt	Units	LCL	UCL	RPD
645	Corrosivity	-	No Units			0		Y			97	103	20		Y			97	103	20

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STL Reference Data Summary

Structured Analysis Code: A-88-AE-01-01

Target Analyte List: All Analytes

Matrix: SOLID
Extraction: NO SAMPLE PREPARATION PERFORMED / DIRECT INJE
Method: Flash Point (1010, Closed Cup)
QC Program: STANDARD TEST SET
Location: STL North Canton

Analyte List		Detection Limits				Check List 1111							Spike List 1111						
Syn	Compound	RL	Units	MDL	Units	Run Date	T	A	Amt	Units	LCL	UCL	RPD	T	A	Amt	Units	LCL	UCL	RPD
2673	Flashpoint		deg F			0		Y			75	125	20		Y			75	125	20

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STL Reference Data Summary

Structured Analysis Code: **A-08-GI-01-01**

Target Analyte List: All Analytes

Matrix: SOLID
Extraction: DISTILLATION, MACRO - Acid
Method: Cyanide, Reactive (SW7.3.3)
QC Program: STANDARD TEST SET
Location: STL North Canton

Analyte List		Detection Limits					Check List 1252							Spike List 1252						
Syn	Compound	RL	Units	MDL	Units	Run Date	T	A	Amt	Units	LCL	UCL	RPD	T	A	Amt	Units	LCL	UCL	RPD
666	Reactive Cyanide	200	mg/kg	71	mg/kg	20020122		Y			10	200	100		Y			10	200	100

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STL Reference Data Summary

Structured Analysis Code: A-08-GJ-01-01

Target Analyte List: All Analytes

Matrix: SOLID
Extraction: DISTILLATION, MACRO - Acid
Method: Sulfide, Reactive (SW7.3.4)
QC Program: STANDARD TEST SET
Location: STL North Canton

Analyte List		Detection Limits					Check List 1253							Spike List 1254					
Syn	Compound	RL	Units	MDL	Units	Run Date	T	A	Amt	Units	LCL	UCL	RPD	T	A	Amt	Units	LCL	UCL	RPD
2365	Reactive Sulfide	500	mg/kg	170	mg/kg	20020123		Y			10	200	100		Y			10	200	100

STL Reference Data Summary

Structured Analysis Code: A-88-SM-01-01

Target Analyte List: All Analytes

Matrix: SOLID
Extraction: NO SAMPLE PREPARATION PERFORMED / DIRECT INJE
Method: Solids, Percent (as TS - 160.3 MOD) - Solids
QC Program: STANDARD TEST SET
Location: STL North Canton

Analyte List		Detection Limits					Check List 1276							Spike List 1276						
Syn	Compound	RL	Units	MDL	Units	Run Date	T	A	Amt	Units	LCL	UCL	RPD	T	A	Amt	Units	LCL	UCL	RPD
3311	Percent Solids	10	%	10	%	20000620	C	Y			80	120	20	C	Y			80	120	20

STL Reference Data Summary

Structured Analysis Code: I-25-QK-72-01

Target Analyte List: NC: OLM03.1/4.2 Volatile List

Matrix: WATER
Extraction: PURGE AND TRAP - 25 mL purge (Waters)
Method: Volatile Organics, GC/MS (8260B)
QC Program: MICHIGAN CRA
Location: STL North Canton

	Target List 4121		Detection Limits				Check List 1630							Spike List 1631						
Syn	Compound	RL	Units	MDL	Units	Run Date	T	A	Amt	Units	LCL	UCL	RPD	T	A	Amt	Units	LCL	UCL	RPD
11	Acetone	25	ug/L	1.1	ug/L	20020313		Y	20	ug/L	22	200	95		Y	20	ug/L	45	128	30
196	Benzene	1	ug/L	0.37	ug/L	20020313	C	Y	20	ug/L	80	116	20	C	Y	20	ug/L	78	118	20
323	Bromodichloromethane	1	ug/L	0.32	ug/L	20020313		Y	20	ug/L	87	130	30		Y	20	ug/L	80	146	30
340	Bromoform	1	ug/L	0.37	ug/L	20020205		Y	20	ug/L	76	150	30		Y	20	ug/L	58	176	30
343	Bromomethane	1	ug/L	0.3	ug/L	20020211		Y	20	ug/L	64	129	30		Y	20	ug/L	55	145	30
372	2-Butanone	25	ug/L	0.59	ug/L	20020313		Y	20	ug/L	28	237	65		Y	20	ug/L	71	123	30
459	Carbon disulfide	5	ug/L	0.24	ug/L	20020313		Y	20	ug/L	73	139	30		Y	20	ug/L	69	138	41
463	Carbon tetrachloride	1	ug/L	0.37	ug/L	20020313		Y	20	ug/L	75	149	30		Y	20	ug/L	63	176	30
521	Chlorobenzene	1	ug/L	0.38	ug/L	20020313	C	Y	20	ug/L	76	117	20	C	Y	20	ug/L	76	117	20
535	Dibromochloromethane	1	ug/L	0.37	ug/L	20020313		Y	20	ug/L	81	138	30		Y	20	ug/L	71	158	30
550	Chloroethane	1	ug/L	0.29	ug/L	20020205		Y	20	ug/L	66	126	30		Y	20	ug/L	59	142	30
569	Chloroform	1	ug/L	0.35	ug/L	20020313		Y	20	ug/L	84	128	30		Y	20	ug/L	83	141	30
574	Chloromethane	1	ug/L	0.49	ug/L	20020313		Y	20	ug/L	48	123	30		Y	20	ug/L	40	137	39
669	Cyclohexane	1	ug/L	0.33	ug/L	20020205														
539	1,2-Dibromo-3-chloropropane	1	ug/L	0.82	ug/L	20020313														
870	1,2-Dibromoethane	1	ug/L	0.34	ug/L	20020313														
904	1,2-Dichlorobenzene	1	ug/L	0.38	ug/L	20020313														
907	1,3-Dichlorobenzene	1	ug/L	0.38	ug/L	20020313														
910	1,4-Dichlorobenzene	1	ug/L	0.38	ug/L	20020313														
924	Dichlorodifluoromethane	1	ug/L	0.49	ug/L	20020205														
933	1,1-Dichloroethane	1	ug/L	0.3	ug/L	20020313		Y	20	ug/L	86	123	30		Y	20	ug/L	88	127	30
936	1,2-Dichloroethane	1	ug/L	0.28	ug/L	20020313		Y	20	ug/L	79	136	30		Y	20	ug/L	71	160	30
948	cis-1,2-Dichloroethene	1	ug/L	0.35	ug/L	20020313		Y	20	ug/L	85	113	30		Y	20	ug/L	87	114	30
950	trans-1,2-Dichloroethene	1	ug/L	0.33	ug/L	20020313		Y	20	ug/L	79	120	30		Y	20	ug/L	85	116	30
943	1,1-Dichloroethene	1	ug/L	0.31	ug/L	20020313	C	Y	20	ug/L	63	130	20	C	Y	20	ug/L	62	130	20
986	1,2-Dichloropropane	1	ug/L	0.41	ug/L	20020313		Y	20	ug/L	82	115	30		Y	20	ug/L	87	114	30
998	cis-1,3-Dichloropropene	1	ug/L	0.35	ug/L	20020313		Y	20	ug/L	84	130	30		Y	20	ug/L	82	130	30
1000	trans-1,3-Dichloropropene	1	ug/L	0.35	ug/L	20020313		Y	20	ug/L	84	130	30		Y	20	ug/L	73	147	30
1332	Ethylbenzene	1	ug/L	0.41	ug/L	20020313		Y	20	ug/L	86	116	30		Y	20	ug/L	86	132	30
1515	2-Hexanone	50	ug/L	0.58	ug/L	20020313		Y	20	ug/L	35	200	52		Y	20	ug/L	81	128	30
1578	Isopropylbenzene	5	ug/L	0.39	ug/L	20020313														
1774	Methyl acetate	10	ug/L	0.54	ug/L	20020313														
1799	Methylcyclohexane	1	ug/L	0.42	ug/L	20020313														
1811	Methylene chloride	5	ug/L	0.29	ug/L	20020313		Y	20	ug/L	78	118	30		Y	20	ug/L	82	115	30
1845	4-Methyl-2-pentanone	50	ug/L	0.26	ug/L	20020104		Y	20	ug/L	78	141	32		Y	20	ug/L	82	135	30
2772	Methyl tert-butyl ether	5	ug/L	0.27	ug/L	20020313														

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Structured Analysis Code: I-25-QK-72-01

Target Analyte List: NC: OLM03.1/4.2 Volatile List

Matrix: WATER
Extraction: PURGE AND TRAP - 25 mL purge (Waters)
Method: Volatile Organics, GC/MS (8260B)
QC Program: MICHIGAN CRA
Location: STL North Canton

	Target List 4121		Detection Limits				Check List 1630							Spike List 1631						
Syn	Compound	RL	Units	MDL	Units	Run Date	T	A	Amt	Units	LCL	UCL	RPD	T	A	Amt	Units	LCL	UCL	RPD
2355	Styrene	1	ug/L	0.35	ug/L	20020313		Y	20	ug/L	85	117	30		Y	20	ug/L	83	120	30
2439	1,1,2,2-Tetrachloroethane	1	ug/L	0.36	ug/L	20020313		Y	20	ug/L	85	118	30		Y	20	ug/L	88	116	30
2445	Tetrachloroethene	1	ug/L	0.42	ug/L	20020313		Y	20	ug/L	88	113	30		Y	20	ug/L	85	121	30
2489	Toluene	1	ug/L	0.39	ug/L	20020313	C	Y	20	ug/L	74	119	20	C	Y	20	ug/L	70	119	20
2515	1,2,4-Trichlorobenzene	5	ug/L	0.4	ug/L	20020313														
2518	1,1,1-Trichloroethane	1	ug/L	0.39	ug/L	20020313		Y	20	ug/L	78	140	30		Y	20	ug/L	71	162	30
2522	1,1,2-Trichloroethane	1	ug/L	0.36	ug/L	20020313		Y	20	ug/L	83	122	30		Y	20	ug/L	86	129	30
2525	Trichloroethene	1	ug/L	0.42	ug/L	20020313	C	Y	20	ug/L	75	122	20	C	Y	20	ug/L	62	130	20
1428	Trichlorofluoromethane	1	ug/L	0.54	ug/L	20020313														
2566	1,1,2-Trichloro-1,2,2-trifluoroethane	1	ug/L	0.32	ug/L	20020313														
2613	Vinyl chloride	1	ug/L	0.36	ug/L	20020313		Y	20	ug/L	61	120	30		Y	20	ug/L	88	126	30
2627	Xylenes (total)	3	ug/L	0.44	ug/L	20020205		Y	60	ug/L	87	116	30		Y	60	ug/L	89	121	30
337	4-Bromofluorobenzene						X	Y	10	ug/L	74	116	0	X	Y	20	ug/L	74	116	0
2735	1,2-Dichloroethane-d4						X	Y	10	ug/L	61	128	0	X	Y	10	ug/L	61	128	0
2740	Toluene-d8						X	Y	10	ug/L	76	110	0	X	Y	10	ug/L	76	110	0
2863	Dibromofluoromethane						X	Y	10	ug/L	73	122	0	X	Y	10	ug/L	73	122	0

STL Reference Data Summary

Structured Analysis Code: I-58-QK-01-01

Target Analyte List: Q: TCLP MSVOA Standard List

Matrix: WATER
Extraction: TCLP(1311-ZHE/filter) -> PURGE-AND-TRAP (Low Level)
Method: Volatile Organics, GC/MS (8260B)
QC Program: STANDARD TEST SET
Location: STL North Canton

Target List 2006		Detection Limits					Check List 924							Spike List 925							
Syn	Compound	RL	Units	MDL	Units	Run Date	T	A	Amt	Units	LCL	UCL	RPD	T	A	Amt	Units	LCL	UCL	RPD
196	Benzene	0.025	mg/L	0.25	ug/L	20020207	C	Y	50	ug/L	79	116	20	C	Y	50	ug/L	73	123	11
373	Methyl ethyl ketone	0.05	mg/L	1.4	ug/L	20020207														
463	Carbon tetrachloride	0.025	mg/L	0.47	ug/L	20020212		Y	50	ug/L	81	126	30		Y	50	ug/L	80	125	30
521	Chlorobenzene	0.025	mg/L	0.38	ug/L	20020207	C	Y	50	ug/L	81	115	20	C	Y	50	ug/L	70	122	14
569	Chloroform	0.025	mg/L	0.37	ug/L	20020207		Y	50	ug/L	87	119	30		Y	50	ug/L	85	124	30
936	1,2-Dichloroethane	0.025	mg/L	0.42	ug/L	20020207		Y	50	ug/L	83	122	30		Y	50	ug/L	84	126	30
946	1,1-Dichloroethylene	0.07	mg/L	0.52	ug/L	20020207														
2446	Tetrachloroethylene	0.07	mg/L	0.51	ug/L	20020207														
2526	Trichloroethylene	0.05	mg/L	0.63	ug/L	20020207														
2613	Vinyl chloride	0.050	mg/L	0.45	ug/L	20020207		Y	50	ug/L	55	121	30		Y	50	ug/L	52	122	30
337	4-Bromofluorobenzene						X	Y	50	ug/L	80	114	0	X	Y	50	ug/L	80	114	0
2735	1,2-Dichloroethane-d4						X	Y	50	ug/L	77	120	0	X	Y	50	ug/L	77	120	0
2740	Toluene-d8						X	Y	50	ug/L	78	111	0	X	Y	50	ug/L	78	111	0
2863	Dibromofluoromethane						X	Y	50	ug/L	78	115	0	X	Y	50	ug/L	78	115	0

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STL Reference Data Summary

Structured Analysis Code: I-59-QL-01-01

Target Analyte List: Q: TCLP MSSemi Standard List

Matrix: WATER
Extraction: TCLP(1311) -> LIQ/LIQ, CONT - Acid->Base
Method: Base/Neutrals and Acids (8270C)
QC Program: STANDARD TEST SET
Location: STL North Canton

Target List 2105		Detection Limits					Check List 1116							Spike List 1117							
Syn	Compound	RL	Units	MDL	Units	Run Date	T	A	Amt	Units	LCL	UCL	RPD	T	A	Amt	Units	LCL	UCL	RPD
2778	m-Cresol & p-Cresol	0.10	mg/L	0.02	mg/L	19991202	C	Y	0.4000	mg/L	46	109	32	C	Y	0.4000	mg/L	46	109	32
910	1,4-Dichlorobenzene	0.050	mg/L	0.00077	mg/L	20010424	C	Y	0.2000	mg/L	28	110	36	C	Y	0.2000	mg/L	18	110	36
1191	2,4-Dinitrotoluene	0.050	mg/L	0.00079	mg/L	20010424	C	Y	0.2000	mg/L	47	131	32	C	Y	0.2000	mg/L	31	131	32
1482	Hexachlorobenzene	0.050	mg/L	0.00074	mg/L	20010205	C	Y	0.2000	mg/L	57	128	22	C	Y	0.2000	mg/L	36	132	22
1489	Hexachlorobutadiene	0.050	mg/L	0.00073	mg/L	20010220	C	Y	0.2000	mg/L	36	116	32	C	Y	0.2000	mg/L	18	116	32
1497	Hexachloroethane	0.050	mg/L	0.00074	mg/L	20010424	C	Y	0.2000	mg/L	30	110	33	C	Y	0.2000	mg/L	18	110	33
1853	o-Cresol	0.05	mg/L	0.0011	mg/L	20010219	C	Y	0.2000	mg/L	33	115	31	C	Y	0.2000	mg/L	33	115	31
1972	Nitrobenzene	0.050	mg/L	0.00081	mg/L	20010424	C	Y	0.2000	mg/L	45	130	50	C	Y	0.2000	mg/L	19	211	59
2118	Pentachlorophenol	0.10	mg/L	0.0024	mg/L	20010329	C	Y	0.2000	mg/L	10	140	56	C	Y	0.2000	mg/L	10	140	56
2256	Pyridine	0.10	mg/L	0.0015	mg/L	20010219	C	Y	0.2000	mg/L	10	148	65	C	Y	0.2000	mg/L	10	148	65
2555	2,4,5-Trichlorophenol	0.050	mg/L	0.0012	mg/L	20010219	C	Y	0.2000	mg/L	41	125	22	C	Y	0.2000	mg/L	24	143	22
2559	2,4,6-Trichlorophenol	0.050	mg/L	0.0017	mg/L	20010219	C	Y	0.2000	mg/L	46	135	27	C	Y	0.2000	mg/L	36	135	27
1425	2-Fluorobiphenyl						X	Y			30	110	0	X	Y			30	110	0
1426	2-Fluorophenol						X	Y			13	110	0	X	Y			13	110	0
2512	2,4,6-Tribromophenol						X	Y			21	122	0	X	Y			21	122	0
2736	Nitrobenzene-d5						X	Y			32	112	0	X	Y			32	112	0
2737	Phenol-d5						X	Y			10	113	0	X	Y			10	113	0
2738	Terphenyl-d14						X	Y			10	144	0	X	Y			10	144	0

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STL Reference Data Summary

Structured Analysis Code: I-34-QO-01-01

Target Analyte List: Q: TCLP Metals ICP Standard List

Matrix: WATER
Extraction: TCLP(1311) -> METALS, TOTAL
Method: Inductively Coupled Plasma (6010B)
QC Program: STANDARD TEST SET
Location: STL North Canton

Target List 2804		Detection Limits					Check List 1900							Spike List 1901						
Syn	Compound	RL	Units	MDL	Units	Run Date	T	A	Amt	Units	LCL	UCL	RPD	T	A	Amt	Units	LCL	UCL	RPD
140	Arsenic	0.5	mg/L	0.0021	mg/L	20020213		Y	2	mg/L	50	150	20		Y	5	mg/L	50	150	20
194	Barium	10	mg/L	0.00094	mg/L	20020209		Y	2	mg/L	50	150	20		Y	50	mg/L	50	150	20
411	Cadmium	0.1	mg/L	0.00028	mg/L	20020213		Y	.05	mg/L	50	150	20		Y	1	mg/L	50	150	20
2952	Chromium	0.5	mg/L	0.0015	mg/L	20020213		Y	.2	mg/L	50	150	20		Y	5	mg/L	50	150	20
1605	Lead	0.5	mg/L	0.0016	mg/L	20020209		Y	.5	mg/L	50	150	20		Y	5	mg/L	50	150	20
2281	Selenium	0.25	mg/L	0.0047	mg/L	20020209		Y	2	mg/L	50	150	20		Y	1	mg/L	50	150	20
2285	Silver	0.5	mg/L	0.00098	mg/L	20020209		Y	.05	mg/L	50	150	20		Y	1	mg/L	50	150	20

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STL Reference Data Summary

Structured Analysis Code: I-0M-O8-01-01

Target Analyte List: All Analytes

Matrix: WATER
Extraction: TCLP(1311) -> METALS, TOTAL (Method exclusive)
Method: Mercury (7470A, Cold Vapor) - Liquid
QC Program: STANDARD TEST SET
Location: STL North Canton

Analyte List		Detection Limits					Check List 1900							Spike List 1901						
Syn	Compound	RL	Units	MDL	Units	Run Date	T	A	Amt	Units	LCL	UCL	RPD	T	A	Amt	Units	LCL	UCL	RPD
1701	Mercury	0.002	mg/L	0.087	ug/L	20020211		Y	5	ug/L	50	150	20		Y	5	ug/L	50	150	20

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STL Reference Data Summary

Structured Analysis Code: I-88-EN-01-01

Target Analyte List: All Analytes

Matrix: WATER
Extraction: NO SAMPLE PREPARATION PERFORMED / DIRECT INJE
Method: Corrosivity (9045)
QC Program: STANDARD TEST SET
Location: STL North Canton

Analyte List			Detection Limits				Check List 1111							Spike List 1111						
Syn	Compound	RL	Units	MDL	Units	Run Date	T	A	Amt	Units	LCL	UCL	RPD	T	A	Amt	Units	LCL	UCL	RPD
645	Corrosivity	-	No Units			0		Y			97	103	20		Y			97	103	20

STL Reference Data Summary

Structured Analysis Code: I-88-AE-01-01

Target Analyte List: All Analytes

Matrix: WATER
Extraction: NO SAMPLE PREPARATION PERFORMED / DIRECT INJE
Method: Flash Point (1010, Closed Cup)
QC Program: STANDARD TEST SET
Location: STL North Canton

Analyte List		Detection Limits				Check List 1111							Spike List 1111						
Syn	Compound	RL	Units	MDL	Units	Run Date	T	A	Amt	Units	LCL	UCL	RPD	T	A	Amt	Units	LCL	UCL	RPD
2673	Flashpoint		deg F			0		Y			75	125	20		Y			75	125	20

STL Reference Data Summary

Structured Analysis Code: I-08-GI-01-01

Target Analyte List: All Analytes

Matrix: WATER
Extraction: DISTILLATION, MACRO - Acid
Method: Cyanide, Reactive (SW7.3.3)
QC Program: STANDARD TEST SET
Location: STL North Canton

Analyte List		Detection Limits					Check List 1252							Spike List 1252						
Syn	Compound	RL	Units	MDL	Units	Run Date	T	A	Amt	Units	LCL	UCL	RPD	T	A	Amt	Units	LCL	UCL	RPD
666	Reactive Cyanide	200	mg/kg	71	mg/kg	20020122		Y			10	200	100		Y			10	200	100

STL Reference Data Summary

Structured Analysis Code: I-08-GJ-01-01

Target Analyte List: All Analytes

Matrix: WATER
Extraction: DISTILLATION, MACRO - Acid
Method: Sulfide, Reactive (SW7.3.4)
QC Program: STANDARD TEST SET
Location: STL North Canton

Analyte List		Detection Limits					Check List 1253							Spike List 1254						
Syn	Compound	RL	Units	MDL	Units	Run Date	T	A	Amt	Units	LCL	UCL	RPD	T	A	Amt	Units	LCL	UCL	RPD
2365	Reactive Sulfide	500	mg/kg	170	mg/kg	20020123		Y			10	200	100		Y			10	200	100

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ATTACHMENT 4

FIELD AUDIT CHECKLIST

APPENDIX 4

FIELD AUDIT CHECKLIST

Briefing with Project Manager

SIGNATURE OF AUDITOR_____ DATE OF AUDIT _____

PROJECT MANAGER _____ PROJECT NO. _____

PROJECT LOCATION_____

TYPE OF INVESTIGATION _____
(authority, agency)

Yes ____ No ____ N/A ___ 1. Was a project plan prepared? If yes, what items are addressed in the Plan?

_____

_____

_____

Yes ____ No ____ N/A ___ 2. Were additional instructions given to project participants (i.e., changes in the project plan)? If yes, describe these changes.

_____

_____

_____

Yes ____ No ____ N/A ___ 3. Is there a written list of sampling locations and descriptions? If yes, describe where documents are.

_____

_____

_____

Yes ____ No ____ N/A ___ 4. Is there a map of sampling locations? If yes, where is the map.

_____

_____

_____

APPENDIX 4

FIELD AUDIT CHECKLIST

Field Observations

Yes ____ No ____ N/A ___ 1. Are the number, frequency and types of field measurements and observations taken as specified in the project plan or as directed by the project manager? If yes, where are they recorded?

_____

_____

_____

Yes ____ No ____ N/A ___ 2. Are samples collected in the types of containers specified for each type of analysis? If no, what kind of sample containers are used?

_____

_____

_____

Yes ____ No ____ N/A ___ 3. Are samples preserved as required? If no or N/A, explain.

_____

_____

_____

Yes ____ No ____ N/A ___ 4. Are the number, frequency and types of samples collected as specified in the project plan or as directed by the project manager? If no, explain why not.

_____

_____

_____

Yes ____ No ____ N/A ___ 5. Are samples packed for preservation when required (i.e., packed in ice, etc.)? If no or N/A, explain why.

_____

_____

_____

Yes ____ No ____ N/A ___ 6. Is sample custody maintained? How?

_____

APPENDIX 4

FIELD AUDIT CHECKLIST

Document Control

Yes ____ No ____ N/A ___ 1. Are samples identified with sample tags? If no, how are samples identified?

_____

_____

_____

Yes ____ No ____ N/A ___ 2. Are sample tags completed (e.g., station no., location, date, time, analyses, signatures on samples, type, preservatives, etc.)? If yes, describe types of information recorded.

_____

_____

_____

Yes ____ No ____ N/A ___ 3. Are samples collected listed on a chain-of-custody record? If yes, describe the type of chain-of-custody record used and what information is recorded.

_____

_____

_____

Yes ____ No ____ N/A ___ 4. If used, are sample tag numbers recorded on chain-of-custody documents?

_____

_____

_____

Yes ____ No ____ N/A ___ 5. Does information on sample tags and chain-of-custody records match?

_____

_____

_____

Yes ____ No ____ N/A ___ 6. Does the chain-of-custody record indicate the method of sample shipment?

_____

_____

Yes ____ No ____ N/A ___ 7. Is the chain-of-custody record included with the samples in the shipping container?

Yes ____ No ____ N/A ___ 8. If used, do the sample traffic reports agree with the sample tags?

Yes ____ No ____ N/A ___ 9. If used, are blank samples identified?

Yes ____ No ____ N/A ___ 10. If collected, are duplicate samples identified on sample tags and chain-of-custody records?

Yes ____ No ____ N/A ___ 11. If used, are spiked samples identified?

Yes ____ No ____ N/A ___ 12. Are logbooks signed by the individual who checked out the logbook from the project coordinator?

Yes ____ No ____ N/A ___ 13. Are logbooks dated upon receipt from the project coordinator?

Yes ____ No ____ N/A ___ 14. Are logbooks project-specific (by logbook or by page)?

Yes ____ No ____ N/A ___ 15. Are logbook entries dated and identified by the author?

Yes ____ No ____ N/A ___ 16. Are photographs documented in logbooks (e.g., time, date, description of subject, photographer, etc.)?

Yes ____ No ____ N/A ___ 17. If film from a self-developing camera is used, are photos matched with logbook documentation?

Yes ____ No ____ N/A ___ 18. Are sample tag numbers recorded? If yes, describe where they are recorded?

Yes ____ No ____ N/A ___ 19. Are calibration of pH meters, conductivity meters, etc., documented? If yes, describe where this is documented.

Yes ____ No ____ N/A ___ 20. Are amendments to the project plan documented? If yes, describe where the amendments are documented.

APPENDIX 4

FIELD AUDIT CHECKLIST

Debriefing with Project Manager

Yes _____ No _____ N/A ___ 1. Was a debriefing held with project manager and/or other participants?

_____

_____

_____

Yes _____ No _____ N/A ___ 2. Were any recommendations made to the project participants during the debriefing? If yes, list recommendations.

_____

_____

_____

_____

_____

_____

_____

_____

_____

_____

ATTACHMENT 5

LABORATORY AUDIT CHECKLIST

ATTACHMENT 5

LABORATORY AUDIT CHECKLIST

The attached laboratory audit checklist is designed for the completion of an on-site laboratory audit primarily in support of an ongoing Haley & Aldrich, Inc (Haley & Aldrich) project or Master Agreement. The checklist consists of a number of charts that will be used to audit the laboratory against the project Quality Assurance Project Plan (QAPP) standard operating procedures (SOP) and/or standard U.S. EPA Methods. Only those checklists that pertain to the project or program of interest shall be covered during the on-site laboratory audit.

The laboratory audit checklist covers the 13 sections detailed below:

1. General Laboratory Information
2. Personnel
3. laboratory Environmental/Facilities
4. equipment and Instrumentation
5. Field Sampling
6. Sample Receipt and Storage
7. Organic Analyses by Gas Chromatography (GC)
8. Organic Analyses by GC/Mass Spectrometry
9. Metals Analysis
10. Other Classical Analyses
11. Data Reduction, Review and Reporting
12. Performance and System Audits

The attached charts (CHARTS I – BB) contain lists on which the availability of written operating procedures is to be checked. These lists cover instrument maintenance and calibration, all aspects of sampling, and the quality control program of the laboratory. The laboratory should be asked to show supporting documents to the auditor(s) during the on-site inspection and to discuss them with the auditor(s).

These checklists are not a demand or request for written procedures (for example, a Quality Control Program) in a particular standard format. The key point is that the principal laboratory controls should be documented in a permanent way. Some procedures may be brief or may not include all of the items to be checked.

GENERAL LABORATORY INFORMATION

1. Laboratory Name: _____

2. Street Address: _____

_____

Mailing Address: _____

_____

3. Telephone No.: _____ FAX No: _____

4. Number of Employees: _____ Years in Operation: _____

5. Name of laboratory Director: _____

Name of Laboratory Project Manager: _____

Name of Quality Assurance (QA) Officer: _____

6. Project Details:

Project Number: _____ Project Name: _____

Laboratory analyses required for project:

Parameters	Matrices	Methods

Completed by: _____ _____ Date: _____

NAME TITLE

1.0. AUDIT CHECKLIST – GENERAL LABORATORY INFORMATION

CHART I

ITEM	YES	NO	COMMENT
Does the lab maintain a Quality Assurance Manual?	____	____	_____
Does the manual address the important elements of a QC program, including the following:			
a. Project Organization and Responsibility	____	____	_____
b. Organization Chart?	____	____	_____
c. Personnel Training/Certification?	____	____	_____
d. Facilities and Equipment?	____	____	_____
e. Quality Assurance Objectives?	____	____	_____
f. Sampling Procedures?	____	____	_____
g. Sample Custody?	____	____	_____
h. Sample Receiving and Disposal?	____	____	_____
i. Analytical Procedures?	____	____	_____
j. Calibration Procedures and Frequency	____	____	_____
k. Preventive Maintenance?	____	____	_____
l. Certification of Reagents and Standards?	____	____	_____
m. Internal Quality Control Checks?	____	____	_____
n. Data Reduction, Review and Reporting?	____	____	_____
o. Reliability of Data?	____	____	_____
p. Feedback and Corrective Action?	____	____	_____
q. Record keeping and Storage?	____	____	_____
r. Performance and System Audits?	____	____	_____
s. Quality Control Reports?	____	____	_____

1.0. AUDIT CHECKLIST - GENERAL LABORATORY INFORMATION

CHART I

ITEM	YES	NO	COMMENT
Is the manual available to all laboratory personnel?	____	____	_____
Is the manual updated regularly with appropriate document control procedures?	____	____	_____
Is line authority for all referenced responsibilities explained by inclusion in an organization chart(s)?	____	____	_____
Is the organizational structure appropriate to accomplish the project QA objectives?	____	____	_____
Are QA/QC responsibilities and reporting relationships clearly defined?	____	____	_____
Are all staff aware of QA/QC and its application?	____	____	_____
Is the QA Officer a full-time function?	____	____	_____
Does the QA Officer operate independently of the analyses?	____	____	_____
Does the QA Officer report directly to senior management?	____	____	_____
Are internal QA reviews conducted at least annually and recorded including any corrective action taken?	____	____	_____
QA Objectives and Criteria:			
a. Are the terms and definitions for precision, accuracy, comparability, representativeness and completeness properly used,	____	____	_____
b. Have the following been defined for each matrix and parameter:			
1) Level of QA effort (frequency of QC, etc.)?	____	____	_____
2) Accuracy (matrix spikes, surrogate spikes, reference samples, etc.)?	____	____	_____

1.0. AUDIT CHECKLIST - GENERAL LABORATORY INFORMATION

CHART I

ITEM		YES	NO	COMMENT
3)	Precision (replicate samples)?	____	___	_____
4)	Sensitivity or MDL?	____	___	_____
5)	Statistical reporting limits?	____	___	_____
c.	Are quantitation limits established for each analytical parameter?	____	___	_____
d.	Are field and lab analyses both covered?	____	___	_____
e.	If appropriate, are completeness objectives quantitatively stated?	____	___	_____
f.	Are representativeness and comparability appropriately addressed?	____	___	_____

Do SOPs include or refer to SOPs addressing in following areas:

a.	Interferences?	____	___	_____
b.	Safety Considerations?	____	___	_____
c,	Apparatus and Equipment?	____	___	_____
d.	Reagents and Supplies?	____	___	_____
e.	Sample Preservation and Storage?	____	___	_____
f.	Sample Preparation?	____	___	_____
g.	Instrumentation Calibration?	____	___	_____
h.	Quality Control Procedures?	____	___	_____
i.	Detailed Step-by-Step Procedures?	____	___	_____
j.	Sample Calculations?	____	___	_____
k.	Method Performance Criteria? (accuracy and precision)	____	___	_____

Are there SOPs for:

a.	Sample collection, preservation, reception storage and handling?	____	___	_____

1.0. AUDIT CHECKLIST - GENERAL LABORATORY INFORMATION

CHART I

ITEM	YES	NO	COMMENT
b. documenting all analytical procedures?	____	___	_____
c. Operation/calibration of instrument?	____	___	_____
d. Preventive maintenance?	____	___	_____
e. Quality Control for each type of test?	____	___	_____
f. Quality Control Charting?	____	___	_____
g. Record keeping and storage?	____	___	_____
h. Data reduction, review and reporting	____	___	_____
i. Personnel training/certification?	____	___	_____
j. Procurement and inventory procedures?	____	___	_____
k. Glassware cleaning?	____	___	_____
l. Waste disposal?	____	___	_____

Is at least the following minimum QC practiced in the lab?

a. For Inorganic/Wet Chemistry:			
1) Minimum 3 concentrations of standards plus blank, and one check standard in 10; the lab shall repeat all samples if check standard is outside $\pm$10% ($\pm$20% for mercury).	____	___	_____
2) One method blank in 20 or per batch	____	___	_____
3) One matrix spike in 20 or per batch	____	___	_____
4) One lab duplicate or matrix spike duplicate in 20 per batch	____	___	_____
5) One laboratory control sample (LCS) (consists of a control matrix spiked with analytes representative of the target analytes) in 20 or per batch.	____	___	_____
b. For Organic Chemistry:			
1) Minimum 5 concentrations of			

CHART I

ITEM	YES	NO	COMMENT
standards plus blank and one check standard in 10; if any are outside control limits, repeat all samples.	____	____	_____
2) One method blank in 20 or per batch.	____	____	_____
3) One matrix spike in 20 or per batch.	____	____	_____
4) One lab duplicate or matrix spike duplicate in 20 or per batch.	____	____	_____
5) Surrogates for all samples.	____	____	_____
Is a QC batch defined as a single event (i.e. one day or less)?	____	____	_____
Are there any exceptions to the above minimum QC practiced in the lab?	____	____	_____
Has the lab established control limits for all of the above types of QC samples?	____	____	_____
Are control limits at least as tight as those stated in the methods?	____	____	_____
Are quality control data (e.g. standard curve, results of duplicates and spikes) accessible for all analytical results?	____	____	_____
Are method detection limits determined and documented?	____	____	_____
Are control charts maintained for each routine analysis?	____	____	_____
Do lab records indicate what corrective action has been taken when results fail to meet QC criteria?	____	____	_____
Is a program of initial and continuing calibration established for each method?	____	____	_____
Does QA Plan include calibration documentation requirements:			
a. Date(s) of calibration?	____	____	_____

1.0. AUDIT CHECKLIST - GENERAL LABORATORY INFORMATION

CHART I

ITEM	YES	NO	COMMENT
b. Identification of standards used?	____	____	_____
c. Personnel performing calibration?	____	____	_____
d. Results of calibration (raw data and summary statistics)?	____	____	_____
e. Corrective actions taken?	____	____	_____
Are the primary reference standards used for calibration only?	____	____	_____
Are all working standards versus primary standards verifies and documented?	____	____	_____
Are reference materials (lab standards) traceable?	____	____	_____
Are reagent grade or higher purity chemicals used to prepare standard?	____	____	_____
Are fresh analytical standards prepared at a frequency consistent with good QC?	____	____	_____
Are reference materials/reagents properly labeled with concentrations, dates of receipt, preparation/expiration and the identity of the person preparing the reagent?	____	____	_____
Are updated equipment operating instructions available?	____	____	_____
Are all analytical procedures written as SOPs available for review?	____	____	_____
Are SOPs provided and maintained in the laboratory or area of use?	____	____	_____
Are all procedural steps and options described in SOPs?	____	____	_____
Are procedures in place for making and controlling revisions to SOPs?	____	____	_____
Are the criteria of method selection included (e.g., in order to obtain a specific Data Quality Objective)?	____	____	_____

1.0. AUDIT CHECKLIST - GENERAL LABORATORY INFORMATION

CHART I

ITEM	YES	NO	COMMENT
If method choice is governed by regulatory requirement (e.g., NPDES, SDWA, RCRA) have the appropriate methods been chosen?	____	___	_____
Are approved methods being used as specified?	____	___	_____
Are procedures documented for data handling reporting and record keeping?	____	___	_____
Are documented validation procedures applied at appropriate levels of all measurement procedures?	____	___	_____
Are documented procedures available for checking the validity of reported analysis values?	____	___	_____
Are predetermined limits available for data acceptability beyond which corrective action is required?	____	___	_____
Are documented procedures available for correcting erroneously reported results?	____	___	_____
Does the lab have a LIMS currently in use? If yes, manufacturer: _____ Model No: _____	____	___	_____

Brief Description: _____

_____

_____

_____

_____

_____

Does the LIMS have an audit trail feature:	____	___	_____

1.0. AUDIT CHECKLIST – GENERAL LABORATORY INFORMATION

CHART I

ITEM	YES	NO	COMMENT

Completed by: _____ _____ Date: _____

NAME TITLE

2.0. AUDIT CHECKLIST - PERSONNEL

CHART J

ITEM	YES	NO	COMMENT
Are there documented protocol for training in quality control methods?	____	____	_____
Do personnel assigned to this project have the appropriate background to successfully accomplish the objectives of this project?	____	____	_____
Does each analyst accountable for performing tasks in any of the following areas meet the specified minimum experience:			
a. General chemistry and instrumentation - 6 months.	____	____	_____
b. Sample preparation - 6 months.	____	____	_____
c. Gas chromatography - 1 year.	____	____	_____
d. Mass spectrometry - 1 year.	____	____	_____
e. Atomic absorption - 1 year.	____	____	_____
f. Atomic emission - 1 year.	____	____	_____
g. spectral/chromatography interpretation - 2 years.	____	____	_____
h. pesticide residue analysis - 2 years.	____	____	_____
Is backup provided for technical staff?	____	____	_____
Are qualifications, training and experience recorded?	____	____	_____
Is there documented evidence of analyst proficiency for each test method performed?	____	____	_____
Is the QA Officer familiar with all test procedures and QC requirements?	____	____	_____
Does the lab have an in-house training program or send staff to training school?	____	____	_____

Completed by: _____ _____ Date: _____

NAME TITLE

3.0. AUDIT CHECKLIST - LABORATORY ENVIRONMENTAL/FACILITIES

CHART K

ITEM	YES	NO	COMMENT
Does the lab building have a security system?	____	____	_____
Is access to the laboratory area controlled?	____	____	_____
Is equipment protected and environment monitored as needed?	____	____	_____
Does the lab have adequate work space, ventilation, light and access to stable power sources at workstation?	____	____	_____
Is the lab free of dust, drifts and temperature extremes?	____	____	_____
Is water free of trace contamination available for preparation of standards and blanks?	____	____	_____
Is the pH and conductivity of water routinely checked and recorded on a daily basis?	____	____	_____
Are exhaust hoods provided to allow contamination-free work with volatile and hazardous materials?	____	____	_____
Is the air flow of the hoods periodically checked and recorded?	____	____	_____
Are adequate facilities, including cold storage, provided for separate storage of samples, extracts, reagents, solvents, reference materials and standards to preserve their identity, concentration, purity and stability?	____	____	_____
Is adequate chemical storage space available and are chemicals properly segregated according to hazard class?	____	____	_____
Are solvent storage cabinets properly vented as appropriate for the prevention of possible lab contamination?	____	____	_____
Does the lab have adequate safety devises such as eye wash stations, spill control stations, showers, first-aid stations, (etc.)?	____	____	_____

3.0. AUDIT CHECKLIST – LABORATORY ENVIRONMENTAL/FACILITIES

CHART K

ITEM	YES	NO	COMMENT
Are these safety devises checked routinely and documented to ensure they are still working properly?	____	____	_____
Are special facilities provided for handling extremely toxic materials such as dioxin (e.g., glove box, controlled air)?	____	____	_____
Are chemical waster disposal policies and procedures well-defined and followed by the lab?	____	____	_____

Completed by: _____ _____ Date: _____

NAME TITLE

4.0. AUDIT CHECKLIST - EQUIPMENT AND INSTRUMENTATION

CHART L

ITEM	YES	NO	COMMENT
Is appropriate equipment/instrumentation available for use in accordance with required methodology?	____	____	_____
Is equipment adequately maintained with sufficient spare parts and are maintenance instructions available?	____	____	_____
Is out-of-service equipment clearly labeled?	____	____	_____
Are instrument maintenance logs kept?	____	____	_____
Are standard curves prepared to adequately cover the expected concentration ranges of samples?	____	____	_____
Are calibration logs maintained?	____	____	_____
Is a new curve prepared annually (or more frequently as specified by the method) or whenever new reagents are prepared, whichever is more frequent?	____	____	_____
Are calibration labels used as applicable?	____	____	_____
Is proper backup equipment available?	____	____	_____
General Equipment Requirements:			
Analytical and Pan Balances:			
a. Are analytical balances capable of weighing 0.1 mg in use?	____	____	_____
b. Is a record of balance calibration kept for at least two ranges with Class S weights? (Please specify the ranges)	____	____	_____
c. Do records show daily functional and calibration checks for analytical balances and weekly for pan balances?	____	____	_____
d. Are the balances services and calibrated at least annually?	____	____	_____

4.0. AUDIT CHECKLIST – EQUIPMENT AND INSTRUMENTATION

CHART L

ITEM	YES	NO	COMMENT
pH Meter:			
a. Is a clean pH meter and appropriate electrode with scale gradations at least 0.1 pH units in use?	____	____	_____
b. Is a thermometer or temperature sensor for automatic compensation in use.	____	____	_____
c. Do records show daily, or before each use, calibration, whichever is less frequent?	____	____	_____
d. Are aliquots of standard pH 4 & pH 7, or pH 7 & pH 10 used only once?	____	____	_____
Conductivity Mater:			
a. Are a conductivity meter and probe of sufficient sensitivity in use?	____	____	_____
b. Do records show a daily, or before each use, calibration check, whichever is less frequent?	____	____	_____
c. Do records show cell constant is determined annually?	____	____	_____
Glassware:			
a. Is glassware cleaned in a manner appropriate for the analytical procedures for which it is used?	____	____	_____
b. Are glassware cleaning SOPs available where cleaning occurs?	____	____	_____
c. Is glassware maintained separately for each department?	____	____	_____
Refrigeration:			
a. Is a thermometer in each refrigerator with a bulb immersed in liquid?	____	____	_____
b. Are thermometers graduated in increments no lager than 1°C?	____	____	_____

4.0. AUDIT CHECKLIST - EQUIPMENT AND INSTRUMENTATION

CHART L

ITEM	YES	NO	COMMENT
c. Are thermometers calibrated against NIST (NBS) - traceable thermometer and documented?	____	____	_____
d. Do records show that refrigerator temperatures are maintained in the range of 2° to 6°C?	____	____	_____
e. Are temperatures for each refrigerator recorded daily?	____	____	_____
f. Are samples stored in separate refrigerators from standards?	____	____	_____
Ovens:			
a. Are thermometers graduated in increments no larger than 1°C?	____	____	_____
b. Are thermometers calibrated against NIST (NBS) - traceable thermometer and documented?	____	____	_____
c. If the oven temperature cannot be read without opening the door, is the bulb of the thermometer in a sand bath?	____	____	_____
d. Is oven temperature adequately monitored (e.g., beginning and end of each use cycle)?	____	____	_____
Thermometers:			
a. Does the lab have access to a NIST (NBS) traceable thermometer?	____	____	_____
b. Is the calibration of each working mercury-in-glass thermometer checked at least annually against a NIST (NBS) traceable certified thermometer?	____	____	_____
c. Is the calibration of each dial0type thermometer checked at least quarterly against a NIST (NBS)-traceable thermometer?	____	____	_____

Completed by: _____ _____ Date: _____

4.0. AUDIT CHECKLIST – EQUIPMENT AND INSTRUMENTATION

CHART L

ITEM		YES	NO	COMMENT
	NAME	TITLE		

5.0. AUDIT CHECKLIST – FIELD SAMPLING: (Complete if this lab will conduct field sampling for Haley & Aldrich).

CHART M

ITEM	YES	NO	COMMENT
Is the Site Specific Quality Assurance Project Plan (QAPP) available to field personnel	___	___	_____
Are field personnel familiar with the QC requirements of the Site specific QAPP	___	___	_____
Do field documentation procedures:			
a. document source of reagents/supplies?	___	___	_____
b. Include procedures/forms for recording the exact location and specific considerations associated with sample collection?	___	___	_____
c. Document specific preservative methods?	___	___	_____
d. Include labels containing all necessary information?	___	___	_____
e. Include forms for tracking sample custody?	___	___	_____
Do sampling procedures follow contract specifications?	___	___	_____
Is there a unique identification number on each sample?	___	___	_____
Is sampling information properly recorded such as sample ID, (grab vs. composite), preservatives, analytes, location, date and time of collection and name of supplier?	___	___	_____
Are written chain-of-custody procedures available for review? Are they in accordance with EPA and QAPP guidelines?	___	___	_____
Are there written sampling procedures covering sampling plans, sampling equipment, sample collections, preservation, identification, storage and lab handling?	___	___	_____

5.0. AUDIT CHECKLIST – FIELD SAMPLING: (Complete if this lab will conduct field sampling for Haley & Aldrich).

CHART M

ITEM	YES	NO	COMMENT
Are there written descriptions of the chain-of-custody of samples? (Attach a copy of chain-of-custody form).	____	____	_____
Are there written procedures for field measurement of flow, dissolved oxygen, residual chlorine, etc.?	____	____	_____
Are there written SOPs for monitoring water supply, effluent, ambient air, stacks, mobile vehicles, pesticides, radiation, etc.?	____	____	_____
Are proper preservation techniques being used for the analytical methods and sample types concerned?	____	____	_____
Are provisions made for the collection of QA/QC split samples?	____	____	_____
Are provisions made for field blanks and duplicate samples at an appropriate percentage (normally 10% or minimum of one per matrix type, whichever is greater, or as specified in Contract)?	____	____	_____
Are adequate facilities available to do compatibility testing?	____	____	_____

Completed by: _____ _____ Date: _____

NAME TITLE

6.0. AUDIT CHECKLIST – SAMPLE RECEIPT/STORAGE

CHART N

ITEM	YES	NO	COMMENT
Are appropriate chain-of-custody procedures documented and followed in the lab?	___	___	_____
Are there adequate written procedures for receipt and storage of samples to ensure that holding times are met?	___	___	_____
Do lab custody procedures:			
a. Identify sample custodian? Name of custodian: _____	___	___	_____
b. Provide for custody record within the lab?	___	___	_____
c. Specify procedures for sample handling, storage, dispersement for analysis, and disposal?	___	___	_____
Does a permanent record exist for sample log-in?	___	___	_____
Are samples assigned an unambiguous sample number when logged in?	___	___	_____
Are there sample preservation records?	___	___	_____
Are the pH values of aqueous samples checked and adjusted in a hood for trace metals, phenols, cyanide and TRPH during sample log-in?	___	___	_____
Is the temperature of sample cooler/shuttle recorded upon receipt?	___	___	_____
Is client notified of receipt temperature outside of 4° $\pm$ 2°C?	___	___	_____
Are discrepancies between sample labels and chain-of-custody documents recorded?	___	___	_____
Is client notified of any discrepancies following sample receipt and log-in?	___	___	_____
Are there adequate facilities for sample receipt and storage of samples?	___	___	_____

6.0. AUDIT CHECKLIST – SAMPLE RECEIPT/STORAGE

CHART N

ITEM	YES	NO	COMMENT
Are samples stored in such a way as to maintain their identity, integrity, stability and concentration?	____	____	_____
How long will the lab store samples before disposing?	____	____	_____

Completed by: _____ _____ Date: _____

NAME TITLE

7.0. AUDIT CHECKLIST - ORGANIC ANALYSES BY GAS CHROMATOGRAPHY (GC):

CHART O

A. Summary of GC Staff:

Position Title	Name of Employee	Years of Experience [1]	Education in Chemistry	Appropriate Training in Analytical Testing Area [2]
GC Group Leader [3] (experience: 2 years minimum required)				
GC Operators [3] (Experience: 1 year minimum required)				
GC Interpretation Experts [3] (Experience: 2 years minimum required)				
PCB and Pesticide Residue Analysis Experts [3] (Experience: 2 years minimum required)				
Purge & Trap Experts [3] (Experience: 1 year minimum required)				
Extraction & Concentration Experts [4] (Experience: 6 months minimum required)				

1. Requirements for experience as listed are minimal and maybe increased for specific projects involving difficult samples or unusual matrices.
2. Manufacturer sponsored class, EPA symposiums, etc.
3. Minimum of Bachelor's degree in chemistry or any scientific/engineering discipline.
4. Minimum of high school diploma and knowledge of general chemistry.

7.0 AUDIT CHECKLIST - ORGANIC ANALYSES BY GC:

CHART P

B. Summary of GC Instrumentation:

No.	Manufacturer	Model Number	Year Acquired	Used for Method [1]	Comments [2]	Haley & Aldrich Use Only S	U
1.							
2.							
3.							
4.							
5.							
6.							
7.							
8.							
9.							
10.							
11.							
12.							
13.							
14.							
15.							
16.							
17.							
18.							
19.							
20.							

1. State EPA method from SW-846 8000 or 40 CFR 136 600 series

7.0 AUDIT CHECKLIST - ORGANIC ANALYSES BY GC:

CHART P

2. Detectors, condition, autosamplers, modification, etc.

7.0 AUDIT CHECKLIST – ORGANIC ANALYSES BY GC:

CHART Q

ITEM	YES	NO	COMMENT
C. Questions about the GC instruments described above. (If one answer does not apply to all of the instruments listed, use the instrument number (1-20) to designate answers as appropriate.			
Are the following detectors available and are they used appropriately?			
a. Flame ionization (603, 604, 609, 8015, 8030, 8040, 8060, 8090, 8100)?	____	____	_____
b. Photoionization (602, 8020)?	____	____	_____
c. Electron capture (604, 606, 608, 609, 612, 8040, 8060, 8080, 8090, 8120, 8150)?	____	____	_____
d. Electrolytic conductivity (601, 611, 8010, 8080, 8140)?	____	____	_____
e. Microcoulometric (601, 611, 8140)?	____	____	_____
f. Thermal Energy Analyzer (607)?	____	____	_____
g. Nitrogen/Phosphorus (607, 8140)?	____	____	_____
h. Flame photometric (8140)?	____	____	_____
Are the column ovens, at a minimum, capable of control within +0.2° C to 220° C?	____	____	_____
Are the injection ports glass lined?	____	____	_____
Are the purge and trap systems subjected to a periodic bake-out and cleaning process and are these actions documented?	____	____	_____
Will the system accept 5mL samples?	____	____	_____
Is the gaseous headspace less than 15mL?	____	____	_____
Is the trap a minimum of 25 cm long?	____	____	_____
Will the system accept 25mL samples?	____	____	_____
Are appropriate confirmation columns or GC/MS analysis in use?	____	____	_____
Is methanol purge and trap quality or equivalent?	____	____	_____

7.0 AUDIT CHECKLIST – ORGANIC ANALYSES BY GC:

CHART Q

ITEM	YES	NO	COMMENT
Id calibration by internal standards?	____	____	_____
If not, is calibration by external standards?	____	____	_____
Is the calibration curve or calibration factor verified every 10 samples?	____	____	_____
Is there a calibration protocol available to the operator?	____	____	_____
Are calibration results kept in a permanent logbook?	____	____	_____
Are SOPs available for each analytical method?	____	____	_____
Are 5-point calibrations used?	____	____	_____
Are surrogate recoveries determined for each sample?	____	____	_____
Is corrective action taken if surrogate recoveries exceed QC limits?	____	____	_____
Does laboratory use EPA CLP protocols to evaluate internal QC data?	____	____	_____
If not, what are the laboratory's criteria for evaluation of internal QC data?	____	____	_____
Are EPA check samples analyzed as appropriate?	____	____	_____
Is a matrix spike and a matrix spike duplicate run with each batch?	____	____	_____
Is corrective action taken if matrix spike recoveries exceed QC limits?	____	____	_____
Are method blanks run with each batch?	____	____	_____
Has method proficiency (acceptable accuracy and precision) been established for all procedures?	____	____	_____
Are method matrix-specific accuracy criteria established and maintained?	____	____	_____
Have laboratory-specific surrogate percent			

7.0 AUDIT CHECKLIST - ORGANIC ANALYSES BY GC:

CHART Q

ITEM	YES	NO	COMMENT
recovery QC limits been established?	____	____	_____
Are manufacturer's operating manuals readily available to the operator?	____	____	_____
Is a permanent logbook kept for each instrument that summarizes instrument problems and servicing records?	____	____	_____
Have any instruments been modified in any way?	____	____	_____
Are the instruments properly vented?	____	____	_____

7.0 AUDIT CHECKLIST – ORGANIC ANALYSES BY GC:

CHART Q

ITEM	YES	NO	COMMENT

Completed by: _____ _____ Date: _____

NAME TITLE

8.0 AUDIT CHECKLIST - ORGANIC ANALYSES BY GC/MASS SPECTROMERY

CHART R

A. Summary of GC/MS Staff:

Position Title	Name of Employee	Years of Experience [1]	Education in Chemistry	Appropriate Training in Analytical Testing Area [2]
GC/MS Group Leader [3] (Experience: 2 years minimum required)				
GC/MS Operator [3] (Experience: 1 year minimum required)				
GC/MS Spectral Interpretation Experts [3] (Experience: 2 years minimum required				
Purge & Trap Experts [3] (Experience: 1 year minimum required)				
Extraction and Concentration Experts [4] (Experience: 6 months minimum required)				

1. Requirements for experience as listed are minimal and maybe increased for specific projects involving difficult samples or unusual matrices.
2. Manufacturer sponsored class, EPA symposiums, etc.
3. Minimum of Bachelor's degree in chemistry or any scientific/engineering discipline.

4. Minimum of high school diploma and knowledge of general chemistry.

8.0 AUDIT CHECKLIST – ORGANIC ANALYSES BY GC/MASS SPECTROMERY

CHART S

B. Summary of GC/MS Instrumentation:

No.	Manufacturer	Model Number	Year Acquired	Used for Method [1]	Comments [2]	Haley & Aldrich Use Only S	U
1.							
2.							
3.							
4.							
5.							
6.							
7.							
8.							
9.							
10.							
11.							
12.							
13.							
14.							
15.							
16.							
17.							
18.							
19.							
20.							

1. State EPA method from SW-846 8000 or 40 CFR 136 600/1600 series

8.0 AUDIT CHECKLIST - ORGANIC ANALYSES BY GC/MASS SPECTROMERY

CHART S

2. Condition, autosamplers, modification, etc.

8.0 AUDIT CHECKLIST - ORGANIC ANALYSES BY GC/MASS SPECTROMERY

CHART T

ITEM	YES	NO	COMMENT
C. Questions about the GC/MS instruments described above. (If one answer does not apply to all of the instruments listed, use the instrument number (1-20) to designate answers as appropriate.			
Are any GCs not programmable? If so, list the instrument number?	____	____	_____
Is a split/splitless capillary injection in place?	____	____	_____
Is the MS capable of scanning from 35 to 500 amu every one second or less?	____	____	_____
Is tuning compound, PFTBA, used to verify mass calibration?	____	____	_____
Do the mass spectra of BFP and DFTPP meet all criteria before each batch is run?	____	____	_____
Are standards containing all of the analytes of interest analyzed to verify response factors and update retention time?	____	____	_____
Is glassware heated at 400°C in a muffle furnace after careful cleaning?	____	____	_____
Is glassware sealed and stored in a clean environment?	____	____	_____
Are magnetic media stored in a secure area?	____	____	_____
Are extensive in-house replacements parts available?	____	____	_____
Are manufacturer's operating manuals readily available to the operator?	____	____	_____
Is there a calibration protocol available to the operator?	____	____	_____
Are calibration results kept in a permanent logbook?	____	____	_____
Are SOPs available for each analytical method?	____	____	_____
Is a permanent logbook kept for each instrument that summarizes instrument problems and servicing records?	____	____	_____
Has the instrument been modified in any way?	____	____	_____

8.0 AUDIT CHECKLIST - ORGANIC ANALYSES BY GC/MASS SPECTROMERY

CHART T

ITEM	YES	NO	COMMENT
Are the instruments properly vented?	____	____	_____
Are 5-point calibrations used?	____	____	_____
Are continuing calibration checks done on a 12-hour basis?	____	____	_____
Are system performance response factors checked on a 12 hour basis?	____	____	_____
Are BFB and DFTPP tuning checks done on a 12-hour basis?	____	____	_____
Are DDT, pentachlorophenol and benzidine included in the DFTPP tuning solution?	____	____	_____
Are low-level methods routinely used for environmental soil/sediment samples?	____	____	_____
Is the most recent version of the EPA/NIST Mass Spectral Library available?	____	____	_____
For tentatively identified compounds, are library searches done for the 10 volatile organics and the 20 semivolatile organics of highest concentration?	____	____	_____
Are surrogate recoveries determined for each sample?	____	____	_____
Is a corrective action taken if surrogate recoveries exceed QC limits?	____	____	_____
Is a matrix spike and a matrix spike duplicate run with each batch?	____	____	_____
Is a corrective action taken if matrix spike recoveries exceed QC limits?	____	____	_____
Is a method blank run with each batch?	____	____	_____
Are samples screened by GC prior to GC/MS analysis?	____	____	_____
Has the laboratory demonstrated initial method proficiency?	____	____	_____
Are method matrix-specific accuracy criteria established and maintained?	____	____	_____

8.0 AUDIT CHECKLIST – ORGANIC ANALYSES BY GC/MASS SPECTROMERY

CHART T

ITEM	YES	NO	COMMENT
Have laboratory-specific surrogate percent recovery QC limits been established?	____	____	_____

Completed by: _____ _____ Date: _____

NAME TITLE

9.0 AUDIT CHECKLIST –METALS ANALYSIS:

CHART U

A. Summary of AA/ICP Staff:

Position Title	Name of Employee	Years of Experience [1]	Education in Chemistry	Appropriate Training in Analytical Testing Area [2]
Metals Group Leader [3] (Experience: 2years minimum required)				
ICP Spectroscopists [3] (Experience: 1 year minimum required)				
Flameless AA Spectroscopists [3] (Experience: 1 year minimum required)				
Flame and Cold Vapor AA Spectroscopists [4] (Experience: 1 year minimum require)				
Inorganic Sample Preparation Experts [4] (Experience: 6 months minimum required)				

9.0 AUDIT CHECKLIST -METALS ANALYSIS:

CHART U

Position Title	Name of Employee	Years of Experience [1]	Education in Chemistry	Appropriate Training in Analytical Testing Area [2]
Wet Lab Manager [3] (Experience: 2 years minimum required)				
UV/VIS Spectroscopist [3] (Experience: 6 months minimum required)				

1. Requirements for experience as listed are minimal and maybe increased for specific projects involving difficult samples or unusual matrices.
2. Manufacturer sponsored class, EPA symposiums, etc.
3. Minimum of Bachelor's degree in chemistry or any scientific/engineering discipline.
4. Minimum of high school diploma and knowledge of general chemistry.

9.0 AUDIT CHECKLIST -METALS ANALYSIS:

CHART V

B. Summary of AA/ICP Instrumentation

No.	Manufacturer	Model Number	Year Acquired	Used for Method [1]	Comments [2]	Haley & Aldrich Use Only S	U
1.							
2.							
3.							
4.							
5.							
6.							
7.							
8.							
9.							
10.							
11.							
12.							
13.							
14.							
15.							
16.							
17.							
18.							
19.							
20.							

1. State EPA method SW-846 6000/7000 or 40 CFR 136 200 series
2. Condition, autosamplers, modification, etc.

9.0 AUDIT CHECKLIST -METALS ANALYSIS:

CHART W

ITEM	YES	NO	COMMENT
C. Questions about the AA/ICP instruments described above. (If one answer does not apply to all of the instruments listed, use the instrument number (1-20) to designate answers as appropriate.			
Atomic absorption spectrophotometer:			
a. Are fuels and oxidants commercial grade?	____	___	_____
b. Is there a filter moisture trap between the air source and the spectrometer	____	___	_____
c. Is nitrous oxide reagent grade?	____	___	_____
d. Are flash-back arrestors and heaters in use when needed?	____	___	_____
e. Are all lamps dated when received and first put into use?	____	___	_____
f. Are lamps available for all elements analyzed?	____	___	_____
g. Does the AA have a deuterium background correction system?	____	___	_____
h. Does the AA have a Zeeman background correction system?	____	___	_____
i. Does the AA have a Smith-Hieftje background correction system?	____	___	_____
ICP-Atomic emission spectrometer:			
a. Is background correction technique in use and documented according to sample matrix at least quarterly?	____	___	_____
b. Has the instrument detection limit for each element been established and documented at least annually?	____	___	_____
c. Where required, has the effect of high dissolved solids and/or acid concentration been controlled?	____	___	_____
d. Has salt build-up on the nebulizer been controlled?	____	___	_____
e. When a new matrix is encountered, is a serial dilution, spike addition, or an alternate method technique in use to eliminate potential interference?	____	___	_____

9.0 AUDIT CHECKLIST –METALS ANALYSIS:

CHART W

ITEM	YES	NO	COMMENT
f. Is the spectrometer equipped with an argon gas supply?	____	___	_____
g. Are ultra high purity grade nitric acid, hydrochloric acid and deionized or distilled water used for sample processing and preparation?	____	___	_____
Are manufacturer's operating manuals readily available to the operator?	____	___	_____
Is there a calibration protocol available to the operator?	____	___	_____
Are calibration results kept in permanent logbooks?	____	___	_____
Are SOPs available for each analytical method?	____	___	_____
Is a permanent logbook kept for each instrument that summarizes instrument problems and servicing records?	____	___	_____
Is ICP calibration checked using a blank and three standards prior to sample analysis?	____	___	_____
Is ICP calibration verified every 10 samples and at the end of the analytical run, using a calibration blank and a check standard?	____	___	_____
Does the result of check standard agree within ±10% of expected value?	____	___	_____
Are interelement and background correction factors checked at the beginning and end of an analytical run or twice during every 8-hour work shift, whichever is more frequent? _____	____	_____	
Does the result of interelement check sample agree with ±20% of expected value?	____	___	_____
Are AA calibrated with a blank and three standards (five standards for mercury)?	____	___	_____
Is the AA calibration verified with a reference standard to within ±10% of expected value prior to sample analysis?	____	___	_____

9.0 AUDIT CHECKLIST -METALS ANALYSIS:

CHART W

ITEM	YES	NO	COMMENT
Is the AA calibration verified every tenth sample with a mid-range of reference standard?	____	___	_____
Does the results of these check standards agree within ±20% of expected value?	____	___	_____
Is a matrix spike duplicate or internal QC duplicate run with each batch?	____	___	_____
Is corrective action taken if matrix spike recoveries exceed QC limits?	____	___	_____
Is a corrective action taken if internal QC duplicate or MS/MSD RPDs exceed QC limits?	____	___	_____
Is an analytical (post-digestion) spike analyzed after each sample?	____	___	_____
Is the method of standard addition in use where needed?	____	___	_____
Has the instrument been modified in any way?	____	___	_____
Are the instruments properly vented?	____	___	_____

Completed by: _____ _____ Date: _____

NAME TITLE

10.0 AUDIT CHECKLIST -OTHER CLASSICAL ANALYSIS:

ITEM	CHART X YES	NO	COMMENT

A. Summary of Classical Analysis Staff:

Position Title	Name of Employee	Years of Experience [1]	Education in Chemistry	Appropriate Training in Analytical Testing Area [2]
Cyanide Analyst [4] (Experience: 6 months minimum required)				
IR Spectroscopists [3] (Experience: 6 months minimum required)				
TPH Analyst [3] (418.1) (Experience: 6 months minimum required)				
HPLC Analysis Experts [3] (Experience: 1 year minimum required)				
Explosives Analyst [3]				
Ion Chromatographic Analysis Experts (Experience: 1 year minimum required)				
Common Ions Analyst [3] Radionuclides Analyst (Experience: 2 years minimum required)				

10.0 AUDIT CHECKLIST -OTHER CLASSICAL ANALYSIS:

CHART X

ITEM	YES	NO	COMMENT

Position Title	Name of Employee	Years of Experience [1]	Education in Chemistry	Appropriate Training in Analytical Testing Area [2]
Microbiological Analysis Experts (Experience: 1 year minimum required)				

Other Classical lab Analysis Experts: (experience: 6 months minimum required). Please specify position, title and analysis.

Position Title	Name of Employee	Years of Experience [1]	Education in Chemistry	Appropriate Training in Analytical Testing Area [2]

1. Requirements for experience as listed are minimal and maybe increased for specific projects involving difficult samples or unusual matrices.
2. Manufacturer sponsored class, EPA symposiums, etc.
3. Minimum of Bachelor's degree in chemistry or any scientific/engineering discipline.
4. Minimum of high school diploma and knowledge of general chemistry.

10.0 AUDIT CHECKLIST –OTHER CLASSICAL ANALYSIS:

CHART Y

B. Summary of Instrumentation

No.	Instrument/ Manufacturer	Model Number	Year Acquired	Used for Method [1]	Comments [2]	Haley & Aldrich Use Only S	U
1.							
2.							
3.							
4.							
5.							
6.							
7.							
8.							
9.							
10.							
11.							
12.							
13.							

1. General classical wet lab/water quality analysis methods.
2. Condition, automation, modifications, etc.

10.0 AUDIT CHECKLIST -OTHER CLASSICAL ANALYSIS:

CHART Z

C. Questions about instruments described above. (If one answer does not apply to all of the instruments listed, use the instrument number (1-13) to designate answers as appropriate.

ITEM	YES	NO	COMMENT
Is the wavelength accuracy and repeatability of all spectrophotometers checked at several wavelengths for each batch of samples?	____	____	_____
Is photometric accuracy and repeatability checked and documented with NIST (NBS) traceable standards?	____	____	_____
Is acid washed glassware retained for phosphorus analyses only?	____	____	_____
Is ammonia free water used in preparation of standards and samples for nitrogen analyses?	____	____	_____
Are manufacturer's operating manuals readily available to operator of each instrument?	____	____	_____
Is there a calibration protocol available to the operator?	____	____	_____
Are calibration results kept in permanent logbooks?	____	____	_____
Are SOPs available for each analytical method?	____	____	_____
Is a permanent logbook kept for each instrument that summarizes instrument problems and servicing records?	____	____	_____
Has any instrument been modified in any way?	____	____	_____
Are 4-point calibrations used?	____	____	_____
Are continuing calibration checks done on a regular basis?	____	____	_____
Are internal QC run per method requirements?	____	____	_____
Is a method blank used with each blank?	____	____	_____

Completed by: _____ _____ Date: _____

NAME TITLE

11.0 AUDIT CHECKLIST -DATA REDUCTION, REVIEW AND REPORTING

ITEM	YES	NO	COMMENT
Are there documented procedures for internal field and lab checks of:			
a. Precision/accuracy?	____	____	_____
b. Routine duplicates, spikes and standard samples?	____	____	_____
c. Statistical methods, including control chart and computer methods?	____	____	_____
Is there a written description of the lab record system including data handling/calculation review and audit?	____	____	_____
Is there a written description of the lab reporting system?	____	____	_____
Is there a system in place that provides for retrievability and traceability of the sample source, analytical methods, results, person performing analysis and date?	____	____	_____
Are records and reports adequately secured for the required amount of time to ensure their integrity per regulatory or H&A contract requirements?	____	____	_____
Are all lab notebooks when filled, raw data, QC data, analytical reports and pertinent documents filed in a secure, controlled archives area?	____	____	_____
Are permanently bound notebooks with consecutively numbered pages being used?	____	____	_____
Is a unique serial number clearly displayed on each notebook cover or spine?	____	____	_____
Have entries been made in a permanent fashion and corrections made without obliterating original entries?	____	____	_____
Are notebooks appropriately controlled?	____	____	_____
Has the supervisor of each individual maintaining a notebook personally examined and reviewed each notebook periodically, signed and dated the review?	____	____	_____

11.0 AUDIT CHECKLIST -DATA REDUCTION, REVIEW AND REPORTING

ITEM	YES	NO	COMMENT

11.0 AUDIT CHECKLIST -DATA REDUCTION, REVIEW AND REPORTING

CHARTAA

ITEM	YES	NO	COMMENT
Do the lab's reports accurately, clearly and unambiguously present results and all other relevant information?	____	____	_____
Does each test report include the following information?			
a. name and address of laboratory	____	____	_____
b. Unique identification and page number?	____	____	_____
c. Name and address of client?	____	____	_____
d. Case narrative?	____	____	_____
e. Sample identification and description?	____	____	_____
f. Dates of sample receipt and test performed, as appropriate?	____	____	_____
g. Identification of sample preparation and analysis methods used?	____	____	_____
h. Description of any deviations from test method?	____	____	_____
i. Disclosure of any subcontractor used?	____	____	_____
j. Results including all method required QC data?	____	____	_____
k. Description of any problems or failures identified?	____	____	_____
Measurement uncertainty, if relevant?	____	____	_____

Completed by: _____ _____ Date: _____

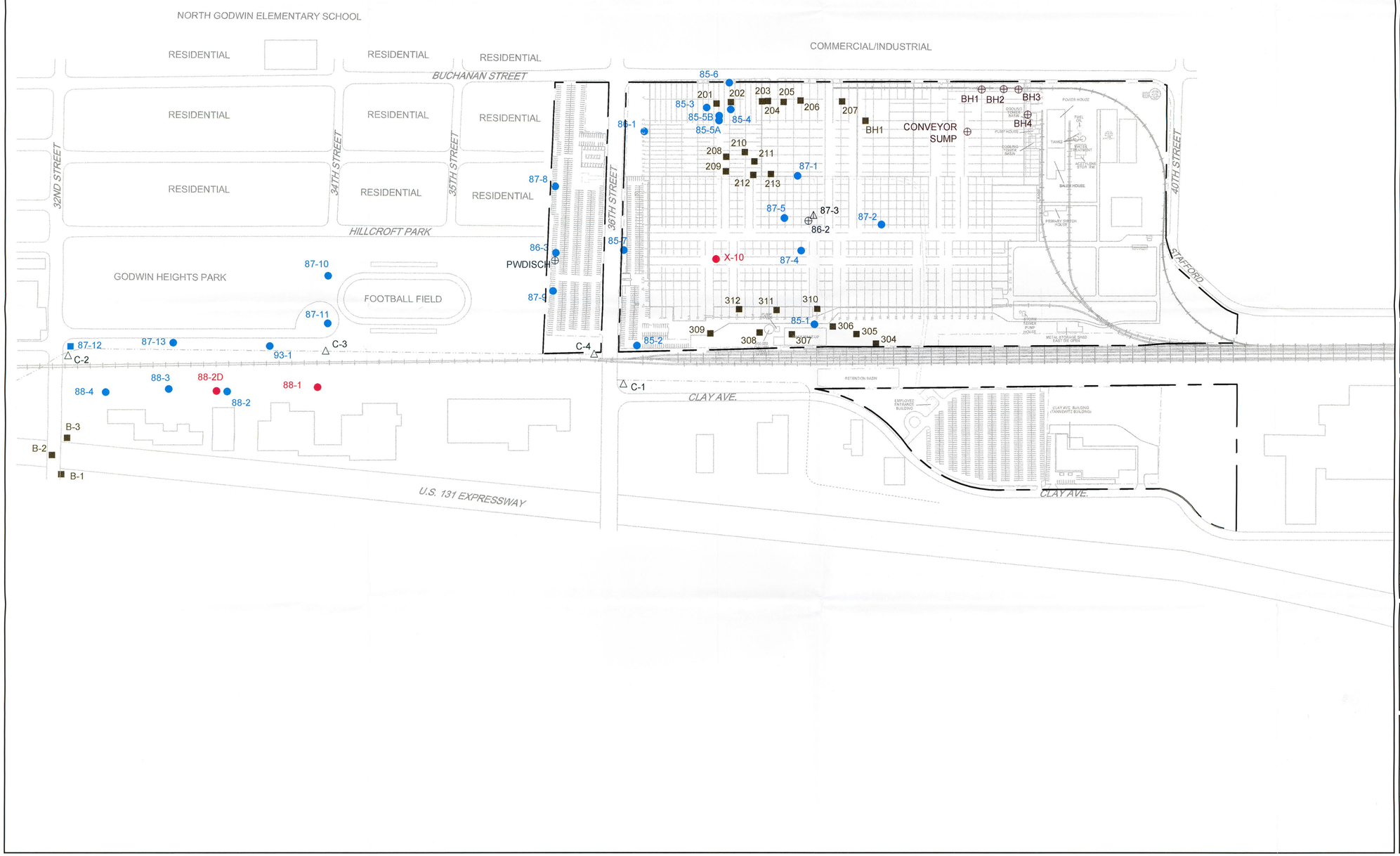
NAME TITLE

12.0 AUDIT CHECKLIST –PERFORMANCE AND SYSTEM AUDITS:

CHART BB

ITEM	YES	NO	COMMENT
Are there audits for both field and lab activities?	____	____	_____
Are there designated persons who will conduct the audits?	____	____	_____
Is there a documented protocol which will be used for audits?	____	____	_____
Are acceptance criteria defined?	____	____	_____
Are audit reports prepared and distributed? To whom?	____	____	_____
Are the type and frequency of audit reports specified?	____	____	_____
Do the reports address:			
a. Status of project (time table)?	____	____	_____
b. Results of performance and system audits?	____	____	_____
c. Data quality assessment?	____	____	_____
d. Significant QA problems and proposed corrective action?	____	____	_____

Completed by: _____ _____ Date: _____
NAME TITLE



NO	Revision	Date	Initial

0 150 250ft

LEGEND

■ 307	SOIL BORING LOCATION
● X-10	DESTROYED/REMOVED MONITORING WELL LOCATION
● 87-2	MONITORING WELL LOCATION
⊕ PWDISCH	PURGE WELL LOCATION
△ C-2	CULVERT LOCATION
⚠ 87-3	AIR PURGE WELL
⊕ BH1	APPROXIMATE LOCATION OF DEWATERING WELLS
— — —	APPROXIMATE SITE BOUNDARY
	FENCE
	RAILROAD
	COLE DRAIN

SOURCE: EDI ENGINEERING & SCIENCE, JUNE 1987 AND JUNE 1988 AND EARTH TECH, SEPTEMBER 2001.

SCALE VERIFICATION

THIS BAR MEASURES 1" ON ORIGINAL. ADJUST SCALE ACCORDINGLY.

Approved

DRAWING STATUS

Status	Date	Initial

GRAND RAPIDS METAL PLANT

WYOMING, MICHIGAN

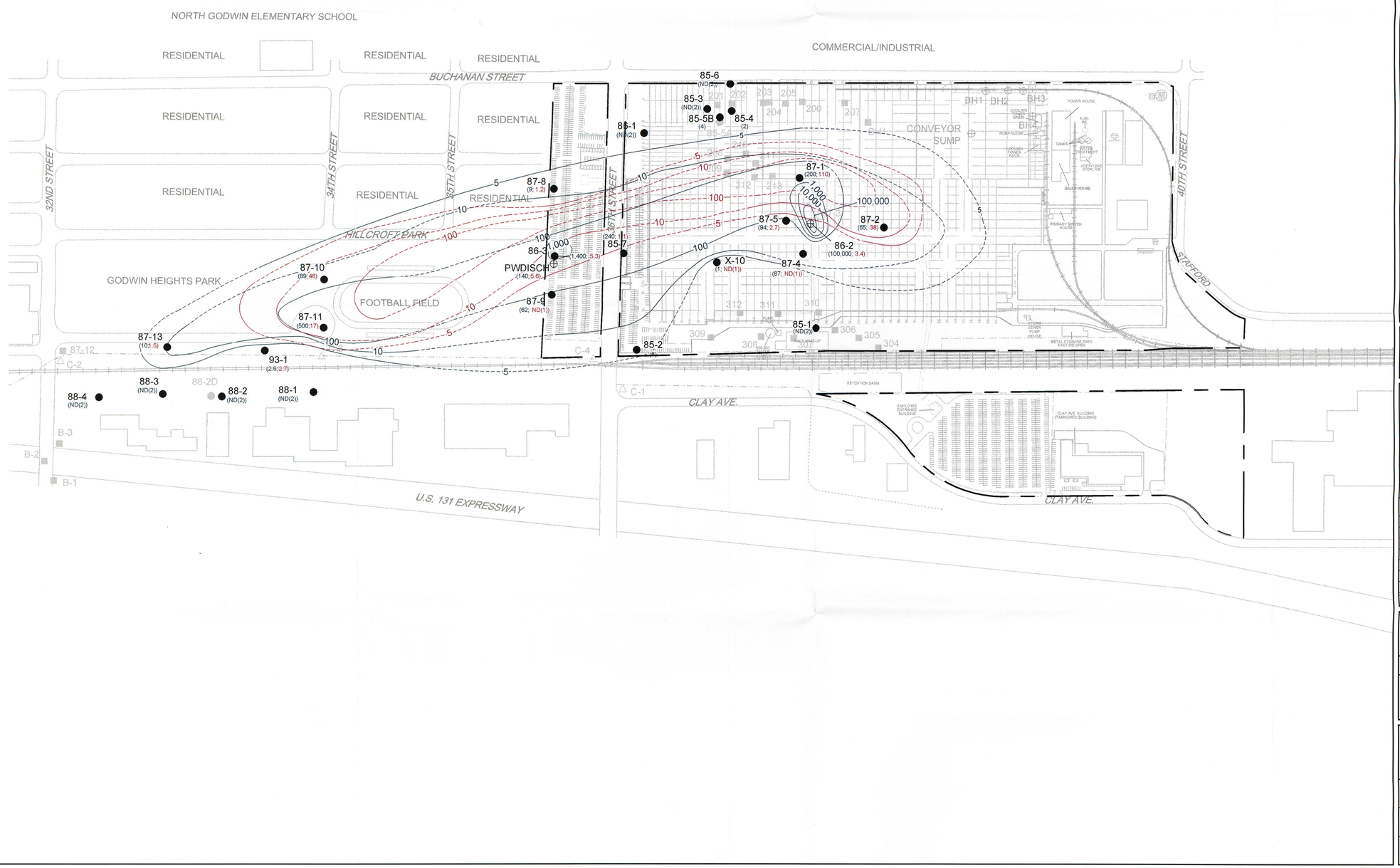
SITE PLAN

CONESTOGA-ROVERS & ASSOCIATES

Source Reference:

Project Manager:	Reviewed By:	Date:	
G.K.	J.Q.	MAY 2002	
Scale: 1"=250'	Project No: 17360-01	Report No: 002	Drawing No: 1

17360-01(002)GN-DE008 DEC 03/2002



NO	Revision	Date	Initial

0 150 250ft

LEGEND

- ■ 307 — SOIL BORING LOCATION
- ● X-10 — ABANDONED MONITORING WELL LOCATION
- ● 87-2 — MONITORING WELL LOCATION
- ⊕ PWDISCH — PURGE WELL LOCATION
- △ C-2 — CULVERTS USED TO MEASURE WATER LEVELS IN COLE DRAIN
- ⚠ 87-3 — AIR PURGE WELL
- ⊕ BH1 — APPROXIMATE LOCATION OF DEWATERING WELLS
- FENCE
- RAILROAD
- COLE DRAIN
- 10 — INITIAL[TCE]SAMPLE TCE CONCENTRATIONS (ug/L) (SAMPLES COLLECTED BETWEEN 1985 AND 1993)
- 10 — DECEMBER 2001 TCE CONCENTRATIONS (ug/L)

SCALE VERIFICATION

THIS BAR MEASURES 1" ON ORIGINAL. ADJUST SCALE ACCORDINGLY.

Approved

DRAWING STATUS

Status	Date	Initial

GRAND RAPIDS METAL PLANT

WYOMING, MICHIGAN

HISTORICAL AND CURRENT CONCENTRATIONS OF TCE IN GROUNDWATER

CONESTOGA-ROVERS & ASSOCIATES

Source Reference:

Project Manager:	Reviewed By:	Date:	
G.K.	J.Q.	MAY 2002	
Scale: 1"=250'	Project No: 17360-01	Report No: 002	Drawing No: 2

17360-01(002)GN-DE009 DEC 03/2002