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QUALITY ASSURANCE PROJECT PLAN

OMC PLANT 2
Waukegan, Illinois

Remedial Investigation

WA No. 237-RICO-0528 / Contract No. 68-W6-0025

January 2005

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Acronyms and Abbreviations

AST	aboveground storage tank
CFR	Code of Federal Regulations
CLP	Contract Laboratory Program
COC	chain-of-custody
CVOC	chlorinated volatile organic compound
DMP	Data Management Plan
DMS	Data Management System
DQO	Data Quality Objective
EDD	Electronic Data Deliverable
FOP	Field Operating Procedure
FSP	Field Sampling Plan
FTL	Field Team Leader
ID	identification number
IEPA	Illinois Environmental Protection Agency
LIMS	Laboratory Information Management System
MIP	membrane interface probe
MS/MSD	matrix spike/matrix spike duplicate
MW	monitoring well
NAPL	nonaqueous phase liquid
OMC	Outboard Marine Corporation
PCB	polychlorinated biphenyl
QAPP	Quality Assurance Project Plan
QA/QC	quality assurance/quality control
RI/FS	remedial investigation/feasibility study
RPD	relative percent difference
SM	Site Manager (not called out in correct place)
SOW	Scope of Work
SPLP	Synthetic Precipitation Leaching Procedure
USEPA	United States Environmental Protection Agency
UST	underground storage tank
WAM	Work Assignment Manager

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SECTION 1

Project Management

1.1 Introduction

The United States Environmental Protection Agency (USEPA) requires that environmental monitoring and measurement efforts mandated or supported by USEPA participate in a centrally managed Quality Assurance Project Plan (QAPP). Parties generating data as part of USEPA environmental monitoring activities must implement procedures so that the precision, accuracy, representativeness, completeness, and comparability of their data are known and documented. To meet this objective, each party must prepare a written QAPP covering each project to be performed. All participants in the project, including subcontractors, must follow the procedures and protocols in this document.

This QAPP presents the organization, objectives, functional activities, and specific quality assurance (QA) and quality control (QC) activities for the remedial investigation (RI) being conducted at the Outboard Marine Corporation's (OMC) Plant 2 site, Waukegan, Illinois.

This section provides an overall approach to managing the project, including:

- Project organization, roles, and responsibilities
- Project definition and background
- Project task description
- Data quality objectives (DQOs)
- Special training requirements
- Documentation and records management

1.2 Project Organization

At the direction of the USEPA Region 5, CH2M HILL is responsible for all phases of RI work to be performed at the OMC Plant 2 site. CH2M HILL will perform the investigation and will provide project management. Table 1 and Figure 1 list the QA and management responsibilities of key project personnel.

1.2.1 USEPA Region 5 Work Assignment Manager

The USEPA Work Assignment Manager (WAM), Kevin Adler, has the overall responsibility for all phases of the RI. The WAM is also responsible for the review and approval of the QAPP.

1.2.2 USEPA Region 5 Quality Assurance Reviewer

The USEPA representative responsible for reviewing and approving this QAPJP and the attached Special Analytical Services (SAS) forms. They are also responsible for overseeing the USEPA data validation effort of the SAS and Contract Laboratory Program Routine Analytical Services (RAS) data.

1.2.3 CH2M HILL Program Manager

Ike Johnson, CH2M HILL's program manager, has overall responsibility for meeting USEPA objectives and CH2M HILL quality standards, as well as technical QC and project oversight.

1.2.4 CH2M HILL QA Manager

Regina Bayer, the QA manager, will remain independent of direct job involvement and day-to-day operations and has direct access to management staff to resolve QA disputes, as necessary. Specific functions and duties include:

- Directing the QA review of the various phases of the project, as necessary
- Directing the review of QA plans and procedures
- Providing QA technical assistance to project staff, as necessary

1.2.5 CH2M HILL Site Manager

Jewelle Keiser is the CH2M HILL Site Manager (SM) responsible for implementing the project and is authorized to commit resources to meet project objectives and requirements. The SM's primary function is to achieve technical, financial, and scheduling objectives. The SM will report directly to the USEPA Region 5 WAM and be the major point of contact for matters concerning the project. More specifically, the SM will:

- Define project objectives and develop a detailed work plan and schedule
- Establish project policy and procedures to address specific needs of the project as a whole, as well as the objectives of each task
- Acquire and apply technical and corporate resources to meet budget and schedule constraints
- Orient field leaders and support staff with regard to the project's special considerations
- Monitor and direct other team members
- Develop and meet ongoing project or task staffing requirements, including mechanisms to review and evaluate each task product
- Review the work performed on each task to ensure quality, responsiveness, and timeliness
- Review and analyze overall task performance with regard to planned schedule and budget
- Review external reports (deliverables) before submission to USEPA Region 5
- Represent the project team at meetings and public hearings

1.2.6 CH2M HILL Review Team Leader

Phil Smith, the review team leader, supports the SM in site management activities, coordinates CH2M HILL internal reviews, and will also be involved in ongoing planning activities.

1.2.7 CH2M HILL Project Chemist

Steven Paukner, the CH2M HILL project chemist, will be responsible for tracking data and overseeing the data evaluation. Specific responsibilities include the following:

- Schedule the analytical laboratories
- Oversee the tracking of samples and data from the time of field collection until results are entered into a database
- Coordinate activities with laboratories and data validators
- Oversee data validation and production of result tables
- Evaluate data usability

1.2.8 CT Laboratories, Analytical Subcontract Laboratory Project Manager

CT Laboratories (CTL) in Baraboo, Wisconsin, will perform the analyses. Eric Korthals is the project manager for CTL. Mr. Korthals will be responsible for coordinating and scheduling the laboratory analyses; supervising the in-house chain-of-custody (COC); accepting requirements outlined within this QAPP; and overseeing the data review and analytical reports preparation.CTL, QA Officer

CTL's QA officer is Dan Elwood. Mr. Elwood will be responsible for overseeing the laboratory QA and the analytical results QA/QC documentation; conducting the data review; selecting any necessary laboratory corrective actions; adherence to applicable in-house standard operating procedures (SOPs); adherence to the QAPP; and approving the final analytical reports.

1.2.9 STL Burlington, Analytical Subcontract Laboratory Project Manager

Severn Trent Laboratories (STL)—Burlington in Colchester, Vermont, will perform the analyses of air samples. Jeannine McCrumb is the project manager for STL-Burlington. Ms. McCrumb will be responsible for coordinating and scheduling the laboratory analyses; supervising the in-house chain-of-custody (COC); accepting requirements outlined within this QAPP; and overseeing the data review and analytical reports preparation.

1.2.10 STL-Burlington, QA Officer

STL-Burlingtons's QA officer is Kirstin McCraken. Ms. McCraken will be responsible for overseeing the laboratory QA and the analytical results QA/QC documentation; conducting the data review; selecting any necessary laboratory corrective actions; adherence to applicable in-house standard operating procedures (SOPs); adherence to the QAPP; and approving the final analytical reports.

1.3 Problem Definition / Background Information

1.3.1 Outboard Marine Corporation Operations/Early Investigations

The OMC Plant 2 site is at 100 E. Seahorse Drive, Waukegan, Illinois. The 65-acre site includes a 1,036,000 ft^2 former manufacturing plant building (i.e., Plant 2) and several

parking lot areas to the north and south of the building complex. The site includes three polychlorinated biphenyl (PCB) containment cells in which PCB-contaminated sediment (dredged from Waukegan Harbor in the early 1990s) and PCB-contaminated soil are managed. The East Containment Cell and the West Containment Cell are located north of OMC Plant 2. The third cell is located south of Seahorse Drive in former harbor Slip 3. OMC performed the harbor dredging work under a 1988 Consent Decree with USEPA and the Illinois Environmental Protection Agency (IEPA) that also required the long-term operations and maintenance of the containment cells.

OMC designed, manufactured, and sold outboard marine engines, parts, and accessories to a worldwide market for many years. Plant 2 was a main manufacturing facility for OMC—the major production lines used PCB-containing hydraulic and lubricating/cutting oils, chlorinated solvent-containing degreasing equipment, and smaller amounts of hydrofluoric acid, mercury, chromic acid, and other similar chemical compounds.

OMC filed for bankruptcy protection on December 22, 2000, and later abandoned the property after completing a limited removal action under USEPA oversight. In November 2001, the bankruptcy trustee filed a motion to abandon OMC Plant 2. USEPA conducted a site discovery inspection in spring 2002 to document the presence of numerous chemical compounds in OMC Plant 2 and support the allegation of imminent and substantial endangerment. Based on the findings, USEPA and the State of Illinois filed a joint objection to the abandonment and alleged that the site posed an imminent and substantial endangerment to public health and welfare and the environment. The bankruptcy trustee negotiated an emergency removal action scope of work with USEPA and IEPA that was approved by the court on July 17, 2002. The waste removal activities for the OMC Trust were completed in November 2002, and OMC Trust abandoned OMC Plant 2 property on December 10, 2002.

OMC Plant 2 history and operations, previous investigations and remediation, and physical and chemical conceptual models are; described in the *Field Sampling Plan* (FSP); (CH2M HILL 2004). Based on a review of existing data, the potential environmental problems and data needs for the OMC Plant 2 site include:

- PCB-contaminated metal structures and piping (i.e., nonporous surfaces), concrete block walls, painted metal walls, painted piping, painted girders (i.e., porous surfaces other than floors), and concrete floors in the Old Die Cast, Parts Storage, and Metal Working Areas. Additional sampling should be conducted to evaluate material handling and disposal options for PCB-contaminated building materials.
- Potential releases to Waukegan Harbor from sanitary sewers and storm sewers that were reportedly plugged and decommissioned or not decontaminated. Sewer lines should be tested to determine effectiveness of previous plugging and capping actions.
- PCB-contaminated sediments that were found in the North Ditch. The volume of sediments that will require remediation needs to be determined.
- Contaminated soils (PCBs and carcinogenic polynuclear aromatic hydrocarbons [CPAHs]) that were found near the former PCB aboveground storage tank (AST) area, northern parking lot areas, areas east of the Former Die Cast underground storage tank (UST) and AST area. Additional surface and subsurface soil samplings in the sand dunes

east of OMC Plant 2 and beneath the building are needed to define the nature and extent of contamination identified by previous investigations

- Chlorinated solvents were detected in soil and groundwater beneath the building where former solvent degreasers were located. Additional investigations, including soil and groundwater sampling, are needed to define nature and extent of hot spot areas beneath the building
- A chlorinated solvent groundwater plume that was identified as potentially migrating into Lake Michigan or Waukegan Harbor. Additional investigations (including soil, groundwater, and air sampling) are needed to define the nature and extent of the plume and related exposure routes.

1.3.2 Remedial Program Activities

OMC Plant 2 became designated as the fourth Operable Unit (OU) of the OMC National Priorities List site by the USEPA remedial program in 2003. CH2M HILL is scheduled to conduct remedial investigation/feasibility study (RI/FS) activities for the USEPA during the period of fall 2004 to fall 2005 to characterize the contamination present within and surrounding Plant 2. RI activities will include Plant 2 building materials investigation, soil and sediment investigation, groundwater investigation, and a soil gas investigation.

The purpose of the RI is to allow the USEPA (in consultation with IEPA) to select a remedial action to eliminate, reduce, or control risks to human health and the environment. The goal is to collect the minimum amount of data necessary to develop an approach for site remediation and to use the results in a well-supported Record of Decision or, if necessary, a Removal Action Memorandum within 24 months of approval of the RI/FS Work Plan.

1.4 Project Description and Schedule

1.4.1 Project Description

The field investigation has been designed to evaluate the impacts of OMC's historical operations and to verify and refine the extent and levels of residual contamination in the building materials in Plant 2, and surface soil, subsurface soil, groundwater, and soil gas sampling to identify potential impacts to air in the vicinity of the Larsen Marine buildings. OMC and USEPA have conducted multiple investigations at and near the site. The data from these investigations were evaluated and used to develop a conceptual model of existing site conditions. Additional sampling has been identified to verify existing data, fill in data gaps, and to collect site-specific information needed to prepare the FS. Specific sampling objectives and approaches were developed for each medium based on the conceptual model and future land use goals.

1.4.2 Project Schedule

Figure 2 shows the project schedule.

1.5 Data Quality Objectives and Criteria for Measurement Data

DQOs are qualitative and quantitative statements that specify the quality of data required to support decisions made during or after site-related activities. Project-specific DQOs are developed with the seven-step process presented below.

1.5.1 Step 1: State the Problem

The purpose of this investigation is to collect the data that will allow the USEPA (in consultation with IEPA) to select a remedial action to eliminate, reduce, or control risks to human health and the environment. Specific sampling objectives were developed for different medium, based on the existing information and the City of Waukegan's future land-use goals. The identified problems for the different media to be investigated are discussed below.

1.5.1.1 OMC Plant 2 Building Materials Investigation

As a result of spills and past waste handling practices within the Old Die Cast, Parts Storage, and Metal Working Areas in OMC Plant 2, 68,000 ft^2 of the concrete floor, various porous nonfloor surfaces, and metal structures and piping in the facility exhibit PCB contamination, specifically Aroclor 1248. Previous decontamination activities within the area proved unsuccessful and this investigation will serve to evaluate material handling and disposal options, and not to evaluate the extent of contamination.

1.5.1.2 Soil and Sediment Investigation

The data from the previous soil and sediment investigations conducted provide a well-defined picture of soil and sediment contamination outside the building, and extensive soil investigation is not necessary. Sediments in the North Ditch contain PCB concentrations above the likely remedial action objective (for Waukegan Harbor the remedial action level for PCB is 1 mg/kg at any single location and a surface-weighted average concentration of 0.25 mg/kg). Further sampling is not needed because the sediment volume is small, but a limited and focused field investigation will be conducted to fill in data gaps identified based on evaluation of the existing data.

1.5.1.3 Groundwater Investigation

The object for groundwater sampling is to define the nature and extent of contamination, to support the assessment of potential risk to human health and the environment, to determine whether remedial actions are necessary and, if so, to allow evaluation of remedial alternatives. The nature and extent of groundwater contamination is well-defined based on the data from the previous investigations. A focused field investigation will be conducted to verify current groundwater flow and water quality conditions indicated by existing data, to define the extent of contamination to the south, around "hot spot" areas and beneath parts of the plant that have no data, and to define the extent of nonaqueous phase liquid (NAPL).

1.5.1.4 Soil Gas and Air Investigation

Previous site data indicate that elevated concentrations of chlorinated volatile organic compounds (CVOCs) are present in groundwater south of the Plant 2 building and in the adjacent Larsen Marine Buildings. A limited and focused field investigation will be conducted by sampling the ambient air the in the Larsen Marine buildings and soil gas in

the subsurface soils south of the Plant 2 buildings to determine if volatilization from the underlying groundwater plume may cause exposure by inhalation.

1.5.2 Step 2: Identify the Decision

The RI monitoring effort has the following objectives.

1.5.2.1 OMC Plant 2 Building Materials Investigation

- Evaluate material handling and disposal options, not the extent of contamination.

1.5.2.2 Soil Investigation

- Define eastern contamination (CPAH and PCB) boundary of Former Die Cast UST/AST area located east of Plant 2
- Characterize sufficiently the soils near the PCB AST area and parking lot areas north of Plant 2 (between the two containment cells) to evaluate the potential for direct contact risk.
- Verify that soils in the uncovered grassy areas surrounding the corporate office buildings south of Plant 2 do not pose direct contact risk related to site-related contaminants.
- Determine contaminant concentrations in soil beneath building at selected groundwater investigation locations.
- Collect soil property data to evaluate contaminant fate and transport and remedial technologies.

1.5.2.3 Groundwater Investigation

- Verify current groundwater flow and water quality conditions indicated by existing data.
- Define the extent of contamination to the south, around "hot spot" areas and beneath parts of the plant that have no data.
- Define the extent of NAPL.

1.5.2.4 Soil Gas and Air Investigation

- Analyze the concentrations of CVOC vapors in subsurface soils south of Plant 2 to determine if volatilization from the underlying groundwater plume may pose an inhalation risk.
- Determine the levels of CVOCs in air within the Larsen Marine buildings.

1.5.3 Step 3: Identify the Inputs to the Decision

1.5.3.1 OMC Plant 2 Building Materials Investigation

Wipe sampling of nonporous surfaces (defined within TSCA [40 CFR 761.3] as a smooth, unpainted solid surface that limits penetration of liquid containing PCBs beyond the immediate surface) such as metal, and porous nonfloor (defined within TSCA [40 CFR 761.3] as "any surface that allows PCBs to penetrate or pass into itself including, but not

limited to, paint or coating on metal; corroded metal . . .") such as concrete block walls, painted metal walls, painted piping, and painted girders that are not visibly contaminated will be conducted and analyzed for PCBs. Analytical results will determine whether decontamination is necessary and, if contaminated (i.e., above 10 µg/100 cm^2), the type of thermal treatment or disposal that may be required.

Walls with PCB concentrations greater than 10 µg/100 cm^2 detected in wipe samples will be core sampled if concrete, or paint chips will be sampled if the surface is metal. Core or chip samples will be collected to determine disposal requirements for the material.

Concrete cores will be collected from porous nonfloor and floor surfaces that are visibly contaminated or exceed the wipe sample criterion of 10 µg/100 cm^2. The PCB results from the core samples will be compared to the 50-mg/kg TSCA disposal criterion to determine the disposal requirements and whether decontamination of walls before offsite disposal is cost-effective.

Sanitary and storm sewer lines outside the main building will be tested to verify their location and that they are no longer connected to Waukegan Harbor. Select sanitary sewer lines beneath the western part of Plant 2 (e.g., the Metal Working Area) also will be tested. The testing will be conducted to verify that the sanitary and storm sewers beneath Plant 2 no longer provide a direct pathway for releases to Waukegan Harbor or to Lake Michigan through the North Ditch.

1.5.3.2 Soil Investigation

Soil samples will be collected from beneath the building and analyzed for VOCs and PCBs. Random unsaturated soil samples beneath the buildings will also be analyzed for TAL metals. The sample locations will coincide with the groundwater investigation locations.

1.5.3.3 Groundwater Investigation

The groundwater investigation will be conducted using direct push technologies. The proposed approach is to use membrane interface probes (MIPs) to get vertical delineation of contamination and lithologic information (soil conductivity). Groundwater grab samples at selected locations will be collected and sent to an offsite laboratory for VOC analysis. The results of the groundwater samples will be used to correlate the MIPs response to a VOC concentration.

The MIP data will be used to determine locations (estimated 5 locations) for "micro wells" to be installed within the building and for permanent monitoring wells (estimated 10 locations) outside the building and their screened intervals. Water level measurements and groundwater samples will be collected from new and existing wells. The water samples will be analyzed for VOCs, SVOCs including PAHs/CPAHs, total and dissolved metals, and natural attenuation parameters.

Groundwater grab samples from beneath the building will be collected and analyzed for CVOCs. In addition, samples in the vicinity of the plating/foundry areas will also be analyzed for hexavalent chromium and filtered for dissolved metals analysis. If NAPL is encountered, samples will be collected and analyzed for VOCs and PCBs.

1.5.3.4 Soil Gas and Air Investigation

The soil gas and air investigation will be conducting using summa canisters and intake airflow regulators. Samples collected will be analyzed to determine what levels of CVOCs, if any, are present and what the potential risk factor is from the inhalation pathway.

1.5.4 Step 4: Define the Study Boundaries

The OMC Plant 2 site consists of about 65 acres, upon which are situated a 1,036,000 ft^2 former manufacturing plant building and several parking lot areas to the north and south of the building complex. To the east of the Plant 2 site is Lake Michigan and to the south is Larsen Marine and Waukegan Harbor. For a sample summary of the investigations described below, see Tables 2, through 5 of this QAPP and the *Field Sampling Plan*, Section 2, Figures 2-1 through 2-5,.

1.5.4.1 OMC Plant 2 Building Materials Investigation

The locations for samples will be determined during the site reconnaissance at the start of the field investigation. Unpainted overhead piping, metal girders, other unpainted metal surfaces, porous nonfloor and floor surfaces in the Old Die Cast, Parts Storage, and Metal Working Areas (i.e., areas where PCB contamination was previously found) will be sketched on a facility map. A photographic record will be made of the nonporous surfaces. Evidence of visual contamination, such as the presence of an oily film, will be noted on the sketch for later correlation to PCB wipe results. Wipe samples will be collected from 50 random sections of the nonporous nonfloor surfaces. Five wipe samples from the most visibly contaminated nonporous nonfloor surfaces will be collected to evaluate potential "worst case" conditions. The number of wipe samples may be reduced based on the results of the reconnaissance survey if a relatively small percentage of metal surfaces are unpainted.

Porous nonfloor surfaces with PCB concentrations greater than 10 $\mu g/100\ cm^2$ detected in wipe samples will be core sampled if concrete, or paint chips will be sampled if the surface is metal. Core or chip samples will be collected to determine disposal requirements for this material.

Concrete cores will be collected from porous nonfloor and porous floor surfaces that are visibly contaminated or exceed the wipe sample criterion of 10 $\mu g/100\ cm^2$. The PCB results from the core samples will be compared to the 50-mg/kg TSCA disposal criterion to determine the disposal requirements and whether decontamination of walls is cost-effective prior to offsite disposal. One porous floor core sample from the Old Die Cast, Parts Storage, and Metal Working Areas and one from the plating room (total of four samples) will be analyzed for total metals and by Synthetic Precipitation Leaching Procedure (SPLP). SPLP testing is proposed to determine the leachability of PCBs and metals in the concrete under a potential remedial alternative including leaving the concrete onsite.

Sanitary and storm sewer lines outside the main building will be tested to verify their location and that they are no longer connected to Waukegan Harbor. Select sanitary sewer lines beneath the western part of Plant 2 (e.g., the Metal Working Area) also will be tested.

1.5.4.2 Soil Investigation

The locations for the soil and sediment samples include the following:

- Former Die Cast UST/AST Area
- PCB Area North of the Plant
- Grassy Area Surrounding Corporate Building
- Beneath Plant 2
- Soil Sampling from New Monitoring Well Borings

1.5.4.3 Groundwater Investigation

The locations for the soil and sediment samples include the following:

- Existing Monitoring Wells
- New Monitoring Wells Outside Building
- New Monitoring Wells Within Building

1.5.4.4 Soil Gas and Air Investigation

The locations for the soil gas samples include the following:

- Subsurface soils south of OMC Plant 2 Building
- Larsen Marine Buildings

1.5.5 Step 5: Develop a Decision Rule

Contaminants of concern are those most likely to pose risk as a result of exposure. Based on the results of previous investigations by OMC and USEPA, the primary contaminants at the site include VOCs (primarily CVOCs), SVOCs, PAHs, PCBs and metals (arsenic, barium, cadmium, chromium, and lead).

The existing data indicate that elevated concentrations of PCB and CVOCs in the soil are likely to pose risk to human health that exceeds the acceptable risk range of 1×10^{-4} to 1×10^{-6} excess lifetime cancer risk (ELCR) and the Hazard Index (HI) of 1. As a result, it may be possible to streamline the risk assessment to an assessment of potential exposure pathways and a qualitative comparison to Illinois TACO Tier I Remediation Objectives or USEPA's preliminary remedial goals, rather than quantifying the risk. The need for a quantitative risk assessment will be reevaluated upon completion of the RI.

Table 6 lists the parameters and associated Illinois TACO Tier I Remediation Objectives. Those objectives are the cleanup criteria for the soils, sediments, and groundwater at the OMC site.

1.5.5.1 OMC Plant 2 Building Materials

PCB Wipe Sample Concentrations < 10 µg/100 cm²

- If the wipe samples collected from unpainted metal structures or piping, wall materials, and floor materials contain PCB concentrations < 10 µg/100cm², the metal can be sold as scrap without treatment or disposal requirements.

- If the wipe samples collected from unpainted metal structures or piping, wall materials, and floor materials that contain no indications of PCB contamination (i.e., no visible oily film) exhibit PCB concentrations < 10 µg/100 cm² the metal can be sold as scrap without treatment or disposal requirements.

PCB Wipe Sample Concentrations >10 µg/100 cm² and < 100 µg/100 cm²

- If the wipe samples collected from unpainted metal structures or piping, wall materials, and floor materials contain PCB concentrations < 100 µg/100cm² and greater than 10 µg/100cm² (40 CFR 761.61 (a)(5)(ii)(B)(1)), the scrap can be smelted directly in a smelter in compliance with 40 CFR 761.72 or disposed of in a RCRA Subtitle D solid waste landfill (40 CFR (a)(5)(ii)(B)(1)).

PCB Wipe Sample Concentrations >100 µg/100 cm²

- If the wipe samples collected from unpainted metal structures or piping, wall materials, and floor materials contain PCB concentrations greater than 100 µg/100cm² the scrap must be thermally treated, per 40 CFR 761.61(a)(5)(ii)(B)(2), in a scrap metal recovery oven in compliance with 40 CFR 761.72 or disposed of in a RCRA Subtitle C hazardous waste landfill or a TSCA chemical waste landfill (40 CFR (a)(5)(ii)(B)(2)).

Unpainted metal structures or piping, wall materials, and floor materials may be decontaminated onsite prior to sale as scrap to reduce PCB concentrations to below 100 µg/100 cm².

1.5.5.2 Porous Surfaces Other Than Floors

PCB Wipe Sample Concentrations < 10 µg/100 cm²

Walls with PCB concentrations < 10 µg/100 cm² detected in wipe samples will be considered uncontaminated, and no additional samples will be collected (40 CFR 761). Wall materials will be disposed of in a RCRA Subtitle D solid waste landfill or potentially considered for onsite disposal.

PCB Wipe Sample Concentrations > 10 µg/100 cm²

Walls with core or chip sample PCB concentrations > 50 mg/kg will be disposed of in a RCRA Subtitle C hazardous waste landfill or a TSCA chemical waste landfill. Walls with core or chip sample PCB concentrations < 50 mg/kg will be disposed of in a RCRA Subtitle D solid waste landfill or considered for onsite disposal.

1.5.5.3 Porous Floor Surfaces

The results from porous floor concrete samples will be compared to the 50-mg/kg TSCA limit to determine the general proportion of the concrete in the Old Die Cast, Parts Storage, and Metal Working Areas that will require disposal in a Subtitle D landfill versus disposal in a Subtitle C or TSCA chemical waste landfill.

1.5.5.4 Sanitary and Storm Sewers

Testing will be conducted to verify that the sanitary and storm sewers beneath Plant 2 no longer provide a direct pathway for releases to Waukegan Harbor or to Lake Michigan through the North Ditch.

1.5.6 Step 6: Specify Limits on Decision Errors

The probability of sampling and measurement errors at any site under investigation necessitates the development of sampling guidelines and the collection of quality control

samples. Field errors are minimized by having each member of the field team follow the same field operating procedures (FOPs) for sampling. Sampling techniques are discussed in detail in the FSP. QC samples are used to verify the accuracy and precision of the data. When a QC sample is outside the established control limits, the data will be qualified and field corrective action implemented when applicable (such as when field duplicates are outside established control limits).

Field data, such as groundwater pH, temperature, specific conductance, dissolved oxygen, and oxidation-reduction potential, will not be subject to data validation.

1.5.7 Step 7: Optimizing the Design

The sampling design objectives are to assess the material handling and disposal options of plant building materials and soils beneath the building, define the contamination boundaries for CPAH and PCB, characterize the PCB contamination in soils, verify that soils will not pose direct contact risk related to site contaminants, verify groundwater flow and water quality conditions, determine the presence or absence of CVOCs in soil gas and air, and define the extent of contamination in the area south of Plant 2 that has no data associated with it.

1.5.8 Measurement Performance Criteria

The measurement performance criteria are checked on several levels:

- Built-in QC standards
- Senior review
- Management controls

The measurement data must abide by specific QC standards. Data that do not meet these standards are qualified accordingly. The analytical data and the QC results are checked by the bench chemist, the Laboratory's QA Manager, CH2M HILL's project chemist, and the USEPA's data validator.

CH2M HILL staff members with relevant technical experience will review all documents that pertain to the project's quality standards. The Field Team Leader (FTL) will supervise activities to assess if FOPs are being followed during field sampling activities. Section 3 describes the specific QC checks and corrective action measures.

1.6 Instructions for Special Training Requirements and Certification

As noted in Subsection 1.2, "Project Organization," the project team members with the necessary experience and technical skills were chosen to perform required project tasks.

CTL and STL-Burlington will meet project-specific requirements and USEPA and Illinois Tier 1 Remediation specifications. One criterion for the new subcontract will be that the laboratory must be Illinois-certified for all analyses.

1.7 Instructions for Documentation and Records

1.7.1 Field Sampling Documentation

Field sampling activities will be recorded in field logbooks. Logbook entries will provide as much detail as possible so that persons going to the site can reconstruct a particular situation without reliance on memory. Modifications to field sampling protocols must be documented in the field logbook. The FTL is responsible for ensuring that modifications to sampling protocols are so documented.

Field logbooks will be bound field survey books or notebooks. Logbooks will be assigned to the field crew, but stored in a secure location when not in use. Project-specific document numbers will identify each logbook, the title page of which will contain:

- The name of the person to whom the logbook is assigned
- Logbook number
- Project name
- Project start date
- Project end date

At the beginning of each entry, the date, start time, weather, names of all sampling team members present, and the signature of the person making the entry will be documented. Measurements and samples collected will be recorded with a detailed description of the location of the station. The number of photographs taken also will be noted. Equipment used to make measurements will be identified, along with the date of calibration.

All entries will be made in ink, and no erasures will be allowed. If an incorrect entry is made, the information will be crossed out with a single strike mark and initialed. Blank pages will be noted as being intentionally blank.

Samples will be collected following the sampling procedures documented in the field sampling FOPs located in the FSP. Sample collection equipment will be identified, along with the time of sampling, sample description, parameters being analyzed, and number of containers. Unique sample identification numbers (IDs) will be assigned to each sample. Field duplicate samples, which will receive an entirely separate sample ID, will be noted in the field logbook.

Field personnel will provide comprehensive documentation of all aspects of field sampling, field analysis, and sample chain of custody (COC). This documentation constitutes a record that allows reconstruction of all field events to aid in the data review and interpretation process. All documents, records, and information relating to the performance of the fieldwork will be retained in the project file.

1.7.2 Data Reporting

For the purpose of this investigation, two data reporting levels have been defined:

- **Level 1—Field Data, Treatment System Test Data, and Health and Safety Reporting.** This level of minimal or "results only" reporting is used for the field data, treatment

system performance data (nonpermit-required data), and health and safety monitoring. This is because they do not generate or require extensive supporting documentation.

- **Level 2—Analytical Reporting.** Full Contract Laboratory Program (CLP)-equivalent reporting is required for all non-field data.

1.7.2.1 Field Data Reporting

Information collected in the field through visual observation, manual measurement, or field instrumentation will be recorded in field notebooks and then entered into an electronic data log. The FTL or project chemist will review the data for adherence to this QAPP and for consistency. Any concerns identified as a result of this review will be discussed with the SM and QA Manager, corrected if possible, and incorporated into the data evaluation process.

Field data calculations, transfers, and interpretations will be conducted by the field crew and reviewed for accuracy by the FTL or project chemist. The appropriate task manager will review field documentation, data reduction, and accuracy of data entries into the data log. The data logs and documents will be checked for:

- General completeness
- Readability
- Use of appropriate procedures
- Whether modifications to sampling procedures are clearly stated
- Appropriate instrument calibration and maintenance records
- Reasonability of data collected
- Correctness of sample locations
- Correctness of reporting units, calculations, and interpretations

Where appropriate, field data forms and calculations will be processed and included in appendixes to the report. Original field logs, documents, and data reductions will be kept in the project file.

1.7.2.2 Laboratory Data Reporting

Calculations for analyses are based on regression analysis of calibration curves. Regression analysis is used to fit a curve through calibration standard data. Sample concentrations are calculated using the resulting regression equations.

Whenever possible, analytical data will be transferred directly from the instrument to a computerized data system. Raw data will be stored electronically and a hard copy file will be maintained. Laboratory data entry will be sufficient to document information used to arrive at reported values.

Electronic data storage shall be used when possible. All electronic data shall be maintained in a manner that prevents inadvertent loss, corruption, and inappropriate alteration. Electronic data shall be accessible and retrievable for a period of 10 years after project completion.

Raw data will be examined to assess compliance with QC guidelines stated in the appropriate analytical SOPs that will be provided by the subcontracted laboratory (Appendix A). Analytical SOPs for non-CLP laboratory work will be submitted for USEPA review on comment upon completion of the subcontract laboratory procurement process.

Surrogate, matrix spike, and QC check sample recoveries will be checked. In addition, samples and lab blanks will be checked for possible contamination or interferences. Chromatograms (where applicable) and concentrations will be checked to ensure that sample results are within the calibration range. If necessary, dilutions will be performed as defined by the initial calibration range.

Deviations from stated guidelines call for corrective action. Deviations caused by factors outside the laboratory's control, such as matrix interference, will be noted with an explanation in the report narrative. Calculations will be checked and the report reviewed for errors and oversights.

Upon completion, a report will be reviewed for discrepancies, errors, or omissions. Data will then be submitted to the Laboratory QA Manager for review and approval. The Laboratory QA Manager will review the package, ensure that any necessary corrections are made, and then give the package to the Laboratory Project Manager for review. A copy of the data package will be filed in the project file. Mailed data packages, along with applicable electronic data deliverables (EDDs), will be sealed in an appropriate shipping container with a custody seal and logged into a document mailing log.

All laboratory hard copy data deliverables will be submitted by CTL and STL-Burlington in the format specified in the laboratory Scope of Work (SOW).

1.7.3 Electronic Analytical Record Format

CH2M HILL requests that three ASCII text files be generated as the EDDs for each batch/ sample delivery group: one for sample data, one for tests and results with QC data, and one for test batch data. The specifications for these files are given to the laboratory in the laboratory contract or SOW.

1.7.4 Project Record Maintenance and Storage

Project records will be stored and maintained in accordance with CH2M HILL's Data Management Plan (DMP), discussed in Subsection 2.10 of this QAPP. Each project team member is responsible for filing all project information or providing it to the project assistant familiar with the project filing system. Individual team members may maintain separate files or notebooks for individual tasks but must provide such materials to the project file room upon completion of each task.

The general project file categories are:

- Correspondence
- Nonlaboratory project invoices and approvals by vendor
- Original unbound reports
- Nonlaboratory requests for proposals, bids, contracts, and statements of work
- Field data
- Data evaluation and calculations
- Site reports from others
- Bound report copies of Category C
- Photographs
- Insurance documentation

- Laboratory analytical data and associated documents/memos
- Regulatory submittals, licensing, and permitting applications
- Site and reference material
- Health and safety plans
- Figures and drawings

A project-specific index of file contents is kept with the project files at all times.

SECTION 2

Data Generation and Acquisition

This section describes the procedures for acquiring, collecting, handling, measuring, and managing data in support of this sampling activity. It addresses these data generation and acquisition aspects:

- Sampling process design
- Sampling method requirements
- Sample handling and custody requirements
- Laboratory analytical methods requirements
- Laboratory QC requirements
- Field and laboratory instrument calibration and frequency
- Inspection and acceptance requirements for supplies and consumables
- Data acquisition requirements
- Data management
- Field and laboratory instrument and equipment testing, inspection, and maintenance requirements

2.1 Sampling Process Design

The sampling locations and sample quantity were chosen to best fulfill the project objectives stated in Step 2 of the DQO process. The sampling design consists of four parts: OMC Plant 2 building materials, soil, groundwater, soil gas, and air. For more information on proposed sample locations and quantities, refer to Tables 2 through 5 of this QAPP and the *Field Sampling Plan*, Section 2, Figures 2-1 through 2-5.

2.1.1 OMC Plant 2 Building Materials

Wipe sampling of nonporous surfaces (defined within TSCA [40 CFR 761.3] as a smooth, unpainted solid surface that limits penetration of liquid containing PCBs beyond the immediate surface) such as metal, and porous nonfloor (defined within TSCA [40 CFR 761.3] as "any surface that allows PCBs to penetrate or pass into itself including, but not limited to, paint or coating on metal; corroded metal . . . ") such as concrete block walls, painted metal walls, painted piping, and painted girders that are not visibly contaminated will be conducted and analyzed for PCBs. Analytical results will determine whether decontamination is necessary and, if contaminated (i.e., above 10 µg/100 cm^2), the type of thermal treatment or disposal that may be required. (See Table 7 for analytes and reporting limits for concrete core and wipe samples.)

Walls with PCB concentrations greater than 10 µg/100 cm^2 detected in wipe samples will be core sampled if concrete or paint chips will be sampled if the surface is metal. Core or chip samples will be collected to determine disposal requirements for this material.

Concrete cores will be collected from porous nonfloor and floor surfaces that are visibly contaminated or exceed the wipe sample criterion of 10 µg/100 cm^2. The PCB results from the core samples will be compared to the 50-mg/kg TSCA disposal criteria to determine the disposal requirements and whether decontamination of walls is cost-effective prior to offsite disposal.

Sanitary and storm sewer lines outside the main building will be tested to verify their location and that they are no longer connected to Waukegan Harbor and no longer provide a direct pathway for releases to Waukegan Harbor or to Lake Michigan through the North Ditch.

2.1.2 Soil and Sediment Sampling

Surface soil samples from locations outside the building will be collected using direct push technology from above the water table (estimated depth of about 4 feet). Additional sample intervals maybe be collected based on visual or olfactory evidence of contamination or high levels of organic vapors as indicated by a photoionization detector or equivalent instrument. These unsaturated soil samples will be analyzed for VOCs, SVOCs, and PCBs. Selected soil samples will be analyzed for total organic carbon and soil oxidant demand. (See Table 8 for analytes and reporting limits for soil and sediment samples.)

A field survey will be performed to estimate the volume of sediment in the North Ditch (measuring width and thickness of sediments along multiple transects). Sediment thickness locations will be staked and survey coordinates determined during site reconnaissance activities. The depth of sediments in the North Ditch will be investigated in a grid pattern using a range pole equipped a metal tip and steel shaft. Personnel performing sediment probing will wear waders and appropriate personal protective equipment. Sediment thickness transects will be spaced every 300 feet. Each transect will include three thickness measurements: one near each shore sediment/water interface and one at the approximate center of each transect.

2.1.3 Groundwater Investigation

The groundwater investigation will be conducted using direct push technologies. The proposed approach is to use MIPs to get vertical delineation of contamination and lithologic information (soil conductivity). Groundwater sample locations will correspond with proposed soil sample locations. Groundwater grab samples at selected locations will be collected and sent to an offsite laboratory for VOC analysis. The results of the groundwater samples will be used to correlate the MIPs' response to a VOC concentration.

The MIP data will be used to determine locations (estimated five locations) for "micro wells" to be installed within the building and locations for permanent monitoring well locations (estimated 10 locations) outside the building and their screened intervals. Water level measurements and groundwater samples will be collected from new and existing wells. The water samples will be analyzed for VOCs, total and dissolved metals, and natural attenuation parameters.

Groundwater grab samples from beneath the building will be collected and analyzed for CVOCs. In addition, samples in the vicinity of the plating/foundry areas will also be

analyzed for hexavalent chromium and filtered for dissolved metals analysis. If NAPL is encountered, samples will be collected and analyzed for VOCs and PCBs.

(See Table 9 for analytes and reporting limits for groundwater samples.)

2.1.4 Soil Gas and Air Investigation

The soil gas investigation will be conducting using Summa™ canisters and 8-hour intake flow regulators. Samples will be taken of the indoor air in the Larsen Marine buildings and soil gas in the subsurface soils south of the Plant 2 buildings. Indoor air samples from within the Larsen Marine buildings will be collected using Summa canisters with 8-hour flow regulators. The canisters will be set up to collect air samples during nonworking hours. Subsurface air samples will be collected via direct push technologies. Samples will be collected in Summa canisters by connecting a hose from the push rod to the canister. Samples collected will be analyzed to determine what levels of CVOCs, if any, are present and what the potential risk factors are for exposure by inhalation. (See Table 10 for analytes and reporting limits for soil gas and air samples.)

2.1.5 Water Level Measurements

Water level measurements will be collected using a standard water level indicator. If encountered during the investigation product levels will be measured using an oil/water interface probe to assess NAPL thickness.

2.1.6 Field Parameters

Dissolved oxygen, pH, oxidation/reductive potential, temperature, and specific conductance measurements will be taken at each groundwater sample location during sampling. Where possible, three well volumes will be extracted from each location before sampling and the field parameter readings will be documented after each well volume is extracted.

2.2 Sampling Method Requirements

The following FOPs are contained in the FSP for field sampling method and decontamination procedures:

- Water level measurement and well purging
- PCB wipe sampling
- Bulk concrete sampling
- Direct-push soil sampling
- MIP
- HSA drilling and sampling
- Monitoring well and soil boring abandonment
- VOC soil sampling
- In situ soil oxidant demand sampling
- Low-flow sampling
- In situ hydraulic testing
- Soil sampling

- Monitoring well sampling
- Soil vapor sampling
- Decontamination

Before sampling at a station, reusable (i.e., nondedicated) sampling equipment will be scrubbed with Alconox, rinsed with distilled water, then rinsed with methanol, again rinsed with distilled water, and air-dried. Large sampling equipment will be washed with a high-pressure water wash using a brush as necessary, to remove any particles. Field blanks will be collected by passing HPLC-grade laboratory water over decontaminated sampling equipment. The field blanks will then be analyzed for the same parameters as the field samples to assess the effectiveness of the decontamination procedures.

2.3 Sample Handling and Custody Requirements

2.3.1 Sample Handling and Preservation

Table 11 summarizes the sample preservation and holding requirements.

Corrective actions will be taken as soon as a problem is identified. Such actions may include discontinuing the use of a specific bottle lot; contacting the bottle suppliers for retesting the representative bottle from a suspect lot; resampling suspect samples; validating the data, taking into account that the contaminants could be introduced by the laboratory (e.g., common lab solvents, sample handling artifacts) as a bottle QC problem; and determining whether the bottles and data are usable.

2.3.2 Sample Identification System

CH2M HILL has devised a sample-numbering system that will be used to identify each sample, including duplicates and blanks. Detailed sample-numbering information is located in Section 4.1.1, Sample Identification of the FSP.

2.3.3 Sample Packaging

Sample handling, packaging and shipping procedures are described in FOP-14, Sample Handling, Packaging, and Shipping, of the FSP.

Sample coolers will be shipped to arrive at the CLP or independent laboratories the morning after sampling (priority overnight) or will be sent by a courier to arrive the same day. For non-CLP samples analyzed at an independent laboratory, the laboratory will be notified of the sample shipment and the estimated date of arrival of the samples being delivered.

2.3.3.1 Shipping Airbills

If samples are shipped, airbills will be retained to provide a record for sample shipment to the laboratory. Completed airbills will accompany shipped samples to the laboratory and be forwarded along with data packages. The airbill number will be documented on the COC form accompanying the samples to the laboratory for sample-tracking purposes. Airbills will be kept as part of the data packages in the project files.

2.3.4 Sample Custody

Accurate records and control of sample and data custody are necessary to provide relevant and defensible data. COC is addressed during field sample collection, data analyses in the laboratory, and through proper handling of project files. Persons will be considered to have custody of samples when samples are in their physical possession, in their view after being in their possession, or in their physical possession and secured to prevent tampering. In addition, when samples are secured in a restricted area accessible only to authorized personnel, they will be deemed to be in the custody of such authorized personnel.

COC forms will provide the record of responsibility for sample collection, transport, and submittal to the laboratory. Field personnel designated as responsible for sample custody will fill out COC forms at each sampling site, at a group of sampling sites, or at the end of each day of sampling. If samples are relinquished by the designated sampling person to other sampling or field personnel, COC forms will be signed and dated by the appropriate personnel to document the custody transfer. Original COC forms will accompany samples to the laboratory, and copies will be forwarded to the project files.

2.3.4.1 Field Custody Procedures

COC forms are required for all samples. The sampling crew in the field will initiate COC forms. COC forms will contain the sample's unique ID, sample date and time, sample description, sample type, preservation (if any), and analyses required. Original COC forms, signed by the sampling crew, will accompany the samples to the laboratory. A copy of relinquished COC forms will be retained with the field documentation. COC forms will remain with the samples at all times. Samples and signed COC forms will remain in the sampling crew's possession until samples are delivered to the express carrier (e.g., Federal Express), hand delivered to the laboratory, or placed in secure storage.

2.3.4.2 Laboratory Custody Procedures

Laboratory custody procedures will be in place to ensure the integrity of sample and laboratory data handling. Laboratory custody procedures for the non-CLP laboratory will be defined in the laboratory's COC Standard Operating Procedure and will be included in Appendix A upon completion of the procurement process for the subcontract laboratory.

2.3.4.3 Laboratory Sample Receipt

Upon sample receipt, the Laboratory Sample Custodian will verify package seals, open the packages, check temperature blanks (and record temperatures), verify sample integrity, and inspect contents against COC forms. The Laboratory Project Manager will be contacted to resolve any discrepancies between sample containers and COC forms. Once the shipment and COC form are in agreement, the Sample Custodian will initiate an internal COC form as well as supply the laboratory task manager with a sample acknowledgement letter. When applicable, sample preservation will be checked and pH documented. If the sample temperatures are outside the required range, the laboratory will contact the project manager or the contractor as to the proper course of action.

Samples will be logged into the Laboratory Information Management System (LIMS), which assigns a unique laboratory number to each sample. LIMS will be used by all laboratory personnel handling samples, to ensure all sample information is captured. Analyses

required will be specified by codes assigned to samples at log-in. Labels containing the laboratory sample number are generated and placed on sample bottles.

2.3.4.4 Laboratory Sample Storage

After the laboratory labels the samples, they will be moved to locked refrigerators where they will be maintained at 4°C. Soil samples may be frozen. If soil samples are frozen, the holding time stops accumulating at the time the sample freezes, and begins accumulating again at the time the sample begins to thaw. Access to refrigerators will be limited to members of the sample management department.

When samples are required, an appropriate member of the sample management department will locate the samples in the locked refrigerator, sign and date the internal sample tracking form and provide the sample(s) to the analyst. When the analyst is finished with samples, unused portions will be returned to an appropriate member of the sample management department for replacement in a secure refrigerator. The analyst will sign and date internal COC forms. In the event that entire samples are depleted during analysis, a notation of "sample depleted" or "entire sample used" will be made on the internal COC forms.

Sample extracts will be stored in designated secure, refrigerated storage areas. Samples and sample extracts will be maintained in secure storage until disposal. No samples or extracts will be disposed of without prior written approval from an appropriate member of the Project Team. The Sample Custodian will note sample disposal date in the sample ledger. The laboratory will dispose of samples in accordance with applicable regulations.

2.3.4.5 Laboratory Logbooks

Workbooks, bench sheets, instrument logbooks, and instrument printouts will be used to trace the history of samples through the analytical process and document important aspects of the work, including associated QC. As such, all logbooks, bench sheets, instrument logs, and instrument printouts will be part of the laboratory's permanent record. In addition, relevant information will be entered into the LIMS at the time information is generated.

Each page or entry will be dated and initialed by the analyst at the time of entry. Entry errors will be crossed out in indelible ink with a single stroke, corrected without obliterating or writing directly over the erroneous entry, and initialed and dated by the individual making the correction. Unused pages of logbooks will be completed by lining out unused portions that are then initialed.

The analyst will record information regarding the sample, the analytical procedures performed, and the results on laboratory forms or personal notebook pages, and enter this information in LIMS. These notes will be dated and will identify the analyst, instruments used, and instrument conditions.

Sufficient raw data records must be retained to permit reconstruction of initial instrument calibrations (e.g., calibration date, test method, instrument, analysis date, each analyte name, concentrations and responses, calibration curves, response factors, or unique equations or coefficients used to reduce instrument responses into concentrations).

The laboratory group leaders will periodically review laboratory notebooks for accuracy, completeness, and compliance with this QAPP. The laboratory group leader will verify all

entries and calculations. If all entries on the pages are correct, the laboratory group leader will initial and date the pages. Corrective action will be taken for incorrect entries before the laboratory group leader signs.

2.3.4.6 Laboratory Project File

Documentation will be placed in a single, secured project file, maintained by the Laboratory Project Manager. This file will consist of these components, all filed chronologically:

- Agreements
- Correspondence
- Memos
- Notes and Data

Reports (including QA reports) will be filed with correspondence. Analytical laboratory documentation and field data will be filed with notes and data. Filed materials may only be removed by authorized personnel on a temporary basis. The name of the person removing the file will be recorded. Laboratories will retain will project files and data packages for a minimum of 7 years unless otherwise agreed.

2.3.4.7 Computer Tape and Hard Copy Storage

All electronic files will be maintained on CD-ROM (preferred media), magnetic tape, or diskette for 10 years; hard copy data packages (including chromatograms) will be maintained in files for 7 years. The computer tape and hard copy storage should include notation of instrument run files and calibration.

2.4 Analytical Method Requirements

Once the samples have been properly collected and documented, they will be sent to a USEPA CLP laboratory for analysis. Certain analyses that cannot be performed by CLP laboratories will be sent to CTL, an offsite laboratory subcontracted by CH2M HILL for analysis. All air samples will be sent to STL-Burlington for analyses.

The analytical methods chosen meet both the USEPA and Illinois Tier 1 Remediation Objectives and the required level of quantification. Table 11 lists the required methodologies and Tables 6 through 9 list the quantification limits for the analyses to be performed during the RI.

The laboratory will use analytical SOPs to ensure that the samples submitted are accurate and analyzed precisely. The analytical SOPs reflect the requirements of the stated methods while including internal QC criteria. The QC criteria used during the analyses will be those stated within the analytical SOPs obtained and included in Appendix A once procurement of the laboratory is completed.

2.5 Quality Control Requirements

The analytical laboratory shall have a QC program to assess the reliability and validity of the analyses being performed. The purpose and creation of QC samples is discussed and summarized below.

2.5.1 Quality Control Samples

2.5.1.1 Field Duplicates

Field duplicate samples will be used to measure the heterogeneity of the sample matrix and the precision of the field sampling and analytical process. Duplicate samples will be collected at a frequency of one duplicate per 10 samples per sampling technique collected for each medium.

For soils, field duplicate samples will be collected by placing the soil in a decontaminated stainless steel bowl, mixing the sample by stirring, and then filling the individual sample and duplicate containers from the bowl. VOC soil duplicate samples will not be collected in this manner. VOC soil duplicates samples will be obtained first by collecting the original sample and then collecting the duplicate sample as close as possible to the original sample.

Groundwater field duplicate samples will be collected by alternately filling first the sample bottle for one analysis and then the duplicate bottle for one analysis. This procedure will be followed until the bottles for all analyses are filled. If dissolved metals samples are collected, a separate inline filter will be used to fill the sample and duplicate containers.

The sample bottles will be labeled as described in this plan. The samples will be preserved and stored in the same manner as the field samples. The frequency of collection will be at least 10 percent.

Wipe sample field duplicates will be collected by locating a compact, contiguous and homogeneous area where a representative wipe sample can be collected. Collect the wipe sample and the duplicate wipe sample within designated sample area using alternating wipe paths, taking care to avoid any overlap.

Concrete core sample field duplicates will be collected from the same core or from multiple cores collected as close to together as possible. The sampling approach will be documented in the field log book.

2.5.1.2 Equipment Blanks

Equipment (field) blanks will be collected and analyzed to determine whether the decontamination procedure has been adequately performed and that there is no cross-contamination of samples occurring due to the equipment or residual decontamination solutions. Equipment blanks will be collected for all matrices to be sampled. A consistent volume of demonstrated analyte-free distilled and deionized water will be poured directly into or over the decontaminated sampling equipment and then collected in a sample container. The sample bottles will be labeled as described in the plan. The samples will be preserved and handled in the same manner as the groundwater samples. The frequency of collection will be at least five percent.

2.5.1.3 Trip Blanks

Trip blanks will be used to determine if any onsite atmospheric contaminants are seeping into the sample bottles, or if any cross-contamination of samples is occurring during shipment or storage of sample containers. Aqueous trip blanks will be included with both groundwater and soil VOC samples.

Aqueous trip blanks will consist of demonstrated analyte-free distilled and deionized water preserved with 1:1 HCl to a pH of less than or equal to 2 standard units in 40-mL Teflon®-lined septum vials. One set of trip blanks will accompany each sample cooler containing one or more VOC samples. The sample bottles will be labeled as described in this plan. The samples will be stored in the same manner as the groundwater samples.

2.5.1.4 Matrix Spike/Matrix Spike Duplicate

Matrix spike/matrix spike duplicate (MS/MSD) samples will be used by the laboratories to assess the precision and accuracy of sample analysis. The MS/MSD samples will be fortified by the laboratories in accordance with the specifications of the analytical methods. Two extra volumes of sample are required for each combination of MS/MSD samples. Sample containers will be filled and stored in the same manner as field duplicate samples. The frequency for collection of MS/MSD samples will be at least 5 percent.

2.5.1.5 Temperature Blanks

A temperature blank will be included in each cooler to allow the laboratory receiving the shipment of samples to determine if the samples have been maintained at the proper temperature. Temperature blanks will consist of a unpreserved sample container filled with distilled water. One temperature blank will accompany each sample cooler being shipped to the laboratory.

2.5.1.6 Laboratory QC

Laboratory QC samples, such as laboratory control samples and surrogates, will be discussed in the analytical SOPs.

2.5.2 Decontamination Procedures

Decontamination of personnel, sampling, monitoring and heavy equipment will follow the procedures presented in the FSP in FOP-17, Decontamination of Drilling Rigs and Equipment and FOP-18 Decontamination of Personnel and Sampling Equipment. The potable water to be used in equipment decontamination will be either from bottles or from a public water supply system. A sample of the water from each source used will be collected at the time of its first use and sent for VOCs, SVOCs, and metals analyses.

2.5.3 Disposal of RI-Generated Wastes

The waste materials generated during a field investigation are known as investigation-derived wastes. Materials that may become investigation-derived wastes requiring proper treatment, storage and disposal are:

- Personnel protective equipment, including disposable coveralls, gloves, booties, and respirator canisters
- Disposable equipment, including plastic ground and equipment covers, aluminum foil, Teflon tubing, broken or unused sample containers, sample container boxes, and tape
- Soil cuttings from drilling, probing or hand auguring
- Groundwater obtained through well development or well purging

- Decontamination water

Management of investigation-derived wastes and materials will be performed consistent with the USEPA guidance *Guide to Management of Investigation-Derived Wastes*, 9345.3-03FS (January 1992). Disposable equipment (including personal protective equipment) and debris will be containerized and appropriately labeled during the sampling events and disposed of accordingly. All purged groundwater and water generated during equipment decontamination will be containerized and staged onsite in a 55-gallon drum or "poly" tank, and will be disposed of appropriately based on analytical results. Equipment will be decontaminated as appropriate, as discussed in the FSP in FOP-17, Decontamination of Drilling Rigs and Equipment, and FOP-18, Decontamination of Personnel and Sampling Equipment. All soil cuttings associated with drilling, direct push technologies, and other subsurface investigations will also be collected and stored onsite in a 55-gallon drum or "roll-off" box and disposed of accordingly following receipt of analytical results. OMC Plant 2 will include support facilities for material storage and staging.

Investigation derived waste samples will be collected and analyzed to determine appropriate disposal procedures. If the total analyses demonstrates that the regulatory levels are not exceeded, the TCLP analysis does not need to be performed. Therefore, the investigation derived waste samples will be extracted as if running TCLP analyses, but the laboratory will first run for total concentrations. If the total concentration of a sample is greater than the TCLP limits, the laboratory will then analyze the extracts using TCLP methods.

2.5.4 Data Precision, Accuracy, and Completeness

Field quality assurance/quality control (QA/QC) samples and laboratory internal QA/QC samples are collected and analyzed to assess the data's usability. Table 12 states the acceptance criteria for precision and accuracy requirements for these QC samples. This criteria is also stated in the laboratory SOW and analytical SOPs. The QA/QC criteria for the internal laboratory QC samples that are not referenced in the appropriate analytical SOPs shall be those stated in the referenced methods. Completeness is the percentage of usable data obtained during the sampling event and its acceptance criteria is project-specific.

2.5.4.1 Precision

The precision of laboratory analysis will be assessed by comparing the analytical results between MS/MSDs. The precision of the field sampling procedures will be assessed by reviewing field duplicate sample results. The relative percent difference (%RPD) will be calculated for the duplicate samples using the equation

$$\%RPD = \{(S - D)/[(S + D)/2]\} \times 100$$

where:

S	=	First sample value (original value)
D	=	Second sample value (duplicate value)

As noted, the precision criteria for duplicate samples will be ± 20 percent for aqueous samples and ± 30 percent for soil. Sample results shall be qualified "J" as estimated in

quantity when the QC limit is exceeded. The acceptable MS/MSD precision criteria are stated in the laboratory SOW.

2.5.4.2 Accuracy

Accuracy of laboratory results will be assessed for compliance with the established QC criteria using the analytical results of method blanks, reagent/preparation blanks, MS/MSD samples, and field blanks. Laboratory results accuracy will be assessed for compliance with the established QC criteria described in the laboratory SOW. The percent recovery (%R) of laboratory control samples will be calculated using the equation

$$\%R = (A/B) \times 100$$

where:

A = The analyte concentration determined experimentally from the laboratory control sample

B = The known amount of concentration in the sample

The accuracy criteria for the QA/QC samples are those stated in the laboratory SOW.

2.5.4.3 Completeness

The data completeness of laboratory analyses results will be assessed for compliance with the amount of data required for decision-making. Complete data are data that are not rejected. Data qualified with qualifiers such as a "J" or a "UJ" are still deemed acceptable and can still be used to make project decisions. The completeness of the analytical data is calculated using the equation

$$\%\ \text{Completeness} = [(\text{Valid data obtained}) \ / \ (\text{Total data planned})] \times 100$$

The completeness goal for the project data is 100 percent. All data have some value; even if data are rejected, they could still be used on the project.

2.5.4.4 Representativeness

Representativeness is the degree that sampling data accurately and precisely represent site conditions, and is dependent on sampling and analytical variability and the variability of environmental media at the site. Representativeness is a qualitative "measure" of data quality.

The goal of achieving representative data in the field starts with a properly designed and executed sampling program that carefully considers the project's overall DQOs. Proper location controls and sample handling are critical to obtaining representative samples.

The goal of achieving representative data in the laboratory is measured by assessing accuracy and precision. A laboratory will provide representative data when all of the analytical systems are in control. Therefore, representativeness is a redundant DQO for laboratory systems if proper analytical procedures are followed and holding times are met.

In addition, laboratories must demonstrate that the staff is qualified to perform the analyses, certified, and proficient in the analytical methods being employed.

2.5.4.5 Comparability

Comparability is the degree of confidence that one data set can be compared to another. Comparability is a qualitative "measure" of data quality.

The goal of achieving comparable data in the field starts with a properly designed and executed sampling program that carefully considers the project's overall DQOs. Proper location controls and sample handling are critical to obtaining comparable samples.

The goal of achieving comparable data in the laboratory is measured by assessing accuracy and precision. A laboratory will provide comparable data when all of the analytical systems are in control. Therefore, comparability is a redundant DQO for laboratory systems if proper analytical procedures are followed and holding times are met.

2.5.4.6 Sensitivity

Sensitivity is defined as the ability of the method or instrument to detect the contaminant of concern and other target compounds at the level of interest. Appropriate sampling and analytical methods will be selected that have QC acceptance limits that support the achievement of established performance criteria. Assessment of sensitivity will require thorough data validation.

2.6 Instrument / Equipment Testing, Inspection, and Maintenance Requirements

Trip blanks are used to detect VOC contamination during sample shipping and handling to assess possible contamination through sample transport. The subcontracted, laboratories will provide trip blank samples to be analyzed. Trip blanks will consist of a preserved, VOC sample vial certified as clean and filled with contaminant-free laboratory water. The vials will contain no air bubbles. One trip blank sample will be sent for each day that VOC samples are shipped to the laboratory, in each cooler containing VOC samples. Corrective action measures will be implemented if analyte concentrations are greater than or equal to the specified reporting limits.

2.6.1 Field Instrument Maintenance

2.6.1.1 Equipment Monitoring

The field equipment will be calibrated daily, checked for indications of poor performance, and the results documented. Any discrepancies will be immediately reported to the appropriate personnel for resolution.

The field team will maintain a sufficient supply of spare parts to minimize downtime. Whenever possible, backup instrumentation will be on hand.

The field equipment will be maintained as stated in the equipment's specific operating manuals. The field equipment to be used in taking field measurements includes:

- Water level indicator
- Oil/water interface probe
- Organic vapor photoionization detector

- Dissolved oxygen, temperature, pH, specific conductance, and oxidation-reduction potential meter

2.6.2 Laboratory Equipment/Instruments

Only qualified personnel will service instruments and equipment. Repairs, adjustments, and calibrations will be documented in the appropriate logbook or data sheet.

2.6.2.1 Instrument Maintenance

Preventive maintenance of laboratory equipment will follow guidelines recommended by the manufacturer. A malfunctioning instrument will be repaired by in-house staff or through a service call to the manufacturer.

The laboratory will maintain a sufficient supply of spare parts for its instruments to minimize downtime. Whenever possible, backup instrumentation will be on hand.

Whenever practical, analytical equipment should be maintained under a service contract. Such contracts allow for preventative system maintenance and repair on an "as-needed" basis. The laboratory should have sufficient trained staff to allow for the day-to-day maintenance of equipment. All laboratory instruments will be maintained in accordance with manufacturer's specifications and within the requirements of the laboratory Quality Assurance Manual.

Preventive maintenance for analyses is described in the laboratory SOW. All maintenance activities are required to be documented in the logbooks to provide a history of maintenance records.

2.6.2.2 Equipment Monitoring

Operation of balances, ovens, refrigerators, and water purification systems will be checked daily and documented. Discrepancies will be reported immediately to the appropriate laboratory personnel for resolution.

Specific laboratory preventative maintenance procedures are found in the laboratory's internal Quality Assurance Manual.

2.7 Instrument Calibration and Frequency

2.7.1 Field Instruments

Calibration of field instruments, as specified by the SOPs, will be performed at the intervals specified by the manufacturer or more frequently as conditions dictate. If an internally calibrated field instrument fails to meet calibration/checkout procedures, the vendor will replace it and return it to the manufacturer for service.

2.7.2 Laboratory Instruments

Calibration procedures for the laboratory equipment will be as specified in the laboratory SOW. The designated laboratory personnel performing QC activities will maintain and file

records of calibration, repairs, or replacement. These records will be filed where the work is performed and subject to a QA audit.

All standards used in equipment will be traceable, directly or indirectly, to the National Institute of Standards and Technology. All standards received will be logged into standard receipt logs maintained by the individual analytical groups. Each group maintains a standards log that tracks the preparation of standards used for calibration and QC purposes.

2.8 Inspection and Acceptance Requirements for Supplies and Consumables

It is expected that several contractors will provide various services to multiple project tasks. The required services must meet the task scope, specified levels of quality, and the submittal schedule. Project contractors or vendors should have contractual arrangements with their suppliers of materials.

2.9 Data Acquisition Requirements for Non-Direct Measurements

The sampling design and rationale of the RI sampling activities were based upon previously collected data. Site maps and other site characterization data were used in the selection of sample locations.

2.10 Data Management Plan

This DMP outlines the procedures for storing, handling, accessing, and securing data collected during this sampling event. Data gathered during this sampling event will be consolidated and compiled into a project database system that can be used to evaluate site conditions and data trends. This DMP will serve as a guide for all database users. The DMP is subject to future revision to allow the database management system to be modified as it is developed and maintained. This plan describes the following:

- The responsibilities of the project team for data management
- The Data Management System (DMS) to be established for the project
- The development of the base maps onto which the data will be plotted
- The types of data that will be entered into the DMS and the process of data entry

2.10.1 Team Organization and Responsibilities

The following are the team members and their responsibilities for the data management process:

Site Manager—Responsible for establishing the sample tracking system.

Project Chemist—Responsible for providing weekly the COC forms and other sampling information to the SM for use in sample tracking. Oversees proper use of the Forms II Lite EPA system and accuracy of the information entered. Reviews lab data for accuracy and

quality and compares electronic outputs for accuracy to Lab hard copies. Conducts tracking of samples, forwards tracking information and received data to the Database Manager, and identifies the data inputs (e.g., sample numbers) to use in generating tables and plots.

Database Manager—Responsible for setting up DMS in consultation with the Project Chemist at the beginning of the data evaluation task. Also oversees the data management process including data conversion/manual entry into DMS, quality control of the entered data, and preparation of the required tables and plots of the data. Coordinate with person responsible for review of the entered data for quality control purposes. Forwards all deliverables to the SM.

GIS Manager—Responsible for coordinating with SM to set up geo-database prior to sampling. Maintains spatial layers and over all geo-database integrity and accuracy. Provides all GIS-related outputs for reports.

2.10.2 Sample Tracking

The Project Chemist is responsible for tracking samples to ensure that the analytical results for all samples sent for analysis are received. Sample tracking will be performed as outlined in Table 13. Copies of COCs from the field team are used to enter in sample IDs, collect date, and analyses. Upon receipt of a sample receipt notice from the laboratory, the date received by the lab and a date the hardcopy is due will be entered. Likewise, upon receipt of the hardcopy and EDD, the date they were received will also be entered. The date the data are sent to the USEPA for validation and the date validation reports are delivered to CH2M HILL will be recorded. The electronic data deliverables will be uploaded when received from the lab, and will be tracked in the sample tracking table. Validation qualifiers will be added to the database and results qualified accordingly.

2.10.3 Data Types

Activities performed at the site will involve accessing a number of different types of data collected or retained for various uses. The following provides a general description of the overall contents of the project database, as based upon the available data and the data to be collected.

2.10.3.1 Historical Data

Sources of historical data for the site include information collected by the USEPA, IDNR, and OMC to characterize site conditions. This information includes both chemical and physical data for the site collected from previous site activities.

2.10.3.2 Site Characterization Data

The QAPP, of which this DMP is a part, identifies additional data to be collected for further site characterization. The data to be collected during the RI include:

- Porous floor, nonporous floor, and nonporous substrate analyte concentrations
- Surface soil and subsurface soil analyte concentrations
- Groundwater/NAPL thickness measurements
- Groundwater field parameter measurements
- Groundwater analyte concentrations

- Soil gas characterization data

These data will be added to the project database as they become available. The data will include new data collected in the field and laboratory and validated by the USEPA. The data source will be noted in the database. Procedures for incorporating the data into the database are presented in subsequent sections of this DMP.

2.10.4 Data Tracking and Management

Every data set received from analytical laboratories will be tracked individually. Analytical laboratory reports of chemical analysis results will be tracked in a consistent fashion. Every data set will be assigned a unique identifier. The date of receipt, status of data validation, and status of database entry for each data set will all be tracked and recorded in the project database.

2.10.4.1 Hard Copy

Measurements made during field data collection activities will be recorded in field logbooks. Field data will be reduced and summarized, tabulated, and stored along with the field logbooks.

All raw analytical laboratory data are stored as the original hard copy. Hard copy information includes COC forms, analytical bench sheets, instrument printouts and chromatograms, certificates of analyses, and QA/QC report summaries. Validation reports will be stored with the hard copy reports.

2.10.4.2 Data Input Procedures

Sampling information, analytical results, applicable QA/QC data, data validation qualifiers, and other field-related information will be entered into the project database for storage and retrieval during data evaluation and report development. The analytical data will be loaded into the database using EDD files received from the analytical laboratory. Validation qualifiers will be entered manually. Printing validated data reports from the database and manually comparing them to the validated summary analytical forms received from the USEPA validators will confirm correct data entry. Other available field-related data collected, such as water levels or newly installed well information, will be manually entered onto standard EDD templates for loading into the database. Historical data, either in hard copy or electronic form, will be manually entered on or formatted to standard EDD templates for database loading. The entry of other field-related data and historical site data will be confirmed by comparing the hard copy printouts from the database against the hard copies used to perform the data entry. All data entry confirmation procedures and results will be documented.

2.10.5 Computer Database

The technical data, field observations, laboratory analytical results and analytical data validation will be managed using EQuIS®, a third-party database system by Earthsoft Inc. that is used in USEPA Region 5 to store and analyze project data submissions. The core EQuIS applications are its Chemistry and Geology modules, each of which is associated with its own underlying Microsoft Access database. CH2M HILL owns licenses for the Geology and Chemistry modules. The EQuIS database system is based on a relational model, in which independent tables, each containing a certain type or entity of data, can be linked through selected fields that are common to two or more tables. This database design

allows for the inclusion of historical data, and allows users to effectively conduct trend analysis and generate a variety of data reports to aid in data interpretation.

The database must be protected from unauthorized access, tampering, accidental deletions or additions, and data or program loss that can result from power outages or hardware failure. The following procedures will be adopted to ensure this protection:

- The master database will be stored on a network file server local to the installation of the EQuIS data management system. Members of the data management team involved in loading, modifying, or querying the database will be given access through EQuIS user accounts and passwords, as well as the appropriate network server permissions.
- Copies of the master database will be stored on the local area network for access by project staff through reporting tools developed to minimize possible database corruption by users. Whenever the master database is updated or modified, it will be recopied to the local area network to ensure that the current copy is available to users.
- Daily backups of the master database and its copies will be made to ensure that the data will not be lost due to problems with the network.

2.10.6 GIS Description

A project geodatabase will be agreed upon and set up prior to sampling by the SM, Database Manager, and GIS Manager. Workflow for creating, maintaining, and organizing geospatial data will follow an SDS format for projects when ever possible.

An ArcView project or extension will be used providing the following functionality: load and display project site basemaps; display sampling station locations and associated sampling data (date, media, results); and perform ad hoc queries to highlight sampling locations meeting user-entered criteria for sampling (e.g. data by date, sample type, analyte, depth/elevation, result value, or any combination there of). Results will be shown as stations highlighted on the map.

2.10.7 Documentation

Documentation of data management activities is critical because it provides:

- A hard copy record of project data management activities
- Reference information critical for database users
- Evidence that the activities have been properly planned, executed, and verified
- Continuity of data management operations when personnel changes occur

The DMP will serve as the initial general documentation of the project data management efforts. Additional documentation will be maintained to document specific issues, such as database structure definitions, database inventories, database maintenance, user requests, database issues and problems, and client contact.

2.10.8 Evidence File

The final evidence file will be the central repository for all documents that constitute evidence relevant to sampling and analysis activities. CH2M HILL is the custodian of the evidence file and maintains the contents of the evidence files for the project, including all

relevant records, reports, logs, field notebooks, pictures, contractor reports, and data reviews in a secured area with limited access.

CH2M HILL will keep all records until project completion and closeout. As necessary, records may be transferred to an offsite records storage facility. The records storage facility must provide secure, controlled-access records storage. Records of raw analytical laboratory data, QA data, and reports will be kept by the subcontract laboratory for at least 7 years.

2.10.9 Presentation of Site Characterization Data

Depending on data user needs, data presentation may consist of any of the following formats:

- Tabulated results of data summaries or raw data
- Figures showing concentration isopleths or location-specific concentrations
- Tables providing statistical evaluation or calculation results
- Presentation tools, such as ARCINFO or similar analysis/presentation aids

In addition to laboratory data, other physical data will be collected during field efforts. This information will be stored in the project database. Other types of data elements may be added as the field investigation needs and activities evolve.

SECTION 3

Assessment / Oversight

3.1 Assessments and Response Actions

Field and laboratory assessments will be performed to assess technical and procedural compliance with this QAPP. Performance and system audits are key to ensuring compliance. The purposes of the audits are to:

- Confirm that appropriate documents are properly completed and kept current and orderly
- Ensure measurement systems are accurate
- Identify nonconformance or deficiencies and to initiate necessary corrective actions
- Verify that field and laboratory QA procedures called for in this QAPP are properly followed and executed

Project managers and the Laboratory QA Manager are responsible for ensuring conformance with SOPs. Activities selected for audit will be evaluated against specified requirements, and the audit will include an evaluation of the method, procedures, and instructions. Documents and records will be examined as necessary to evaluate whether the QA program is effective and properly implemented. Reports and recommendations must be prepared on all audits and submitted to the QA Manager for retention in the project files.

3.1.1 Field Audits

Planning, scheduling, and conducting QA audits and surveillance are required to verify that site activities are being performed efficiently in conformance with approved plans, standards, federal and state regulatory requirements, sound scientific practices, and contractual requirements. Planned and scheduled audits may be performed to verify compliance with aspects of the QA program and to evaluate the effectiveness of the QA program.

Audits include:

- Objective examination of work areas, activities, and processes
- Review of documents and records
- Interviews with project personnel
- Review of plans and standards

The FTL will regularly conduct internal review of the sampling program during the investigation and pay particular attention to the sampling program with respect to representativeness, comparability, and completeness of the specific measurement parameters involved.

The FTL or a designee will review field documentation (COC forms, field daily sheets, and logbooks) as it is generated for accuracy, completeness, and compliance with QAPP requirements. The FTL will also periodically audit field sampling procedures for compliance with QAPP procedures. The auditor will check that:

- Sampling protocols are followed
- Samples are placed in proper containers
- Samples are stored and transported properly
- Field documentation is completed

3.1.1.1 Field Corrective Action

Any project team member may initiate a field corrective action process, which action process consists of identifying a problem, acting to eliminate it, monitoring the effectiveness of the corrective action, verifying that the problem has been eliminated, and documenting the corrective action.

Corrective actions include correcting COC forms, problems associated with sample collection, packaging, shipping, field record-keeping, or additional training in sampling and analysis. Additional approaches may include resampling or evaluating and amending sampling procedures. The FTL will summarize the problem, establish possible causes, and designate the person responsible for a corrective action. The FTL will verify that the initial action has been taken and appears effective, as well as follow up to verify that the problem has been resolved.

Technical staff and project personnel will be responsible for reporting suspected technical or QA nonconformances or suspected deficiencies by reporting the situation to the FTL, who will be responsible for assessing suspected problems in consultation with the laboratory QA Manager and the Site Manager, and make a decision based on the situation's potential to impact data quality. If it is determined that the situation warrants a reportable nonconformance requiring corrective action, the FTL will initiate a nonconformance report.

The FTL will be responsible for ensuring that corrective actions for non-conformances are initiated by:

- Evaluating all reported nonconformances
- Controlling additional work on nonconforming items
- Determining disposition or action to be taken
- Maintaining a log of nonconformances
- Reviewing nonconformance reports and corrective actions taken
- Ensuring nonconformance reports are included in the final documentation in the project files

The USEPA holds the right to perform field audits during sampling activities.

3.1.2 Laboratory Audits

The Laboratory QA Manager may conduct internal system audits, which are qualitative evaluations of all components of the laboratory QC measurement system. The audit serves to determine if all measurement systems are used appropriately. The system audits are conducted to evaluate the following:

- Sample handling procedures
- Calibration procedures
- Analytical procedures
- QC results

- Safety procedures
- Record-keeping procedures
- Timeliness of analysis and reporting.

Laboratories also are subject to external audits, which focus on assessing general laboratory practices and conformance to this QAPP. Laboratory audits may be performed prior to the start of analyses and at any time during the course of the project as deemed necessary.

The Laboratory QA Manager will review internal laboratory performance. The Laboratory QA Manager will evaluate laboratory precision and accuracy by comparing results of duplicate samples, QC samples, spikes, and blanks. The laboratory QA manager or other client services individual will check the analytical prior to distribution when a beyond-control-limit situation is encountered

External laboratory performance reviews may also be conducted based on evaluation of the results of check samples analyzed as part of the USEPA and/or state certification requirements. In addition, performance audits may be conducted by sending "double blind" performance evaluation samples (those that are not discernable from routine field samples) to the analytical laboratory. USEPA Region 5 or the IEPA may conduct external audits.

3.1.1.2 Laboratory Corrective Action

Corrective actions may be required for two classes of problems: analytical/equipment problems and noncompliance problems. Analytical/equipment problems may occur during sampling, sample handling, sample preparation, laboratory instrumental analysis, or data review.

A corrective action program will be determined and implemented when a noncompliance problem is identified. The person identifying the problem will be responsible for notifying the proper project member. If the problem is analytical in nature, information on these problems will be communicated to the Laboratory QA Manager and the QA Manager, who will in turn direct information to proper project members. Implementation of corrective action will be confirmed through similar channels.

Implementation of all corrective actions will be documented. No staff member will initiate corrective action without prior communication of the action needing correction and the proposed corrective action through the proper channels. If corrective actions are insufficient, the Site Manager or the QA Manager may issue a stop-work order.

Corrective actions are required whenever an actual or potential out-of-control event or out-of-control event is noted. The investigative action taken depends somewhat on the analysis and the event. Laboratory personnel are alerted that corrective actions may be necessary if:

- QC data are outside the warning or acceptable windows for precision and accuracy
- Blanks contain target analytes above acceptable levels
- Undesirable trends are detected in spike recoveries or RPD between duplicates
- Unusual changes in detection limits occur
- Inquiries concerning data quality are received
- Deficiencies are detected by the Laboratory QA Manager during internal or external audits or from results of performance evaluation samples

Corrective action procedures are often handled at the bench level by the analyst. The analyst reviews preparation or extraction procedures for possible errors, checks instrument calibrations, spike and calibration mixes, and instrument sensitivity. If problems persist, or cannot be identified, matters are referred to the Laboratory Supervisor, Laboratory Project Manager, or Laboratory QA Manager for further investigation. Once resolved, full documentation of the corrective action procedures is filed with the Laboratory QA Manager after approval by CH2M HILL. Corrective action may include:

- Resampling and analyzing
- Evaluating and amending sampling procedures
- Evaluating and amending analytical procedures
- Accepting data and acknowledging the level of uncertainty
- Reanalyzing the samples, if sample or extract volume is adequate and holding time criteria permit

If resampling is deemed necessary due to laboratory problems, the Site Manager must identify the appropriate approach including cost recovery from the laboratory for the additional sampling effort.

3.2 Reports to Management

In addition to the audit reports that may be submitted to the SM in accordance with this QAPP, a monthly progress report is prepared by the SM, addressing all QA issues and corrective actions proposed or already taken, and is submitted to the USEPA. Also, after the sample results are received from the laboratory, evaluated, reduced, and tabulated, a data evaluation report will be submitted that documents the field investigation.

SECTION 4

Data Validation and Usability

4.1 Data Review, Verification, and Validation

Data validation is the process of reviewing project data against the data QA/QC requirements. The data are evaluated for precision and accuracy against the analytical protocol requirements stated in the laboratory SOW and analytical SOPs. Nonconformance issues or deficiencies that could affect the reported result's precision or accuracy are identified and considered when assessing whether the result is sufficient to achieve DQOs.

All data collected as part of this monitoring plan will be consistent with this QAPP. All CLP-equivalent data reports (Level 3 analyses) will be validated using the USEPA CLP National Functional Guidelines for Organic Data Review (October 1999) and Region 5 Standard Operating Procedures for Validation of CLP Organic Data (Revised February 1997) as templates. Criteria for assessment (e.g., DQOs contained in these documents) are superceded by the laboratory SOW and analytical SOPs.

USEPA will conduct the validation. Validation of laboratory data packages will include an assessment of compliance with method guidelines, specifically including an evaluation of:

- Holding times
- Blank contamination
- Calibration requirements (initial and continuing)
- Matrix spike and duplicate recoveries
- Surrogate spike recoveries
- Instrument performance
- Compound identification and quantitation

The following steps are included as part of the data validation process:

- Evaluation of completeness of data package.
- Verification that field COC forms were completed and that the samples were handled properly.
- Verification that holding times were met for each parameter. Holding time exceedances will be documented. Data for all samples exceeding holding time requirements will be flagged as holding time exceeded. The validator will decide which qualifiers are most appropriate on a case-by-case basis.
- Verification that parameters were analyzed according to methods specified.
- Review of QA/QC data (assurance that duplicates, blanks, and spikes were analyzed on the required number of samples as specified in the method; verification that duplicate and matrix spike recoveries were acceptable).

- Investigation of anomalies identified during review, which will be discussed with the QA Manager and the Laboratory QA Manager.

Deficiencies discovered as a result of data validation, as well as corrective actions implemented in response, will be documented and submitted in the form of a written report with supporting documentation supplied as check sheets. USEPA Functional Guidelines will be used as guidance on data validation procedures. QC requirements specified in the laboratory SOW and analytical SOPs shall take precedence over the Functional Guidelines requirements when listed.

4.2 Validation and Verification Methods

The data validation process is conducted to assess the effect of the overall sampling and analysis process on the usability of the data. There are two areas of review: laboratory performance evaluation and the effect of matrix and sampling interference. The laboratory performance evaluation is a check for compliance with the method requirements and a straightforward examination. The laboratory either did or did not analyze the samples within the QC limits of the analytical method and according to protocol requirements. The assessment of potential matrix and sampling affects consists of a QC evaluation of the analytical results; the results of testing blank, duplicate, and matrix spike samples; and then assessing how, if at all, this could affect the usability of the data.

All analytical data will be supported by a data package. The data package will contain the supporting QC data for the associated field samples. Before the laboratory will release each data package, the Laboratory QA Manager (or the analytical section supervisor) must carefully review the sample and laboratory performance QC data to verify sample identity, the completeness and accuracy of the sample and QC data, and compliance with method specifications.

The USEPA will perform data validation for laboratory-generated data in a manner consistent with the *USEPA Contract Laboratory Program National Functional Guidelines for Organic and Inorganic Data Review*. Sample results will then be assigned a degree of usability based upon overall data quality.

The CH2M HILL project team will evaluate the data validation results. This evaluation will assess how the data, as qualified by the data validation, can be used on the project.

The data, after validation, will also be verified to assess if the correct samples were analyzed and the correct parameters reported. The data are also verified to assess if the EDDs and the hard copy data deliverables are consistent with one another to assure an accurate database. Also, the data will be looked at in such a way as to see if the results make sense if compared to what is anticipated. If the data are consistent with anticipated results, no corrective action will be deemed necessary. However, if the data obtained from the laboratory are not consistent with the anticipated results, an in-depth evaluation of the results may be necessary to interpret the deviation.

4.3 Reconciliation with Data Quality Objectives

The final activity of the data validation process is to assess whether the data fulfill the objectives for the project. The final results, as adjusted for the findings of any data validation/data evaluation, will be checked against the DQOs. The data acquired from the additional site investigation should fulfill the following project objectives:

- Evaluate material handling and disposal options but not the extent of contamination.
- Define eastern contamination (CPAH and PCB) boundary of Former Die Cast UST/AST area located east of Plant 2.
- Characterize the soils in the vicinity of PCB AST area and parking lot areas north of Plant 2 (between the two containment cells) sufficiently to evaluate the potential for direct contact risk.
- Verify that soils in the uncovered grassy areas surrounding the corporate office buildings south of Plant 2 will not pose direct contact risk related to site contaminants.
- Determine contaminant concentrations in soil beneath building at selected groundwater investigation locations.
- Collect soil property data to evaluate contaminant fate and transport and remedial technologies.
- Verify current groundwater flow and water quality conditions indicated by existing data.
- Define the extent of contamination to the south, around hot spot areas and beneath parts of the plant that have no data.
- Define the extent of NAPL.
- Analyze the concentrations of CVOC vapors in subsurface soils south of Plant 2 to determine whether they pose a risk.
- Determine if present and subsequently quantify any ambient CVOC vapors in the Larsen Marine buildings.

The RI data will be evaluated to assess whether the project objectives have been met. The objectives will be met if all scheduled samples and data readings documented in the QAPP are obtained, data are managed according to the *Data Management Plan* (see Section 2.10), and all the data are deemed usable after sufficient validation and evaluation. If the objectives are not met, future data collection will be required and implemented accordingly. If the data, after validation and evaluation, are sufficient to achieve project objectives, the SM will release the data and work may proceed.

SECTION 5

References

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Tables

TABLE 1
RI/FS Project Staff
OMC Plant 2

Staff	Role	Highest Degree	Total Years of Experience	P-Grade
Ike Johnson	PM	MS	25	P4
Jewelle Keiser	SM	MS	20	P3
Paul Rohde	ASM/Project Hydrogeologist	BS	6	P2
Dan Plomb	Senior Reviewer	MS	19	P3
Keli McKenna	Project Engineer	BS	7	P2
Phil Smith	RTL	BS	27	P4

TABLE 2
Summary of Sample Locations and Rationale for Building Material Investigation
OMC Plant 2

Overall Objective of Sampling: Collect PCB data to evaluate material handling and disposal options of plant building materials.

Media	General Location Description	Collection Method	Number of Sampling Locations	Sample Depth	Number of Samples[a]	Analysis[b]	Rational of Selection of Sampling Locations
Nonporous Surfaces: Unpainted Metal Structures and Piping	Random locations within the Old Die Cast Area, Parts Storage Area, and the Metal Working Area	Wipe samples	50 random locations 5 visually contaminated locations	Surface	55	TCL PCBs	To determine whether these nonporous media are contaminated and will need to be decontaminated and, if contaminated, the type of thermal treatment or disposal required.
Porous Surfaces Other than Floors	Random locations within the Old Die Cast Area, Parts Storage Area, and the Metal Working Area	Wipe samples	50 random locations	Surface	55	TCL PCBs	To determine relative proportion of porous surfaces that are contaminated (i.e., PCB concentration > 10 µg/100 cm^2) and to determine if further bulk sampling is needed to determine disposal requirements.
	Visually contaminated areas or where results from wipe samples > 100 µg/100 cm^2	Concrete core samples	5 core locations	0 to 4 inches	5[c]	TCL PCBs	To determine if contaminated materials contain PCB concentrations > the TSCA disposal criteria of 50 mg/kg.
Porous Floor Surfaces	Random locations within the Old Die Cast Area, Parts Storage Area, and the Metal Working Area	Concrete core samples	5 random locations in Old Die Cast Area 5 random location in Parts Storage Area 10 random locations in Metal Working Area	0 to 4 inches	20[c]	TCL PCBs	To determine if contaminated materials contain PCB concentrations > the TSCA disposal criteria of 50 mg/kg.
	Northwest corner of Chemical Storage Building	Concrete core samples	1 location	0 to 4 inches	1	TCL PCBs	Previous samples from this area contained PCB concentrations > 10 µg/100 cm^2 in wipe samples. Core samples will be analyzed to determine if contaminated materials contain PCB concentrations > the TSCA disposal criteria of 50 mg/kg.
	Northwest corner of New Die Cast Area	Concrete core samples	1 location	0 to 4 inches	1	TCL PCBs	Previous samples from this area contained PCB concentrations > 10 µg/100 cm^2 in wipe samples. Core samples will be analyzed to determine if contaminated materials contain PCB concentrations > the TSCA disposal criteria of 50 mg/kg.
	Random locations within the Old Die Cast Area, Parts Storage Area, and the Metal Working Area	Concrete core samples	1 from each area	0 to 4 inches	3	TCL PCBs TAL metals & cyanide (total) SPLP PCBs SPLP metals	Evaluate potential impacts of leaching from contaminated concrete to allow evaluation of onsite disposal alternatives.
	Plating Room	Concrete core samples	1 location	0 to 4 inches	1	TCL PCBs TAL metals & cyanide (total) SPLP PCBs SPLP metals	Evaluate potential impacts of leaching from contaminated concrete to allow evaluation of onsite disposal alternatives.

[a]Number of samples does not include quality control samples.
[b]The parameter list for each of the analyses identified are provided in Table 7.
[c]The 4-inch cores maybe subdivided into different depth intervals (0-to-1-inch and 3-to-4-inch) based on visual contamination

TABLE 3
Summary of Sample Locations and Rationale for Soil Investigation
OMC Plant 2

Overall Objective of Sampling: Confirm the nature and extent of contamination identified by previous investigations; Fill data gaps; Collect geotechnical characteristics of the soils

Media	General Location Description	Collection Method	Number of Sampling Locations	Sample Depth	Number of Samples[a]	Analysis[b]	Rational of Selection of Sampling Locations
Unsaturated soils	Former Die Cast UST/AST Area and along access road adjacent to dune area east of the site	Direct push methods	6 locations around area 4 locations along north-south access road	0 to 6 inches 2-foot interval above water table	20	TCL VOCs TCL SVOCs[c] TCL PCBs	Define eastern contaminant boundary. Additional locations will be stepped out at 100-foot intervals based on results from initial locations.
Unsaturated soils	PCB Area North of the Plant	Direct push methods	34	0 to 6 inches 2-foot interval above water table	68	TCL VOCs TCL SVOCs[c] TCL PCBs	Define limits of soil contamination in vicinity of PCB AST area and northern parking lot area.
Unsaturated soils	Uncovered grassy area surrounding the Corporate Building	Direct push methods	5	0 to 6 inches 2-foot interval above water table	10	TCL VOCs TCL SVOCs[c] TCL PCBs	Determine if soil contamination exists in the nonpaved areas south of the plant. High VOC concentrations have been observed in the groundwater in this general area.
Unsaturated and saturated soils	Selected locations in area of elevated groundwater contamination	Direct push methods	10	0 to 4 feet Top of aquifer Bottom of aquifer	30	TCL VOCs TCL PCBs Total organic carbon Porosity Bulk density Grain size Moisture content Soil oxidant demand	Determine contaminant concentrations in soil beneath building to allow comparison to groundwater concentrations and to allow evaluation of remedial technologies.
Unsaturated soils	Random samples beneath building	Direct push methods	7 to 10 random locations (estimated based on 10 percent of the MIPs locations)	0 to 4 feet	7 to 10	TCL VOCs TAL metals & cyanide[d]	Determine contaminant concentrations in soil beneath building and to correlate MIPs response to concentrations in soil.
Unsaturated and saturated soils	Samples from borings for new monitoring wells installed outside of building	Hollow-stem augers/split-spoon samplers	10	Unsaturated zone sample Top of aquifer Bottom of aquifer	30	Total organic carbon Grain size Porosity Bulk density	Samples will be collected to evaluate transport properties of unsaturated zone and groundwater flow and transport characteristics of the aquifer

[a]Number of samples does not include quality control samples.
[b]The parameter list for each of the analyses identified are provided in Table 8.
[c]PAHs and CPAHs will be analyzed as part of the TCL SVOC list.
[d]Soil samples taken near the plating/foundry areas will be analyzed for metals and cyanide (total).

TABLE 4
Summary of Sample Locations and Rationale for Groundwater Investigation
OMC Plant 2

Overall Objective of Sampling: Determine site-specific hydraulic gradients and groundwater velocities; Confirm the nature and extent of contamination identified by previous investigations; Fill data gaps

Monitoring Point	General Location Description	Collection Method	Number of Sampling Locations	Sample Depth	Number of Samples[a]	Analysis[b]	Rational of Selection of Sampling Locations
Temporary borehole	Randomly selected borings adjacent to MIPs locations	Discrete groundwater grab sample	7 to 10 random locations (estimated based on 10 percent of the MIPs locations)	Shallow zone (0 to 10 ft) Intermediate Zone (10 to 20 ft) Deep Zone (20 to 30 ft)	21	TCL VOCs Cr^{6+}, TAL metals (dissolved) & cyanide (total)[c] Note: If NAPL encountered samples will be also be analyzed for TCL PCBs	Correlate MIPs response and CVOC groundwater concentrations.
Existing monitoring wells[d]	Shallow (0 to 10 ft): W-2A, W-3, W-4A, W-12A, W-13, MW-14, MW-15 Intermediate (10 to 20 ft): W-2B, W-4B, W-12, W-06, W-10, W-09 Deep (20 to 30 ft): W-4C, W-05, W-7, W-11, W-4, MW-T101, MW-T104, MW-T105, MW-T106, MW-T107	Low flow sampling	23	6 shallow 6 intermediate 11 deep	23	TCL VOCs TCL SVOCs[e] TCL PCBs TAL metals (total and dissolved) & cyanide (total) Natural attenuation parameters[f] Field analyses[g]	Verify water quality conditions identified by previous investigations.
New monitoring wells	Southwestern corner of site near Chemical Storage Building	Low flow sampling	1	2 well nests: shallow water table well (0 to 10 ft) deep well (20 to 30 ft)	2	TCL VOCs TCL SVOCs[e] TCL PCBs TAL metals (total and dissolved) & cyanide (total) Natural attenuation parameters[f] Field analyses[g]	Determine groundwater flow onto site from former OMC Plant 3.
	Northwestern portion of site.	Low flow sampling	1	2 well nests: shallow water table well (0 to 10 ft) deep well (20 to 30 ft)	2	TCL VOCs TCL SVOCs[e] TCL PCBs TAL metals (total and dissolved) & cyanide (total) Natural attenuation parameters[f] Field analyses[g]	TP-16 contained high VOC concentrations in the deep groundwater (25,019 µg/L). The source of contaminant concentrations in this area needs to be examined. The exact location for this well may be located west of the railroad.
	Outside of chip dock area	Low flow sampling	1	2 well nests: shallow water table well (0 to 10 ft) deep well (20 to 30 ft)	2	TCL VOCs TCL SVOCs[e] TCL PCBs TAL metals (total and dissolved) & cyanide (total) Natural attenuation parameters[f] Field analyses[g]	Monitor contamination observed in HY-35 that previously contained high VOC concentrations in the deep groundwater (36,569.4 µg/L).
	Outside of chip room	Low flow sampling	1	2 well nests: shallow water table well (0 to 10 ft) deep well (20 to 30 ft)	2	TCL VOCs TCL SVOCs[e] TCL PCBs TAL metals (total and dissolved) & cyanide (total) Natural attenuation parameters[f] Field analyses[g]	Monitor contamination observed in HY-2 and GP-8 that previously contained high VOC concentrations in the groundwater.
	Parking lot between Old Die Cast Area and	Low flow	1	2 well nests:	2	TCL VOCs	Monitor contamination observed in HY-22 and HY-34

TABLE 4
Summary of Sample Locations and Rationale for Groundwater Investigation
OMC Plant 2

Overall Objective of Sampling: Determine site-specific hydraulic gradients and groundwater velocities; Confirm the nature and extent of contamination identified by previous investigations; Fill data gaps

Monitoring Point	General Location Description	Collection Method	Number of Sampling Locations	Sample Depth	Number of Samples[a]	Analysis[b]	Rational of Selection of Sampling Locations
	New Die Cast Area, south of former PCB ASTs	sampling		shallow water table well (0 to 10 ft) deep well (20 to 30 ft)		TCL SVOCs[e] TCL PCBs TAL metals (total and dissolved) & cyanide (total) Natural attenuation parameters[f] Field analyses[g]	that previously contained high VOC concentrations in the groundwater. This location was also identified to potentially be a low spot in the till.
	Near Corporate Offices	Low flow sampling	2	2 well nests: shallow water table well (0 to 10 ft) deep well (20 to 30 ft)	4	TCL VOCs TCL SVOCs[e] TCL PCBs TAL metals (total and dissolved) & cyanide (total) Natural attenuation parameters[f] Field analyses[g]	Monitor contamination observed in HY-18, HY-9, HY-17 and TP-13 that previously contained high VOC concentrations in the groundwater. This source of the contamination in this area is unknown.
	Larson Marine Property – near Slip 4	Low flow sampling	2	2 well nests: shallow water table well (0 to 10 ft) deep well (20 to 30 ft)	4	TCL VOCs TCL SVOCs[e] TCL PCBs TAL metals (total and dissolved) & cyanide (total) Natural attenuation parameters[f] Field analyses[g]	Groundwater contamination has not been observed in previous groundwater grab samples collected in this area. Based on groundwater flow data, this location may serve to monitor potential groundwater discharges to Waukegan Harbor.
	Within the building	Low flow sampling	5	2 well nests: shallow water table well (0 to 10 ft) deep well (20 to 30 ft)	10	TCL VOCs TCL SVOCs[e] TCL PCBs TAL metals (total and dissolved) & cyanide (total) Natural attenuation parameters[f] Field analyses[g]	These locations will be selected based on the results of the MIPs investigation. These locations will be selected to monitor the contaminated groundwater plume under the building and will include high concentration areas as well as the plume boundaries.

[a]Does not include quality control samples.
[b]The parameter list for each of the analyses identified are provided in Table 9.
[c]Groundwater grab samples taken near the plating/foundry areas will be analyzed for dissolved metals, cyanide (total) and hexavalent chromium.
[d]Number of existing wells and condition will be determined during the site reconnaissance.
[e]CPAHs and CPAHs will be analyzed as part of the TCL SVOC list.
[f]Natural attenuation parameters include: methane, ethane, ethene, dissolved iron, total alkalinity, chloride, nitrate, nitrite, sulfate, sulfide, total organic carbon
[g]Field analysis includes: water levels, temperature, pH, specific conductance, conductivity, dissolved oxygen, oxidation-reduction potential, and turbidity.

TABLE 5
Summary of Sample Locations and Rationale for Air Investigation
OMC Plant 2

Overall Objective of Sampling: Determine the nature of potential soil vapor levels above the groundwater plume in the vicinity of Larsen Marine; Fill data gaps

Monitoring Point	General Location Description	Collection Method	Number of Sampling Locations	Sample Depth (feet)	Number of Samples[a]	Analysis[b]	Rational of Selection of Sampling Locations
Temporary borehole	Soil boring locations selected based on the plume boundaries in the vicinity of Larsen Marine.	Collection of soil vapor samples from soil gas probes (with PRT adapters) using Summa canisters. Approximately 5 minutes of soil gas sampling per Summa canister.	5 to 10[c]	From unsaturated zone (water table estimated to be about 5 feet bgs).	10	TO-15 SIM VOCs	Assist in evaluating if gas migration is a potential migration pathway.
Within Larsen Marine buildings	Three sample locations-one in each of the main buildings on the Larsen Marine property and one outdoor ambient air sample (background).	VOC samples are collected with SUMMA canisters by opening the flow controlled valve and slowly filling the canister using a flow controller to collect a time-integrated sample. Typically, samples are collected over an 8-hour period.	4	Above ground	4	TO-15 SIM VOCs	Assist in defining indoor air concentrations within Larsen Marine buildings.

[a]Number of samples does not include quality control samples.
[b]The parameter list for each of the analyses identified are provided in Table 10
[c]An initial five locations were identified based on historical site groundwater data. Five additional locations may be sampled based on the results of the MIPs investigation south of Plant 2

TABLE 6
Illinois Tier I Remediation Objectives for Chemicals Detected at the Site
OMC Plant 2

Chemical Name	Water (mg/L) Groundwater[a] Class I Aquifer	Soil[b] (mg/kg) Industrial/ Commercial Properties[c] Industrial/ Commercial	Industrial/ Commercial Properties[c] Construction Worker	Residential[d]	Soil Component of Groundwater Ingestion (Class I)[e]	Acceptable Detection Limit[e]
Acenaphthene	0.42	120,000[f]	120,000[f]	4,700[f]	570[f]	*
Acetone	0.7	100,000[k]	100,000[k]	7,800[f]	16[f]	*
Anthracene	2.1	610,000[f]	610,000[f]	23,000[f]	12,000[f]	*
Benzene	0.005[g]	1.6[h]	2.2[h]	0.8[h]	0.03	*
Benzo(a)anthracene	0.00013[i]	8[h]	170[h]	0.9[h]	2	*
Benzo(b)fluoranthene	0.00018[i]	8[h]	170[h]	0.9[h]	5	*
Benzo(k)fluoranthene	0.00017[i]	78[h]	1,700[h]	9[h]	49	*
Benzo(a)pyrene	0.0002[g,i]	0.8[h]	17[h]	0.09[h,j]	8	*
Bis(2-chloroethyl)ether	0.01[i]	0.47[h]	0.66[h]	0.2[h,j]	0.0004[h,j]	0.66
Bis(2-ethylhexyl)phthalate	0.006[g]	410[h]	4,100[f]	46[h]	3,600	*
Bromodichloromethane	0.0002[i]	92[h]	2,000[h]	10[h]	0.6	*
Bromoform	0.001[i]	100[h]	140[h]	53[h]	0.8	*
Carbon disulfide	0.7	720[k]	9.0[f]	720[k]	32[f]	*
Carbon tetrachloride	0.005[g]	0.64[h]	0.90[h]	0.3[h]	0.07	*
Chlorobenzene	0.1[g]	210[f]	1.3[f]	130[f]	1	*
Chloroform	0.0002[i]	0.54[h]	0.76[h]	0.3[h]	0.6	*
Chrysene	0.0015[i]	780[h]	17,000[h]	88[h]	160	*
Dibenzo(a,h)anthracene	0.0003[i]	0.8[h]	17[h]	0.09[h,j]	2	*
1,2-Dibromo-3-chloropropane	0.0002[g]	4[n]	0.11[l]	0.46[e]	0.002	*
Di-n-butyl phthalate	0.7	2,300[k]	2,300[k]	2,300[k]	2,300[k]	*
1,2-Dichlorobenzene	0.6[g]	560[k]	310[f]	560[k]	17	*
1,4-Dichlorobenzene	0.075[g]	17,000[f]	340[f]	11,000[f]	2	*
3,3'-Dichlorobenzidine	0.02[i]	13[h]	280[h]	1[h]	0.007[h,j]	1.3
1,1-Dichloroethane	0.7	1,700[k]	130[f]	1,300[f]	23[f]	*
1,2-Dichloroethane	0.005[g]	0.70[h]	0.99[h]	0.4[h]	0.02	*
1,1-Dichloroethylene	0.007[g]	1,500[k]	300[m]	700[f]	0.06	*
cis-1,2-Dichloroethylene	0.07[g]	1,200[k]	1,200[k]	780[f]	0.4	*
trans-1,2-Dichloroethylene	0.1[g]	3,100[k]	3,100[k]	1,600[f]	0.7	*
1,2-Dichloropropane	0.005[g]	23[f]	0.50[l]	9[h]	0.03	*
1,3-Dichloropropene	0.001[i]	2.1[h]	0.39[f]	1.1[h]	0.004[h]	0.005
Diethyl phthalate	5.6	2,000[k]	2,000[k]	2,000[k]	470[f]	*
2,4-Dimethylphenol	0.14	41,000[f]	41,000[f]	1,600[b]	9[b]	*
2,4-Dinitrotoluene	0.00002[i]	8.4[h]	180[h]	0.9[h]	0.0008[e,f]	0.250
2,6-Dinitrotoluene	0.00031[i]	8.4[h]	180[h]	0.9[e]	0.0007[e,f]	0.260
Di-n-octyl phthalate	0.14	10,000[k]	4,100[f]	1,600[f]	10,000[k]	*
Ethylbenzene	0.7[g]	400[k]	58[f]	400[k]	13	*

TABLE 6
Illinois Tier I Remediation Objectives for Chemicals Detected at the Site
OMC Plant 2

Chemical Name	Water (mg/L) Groundwater[a] Class I Aquifer	Soil[b] (mg/kg) Industrial/ Commercial Properties[c] Industrial/ Commercial	Industrial/ Commercial Properties[c] Construction Worker	Residential[d]	Soil Component of Groundwater Ingestion (Class I)[e]	Acceptable Detection Limit[e]
Fluoranthene	0.28	82,000[f]	82,000[f]	3,100[f]	4,300[f]	*
Fluorene	0.28	82,000[f]	82,000[f]	3,100[f]	560[f]	*
Hexachlorobenzene	0.00006[f]	1.8[h]	2.6[h]	0.4[h]	2	*
Hexachlorocyclopentadiene	0.05[g]	16[f]	1.1[f]	10[f]	400	*
Hexachloroethane	0.007	2,000[f]	2,000[f]	78[f]	0.5[f]	*
Indeno(1,2,3-c,d)pyrene	0.00043[i]	8[h]	170[h]	0.9[h]	14	*
Isophorone	1.4	4,600[k]	4,600[k]	4,600[k]	8[f]	*
Methylene chloride (Dichloroethane)	0.005[g]	24[h]	34[h]	13[h]	0.02[h]	*
Naphthalene	0.14	270[f]	1.8[f]	170[f]	12[f]	*
Nitrobenzene	0.0035	140[b]	9.4[f]	39[f]	0.1[f,j]	0.26
N-nitrosodiphenylamine	0.0032[i]	1,200[h]	25,000[h]	130[h]	1[h]	*
N-Nitrosodi-n-propylamine	0.0018[i]	0.8[h]	18[h]	0.09[h,j]	0.00005[h,j]	0.0018
Phenol	0.1[g]	1,000,000[f]	120,000[f]	47,000[f]	100[f]	*
Polychlorinated biphenyls (PCBs)	0.0005[g]	1[f]	1[f]	1[f]	[illegible]	*
Pyrene	0.21	61,000[f]	61,000[f]	2,300[f]	4,200[f]	*
Styrene	0.1[g]	1,500[k]	430[f]	1,500[k]	4	*
Tetrachloroethylene (PCE)	0.005[g]	20[h]	28[h]	11[h]	0.06	*
Toluene	1.0[g]	650[k]	42[k]	650[k]	12	*
1,2,4-Trichlorobenzene	0.07[g]	3,200[k]	920[f]	780[f]	5	*
1,1,1-Trichloroethane	0.2[g]	1,200[k]	1,200[k]	1,200[k]	2	*
1,1,2-Trichloroethane	0.005[g]	1,800[k]	1,800[k]	310[b]	0.02	*
Trichloroethylene (TCE)	0.005[g]	8.9[h]	12[h]	5[h]	0.06	*
Vinyl Acetate	7	1,600[f]	10[f]	1,000[f]	170[f]	*
Vinyl Chloride	0.002[g]	1.1[h]	1.1[f]	0.28[h]	0.01[f]	*
m-Xylene (1,3-dimethylbenzene)		420[k]	420[k]	420[k]	210	*
o-Xylene (1,2-dimethylbenzene)		410[k]	410[k]	410[k]	190	*
p-Xylene (1,4-dimethylbenzene)		460[k]	460[k]	460[k]	200	*
Xylenes, total	10.0[g]	320[k]	320[k]	320[k]	150	*
Ionizable Organics						
2-Chlorophenol	0.035	10,000[f]	10,000[f]	390[f]	4[f,n]	*
2,4-Dichlorophenol	0.021	6,100[f]	6,100[f]	230[f]	1[f,n]	*
2,4-Dinitrophenol	0.014	4,100[f]	410[f]	160[f]	0.2[f,j]	3.3

TABLE 6
Illinois Tier I Remediation Objectives for Chemicals Detected at the Site
OMC Plant 2

Chemical Name	Water (mg/L) Groundwater[a] Class I Aquifer	Soil[b] (mg/kg) Industrial/ Commercial Properties[c] Industrial/ Commercial	Industrial/ Commercial Properties[c] Construction Worker	Residential[d]	Soil Component of Groundwater Ingestion (Class I)[e]	Acceptable Detection Limit[e]
Pentachlorophenol	0.001[g]	24[h,o]	520[h,o]	3[h,o]	0.03[f,i]	*
2,4,6-Trichlorophenol	0.01[l]	390[h]	540[h]	58[h]	0.2[h,j,n]	0.66
Inorganics						
Arsenic	0.05[g]	1,200[e]	61[b]	750[e]	0.05[m]	*
Barium	2.0[g]	140,000[b]	14,000[b]	5,500[b]	2.0[m]	*
Cadmium	0.005[g]	2,000[b,r]	200[b,r]	78[b,r]	0.005[m]	*
Chloride	200[g]	c	c	c	200[m]	*
Chromium, total	0.1[g]	420[e]	690[b]	230[b]	0.1[m]	*
Chromium, ion, trivalent		1,000,000[b]	310,000[b]	120,000[b]	g	*
Chromium, ion, hexavalent		420[e]	690[b]	230[b]		*
Cyanide, amenable	0.2[g,p]	41,000[b]	4,100[b]	1,600[b]	0.2[g,m]	*
Iron	5.0[g]	c	c	c	5.0[m]	*
Lead	0.0075[g]	400[k]	400[k]	400[k]	0.0075[m]	*
Mercury	0.002[g]	610[b]	61[b]	10[b]	0.002[m]	*
Selenium	0.05[g]	10,000[b]	1,000[b]	390[b]	0.05[m]	*
Silver	0.05[g]	10,000[b]	1,000[b]	390[b]	0.05[m]	*
Sulfate	400[g]	c	c	c	400[m]	*

"*" indicates that the ADL is less than or equal to the specified remediation objective

[a] From Illinois Section 742.Appendix B. Table E: Tier 1 Groundwater Remediation Objectives for the Groundwater Component of the Groundwater Ingestion Route

[b] Soil remediation objectives based on human health criteria only.

[c] From Illinois Section 742.Appendix B. Table B: Tier 1 Soil Remediation Objectives for Industrial/Commercial Properties Value is the lower of the ingestion and Inhalation exposure route-specific values for soils

[d] From Illinois Section 742.Appendix B. Table A: Tier 1 Soil Remediation Objectives for Residential Properties Value is the lower of the ingestion and inhalation exposure route-specific values for soils

[e] From Illinois Section 742.Appendix B. Table B: Tier 1 Soil Remediation Objectives for Industrial/Commercial Properties

[f] Calculated values corresponds to a target hazard quotient of 1

[g] Value listed is also the Groundwater Quality Standard for this chemical pursuant to 35 IAC 620.410 for Class I

[h] Calculated value correspond to a cancer risk of 1 in 1,000,000

[i] The groundwater remediation objective is equal to the ADL for carcinogens according to the procedures specified in 35 I.

[l] Level is at or below Contract Laboratory Program required quantitation limit for Regular Analytical Services (RAS)

[k] Soil saturation concentration have been reached and alternative modeling approaches are required.

[l] 40 CFR 761 contains applicability requirements and methodologies for the development of PCB remediation objectives.

[m] The soil remediation objectives are in mg/L. These values can be compared to either TCLP or SPLP test results.

[n] Soil remediation objective for pH of 6.8

[o] Ingestion soil remediation objective adjusted by a factor of 0.5 to account for dermal route.

[p] Remediation objective for groundwater is for total cyanide

TABLE 7
Building Materials Analytes and Reporting Limits
OMC Plant 2

Parameter	CAS Number	Project Action Limit	Project Reporting Limit	Achievable Laboratory MDLs	Project Method
Concrete Cores		**N/A**			
TAL Metals					SW-846 6010 or 7000series
Aluminum	7429-90-5	—	40 mg/Kg	12 mg/Kg	
Antimony	7440-36-0	—	1.8 mg/Kg	0.53 mg/Kg	
Arsenic	7440-38-2	—	0.22 mg/Kg	0.07 mg/Kg	
Barium	7440-39-3	—	0.86 mg/Kg	0.26 mg/Kg	
Beryllium	7440-41-7	—	0.061 mg/Kg	0.018 mg/Kg	
Cadmium	7440-43-9	—	0.22 mg/Kg	0.0676 mg/Kg	
Calcium	7440-70-2	—	25 mg/Kg	7.4 mg/Kg	
Chromium	7440-47-3	—	0.88 mg/Kg	0.27 mg/Kg	
Cobalt	7440-48-4	—	6.3 mg/Kg	1.9 mg/Kg	
Copper	7440-50-8	—	0.8 mg/Kg	0.24 mg/Kg	
Iron	7439-89-6	—	15 mg/Kg	4.6 mg/Kg	
Lead	7439-92-1	—	0.41 mg/Kg	0.13 mg/Kg	
Magnesium	7439-95-4	—	9.6 mg/Kg	2.9 mg/Kg	
Manganese	7439-96-5	—	0.83 mg/Kg	0.25 mg/Kg	
Mercury	7439-97-6	—	0.1 mg/Kg	0.006 mg/Kg	
Nickel	7440-02-0	—	5.3 mg/Kg	1.6 mg/Kg	
Potassium	7440-09-7	—	27.5 mg/Kg	8.24 mg/Kg	
Selenium	7782-49-2	—	0.27 mg/Kg	0.08 mg/Kg	
Silver	7440-22-4	—	0.66 mg/Kg	0.2 mg/Kg	
Sodium	7440-23-5	—	42.6 mg/Kg	12.8 mg/Kg	
Thallium	7440-28-0	—	2 mg/Kg	1.2 mg/Kg	
Vanadium	7440-62-2	—	4.6 mg/Kg	1.4 mg/Kg	
Zinc	7440-66-6	—	1.5 mg/Kg	0.46 mg/Kg	
Cyanide	57-12-5	—	0.13 mg/Kg	0.04 mg/Kg	
TCL PCBs		—			SW-846 8082
Aroclor 1016	12674-11-2	—	0.04 mg/Kg	0.011 mg/Kg	
Aroclor 1221	11104-28-2	—	0.05 mg/Kg	0.015 mg/Kg	
Aroclor 1232	11141-16-5	—	0.04 mg/Kg	0.013 mg/Kg	
Aroclor 1242	53469-21-9	—	0.04 mg/Kg	0.011 mg/Kg	
Aroclor 1248	12672-29-6	—	0.05 mg/Kg	0.015 mg/Kg	
Aroclor 1254	11097-69-1	—	0.03 mg/Kg	0.01 mg/Kg	
Aroclor 1260	11096-82-5	—	0.02 mg/Kg	0.01 mg/Kg	
Total Aroclors	—	—	1.0 mg/Kg	0.085 mg/Kg	
SPLP Metals (incl. Be)					SW-846 1312/6010 or 6020/7000 series
Aluminum	7429-90-5	—	373 ug/L	112 ug/L	6010[a]
Antimony	7440-36-0	—	16 ug/L	4.9 ug/L	6010[a]
Arsenic	7440-38-2	—	2.57 ug/L	0.72 ug/L	7060
Barium	7440-39-3	—	4.5 ug/L	1.4 ug/L	6010[a]
Beryllium	7440-41-7	—	0.75 ug/L	0.23 ug/L	6010[a]
Cadmium	7440-43-9	—	2.9 ug/L	0.88 ug/L	6010[a]
Calcium	7440-70-2	—	330 ug/L	99 ug/L	6010[a]

TABLE 7
Building Materials Analytes and Reporting Limits
OMC Plant 2

Parameter	CAS Number	Project Action Limit	Project Reporting Limit	Achievable Laboratory MDLs	Project Method
Chromium	7440-47-3	—	14ug/L	4.1 ug/L	6010[a]
Cobalt	7440-48-4	—	3.3 ug/L	0.99 ug/L	6010[a]
Copper	7440-50-8	—	9.1 ug/L	2.7 ug/L	6010[a]
Iron	7439-89-6	—	222 ug/L	67 ug/L	6010[a]
Lead	7439-92-1	—	0.49 ug/L	0.15 ug/L	7421
Magnesium	7439-95-4	—	139 ug/L	42 ug/L	6010[a]
Manganese	7439-96-5	—	4.3 ug/L	1.3 ug/L	6010[a]
Mercury	7439-97-6	—	0.2 ug/L	0.1 ug/L	7470
Nickel	7440-02-0	—	30 ug/L	9 ug/L	6010[a]
Potassium	7440-09-7	—	3200 ug/L	934 ug/L	6010[a]
Selenium	7782-49-2	—	1.7 ug/L	0.42 ug/L	7740
Silver	7440-22-4	—	9.1 ug/L	2 ug/L	6010[a]
Sodium	7440-23-5	—	1470 ug/L	442 ug/L	6010[a]
Thallium	7440-28-0	—	5.03 ug/L	1.51 ug/L	7841
Vanadium	7440-62-2	—	2.73 ug/L	0.82 ug/L	6010[a]
Zinc	7440-66-6	—	16 ug/L	4.9 ug/L	6010[a]
Cyanide	57-12-5	—	29 ug/L	8.6 ug/L	9012
SPLP PCBs					SW-846 1312/8082[b]
Aroclor 1016	12674-11-2	—	0.5 ug/L	0.15 ug/L	
Aroclor 1221	11104-28-2	—	0.6 ug/L	0.18 ug/L	
Aroclor 1232	11141-16-5	—	0.61 ug/L	0.18 ug/L	
Aroclor 1242	53469-21-9	—	0.69 ug/L	0.2 ug/L	
Aroclor 1248	12672-29-6	—	0.56 ug/L	0.16 ug/L	
Aroclor 1254	11097-69-1	—	0.78 ug/L	0.23 ug/L	
Aroclor 1260	11096-82-5	—	0.47 ug/L	0.14 ug/L	
Total Aroclors	–	—	4.21 ug/L	1.24 ug/L	
Wipes		**N/A**			
TCL PCBs					SW-846 8082
Aroclor 1016	12674-11-2	—	0.04 mg/Kg	0.011 mg/Kg	
Aroclor 1221	11104-28-2	—	0.05 mg/Kg	0.015 mg/Kg	
Aroclor 1232	11141-16-5	—	0.04 mg/Kg	0.013 mg/Kg	
Aroclor 1242	53469-21-9	—	0.04 mg/Kg	0.011 mg/Kg	
Aroclor 1248	12672-29-6	—	0.05 mg/Kg	0.015 mg/Kg	
Aroclor 1254	11097-69-1	—	0.03 mg/Kg	0.02 mg/Kg	
Aroclor 1260	11096-82-5	—	0.02 mg/Kg	0.01 mg/Kg	
Total Aroclors	–	—	1 mg/Kg	0.095 mg/Kg	

[a] Concentration of samples will result in a 2x lower reporting limit, if required

[b] extraction of 1L samples vs. standard 100 ml will result in a 10x lower reporting limit

TABLE 8
Soil and Sediment Analytes and Reporting Limits
OMC Plant 2

Parameter	CAS Number	Project Action Limit	Project Reporting Limit	Achievable Laboratory MDLs[a]	Required Quantization Limit (CRQL)	Project Method
TAL Metals						ILM05.3
Aluminum	7429-90-5	—			20 mg/Kg	
Antimony	7440-36-0	—			6 mg/Kg	
Arsenic	7440-38-2	—			1 mg/Kg	
Barium	7440-39-3	—			20 mg/Kg	
Beryllium	7440-41-7	—			0.5 mg/Kg	
Cadmium	7440-43-9	—			0.5 mg/Kg	
Calcium	7440-70-2	—			500 mg/Kg	
Chromium	7440-47-3	—			1 mg/Kg	
Cobalt	7440-48-4	—			5 mg/Kg	
Copper	7440-50-8	—			2.5 mg/Kg	
Iron	7439-89-6	—			10 mg/Kg	
Lead	7439-92-1	—			1 mg/Kg	
Magnesium	7439-95-4	—			500 mg/Kg	
Manganese	7439-96-5	—			1.5 mg/Kg	
Mercury	7439-97-6	—			0.1 mg/Kg	
Nickel	7440-02-0	—			4 mg/Kg	
Potassium	7440-09-7	—			500 mg/Kg	
Selenium	7782-49-2	—			3.5 mg/Kg	
Silver	7440-22-4	—			1 mg/Kg	
Sodium	7440-23-5	—			500 mg/Kg	
Thallium	7440-28-0	—			2.5 mg/Kg	
Vanadium	7440-62-2	—			5 mg/Kg	
Zinc	7440-66-6	—			6 mg/Kg	
Cyanide	57-12-5	—			2.5 mg/Kg	
TCL PCBs			—			OLM04.2
Aroclor 1016	12674-11-2	—			33 µg/Kg	
Aroclor 1221	11104-28-2	—			67 µg/Kg	
Aroclor 1232	11141-16-5	—			33 µg/Kg	
Aroclor 1242	53469-21-9	—			33 µg/Kg	
Aroclor 1248	12672-29-6	—			33 µg/Kg	
Aroclor 1254	11097-69-1	—			33 µg/Kg	
Aroclor 1260	11096-82-5	—			33 µg/Kg	
Total Aroclors	—	—	1.0 mg/Kg		—	
SPLP Metals (incl. Be)						SW-846 1312/6010 or 6020/7000 series
Aluminum	7429-90-5	—	373 µg/L	112 µg/L		
Antimony	7440-36-0	—	16 µg/L	4.9 µg/L		
Arsenic	7440-38-2	—	2.57 µg/L	0.72 µg/L		
Barium	7440-39-3	—	4.5 µg/L	1.4 µg/L		
Beryllium	7440-41-7	—	0.75 µg/L	0.23 µg/L		
Cadmium	7440-43-9	—	2.9 µg/L	0.88 µg/L		
Calcium	7440-70-2	—	330 µg/L	99 µg/L		
Chromium	7440-47-3	—	14 µg/L	4.1 µg/L		

TABLE 8
Soil and Sediment Analytes and Reporting Limits
OMC Plant 2

Parameter	CAS Number	Project Action Limit	Project Reporting Limit	Achievable Laboratory MDLs[a]	Required Quantization Limit (CRQL)	Project Method
Cobalt	7440-48-4	---	3.3 µg/L	0.99 µg/L		
Copper	7440-50-8	---	9.1 µg/L	2.7 µg/L		
Iron	7439-89-6	---	222 µg/L	67 µg/L		
Lead	7439-92-1	---	0.49 µg/L	0.15 µg/L		
Magnesium	7439-95-4	---	139 µg/L	42 µg/L		
Manganese	7439-96-5	---	4.3 µg/L	1.3 µg/L		
Mercury	7439-97-6	---	0.2 µg/L	0.1 µg/L		
Nickel	7440-02-0	---	30 µg/L	9 µg/L		
Potassium	7440-09-7	---	3200 µg/L	934 µg/L		
Selenium	7782-49-2	---	1.7 µg/L	0.42 µg/L		
Silver	7440-22-4	---	9.1 µg/L	2 µg/L		
Sodium	7440-23-5	---	1470 µg/L	442 µg/L		
Thallium	7440-28-0	---	5.03 µg/L	1.51 µg/L		
Vanadium	7440-62-2	---	2.73 µg/L	0.82 µg/L		
Zinc	7440-66-6	---	16 µg/L	4.9 µg/L		
Cyanide	57-12-5	---	29 µg/L	8.6 µg/L		
SPLP PCBs						SW-846 1312/8082
Aroclor 1016	12674-11-2	---	0.5 µg/L	0.15 µg/L		
Aroclor 1221	11104-28-2	---	0.6 µg/L	0.18 µg/L		
Aroclor 1232	11141-16-5	---	0.61 µg/L	0.18 µg/L		
Aroclor 1242	53469-21-9	---	0.69 µg/L	0.2 µg/L		
Aroclor 1248	12672-29-6	---	0.56 µg/L	0.16 µg/L		
Aroclor 1254	11097-69-1	---	0.78 µg/L	0.23 µg/L		
Aroclor 1260	11096-82-5	---	0.47 µg/L	0.14 µg/L		
Total Aroclors	---	---	4.21 µg/L	1.24 µg/L		
TCL VOCs						OLM04.2
acetone	67-64-1	---			10 µg/Kg	
benzene	71-43-2	---			10 µg/Kg	
bromodichloromethane	75-27-4	---			10 µg/Kg	
bromoform	75-25-2	---			10 µg/Kg	
bromomethane	74-83-9	---			10 µg/Kg	
2-butanone (MEK)	78-93-3	---			10 µg/Kg	
carbon disulfide	75-15-0	---			10 µg/Kg	
carbon tetrachloride	56-23-5	---			10 µg/Kg	
chlorobenzene	108-90-7	---			10 µg/Kg	
chloroethane	75-00-3	---			10 µg/Kg	
chloroform	67-66-3	---			10 µg/Kg	
chloromethane	74-87-3	---			10 µg/Kg	
cyclohexane	110-82-7	---			10 µg/Kg	
dibromochloromethane	124-48-1	---			10 µg/Kg	
dichlorodifluoromethane	75-71-8	---			10 µg/Kg	
1,2-dibromo-3-chloropropane	96-12-8	---			10 µg/Kg	
1,2-dibromomethane	106-93-4	---			10 µg/Kg	
1,2-dichlorobenzene	95-50-1	---			10 µg/Kg	
1,3-dichlorobenzene	541-73-1	---			10 µg/Kg	

TABLE 8
Soil and Sediment Analytes and Reporting Limits
OMC Plant 2

Parameter	CAS Number	Project Action Limit	Project Reporting Limit	Achievable Laboratory MDLs[a]	Required Quantization Limit (CRQL)	Project Method
1,4-dichlorobenzene	106-46-7	—			10 µg/Kg	
1,1-dichloroethane	75-34-3	—			10 µg/Kg	
1,2-dichloroethane	107-06-2	—			10 µg/Kg	
1,1-dichloroethene	75-35-4	—			10 µg/Kg	
cis-1,2-dichloroethene	156-59-2	—			10 µg/Kg	
trans-1,2-dichloroethene	156-60-5	—			10 µg/Kg	
1,2-dichloropropane	78-87-5	—			10 µg/Kg	
ethylbenzene	100-41-4	—			10 µg/Kg	
2-hexanone	591-78-6	—			10 µg/Kg	
4-methyl-2-pentanone	108-10-1	—			10 µg/Kg	
isopropylbenzene	98-82-8	—			10 µg/Kg	
methylene chloride	75-09-2	—			10 µg/Kg	
methyl acetate	79-20-9	—			10 µg/Kg	
methyl tert-butyl ether	1634-04-4	—			10 µg/Kg	
methylcyclohexane	108-87-2	—			10 µg/Kg	
1,1,2,2-tetrachloroethane	79-34-5	—			10 µg/Kg	
1,1,2-trichloro-1,2,2-trifluoroethane	76-13-1	—			10 µg/Kg	
styrene	100-42-5	—			10 µg/Kg	
tetrachloroethene	127-18-4	—			10 µg/Kg	
toluene	108-88-3	—			10 µg/Kg	
trans-1,3-dichloropropene	142-28-9	—			10 µg/Kg	
trichlorofluoromethane	75-69-4	—			10 µg/Kg	
1,2,4-trichlorobenzene	120-82-1	—			10 µg/Kg	
1,1,1-trichloroethane	71-55-6	—			10 µg/Kg	
1,1,2-trichloroethane	79-00-5	—			10 µg/Kg	
trichloroethene	79-01-6	—			10 µg/Kg	
vinyl chloride	75-01-4	—			10 µg/Kg	
xylenes (total)	1330-20-7	—			10 µg/Kg	
TCL SVOCs			---			OLMO4.2
acenaphthene	83-32-9	—			33 µg/Kg	
acetophenone	98-86-2				33 µg/Kg	
acenaphthylene	208-96-8				33 µg/Kg	
anthracene	120-12-7	—			33 µg/Kg	
atrazine	1912-24-9				33 µg/Kg	
benzo(a)anthracene	56-55-3	—			33 µg/Kg	
benzo(b)fluoranthene	205-99-2	—			33 µg/Kg	
benzo(k)fluoranthene	207-08-9	—			33 µg/Kg	
benzo(g,h,I)perylene	191-24-2				33 µg/Kg	
benzo(a)pyrene	50-32-8	—			33 µg/Kg	
benzaldehyde	100-52-7				33 µg/Kg	
bis(2-chloroethyl)ether	111-44-4	—			33 µg/Kg	
bis(2-ethylhexyl)phthalate	117-81-7	—			33 µg/Kg	
bis-(2-chloroethoxy) methane	111-91-1				33 µg/Kg	
butylbenzylphthalate	85-68-7				33 µg/Kg	
chrysene	218-01-9	—			33 µg/Kg	

TABLE 8
Soil and Sediment Analytes and Reporting Limits
OMC Plant 2

Parameter	CAS Number	Project Action Limit	Project Reporting Limit	Achievable Laboratory MDLs[a]	Required Quantization Limit (CRQL)	Project Method
caprolactam	105-60-2				33 µg/Kg	
carbozole	---				33 µg/Kg	
dibenzo(a,h)anthracene	53-70-3	---			33 µg/Kg	
dimethylphthalate	131-11-3				33 µg/Kg	
dibenzofuran	132-64-9				33 µg/Kg	
di-n-butyl phthalate	84-74-2	---			33 µg/Kg	
1,1'-biphenyl	92-52-4				33 µg/Kg	
3,3'-dichlorobenzidine	91-94-1	---			33 µg/Kg	
diethyl phthalate	84-66-2	---			33 µg/Kg	
2-chloronaphthalene	91-58-7				33 µg/Kg	
2-methylphenol	95-48-7				33 µg/Kg	
2-nitrophenol	88-75-5				33 µg/Kg	
2-nitroaniline	88-74-4				830 µg/Kg	
2,2'-oxybis (1-chloropropane)	540-54-5				33 µg/Kg	
2,4-dimethylphenol	105-67-9	---			33 µg/Kg	
2,4-dinitrotoluene	121-14-2	---			33 µg/Kg	
2,6-dinitotoluene	606-20-2	---			33 µg/Kg	
2-methylnaphthalene	91-57-6				33 µg/Kg	
di-n-octyl phthalate	117-84-0	---			33 µg/Kg	
3-nitroaniline	---				830 µg/Kg	
4-bromophenyl-phenylether	101-55-3				33 µg/Kg	
4-chloroaniline	106-47-8				33 µg/Kg	
4-chloro-3-methylphenol	35421-08-0				33 µg/Kg	
4-chlorophenyl-phenyl ether	7005-72-3				830 µg/Kg	
4-methylphenol	106-44-5				33 µg/Kg	
4-nitrophenol	100-02-7				830 µg/Kg	
4-nitroaniline	100-01-6				830 µg/Kg	
4,6-dinitro-2-methylphenol	534-52-1				830 µg/Kg	
fluoranthene	206-44-0	---			33 µg/Kg	
fluorene	86-73-7	---			33 µg/Kg	
hexachlorobenzene	118-74-1	---			33 µg/Kg	
hexachlorocyclopentadiene	77-47-4	---			33 µg/Kg	
hexachlorobutadiene	87-68-3				33 µg/Kg	
hexachloroethane	67-72-1	---			33 µg/Kg	
indeno(1,2,3-c,d)pyrene	193-39-5	---			33 µg/Kg	
isophorone	78-59-1	---			33 µg/Kg	
naphthalene	91-20-3	---			33 µg/Kg	
nitrobenzene	98-95-3	---			33 µg/Kg	
n-nitrosodiphenylamine	86-30-6	---			33 µg/Kg	
n-nitrosodi-n-propylamine	621-64-7	---			33 µg/Kg	
phenol	108-95-2	---			33 µg/Kg	
phenanthrene	85-01-8				33 µg/Kg	
pyrene	129-00-0	---			33 µg/Kg	
2-chlorophenol	95-57-8	---			33 µg/Kg	
2,4-dichlorophenol	120-83-2	---			33 µg/Kg	

TABLE 8
Soil and Sediment Analytes and Reporting Limits
OMC Plant 2

Parameter	CAS Number	Project Action Limit	Project Reporting Limit	Achievable Laboratory MDLs[a]	Required Quantization Limit (CRQL)	Project Method
2,4-dinitrophenol	51-28-5	—			830 µg/Kg	
2,4,5-trichlorophenol	95-95-4				830 µg/Kg	
pentachlorophenol	87-86-5	—			830 µg/Kg	
2,4,6-trichlorophenol	88-06-2	—			33 µg/Kg	
TOC	N/A	—	1.0 mg/Kg	73 mg/Kg		Lloyd Kahn
Porosity	N/A	—	—	—		ASTM D4404-84
Bulk Density	N/A	—	—	—		ASTM D854 (Specific Gr
Grain Size	N/A	—	—	—		ASTM D422-63
Moisture Content	N/A	—	—	—		EPA 160.3
Soil Oxidant Demand	N/A	—	—	—		TBD

[a] Analyses to be performed by a CLP lab do not have Achievable Laboratory MDLs listed because they are lab specific and the CLP lab to run the analyses will not be chosen until approximately a week before samples are collected.

TABLE 9
Groundwater Investigation Analytes and Reporting Limits
OMC Plant 2

Parameter	CAS Number	Project Action Limit	Project Reporting Limit	Achievable Laboratory MDLs[a]	Contract Required Quantiation Limit (CRQL)	Project Method
TCL VOCs						OLCO3.2
acetone	67-64-1	700 µg/L			5.0 µg/L	
benzene	71-43-2	5.0 µg/L			0.5 µg/L	
bromodichloromethane	75-27-4	0.2 µg/L			0.5 µg/L	
bromoform	75-25-2	1.0 µg/L			0.5 µg/L	
bromomethane	74-83-9	---			0.5 µg/L	
bromochloromethane	74-97-5	---			0.5 µg/L	
2-butanone (MEK)	78-93-3	---			5.0 µg/L	
carbon disulfide	75-15-0	700 µg/L			0.5 µg/L	
carbon tetrachloride	56-23-5	5.0 µg/L			0.5 µg/L	
chlorobenzene	108-90-7	100 µg/L			0.5 µg/L	
chloroethane	75-00-3	---			0.5 µg/L	
chloroform	67-66-3	0.2 µg/L			0.5 µg/L	
cyclohexane	110-82-7	---			0.5 µg/L	
chloromethane	74-87-3	---			0.5 µg/L	
dibromochloromethane	124-48-1	---			0.5 µg/L	
dichlorofluoromethane	75-43-4	---			0.5 µg/L	
1,2-dibromo-3-chloropropane	96-12-8	0.2 µg/L			0.5 µg/L	
1,2-dichlorobenzene	95-50-1	600 µg/L			0.5 µg/L	
1,4-dichlorobenzene	106-46-7	75 µg/L			0.5 µg/L	
1,1-dichloroethane	75-34-3	700 µg/L			0.5 µg/L	
1,2-dichloroethane	107-06-2	5.0 µg/L			0.5 µg/L	
1,2-dibromoethane	106-93-4	---			0.5 µg/L	
1,1-dichloroethene	75-35-4	7.0 µg/L			0.5 µg/L	
cis-1,2-dichloroethene	156-59-2	70.0 µg/L			0.5 µg/L	
cis-1,3-dichloropropene	10061-01-5	---			0.5 µg/L	
trans-1,2-dichloroethene	156-60-5	100 µg/L			0.5 µg/L	
trans-1,3-dichloropropane	142-28-9	---			0.5 µg/L	
1,2-dichloropropane	78-87-5	5.0 µg/L			0.5 µg/L	
1,3-dichlorobenzene	541-73-1	---			0.5 µg/L	
ethylbenzene	100-41-4	700 µg/L			0.5 µg/L	
2-hexanone	591-78-6	---			5.0 µg/L	
4-methyl-2-pentanone	108-10-1	---			5.0 µg/L	
methylene chloride	75-09-2	5.0 µg/L			0.5 µg/L	
methylcyclohexane	108-87-2	---			0.5 µg/L	
methyl tert-butyl ether	1634-04-4	---			0.5 µg/L	
methyl acetate	79-20-9	---			0.5 µg/L	
isopropylbenzene	98-82-8	---			0.5 µg/L	
1,1,2,2-tetrachloroethane	79-34-5	---			0.5 µg/L	
1,1,2-trichloro-1,2,2-trifluoroethane	76-13-1	---			0.5 µg/L	
styrene	100-42-5	---			0.5 µg/L	
tetrachloroethene	127-18-4	5.0 µg/L			0.5 µg/L	
toluene	108-88-3	1000 µg/L			0.5 µg/L	
trichlorofluoromethane	75-69-4	---			0.5 µg/L	

TABLE 9
Groundwater Investigation Analytes and Reporting Limits
OMC Plant 2

Parameter	CAS Number	Project Action Limit	Project Reporting Limit	Achievable Laboratory MDLs[a]	Contract Required Quantiation Limit (CRQL)	Project Method
1,2,4-trichlorobenzene	120-82-1	70 µg/L			0.5 µg/L	
1,1,1-trichloroethane	71-55-6	200 µg/L			0.5 µg/L	
1,1,2-trichloroethane	79-00-5	5.0 µg/L			0.5 µg/L	
1,2,3-trichlorobenzene	87-61-6	—			0.5 µg/L	
trichloroethene	79-01-6	5.0 µg/L			0.5 µg/L	
vinyl chloride	75-01-4	2.0 µg/L			0.5 µg/L	
xylenes (total)	1330-20-7	10,000 µg/L			0.5 µg/L	
TCL SVOCs		—				OLCO3.2
acenaphthene	83-32-9	420 µg/L			5.0 µg/L	
acetophenone	98-86-2	—			5.0 µg/L	
anthracene	120-12-7	2100 µg/L			5.0 µg/L	
atrazine	1912-24-9	—			5.0 µg/L	
benzaldehyde	100-52-7	—			5.0 µg/L	
benzo(a)anthracene	56-55-3	0.13 µg/L			5.0 µg/L	
benzo(b)fluoranthene	205-99-2	0.18 µg/L			5.0 µg/L	
benzo(k)fluoranthene	207-08-9	0.17 µg/L			5.0 µg/L	
benzo(a)pyrene	50-32-8	0.20 µg/L			5.0 µg/L	
benzo(g,h,I)perylene	191-24-2	—			5.0 µg/L	
bis(2-chloroethyl)ether	111-44-4	10 µg/L			5.0 µg/L	
bis(2-ethylhexyl)phthalate	117-81-7	6.0 µg/L			5.0 µg/L	
bis (2-chloroethoxy) methane	111-91-1	—			5.0 µg/L	
butylbenzylphthalate	85-68-7	—			5.0 µg/L	
chrysene	218-01-9	1.5 µg/L			5.0 µg/L	
caprolactam	105-60-2	—			5.0 µg/L	
dibenzo(a,h)anthracene	53-70-3	0.3 µg/L			5.0 µg/L	
di-n-butyl phthalate	84-74-2	700 µg/L			5.0 µg/L	
dibenzofuran	132-64-9	—			5.0 µg/L	
3,3'-dichlorobenzidine	91-94-1	20 µg/L			5.0 µg/L	
diethyl phthalate	84-66-2	5600 µg/L			5.0 µg/L	
dimethylphthalate	131-11-3	—			5.0 µg/L	
1,1'-biphenyl	92-52-4	—			5.0 µg/L	
1,2,4,5-tetrachlorobenzene	95-94-3	—			5.0 µg/L	
2-methylnaphthalene	91-57-6	—			5.0 µg/L	
2,'-oxybis (1-chloropropane)	540-54-5	—			5.0 µg/L	
2-nitrophenol	88-75-5	—			5.0 µg/L	
2-chloronaphthalene	91-58-7	—			5.0 µg/L	
2-methylphenol	95-48-7	—			5.0 µg/L	
2-nitroaniline	88-74-4	—			20 µg/L	
2,4-dimethylphenol	105-67-9	140 µg/L			5.0 µg/L	
2,4-dinitrotoluene	121-14-2	0.02 µg/L			5.0 µg/L	
2,6-dinitotoluene	606-20-2	0.31 µg/L			5.0 µg/L	
3-nitroaniline	—	—			20 µg/L	
4-methylphenol	106-44-5	—			5.0 µg/L	
4-nitrophenol	100-02-7	—			20 µg/L	

TABLE 9
Groundwater Investigation Analytes and Reporting Limits
OMC Plant 2

Parameter	CAS Number	Project Action Limit	Project Reporting Limit	Achievable Laboratory MDLs[a]	Contract Required Quantiation Limit (CRQL)	Project Method
4-nitroaniline	100-01-6	—			20 µg/L	
4-bromophenyl-phenylether	101-55-3	—			5.0 µg/L	
4-chloroaniline	106-47-8	—			5.0 µg/L	
4-chloro-3-methylphenol	35421-08-0	—			5.0 µg/L	
4-chlorophenyl-phenylether	7005-72-3	—			5.0 µg/L	
4,6-dinitro-2-methylphenol	534-52-1	—			20 µg/L	
di-n-octyl phthalate	117-84-0	140 µg/L			5.0 µg/L	
fluoranthene	206-44-0	280 µg/L			5.0 µg/L	
fluorene	86-73-7	280 µg/L			5.0 µg/L	
hexachlorobutadiene	87-68-3	—			5.0 µg/L	
hexachlorobenzene	118-74-1	0.06 µg/L			5.0 µg/L	
hexachlorocyclopentadiene	77-47-4	50 µg/L			5.0 µg/L	
hexachloroethane	67-72-1	7.0 µg/L			5.0 µg/L	
indeno(1,2,3-c,d)pyrene	193-39-5	0.43 µg/L			5.0 µg/L	
isophorone	78-59-1	1400 µg/L			5.0 µg/L	
naphthalene	91-20-3	140 µg/L			5.0 µg/L	
nitrobenzene	98-95-3	3.5 µg/L			5.0 µg/L	
n-nitrosodiphenylamine	86-30-6	3.2 µg/L			5.0 µg/L	
n-nitrosodi-n-propylamine	621-64-7	1.8 µg/L			5.0 µg/L	
phenol	108-95-2	100 µg/L			5.0 µg/L	
pyrene	129-00-0	210 µg/L			5.0 µg/L	
phenanthrene	85-01-8	—			5.0 µg/L	
2-chlorophenol	95-57-8	35 µg/L			5.0 µg/L	
2,4-dichlorophenol	120-83-2	21 µg/L			5.0 µg/L	
2,4-dinitrophenol	51-28-5	14 µg/L			20 µg/L	
pentachlorophenol	87-86-5	1.0 µg/L			5.0 µg/L	
2,4,5-trichlorophenol	95-95-4	—			20 µg/L	
2,4,6-trichlorophenol	88-06-2	10 µg/L			5.0 µg/L	
TCL PCBs						OLCO3.2
Aroclor 1016	12674-11-2	—			0.2 µg/L	
Aroclor 1221	11104-28-2	—			0.4 µg/L	
Aroclor 1232	11141-16-5	—			0.2 µg/L	
Aroclor 1242	53469-21-9	—			0.2 µg/L	
Aroclor 1248	12672-29-6	—			0.2 µg/L	
Aroclor 1254	11097-69-1	—			0.2 µg/L	
Aroclor 1260	11096-82-5	—			0.2 µg/L	
Total Aroclors	—					
TAL Metals						ILMO5.3
Aluminum	7429-90-5	—			200 µg/L	
Antimony	7440-36-0	—			60 µg/L	
Arsenic	7440-38-2	50 µg/L			10 µg/L	
Barium	7440-39-3	2000 µg/L			200 µg/L	
Beryllium	7440-41-7	—			5 µg/L	
Cadmium	7440-43-9	5.0 µg/L			5 µg/L	

TABLE 9
Groundwater Investigation Analytes and Reporting Limits
OMC Plant 2

Parameter	CAS Number	Project Action Limit	Project Reporting Limit	Achievable Laboratory MDLs[a]	Contract Required Quantiation Limit (CRQL)	Project Method
Calcium	7440-70-2	—			5000 µg/L	
Chromium	7440-47-3	100 µg/L			10 µg/L	
Cobalt	7440-48-4	—			50 µg/L	
Copper	7440-50-8	—			25 µg/L	
Iron	7439-89-6	5000 µg/L			100 µg/L	
Lead	7439-92-1	7.5 µg/L			10 µg/L	
Magnesium	7439-95-4	—			5000 µg/L	
Manganese	7439-96-5	—			15 µg/L	
Mercury	7439-97-6	—			0.2 µg/L	
Nickel	7440-02-0	—			40 µg/L	
Potassium	7440-09-7	—			5000 µg/L	
Selenium	7782-49-2	50 µg/L			35 µg/L	
Silver	7440-22-4	50 µg/L			10 µg/L	
Sodium	7440-23-5	—			5000 µg/L	
Thallium	7440-28-0	—			25 µg/L	
Vanadium	7440-62-2	—			50 µg/L	
Zinc	7440-66-6	—			60 µg/L	
Cyanide (ammenable)	57-12-5	200 µg/L			10 µg/L	
Hexavalent Chromium		—	5.0 µg/L			SW-846 7196
General Chemistry						
Alkalinity ($CaCO_3$)	471-34-1	—	5.0 mg/L			EPA 310.1
Chloride	16887-00-6	200 mg/L	1.0 mg/L			EPA 300.0
Sulfate	14808-79-8	400 mg/L	50 mg/L			EPA 300.0
Sulfide	18496-25-8	—	1.0 mg/L			EPA 376.1
Nitrate	7697-37-2	—	1.0 mg/L			EPA 300.0
Nitrite	14797-65-0	—	1.0 mg/L			EPA 300.0
Methane	74-82-8	—	10 µg/L			RSK 175
Ethane	74-84-0	—	10 µg/L			RSK 175
Ethene	74-85-1	—	10 µg/L			RSK 175
Total Organic Carbon		—	1.0 mg/L			SW-846 9060

a Analyses to be performed by a CLP lab do not have Achievable Laboratory MDLs listed because they are lab specific and the CLP lab to run the analyses will not be chosen until approximately a week before samples are collected.

TABLE 10
Air and Soil Gas Analytes and Reporting Limits
OMC Plant 2

Parameter	CAS Number	Project Action Limit	Project Reporting Limit	Achievable Laboratory MDLs	Project Method
TCL VOCs					TO-15
Chloromethane	74-87-3	—	0.2 ppbv	0.301 ppbv	
Vinyl Chloride	75-01-4	—	0.2 ppbv	0.119 ppbv	
Bromomethane	74-83-9	—	0.2 ppbv	0.0740 ppbv	
Chloroethane	75-00-3	—	0.2 ppbv	0.145 ppbv	
1,1-Dichloroethene	75-35-4	—	0.2 ppbv	0.0839 ppbv	
Methylene Chloride	75-09-2	—	0.5 ppbv	0.159 ppbv	
1,1-Dichloroethane	75-34-3	—	0.2 ppbv	0.0951 ppbv	
cis-1,2,-Dichloroethene	156-59-2	—	0.2 ppbv	0.0763 ppbv	
trans-1,2-Dichloroethene	156-60-5	—	0.2 ppbv	0.107 ppbv	
Chloroform	67-66-3	—	0.2 ppbv	0.0701 ppbv	
1,1,1-Trichloroethane	71-55-6	—	0.2 ppbv	0.0709 ppbv	
Carbon Tetrachloride	56-23-5	—	0.2 ppbv	0.0599 ppbv	
Benzene	71-43-2	—	0.2 ppbv	0.0784 ppbv	
1,2-Dichloroethane	107-06-2	—	0.2 ppbv	0.0661 ppbv	
Trichloroethene	79-01-6	—	0.2 ppbv	0.109 ppbv	
1,2-Dichloropropane	78-87-5	—	0.2 ppbv	0.102 ppbv	
Toluene	108-88-3	—	0.2 ppbv	0.0703 ppbv	
trans-1,3-Dichloropropene	10061-02-6	—	0.2 ppbv	0.0940 ppbv	
1,1,2-Trichloroethane	79-00-5	—	0.2 ppbv	0.0799 ppbv	
Tetrachloroethene	127-18-4	—	0.2 ppbv	0.0593 ppbv	
Chlorobenzene	108-90-7	—	0.2 ppbv	0.0623 ppbv	
Ethyl Benzene	100-41-4	—	0.2 ppbv	0.0708 ppbv	
p-xylene	106-42-3	—	0.2 ppbv	0.121 ppbv	
m-xylene	108-38-3	—	0.2 ppbv	0.121 ppbv	
o-xylene	95-47-6	—	0.2 ppbv	0.0612 ppbv	
Styrene	100-42-5	—	0.2 ppbv	0.0544 ppbv	
1,1,2,2-Tetrachlorethane	79-34-5	—	0.2 ppbv	0.0520 ppbv	
Acetone	67-64-1	—	5.0 ppbv	0.669 ppbv	
Carbon Disulfide	75-15-0	—	0.5 ppbv	0.144 ppbv	
2-Butanone (MEK)	78-93-3	—	0.5 ppbv	0.0763 ppbv	
Bromodichloromethane	75-27-4	—	0.2 ppbv	0.0695 ppbv	
4-Methyl-2-pentanone	108-10-1	—	0.5 ppbv	0.109 ppbv	
2-Hexanone	591-78-6	—	0.2 ppbv	0.171 ppbv	
Dibromochloromethane	124-48-1	—	0.2 ppbv	0.0543 ppbv	
Bromoform	75-25-2	—	0.2 ppbv	0.0436 ppbv	

TABLE 11
Sample Containers, Preservatives, and Holding Times
OMC Plant 2

Analysis	Method a, d	Container	Preservation/ Storage	Maximum Hold Time
Building (core samples)				
TAL Metals	ILM05.3	Concrete core plug in ziploc bag	4°C	180 days; mercury 28 days
Cyanide (total)	ILM05.3	Concrete core plug in ziploc bag	4°C	14 days
TCL PCBs	OLM04.2	Concrete core plug in ziploc bag	4°C	14 days to extraction, 40 days from extraction to analysis
SPLP Metals (including Be)	SW-836 1312/6010	Concrete core plug in ziploc bag	4°C	180 days
SPLP PCBs	SW-846 1312[a]/8082	Concrete core plug in ziploc bag	4°C	14 days to extraction, 40 days from extraction to analysis
Building (wipe samples)				
TCL PCBs	OLM04.2	Cotton Gauze + 40-mL glass jar	4°C, 15 mL hexane	14 days
Soil				
TAL Metals	ILM05.3	One 8-oz amber glass	4°C	180 days; mercury 28 days
Cyanide (total)	ILM05.3	One 8-oz amber glass	4°C	14 days
TCL PCBs	OLM04.2	One 8-oz amber glass	4°C	14 days to extraction, 40 days from extraction to analysis
TCL VOCs	OLM04.2	One 2-oz or 4-oz glass – no head space (must have 5g of soil)	4°C, MeOH	14 days to extraction, 40 days from extraction to analysis
TCL SVOCs	OLM04.2	One 8-oz amber glass	4°C	14 days to extraction, 40 days from extraction to analysis
SPLP PCBs	SW-846 1312[a]/8082	One 8-oz amber glass	4°C	14 days to extraction, 40 days from extraction to analysis
SPLP Metals (including Be)	SW-836 1312/6010 or 7000 series (Mercury)	One 8-oz amber glass	4°C	180 days; mercury 28 days
Total Organic Carbon	415.1 or SW-846 9060	One 8-oz amber glass	4°C	48 hours
Porosity	ASTM D4404-84	4-oz glass jar	—	—
Bulk Density	ASTM D854 (Specific Gravity)	4-oz glass jar	—	—
Grain Size	ASTM D422-63	4-oz glass jar	—	—
Moisture Content	EPA 160.3	4-oz glass jar	4°C	—

TABLE 11
Sample Containers, Preservatives, and Holding Times
OMC Plant 2

Analysis	Method a, d	Container	Preservation/ Storage	Maximum Hold Time
Soil Oxidant Demand[b]	Potassium Permanganate Demand	4-oz glass jar	4°C	Upon receipt of samples
Groundwater				
TCL PCBs	OLC03.2	Two 1-L amber glass	4°C	7 days to extraction, 40 days from extraction to analysis
TCL VOCs	OLC03.2	Three 40-mL VOA vials	HCl to pH ≤ 2, 4°C	14 days to extraction, 40 days from extraction to analysis
TCL SVOCs	OLC03.2	Two 1-L amber glass	4°C	7 days to extraction, 40 days from extraction to analysis
TAL Metals (total and dissolved)	ILM05.3	1-L poly	HNO_3 to pH ≤ 2	180 days; mercury 28 days
Cyanide (total)	ILM05.3	1-L poly	NaOH to pH ≥12	14 days
Chromium (hexavalent)	SW-846 7196	250-mL poly	4°C	24 hours
Sulfate[c]	EPA 375.4	250-mL poly	4°C	28 days
Sulfide[c]	EPA 376.1	500-mL poly	4°C, Zn acetate, NaOH to pH>9	7 days
Nitrate[c]	EPA 300.0	100-mL poly	4°C	48 hours
Chloride[c]	EPA 300.0	250-mL poly	4°C	28 days
Methane/Ethene/ Ethane[c]	RSK 175	Three 40mL VOA vials	4°C	14 days
Total Alkalinity[c]	EPA 310.2	100-mL poly	4°C	14 days
TOC[c]	SW-846 9060	100-mL poly	HCl to pH <2, 4°C	28 days
Nitrite[c]	EPA 354.1	100-mL poly	4°C	48 hours
Investigation Derived Waste (characterization sampling)				
Soil				
TCLP VOCs	SW 846 1311/8260B	One 2-oz or 4-oz glass – no head space (must have 5g of soil)	4°C, MeOH	14 days
TCLP SVOCs	SW-846 1311/8270C	One 8-oz amber glass	4°C	14 days
TCLP Metals	SW-846 1311/6010B or 7000 series (Mercury)	One 8-oz amber glass	4°C	180 days; mercury 28 days
TCL VOCs	OLM04.2	One 2-oz glass – no head space	4°C, MeOH	14 days
TCL SVOCs	OLM04.2	One 8-oz amber glass	4°C	14 days

TABLE 11
Sample Containers, Preservatives, and Holding Times
OMC Plant 2

Analysis	Method a, d	Container	Preservation/ Storage	Maximum Hold Time
TCL PCBs	OLM04.2	One 8-oz amber glass	4°C	14 days
TAL Metals	ILM05.3	One 8-oz amber glass	4°C	180 days; mercury 28 days
Cyanide	ILM05.3	One 8-oz amber glass	4°C	14 days
Investigation-Derived Waste (characterization sampling)				
Groundwater				
TCL VOCs	OLM04.3	Three 40-mL VOA vials	HCl to pH ≤ 2, 4°C	7 days to extraction, 40 days from extraction to analysis
TCL SVOCs	OLM04.3	Two 1-L amber glass	4°C	7 days to extraction, 40 days from extraction to analysis
TCL PCBs	OLM04.3	Two 1-L amber glass	4°C	7 days to extraction, 40 days from extraction to analysis
TAL Metals	ILM05.3	1-L poly	HNO_3 to pH ≤ 2	180 days; mercury 28 days
Cyanide (total)	ILM05.3	1-L poly	NaOH to pH ≥12	14 days
Soil Gas & Air				
VOCs	TO-15	SUMMA canister	None	14 days

a. Identified method may be modified in QAPP based on quantitation limits to achieve Illinois TACO Tier 1 remediation objectives or ADLs.
b. Soil Oxidant Demand – Analysis, containers, storage, and holding times are different depending on laboratory used.
c. Indicates natural attenuation parameter selected from Table 2.3 of *EPA's Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Groundwater*, 1998.

d. CLP method listed or equivalent

— = not applicable/not required

TABLE 12
QC Acceptance Criteria
OMC Plant 2

Audits Required	Frequency of Audits	Limits
Preparation Blank	1 per group of 10 or fewer samples	< RL
Lab Duplicate	1 per group of 10 or fewer samples	< 20% RPD
Matrix Spike/ Matrix Spike Duplicate	1 per group of 20 or fewer samples	70-130% Recovery
Lab Control Spikes	1 per group of 20 or fewer samples	80-120% Recovery

TABLE 13
Sample Tracking Sheet

OMC Plant 2 Building Data 2004–2005

SDG No.	Sample Nos.	Matrix	VOCs	TOC	Porosity	Bulk Density	Grain Size	Moisture Content	Soil Oxidant Demand	Dissolved Iron	Hexavalent Chromium	Sulfate	Sulfide	Nitrate	Nitrite	Chloride	Methane/Ethene/Ethane	Total Alkalinity	TOC	TAL Metals	TCL PCBs	SPLP Metals	SPLP PCB's	TCLP VOCs	TCLP SVOCs	TCLP Pesticides	TCLP Metals

TABLE 13
Sample Tracking Sheet

OMC Plant 2 Building Data 2004–2005

										EPA Validated								
Sample Date	Date Recv'd by Lab	TAT (days)	Date Due	Date Hard Copy Recv'd by CH2M	No. of Days Late	Date EDD Recv'd by CH2M	Invoice Approved	1st Hard Copy Filed	Date Sent to EPA	Validation back from EPA	VOCs	As & Pb	SVOCs	Gen Chem	2nd Hard Copy Filed	Comments	EDD Uploaded	Validation Qualifiers/ Comments Uploaded

Figures

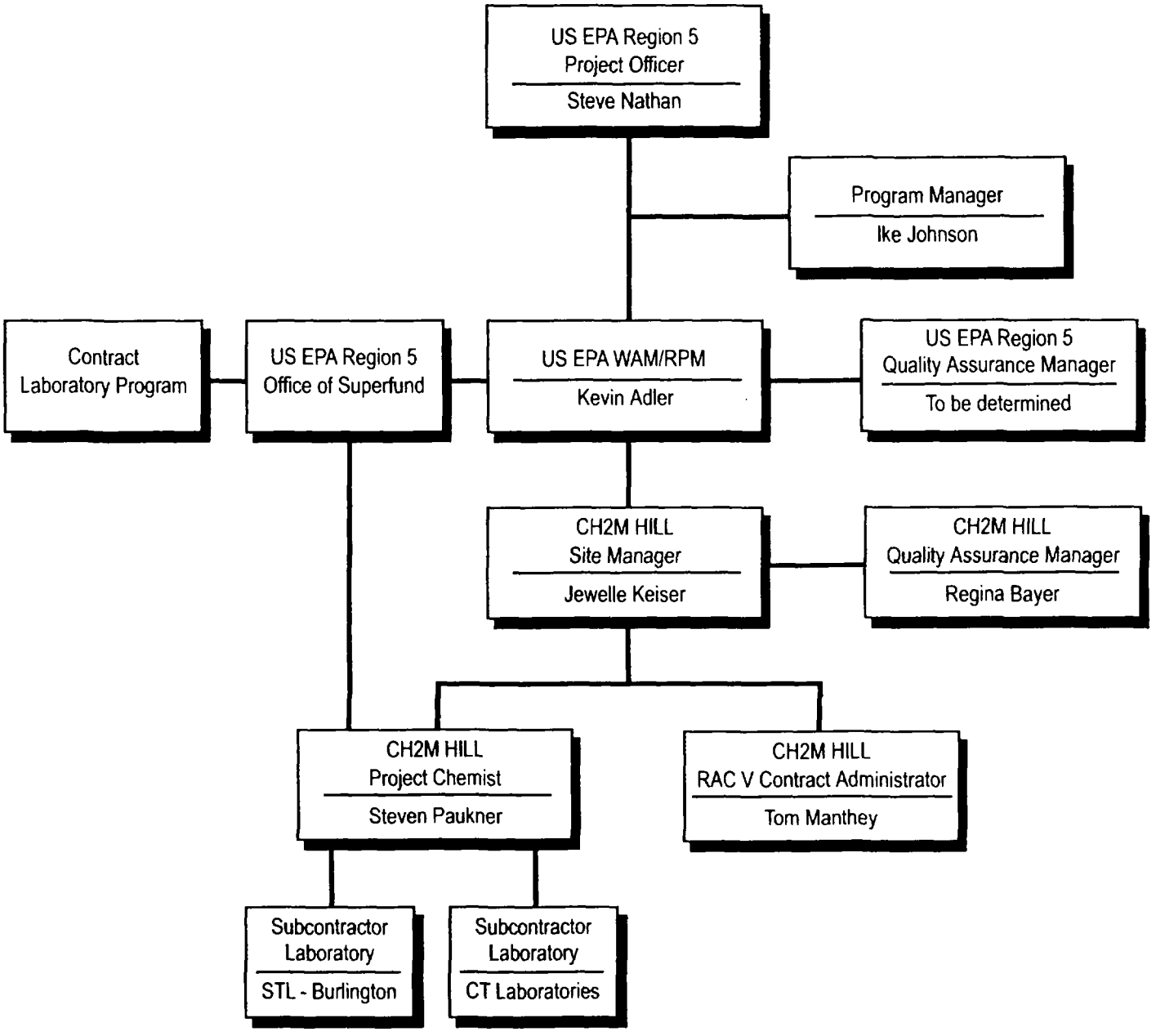
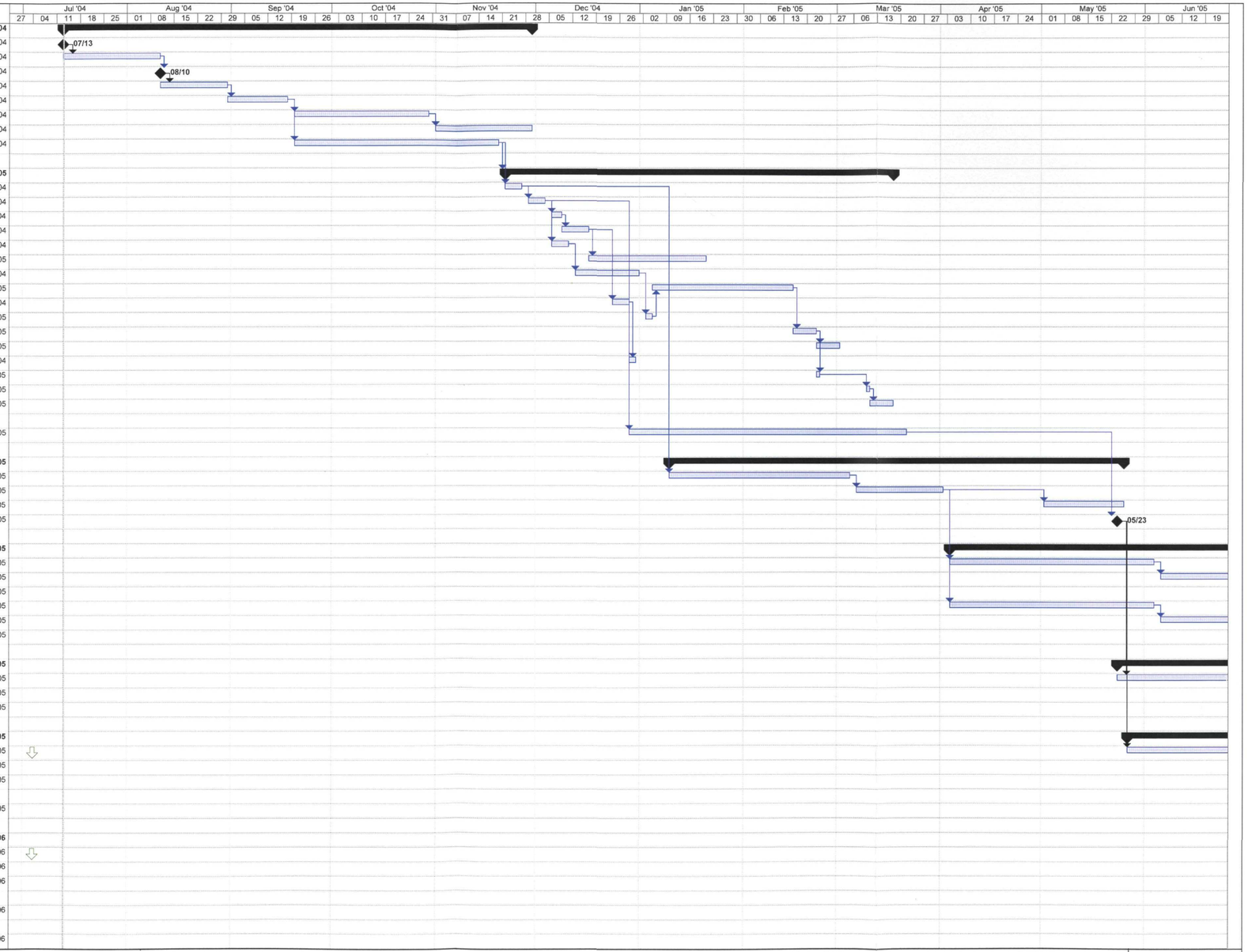


FIGURE 1
Project Organization Chart
OMC Plant 2
Remedial Investigation

ID	Task Name	Duration	Start	Finish
1	**Task 1 Project Planning**	**100 days**	**Tue 07/13/04**	**Mon 11/29/04**
2	Submit RI/FS Work Plan	0 days	Tue 07/13/04	Tue 07/13/04
3	USEPA Review Work Plan	21 days	Tue 07/13/04	Tue 08/10/04
4	Negotiation meeting	0 days	Tue 08/10/04	Tue 08/10/04
5	Revised work plan	14 days	Wed 08/11/04	Mon 08/30/04
6	USEPA Review Work Plan	14 days	Tue 08/31/04	Fri 09/17/04
7	Prepare Site Plans	30 days	Mon 09/20/04	Fri 10/29/04
8	USEPA Review Plans	21 days	Mon 11/01/04	Mon 11/29/04
9	Procure Subcontractors	45 days	Mon 09/20/04	Fri 11/19/04
10				
11	**Task 3 Data Acquisition**	**84 days**	**Mon 11/22/04**	**Thu 03/17/05**
12	Site Reconnaisance	5 days	Mon 11/22/04	Fri 11/26/04
13	Mobilization	5 days	Mon 11/29/04	Fri 12/03/04
14	Wipe Sampling	3 days	Mon 12/06/04	Wed 12/08/04
15	Concrete Core Sampling	6 days	Thu 12/09/04	Thu 12/16/04
16	Confirmatory MIP GW and Soil Sam	5 days	Mon 12/06/04	Fri 12/10/04
17	MIP Investigation	25 days	Fri 12/17/04	Thu 01/20/05
18	Soil Investigation	15 days	Mon 12/13/04	Fri 12/31/04
19	Monitoring Well Installation and Dev	30 days	Wed 01/05/05	Tue 02/15/05
20	Storm and Sanitary Sewer Testing	3 days	Fri 12/24/04	Tue 12/28/04
21	Soil Vapor and Air Investigation	2 days	Mon 01/03/05	Tue 01/04/05
22	Groundwater Sampling	5 days	Wed 02/16/05	Tue 02/22/05
23	In-situ Hydraulic Testing	5 days	Wed 02/23/05	Tue 03/01/05
24	Ecological Investigation	2 days	Wed 12/29/04	Thu 12/30/04
25	IDW Sampling	1 day	Wed 02/23/05	Wed 02/23/05
26	Disposed of IDW	1 day	Thu 03/10/05	Thu 03/10/05
27	Site Demobilization	5 days	Fri 03/11/05	Thu 03/17/05
28				
29	**Task 5 Analytical Support and Data Va**	59 days	Wed 12/29/04	Mon 03/21/05
30				
31	**Task 6 Data Evaluation**	**98 days**	**Mon 01/10/05**	**Wed 05/25/05**
32	Data Usability	40 days	Mon 01/10/05	Fri 03/04/05
33	Data Reduction, Tabulation and Eva	20 days	Mon 03/07/05	Fri 04/01/05
34	Develop Data Evaluation Report	18 days	Mon 05/02/05	Wed 05/25/05
35	Submit Data Evaluation Report	0 days	Mon 05/23/05	Mon 05/23/05
36				
37	**Task 7 Risk Assessment**	**96 days**	**Mon 04/04/05**	**Mon 08/15/05**
38	Draft HHRA	45 days	Mon 04/04/05	Fri 06/03/05
39	USEPA Review	21 days	Mon 06/06/05	Mon 07/04/05
40	Final HHRA	30 days	Tue 07/05/05	Mon 08/15/05
41	Draft ERA	45 days	Mon 04/04/05	Fri 06/03/05
42	USEPA Review	21 days	Mon 06/06/05	Mon 07/04/05
43	Final ERA	30 days	Tue 07/05/05	Mon 08/15/05
44				
45	**Task 9 Remedial Investigation Report**	**126 days**	**Tue 05/24/05**	**Tue 11/15/05**
46	Draft RI Report	60 days	Tue 05/24/05	Mon 08/15/05
47	USEPA Review	21 days	Tue 08/16/05	Tue 09/13/05
48	Final RI Report	45 days	Wed 09/14/05	Tue 11/15/05
49				
50	**Task 10 Remedial Alternative Screeni**	**126 days**	**Fri 05/27/05**	**Fri 11/18/05**
51	Draft Remedial Alternatives Memora	75 days	Fri 05/27/05	Thu 09/08/05
52	USEPA Review	21 days	Fri 09/09/05	Fri 10/07/05
53	Final Remedial Alternatives Memora	30 days	Mon 10/10/05	Fri 11/18/05
54				
55	**Task 11 Remedial Alternative Evaluati**	30 days	Mon 11/07/05	Fri 12/16/05
56				
57	**Task 12 FS Report and RI/FS Report**	**96 days**	**Mon 12/05/05**	**Mon 04/17/06**
58	Draft FS Report	45 days	Mon 12/05/05	Fri 02/03/06
59	USEPA Review	21 days	Mon 02/06/06	Mon 03/06/06
60	Final FS Report	30 days	Tue 03/07/06	Mon 04/17/06
61				
62	**Task 13 Post RI/FS Support**	60 days	Tue 04/18/06	Mon 07/10/06
63				
64	**Task 16 Work Assignment Closeout**	4 days	Tue 07/11/06	Fri 07/14/06



Project: OMC_Plant2_jk
Date: Tue 07/13/04

Task | Split | Progress | Milestone | Summary | Project Summary | External Tasks | External Milestone | Deadline

FIGURE 2
Project Schedule

Appendix A
Analytical Standard Operating Procedures

APPENDIX A
ANALYTICAL STANDARD OPERATING PROCEDURES (SOPs)
CT LABORATORIES (CTL), BARABOO, WISCONSIN

COMMENT: CTL Method Detection Limits (MDLs) and Reporting Limits (RLs) should be included in the SOPs, to demonstrate that **CTL** can achieve the project required MDLs and RLs specified in QAPP TABLES 7, 8, and 9.

MDLs and RLs are not static and change at least on an annual basis (i.e., MDLs) or are project-specific (i.e., RLs). It is our contention that these do not belong in a standard operating procedure but are best managed and updated, as needed, in separate documents or tables. We will or have provided this information but can provide, if necessary, in a format suitable to append to the SOPs.

I Total and Amenable Cyanide SOP No: CC-1

Section 11.2.2
Describe preparation procedures for Concrete Core samples.

See attached CTLaboratories facility SOP for sub-sampling, FO-10. This SOP is separate from analytical SOPs. The same procedure for sample reduction will be same in each case. Once the concrete core has been broken up into particulate material, the concrete is treated in the analytical methods as soil matrix.

II Hexavalent Chromium, Automated Colorimetric SOP No: CC-34

Section 8.2.5
Can this method achieve the project required RL of 5 ug/L? See QAPP TABLE 9.

CTLaboratories current MDL of 5.2 ug/L does not meet the project reporting limit of 5.0 ug/L. This information was provided in our solicitation response.

III Mercury Cold Vapor Atomic Absorption SOP No: 6120B

A Section 8.4.3
Can this method achieve the project required RL of 0.2 ug/L? See QAPP TABLES 7 and 8.

CTLaboratories current MDL of 0.11 ug/L meets the project reporting limit.

B Section 11.3
Describe preparation procedures for Concrete Core samples.

See information in Section I.

IV Graphite Furnace Atomic Absorption SOP No: 6110B

A Section 1.0, editorial
Reference the applicable digestion procedures.

CTLaboratories will consider including digestion method references in our next revision to the SOP. Individual SOPs have been provided for the digestion/sample preparation procedures.

B Appendix A
Can this method achieve the project required RLs for Arsenic, Lead, and Selenium specified in QAPP TABLE 7?

CTLaboratories current MDLs for As, Pb, and Se are 0.07, 0.13, and 0.08 mg/kg, respectively. These MDLs meet the project reporting limits of 2, 0.6, and 1 mg/kg, respectively.

V Acid Digestion of Solids and Semi-solids for Total Metals SOP No: 6230B

A Section 11.2
Include procedures for determining % Dry Weight, or provide SOP for determining % Moisture, likely, method based on EPA 160.3.

See attached CTLaboratories SOP # CC29 for Total Solids.

B Section 11.2
Describe preparation procedures for Concrete Core samples.

See information in Section I.

VI Semi-Volatile PCB as Aroclor Analysis SOP NO: 8082

A Section 9.0
Describe preparation procedures for Building (wipe samples).

See attached updated CTLaboratories SOP # 8082.

B Section 9.2.3
Describe preparation procedures for Concrete Core samples.

See information in Section I.

VII Semi-Volatile Organochlorine Pesticide Analysis SOP NO: 8081A

This SOP may not be needed, unless the project requires pesticide analysis for soil, groundwater, and TCLP/SPLP extracts.

N/A

VIII Sulfide, Titrimetric Method SOP No: CC-32

Section 16.0

CTL should consider adding a Matrix Spike and Laboratory Control Sample.

Per the method, MS and LCS are not required. Spikes for sulfide typically have low recovery due to sulfide oxidation during the preparation procedure and are, therefore, a poor quality control representation of the procedure.

IX Analysis of Semivolatile Organic Compounds by GC/MS SOP No: 5260

A This SOP may not be needed, unless the project requires Semivolatile analysis for Soil, Groundwater, and TCLP/SPLP extracts.

B Table 1
The compounds 3-Methylphenol and 4-Methylphenol must be included if TCLP extracts are going to be analyzed.

These compounds weren't indicated in the TAL in the SAS or the project solicitation. These compounds are part of our normal reporting list but co-elute.

C Section 11.0
Provide all the applicable Semivolatile preparation procedures, if used.

See CTLaboratories SOP # 8270EXT for the applicable procedures.

X Total Organic Carbon in Water SOP No: CC-TOC

A Section 10.0
Describe preparation procedures for TOC in Soil samples. See QAPP TABLE 8.

Only the water SOP has been provided. CTLaboratories will need to provide the soil SOP for the Lloyd-Kahn method. SOP is currently in draft format.

B Section 10.8.4
Will samples be done in quadruplicate? See item 15 page 12/12.

Strike item 15 on page 12/12. This is not appropriate to water samples. Soil samples will not be performed in quadruplicate unless required, and then only 1 of 20 samples or one per analytical run would be applicable.

XI Analysis of Volatile Organic Compounds by GC/MS SOP NO: 5280B

This SOP may not be needed, unless the project requires volatile analysis for soil, groundwater, and TCLP/SPLP extracts.

CT Laboratories, Inc.
Baraboo Laboratory Divison

Title: **Alkalinity, Titrimetric Method**

SOP Number: **CC-11**

Prepared by: _____
Date

Technical Review by: _____
Date

Reviewed by: _____
Quality Assurance ***Date***

_____
Laboratory Director ***Date***

SOP Manual Control Number:_____

1.0 SCOPE AND APPLICATION

1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.

2.0 METHOD SUMMARY

2.1 Hydroxyl ions present in a sample as a result of dissociation or hydrolysis of solutes react with additions of standard acid. The end point of pH 4.5 is determined either by the use of Bromcresol Green/Methyl Red initcator or by use of a pH meter.

3.0 DEFINITIONS

3.1 Lab Control Sample (LCS): A known concentration obtained from a second source. The LCS is analyzed exactly like a sample.

3.2 Continuing Calibration Verification (CCV): A check standard analyzed after every ten samples and at the end of the analytical run.

3.3 Duplicate Analysis: Two aliquots of a given sample are analyzed. The relative percent difference (RPD) is then determined from the two results and compared to the lab control limits for that particular matrix.

3.4 Method Blank (MB): DI water taken through the same process as the samples.

4.0 HEALTH AND SAFETY

4.1 Gloves and protective clothing should be worn to protect against unnecessary exposure to possibly hazardous chemicals and contaminants in samples. All activities performed while following this procedure should utilize appropriate laboratory safety systems (see CTI Health and Safety Manual).

5.0 CAUTIONS

5.1 Drinking water samples must be analyzed using a pH meter.

5.2 ACOE protocol samples must be analyzed using a pH meter.

6.0 INTERFERENCES

6.1 Color can interfere with the bromcresol green/methyl red indicator solution. If you cannot clearly see the endpoint. titrate the sample using a pH meter.

6.2 Soaps, oily matter, suspended solids, or precipitates may coat the glass electrode and cause a sluggish response. Clean electrode between samples.

6.3 If the sample is altered in any way. the analysis is in error.

7.0 PERSONNEL QUALIFICATIONS

7.1 All personnel need to demonstrate capability by completing a valid IDC, initial demonstration of capability, study prior to performing analysis on actual samples.

8.0 APPARATUS AND MATERIALS

8.1 Calibrated pH meter, capable of reading 0.05 pH units.
8.2 Magnetic stir plate with Teflon coated stir bar
8.3 25.0 ml self-zeroing buret.
8.4 Pipets, volumetric.
8.5 Erlenmeyer flasks.
8.6 Graduated cylinders.
8.7 Sulfuric acid, 0.02 N;. Certified normality 0.0202-0198 N.
8.8 *Mixed bromcresol green/methyl red indicator: purchased commerically*

9.0 INSTRUMENT OR METHOD CALIBRATION

9.1 Calibrate meter daily.
9.2 Check internal reference solution and fill if necessary.
9.3 Press Calibrate. The word CALIBRATE is displayed.
9.4 After a few seconds ENTER NO. BUFFERS is displayed. Press 3 and then press Yes.
9.5 When the BUFFER 1 prompt appears, place the electrode into the pH 4.0 buffer. Always use fresh buffers daily.
9.6 When the electrode signal has stabilized, the prompt READY CAL AS will appear. Record the pH displayed in the pH calibration log book. Press Yes. Rinse the probe.
9.7 Repeat steps 9.5 and 9.6 for the pH 7.0 and 10.0 buffers.
9.8 The slope of the line should appear. This appears *very briefly* after you press YES following the pH 10 buffer. Record the slope in the pH calibration log book.
9.9 The meter will automatically go to the MEASURE mode.
9.10 The acceptable range for the electrode slope is 90-110%. Generally, the slope value is closer to 95-105%. Slope values below 92% indicate that the probe may need cleaning. Follow the manufacturer recommendations, then recalibrate.

10.0 SAMPLE COLLECTION, HANDLING AND PRESERVATION

10.1 A minimum of 125 mL of sample may be collected.
10.2 The sample must not be filtered, diluted, concentrated, or altered in any way.
10.3 Cool to 4° C. Hold time is 14 days.
10.4 Plastic or glass containers.

11.0 SAMPLE PREPARATION AND ANALYSIS

11.1 Using a pH meter:
- 11.1.1 Use a graduated cylinder to measure sample (25 to 100 ml). Pour sample into a clean 125mL Erlenmeyer flask.
- 11.1.2 Place the flask on the stir plate, stir with the stir bar, and submerge the pH probe. Allow at least 30 seconds for the pH probe to stabilize.
- 11.1.3 Begin to titrate with 0.02 N H2SO4. Note the pH change.

11.1.4 Titrate to a pH of between 4.7 to 4.3 and record the amount of titrant used.

11.1.5 Continue to titrate to reduce the pH of the sample an additional 0.3 pH units from the pH value recorded in Step 8.4. Again record the amount of titrant used.

11.1.6 Record the amount of sample used, the amount of titrant used to obtain the first pH, the amount used to obtain the second pH, and the calculated alkalinity on the proper bench sheet.

11.1.7 If the volume of titrant required to reach a pH of 4.5 using a 50 ml aliquot of sample is < 10 ml, calculate the alkalinity using calculation 13.1.

11.1.8 If the amount of titrant used exceeds 10 ml for a 50 ml sample, titrate only to pH 4.5. This is known as the one end point method. To calculate the alkalinity in this case, use calculation 13.2.

11.1.9 Rinse the probe and beaker with de-ionized water before you proceed to the next sample.

11.2 Using bromcresol green/methyl red indicator:

11.2.1 Use a graduated cylinder to measure sample (25 to 100 ml). Pour sample into a clean 125mL Erlenmeyer flask.

11.2.2 Place the flask on the stir plate, stir with the stir bar, and add several drops of bromcresol green/ methyl red indicator.

11.2.3 Titrate with 0.02 N H2SO4 until you see a color change from blue to red.

11.2.4 Record the amount of titrant used.

11.2.5 To calculate the alkalinity, use calculation 13.2.

12.0 INSTRUMENT MAINTENANCE AND TROUBLESHOOTING

12.1 Refer to Benchtop pH/ISE meters Model 920A Instruction Manual for further instructions.

13.0 DATA ACQUISITION, CALCULATION AND REDUCTION

13.1 High level:

A = Volume of titrant (ml) used to obtain the first pH.
B = Total volume of titrant (ml) used to obtain the second pH.
N = Normality of titrant; normality of H_2SO_4.

Use the following formula to calculate the alkalinity:

$$\frac{A \times N \times 50000}{\text{mL sample}}$$

13.2 Low level. If the amount of titrant used exceeds 10 ml, titrate only to pH 4.5. Use the following formula to determine the alkalinity:

$$\frac{(2a-b) \times N \times 50000}{\text{mL sample}}$$

13.3 **Precision- Relative percent difference (RPD):**

$$\% \ RPD = \frac{Abs.^{**}\ [sample\ conc. - dup\ conc.]\ x\ 100}{ave.\ of\ sample\ \&\ dup\ conc.}$$

***Absolute Value*

14.0 COMPUTER HARDWARE AND SOFTWARE

14.1 Computer with StarLIMS

15.0 DATA MANAGEMENT AND RECORD MANAGEMENT

15.1 After data has been entered into LIMS, it is reviewed by the analyst for accuracy and completeness. See checklist for data review guidance.

15.2 Once analyst has reviewed and approved the data, it is given to a peer or supervisor for review.

15.3 After the second reviewer approves the data, the reviewer sends the data to "validated" status in LIMS.

15.4 The original data is filed by test in the file cabinet and periodically the contents of the file cabinet are archived.

16.0 QUALITY CONTROL/QUALITY ASSURANCE

16.1 The analyst must run a CCV/LCS every 10 samples. The check standard must have a percent recovery of 90 – 110%.. If the check standard is not within this range replace sulfuric acid titrant.

16.2 A duplicate sample must be run at a 10% frequency for drinking water samples and at a frequency of 5% for all other matrices.

16.3 Duplicate sample RPDs must fall within in-house limits. If RPD is outside of limits, repeat analysis or qualify associated results.

16.4 A method blank must be once per analytical batch. Result must be less than MDL. If result is greater than the MDL, repeat analysis or qualify associated results.

17.0 REFERENCES

17.1 *Standard Methods for the Examination of Water and Wastewater*. 1985, 16th Edition, APHA, AWWA, WPCF, Method 403.

17.2 *Methods for Chemical Analysis of Water and Wastes*. 1983, EPA, EPA-600/4-79-20, Method 310.1.

17.3 *Benchtop pH/ISE meters Model 920A Instruction Manual*, Orion.

SUMMARY OF QUALITY CONTROL REQUIRED

Procedure	Frequency of Procedure	Acceptance Criteria	Corrective Action if Unacceptable
Check Standard (LCS/CCV)	1 every 10 samples	Percent recovery of 90 – 110%	Replace titrant and re anlayze
Method Blank (MB)	1 per analytical batch	MB<RL	Replace titrant and re anlayze or qualify results
Sample duplicate (DUP)	One (1) per 20 per matrix except drinking waters 1 per 10	In-house derived limits Default: RPD ≤ 20% if analytes > RL for all matrices except drinking water RPD≤5% if analytes >RL	Investigate problem. if system precision in control qualify results. If system precision out of control reanalyze entire batch

Alkalinity by Titration

Analyst	Date	LIMS Number

	Sample Number	MLs of Sample	MLs of 0.0202N H2SO4	Alkalinity
1	Chk Std=375			
2	**Blank**			
3				
4				
5				
6				
7				
8				
9				
10				
11				
12				
13	Chk Std=375			
14				
15				
16				
17				
18				
19				
20				
21				
22				
23				
24	Chk Std=375			
25				
26				
27				
28				
29				
30				
31	Chk Std=375			

Data Validation Checklist

LIMS #:	Method: Alkalinity by Titration EPA310.1			
Analysis Date	**Analyst / Data Interpreter**	**Independent Reviewer**	**Date of Review**	**Approved**
				Yes ... No

Instructions: Complete one checklist per *analytical run*. Enter the appropriate response for each question. Each "No" response requires an explanation in the Comments section, and may require the initiation of a Nonconformance Report.

Requirement:	Acceptance Criteria	Analyst Review		Independent Review		Comments:
		Yes	No	Yes	No	(indicate reference to an attachment if necessar
1. Does a titration bench sheet accompany the run?	---					
2. Were the samples analyzed within hold time?	14 days					
3. Was a blank titrated along with the samples?	---					
4. Was the blank result acceptable?	< LOD					
5. Were the check standards analyzed at the required frequency?	1 per 10 samples					
6. Were the recoveries acceptable for the check standards?	90-110%					
7. Were duplicates analyzed at the required frequency?	1 per 20 samples of the same matrix					
8. Was the RPD of the duplicates acceptable?	Within in house QC limits					
9. Are all samples on the job lists accounted for?	---					

CT Laboratories.

Title: **Ion Chromatography**

SOP Number: **CC-IC**

Prepared by: _____
Date

Technical Review by: _____
Date

Reviewed by: _____
Quality Assurance ***Date***

_____
Laboratory Director ***Date***

SOP Manual Control Number:_____

1.0 SCOPE AND APPLICATION

1.1 This method covers the sequential determination of the anions chloride, fluoride, nitrite, nitrate, *ortho*-phosphate, and sulfate in all water samples as well as soil and sludge samples that have been extracted according to the procedure in this SOP.

2.0 METHOD SUMMARY

2.1 A small volume of a water or extracted sample is injected into an ion chromatograph to flush and fill a 25 or 50uL constant volume sample loop. The sample is then injected into a stream of carbonate-bicarbonate eluent.

2.2 The sample is pumped through three different ion exchange columns and into a conductivity detector. The first two columns, a guard column and a separator column, are packed with low-capacity, strongly basic anion exchanger. Ions are separated into discrete bands based on their affinity for the exchange sites of the resin. The last column is a self-regenerating suppressor 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 area and comparing it to a calibration curve generated from known standards.

3.0 DEFINITIONS

3.1 Calibration Blank (CB)—A volume of reagent water fortified with the same matrix as the calibration standards. It is analyzed immediately following the calibration standards (Initial Calibration Blank-ICB), at a frequency of 1 per 10 samples during a run (Continuing Calibration Blank-CCB), and at the end of a run to check for drifts in calibration, or possible analyte carry-over. Control criteria consist of the absolute value being less than or equal to the MDL for a given analyte. If this range is exceeded, a new calibration will be necessary or data flagged appropriately.

3.2 Calibration standard (CAL)—A solution prepared from the stock standard solutions. The CAL solutions are used to calibrate the instrument. Acceptance of the calibration requires a correlation coefficient of 0.995 or better. No samples will be analyzed without acceptable calibration.

3.3 Laboratory Control Standard (LCS)-- A mid-range standard prepared from a source different from that used for calibration standards. The LCS is analyzed exactly like a sample and its purpose is to determine whether the methodology is in control. The retention times of the analytes in the LCS must be within 10% of the retention time of the those analytes in the calibration curve.

3.4 Matrix duplicate (DUP)—Two separate aliquots of a sample are analyzed at a rate of one per 10 samples of a given matrix per day for 9056 and 300.0. ACOE duplicates should be analyzed at a rate of one per project per run or as specified by

the client. To be considered acceptable RPD between the sample and the sample duplicate must meet in house acceptance criteria.

3.5 Matrix spike (MS)—An aliquot of a sample to which known quantities of the analytes of interest are added. The MS is analyzed exactly like the samples and its purpose is to determine whether the sample matrix contributes bias to the analytical results. An MS is prepared for every 20 samples of a given matrix per day for 9056 or CLP, for every 10 samples of a given matrix per day for 300.0, and at the same rate as the matrix duplicates for ACOE work. Failure to meet criteria may be due to matrix interference within the sample. To be considered acceptable, MS must meet in house % recovery criteria.

3.6 Matrix spike duplicate (MSD)—An additional aliquot of sample treated exactly as the MS. The MSD is run along with the DUP and MS for ACOE work. To be considered acceptable it must meet the same RPD criteria as the DUP and % recovery criteria as the MS.

3.7 Method blank (MB)—An aliquot of reagent water that is treated exactly as a sample including exposure to all glassware, equipment, solvents, and reagents that are used with other samples. The MB is used to determine if method analytes or other interferences are present in the lab environment, the reagents or the apparatus. A minimum of one MB is prepared per batch of 20, and is analyzed at the beginning of an analytical batch. Blank recovery should be less than the MDL.

3.8 Linear calibration range (LR)—the concentration range over which the instrument response is linear. Samples with results greater than the highest calibration standard should be diluted to a concentration that falls within the calibration curve range and reanalyzed.

3.9 Method detection limit (MDL)—The minimum concentration of an analyte that can be identified, measured and reported with 99% confidence that the analyte concentration is greater than zero.

3.10 Calibration Verification Standard-Initial (ICV) & Continuing (CCV) - A midpoint calibration standard which is analyzed at the beginning of the run (ICV), at a frequency of 1 per 10 samples during a run (CCV), and at the end of a run to verify calibration throughout the run. The ICV must be from a second source different than that of the calibration standards, while the CCV may be from the same source as the calibration standards.

3.11 Contract Required Detection Limit (CRDL) Standard--Detection level standard at a level near the reporting limit, or at a level specified by client contract. When required, it is to be analyzed following the ICB, and prior to the last CCV standard in the run.

4.0 HEALTH AND SAFETY

4.1 The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonable achievable.

4.2 Gloves and protective clothing should be worn to protect against unnecessary exposure to hazardous chemicals and contaminants in samples. All activities performed while following this procedure should utilize appropriate laboratory safety systems.

5.0 CAUTIONS

5.1 Nitrate, Nitrite and *o*-Phosphate have 48 hour holding times. Nitrate and nitrite can be analyzed together when they are preserved with sulfuric acid. The combined Nitrate/Nitrite test has a 14 day holding time when preseverd with acid but cannot be used to speciate between Nitrate and Nitrite. Chloride, Sulfate and Fluoride have a 28 day holding time when stored at 4^0C.

5.2 Standards should be stored at 4° C.

6.0 INTERFERENCES

6.1 Any species with a retention time similar to that of the desired ion will interfere. Large quantities of ions eluting close to the ion of interest will also result in an interference. Separation can be improved by adjusting the eluent concentration and/or flow rate. Sample dilution and/or the use of the method of standard additions can also be used. Two common species, formate and acetate, elute between fluoride and chloride.

6.2 Because bromide and nitrate elute very close together, they are potential interferences for each other. It is advisable not to have Br^- /$N0_3^-$ ratios higher than 1:10 or 10:1 if both anions are to be quantified.

6.3 Method interferences may be caused by contaminants in the reagent water, reagents, glassware, and other sample processing apparatus that lead to discrete artifacts or elevated baseline in ion chromatograms. Insure that all glassware is rinsed with Milli-Q water prior to use and use only Milli-Q water for making standards and reagents.

6.4 Samples that contain particles larger than 0.45 µm and reagent solutions that contain particles larger than 0.20 µm require filtration to prevent damage to instrument columns and flow systems.

6.5 Large amounts of an anion can interfere with the peak resolution of an adjacent anion. Sample dilution can be used to solve most interference problems associated with retention times.

6.6 The water dip or negative peak that elutes near, and can interfere with, the fluoride peak. This is taken care of by using the void volume function of the software for the fluoride peak.

6.7 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.

6.8 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.

7.0 PERSONNEL QUALIFICATIONS

Personnel operating the IC should have background knowledge of the scientific principles used during this application. All operators should perform an initial demonstration of capability (IDC) prior to analyzing any samples. It is preferable for the operator to have at least two semesters of college chemistry.

8.0 APPARATUS AND MATERIALS

8.1 Dionex DX-120 Ion chromatograph

- 8.1.1 Guard column, Dionex AG14A-7uM, placed before the separator column to protect the separator column from being fouled by particulates or certain organic constituents (4 x 50 mm, Dionex P/N 056897 or equivalent)
- 8.1.2 Separator column, Dionex AS14A-7uM,a column packed with low-capacity pellicular anion exchange resin that is etheylvinylbenzene crossed with divinylbenzene (4 x 250 mm, Dionex P/N 056904 or equivalent)
- 8.1.3 Self-regenerating suppressor, Dionex SRS-Ultra, a column that is capable of converting the eluent and separated anions to their respective acid forms (Dionex P/N 53946 or equivalent)
- 8.1.4 Detector, a low-volume, flow-through, temperature-compensated, electrical conductivity cell (approximately 1.25 µL volume, Dionex DS4 or equivalent) equipped with a meter capable of reading from 0 to1,000 µseconds/cm on a linear scale.
- 8.1.5 Pump, capable of delivering a constant flow of 0.5 to 4 mL/min throughout the test.
- 8.1.6 Autosampler, Dionex AS40 with autosampler trays (Dionex P/N 046032 or equivalent), tubes and filter tops (Dionex P/N 038141 or equivalent).
- 8.1.7 Eluent reservoirs, suitable containers for storing eluent under pressure.
- 8.1.8 Computer with PeakNet 5.1 software and a printer, to integrate the area under the chromatogram. Software controls the DX-120 as well as processing and calculating data for the DX-120. Printer generates a paper copy of the data for archival purposes.
- 8.1.9 Bed support assembly- (Dionex P/N 042955 044689 or equivalent)

8.2 Analytical balance, capable of weighing to the nearest 0.0001 g.
8.3 Pipets, Class A volumetric flasks, beakers: assorted sizes
8.4 Autopipettors of various volumes (Oxford Macro and Eppendorf micro)
8.5 Syringes
8.6 Glass Fiber Syringe Pre-Filters
8.7 *0.45um Syringe filters with pre-filter*

8.8 Reagents

8.8.1 Reagent water--Milli-Q water

8.8.2 Eluent Concentrate—Into a 2L volumetric flask add 84.0g dried sodium bicarbonate and 371.0g dried sodium carbonate and bring to volume with Milli-Q water.

8.8.3 Eluent—Use 20mL eluent concentrate (8.8.2) and bring to 10 liters with Milli-Q water in carboy. Helium purge to remove bubbles prior to use. Filter if necessary. Store on counter in IC lab.

8.8.4 Nitrate Nitrogen-200mg/L- Into a 1L volumetric flask, add 1.444g of Potassium Nitrate and 2.0mL of chloroform. Bring to volume with Milli-Q water. Store in standards refrigerator in wet chem lab.

8.8.5 Nitrite Nitrogen-200mg/L- Into a 1L volumetric flask, add 1.214g of Potassium Nitrite and 2.0mL of chloroform. Bring to volume with Milli-Q water. Store in standards refrigerator in wet chem lab.

8.8.6 LCS/ICV/CCV Concentrate #1—Into a 1L volumetric flask add 40mL 100mg/L Flouride, 20mL 1000mg/L Chloride, 26.55mL 226mg/L Nitrogen in the form of Nitrate (alternately use 6.0mL 1000mg/L N as NO3 or 30mL 200mg/L N as NO3(8.8.4)), 4mL 1000 mg/L *ortho*-phosphate and 20mL 1000mg/L Sulfate. Bring to volume with Milli-Q water. Store in the refrigerator in the wet chemistry laboratory. TV = 4mg/L F, 20mg/L Cl, 6mg/L N as NO3, 4mg/L O-Phos and 20mg/L SO4. Expires after one year or sooner if stock solutions expire first.

8.8.7 LCS/ICV/CCV Concentrate #2—Into a 1L volumetric flask add 6mL 1000mg/L Nitrogen in the form of Nitrite (alternately use 30mL 200mg/L N as NO2 (8.8.5)) and fill to volume with Milli-Q water. Store in the refrigerator in the wet chemistry laboratory. TV = 6mg/L N as NO2. Expires after one month.

8.8.8 LCS/ICV/CCV- Into a 100mL beaker add 30mL LCS Concentrate #1 (8.8.6) and 30mL LCS Concentrate #2 (8.8.7). Mix well. Use immediately. True value for solution is Fluoride and Phosphorus 2mg/L, Chloride and Sulfate 10mg/L and Nitrate and Nitrite Nitrogen 3 mg/L. ***NOTE: ACOE requires that the LCS/ICV/CCV be exactly one-half the value of the high calibration standard. Adjust concentrations accordingly.***

8.8.9 100mg/L Chloride--add 10mL of 1000 mg/L Chloride to a final volume of 100mL with Milli-Q water.

8.8.10 100mg/L Nitrite Nitrogen—add 10mL of 1000 mg/L Nitrite Nitrogen (alternately use 50mL of 200mg/L Nitrite Nitrogen) to a final volume of 100mL with Milli-Q water.

8.8.11 100mg/L Nitrate Nitrogen—add 10mL of 1000 mg/L Nitrate Nitrogen (alternately use 50mL of 200mg/L Nitrate Nitrogen or 44.25mL of 226mg/L Nitrate Nitrogen) to a final volume of 100mL with Milli-Q water.

8.8.12 100 mg/L Phosphorus--add 10mL of 1000 mg/L Phosporus to a final volume of 100mL with Milli-Q water.

8.8.13 Calibration standards- Into 8-100mL volumetric flasks pipet the following and fill to volume with Milli-Q water.

Level	1	2	3	4	5	6	7	8
Vol of 100mg/L F	0	0.02	0.10	0.5	1.0	2.0	5.0	7.0mL
Vol of 100mg/L Cl	0	0.04	0.50	1.0	5.0	10.0	20.0	30.0mL
Vol of 100mg/L NO2	0	0.02	0.10	0.5	1.0	2.0	5.0	7.0mL
Vol of 100mg/L NO3	0	0.02	0.10	0.5	1.0	2.0	5.0	7.0mL
Vol of 100mg/L P	0	0.02	0.10	0.5	1.0	2.0	5.0	7.0mL
Vol of 1000mg/L SO4	0	0.025	0.05	0.1	0.5	1.0	2.0	5.0mL

Prepare fresh daily. **Calibration Standards must be made from different sources than the LCS.**

8.8.14 Calibration check concentrate #1—Prepared as the LCS/ICV/CCV Concentrate #1 (8.8.6) with standards from the same source as the calibration. Store in the wet chemistry refrigerator.

8.8.15 Calibration check concentrate #2—Prepared as the LCS/ICV/CCV Concentrate #2 (8.8.7) with the same standard used to make the calibration. Store in the wet chemistry refrigerator.

8.8.16 Calibration Check—Into a portion cup combine 5.0mL of Calibration Check Concentrate #1 (8.8.15) and 5.0mL of Calibration Concentrate Concentrate #2 (8.8.16). Mix well. Prepare fresh daily.

8.8.17 Spiking solution #1- Into a 200mL volumetric flask pipet 64mL 100mg/L F, 51.2mL 1000mg/L Cl, 12.8mL 1000mg/L N as NO3 (alternately 60.64mL 200mg/L N as NO3 or 56.64mL 226mg/l N as NO3), 6.4mL 1000mg/L P and 51.2mL 1000mg/L SO4. Bring to volume with Milli-Q water. True value is 256mg/L Cl and SO4, 64mg/L N as NO3 and 32mg/L F and P. Add 0.1mL to 3.0mL of sample for a true value of 8mg/L Cl and SO4, 2mg/L N as NO3 and 1mg/L F and P. Store solution in wet chem refrigerator. Expires after one year.

8.8.18 Spiking solution #2- Into a 200mL volumetric flask pipet 12.8mL 1000mg/L N as NO2 (alternately 60.64mL 200mg/L N as NO2). Bring to volume with Milli-Q water. True value is 64mg/L N as NO2 . Add 0.1mL to 3.0mL of sample for a true value of 2mg/L N as NO2. Store solution in wet chem refrigerator. Expires after one month.

8.8.19 Sodium Chloride (NaCl)- 1M- Dissolve 58.5g of NaCL in DI water in a 1 Liter volumetric flask and dilute to volume with DI water. Adjust the pH to 2.0 using HCl. Stored in plastic bottle on top of IC.

8.8.20 pH 2.0 200 mM NaCl in 80% acetonitrile- Into a 500mL volumetric flask, combine 100mL of 1M NaCl solution (8.8.12) and 400mL of Acetonitrile (stored in extraction lab). This solution needs to be made fresh for each use.

8.8.21 10X Eluent--Into a 500mL volumetric flask, add 10.0mL of Eluent Concentrate (8.8.2) and dilute to volume with Milli-Q water.
8.8.22 Oxalic Acid solution- 0.1 M
8.8.23 200mN sulfuric acid- Into a 1 liter volumetric flask, add 5.6 mLs of concentrated sulfuric acid and dilute to volume with DI water.

9.0 INSTRUMENT CALIBRATION

9.1 Start DX-120 and allow to equilibrate. See section 11.0 for further instructions on start up and method development.

9.2 In the PeakNet software, go to the Method Editor. Open a new file. See Section 11.3 for further instructions on method set-up.

9.2.1 Click on the Calibration Parameters icon.

9.2.1.1 Choose the General page. Choose the method of standardization to be external, the number of replicates is 1 the linear weighting is equal and the calibration standard volume is 1. Check the Replace Retention Time and Update Response/replace under the Update Data.

9.2.1.2 Choose the Defaults page. The sample volume, sample weight and dilution factor should all default to 1. The unknown response factor should default to 0 and the response for unknowns should default to area.

9.2.2 Click on the Component table icon.

9.2.2.1 On the Identification page:

9.2.2.1.1 The components for the anions group will elute in the following order: Fluoride, Chloride, Nitrite, Nitrate, *ortho*-Phosphate and Sulfate.

9.2.2.1.2 The retention times will be set based on the elution time of the analytes in a known standard. See method set up in Section 11.0 for further instructions.

9.2.2.1.3 For the Tolerance, choose 0.5 minutes.

9.2.2.1.4 For the Reference Component, choose none.

9.2.2.2 On the calibration Standards page:

9.2.2.2.1 The concentrations for each level in mg/L are:

Level	1	2	3	4	5	6	7	8
F	0	0.02	0.1	0.5	1	2	5	7
Cl	0	0.04	0.5	1	5	10	20	30
NO_2	0	0.02	0.1	0.5	1	2	5	7
NO_3	0	0.02	0.1	0.5	1	2	5	7
o-Phos	0	0.02	0.1	0.5	1	2	5	7
SO_4	0	0.25	0.5	1	5	10	20	50

9.2.2.3 On the Calibration page:

9.2.2.3.1 For the curve fit type, choose linear.

9.2.2.3.2 For the Origin, choose ignore

9.2.2.3.3 For Calibrate by, choose Area.

9.2.3 Save the method under C:\Instrument Archive\Method\Sytstem x\W####, where x is the system number and #### is the calibration standard number for the calibration curve.

9.3 Go to the Schedule Editor.

9.3.1 Under sample name, enter Level number. Repeat this for all eight levels.

9.3.2 Under the Sample type, choose calibration standard

9.3.3 Under Level, choose the appropriate level number for each level

9.3.4 Under the method name, choose the method just created (C:\instrument archive\method\system x\W####)

9.3.5 Under data file copy and paste the entries from the sample name column.

9.3.6 Save schedule under c:\instrument archive\schedule\system *\W####

9.4 Go to the Run Menu.

9.4.1 Go to file and choose load schedule.

9.4.1.1 Choose the schedule that you saved under c:\instrument archive\schedule\system *\W####

9.4.2 On the Sample page:

9.4.2.1 *Under Data File, choose Browse.*

9.4.2.2 Create a new directory under c:\instrument archive\data\system *. Name the new directory by the calibration standard number. Click OK

9.4.2.3 Under Data Collection, confirm that the defaults of DX-120 and the method run time appear.

9.4.3 On the Modes page:

9.4.3.1 Choose upon receiving signal at module.

9.5 On the AS-40 Autosampler:

9.5.1 Load the calibration standards in order.

9.5.2 Press the Run button to begin running.

10.0 SAMPLE COLLECTION, HANDLING AND PRESERVATION

10.1 For Nitrate, Nitrite and *o*-Phosphate, refrigerate water and soil samples at 4^0C until analyzed. Hold time for samples is 48 hours.

10.2 For Chloride, Sulfate, and Fluoride, refrigerate water and soil samples at 4^0C until analyzed. Hold time for samples is 28 days.

10.3 For Nitrate + Nitrite, preserve samples to a pH <2 with sulfuric acid. Refrigerate samples at 4^0C until analyzed. Hold time for samples is 14 days.

11.0 SAMPLE PREPARATION AND ANALYSIS

11.1 Sample Preparation

11.1.1 For water samples, filter, if necessary, with a 0.45um syringe filter 3-5mL of an appropriately preserved sample into an autosampler vial and cap with a filter cap.

11.1.2 For soil samples, place 5g $\pm$0.01g of sample in a specimen cup and add 50mL of Milli-Q water. Place on shaker table for 30 minutes then filter 3-5 mL of sample through a 0.45um syringe filter into an autosampler vial and cap with a filter cap.

11.2 Instrument equilibration

11.2.1 Turn on DX-120.
11.2.2 Ensure that Helium tank has an adequate supply of Helium for the run.
11.2.3 Fill the eluent containers on the top of the instrument with degassed eluent.
11.2.4 Turn on the Helium supply for the DX-120.
11.2.5 Press the Local/Remote button on the front of the DX-120. Make sure that the instrument screen on the front of the DX-120 says Local.
11.2.6 Press the Eluent pressure button. A green light should indicate that it is on.
11.2.7 Open the front cover of the instrument and locate the small screw, in the middle of the panel, that controls the purge for the pump.
11.2.8 Loosen the screw by turning 2 or 3 times
11.2.9 Press the pump button on the front of the instrument. A green light should indicate that it is on.
11.2.10 Allow the pump to prime for approximately one minute. If air is not purged from the system, increase the flow rate by pulling the knob adjacent to the pump and turning it clockwise. Turn the knob until the air is purged or until the flow rate is approximately 2.0mL/min. Allow the pump the prime for approximately one minute.
11.2.11 Close the pump screw
11.2.12 Press the SRS button on the front of the instrument. A green light should indicate that it is on. If the flow rate was increased to prime the pump return it to its original setting by turning the knob counterclockwise.
11.2.13 Allow instrument to stabilize for 20-30 minutes prior to analysis.

11.3 Method creation in PeakNet software
11.3.1 Turn on computer
11.3.2 Open the PeakNet software by double clicking on the icon
11.3.3 Open the Method editor by left clicking on the Method icon.
11.3.4 Click on the new file icon (blank sheet) in the toolbar to open a new method file.
11.3.5 Highlight DX-120 under modules and then click add. Press Exit.
11.3.6 After the dialog box opens
11.3.6.1 Set the data collection time to 15 minutes.
11.3.6.2 Set the rate to 5.00 Hz
11.3.6.3 Set the Detector Unit to uS
11.3.6.4 Set the Plot Scales to 30.0 uS for the maximum and –3uS for the minimum.
11.3.6.5 Click on the timed events icon (stopwatch).
11.3.6.5.1 For time INIT, place a check mark next to TTL1. All others should be unchecked. Click enter.
11.3.6.5.2 For time 0.0, place a check mark next to offset. All others should be unchecked. Click enter.
11.3.6.5.3 For time 0.01, place a check mark next to begin. All others should be unchecked. Click enter.
11.3.6.5.4 Click exit.
11.3.6.6 Click on the integration icon (peak).
11.3.6.6.1 Set the Peak detection algorithm to standard
11.3.6.6.2 Set the peak width to 10.00 seconds.
11.3.6.6.3 Set the peak threshold to 0.01

11.3.6.6.4 Set the area reject to 100
11.3.6.6.5 Set the reference area reject to 100
11.3.6.6.6 Click OK
11.3.6.7 Click on the smoothing parameters icon.
11.3.6.7.1 Set the filter type to none.
11.3.6.8 Click on the data events icon (baseline)
11.3.6.8.1 Move the time line to the time that corresponds to the elution time of Fluoride (usually around 3 minutes).
11.3.6.8.2 Highlight the event option, void volume treatment for this peak.
11.3.6.8.3 Click add event
11.3.6.8.4 Click exit
11.3.6.9 For the calibration and component table icons, refer to section 9.0 to determine the correct settings.
11.3.6.10 Save the method as C:\INSTRUMENT ARCHIVE\METHOD\ SYSTEMx\ W####where x = the system number the method is for and the #### is for the W number of the standard prep.
11.3.6.11 Close the method editor.
11.3.6.12 NOTE: a calibration must be run for the method before it can be used to analyze samples. See Section 9.0 for further details.

11.4 Creating a schedule
11.4.1 Open the schedule editor by clicking on the icon.
11.4.2 A new file should appear. If not, click on the new file icon in the toolbar.
11.4.3 Under the sample column
11.4.3.1 Type in the CTI sample ID for the sample to be analyzed. For DUP, MS and MSD samples, place the letters DUP, MS or MSD in front of the CTI sample ID.
11.4.3.2 The first line in the schedule editor should be the CAL CHECK.
11.4.3.3 The second line in the schedule editor should be ICV.
11.4.3.4 The third line in the schedule editor should be ICB.
11.4.3.5 After every ten samples and at the end of the run, a CCV, which is also used as an LCS, and CCB, which is also used as a MB, should be run.
11.4.4 Under the Method column, all lines should haveC:\ INSTRUMENT ARCHIVE\Method\System x\ W####.met, where W#### is the calibration standard number and x is the system number you are using.
11.4.5 Under the data file column, enter the same thing as the sample field. It is easier to copy and paste the sample column for this rather than hand entering all the information again.
11.4.6 Under the comments column, enter any dilution factors that you might have.
11.4.7 Save the schedule as c:\ INSTRUMENT ARCHIVE\Sequences\System X****** where x is the system number you are using and ****** is the LIMS run number.
11.4.8 Exit the schedule editor.

11.5 The run program in PeakNet
11.5.1 Click on the Run icon (center of screen)
11.5.2 Click on the window for the system you want to use.
11.5.3 Click on file. Choose Load Schedule.

Select the schedule for that corresponds to the LIMS run number you want to run.

11.5.4 Click Open

11.5.5 Under data on the load schedule page

11.5.5.1 Click on browse

11.5.5.2 Double click on the folder under C:\instrument archive\data\system x

11.5.5.3 In the new directory box type in the LIMS run number that you want to run.

11.5.5.4 Click Create to create the file folder

11.5.5.5 Click OK to get back to the load schedule page

11.5.6 Under modes on the load schedule page

11.5.6.1 Click on the "upon receiving signal at module" button.

11.5.7 Click OK at the bottom of the Load Schedule page. The computer will be waiting for the autosampler to signal that a sample has been injected.

11.6 Load the autosampler with the samples in the order indicated in the schedule editor.

11.7 Press the Run/Hold button on the Autosampler. A green light will indicated that the autosampler is running.

11.8 To turn off the DX-120

11.8.1 Close the run in PeakNet

11.8.2 Close PeakNet software

11.8.3 On the DX-120:

11.8.3.1 Press the SRS button. The green light next to SRS should shut off.

11.8.3.2 Press the pump button. The green light next to pump should shut off.

11.8.3.3 Press the eluent pressure button. The green light next to the eluent pressure should shut off.

11.9 If system will remain off for an extended period of time

11.9.1 Press the button on the front of the DX-120 to turn off the power to it.

11.9.2 Turn off the power to the autosampler using the button on the left rear.

12.0 DATA CAPTURE

12.1 Select Batch in the PeakNet Main Menu.

12.2 Under File click open

12.2.1 Open C:\PeakNet\Schedule\DC.bch

12.3 Under Processing select Input

12.3.1 Click Select

12.3.1.1 Select the schedule you want to data capture. C:\Insturment Archive\Schedule\System x***** where ***** is the LIMS run number.

12.3.1.2 Click Open

12.3.2 Process Injection should default to 1 through the last line of your schedule. If there are more than 100 lines in the schedule capture it in parts. For example when capturing a schedule that has 129 lines change the 129 to 100. Capture the schedule then repeat the process changing the 1 to 101 and leaving the 129.

12.3.3 Select All under included Detectors

12.3.4 Choose from schedule for process method

12.4 Under Output unselect all options.

12.5 Select Export

12.5.1 Change the file name to I:\DX120***** +.csv where ***** is the LIMS run number followed by +, an arbitrary letter. If capturing more than once to the same run, changing this letter prevents the files from being overwritten.

12.5.2 Select summary as the report type.

12.5.3 Choose Peak as the summary option.

12.6 Click OK

12.7 Click the Start Button

12.8 Exit the batch program. Do not save the changes.

13.0 TROUBLESHOOTING AND MAINTENANCE

13.1 See Dionex PeakNet Software User's Guide, Dionex DX-120 Operator's manual, Dionex Installation Instructions, Troubleshooting Guide for the IonPac AS14, Column Care Guide for IonPac AS14 and ASRS-Ultra Installation Instructions and Troubleshooting Guide for troubleshooting instructions not covered in this section.

13.2 The column bed support assemblies should be replaced when they become clogged. A clog usually causes an increase in the pressure of the system. NOTE Replace the outlet bed support ONLY if high pressure persists after replacement of the inlet fitting.

13.2.1 Disconnect the column from the system.

13.2.2 Carefully unscrew the inlet (top) column fitting. Use two open-end wrenches.

13.2.3 Remove the bed support. Turn the end fitting over and tap it against a benchtop or other hard, flat surface to remove the bed support and seal assembly. If the bed support must be pried out of the end fitting, use a sharp pointed object such as a pair of tweezers, but be careful that you DO NOT SCRATCH THE WALLS OF THE END FITTING. Discard the old bed support assembly.

13.2.4 Place a new bed support assembly into the end fitting. Make sure that the end of the column tube is clean and free of any particulate matter so that it will properly seal against the bed support assembly. Use the end of the column to carefully start the bed support assembly into the end fitting. If the column tube end is not clean when inserted into the end fitting, particulate matter may obstruct a proper seal between the end of the column tube and the bed support assembly. If this is the case, additional tightening may not seal the column but instead damage the column tube or the end fitting.

13.2.5 Screw the end fitting back onto the column. Tighten it fingertight, then an additional 1/4 turn (25 in x lb). Tighten further only if leaks are observed.

13.2.6 Reconnect the column to the system and resume operation.

13.3 The column will need to be cleaned when the retention time window shift more than 10%, calibrations are no longer linear or the column becomes contaminated from a sample.

13.3.1 Prepare a 500 mL solution of pH 2.0 200 mM NaCl in 80% acetonitrile

13.3.2 Disconnect the ASRS-Ultra from the IonPac AS14 Analytical Column. Reverse the order of the guard and analytical column in the eluent flow path. Double check that the eluent flows in the direction designated on each of the column labels.CAUTION When cleaning an analytical column and a guard column in series, ensure that the guard column is placed after the analytical column in the eluent flow path. Contaminants that have accumulated on the guard column can be eluted onto the analytical column and irreversibly damage it. If in doubt, clean each column separately.

13.3.3 Set the pump flow rate to 1.0 mL/min

13.3.4 Rinse the column for 15 minutes with deionized water before pumping the NaCl/Acetonitrile cleanup solution over the column.

13.3.5 Pump the NaCl/Acetonitrile cleanup solution through the column for 60 minutes.

13.3.6 Rinse the column for 15 minutes with deionized water before pumping the Oxalic acid cleanup solution over the column.

13.3.7 Pump the Oxalic Acid cleanup solution through the column for 60 minutes.

13.3.8 Rinse the column for 15 minutes with deionized water before pumping the 10X eluent cleanup solution over the column.

13.3.9 Pump the 10X eluent cleanup solution through the column for 60 minutes.

13.3.10 Rinse the column for 15 minutes with deionized water before pumping eluent over the column.

13.3.11 Equilibrate the column(s) with eluent before resuming normal operation for at least 30 minutes.

13.3.12 Reconnect the ASRS-Ultra to the AS14 Analytical Column and place the guard column in line between the injection valve and the analytical column.

13.4 Small analyte peak area is caused by running eluent through the ASRS while the power is off to the ASRS. To regenerate the ASRS:

13.4.1 Disconnect the eluent line from the analytical column attached to the ELUENT IN port of the ASRS-ULTRA at the analytical column end of the line. Direct this line to a separate waste beaker.

13.4.2 Disconnect the eluent line from the ELUENT OUT port of the ASRS-ULTRA.

13.4.3 Using a plastic syringe push approximately 3 mL of 200 mN sulfuric acid through the ELUENT OUT port and approximately 5 mL of 200 mN sulfuric acid through the REGEN IN port.

13.4.4 Reconnect the eluent line from the ELUENT IN port of the ASRS-ULTRA to the analytical column and the eluent line from the **ELUENT OUT** port of the ASRS-ULTRA to the conductivity detector cell.

13.4.5 Turn on the power and then begin pumping eluent.

14.0 DATA ACQUISITION, CALCULATIONS AND DATA REDUCTION

13.1 LIMS will calculate the following according to these equations:

13.1.1 *Liquid Concentration (mg/L)* = A x C
where A = instrument reading for sample (mg/L)
C= dilution factor

13.1.2 *Solid Concentrations (mg/kg)* = $\frac{A \times B \times C}{D \times E}$,
where A = instrument reading for sample (mg/L)
B = total volume of extraction (L)
C= dilution factor
D = amount of sample used in extraction (Kg)
E = percent solids/100 (if reporting on a Dry Weight Basis)

13.1.3 *Spike Recovery (%)*= $\frac{\text{(Spiked sample value – Sample value) x 100}}{\text{(Spike amount)}}$

13.1.4 *%RSD* = $\frac{|\text{(Sample – DUP)}| \times 100}{\text{(Sample + DUP)/2}}$,
where DUP = Duplicate concentration

15.0 COMPUTER HARDWARE AND SOFTWARE

15.1 Computer with LIMS
15.2 Printer
15.3 PeakNet 5.0 Software

16.0 DATA MANAGEMENT AND RECORD MANAGEMENT

16.1 After data has been captured by LIMS, it is reviewed by the analyst for accuracy and completeness. See checklist for data review guidance.
16.2 Once analyst has reviewed and approved the data, it is given to a peer or supervisor for review.
16.3 After the second reviewer approves the data, the reviewer sends the data to "validated" status in LIMS.
16.4 The original data is filed by test in the file cabinet and periodically the contents of the file cabinet are archived.

17.0 QUALITY CONTROL AND QUALITY ASSURANCE

17.1 After every 10 injections, analyze a CCV, a midrange calibration standard. If the instrument retention time has changed by more than 10% or recovery is outside of 90-110%, remake solution and analyze the fresh solution. If it still does not fall within the above criteria, recalibrate.
17.2 Analyze one in every ten samples in duplicate for 300.0 or every twenty samples in duplicate for 9056A. Take the duplicate sample through the entire sample preparation and analytical process.
17.3 A matrix spiked sample should be run for each analytical batch or twenty samples for 9056A or 10 samples for 300.0, whatever is more frequent, to determine matrix effects.
17.4 Prior to analyzing samples, each analyst must perform an IDC, initial demonstration of capability. The IDC consists of running a standard solution in quadruplicate and getting a recovery and RPD within method limits.

17.5 Method Detection Limit (MDL)—MDLs must be established for all analytes, using reagent water fortified at a concentration of 3-5 times the estimated instrument detection limit. To determine MDL values, take seven or eight replicate aliquots of the fortified reagent water and process through the entire analytical method. Calculate the MDL using the spreadsheet in H:\MDLs\classical\MDL water blank workbook.xls for waters of h:\MDLs\classical\MDL soil blank workbook.xls for soils. MDLs should be determined annually or whenever there is a significant change in background or instrument response.

17.6 Calibration check standard—A mid-point calibration standard run as a sample. If the instrument retention time has changed by more than 10% or recovery is outside of 90-110%, remake solution and analyze the fresh solution. If it still does not fall within the above criteria, recalibrate. A calibration check standard should be run once a day.

17.7 Calibration Blank (CB)—A volume of reagent water fortified with the same matrix as the calibration standards. It is analyzed immediately following the calibration standards (Initial Calibration Blank-ICB), at a frequency of 1 per 10 samples during a run (Continuing Calibration Blank-CCB), and at the end of a run to check for drifts in calibration, or possible analyte carry-over. Control criteria consist of the absolute value being less than or equal to the MDL for a given analyte. If this range is exceeded, a new calibration will be necessary or data flagged appropriately.

Standard Quality Control Requirements and Corrective Action Guidelines

QC Type	Frequency	Conc. Level	*Acceptance Criteria*	*Corrective Action*
ICAL	As needed		$R \geq 0.995$	Recalibrate Instrument
ICV	1 per calibration	Midpoint of cal curve	90-110%	Reanalyze or recalibrate
ICB	1 per calibration		<MDL	Correct problem and reanalyze or qualify data that is not > 20 times the ICB or <MDL
CCV	1 after every 10th sample	Midpoint of cal curve	90-110%	Correct problem and reanalyze.

CCB	Immediately following each CCV		<MDL	Correct problem and reanalyze or qualify data that is not > 20 times the ICB or <MDL
LCS	1 per batch of 20 samples	Midpoint of cal curve	90-110%	Correct problem and reanalyze.
DUP	10% (1 for every 10 samples) per matrix		In house limits. Default is 20%	Identify source of problem. Qualify data or reanalyze depending on source of problem.
MS-MSD	5% (1 in 20) of samples per batch per matrix		In-house limits. Default limits are 80-120%	Identify source of problem. Qualify data or reanalyze depending on source of problem.

Data Validation Checklist

LIMS #:	Method: Anions by Ion Chromatography 300.0/9056			
Analysis Date	Analyst / Data Interpreter	Independent Reviewer	Date of Review	Approved
				Yes .. No

Instructions: Complete one checklist per *analytical run*. Enter the appropriate response for each question. Each "No" response requires an explanation in the Comments section, and may require the initiation of a Nonconformance Report.

Requirement:	Acceptance Criteria	Analyst Review		Independent Review		Comments: (indicate reference to an attachment if necessary)
		Yes	No	Yes	No	
1. Were the samples analyzed within hold time?	28 days for Cl, F, SO_4; 14 days for preserved NO_2+NO_3; 48 hours for O.Phos, and unpreserved NO_2 and NO_3					
2. Was the calibration performed using the required number of standards?	Three plus a blank					
3. Is the standard prep log number noted on the analytical report?	---					
4. Was the correlation coefficient acceptable?	> 0.995					
5. Was Calibration Check standard run prior to analysis of samples?	---					
6. Was the Calibration Check standard recovery acceptable?	90 – 110 %					
7. Were the ICV and ICB run immediately after the calibration check standard?	---					
8. Was the ICV recovery acceptable?	90 – 110 %					
9 Was the ICB result acceptable?	< LOD					
11. Were the CCV's and the CCB's analyzed at the required frequency?	1per 10 samples					
12. Were the CCV recoveries acceptable?	90 – 110 %					
13. Were the CCB results acceptable?	< LOD					
14. Was a LCS run at the required frequency?	1 per 20 samples					
15. Was the LCS recovery acceptable?	90-110 %					

16. Was the LCS used before the indicated expiration date?	---					
17. Were the MS and MSD prepared at the required frequency?	1per 20 field samples					
18. Were the MS and MSD recoveries acceptable?	Within in house QC limits					
Requirement:	Acceptance	Analyst Review		Independent Review		Comments:
	Criteria	Yes	No	Yes	No	(indicate reference to an attachment if necessary)
19. Was the RPD between the MS and MSD acceptable?	Within in house QC limits					
20. Were all chromatograms checked to ensure accurate peak identification?	---					
21. Are all samples on the job lists accounted for?	---					

CT Laboratories
Baraboo Laboratory Division

Title: **Total Solids**

SOP Number: **CC-29**

Prepared by: _____
Date

Technical Review by: _____
Date

Reviewed by: _____
Quality Assurance ***Date***

_____
Laboratory Director ***Date***

SOP Manual Control Number:

1.0 SCOPE AND APPLICATION

1.1 This method is used to determine the percentage of solids in a sample. It is applicable to sludges, soils, and surface waters, groundwaters, and wastewaters (both domestic and industrial).

1.2 The result is given as a percentage of the total weight, for sludges and soils, and as mg/L for surface waters, groundwaters, and wastewaters.

1.3 The limit of detection (LOD) for this method is 1 mg/L for liquid samples, 0.02% for sludges, and 0.2% for soils.

2.0 METHOD SUMMARY

2.1 A well-mixed sample is evaporated in a weighed dish and dried to a constant weight in an oven at 103-105^{0}C. the increase in weight over that of the empty dish represents the total solids.

3.0 DEFINITIONS

3.1 Duplicate Analysis: Two aliquots of a given sample are analyzed. The difference is then determined from the two results and compared to the lab control limit.

4.0 HEALTH AND SAFETY

4.1 Gloves and protective clothing should be worn to protect against unnecessary exposure to possibly hazardous chemicals and contaminants in samples. All activities performed while following this procedure should utilize appropriate laboratory safety systems (see CTI Health and Safety Manual).

5.0 CAUTIONS

There are no caution

6.0 INTERFERENCES

6.1 Highly mineralized water, with a significant concentration of calcium, magnesium, chloride and/or sulfate, may be hygroscopic and require prolonged drying, proper desiccation, and rapid weighing.

6.2 Exclude, floating particles or submerged agglomerates of non-homogeneous materials from the sample if it is determined that their inclusion is not desired in the final result.

6.3 Because excessive residue in the dish may form a water-trapping crust, limit sample to no more than 200 mg residue.

6.4 The determination of total solids in solid and semisolid materials is subject to negative error due to loss of ammonium carbonate and volatile organic matte during drying. Although this is true also for wastewater, the effect tends to be more pronounced with sediments, and especially with sludges and sludge cakes. The mass of organic matter recovered from sludge and sediment requires a longer ignition time than that specified for wastewaters, effluents, or polluted waters. Carefully observe specified ignition time and temperature to control losses of volatile inorganic salts if

these are a problem. Make all weighings quickly because wet samples tend to lose weight by evaporation. After drying or ignition, residues often are very hygroscopic and rapidly absorb moisture from the air.

7.0 PERSONNEL QUALIFICATIONS

7.1 The analyst must show an initial demonstration of capability (IDC) to generate acceptable data, by successfully analyzing four matrix replicates. The relative percent difference of the replicates must be within 5%. If this percentage is exceed the analyst must reanalyze four replicates until the relative percent difference is within 5%.

8.0 APPARATUS AND MATERIALS

8.1 Aluminum weighing dishes or porcelain evaporation dish.
8.2 Drying oven, capable of 103-105°C
8.3 Top Loading balance, capable of weighing to 0.1 mg (used for liquids and sludges)
8.4 Analytical balance, capable of weighing to 10mg (used for soils)
8.5 Scoop or spatula.
8.6 Wide-bore pipets.
8.7 Desiccator, provided with a desiccant containing a color indicator of moisture.

9.0 INSTRUMENT OR METHOD CALIBRATION

9.1 Follow manufacturer's instructions to calibrate the balances.

10.0 SAMPLE COLLECTION, HANDLING AND PRESERVATION

10.1 Samples should be collected in resistant-glass or plastic bottles 4 oz jar, provided that the material in suspension does not adhere to container walls.
10.2 Preservation of the sample is not practical; analysis should begin as soon as possible. Refrigeration or icing to 4°C, to minimize microbiological decomposition of solids, is recommended.

11.0 SAMPLE PREP AND ANALYSIS

11.1 If only total solids are requested, heat clean aluminum dishes to 103 – 105° C for 1 hour. If sample also needs a total volatile solids, use an evaporating dish that has been ignited at 500 ° ± 50°C for one hour and pre weighed.
11.2 Transfer sample (amount specified below) to a pre weighed dish, and weigh both dish and sample. Record weight.
11.2.1 For soil samples: utilizing the Denver Instrument Company XD-2200 balance, transfer 5-10 g of well mixed sample to a weigh dish, with a scoop or spatula.
11.2.2 For water samples (groundwater, wastewater, or surface water): utilizing the Fisher Scientific A-200DS balance, transfer 25-30 mL of well mixed sample to weigh dish, with a pipet. NOTE: If the

sample contains suspended solids, it is necessary to use a wide-bore pipet.

11.2.3 For sludge samples: utilizing the Fisher Scientific A-200DS balance, transfer 25-50 g of well mixed sample to dish. NOTE: If the sludge is a fluid, stir to homogenize before transferring aliquot. If the sludge is a solid, pulverize the sample before transferring to the weigh dish.

11.3 Place the dish(es) into an oven at 103-105°C, dry overnight (at least 8 hrs.).

11.4 When drying is complete, the samples may be removed from the oven, cooled in a desiccator, weighed back and reported.

12.0 INSTRUMENT MAINTENANCE AND TROUBLESHOOTING

12.1 Refer to balance manufacturer's instructions.

13.0 DATA ACQUISITION, CALCULATION AND REDUCTION

13.1 For solid sample, use the spreadsheet located in H:\INSTRMNT\SOLIDS\TS. For sludge and water samples, use the spreadsheet located in H:\INSTRMNT\SOLIDS\LQTSTVS.

13.2 **Total Solids (Percent)** = $\frac{(A - B) \times 100}{C - B}$

where:

A = Dry weight of sample and dish, g
B = Tared weight of dish, g
C = Weight of sample and dish, g

13.3 **Total Solids (mg/L)** = $\frac{(A-B) \times 1000}{\text{sample volume, mL}}$

where:

A = weight of dried residue + dish, mg
B = weight of dish, mg

13.4 **Precision- Relative percent difference (RPD*):***

$$\frac{|\text{sample result} - \text{duplicate sample result}|}{(\text{sample result} + \text{duplicate sample result})/2} \times 100 = \%RPD$$

14.0 COMPUTER HARDWARE AND SOFTWARE

14.1 Computer with StarLIMS
14.2 Computer with Excel
14.3 Computer with balance data capture software

15.0 DATA MANAGEMENT AND RECORD MANAGEMENT

15.1 After data has been entered into LIMS, it is reviewed by the analyst for accuracy and completeness. See checklist for data review guidance.

15.2 Once analyst has reviewed and approved the data, it is given to a peer or supervisor for review.

15.3 After the second reviewer approves the data, the reviewer sends the data to "validated" status in LIMS.

15.4 The original data is filed by test in the file cabinet and periodically the contents of the file cabinet are archived.

16.0 QUALITY CONTROL AND QUALITY ASSURANCE

16.1 Duplicate analysis should be done every 20 samples per matrix. The relative percent difference (RPD) (9.3) for the duplicates must be less than of equal to the quarterly control limits. If the result of the replicate exceeds the quality control limit corrective action must take place. Corrective action shall include reanalysis of affected samples or qualifying the results back to the last acceptable quality control check, unless the laboratory determines the sample results are unaffected (in this case, the rationale must be noted along with the data package).

16.2 Calibration of the analytical balance prior to use will ensure accurate measurements.

16.3 Weighing the sample to constant weight ensures that the sample is not gaining moisture once removed from the oven.

17.0 REFERENCES

17.1 *Standard Methods for Determination of Water and Wastewater*, 18th Edition, 1992, APHA-AWWA-WEF, Method 2540B & 2540G.

SUMMARY OF QUALITY CONTROL REQUIREMENTS

Procedure	Frequency of Procedure	Acceptance Criteria	Corrective Action if Unacceptable
Sample duplicate (DUP)	One (1) per analytical batch per matrix	In-house derived limits Default: RPD $\leq$ 20% if analytes > RL	Investigate problem, if system precision in control qualify results, if system precision out of control reanalyze entire batch
Weigh sample to a constant weight	Check one (1) sample per batch	Weigh until constant weight of or until the weights agree within 0.5 mg.	Place back in oven and repeat weighing process until constant weight is achieved
Capability demonstration sample (IDC)	Four (4) prepared samples analyzed one time prior to any sample analyses	In-house determined criteria for LCS recovery and precision	Repeat until acceptable

Data Validation Checklist

LIMS #:	Method: Total Solids SM2540B&G / Percent Solids SW846-5030A			
Analysis Date	**Analyst / Data Interpreter**	**Independent Reviewer**	**Date of Review**	**Approved**
				Yes ... No

Instructions: Complete one checklist per *analytical run*. Enter the appropriate response for each question. Each "No" response requires an explanation in the Comments section, and may require the initiation of a Nonconformance Report.

Requirement:	Acceptance Criteria	Analyst Review		Independent Review		Comments: (indicate reference to an attachment if necessary)
		Yes	No	Yes	No	
1. Were samples analyzed within hold time?	7 days					
2. Were samples dried overnight?	> 8hours					
3. Were drying start and stop times recorded?	---					
4. Were duplicates analyzed at the appropriate frequency?	1 per 20 of similar matrix					
5. Were the duplicates within acceptable limits?	Within in house QC limits					
6. Are all samples on the job lists accounted for?	---					

CT Laboratories.
Baraboo WI

Title: **Soil Oxidant Demand**

SOP Number: **CC- Soil Oxidant Demand**

Prepared by: _____
Date

Technical Review by: _____
Date

Reviewed by: _____
Quality Assurance ***Date***

_____
Laboratory Director ***Date***

SOP Manual Control Number:_____

1.0 SCOPE AND APPLICATION

1.1 This method is used to determine the oxidant (i.e., potassium permanganate) demand of soils and sludges.

2.0 METHOD SUMMARY

2.1 Oxidant demand is a colorimetric technique that uses varing ratios of oxidant mass to soil mass prepareed in separate containers. Potasssium permanganate serves as the oxidant and color indicator, i.e., purple coloration. The varying ratios of oxidant/soil mixtures are allowed to react, and the color is observed. The soil oxidant demand (SOD) can be narrowed down to the mixture ratio where color remains and the mixture ratio where the color is depleted.

3.0 DEFINITIONS

There are no definitions

4.0 HEALTH AND SAFETY

4.1 Gloves and protective clothing should be worn to protect against unnecessary exposure to possibly hazardous chemicals and contaminants in samples. All activities performed while following this procedure should utilize appropriate laboratory safety systems (see CTLaboratory Health and Safety Manual).

5.0 CAUTIONS

There are no cautions

6.0 INTERFERENCES

6.1 Suspended soil material, especially fine silts or clays, may make a determination of the solution color difficult. Decanting the solution from the specimen cups into test tubes may make the color determination easier. Centrifuging the solutions in the test tubes may further clear the soil/water suspensions.

7.0 PERSONNEL QUALIFICATIONS

7.1 Analyst must read SOP and be familiar with the operation of the analytical balance.

8.0 APPARATUS AND MATERIALS

8.1 Stock potassium permanganate solution; $KMnO_4$; dissolve 0.891 g of $KMnO_4$ in 1000 ml deionized water. Expires in 6 months
8.2 Scoop or spatula
8.3 Graduated pipets
8.4 Specimen cups
8.5 Graduated cylinder
8.6 Analytical balance
8.7 Disposable test tubes (if necessary)

8.8 Centrifuge (if necessary)

9.0 INSTRUMENT METHOD OR CALIBRATION

None

10.0 SAMPLE COLLECTION, HANDLING AND PRESERVATION

10.1 Samples should be collected in resistant glass or plastic bottles. Refrigerate sample at 4 degrees C until analysis.

11.0 SAMPLE PREPARATION AND ANALYSIS

11.1 The amount oxidant demand in a solid will be dependent on a wide variety of factors but in general saturated soils from carbonate aquifiers will have a lower SOD than an organic rich soil under reducing conditions. The variability in the SOD based on soil type may dictate using more or less soil or more or less potassium permanganate. A typical starting point would be to use 10, 5, 2.5, 1, and 0.5 g portions of soil and then refine, if necessary, the soil weights based on this initial weight series.

11.2 Tare each specimen cup on the top loader balance and add the soil directly to the cup. Label the container and record the soil weight on the container. Proceed with the next specimen cup and weigh the apprpriate amount of soil until the series is completed.

11.3 Add 90 milliliters of deionized water to a graduated cylinder (note: use 90 milliliters of deionized water if 10 milliliters of potassium permanganate solution will be added. Alternatively, add 99 milliliters of deionized water if 1 milliliter of potassium permanganate will be added) and then pour into the specimen cup containing the soil. Repeat procedure with each specimen cup.

11.4 Add, with a pipet, 10 milliliters of potassium permangante to each specimen cup. See note in 11.3 if 99 milliliters of deionized water was used.

11.5 Cap each specimen cup tightly and place on a shaker table for approximately one hour to agitate the the soil/oxidant mixture. Allow the mixture to stand for an hour before reading the color reaction.

11.6 After settling, decant the supernantants into separate test tubes. If the color change end-point is not readily visible because of turbidity, centrifuge the test tubes at full speed for 10 minutes to calrify the solution.

11.7 Repeat steps 11.1 through 11.6 if no color change has occurred (all samples still pink) by using less potassium permanganate, i.e., 1 milliliter instead of 10. These steps may also be repeated if the soil weight range needs further refinement. For example, if the 10 gram sample has a color change but the 5 gram sample is still pink, then soils weights between 10 and 5 grams may be used to narrow the range.

12.0 INSTRUMENT MAINTENANCE AND TROUBLESHOOTING

There is no maintenance or troubleshooting for this method.

13.0 DATA ACQUISITION, CALCULATION AND REDUCTION

13.1 Calculate the weight (grams) of potassium permanganate to kilogram of soil (wet weight) to affect the color change (the solution no longer demonstrating the intense pink coloration).

Example: color change occurred in the 2.48 gram soil sample to which 10 milliliters of stock solution was added.

1 milliliter of stock solution contains 0.000891 g of potassium permanganate

10 ml x 0.000891 g/ml = 0.00891 g/ 2.48 g of soil or 0.00359 g/g
0.00359 g/g) x 1000 g/Kg = 3.592 g / Kg
SOD = 3.592 g of KMnO4 / Kg wet weight

14.0 COMPUTER HARDWARE AND SOFTWARE

14.1 Computer with StarLIMS

15.0 DATA MANAGEMENT AND RECORD MANAGEMENT

15.1 After data has been captured by LIMS, it is reviewed by the analyst for accuracy and completeness. See checklist for data review guidance.

15.2 Once analyst has reviewed and approved the data, it is given to a peer or supervisor for review.

15.3 After the second reviewer approves the data, the reviewer sends the data to "validated" status in LIMS.

15.4 The original data is filed by test in the file cabinet and periodically the contents of the file cabinet are archived.

16.0 QUALITY CONTROL

16.1 Balance should be calibrated prior to use to ensure accurate measurements

17.0 REFERENCES

none

CT Laboratories
Baraboo Laboratory Divison

Title: Total and Amenable Cyanide

SOP Number: CC-1

Prepared by: _____
Date

Technical Review by: _____
Date

Reviewed by: _____
Quality Assurance *Date*

_____
Laboratory Director *Date*

SOP Manual Control Number:_____

1.0 SCOPE AND APPLICATION

1.1 This method covers the determination of cyanide in drinking, ground, surface and saline waters, domestic, industrial wastes, soil and sediment. The working range is approximately 5-200 ug/L or 5-200 mg/kg. Samples greater than that may be diluted into the working range.

1.2 The method detects inorganic cyanides that are present as either soluble salts or complexes. It is used to determine values for both total cyanide and cyanide amenable to chlorination.

2.0 METHOD SUMMARY

2.1 The cyanide, as hydrocyanic acid (HCN), is released from samples containing cyanide by means of a reflux-distillation operation under acidic conditions and absorbed in a scrubber containing sodium hydroxide solution. The cyanide ion in the absorbing solution is then determined by automated UV colorimetry.

2.2 In the automated colorimetric measurement, the cyanide is converted to cyanogen chloride (CNCl) by reaction with Chloramine-T at a pH less than 8 without hydrolyzing to the cyanate. After the reaction is complete, color is formed on the addition of pyridine-barbituric acid reagent. The concentration of NaOH must be the same in the standards, the scrubber solutions, and any dilution of the original scrubber solution to obtain colors of comparable intensity.

3.0 DEFINITIONS

3.1 Initial Calibration Verification (ICV): A midrange check standard analyzed after the calibration has been completed, to evaluate calibration curve and or instrument performance. The ICV is non-distilled and from a different source than the calibration standards.

3.2 Lab Control Sample (LCS): A known concentration obtained from a second source.

3.3 Continuing Calibration Verification (CCV): A check standard analyzed after every ten samples and at the end of the analytical run, to evaluate instrument performance.

3.4 Matrix spike-matrix spike duplicate (MS-MSD): To two of three aliquots of a given sample a known amount of spike solution is added. Matrix spikes and matrix spike duplicates are taken through all steps of preparation and analysis, exactly like a sample. The amount of spike recovered helps to assess the effect of the sample matrix on the analysis. The precision of the method is also determined, by calculating the relative percent difference (RPD) (10.3) of the two spiked aliquots. An MS-MSD should be prepared for every 20 samples in each matrix.

3.5 Method Blank (MB): Reagent water treated exactly as a sample, including exposure to all glassware, reagents, and treatments used with other samples.

3.6 Low Distillation Standard (LDS): Low level calibration standard distilled to check low end efficiency of calibration.

3.7 High Distillation Standard (HDS): High level calibration standard distilled to check high end efficiency of calibration.

4.0 HEALTH AND SAFETY

4.1 Cyanogen chloride may form during this reaction. This is a very toxic gas and the distillation should always be performed in a hood.

4.2 Caution should be used during the distillation step. If the vacuum pressure is not adequately maintained, sulfuric acid or sodium hydroxide could be expelled from the distillation apparatus.

4.3 Caution: KCN is highly toxic. Avoid inhalation of dust or contact with the solid or solutions.

5.0 CAUTIONS

5.1 A minimum of 50 mL of sample is required for liquid analysis. Samples must be preserved with sodium hydroxide to pH of >12 , and cooled to 4 ^{o} C at the time of collection (approximately 2 mL NaOH/1-L sample). Soil samples can be taken in unpreserved 4 oz. jars and cooled to 4° C until analysis.

5.2 If sample contains chlorine or hydrogen sulfide, see section 6.0 for treatment. Document any sample pretreatment in sample prep book.

5.3 Samples may not be stored for longer than 14 days.

5.4 Samples for ACOE work must be analyzed in duplicate and the average result reported.

6.0 INTERFERENCES

6.1 Chlorine: Oxidizing agents, such as chlorine, decompose most of the cyanides. To determine if there is significant chlorine present, test a drop of the sample with potassium-iodide starch paper. If the paper turns blue, treatment with ascorbic acid will be necessary prior to analysis. Add a few crystals of ascorbic acid a time, until a drop of sample produces no color on the indicator paper; then add an additional 0.6 g of ascorbic acid for each liter of sample.

6.2 Sulfides: Test for presence of sulfide by placing a drop of sample on lead acetate test paper. Darkening of paper indicates presence of sulfide. Treat 75 mL of the reserved sample (pH>12) as follows: Add powdered Cadmium Carbonate to sample gradually. Yellow cadmium sulfide precipitates if the sample contains sulfide. Test the treated sample periodically by adding a drop of the solution to the lead acetate paper. When the paper does not darken, the sulfide has been removed sufficiently. Filter the treated solution through a dry filter paper into a dry beaker. From this filtrate measure out the sample aliquot to be used for analysis. Note any treatment in the sample prep logbook. Avoid a large excess of cadmium and a long contact time.

6.3 NO_3/NO_2: Remove by adding excess (0.2 g) sulfamic acid before distillation.

6.4 If fatty acids, detergents, and surfactants are a problem, they may be extracted using the following procedure. Acidify the sample with acetic acid (1.6M) to pH 6.0 to 7.0. **CAUTION: This procedure can produce lethal HCN gas.** Extract with hexane with solvent volume equal to 20% of the sample volume. One extraction is usually adequate to reduce the compounds below the interference level. Avoid multiple extractions or a long contact time at low pH in order to keep the loss of HCN at a minimum. When the extraction is completed, immediately raise the pH of thesample to above 12 with 50% NaOH solution.

6.5 Most interferences are eliminated reduced by the distillation procedure.

7.0 PERSONNEL QUALIFICATIONS

7.1 Analysts should be familiar with safety requirements for the lab.

7.2 Analysts should have a working knowledge of the midi-distillation system.

7.3 Analysts should have a working knowledge of the Lachat AE system.

7.4 Analysts should have a valid IDC on file.

8.0 APPARATUS AND MATERIALS

8.1 Materials

8.1.1 Fisher Analytical Balance: To weigh accurately to the nearest 0.0001 g.

8.1.2 Glassware: Class A volumetric flasks and pipets.

8.1.3 Midi-dist Apparatus: Easy-Dist model, with timed controlled heating block, vacuum controls, digestion tubes, and cold finger condensers, gas scrubbers.

8.1.4 Lachat Continuous Flow Autoanalyzer:

8.1.4.1 Sampler

8.1.4.2 Pump

8.1.4.3 Injection Module: 150 cm, 0.8 mm i.d. sample loops

8.1.4.4 Colorimetric Detector with 10mm-flow cell, and 570nm-wavelength interference filter.

8.1.4.5 Heating Bath: Temperature must be 60° C.

8.1.4.6 Reaction Module for Cyanide, 10-204-00-21-A

8.1.4.7 QuikCalc II software.

8.1.5 Twistcap plastic centrifuge tubes. Stored in wet lab beneth bench

8.1.6 PTFE boiling stone. Stored in drawer with CN glasware

8.2 Reagents

8.2.1 All reagents are prepared with deionized water.

8.2.2 To prevent bubble formation, all solutions except the standards are degassed with helium.

8.2.3 Potassium iodide test paper: For checking for chlorine residual and to be used in preparing cyanides amenable to chlorination. Stored on reagent shelf in wet lab.

8.2.4 Lead acetate test paper: Used in checking for potential sulfide interference. Stored on reagent shelf in wet lab.

8.2.5 Ascorbic Acid: Crystal. Stored on reagent shelf in wet lab.

8.2.6 Chloramine T: Dissolve 1.0 g in 50 mL of reagent water in a 250mL volumetric flask. Bring to volume with DI water. Prepare fresh daily. Do not keep solid reagent for longer than one year. Stored on reagent shelf in wet lab.

8.2.7 Magnesium Chloride Solution: To a 1000-mL volumetric flask, add 500 mL of reagent water. Add 510 g of MgCl2-6H2O (stored on shelf in wet lab) and dilute to 1000 mL with reagent water. Store in plastic container on shelf under hood.

8.2.8 Pyridine-Barbituric Acid Reagent: In a fume hood, place 15.0 g of barbituric acid (stored on reagent shelf in wet lab) in a 1L beaker. Wash the sides of the beaker with about 100-mL reagent water to wet the barbituric acid. Add 75 mL of pyridine (stored under hood in extraction lab) and mix. Add 15-mL conc. Hydrochloric acid (stored under hood in glassware room) and mix. Mix until all the barbituric acid is dissolved. Transfer the solution to a 1L volumetric flask and dilute to the mark with reagent water. Stable for approximately 6 months if kept in amber bottle in the refrigerator. **Safety Note: Barbituric acid comes in a fine powder form. When weighing this reagent, be sure to take precautions to avoid breathing the powder while weighing the reagent or adding to the beaker.** Bring to room temperature prior to analysis

8.2.9 Potassium dihydrogen phosphate (KH_2PO_4), also know as Potassium phosphate monobasic, buffer: 1M: Dissolve 97 g of anhydrous KH_2PO_4 (stored on reagent shelf in wet lab)in 500mL reagent water in a 1L flask. Stir with a magnetic stirrer for 30 minutes. Bring to volume with DI water Prepare fresh monthly and keep refrigerated. Bring to room temperature prior to analysis.

8.2.10 Sodium Hydroxide Solution, 0.25 M: Into a large carboy, dissolve 60 g of NaOH (stored under hood in wet lab) pellets in reagent water. Bring to 6L with DI water. Prepare as needed and store in caustic cabinet under hood in wet lab.

8.2.11 Sodium Thiosulfate, ($Na_2S_2O_3$) as crystals. (Stored on reagent shelf in wet lab)

8.2.12 Standardized Silver Nitrate Solution, 0.0192 N: NIST traceable. (stored under the hood in the extraction lab.)

8.2.13 Indicator solution: 0.02% p-dimethylaminobenzalrhodanine w/v in acetone.

8.2.14 Stock Cyanide Solution (1000 mg CN/L): Ricca Chemical. NIST traceable. (Keep stock refrigerated in an amber bottle and standardize biweekly).

8.2.14.1 To standardize the 1000 mg/L CN stock standard, fill buret with 0.0192N $AgNO_3$ solution and zero. With a

Class A volumetric pipet, pipet 15 mL of stock standard into a 250 mL beaker and into another beaker, pipet 20 mLs of stock standard. To both beakers, add approximately 4 drops of indicator solution (6.13) and place a magnetic stirrer in each. The initial color, when indicator is added, should be a canary yellow. The indicator turns to a salmon hue when the end point is reached. With burette zeroed, begin dispensing the 0.0192N $AgNO_3$ solution into the beaker containing either 15 or 20 mLs of standard. The beaker with the standard should be stirring continuously while dispensing the 0.0192N $AgNO_3$. When the end point is reached (the standard turns from yellow to salmon), take reading off of the burette and record in reagent Standardization Log. Calculate the concentration of the standard using calculation 10.5. An acceptable range for the calculated concentration is 995-1005 mg/L of CN. If the concentration is outside of this range a new stock standard must be ordered.

8.2.15 Working Stock Standard Solution (10 mg/L): Add 1.0 mL of standardized 1000 mg/L CN- stock solution (8.2.14) to a 100 mL volumetric flask. Dilute to the mark with 0.25M NaOH (8.2.10) and mix. Prepare fresh weekly. This standard will be used for spiking and also to prepare working standards.

8.2.16 Working Standards: Prepare fresh daily. Using the 10 mg/L working stock solution (8.2.16), transfer volumetrically, into volumetric flasks, the following amounts:

Standard	mLs of	solution	into Vol Flask
200 ug/L	2.0	10 mg/L	100 mLs
100 ug/L	2.0	10 mg/L	200 mLs
50 ug/L	0.5	10 mg/L	100 mLs
30 ug/L	30.0	100 ug/L	100 mLs
20 ug/L	10.0	100 ug/L	50 mLs
10 ug/L	5.0	100 ug/L	50 mLs
0 ug/L	0	---------	---------

Dilute to volume with 0.25M NaOH and mix well.

8.2.17 Cadmium carbonate: powdered reagent: for reduction of sulfide interference (stored on reagent shelf in wet lab).

8.2.18 Sulfamic Acid: for Nitrate/Nitrite interference: ACS Dry reagent (stored on reagent shelf in wet lab).

8.2.19 Sulfuric Acid 18N: Slowly add 500 mL of concentrated H2SO4 (stored under hood in glassware room) to 500 mL of reagent water in pyrex 2L beaker while under a hood.
CAUTION: This solution will get very hot. Do not attempt to do this in plastic beakers because they will melt. Only a large Pyrex

beaker should be used. It will take time to bring it down to ambient temperature for use in the test.

8.2.20 Calcium hypochlorite solution (0.35M) $Ca(OCl)_2$: Combine 5 g of calcium hypochlorite (Stored on reagent shelf in wet lab) and approximately 50 mL of water in a 100mL volumetric flask. Bring to volume with DI water Shake before using. Store under hood in wet lab.

8.2.21 Sodium hydroxide solution (1.25N) NaOH: Dissolve 50 g of NaOH (stored under hood in wet lab)into DI water in a 1L volumetric flask. Bring to volume with DI water. Store under hood in wet lab.

8.2.22 Hexane: ACS grade (Stored at ambient temperature in extraction lab).

8.2.23 Sodium hydroxide solution (50%) NaOH: Dissolved 50g of NaOH (stored under hood in wet lab) in 100mL of DI water in a large pyrex beaker. **CAUTION: This solution will get very hot.** Do not attempt to do this in plastic beakers because they will melt. Only a large Pyrex beaker should be used. It will take time to bring it down to ambient temperature for use in the test. Store under hood in wet lab.

8.2.24 Acetic Acid (1.6M): Into a 1L volumetric flask, combine 92mL of glacial acetic acid (stored at ambient temperature under the counter in the extraction lab) with 500mL of DI water. Bring to volume with DI water.

9.0 INSTRUMENT OR METHOD CALIBRATION

See Sample preparation and analysis section 11.0.

10.0 SAMPLE COLLECTION, HANDLING AND PRESERVATION

10.1 A minimum of 50 mL of sample is required for liquid analysis. Samples must be preserved with sodium hydroxide to pH of >12 , and cooled to 4 ° C at the time of collection (approximately 2 mL NaOH/1-L sample). Soil samples can be taken in unpreserved 4 oz. jars and cooled to 4° C until analysis.

10.2 If sample contains chlorine or hydrogen sulfide, see section 6.0 for treatment. Document any sample pretreatment in sample prep book.

10.3 Samples may not be stored for longer than 14 days.

11.0 SAMPLE PREPARATION AND ANALYSIS

11.1 Pretreatment for Cyanides Amenable to Chlorination

11.1.1 To one 50-mL sample or to a sample diluted to 50 mL, add calcium hypochlorite solution dropwise while stirring. Maintain the pH of the sample between 11 and 12 with 1.25N NaOH. Test for chlorine with KI starch paper by adding a drop of sample to a test strip. When excess chlorine is present a drop of sample added to the paper will turn it blue. **CAUTION: Cyanogen chloride**

may form during this reaction. This is a very toxic gas and this step should always be performed in a hood.

11.1.2 Maintain this excess chlorine for one hour with continuous stirring. Periodically spot check with the KI paper and add more calcium hypochlorite solution as necessary.

11.1.3 After one hour, add a few crystals of ascorbic acid at a time until a drop of sample produces no color on the indicator paper. Then add an additional 0.03 g of ascorbic acid to each 50 mLs of sample. Note this in the sample prep book.

11.1.4 Test for total cyanide as described in the following procedure in both the chlorinated and the unchlorinated samples. The difference of total cyanide in the chlorinated (listed as Cyanide + Chlorine in LIMS) and the unchlorinated (listed as Cyanide or Total Cyanide in LIMS) samples is the cyanide amenable to chlorination.

11.2 Distillation Procedure:

11.2.1 Pour 50 mL 0.25 M NaOH into each scrubber tube.

11.2.2 For liquid samples, add 50 mL of sample or an aliquot diluted to 50 mL to the midi-distillation boiling tube. For soil samples: weigh up approximately 2 g of soil and place in boiling tube, then add 50 mLs of 0.25 NaOH. Add PTFE boiling chips as required.

11.2.3 Add 0.2 g of sulfamic acid to tube before assembly of apparatus.

11.2.4 For low distillation standard, add 50 ml of 30ug/L working standard to midi-distillation boiling tube.

11.2.5 For high distillation standard, add 50 ml of 100ug/L working standard to midi-distillation boiling tube.

11.2.6 Assemble each apparatus. Start the vacuum and water after all connections are made and checked. Adjust the vacuum bubble rate at approximately 2 bubbles/ second. If you are distilling a soil the bubble rate should be higher to ensure adequate mixing of reagent with the soil in suspension. Let bubbles mix the solution for about 3 minutes. For spiked samples, add 0.25 mL of 10mg/L cyanide standard with a calibrated pipettor through the air inlet at this point. Rinse down with a small amount of reagent water, then let the solution mix for 3 minutes.

11.2.7 Slowly add 5 mL of 18N H_2SO_4 through the air inlet tube. Rinse down with a small amount of reagent water, continue to bubble 3 minutes. Add 2 mL of Magnesium Chloride (6.7) into the inlet tube and wash down with a small amount of reagent water.

11.2.8 Turn on the Easy-Dist. Set the controller to the following settings: Rate1 15^{0}C, Rate2 0, Temp1 190^{0}C, Temp2 190^{0}C, Time1 1.5 hour, Time2 0.

11.2.9 Press Start. The system should be monitored periodically to make sure the apparatus is working correctly.

11.2.10 After distillation time finishes, continue the vacuum and water flow until the temperature displayed for the Easy-Dist is less than 100 ^{0}C.

11.2.11 Disconnect the absorber tube, shut off the vacuum and remove the absorber tube.

11.2.12 Pour off the trapped cyanide solutions into 50 mL twistcap plastic centrifuge tubes. Prepped samples can be stored for later analysis for up to 3 days. Keep refrigerated at 4°C in the walk-in cooler until analysis.

11.3 Calibration and Analysis:

11.3.1 Set up Lachat programs to include the following timing guidelines. Save as the appropriate method. Load program needed for analysis.
Injection Timing:
Pump Speed: 35
Cycle Period: 60 sec.
Sample loop: 150 cm
Load Period: 35 sec.
Inject period: 20 sec.
Inject to start of peak: 20 sec.
Inject to end of peak: 60 sec

11.3.2 Turn on and set heating bath at 60°C. It should take approximately 15 minutes to reach desired temperature.

11.3.3 Inspect modules for proper connections.

11.3.4 Turn on power to all modules.

11.3.5 Place reagent lines into proper containers. Apply tension on pump tube cassettes. Refer to Lachat Manuals for specific details and a diagram of the manifold.

11.3.6 Pump system until a stable baseline is attained.

11.3.7 Place calibration standards and blank in sample tray in descending order of concentration followed by check standards and unknowns. For samples for ACOE work, samples must be analyzed in duplicate and the average result reported. The concentrations of the unknowns (samples) as well as the check standards and other QC will be evaluated in relation to the absorbencies of the calibration standards. The Lachat program prints out the raw data in ug/L.

11.3.8 For samples that have results higher than the highest calibration standard, dilute samples using 0.25M NaOH as the diluent and reanalyze.

11.3.9 At end of run, place all transmission lines in water, and flush system. Pump lines dry.

11.3.10 Turn off pump, all modules, and release tension levers on pump tube cassettes.

11.3.11 Clean area thoroughly.

12.0 TROUBLESHOOTING AND MAINTENANCE

Refer to Lachat and Easy-Dist operation manuals for troubleshooting and maintenance instructions.

13.0 DATA ACQUISITION, CALCULATIONS AND DATA REDUCTION

Liquid Concentration (ug/L) = A x C

Solid Concentrations (mg/kg) = $\frac{A \times B \times C}{D \times E}$,

where A = instrument reading for sample (ug/L)
B = total volume of digestion (L)
C= analyst dilution factor, if necessary (ex. For a 1 to 10 dilution, C = 10)
D = amount of sample used in digestion (g)
E = percent solids/100, if necessary

Spike Recovery (%)= $\frac{\text{(Spiked sample concentration – Sample concentration) x 100}}{\text{(Spike amount)}}$

%RSD = $\frac{\text{(MS – MSD) x 100}}{\text{(MS + MSD)/2}}$

where MS = Matrix spike concentration
MSD = Matrix spike duplicate concentration

14.0 COMPUTER HARDWARE AND SOFTWARE

14.1 Computer with StarLIMS
14.2 Lachat QuickChem AE software

15.0 DATA MANAGEMENT AND RECORD MANAGEMENT

15.1 After data has been captured by LIMS, it is reviewed by the analyst for accuracy and completeness. See checklist for data review guidance.
15.2 Once analyst has reviewed and approved the data, it is given to a peer or supervisor for review.
15.3 After the second reviewer approves the data, the reviewer sends the data to "validated" status in LIMS.
15.4 The original data is filed by test in the file cabinet and periodically the contents of the file cabinet are archived.

16.0 QUALITY CONTROL AND QUALITY ASSURANCE

16.1 The analyst must show an initial demonstration of capability (IDC) to generated acceptable data, by successfully analyzing four replicates of a known standard and having acceptable results for a blind sample.
16.2 ICV (initial calibration verification): This mid range check standard is analyzed after calibration. Control limits are +/- 10% of the true value. If the recovery is outside of this range, terminate the run and correct the problem before proceeding.
16.3 ICB (initial calibration blank): Analyzed immediately after the ICV. The value of the ICB must be below the method LOD. If not, terminate the analysis and correct the problem before proceeding or qualify results less than 20 times the ICB with a 'B' flag.

16.4 LCS (lab control sample): Analyze a LCS (reference obtained from a second source) per 20 samples. Control limits are +/- 15% of the true value. An out of control LCS may indicate that the calibration standard stock solution is inaccurate or that there was a problem with the distillation process. If the recovery exceeds this, terminate the analysis and correct the problem before proceeding

16.5 CCV (continuing calibration verification): Analyze a CCV following every ten samples and at the end of the analysis. Control limits are +/- 10% of the true value. If recovery is outside these limits, recalibrate and reanalyze all samples back to the last acceptable CCV or ICV.

16.6 CCB (continuing calibration blank): Analyzed immediately after the CCV. The value of the CCB must be below the method LOD. If not, terminate the analysis and correct the problem before proceeding. If CCB is outside these limits, recalibrate and reanalyze all samples back to the last acceptable CCB or ICB or qualify results less than 20 times the CCB with a 'B' flag.

16.7 MS-MSD (matrix spike-matrix spike duplicate):A MS-MSD is required every analytical run at a frequency of 5% (1 for every 20 samples) per matrix type. Refer to the control limits for acceptance criteria for both accuracy and precision. Unless otherwise specified in a contract if recovery is outside of acceptable range, flag the sample with an 'M' qualifer. If the RPD is outside of the acceptable range, flag the sample with a 'Y' qualifier.

16.8 Method blank: analyze one method blank per digestion batch. This is a reagent water blank that is taken through all of the processes that the samples are. The value of the method blank must be below the method LOD. If not, terminate the analysis and correct the problem before proceeding or qualify results less than 20 times the method blank with a 'B' flag.

16.9 Low Distillation standard: prepare once per calibration. Recovery should fall within 90-110%. An out of control standard may indicate there was a problem with the distillation process. If the recovery exceeds this, terminate the analysis and correct the problem before proceeding.

16.10 High Distillation standard: prepare once per calibration. Recovery should fall within 90-110%. An out of control standard may indicate there was a problem with the distillation process. If the recovery exceeds this, terminate the analysis and correct the problem before proceeding.

16.11 1000 mg/L CN stock standard is standardized against a 0.0192N $AgNO_3$ solution biweekly. Acceptance criteria, is 995 – 1005 mg/L CN.

16.12 Contract Specific Sample Analysis: For certain samples, limits are specified by the QAPP (Quality Assurance Project Plan) associated with a given project. For these samples follow the limits specified in the QAPP for that project.

17.0 REFERENCES

17.1 *Methods for the Determination of Inorganic Substances in Environmental Samples*, EPA-600/R-93/ 100, August 1993, Method 335.4.
17.2 *Standard Methods for the Examination of Water and Wastewater*, 18th Edition, 1992, APHA-AWWA-WEF, Method 4500-CN.
17.3 *SW 846*, 3rd Edition, Update III, 1997 Method 9010B, 9012A and 9013.
17.4 *EASY-Dist Environmental Methods Manual*, Rev 6/23/97, Cyanide Methods
17.5 *Lachat QuickChemAE Operating Manual,* Issued: 10/01/93
17.6 *Lachat QuickChem Methods Manual,* Revision Date: 18 January 1996
17.7 *Lachat QuickChemAE Software Reference Manual,* 24 January 1994 release

SUMMARY OF QUALITY CONTROL REQUIREMENTS

Procedure	Frequency of Procedure	Acceptance Criteria	Corrective Action if Unacceptable
Six-point initial calibration plus blank (ICAL)	Initially and as needed	$r \geq 0.995$ for regression line	Repeat until acceptable
Initial calibration verification (ICV)	After each ICAL, prior to sample analysis	%R: 90-110% for all analytes	Remake and reanalyze ICV standard, if still unacceptable repeat ICAL
Initial calibration blank (ICB)	After each ICV, prior to sample analysis	< RL	Remake and reanalyze CB once, if still unacceptable investigate and correct problem or flag results less than 20 X's the ICB with a 'B' qualifier
Continuing calibration verification (CCV)	Daily, prior to sample analysis, after every 10 samples, and at end of run	%R: 90-110% for all analytes	Remake and reanalyze CCV, if still unacceptable investigate and correct problem. Reanalyze all samples after last acceptable CCV.
Continuing calibration blank (CCB)	After each CCV	<RL or <20 times less than the lowest sample result	Remake and reanalyze CB once, if still unacceptable investigate and correct problem then reanalyze all samples after the last acceptable CCB or flag results less than 20 X's the CCB with a 'B' qualifier
Capability demonstration sample (IDC)	Four (4) prepared samples analyzed one time prior to any sample analyses and one blind sample	In-house determined criteria for LCS recovery and precision	Repeat until acceptable
Method Blank (MB)	One (1) per analytical batch	<RL or <20 times less than the lowest sample result	Clean analytical system, repeat. If still unacceptable, redistill batch or flag all results less than 20 X's the MB with a 'B' qualifier.
Sample duplicate (DUP) or matrix spike duplicate (MSD)	One (1) per analytical batch per matrix	In-house derived limits	Investigate problem, if LCS in control qualify results. Qualify results with a 'Y' flag if necessary
Matrix spike sample (MS)	One (1) per analytical batch per matrix	In-house derived limits	Investigate problem, if LCS in control qualify results. Qualify results with a 'M' flag if necessary
Low Distillation Standard (LDS)	One (1) per calibration	$90\% \leq \%R \leq 110\%$	Redistill samples
High Distillation Standard (HDS)	One (1) per calibration	$90\% \leq \%R \leq 110\%$	Redistill samples
1000 mg/L CN stock standard	standardized weekly	995 – 1005 mg/L CN	Order new stock standard if outside this range.
Laboratory control sample (LCS)	One per analytical batch	In-house derived limits	Halt analysis, fix problem, repeat associated sample analyses. If still unacceptable, redistill batch

Data Validation Checklist

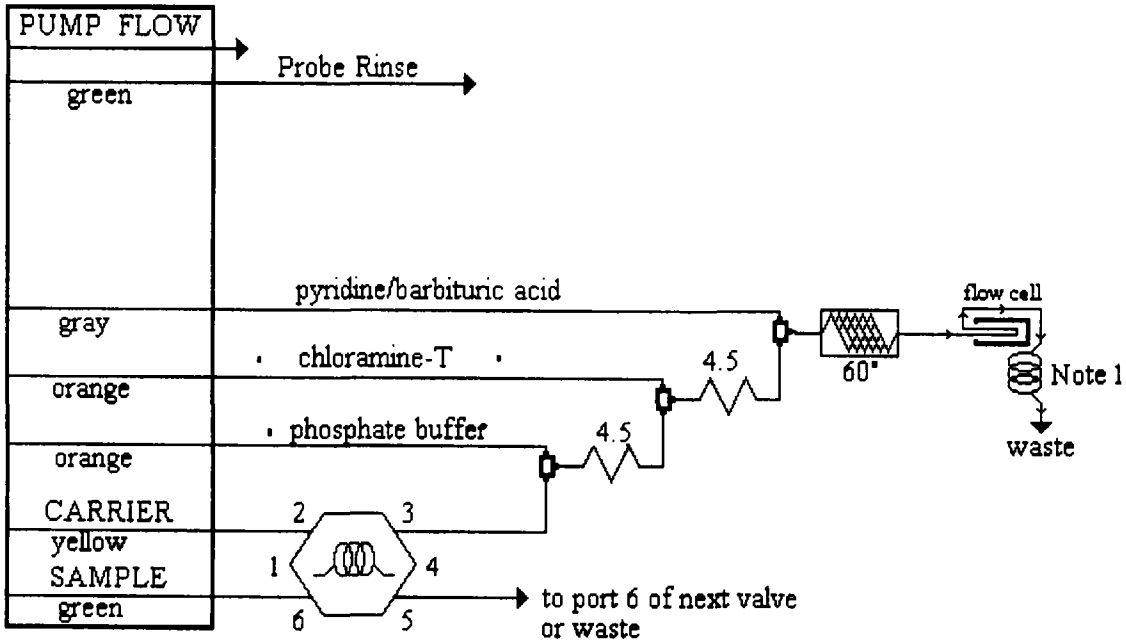
LIMS #:	Method: CYANIDE EPA335.4			
Analysis Date	**Analyst / Data Interpreter**	**Independent Reviewer**	**Date of Review**	**Approved**
				Yes ... No

Instructions: Complete one checklist per *analytical run*. Enter the appropriate response for each question. Each "No" response requires an explanation in the Comments section, and may require the initiation of a Nonconformance Report.

Requirement:	Acceptance Criteria	**Analyst Review**		**Independent Review**		Comments: (indicate reference to an attachment if necessar
		Yes	No	Yes	No	
1. Does a distillation sheet accompany the data package?	---					
2. Does the distillation sheet include all reagent and standard prep log numbers?	---					
3. Is a copy of the stock standard standardization log included?	---					
4. Is the stock standard within acceptance limits?	995-1005 ug/L CN					
5. Were samples checked for chlorine and sulfide?	---					
6. Were the samples distilled within hold time?	14 days					
7. Were method blanks prepared at the required frequency?	1per 20 samples					
8. Was the method blank result acceptable?	< LOD					
9. Were LCS's prepared at the required frequency?	1per 20 samples					
10. Was the LCS used before the indicated expiration date?	---					
11. Was the LCS recovery acceptable?	Within in house QC limits					
12. Were the MS and MSD prepared at the required frequency?	1per 20 samples of the same matrix					
13. Were the MS and MSD recoveries acceptable?	Within in house QC limits					
14. Was the RPD between the MS and MSD acceptable?	Within in house QC limits					

	Acceptance Criteria	Yes		Yes		Comments: (indicate reference to an attachment if necessa
15. Was calibration performed using required number of standards	6 plus a blank					
16. Is the standard prep log number noted on the analytical report?	---					
17. Was the correlation coefficient acceptable?	>= 0.995					
18. Were distilled calibration standard recoveries acceptable?	90-110					
19. Were the ICV and ICB run immediately after the calibration curve?	---					
20. Was the ICV recovery acceptable?	90 – 110 %					
21. Was the ICB result acceptable?	< LOD					
22. Were the CCV's and the CCB's analyzed at the required frequency?	1per 10 samples					
23. Were the CCV recoveries acceptable?	90 – 110 %					
24. Were the CCB results acceptable?	< LOD					
25. Were the samples analyzed within 3 days of being distilled?	---					
26. Are all samples on the job lists accounted for?	---					

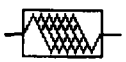
Cyanide MANIFOLD diagram



Sample loop = 150 cm x 0.8 mm i.d.
QC8000 Sample loop = 150 cm x 0.8 mm i.d.

Interference Filter = 570 nm

CARRIER is 0.25 M sodium hydroxide solution (Reagent 1).
All manifold tubing is **0.8 mm (0.030 in) i.d.** This is **5.2 uL/cm**.
4.5 is **70** cm of tubing on a **4.5** cm coil support

APPARATUS: An injection valve, a 10 mm path length flow cell, and a colorimetric detector module are required. The  shows **650 cm of tubing** wrapped around the heater block at the specified temperature.
Note 1: 2 meter back pressure loop, 0.52 mm i.d.

CT Laboratories.
Baraboo, WI

Title: **Subsampling Guidance**

SOP Number: **FO-10**

Prepared by: _____
Date

Reviewed by: _____
Quality Assurance ***Date***

_____
Laboratory Director ***Date***

SOP Manual Control Number:_____

Subsampling Guidance

1.0 Scope and Application

1.1 This SOP is designed to provide guidance on the representative subsampling of analytical aliquots from environmental samples received in typically sized field containers (e.g., bottles, split spoon liners, VOA vials, etc.). It should be noted that specific samples might require special techniques due to problematic matrices or project specific requirements. The intent is to address the following matrix groups and subgroups:

LIQUIDS
Aqueous liquids: surface water, groundwater, TCLP extracts, wastewaters, and leachates (< 1% solids)
Nonaqueous liquids: oils

SOLIDS
Soil, sediment, heterogeneous solid substances, concrete, paint chips, ash

MULTIPHASE (LIQUID/SOLIDS) SLUDGES
Aqueous sludges: liquid sludges, solid sludges, emulsions
Nonaqueous sludges

1.2 This procedure is not applicable to VOA samples, or wipe and air samples for which duplicate field samples should be collected to replace subsamples.

2.0 Method Summary

The subsampling approaches presented in this SOP are based in large part on the most common characteristics and properties found within each matrix group. However, sampling theory cannot replace experience and common sense. Bulk samples received at the laboratory must be thoroughly homogenized, if applicable, prior to subsampling into appropriate containers for analysis and/or shipments to another laboratory.

3.0 Health and Safety

3.1 All subsampling activities should be performed using appropriate personal protective equipment protecting the analyst from direct sample contact, potential vapor inhalation, splashes, and sharp objects.

3.2 Whenever possible or necessary, subsampling should be performed in a laboratory fume hood.

4.0 Sample Preservation, Containers, Handling, and Storage

Not Applicable

5.0 Interferences and Potential Problems

5.1 The most significant potential problem is the high probability of a subsample taken from a heterogeneous waste being non-representative.

5.2 Care must be exercised so that the introduction of contamination or potential for cross-contamination from equipment used to manipulate the sample is minimized. Full decontamination protocols must be performed on equipment used between each use, and/or sufficient materials available for individual sample usage. Recommend implementing the appropriate quality controls to ensure that samples are not contaminated.

5.3 Aqueous samples containing hydrophobic analytes, e.g., petroleum hydrocarbons, should not be subsampled. The entire bottle contents should be used to avoid loss of analytes to container walls or cap.

6.0 Equipment/Apparatus

The specific equipment used for subsampling is dependent on the analyses and methods to be performed. Specific methods should be consulted prior to performing these activities. Specific equipment should be selected from the options presented below.

6.1 Spatulas, spoons, scoops, PTFE-coated or stainless steel, various sizes

6.2 Stirring rods, glass

6.3 Magnetic stirrers, PTFE-coated magnetic stir bars

6.4 Laboratory trays, metal, plastic or glass.

6.5 Laboratory beakers, PTFE or glass

6.6 Class A Pipet, serological and volumetric (TD, to deliver), various sizes

6.7 Class A Graduate Cylinders (TD to deliver), various sizes up to 2L

6.8 Weigh pans, various sizes

6.9 Laboratory drying oven

6.10 Balance, top-loader with readability to 1 mg or analytical with readability to 0.1 mg.

6.11 Laboratory grinders (mortar/pestle or Braun)

6.12 Sieve; the sieves to have available are dependent upon the analyses performed by the lab. For example, Methods 3540/3550 require a 1 mm sieve, 8330 a 30 mesh sieve, 1311 a 9.5 mm sieve, etc..

6.13 Centrifuge - International Equipment Company – HN-SII Centrifuge or equivalent.

6.14 Separatory Funnel, glass

6.15 Filtering apparatus; 124 mm, Fisher cat.# 09-753-17E or equivalent.

6.16 Syringe filters with Teflon filtering discs

6.17 Syringes, glass, air-tight, various sizes, with Luer-Lok valves

6.18 Kimwipes, or equivalent

6.19 Coring device; remove injection end of a disposable plastic 10 cc syringe. Remove Luer Lok end of the syringe with a razor edge knife, creating a smooth clean barrel neck.

6.20 Miscellaneous equipment or tools for reducing material size or sub-sampling from substrate or surface, e.g., sledge hammer, chisels (wood and/or cold chisels), tungsten-carbide rotary burrs, etc…

7.0 Reagents

7.1 Methanol and Acetone, Residue Grade or equivalent.

7.2 Non-phosphate detergent, such as Micro-90.

7.3 Tap water

7.4 Reagent water

8.0 Procedure

The matrices have been grouped to process samples of similar physical nature. This is by no means a "hard and fast" division. Subsampling routines should always be evaluated on a continuous basis, based upon subsequent analysis to be performed and the intended use of data resulting from sample analysis.

Inspect each sample to determine if the sample is a liquid, solid, or a combination (multiphase). Depending upon the matrix, refer to sections 8.1, 8.2, and/or 8.3, respectively.

8.1 Subsampling Liquids

Evaluate the liquid sample, looking for suspended matter, multiple phases, or any other features that may require specific measures to obtain a representative subsample. If the samples contain no detectable suspended matter, follow guidance presented in section 8.1.1. Samples, which contain suspended matter, but will be analyzed as a single liquid phase should follow the guidance presented in section 8.1.2. Multiphase samples should follow guidance established in section 8.3.

8.1.1 Aqueous Liquids; Surface Water, Groundwater, TCLP Extracts, Wastewater, and Leachates (< 1.0% solids)

8.1.1.1 Inorganics and Metals (Total Analysis)

- Make sure sample lid is securely attached to sample jar.
- Invert, or shake the sample in an up and down fashion a minimum of 7 times.
- Remove lid and quickly yet smoothly transfer desired aliquot into an appropriately sized graduated cylinder. This will be dependent on the required accuracy necessary for the measurement as specified in the applicable method. If the required sample volume is small, a serological or volumetric pipet (depending on required accuracy of measurement) may be used to obtain sample.
- Transfer the sample from the pipet or graduated cylinder into an appropriate container used to either process the subsample further or to ship to a contract laboratory for analyses. The sample can be transferred directly into the process apparatus or testing vessel, if appropriate (e.g., cyanide distillation unit).
- If sample results are not affected by volume additions, rinse the delivery glassware with a small volume (1-2 mL) of reagent water approximately 3 times and transfer the rinsate into the container or test vessel, which contains the sample to ensure a quantitative transfer.
- If the cylinder or pipet used to subsample is to be reused for other samples, thoroughly clean the transfer glassware appropriately.

8.1.1.2 Dissolved Inorganics and Dissolved Metals

When dissolved analytes are required, field filtration followed by appropriate field preservation techniques is optimum. However, if this is not practical, project personnel may elect to send unpreserved samples to the laboratory for filtration and preservation. The appropriate regulatory authorities should be consulted and concur with this

approach.

- Generally, the only difference between this and 8.1.1 is that the sample is filtered through a 0.45 µm filter before processing the filtrate through the appropriate procedures. The precipitate is discarded.

- The filtering device needs to be thoroughly decontaminated in between uses as appropriate.

8.1.1.3 Volatile Organics

VOA vials should never be split for analysis by another laboratory. If split samples are required, separate VOA vials must be collected in the field.

- VOA samples should be brought to room temperature before subsampling for analysis. For subsampling VOA vials, the best alternative is to collect the subsample through the vial septum using a syringe and needle. If this is not possible, use an air-tight syringe fitted with a Luer-Lok valve as follows. Open the VOA vial and smoothly fill the syringe by pulling the plunger smoothly and quickly to minimize loss of volatiles. Invert the syringe, and express any air bubbles out through the Luer-Lok. A 5-ml syringe is large enough to aspirate more than the 5 mL required for a sample. Duplicate analysis can be accomplished by multiple fillings of the 5-ml syringe. In the event that a sample is in insufficient quantity to provided for multiple analysis the use of a second (duplicate) sample vial, if available, may be necessary.

- Adjust the plunger to the desired sample volume and close the Luer-Lok valve. The sample is now ready for insertion into the purge vessel (after all appropriate surrogates or spikes are added, if this is part of the analytical procedure).

8.1.1.4 Semivolatile Organics

It is not recommended to subsample a 1-L aliquot from a 1-Gallon container, for residual analytes may adhere to the container inner surfaces. Utilizing a 1-L sample container, and rinsing the bottle with the appropriate solvent is recommened.

- Most semivolatile organic analyses begin by extracting a 1-liter subsample, and therefore the following reflects this commonality. Subsample volumes and glassware can be adjusted based on laboratory or project needs.
- Make sure sample lid is attached securely and shake the sample in an up and down (or end over end) fashion a minimum of 3 times.

- If a 1-liter bottle is received, mark the volume on the sample bottle.

- Pour the sample smoothly into the extraction vessel.

- Rinse the sample bottle 3 times with small volumes of the appropriate organic solvent and transfer these rinsates into the extraction vessel containing the sample.

- Fill the sample bottle to the mark with tap water, and pour into a graduated cylinder to determine the sample volume.

  Note: If a bottle greater that 1-liter is received, an aliquot should be poured into a graduated cylinder and then transferred into the extraction vessel. The appropriate organic solvent is then used to rinse the graduated cylinder.

8.1.2 Liquid Samples with Suspended Matter (1.0%)

Sampling procedures for liquid samples that contain suspended matter are very similar to the procedures outlined in section 8.1.1 with some minor deviations.

8.1.2.1 Inorganics and Metals (Total Analysis)

- Invert, or shake the sample in an up and down fashion a minimum of 7 times, or until the sample appears uniformly mixed.

- Evaluate whether the rate that the suspended matter settles allows sufficient time to acquire a representative aliquot.

- If the suspended matter settles slowly, the sample will be shaken repeatedly and an aliquot taken immediately.

- If the suspended matter settles rapidly, the sample shaken repeatedly and immediately transferred to a large beaker. A magnetic stir bar is added and the sample is magnetically stirred until uniformly mixed. While stirring continues, an aliquot is taken by pipet or other subsampling means.

- Refer to remaining protocol presented in section 8.1.1.1.

8.1.2.2 Dissolved Inorganics and Dissolved Metals

- Due to the physical separation of the suspended matter, refer to the procedures outlined in section 8.1.1.2.

8.1.2.3 Volatile Organics

- Recommend allowing the suspended particles to settle and follow procedures outlined in section 8.1.1.3.

8.1.2.4 Semivolatile Organics

- Due to the assumption that the entire 1 Liter sample is processed through the preparatory process, refer to the procedures outlined in section 8.1.1.4. In the event that only an aliquot of the sample is desired refer to section 8.1.2.1 for guidance.

8.1.3 Nonaqueous Liquids-Oils

The need for mixing of these nonaqueous liquids must be investigated. Verify whether minor amounts of particles are present which would require redistribution into the liquid prior to subsampling. Samples with substantial amounts of separated phases should refer to section 8.1.3.

8.1.3.1 Due to the different viscosities, densities, coating properties, etc., the weight of the subsample should typically be determined, rather than attempting to express the subsample in terms of volume. If it is difficult to volumetrically measure a sample because it adheres to glassware walls, weight must be used.

8.1.3.2 If a specific and accurate weight needs to be aliquoted, a serological pipet is a good option for subsampling. Aspirate the sample, and then carefully transfer the sample into a tared vessel, controlling the addition by finger pressure on the top of the serological pipet.

8.2 Subsampling Solids ; Soil, Sediment, Heterogeneous Solid Substances, Concrete, Paint Chips, Ash

When subsampling these matrices, first examine the particle size distribution. A decision must be made as to whether a representative subsample can be obtained without prior sample manipulation. This may entail mixing, particle size reduction (PSR), or particle size separation (PSS) techniques. The decision depends on whether the sample is homogenous or heterogeneous in nature. This is determined visually and based on the physical attributes of the sample. Questions to be considered at this time include:

- Is there a significant amount of oversized material (be it either naturally occurring [rocks] or artificially introduced material [debris])?
- Are there obvious soil, chemical, or ash inclusions where indiscriminate subsampling might bias the analytical results or caution against specific protocols (e.g., lead chunks, tar balls, solid (grayish-white) explosives material)?
- Does the sample tend to segregate into various size fractions easily?

If the answer to each of the above considerations is no, then taking a subsample as described in 8.2.1 will likely yield a representative sample. If any answer was yes, then the sample is likely heterogeneous material,

and guidance in Sections 8.2.2 should be observed.

SW-846 states "Decant or discard any water layer on a sediment sample." "Discard any foreign objects such as sticks, leaves, and rocks." USACE default procedures include these practices.

Another important aspect of subsampling depends on the method of analysis, and the size of the aliquot being taken. Analysis requiring smaller (1-2 grams) aliquots (metals, explosives, etc.) require special considerations compared to analysis requiring larger (30 grams) subsamples (semivolatile organics). Achieving a representative subsample must consider whether PSR or PSS techniques are required. If PSR or PSS techniques are used, implement the appropriate quality controls to ensure that samples are not contaminated.

8.2.1 Homogeneous Material

8.2.1.1 Inorganics, Metals, or Semivolatile Organics

- Even if the material received appears homogeneous, the entire sample should be thoroughly mixed using an inert, non-contaminating spatula or rod. This may be performed within the original sample container, or the material may be transferred onto a laboratory tray or pan and mixing performed there.

- For cohesive material, the bulk material should first be size reduced using a stiff bladed utensil such that the average size of any clump is approximately pea-sized (approximately 6mm), if this is possible.

- The material is then mixed by turning the volume of material over a minimum of three times, followed by taking an appropriately sized subsample and transferring this subsample as before into the preparation or test vessel. (An attempt should be made to subsample equivalent aliquots from different areas of the container or tray until the method prescribed amount is achieved.)

- Some samples may be received in brass liners or sections of brass liners. These samples must first be extruded onto a laboratory tray or pan and mixed as described above.

8.2.1.2 Volatile Organics

The volatility of the target analytes must be considered when taking a subsample. An alternative method to that described below, is to place the field sample directly into an aliquot of purge and trap grade methanol (addition of methanol may elevate MDL) or organic-free reagent water preserved with $HgCl_2$ so that the soil to liquid ratio is approximately 1:1 The soil sample must be completely dispersed in liquid prior to VOC analysis of the liquid portion.

The ideal manner in which to take a volatile subsample is to use a coring device (Section 6.20) that takes a representation from non-disturbed soil within the container upon being pushed through the sample. If duplicate analysis is required, a separate collocated field sample should ideally be collected.

- Discard the top layer of the solid sample.
- Take approximately equal aliquots from several places within the container.
- Work should be performed quickly so as to minimize the potential loss of volatile constituents.

8.2.2 Heterogeneous Material

If a solid sample is determined to be heterogeneous (see Section 8.2), a decision must be made as to how a subsample is to be taken so project needs are met. This decision must be made in conjunction with the project manager who submitted the samples for analysis. The following options are possible techniques that can be used to produce a representative subsample of a heterogeneous material. Achieving a representative subsample must consider whether PSR or PSS techniques are required. If PSR or PSS techniques are used, implement the appropriate quality controls to ensure that samples are not contaminated.

8.2.2.1 Inorganics, Metals, or Semivolatile Organics

PSR should be avoided for semivolatile organic procedures due to the potential loss of more volatile analytes. Other general considerations include contamination that may result from these techniques. If PSR is necessary, mortar and pestle is usually the best alternative for semivolatile methods. Milling is also an effective technique, but samples must be dry or dried, therefore less desirable for semivolatile methods.

- If PSR techniques are used which require dry samples, they should be dried at room temperature to a constant weight without exposure to direct sunlight.
- If the sample is amenable to PSR (e.g., grinding or milling), refer to general guidance above and process the entire sample in an appropriate device (appropriate meaning that target analytes are unaffected by the use of the particular grinding apparatus).
- After PSR has been accomplished, use of an appropriate sieve to check for oversized material.
- Rework the oversized material.

- Following PSR/PSS techniques, mix the sample until homogenous and subsample as outlined in 8.2.1.

OR

- If the heterogeneity is due to foreign material or debris, physically separate the foreign material, mix the remaining homogenous sample, and transfer an appropriately homogeneous sample to an appropriately sized aliquot to the tared testing vessel(s).

OR

- Cone and quarter the samples, repeating this procedure until the subsample obtained meets the sample size of the analytical procedure, as per ASTM Method C702, Method B.

OR

- For samples that segregate into size fractions easily, perform a particle size separation (PSS) procedure (e.g., sieving)
- Determine the percentage of each size fraction
- Compose a subsample that takes an appropriate percentage of each fraction.

8.2.2.2 Volatile Organics

Volatile sample subsampling precludes any aggressive mixing or manipulation of original sample. In this case, the project manager must be consulted to determine the most appropriate manner in which to subsample the container. A good alternative is to use methanol as described in Section 8.2.1.2, if this will meet project needs.

8.2.3 Miscellaneous Solid Materials

Certain materials as they originally present themselves cannot be classified in terms as specified in Sections 8.2.1 and 8.2.2. These materials do not have well defined procedures for reducing the size of the material or for obtaining manageable susb-samples of the material. These materials may include but are not limited to concrete blocks or pieces, wooden planks or pieces, filters of various material. The equipment selected for size reduction is simplistically based on what will work for the material but not contaminate the material with the analyte of interest. Once these materials have been sub-sampled or reduced to a manageable particle size then they are treated by laboratory preparation procedures or analytical procedures as a solid or soil matrix.

8.3 Subsampling Multiphase (Liquids/Solids) Sludges (Both Aqueous-Based and Nonaqueous)

This section is meant to address samples considered multiphasic based on physical characteristics (mixture of solids and liquids). The choice of the procedure for handling multiphasic samples is highly dependent on

project needs. There are no specific procedures describing how samples with certain volume distributions of liquid/solid are handled. It is essential that the project manager be consulted before selecting one of the approaches outlined below. If no clear guidance is provided, analyst judgement must be used to decide what portions will be sampled and analyzed. Regardless of the approach used, it must be adequately documented.

Three approaches are provided in the following subsections:

8.3.1 Subsampling of samples analyzed as a Single Mixed Phase (as received)

This approach will not provide information on the abundance of analytes in the individual phases other than what can be implied by solubility.

8.3.1.1 The sample is mixed sufficiently so as to create a homogenous sample. This is usually assessed on a visual basis. A single analysis will then be performed.

- The manner in which the sample is mixed is highly dependent on sample consistency and how easily the phases mix. Some samples can simply be shaken, while others will require a spatula or mixing rod, or laboratory blender. If this is necessary, the device used to mix the sample must be noncontaminating, inert, and easily decontaminated. Usually a glass, or Teflon-coated device is appropriate.

8.3.1.2 The sample is then poured, subsampled with a scoop, or transferred by some other physical means into a tared vessel and the weight of sample is recorded. This transfer is dependent upon sample viscosity/consistency. Another consideration is to not allow the sample to resegregate into the phases when aliquoting the sample.

8.3.2 Subsampling of samples analyzed as Separate Phases

8.3.2.1 When the phases of a multiphasic sample are to be tested individually, the phases are separated by physical means (i.e., filtration [either pressurized or non-pressurized], centrifugation, settling, or use of a separatory funnel). The technique used is dependent on items such as laboratory capabilities, sample characteristics, and analytes of interest.

If an aliquot (subsample) of a sample is to be phase separated, this aliquot must be representative of the original sample. This means that the solid and liquid ratio of the aliquot needs to be the same as the original sample.

8.3.2.2 To accomplish this, follow the procedures listed in Section 8.3.1, except that the final step is to aliquot the subsample into the device used to accomplish phase separation.

Items to consider when performing the phase separation include:

- Device is non-contaminating.
- Device is non-absorbent for analytes of interest.
- Device does not cause the loss of analytes through other means other than noted above.

8.3.2.3 Once the phases are separated, the solid and liquid ratios are recorded. The two portions are transferred into either sample preparation vessels, testing vessels, or into appropriate storage containers for later analysis.

If the liquid portion is subsequently subsampled, follow procedures listed in 8.1. If the solid portion is subsequently subsampled, follow the solids handling procedures described in 8.2.

8.3.3 Subsampling of samples analyzed as Separated Phases and only select phases are desired

This approach requires the separation of the phases and the analysis of only those phases of interest. For example, it may be decided that a phase which constitutes only 0-20% of a total sample may be discarded

8.3.3.1 Separate the phases as described in Section 8.3.2.1.

8.3.3.2 Discard those phases which are not of interest.

8.3.3.3 Transfer portions of the phase(s) to be analyzed into appropriate vessels as described in Section 8.3.2.3.

9.0 Calculations

When phases are separated and analyzed separately, the final concentration for the total sample must be calculated.

$$Final\ Analyte\ Concentration = \frac{(V_1)(C_1) + (V_2)(C_2)}{V_1 + V_2}$$

The final analyte concentration is expressed as µg/mL or µg/g.

where:

V_1 = volume (mL) or weight (g) of first phase

C_2 = concentration of analyte in first phase (µg/mL or µg/g)

V_2 = volume (mL) or weight (g) of second phase

C_2 = concentration of analyte in second phase (µg/mL or µg/g)

10.0 Quality Assurance/Quality Control

10.1 When processing samples, be sure to fully document the actual procedure used (describing the manipulations as completely as possible), and any irregularities or observations made into the appropriate log book, or bench sheet.

10.2 Check to make sure subsample weights/volumes have been properly recorded in sample preparation log books.

10.3 Implement the appropriate quality control samples to allow an assessment of the potential cross-contamination (blanks), and overall effectiveness of the subsampling techniques (duplicates).

11.0 Data Validation

If ineffective subsampling is indicated, the initial subsampling procedure used will be reevaluated. If a more effective method is available, and the holding times are not exceeded, the sample will be resubsampled using the alternative technique, and the analysis repeated.

12.0 Waste Disposal

12.1 Disposal of samples will adhere to local regulatory and/or internal laboratory policies as described in the laboratory's Waste Management Plan.

13.0 References

13.1 *Test methods for Evaluating Solid Wastes*, U.S.EPA SW-846, Third Edition, through Update III, 1997.

13.2 *Sampling for Chemical Analysis*, Analytical Chemistry, Kratochvil, B, and Taylor, J.K., American Chemical Society, July 1981, pp. 924-938.

13.3 *Soil Sampling and Analysis for Volatile Organic Compounds*, U.S.EPA, Office of Solid Waste and Emergency Response, EPA/540/4-91/001, February 1991.

13.4 American Society for Testing and Materials, Method Designation C702, Annual Book of ASTM Standards, Vol. 04.08.2

13.6 *Sampling Theory and Sampling Practice*, F. F. Pitard, Pierre Gy, Volume I and II, 1989, CRC Press,

Inc., Boca Raton, Florida.

CT Laboratories .
Baraboo Laboratory Division

Title: ***Dissolved Methane, Ethene, Ethane, Acetylene and Carbon Dioxide in Water***

SOP Number: **5200**

Prepared by: _____
Date

Technical Review by: _____
Date

Reviewed by: _____
Quality Assurance ***Date***

_____
Laboratory Director ***Date***

SOP Manual Control Number:_____

1.0 Identification of Test Method

1.1 This method is designed to follow procedures and QC requirements consistent with other GC methods utilized by this laboratory

2.0 Applicable Matrix or Matrices

2.1 This method is used to quantify Methane, Ethane, Ethene, Acetylene and Carbon dioxide in water. Results are reported in μg/L. Results can be converted to units that may better satisfy client or program needs.

3.0 Detection Limits

3.1 The reported levels of detection (RL) are 0.5μg/L for each compound (the RL currently used for Carbon dioxide is 200 ug/L).

4.0 Scope and Application

4.1 Target compounds for this method include Methane (CH_4), Ethane (C_2H_6), Ethene (C_2H_4), Acetylene (C_2H_2) and Carbon dioxide (CO_2). With proper detector configurations, oxygen (O_2) and carbon monoxide (CO), as well as other dissolved gases, may be prepared and analyzed by this procedure.

5.0 Method Summary

5.1 Gas chromatographic conditions are utilized for the detection of dissolved gases. Quantification is achieved through analysis of headspace created in each sample vial. The gas chromatograph (GC) is temperature programmed to facilitate separation of organic compounds. The GC uses a flame ionization detector (FID).

5.2 Identification of the dissolved gases is performed by comparison of samples with commercially purchased external standards. Quantification is achieved through calibration of the instrument using the FID's response to the external standards.

6.0 Definition

6.1 Dissolved gas quantification is based on a direct comparison of the areas of each constituent.

6.1.1 An initial calibration check verification standard (ICV) is analyzed immediately following a calibration curve to verify the linearity of the curve and as a check on the integrity of the calibration standard.

6.1.2 An initial calibration blank (ICB) is analyzed after calibrating the instrument to demonstrate that the instrument, purge gas, and preparation water are free from contamination.

6.1.3 A calibration check verification standard (CCV) is analyzed at the beginning of a sequential run of 20 or fewer samples, and again after every ten samples. The CCV functions in verifying the compliance of the calibration curve and the stability of retention times.

6.1.4 A laboratory control spike (LCS) is analyzed with each batch of samples as a system control and method control check. An LCS should be analyzed with every batch of samples (20 or fewer).

6.1.5 A method blank (MB) is run with each batch of 20 or fewer samples to ensure the instrument, purge gas, and preparation water are free from contamination.

6.1.6 A matrix spike, matrix spike duplicate (MS/MSD) pair are run with every batch of 20 or fewer samples as a matrix interference and control check. If not enough sample is available to run an MS and MSD a laboratory control spike duplicate (LCSD) can be analyzed along with the LCS.

6.1.7 One sample per batch (20 or fewer) is also prepared in duplicate and is used as a precision sample preparation check.

6.1.8 A particularly dirty sample can possibly contaminate sampling syringes. After a dirty sample, the syringe should be flushed with the inert purge gas.

7.0 Interferences

7.1 High levels of heavy hydrocarbons may contain constituents that fall among the dissolved gas retention times. These contaminants may adversely affect the baseline during analysis. In this case, dilute the sample and reanalyze to confirm hydrocarbon contamination.

7.2 Moisture can interfere with analysis. Procedures to minimize the injection of moisture into the GC are advisable.

8.0 Safety

8.1 Gloves, safety goggles, and protective clothing should be worn to protect against unnecessary exposure to hazardous chemicals and contaminants in samples. All activities performed while following this procedure should utilize appropriate laboratory safety systems.

9.0 Equipment and Supplies

9.1 10 uL, 25µL, 100µL, 500µL, and 1mL gas-tight syringes (Hamilton or equivalent).

9.2 40mL VOA vials with Teflon-lined caps (QEC or equivalent).

9.3 Ring stand with three-finger clamps.

9.4 15mL graduated vial (Fisher brand or equivalent).

9.5 Thermometer (NIST traceable).

9.6 Water bath (ambient temperature).

9.7 Gas chromatographs (Hewlett Packard 5890 or SRI 8610) equipped a packed column (Supelco, Haysep D, 80/100 mesh size) and a FID.

9.8 Data management system (EZ Chrom-Elite, ver. 3.1 or Peak Simple II).

10.0 Reagents and Materials

10.1 200ppmV CH_4, C_2H_6, and C_2H_4 certifide gas standard (Scotty II or equivalent), prepared in helium.

10.2 200ppmV C_2H_2 certifide gas standard (Scotty II or equivalent) prepared in helium.

10.3 10,000ppmV certifide CO_2 (Scotty II or equivalent) prepared in helium.

10.4 Deionized water (Milipore).

10.5 Inert gas (He or N_2) for purging (4.7 grade or better, 99.999%)

11.0 Sample Preservation and Storage

11.1 Samples to be analyzed for methane, ethane, ethene, and acetylene require preservation by acidification (pH < 2). Samples requiring CO_2 analysis are to be analyzed unpreserved. All samples are to be stored in the volatiles double door refrigerator, inverted, at 4°C ±2°. Hold time is 14 days from sample collection except for CO2 which requires analysis within 7 days from sampling.

12.0 Quality Control

12.1 Table 1 is designed to outline the control steps and provisions required to produce acceptable data.

13.0 Calibration and Standardization

13.1 Six injections of varying standard concentrations are introduced into the GC via the direct injection port. The standards range from 2ppmV to 100ppmV. The results are then plotted on a calibration curve by the instrument's computer software. Procedures for programming the calibration are outlined in the reference manuals supplied with the EZChrom software. The plotted curves for each compound should have a correlation coefficient (r^2) of 0.990 (or $r \geq 0.995$) in order for the curve to be considered valid.

13.1.1 The standard concentrations are made using the 200ppmV dissolved gas standard (or 10,000 ppmV for CO_2), as follows:

Methane/Ethene/Ethane and Acetylene

Standard Concentration	Standard added (in μL)
2ppmV	10
5ppmV	25
10ppmV	50
20ppmV	100
50ppmV	250

100ppmV	500

Carbon dioxide

Standard Concentration	Standard added (in μL)
50ppmV	5
100ppmV	10
250ppmV	25
500ppmV	50
1000ppmV	100
2500ppmV	250

An ICV is analyzed immediately following a successful calibration. To analyze an ICV, inject 250μL of the dissolved gases standard directly into the GC (concentration = 50ppmV) for Methane, Ethene, Ethane, and Acetylene. Inject 50 ul of the gases standard for CO_2 (conc. = 500 ppmV).

13.2 An ICB should follow the ICV, before samples are analyzed. The ICB is prepared in the same way as a method blank, with the same requirements.

14.0 Procedures

14.1 Samples are collected in 40mL VOA vials with zero headspace. Following login, they are stored inverted in the volatiles refrigerator (<4°C ± 2°).

14.2 To prepare the samples for analysis, each sample is purged with an inert gas in order to obtain a 4mL headspace. The sample vial is placed in a 3-finger clamp, at an inverted 45° angle. A large bore needle is inserted through the septum, directly over the graduated collection device. Another needle (connected to the purge gas source) is inserted through the septum. The purge gas pressurizes the sample, expelling the 4mL (the purge rate should be no faster than 5mL/min).

14.3 When all samples have been prepared, they are shaken for five minutes on a shaker table, allowing the gas and liquid phases to equilibrate. Before analysis, the samples should be placed in an ambient temperature water bath, to allow samples to reach a constant temperature.

14.4 A method blank (MB) is to be analyzed with each batch of samples (one per 20 samples). Method blanks are prepared by reversing the flow of the purge gas through the system, filling the VOA vial with degassed water. The vial should have no headspace, and should then be prepared in the same manner as the other samples.

14.5 An LCS is prepared in the same manner as a method blank. Once the 4mL headspace has been provided, withdraw 500μL of the headspace and immediately inject 500μL of the a 200 ppmV dissolved gases standard (Methane, Ethane, Ethene, and Acetylene) into the headspace. Analyze 1mL of the spiked headspace by directly injecting it into the GC (final concentration: 25ppmV). For CO_2 withdraw 100 uL of the headspace and immediately inject 100 uL of the 10,000 ppmV CO_2 gas standard. Analyze 1mL of the spiked headspace by directly injecting it into the GC (final concentration: 250ppmV). The final concentration values are converted to ug/L via a series of calculations (see sec. 15.0) to obtain recoveries values in the LIMS system.

14.6 If sample volume is sufficient (e.g. the client has provided at least three to four vials for a

sample), an MS/MSD set should be analyzed. This sample is prepared in the same way as the other samples. Withdraw 500μL of the headspace and immediately inject 500μL of the 200ppmV dissolved gas standard (Methane, Ethane, Ethene, and Acetylene). Analyze 1mL of the spiked headspace by directly injecting it into the GC (final concentration: 25ppmV). For CO_2 withdraw 100 uL of the headspace and immediately inject 100 uL of the 10,000 ppmV CO_2 gas standard. Analyze 1mL of the spiked headspace by directly injecting it into the GC (final concentration: 250ppmV). The final concentration values are converted to ug/L via a series of calculations (see sec. 15.0) to obtain recoveries and precision values in the LIMS system.

14.7 A CCV analysis begins and ends each sequential run (also injected after every ten sample analyses) 250μL of dissolved gas standard is directly injected into the GC. Inject 50 ul of the gases standard for CO_2 (conc. = 500 ppmV).
All target compound recoveries must be within QC limits in order for analysis to continue. A method blank follows the CCV, and samples analyses follow the MB.

14.8 The GC's are either run isothermally at 95°C or slightly ramped to facilitate sample peak separation. The CO_2 sample are currently analyzed on the SRI GC equipped with a methanizer (set at approximately 380°C) used for catalytically reduce CO_2 to Methane in order to get an FID response. Helium or Nitrogen are typically used as carrier gases and hydrogen mix with in-house compressed air is used as the reaction gas to burn in the FID. To better separate Acetylene from Ethene two Haysep D columns are connected in series. Carrier flow rates are adjusted for optimum separation (usually between 15 and 20 mL/minute).

15.0 Calculations

15.1 EZChrom will produce results in ppmV (or partial pressure result). Peak Simple II provides a peak area that is converted into partial pressure. An Excel spreadsheet is set up in which the results in ppmV are converted to μg/L. This is achieved, in part, by the use of Henry's Law Constant. Each analyte has a different value for this constant, as seen in Table 2. The spreadsheet contains several other values. Vial volume (ave. vol. = 43mL), the headspace volume (normally 4mL), sample temperature (°C), equilibrium mole fractions , moles of gas, saturation concentrations, and densities must all be known or calculated to obtain the correct final result. Each gas also has a unique molecular weight (as outlined in Table 3).

15.2 The partial pressure of each compound is found using the linear equation:

$$P_g = mx + b$$

Where:

- P_g = partial pressure
- m = slope of calibration curve
- x = area obtained from sample analysis
- b = y-intercept of calibration curve

15.3 The partial pressure is converted to a decimal equivalent. For instance, 10ppm = 0.000010 (1.0×10^{-5}).

15.4 The equilibrium mole fraction is then determined by dividing the partial pressure by the Henry's Law Constant for that compound (see Table 2).

$$X_g = P_g \div H$$

Where:

- X_g = equilibrium mole fraction
- P_g = partial pressure
- H = Henry's Law Constant

15.5 The moles of gas (N_g) is found by multiplying the equilibrium mole fraction (X_g) by 55.5, where 55.5 = gram·moles of 1L of water.

15.6 The saturation concentration C of the gas is calculated as follows:

$$C = N_g\,(MW)(1000mg/g)$$

Where:

- MW = molecular weight of gas (see Table 3)

15.7 To adjust gas density for pressure:

$$D = (MW) \div (22.4\ L{\cdot}mol)(T/273)$$

Where:

- T = sample temperature in Kelvin

15.8 Determine the milliliters of analyte in the headspace (A_h):

$$A_h = (mL\ of\ headspace)(P_g)$$

15.9 To determine the amount of analyte in the liquid phase:

$$A_l = (A_h/V)(D)(1000mg/g)(1L/1000mL{\cdot}L)$$

Where:

- V = volume of water (vial volume – headspace volume) in liters

15.10 Finally, the total concentration(TC) of an analyte in the original sample is found by adding the concentration in water to the saturation concentration. This result will be in mg/L. Convert to μg/L.

$$TC = A_l + C$$

$$TC\ (mg/L) \times 1000 = TC\ (\mu g/L)$$

16.0 Method Performance

16.1 Certified standards, properly maintained instrumentation, and analyst experience and expertise are critical elements in producing accurate results.

16.2 Initial demonstration of capability (IDC) is a technique used to ensure acceptable method performance. An analyst must demonstrate initial precision and accuracy through the analysis of five laboratory control spikes. After analysis, the analyst determines the average recovery in µg/L, as well as the relative standard deviation (RSD of the recoveries for each analyte. The default criteria of 70-130% recovery and 20% RSD are used until internal limits are generated.

16.2.1 IDCs are analyzed in the same way as a laboratory control spike.

17.0 Data Assessment and Acceptance Criteria for QC Measures

17.1 If the initial analysis of a sample or a dilution of the sample has a concentration of a particular analyte that exceeds the calibration range, the sample must be reanalyzed at a higher dilution (i.e. smaller injection volume). If the blank analysis is not free of interferences, the system must be decontaminated. Sample analyses cannot resume until a blank that is free of interferences can be analyzed.

17.2 When the analysis of an analytical batch or sequence has completed, the data is processed and prepared for reporting. Assessments of all spiked and calibration control samples and standards should also be finalized before reporting the data. When the analyst has finished processing the analytical batch, the results are manually entered into the LIMS system where dilution factor adjustments are made. Once the final results have been verified, the data is turned over to another qualified analyst for final validation. The second analyst confirms the results and electronically validates them. Finally, the validated results are made available to the client services personnel in order for the data to be given to the client or appropriate agencies.

18.0 Waste Management

18.1 Samples are routinely held (refrigerated) for up to six weeks from analysis date before they enter the waste stream. Waste disposal of samples and standards follows the procedures documented in the Laboratory Waste Disposal SOP (Quality Assurance Section, SOP No. FO-8, Rev. 4).

19.0 References

19.1 USEPA, Methane, Ethane, Ethene Analysis Guidance, Rev. 1, February 21, 2002

19.2 RSK SOP 175, Analysis of Dissolved Methane, Ethane, and Ethylene in Ground Water by Standard Gas Chromatographic Technique. Region 1 Library, 1997

Table 1-QC Requirements

QC Item	Frequency	Acceptance Criteria	Corrective Actions
Initial calibration (ICAL)	Each time the instrument is set up. Established initially with a minimum of five concentration levels, with the low standard at or below the reporting limit (RL).	Coefficient of determination (r^2) should be > 0.990. (r > 0.995)	Correct system and recalibrate. Criteria should be met before sample analyses can begin.
Continuing Calibration Check Standard (CCV) and Initial Calibration Verification (ICV)	Analyzed at the beginning and end of each sequential run and after every 10 samples. ICV analyzed after intial calibration.	Within 20% of spiked value or within project/program specified criteria.	Reanalyze CCV and affected samples. If CCV recoveries are still unacceptable, correct problems and recalibrate.
Method Blank (MB) and Initial Calibration Blank (ICB)	Analyzed with each batch of samples (20 or less).	Recoveries less than adjusted reporting limit. Blank subtraction is not allowed.	Reprep with fresh water and reanalyze.
Matrix Spike/Matrix Spike Duplicate (MS/MSD)	Analyzed with each batch of samples (one set per 10 samples).	Recoveries: Default 70 to 130%. Precision: Default 20%. Or use internally generated or project/ program specific limits.	Repeat injection, check calculations. Recoveries reported exceeding limits should be qualified (M)
Laboratory Control Spike (LCS)	Analyzed if sample volume is insufficient for MS/MSD analysis (every 10 samples). Second source standard is optional because of difficulty of obtaining a second source.	Default: 70-130% Recovery. Or use internally generated or project/ program specific limits.	Reanalyze LCS and affected samples. If LCS recoveries are still unacceptable, correct problems and recalibrate. Sample results reported with associated LCS recoveries exceeding limits should be qualified (Q).
Qualitative/Quantitative Issues	If analyte(s) in a sample exceeds the working calibration range of the instrument, the sample must be diluted and reanalyzed so that the compound(s) fall around the midpoint of the calibration curve. If the concentration of the target analyte that exceeded the calibration range is present in the subsequent sample(s) (>RL but <20xRL), the sample(s) should be reanalyzed to confirm the sample syringe is clean.	The detection level of all compounds must be within the working range of the calibration curve. Potential carryover may occur only if the sample syringe contains the contamination from one sample to the next. Proper flushing of the syringes with an inert gas will eliminate this problem.	Dilute the sample to bring the level of the highest concentration of target compounds within the working range of the calibration curve. If a sample is reanalyzed to determine whether or not c carryover has occurred, and the results do not confirm in the second analysis, then report only the second analysis. Once more than 10 % of the head space is removed from a vial for analysis then another vial should be prepared before reanalyzing the sample.

Table 2-Henry's Law Constants

Compound	Temperature Range (in °C)	Henry's Law Constant
Methane	13-16	3.37×10^4
	17-22	3.76×10^4
	23-27	4.13×10^4
Ethane	13-16	2.26×10^4
	17-22	2.63×10^4
	23-26	3.02×10^4
Ethene	13-16	8.95×10^3
	17-22	1.02×10^4
	23-26	1.14×10^4
Acetylene	13-16	1.08×10^5
	17-22	1.21×10^5
	23-27	1.33×10^5
Carbon Dioxide	13-16	1.22×10^3
	17-22	1.42×10^3
	23-26	1.64×10^3

Table 3-Molecular Weights

Compound	Molecular Weight (in amu)
Methane	16
Ethane	30
Ethene	28
Acetylene	26
Carbon Dioxide	44

CT Laboratories
Baraboo Laboratory Division

Title: **Hexavalent Chromium, Automated Colorimetric**

SOP Number: **CC-34**

Prepared by: _____
Date

Technical Review by: _____
Date

Reviewed by: _____
Quality Assurance ***Date***

_____
Laboratory Director ***Date***

SOP Manual Control Number:

1.0 SCOPE AND APPLICATION

1.1 This method is used to determine Cr(VI) in surface waters, drinking waters, domestic wastewaters and industrial wastewaters.

1.2 The method may not be used for preserved samples or solids.

2.0 METHOD SUMMARY

2.1 Dissolved hexavalent chromium, in the absence of interfering amounts of substances such as molybdenum, vanadium, and mercury, may be determined colorimetrically by reaction with diphenylcarbazide in acid solution. A red-violet color of unknown composition is produced. The reaction is very sensitive, the absorbancy index per gram atom of chromium being about 40,000 at 540 nm. Addition of an excess of diphenylcarbazide yields the red-violet product, and its absorbance is measured photometrically at 540 nm.

3.0 DEFINITIONS

3.1 Initial Calibration Verification (ICV): A midrange check standard analyzed immediately after the calibration has been completed, to evaluate calibration curve and or instrument performance.

3.2 Initial Calibration Blank (ICB): An aliquot of reagent water analyzed fortified with the same matrix as the calibration standards analyzed immediately after the ICV.

3.3 Lab Control Sample (LCS): A known concentration obtained from a second source.

3.4 Continuing Calibration Verification (CCV): A check standard analyzed after every ten samples and at the end of the analytical run, to evaluate instrument performance.

3.5 Continuing Calibration Blank (CCB): An aliquot of reagent water analyzed fortified with the same matrix as the calibration standards analyzed immediately after the CCV.

3.6 Matrix spike-matrix spike duplicate (MS-MSD): To two of three aliquots of a given sample a known amount of spike solution is added. Matrix spikes and matrix spike duplicates are taken through all steps of preparation and analysis, exactly like a sample. The amount of spike recovered helps to assess the effect of the sample matrix on the analysis. The precision of the method is also determined, by calculating the relative percent difference (RPD)of the two spiked aliquots. An MS-MSD should be prepared for every 20 samples in each matrix.

4.0 HEALTH AND SAFETY

4.1 Gloves and protective clothing should be worn to protect against unnecessary exposure to possibly hazardous chemicals and contaminants in samples. All activities performed while following this procedure should utilize appropriate laboratory safety systems (see CTI Health and Safety Manual).

5.0 CAUTIONS

There are no cautions

6.0 INTERFERENCES

6.1 Substances which can reduce Cr(VI) upon acidification (e.g. cyanides, thiosulfate, organic matter) will cause negative interferences in the determination of Cr(VI).

6.2 Hexavalent molybdenum and mercury salts will react to form color with the reagent but the intensities are much lower than that for chromium at the specified pH. Concentrations as high as 200mg Mo or Hg/L can be tolerated.

6.3 Vandadium interferes strongly but concentrations up to 10 times that of chromium will not cause trouble.

6.4 Iron in concentrations greater than 1 mg/L may produce a yellow color but the ferric ion (Fe^{+3}) color in not strong and no difficulty is encountered normally if the absorbance is measured photometrically at the appropriate wavelength.

6.5 Samples with a native color can cause positive interference. Correct for this interference by analyzing the sample following section 11 but do not use diphenylcarbize in the color reagent.

7.0 PERSONNEL QUALIFICATIONS

7.1 Analysts should be familiar with safety requirements for the lab.

7.2 Analysts should have a working knowledge of the Lachat AE system.

7.3 Analysts should have a valid IDC on file.

8.0 APPARATUS AND MATERIALS

8.1 Lachat QuikChem automated flow injection ion analyzer, which includes:

- 8.1.1 Automated sampler
- 8.1.2 Proportioning pump
- 8.1.3 Injection module with a 120cm, 0.8 mm I.D. sample loop
- 8.1.4 Colorimeter
  - 8.1.4.1 Flow cell, 10mm, 80 uL
  - 8.1.4.2 Interference filter, 540nm
- 8.1.5 Reaction module 10-124-13-1-A
- 8.1.6 QuikCalc II software system

8.2 **REAGENTS**

- 8.2.1 Prepare all standards and solutions using deionized water.
- 8.2.2 <u>Color Reagent</u>: in a 1 L volumetric flask, dissolve 0.40 g of s-diphenylcarbazide (1, 5–dephenylcarbohydrazide, 2 2 – diphenycarbonic dihydazide, $C_{13}H_{14}N_4O$) in 200 mL Purge and Trap Grade Methanol. Add 720 mL of deionized water, then 80.0 mL of concentrated sulfuric acid. Dilute to mark with additional DI water. This solution is good for one month.
- 8.2.3 <u>Stock Standard, 100 mg Cr/L as K_2CrO_4</u>: in a 1L volumetric flask add 0.3735g of dreid (2 hours at 104°C) potassium chromate

(K_2CrO_4 Analytical Reagent Grade). Dilute to the mark with deionized water, invert or shake until dissolved.

8.2.4 Intermediate Stock Standard, 1.00 mg/L as K_2CrO_4: to a 1 L volumetric flask, add 10 mL of stock standard (6.3) and bring up to volume with DI water. Mix by inverting three times.

8.2.5 Working standards: into 5 – 250 mL volumetric flasks pipet, 100, 50, 25, 12.5, & 5 mL of the intermediate stock standard (6.4) and bring up to volume with DI water. Invert three times. This yields standards of 400, 200, 100, 50, and 20 ug Cr/L respectively.

9.0 INSTRUMENT OR METHOD CALIBRATION

See section 11.0 for calibration instructions

10.0 SAMPLE COLLECTION, HANDLING AND PRESERVATION

10.1 Collect a minimum of 125 mL of sample in plastic or glass containers.

10.2 Samples should be kept at 4°C without chemical preservative until analysis. Hold time is 24 hours.

11.0 SAMPLE PREP AND ANALYSIS

11.1 Set up Lachat program to include the following timing guidelines. Save as the Hexavalent Chromium method. Load test for analysis.

Injection timing:

Pump speed:	35
Cycle speed:	50s
Load speed:	20s
Injection period:	20s
Inject to peak start period:	14s
Inject to peak end period:	60s
Sample loop length:	120 cm

11.2 Inspect modules for proper connections.

11.3 Turn on power to all modules.

11.4 Place reagent lines into proper containers. Raise tension on pump tube cassettes. Refer to Lachat Manual for specific details and a diagram of the manifold.

11.5 Pump system until a stable baseline is attained.

11.6 Place calibration standards and blank in sample tray in descending order of concentration followed by unknowns and check standards. Analyze and develop a standard curve based on plotting absorbance against the known concentrations. The concentrations of the unknowns (samples) as well as the check standards and other QC will be evaluated in relation to the absorbencies of the calibration standards. The Lachat program prints out the raw data in ug/L.

11.7 Using the calibration curve developed using the color reagent, reanalyze the sample using the color reagent solution without the diphenylcarbazide.

11.8 Subtract the results of the sample without diphenylcarbazide from the sample with diphenylcarbazide and report this as your final result.

11.9 At end of run, place all transmission lines in water, and flush system. Pump lines dry.

11.10 Turn off pump, all modules, and release tension levers on pump tube cassettes.

12.0 INSTRUMENT MAINTENANCE AND TROUBLESHOOTING

12.1 If baseline drifts, peaks are too wide, or other problems with precision arise, clean the manifold by the following procedure:

12.1.1 Place all reagent lines in deionized water and pump to clear reagents (2-5 minutes).

12.1.2 Place reagent lines and carrier in a 1 M hydrochloric acid (1 volume conc. HCl added to 11 volumes of DI water) and pump for several minutes.

12.1.3 Place all lines in DI water and pump for several minutes.

12.2 See Lachat Operator's Manual for further guidance on troubleshooting and maintenance.

13.0 DATA ACQUISITION, CALCULATION AND REDUCTION

13.1 Accuracy- MS-MSD

$$\textit{Spike Concentration, ug/L} = \frac{\textit{(mLs of spike used) (conc. of spiking soln, ug/L)}}{\textit{(combined vol. of sample + spike, mL)}}$$

$$\textit{\% Spike Recovery} = \frac{\textit{[spike + sample] - [sample x C.F.*]}}{\textit{spike value}}$$

$$\textit{*C.F (volume correction factor)} = \frac{\textit{Volume of sample, mLs}}{\textit{vol. of sample + spike, mLs}}$$

13.2 **Accuracy- check standards**

$$\textit{\% Recovery of Standard} = \frac{\textit{measured value}}{\textit{true value}} \times 100$$

13.3 **Precision- Relative percent difference (RPD)*:***

$$\textit{\% RPD} = \frac{\textit{Abs.** [sample conc. - dup conc.] x 100}}{\textit{ave. of sample \& dup conc.}}$$

***Absolute Value*

14.0 COMPUTER HARDWARE AND SOFTWARE

14.1 Computer with StarLIMS

14.2 Lachat QuickChem AE software

15.0 DATA MANAGEMENT AND RECORD MANAGEMENT

15.1 After data has been captured by LIMS, it is reviewed by the analyst for accuracy and completeness. See checklist for data review guidance.

15.2 Once analyst has reviewed and approved the data, it is given to a peer or supervisor for review.

15.3 After the second reviewer approves the data, the reviewer sends the data to "validated" status in LIMS.

15.4 The original data is filed by test in the file cabinet and periodically the contents of the file cabinet are archived.

16.0 REFERENCES

16.1 *Standard Methods for the Examination of Water and Wastewater*, 18th Edition 1992, APHA-AWWA-WEF, Method 4500 D.

16.2 *Test Methods for Evaluating Solid Waste*, SW-846, Third Edition, July 1992, Method 7196A.

16.3 *Lachat QuickChemAE Operating Manual,* Issued: 10/01/93

16.4 *Lachat QuickChem Methods Manual,* Revision Date: 18 January 1996

16.5 *Lachat QuickChemAE Software Reference Manual,* 24 January 1994 release

SUMMARY OF QUALITY CONTROL REQUIREMENTS

Procedure	Frequency of Procedure	Acceptance Criteria	Corrective Action if Unacceptable
Five-point initial calibration	Initially and as needed	$r \geq 0.995$ for regression line	Repeat until acceptable
Initial calibration verification (ICV)	After each ICAL, prior to sample analysis	%R: 90-110% for all analytes	Remake and reanalyze ICV standard once, if still unacceptable repeat ICAL
Initial calibration blank (ICB)	After ICV, prior to sample analysis	< RL	Remake and reanalyze CB once, if unacceptable investigate and correct problem. Reanalyze along with associated samples.
Continuing calibration verification (CCV)	Daily, prior to sample analysis, after every 10 samples, and at end of run	%R: 90-110% for all analytes	Reanalyze CCV once, if unacceptable investigate and correct problem. Reanalyze all samples after last acceptable CCV.
Continuing calibration blank	After each CCV	<RL	Halt operation, fix problem and reanalyze all samples back to the last acceptable CCB
Capability demonstration sample (IDC)	Four (4) prepared samples analyzed one time prior to any sample analyses	In-house determined criteria for LCS recovery and duplicate precision	Repeat as needed until acceptable
Sample duplicate (DUP) or matrix spike duplicate (MSD)	One (1) per of 20 samples of the same matrix	In-house derived limits Default: RPD $\leq$20% if analytes > RL	Investigate problem, if LCS in control qualify results.
Matrix spike sample (MS)	One (1) per of 20 samples of the same matrix	In-house derived limits Default: 80% $\leq$ %R $\leq$ 120%	Investigate problem, if LCS in control qualify results as matrix interference.
Laboratory control sample (LCS)	One (1) per of 20 samples of the same matrix	In-house derived limits Default: 90% $\leq$ %R $\leq$ 110%	Reanalyze once, if unacceptable investigate and correct problem. Reanalyze along with associated samples.

Commonwealth Technology, Inc.

Data Validation Checklist

LIMS #:	Method: Hexavalent Chromium SW846-7196A			
Analysis Date	**Analyst / Data Interpreter**	**Independent Reviewer**	**Date of Review**	**Approved**
				Yes ... No

Instructions: Complete one checklist per *analytical run*. Enter the appropriate response for each question. Each "No" response requires an explanation in the Comments section, and may require the initiation of a Nonconformance Report.

Requirement:	Acceptance Criteria	Analyst Review		Independent Review		Comments: (indicate reference to an attachment if necessary)
		Yes	No	Yes	No	
1. Were the samples analyzed within hold time?	24 hours					
2. Was the calibration performed using the required number of standards?	Five plus a blank					
3. Is the standard prep log number noted on the analytical report?	---					
3. Was the correlation coefficient acceptable?	>= 0.995					
4. Were the ICV and ICB run immediately after the calibration curve?	---					
5. Was the ICV recovery acceptable?	90 – 110 %					
6. Was the ICB result acceptable?	< LOD					
7. Were the CCV's and the CCB's analyzed at the required frequency?	1per 10 samples					
8. Were the CCV recoveries acceptable?	90 – 110 %					
9. Were the CB results acceptable?	< LOD					
10. Was a LCS ran at the required frequency?	1 per 20 samples					
11. Was the LCS recovery acceptable?	80-120 %					
12. Was the LCS used before the indicated expiration date?	---					
13. Were samples results corrected for sample color affects?						
14. Were the MS and MSD prepared at the required frequency?	1per 20 field samples					
15. Were the MS and MSD recoveries acceptable?	Within in house QC limits					
16. Was the RPD between the MS and MSD acceptable?	Within in house QC limits					
17. Are all sample on the job lists accounted for?	---					

CT Laboratories
Baraboo Laboratory Divison

Title: **Mercury Cold Vapor Atomic Absorption**

SOP Number: **6120B**

Prepared by: _____
Date

Technical Review by: _____
Date

Reviewed by: _____
Quality Assurance ***Date***

_____
Laboratory Director ***Date***

SOP Manual Control Number:_____

1.0 SCOPE AND APPLICATION

This method is appropriate for measuring mercury concentrations in groundwater, wastewater, drinking water, TCLP extracts, soils, sediments, and sludge-type materials.

2.0 METHOD SUMMARY

2.1 Prior to analysis, the samples must be prepared according to the procedures discussed in this SOP.

2.2 This is a cold-vapor atomic absorption technique, based on the absorption of radiation at 254-nm by mercury vapor. The mercury is reduced to the elemental state 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 (peak height) is measured as a function of mercury concentration.

3.0 DEFINITIONS

3.1 Reagent Blank - A solution of deionized water, (containing in correct proportion, all reagents required by the method), used with the calibration standards to standardize the instrument, as a calibration blank, and for sample dilution.

3.2 Calibration Standards - A series of known standard solutions used for calibration of the instrument within the measurable linear range. Calibration standards shall contain, in correct proportion, all reagents required by the method. A total of 5 calibration points are used for Mercury calibration. Acceptance of the calibration requires a correlation coefficient of 0.995 or better. No samples shall be analyzed without acceptable calibration.

3.3 Calibration Verification Standards-Initial (ICV) & Continuing (CCV) - A midpoint calibration standard which is analyzed at the beginning of the run (ICV), at a frequency of 1 per 10 samples during a run (CCV), and at the end of a run to verify calibration throughout the run. The ICV must be from a second source different than that of the calibration standards, while the CCV may be from the same source as the calibration standards. Note that limits for ICV are tighter than those for CCV (see section 16).

3.4 CB (Calibration Blanks- Initial and Continuing) - A reagent blank solution, which is analyzed immediately following the calibration standards (Initial Calibration Blank-ICB), at a frequency of 1 per 10 samples during a run (Continuing Calibration Blank-CCB), and at the end of a run to check for drifts in calibration or possible analyte carry-over. Control criteria consist of the highest of the following: the absolute value being less than or equal to the MDL for a given

analyte for routine work or ½ the MRL for ACOE work, five percent of the regulatory limit, or five percent of the measure concentration in the sample. If this range is exceeded, a new calibration will be necessary.

3.5 LCS (Laboratory Control Sample)- A mid-range standard prepared from a source different from that used for calibration standards. The LCS is used to verify the accuracy of the digestion and is analyzed at the beginning of the analytical batch.

3.6 MB (Method Blank) - A Reagent Blank which is carried through the entire preparation and analytical method. The method blank is used to detect possible contamination that may occur prior to or during the sample preparation. A minimum of one MB is prepared per batch, and is analyzed at the beginning of an analytical batch. Method blank value should be lower than the highest of the following: the absolute value being less than or equal to the MDL for a given analyte, five percent of the regulatory limit of five percent of the measure concentration in the sample.

3.7 MS-MSD (Matrix Spike-Matrix Spike Duplicate): - Two separate sample aliquots to which a known concentration of analyte has been added which is carried through the entire preparation and analytical procedure. The purpose of a matrix spike is to reveal any matrix effect from the sample on the recovery of the analyte by the method being used. An MS-MSD pair is prepared for every 20 samples per matrix of routine samples or for ACOE a DUP/MS pair is prepared for every 20 samples of a given matrix per day. Failure to meet criteria may be due to poor recovery during the preparation method or due to matrix interference within the digestate. To be considered acceptable, MSD must meet both the same % recovery criteria as an MS, and the same % RPD as a duplicate sample. MS/MSD %RPD and may be used as acceptance criteria for duplicate analysis.

3.8 Method Reporting Limit (MRL) or Contract Required Detection Limit (CRDL) Standard: Detection level standard at a level near but below the reporting limit, or at a level specified by client contract. When required, it is to be analyzed following the ICB, and prior to the last CCV standard in the run.

3.9 Duplicate (DUP)- A separate aliquot of sample which has been carried through the entire preparation and analytical procedure the same as the original sample. One duplicate per batch is prepared for ACOE work.

4.0 HEALTH AND SAFETY

4.1 Gloves and protective clothing shall be worn to protect against unnecessary exposure to hazardous chemicals and contaminants in samples. All activities performed while following this procedure shall utilize appropriate laboratory safety systems.

5.0 CAUTIONS

5.1 Mercury is a toxic substance and care should be taken to avoid contact with it. This includes wearing gloves and using ventilation devices when working with Mercury.

5.2 This method allows for detection of small quantities of Mercury. All potential sources of Mercury contamination should be avoided. This would include sources of Mercury present in other lab areas.

6.0 INTERFERENCES

6.1 Potassium permanganate is added to eliminate possible interference from sulfide. Concentrations as high as 20 mg/L of sulfide as sodium sulfide do not interfere with the recovery of added inorganic mercury from reagent water.

6.2 Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/L had no effect on recovery of mercury from spiked samples.

6.3 Seawaters, brines, and industrial effluents high in chlorides require additional permanganate (as much as 25 mL) because, during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation of 254 nm. Care must therefore be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine sulfate reagent (25 mL).

6.4 Certain volatile organic materials that absorb at this wavelength mayalso cause interference. A preliminary run without reagents should determine if this type of interference is present.

7.0 PERSONNEL QUALIFICATIONS

7.1 Personnel operating the CVAA shall have background knowledge of the scientific principles used during this application. All operators shall perform an initial demonstration of capability (IDC) prior to analyzing any samples. It is preferable for the operator to have at least two semesters of college chemistry.

8.0 APPARATUS AND MATERIALS

8.1 APPARATUS & MATERIALS

8.1.1 Cetac M-6000A Mercury Analyzer with ASX-500 autosampler.

8.1.2 Argon gas, HP grade.

8.1.3 50 mL disposable centrifuge tubes and caps. (Fisher p/n 05-539-9 or equivalent)

8.1.4 25 mL Class A volumetric pipettes

8.1.5 100 mL volumetric flasks

8.1.6 25 mL glass Class A, TD, graduated cylinders

8.1.7 1, 2, 3, 4, 5 mL Class A volumetric pipettes.

8.1.8 Eppendorf pipette, 0.100 to 1.000 mL range.

8.1.9 Environmental Express Hot Blocks set at 90-95 ^{0}C.

8.2 REAGENTS

8.2.1 Sulfuric acid, H_2SO_4, concentrated: Trace metal grade (Fisher p/n A300C-212)

8.2.2 Nitric acid, HNO_3, concentrated: Trace metal grade. (Fisher p/n A509-212 or equivalent)

8.2.3 Hydrochloric acid, HCl, concentrated: Trace metal grade. (Fisher p/n A508SK212 or equivalent)

8.2.4 Potassium permanganate solution, 5% w/v: Prepared by dissolving 50g Potassium Permanganate (Fisher p/n P279-212 or equivalent) in 1000 ml of deionized water. Prepare as needed. Expires 6 months from date of preparation. Store at room temperature in metals lab.

8.2.5 Potassium persulfate solution, 5% w/v: Prepared by dissolving 50 g Potassium Persulfate (Fisher p/n P282-500 or equivalent)in 1000 ml of DI water. Prepare as needed. Expires 6 months from date of preparation. Store at room temperature in metals lab.

8.2.6 Sodium chloride-hydroxylamine sulfate solution, 12% w/v: Prepared by dissolving 60 g Sodium Chloride (Fisher p/n) and 60 g of Hydroxylamine Sulfate in 500 ml of DI water. Prepare as needed. Expires 6 months from date of preparation. Store at room temperature in metals lab.

8.2.7 Stannous chloride (10% $SnCl_2$ w/v in 7% HCl v/v): to a 1000mL volumetric flask dissolve 100 gm Stannous Chloride(VWR part number MK817604) in 70mL conc. HCl. Stir until $SnCl_2$ is completely dissolved. Additional heat may be necessary to get complete dissolution. Once dissolved, dilute to line and cool. Prepare as needed. Expires 6 months from date of preparation. Store at room temperature in metals lab.

8.2.8 Aqua regia: In a fume hood, carefully add three volumes of concentrated HCl to one volume of concentrated HNO_3. Prepare fresh daily.

8.3 Stock Standards

8.3.1 Mercury stock standards, 1000 mg/L certified solutions, two sources. One is to be used for the calibration standards and the other for the LCS. (Ultra Scientific ICP-080 and JT Baker 6934-04 or equivalents). Store at room temperature in the metals lab. Expiration dates are given by the manufacturer.

8.4 Calibration Standards:

8.4.1 Intermediate Stock #1 (10,000 ug/L): To a 100 ml volumetric flask add 50 ml DI water and 0.2 ml conc. HNO_3 and 0.2 mL HCl. Transfer 1.0mL of 1000 mg/L Hg stock standard. Dilute to 100 ml with DI water and mix. Prepare fresh daily.

8.4.2 Intermediate Stock #2 (100 ug/L): To a 100 ml volumetric flask add 50 ml DI water and 0.2 ml conc. HNO_3 and 0.2 mL HCl. Transfer 1.0mL of 10,000 ug/L intermediate stock #1. Dilute to 100 ml and mix. Prepare fresh daily.

8.4.3 Use 100mL volumetric flasks. To each, add 50 mL DI water and 0.2mL conc. HNO3 and 0.2 mL conc. HCl. Add the following volumes of 100ug/L intermediate, dilute to volume with DI water, and mix well.

Std Conc. ug/L	Vol. 100ug/L Intermediate #2 Std	Final Volume
0.5	0.5 mL	100 mL
1.0	1.0 mL	100 mL
2.0	2.0 mL	100 mL
4.0	4.0 mL	100 mL
5.0	5.0 mL	100 mL

Using a 25 mL volumetric pipette, transfer 25 mL of each to 50 mL centrifuge tubes. Add 25 mL reagent water to another centrifuge tube for the calibration blank.

8.5 ICV/LCS and CCV: (ICV/LCS from second source, CCV from same source as standards)

8.5.1 Intermediate Stock #1 (10,000 ug/L): To a 100 ml volumetric flask add 50 ml DI water and 0.2 ml conc. HNO_3 and 0.2 mL HCl. Transfer 1.0mL of 1000 mg/L Hg stock standard. Dilute to 100 ml and mix. Prepare fresh daily.

8.5.2 Intermediate Stock #2 (100 ug/L): To a 100 ml volumetric flask add 50 ml DI water and 0.2 ml conc. HNO_3 and 0.2 mL HCl. Transfer 1.0mL of 10,000 ug/L intermediate stock #1. Dilute to 100 ml and mix. Prepare fresh daily.

8.5.3 Check Standard/LCS: To a 100 mL volumetric flask add 50 mL DI and 0.2 ml conc. HNO_3 and 0.2 mL HCl . Add 3.0 mL of the 100 ug/L intermediate stock from the second source standard, dilute to the line and mix.

8.5.4 Using a 25 mL volumetric pipette, transfer 25 mL of each to 50 mL centrifuge tubes.

8.5.4.1 Note: Due to different digestion matrices for aqueous and solid samples, two sets of standards must be prepped to match the matrix for each digestion.

9.0 INSTRUMENT CALIBRATION

In the upper window menu bar select Instrument then calibrate. Enter the calibration information which consists of the standard number and standard concentration in ug/L and press continue. The calibration data will now be available for sample analysis. See section 11.0 for futher calibration instructions.

10.0 SAMPLE COLLECTION, HANDLING AND PRESERVATION

	Water	Soil
Preservative:	pH < 2 with HNO_3	4 °C
Hold Time:	28 days	28 days

11.0 SAMPLE PREPARATION AND ANALYSIS

11.1 Turn on the Hot Block and allow it to heat to 95^0 C while the samples are being prepared.

11.2 Sample Preparation-Aqueous:

11.2.1 Waters: Using a 25 mL graduated cylinder, transfer 25 mL of sample to a 50 mL polyethylene centrifuge tube. For drinking water analysis, a 25 mL Class A pipette must be used.

11.2.1.1 MS-MSD Prep: Add 0.50 mL of the 100 ug/L intermediate to a 25 mL final volume for a spike concentration of 2.0 ug/L.

11.2.1.2 To each of the samples, MS-MSD, LCS, standards, and blanks add the following (under a hood):1.25 mL conc. H_2SO_4. 0.625 mL conc. HNO_3

11.2.1.3 To all samples, standards, and blanks add 3.75 mL Potassium permanganate ($KMnO_4$) solution.

11.2.1.4 Tightly cap the samples and mix by inverting several times.

11.2.1.5 The purple permanganate color should remain for at least 15 minutes. If it does not, add additional permanganate in 1 mL aliquots until the purple color remains for at least 15 minutes. Record any extra permanganate added in the logbook. The same amount of extra permanganate will have to be added to all other samples and standards.

11.2.1.6 To all samples, standards, and blanks add 2.0 mL Potassium persulfate solution.

11.2.1.7 Place the samples and standards in the Hot Block. Heat at 90-95^{0}C for 2 hours. Record initial and final Hot Block temperatures in the logbook.

11.2.1.8 Following digestion, remove the samples and place under a hood to cool. Alternately, the racks may be placed in a sink of cold water to hasten the cooling.

11.2.1.9 When the samples are cool, add 1.5 mL Sodium chloride-hydroxylamine sulfate solution to all samples, standards, and blanks. Tightly cap and mix by inverting until samples are clear. Samples are now ready for analysis.

11.3 Sample Preparation-Solids

11.3.1 Weigh 0.50 g – 1.00 g of sample into a 50 mL polyethylene centrifuge tube with a plastic spatula. Do not use metal spatulas. Record the weight in the mercury prep book. See the subsampling SOP FO-10 for futher instructions on how to obtain a subsample for analysis.

11.3.2 Method Blank and LCS Prep: Weigh 0.50 g of sand blank into each of two 50 mL polyethylene centrifuge tubes. For the LCS, add 0.5 mL of the 100 ug/L second source intermediate stock solution #2.

11.3.3 MS-MSD Prep: Add 0.50 mL of the 100 ug/L intermediate to a 25 mL final volume for a spike concentration of 2.0 ug/L.

11.3.4 To all tubes, add 1.25 mL aqua regia reagent, and heat for 2 minutes in Hot Block at 95 ^{o}C.

11.3.5 Cool, and then add 25 mL of DI water and 3.75 mL of Potassium Permanganate solution to each vial.

11.3.6 Tightly cap all vials and mix by inverting several times.

11.3.7 The purple permanganate color should remain for at least 15 minutes. If it does not, add additional permanganate in 1 mL aliquots until the purple color remains for at least 15 minutes. Record any extra permanganate added in the logbook. The same amount of extra permanganate must be added to all other samples and standards.

11.3.8 Place the samples and standards in the Hot Block. Heat at 90-95 ^{0}C for 30 minutes. Record initial and final Hot Block temperatures in the logbook.

11.3.9 Cool, and then add 1.5 mL of Sodium Chloride-hydroxylamine sulfate to each sample and mix by inverting. The samples should turn clear.

11.4 Instrument Set-up

11.4.1 Power up the M-6000A and autosampler and allow to warm up for one hour.

11.4.2 Turn on lamp and gas supply and allow to warm up for 15 minutes.

11.4.3 Place autosampler tubing into rinse water (1%hydrochloric acid/1%nitric acid solution)

11.4.4 Verify that the sample capillary (inlet insert) is 0.5mm above the gas/liquid separator center post.

11.4.5 Open vents on waste container

11.4.6 Inspect peristaltic pump tubing for wear and flat spots and replace if necessary.

11.4.7 Place the peristaltic pump tubing in their appropriate holes and holder clips. Do not lock shoe clamps at this time.

11.4.8 Initiate M-6000A program by clicking on the M6000 icon, then controls then autosampler page.

11.4.9 Start the autosampler rinse pump by clicking the pump on and the probe down.

11.4.10 Place reagent capillary in a beaker of DI water and start the peristaltic pump in a clockwise rotation.

11.4.11 Lock down the peristaltic shoe clamps.

11.4.12 Inspect liquid flows. The GLS drain should be flowing smoothly with no build up or pulsing of liquid. The waste line from the peristaltic pump to the waste container should be liquid/gas with no vibration. If this is not the case upon inspection, stop

11.4.13 Immediately and change the GLS drain line and/or waste line.

11.4.14 Wet the GLS center post. Pinch the drain line prior to the tee of the peristaltic pump drain tubing. Let two or three liquid bubbles go to the top of the GLS center post and release the drain line. If the liquid does not bubble, then fill the GLS to the top of the center post and release the drain line.

11.4.15 Attach GLS exhaust tube to the GLS

11.4.16 Place reagent capillary in the reagent bottle

11.4.17 Open the appropriate worksheet and verify that the gas flow of the worksheet matches what is listed in the controls, if the flow is not the same make the necessary change and click set gas.

11.4.18 Zero the M-6000A using the autozero. This is under Instrument and then Zero Instrument.

11.4.19 Peak profile the high standard and verify baseline and sample integration times. Do this by clicking on Analysis and then read then standard and then choose the highest standard. If there are any adjustments needed to the peak, refer to the M6000A software manual 5.6.12.

11.5 Analysis

11.5.1 Insert sample labels by clicking on labels and then entering the sample ID numbers.

11.5.2 Right click to enter the QC standards after all the samples are entered. Choose "QC standard" for the CCV and "QC blank for the CCB.

11.5.3 Click on Analysis and then Click on start.

11.5.4 Choose the appropriate box and then click OK.

11.5.5 After analysis, click on file and choose return to main index.

11.5.6 Choose reports

11.5.7 Click on the data tab and choose the data that you want to report

11.5.8 Click on the Reports tab

11.5.9 Click on Write test to file and then enter the LIMS run number and make sure it is saved in the Cetac folder on the I drive.

11.6 Shutdown

11.6.1 Place the reagent capillary in a beaker of 10% nitric acid and cap the reagent bottle. Rinse the system for a minimum of ten minutes.

11.6.2 Place the reagent capillary in a beaker of DI water and rinse the system for one minute

11.6.3 Raise sample probe by clicking on controls then autosampler and click probe up and pump off.

11.6.4 Remove reagent capillary from DI water.

11.6.5 Allow the drain and waste lines to run completely dry

11.6.6 Turn off peristaltic pump

11.6.7 Release peristaltic shoe clamps and release the pump tubing from their holder clips.

11.6.8 Close vents on waste container.

11.6.9 Remove GLS exhaust line from GLS

11.6.10 Turn off gas and lamp

11.6.11 Exit software and run off the autosampler and instrument

12.0 TROUBLESHOOTING

12.1 See Cetac operator's manual for further troubleshooting instructions.

12.2 Preventative maintenance is recorded in the logbook located with the instrument. Follow the recommendations listed in the maintenance section of the Cetac M6000 Operators manual.

13.0 DATA ACQUISITION, CALCULATION AND DATA REDUCTION

Sample Calculations:

Liquid Concentration (ug/L) = A x C

Solid Concentrations (mg/kg) = $\frac{A \times B \times C}{D \times E}$

where A = instrument reading for sample (ug/L)
B = total volume of digestion (L)
C= analyst dilution factor, if necessary (ex. For a 1 to 10 dilution, C = 10)
D = amount of sample used in digestion (g)
E = percent solids/100, if necessary

Spike Recovery (%) = $\frac{\text{(Spiked sample concentration – Sample concentration)} \times 100}{\text{(Spike amount)}}$

%RSD = $\frac{(MS - MSD) \times 100}{(MS + MSD)/2}$,

where MS = Matrix spike concentration
MSD = Matrix spike duplicate concentration

14.0 COMPUTER HARDWARE AND SOFTWARE

14.1 Computer

14.2 LIMS software

14.3 M6000A software

15.0 DATA MANAGEMENT AND RECORD MANAGEMENT

15.1 After data has been captured by LIMS, it is reviewed by the analyst for accuracy and completeness. See checklist for data review guidance.

15.2 Once analyst has reviewed and approved the data, it is given to a peer or supervisor for review.

15.3 After the second reviewer approves the data, the reviewer sends the data to "validated" status in LIMS.

15.4 The original data is filed by test in the file cabinet and periodically the contents of the file cabinet are archived.

16.0 QUALITY CONTROL AND QUALITY ASSURANCE

16.1 Non-CLP (Solid Waste and Wastewater-7470A &7471A):

16.1.1 For every analytical run, calibrate with the blank and 0.50, 1.00, 2.00, 4.00, and 5.00 ug/L standards.

16.1.2 ICV (initial calibration verification): Following instrument calibration, analyze the 3.0 ug/L ICV/CCV standard. Control limits are +/-10%. If the recovery exceeds this, terminate the run and correct the problem before proceeding.

16.1.3 CCV (Continuing Calibration Verification): Anazlyzed after every 10 samples and at end of run. A 3.0 ug/L standard. Control limits are +/-20%.

16.1.4 ICB/CCB (initial and continuing calibration blank): After the ICV and any CCV, analyze a blank. The absolute value of the result for the blank must be below the highest of the following: the absolute value being less than or equal to the MDL for a given analyte, five percent of the regulatory limit or five percent of the measure concentration in the sample. If the result exceeds this, terminate the analysis and correct the problem before proceeding or appropriately qualify the data.

16.1.5 LCS (laboratory control sample): An alternate source standard from the same digestion set as the samples. It is prepared for every 20 samples per medium. Control limits are generated in-house control limits or as specified by client QAPP. If the recovery exceeds this, terminate the run, reprep, and reanalyze all samples.

16.1.6 MB (method blank): From the same digestion set as the samples. Blank recovery should be less than the highest of the following: the absolute value being less than or equal to the MDL for a given analyte, five percent of the regulatory limit or five percent of the measure concentration in the sample. If the result is exceeded, reanalyze. If still exceeded, reprep samples associated with this blank or appropriately qualify results.

16.1.7 MS/MSD (matrix spike/matrix spike duplicate): A MS/MSD is required every analytical run at a frequency of 5% per digestion batch for 7000 series or at a frequency of 10% per digestion batch for 200 series To be considered acceptable, MSD must meet both the same % recovery criteria as an MS, and the same % RPD as a duplicate sample. For routine work, use in-house generated limits for the recovery and RPD limits

16.2 CLP-Like Protocol (ACOE work):

16.2.1 For every analytical run, calibrate with the blank and 0.50, 1.00, 2.00, 4.00, and 5.00 ug/L standards..

16.2.2 ICV (initial calibration verification): Following instrument calibration, analyze the 3.0 ug/L ICV/CCV standard. Control limits are +/-10%. If the recovery exceeds this, terminate the run and correct the problem before proceeding.

16.2.3 ICB (initial calibration blank): Following the ICV, analyze a blank. The absolute value of the result for the ICB must be below ½ the MRL. If the result exceeds this, terminate the analysis and correct the problem before proceeding or appropriately qualify the results.

16.2.4 LCS (laboratory control sample): Following the calibration verification standard and the calibration verification blank, and every 20 samples thereafter, analyze the 3.0 ug/L alternate source standard. Control limits are specified within the client QAPP or use default limits of 80-120%. If the recovery exceeds this, terminate the run, reprep, and reanalyze all samples.

16.2.5 MRL/CRDL standard (Method Reporting limit/contract required detection limit standard): Analyze a standard at the MRL or the CRDLas specified by the client QAPP. Limits are listed within the client QAPP or use a default of 70-130%.

16.2.6 MB (method blank): From the digestion set. If the result exceeds the ½ the MRL, re-digest all samples associated with the MB or appropriately qualify associated results.

16.2.7 CCV (continuing calibration verification): Analyze the 3.0 ug/L calibration standard following every ten samples, and at the end of the analysis. Control limits are +/-20% true value. If the recovery exceeds this, recalibrate and reanalyze all samples back to the last acceptable CCV.

16.2.8 CCB (continuing calibration blank): Analyze a blank following every CCV. The absolute value of the result for the CCB must be below the ½ the MRL. If the result exceeds this, reanalyze all samples back to the last acceptable CCB or appropriately qualify results.

16.2.9 Matrix Spike: A matrix spike is required every for every sample delivery group of 20 samples or less. The matrix spike shall be prepared at the time of digestion. Default control limits are +/- 25% true value or as specified in client QAPP. If recovery is outside of limits, refer to client QAPP for further instruction.

16.2.10 Duplicate: A duplicate is required for every sample delivery group of 20 samples or less and is prepared at the time of digestion. For results exceeding five times the MRL, the default control limit is 20% RPD or as specified in the client QAPP. For results that are less than five times the MRL, the default control limit is +/- MRL. If the recovery is outside this, see client QAPP for further instruction.

16.3 SDWA Protocol (245.1)

16.3.1 For every analytical run, calibrate with the blank and 0.50, 1.00, 2.00, 4.00, and 5.00 ug/L standards

16.3.2 ICV (initial calibration verification): Following instrument calibration, analyze the 3.0ug/L ICV/CCV standard. Control limits are +/-5%. If the recovery exceeds this, terminate the run and correct the problem before proceeding.

16.3.3 ICB (initial calibration blank): Following the ICV, analyze a blank. The absolute value of the result for the ICB must be below the MDL for the method. If the result exceeds this, terminate the analysis and correct the problem before proceeding or appropriately qualify the data.

16.3.4 LCS (laboratory control sample): Following the calibration verification standards, and every 20 samples thereafter, analyze the 3.0 ug/L alternate source standard. Control limits are generated control limits. If the recovery exceeds this, terminate the run, reprep, and reanalyze all samples associated with the LCS.

16.3.5 MB (method blank): From the same digestion set as the samples. Limits: the highest of the MDL, 5% of the measured concentration in the sample, or 5% of the regulatory limit for that analyte. If the results exceed this, terminate the run, reprep and reanalyze all samples associated with MB or appropriately qualify the data.

16.3.6 CCV (continuing calibration verification): Analyze the 3.0ug/L calibration standard following every ten samples, and at the end of the analysis. Control limits are +/-10% true value. If the recovery exceeds this, recalibrate and reanalyze all samples back to the last acceptable CCV.

16.3.7 CCB (continuing calibration blank): Analyze a blank following every CCV. The absolute value of the result for the CCB must be below the highest of the MDL, 5% of the measured concentration in the sample, or 5% of the regulatory limit for that analyte. If the result exceeds this, reanalyze all samples back to the last acceptable CCB or appropriately qualify results.

16.3.8 MS/MSD (matrix spike/matrix spike-duplicate): A MS/MSD is required every analytical run at a frequency of 10% per matrix type. For digested samples, appropriate samples are designated and spiked at the time of the digestion. Control limits are in-house limits.

16.4 Data Review Prior to Shutdown: Check results for the following criteria. It may be possible to correct some problems within the same analytical run.

16.4.1 ICV/CCV, LCS, MB, MRL acceptance. See above for corrective action.

16.4.2 Results over the calibration range of 5 ug/L. Dilute affected samples within calibration range with dilution blank.

16.4.3 MS-MSD recovery outside of acceptance range. If both are out of range, but all other CCV, CCB, and LCS associated with the MS/MSD are within specs, then the problem is matrix related-not instrument related. Sample data may be reported but flagged with the appropriate comment.

16.5 Analysis data review checklist- the checklist will be completed by the analyst and the data reviewer and attached to the analytical data package.

17.0 REFERENCES

17.1 *Test Methods for Evaluating Solid Waste*, EPA, SW-846, Methods 7470A, 7471A.

17.2 Statement of Work for Inorganic Analysis, USEPA Contract Laboratory Program,. ILM04.0.

17.3 *Methods for the Determination of Metals in Environmental Samples.* EPA/600/R94/111, Method 245.1

17.4 Cetac M6000A operations manual and software manual.

18.0 TABLES

18.1.1 Mercury Spike Prep

COLD VAPOR Element	Spike Amt. mL	Spike Solution Supplier	Stock Conc. ug/L	Final Vol. mL	Expected Conc. ug/L
Hg	0.50	Ultra 1000 mg/L	100.0	25.0	2.0

Standard Quality Control Requirements and Corrective Action

QC Type	Frequency	Conc. Level	*Acceptance Criteria*	*Corrective Action*
ICal	Each time the instrument is set up. The ICal consists of five standards and a blank.	0 + 0.5 – 5.0 ug/L	Correlation coefficient of .995 or greater	Terminate analysis, correct problem and recalibrate.
ICV	Immediately after the ICal	3 ug/L	Second source standard, SDWA: 95-105% SW846:90-110% ACOE- see client QAPP	Reanalyze once, if still unacceptable terminate analysis, correct problem and recalibrate
ICB	Immediately after the ICV	0	The highest of : The MDL, 5% of the Reg. Limit or 5% of the sample concentration for routine sample and ½ the MRL for ACOE work	Reanalyze once, if still unacceptable terminate analysis, correct problem and recalibrate or appropriately qualify data
LCS	1 per batch of ≤ 20 samples per matrix per day	mid cal. Range	SDWA; 90-110% SW846; 80-120% ACOE- see client QAPP	Reanalyze once, if still unacceptable terminate analysis, correct problem reanalyze all associated samples. High bias is acceptable for associated samples that have results less than the MDL for routine work or the MRL for ACOE work.
CCV	After every 10th sample and at the end of the analytical sequence	mid cal range	SDWA; 90-110% SW846; 80-120% ACOE- see client QAPP	Reanalyze once, if still unacceptable recalibrate and reanalyze all samples back to the last acceptable CCV or ICV. High bias is acceptable for associated samples that have results less than the MDL for routine work or the MRL for ACOE work.
CCB	Immediately following each CCV	0	The highest of : The MDL, 5% of the Reg. Limit or 5% of the sample concentration for routine work. ACOE- ½ the MRL	Reanalyze once, if still unacceptable reanalyze all samples back to the last acceptable CCB or ICB or appropriately qualify results.
MS-MSD (routine work) or MS-DUP (ACOE)	5% of samples per matrix per day	See attached spike chart	≤ ± 20%, Applicable when spike level is >25% of original analyte level in the sample and RPD ≤ ± 20% or as specified in client QAPP	Perform PDS
Post Digestion Spike (PDS)	Upon failure of MS or per batch for ACOE work	Same level as MS	85-115%	Qualify data as matrix interference or perform MSA

Method Blank	1 per batch of 20 samples	0	The highest of : The MDL, 5% of the Reg. Limit or 5% of the sample concentration for routine sample and ½ the MRL for ACOE work	Reanalyze all associated samples, if possible, or qualify data

CT Laboratories
Baraboo Laboratory Divison

Title: **Graphite Furnace Atomic Absorption**

SOP Number: **6110B**

Prepared by: _____
Date

Technical Review by: _____
Date

Reviewed by: _____
Quality Assurance ***Date***

_____
Laboratory Director ***Date***

SOP Manual Control Number:_____

1.0 SCOPE AND APPLICATION

A large number of metals in solution may be determined by graphite furnace atomic absorption spectroscopy. This procedure is used for low-level metals analysis of drinking water, groundwater, wastewater, soil, and sludge. SDWA samples and clean groundwater samples, properly preserved, with <1 NTU of turbidity may be analyzed directly; otherwise, sample digestion is required. All other sample matrices require digestion prior to analysis.

2.0 METHOD SUMMARY

A representative aliquot of a sample is placed in the graphite tube in the furnace, evaporated to dryness, charred, and atomized. Radiation from a hollow cathode lamp specific to the analyte of interest is passed through the center of the graphite tube. The intensity of the transmitted radiation decreases in proportion to the amount of the analyte specific ground-state atoms present in the graphite tube upon atomization. A monochromator isolates the characteristic radiation from the hollow cathode lamp, and a photosensitive device measures the transmitted radiation. The SIMAA can measure up to 4 elements simultaneously. The SIMAA employs the Zeeman background correction technique. Matrix interferences from organic and inorganic constituents are minimized when the appropriate background correction technique is used in conjunction with the appropriate matrix modifiers.

3.0 DEFINITIONS

3.1 Reagent Blank - A solution of de-ionized water, (containing in correct proportion, all reagents required by the method), used with the calibration standards to standardize the instrument, as a calibration blank, and for sample dilution.

3.2 Calibration Standards - A series of known standard solutions, which may include the reagent blank, used for calibration of the instrument within the measurable linear range. Calibration standards should contain, in correct proportion, all reagents required by the method. A minimum of 4 calibration points plus a reagent blank are used for calibration. Acceptance of the calibration requires a correlation coefficient of 0.995 or better. No samples will be analyzed without acceptable calibration. AA calibrations are performed daily.

3.3 Calibration Verification Standards-Initial (ICV) & Continuing (CCV) - A midpoint calibration standard which is analyzed at the beginning of the run (ICV), at a frequency of 1 per 10 samples during a run (CCV), and at the end of a run to verify calibration throughout the run. Note that the ICV must be from a different source than that of the calibration standards and the CCV, and that limits for ICV are tighter than those for CCV.

3.4 (ICB/CCB (Calibration Blanks- Initial and Continuing) - A reagent blank solution, which is analyzed immediately following the calibration standards (Initial Calibration Blank-ICB), at a frequency of 1 per 10 samples during a run (Continuing Calibration Blank-CCB), and at the end

of a run to check for drifts in calibration, or possible analyte carry-over.. Warning criteria include that the absolute value be less than or equal to the MDL for a given analyte. Control criteria consist of the absolute value being less than or equal to 2 times the MDL for a given analyte. If this range is exceeded, a new calibration will be necessary.

3.5 LCS (Laboratory Control Sample)- A mid-range standard prepared from a source different from that used for calibration standards. The LCS is used to verify the accuracy of the calibration at the start of an analytical run, and is analyzed immediately after the initial CB (ICB).

3.6 PB or MB (Prep Blank/ Method Blank) - A Reagent Blank which is carried through the entire preparation and analytical method. The method blank is used to detect possible contamination that may occur prior to or during the sample preparation. A minimum of one MB is prepared per batch, and is analyzed at the beginning of an analytical batch.

3.7 MS-MSD (Matrix Spike-Matrix Spike Duplicate): - Two separate sample aliquots to which a known concentration of analyte has been added which is carried through the entire preparation and analytical procedure. The purpose of a matrix spike is to reveal any matrix effect from the sample on the recovery of the analyte by the method being used. An MS-MSD pair is prepared for every 20 samples of a given matrix per day for 7000 series and CLP and every 10 samples of a given matrix per day for 200 series. Failure to meet criteria may be due to poor recovery during the preparation method or due to matrix interference within the digestate. To be considered acceptable, MSD's must meet both the same % recovery criteria as an MS, and the same % RPD as a duplicate sample. MS/MSD %RPD and may be used as acceptance criteria for duplicate analysis.

3.8 Detection Limit (DL) or Contract Required Detection Limit (CRDL) Standard: Detection level standard at a level near the reporting limit, or at a level specified by client contract. When required, it is to be analyzed following the ICB, and prior to the last CCV standard in the run.

4.0 HEALTH AND SAFETY

4.1 Gloves and protective clothing should be worn to protect against unnecessary exposure to hazardous chemicals and contaminants in samples. All activities performed while following this procedure should utilize appropriate laboratory safety systems.

5.0 CAUTIONS

The SIMAA employs high magnetic fields during operation. People with pacemakers should be kept away from the instrument area.

6.0 INTERFERENCES

6.1 Direct aspiration

6.1.1 The most troublesome type of interference in atomic absorption spectrophotometry is usually termed "chemical" and is caused by lack of absorption of atoms bound in molecular

combination in the flame.This phenomenon can occur when the flame is not sufficiently hot to dissociate the molecule, as in the case of phosphate interference with magnesium, or when the dissociated atom is immediately oxidized to a compound that will not dissociate further at the temperature of the flame.

6.1.2 Chemical interferences may also be eliminated by separating the metal from the interfering material. Although complexing agents are employed primarily to increase the sensitivity of the analysis, they may also be used to eliminate or reduce interferences.

6.1.3 The presence of high dissolved solids in the sample may result in an interference from nonatomic absorbance such as light scattering.

6.1.4 Spectral interference can occur when an absorbing wavelength of an element present in the sample but not being determined falls within the width of the absorption line of the element of interest. The results of the determination will then be erroneously high, due to the contribution of the interfering element to the atomic absorption signal. Interference can also occur when resonant energy from another element in a multielement lamp, or from a metal impurity in the lamp cathode, falls within the bandpass of the slit setting when that other metal is present in the sample. This type of interference may sometimes be reduced by narrowing the slit width.

6.1.5 Samples and standards should be monitored for viscosity differences that may alter the aspiration rate All metals are not equally stable in the digestate, especially if it contains only nitric acid, not nitric acid and hydrochloric acid. The digestate should be analyzed as soon as possible, with preference given to Sn, Sb, Mo, Ba, and Ag.

6.2 Furnace procedure

6.2.1 Although the problem of oxide formation is greatly reduced with furnace procedures because atomization occurs in an inert atmosphere, the technique is still subject to chemical interferences. The composition
of the sample matrix can have a major effect on the analysis. It is those effects which must be determined and taken into consideration in the analysis of each different matrix encountered. To help verify the absence of matrix or chemical interference, the serial dilution technique may be used. Those samples which indicate the presence of interference should be treated in one or more of the following ways:
1) Successively dilute and reanalyze the samples to eliminate interferences.
2) Modify the sample matrix either to remove interferences or to stabilize the analyte. Examples are the addition of ammonium nitrate to remove alkali chlorides and the addition of ammonium

phosphate to retain cadmium. The mixing of hydrogen with the inert purge gas has also been used to suppress chemical interference. The hydrogen acts as a reducing agent and aids in molecular dissociation.
3) Analyze the sample by method of standard additions while noticing the precautions and limitations of its use.

6.2.2 Gases generated in the furnace during atomization may have molecular absorption bands encompassing the analytical wavelength. When this occurs, use either background correction or choose an alternate wavelength. Background correction may also compensate for nonspecific broad-band absorption interference.

6.2.3 Interference from a smoke-producing sample matrix can sometimes be reduced by extending the charring time at a higher temperature or utilizing an ashing cycle in the presence of air. Care must be taken, however, to prevent loss of the analyte.

6.2.4 Samples containing large amounts of organic materials should be oxidized by conventional acid digestion before being placed in the furnace. In this way, broad-band absorption will be minimized.

6.2.5 Cross-contamination and contamination of the sample can be major sources of error because of the extreme sensitivities achieved with the furnace. The sample preparation work area should be kept scrupulously clean. Pipet tips are a frequent source of contamination. If suspected, they should be acid soaked with 1:5 nitric acid and rinsed thoroughly with tap and reagent water. Special attention should be given to reagent blanks in both analysis and in the correction of analytical results. Lastly, pyrolytic graphite, because of the production process and handling, can become contaminated. As many as five to ten high-temperature burns may be required to clean the tube before use.

7.0 PERSONNEL QUALIFICATIONS

Personnel operating the graphite furnace should have background knowledge of the scientific principles used during this application. All operators should perform an initial demonstration of capability (IDC) prior to analyzing any samples. It is preferable for the operator to have at least two semesters of college chemistry.

8.0 APPARATUS AND MATERIALS

8.1 Apparatus and Materials

8.1.1 Perkin-Elmer SIMAA simultaneous spectrophotometer with autosampler.

8.1.2 Graphite furnace tubes: THGA platform tubes.

8.1.3 Sample carousel standard cups.

8.1.4 Plastic autosampler vials.

8.1.5 Electrodeless Discharge Lamps (EDL).

8.1.6 Argon: high purity.

8.1.7 Class 'A' volumetric flasks and pipettes.
8.1.8 Eppendorf pipettes.

8.2 REAGENTS

8.2.1 Alternate source multi-element stock standard, purchased Inorganic Ventures, # CTI-GFCAL-1 or equivalent.
10 ug/mL Sb, As, Cr, Pb, Se, Tl
1 ug/mL Cd, Ag.

8.2.2 Multi-element stock standard, purchased Inorganic Ventures, #CTI-SPK-1 or equivalent
100 ug/mL Sb, As, Cr, Pb, Se Tl
15 ug/mL Ag
5 ug/mL Cd

8.2.3 Single-element standard-1000 ug/mL Sn

8.2.4 Single-element standard- purchased 1000 ug/mL Sn- source alternate to 8.2.3

8.2.5 Concentrated nitric acid (HNO_3): Trace metals grade.

8.2.6 Type II water: 18-megohm Deionized water.

8.2.7 1% Palladium solution, purchased

8.2.8 1% Magnesium Nitrate solution, purchased

8.2.9 Citric Acid (powdered).

8.2.10 Ammonium Dihydrogen Phosphate (powdered).

8.2.11 Standard preparation:

8.2.11.1 Base Standard: To a 200-mL volumetric flask, add 0.5 mL conc. HNO3 and 0.1mL Inorganic Ventures CTI-SPK-1 or equivalent (8.2.2). Bring to volume with Milli-Q water and invert several times to mix. Prepare annually or as needed. Concentration: 50 ug/L Sb, As, Pb, Se, Tl and 7.5 ug/L Ag

8.2.11.2 Base Standard: To a 200-mL volumetric flask, add 0.5 mL conc. HNO3 and 0.02mL 1000mg/L Sn (8.2.3). Dilute to volume with Milli-Q water and invert several times to mix. Prepare annually or as needed. Concentration: 100 ug/L Sn

8.2.11.3 ICV/CCV-Check Standard: To a 200-mL volumetric flask, add 0.5 mL conc. HNO3 and 0.5 mL of Inorganic Ventures CTI-GFCAL-1 (8.2.1) or equivalent. Dilute to volume with Milli-Q water. Prepare annually or as needed. Concentrations: 25 ug/L Sb, As, Pb, Se, Tl and 2.5 ug/L Ag

8.2.11.4 ICV/CCV-Check Standard: To a 200-mL volumetric flask, add 0.5 mL conc. HNO3 and 0.01 mL of 1000 mg/L Sn (8.2.4). Dilute to volume with Milli-Q water and invert several times to mix . Prepare fresh annually or as needed. Concentrations: 50 ug/L Sn

8.2.12 Matrix modifier preparation:

8.2.12.1 Palladium Nitrate 0.05%: To a 200-mL volumetric flask, add 100 ml DI H2O. Add 4 g. citric acid, 10 ml 1% Palladium Nitrate solution, and 1 mL 1% Magnesium Nitrate solution. Dilute to volume with DI H2O. Prepare fresh every 6 months. To be used for the analysis of Sb, Tl, As, Se, Sn.

8.2.12.2 Ammonium Phosphate 0.5%: To a 200-mL volumetric flask, add 1.0 g. Ammonium Dihydrogen Phosphate. Dilute to volume with DI H2O. Prepare fresh every month. To be used for the analysis of Cd and Pb.

9.0 INSTRUMENT CALIBRATION

See section 11.0 for calibration details.

10.0 SAMPLE COLLECTION, HANDLING AND PRESERVATION

	Aqueous	Solids
Preservative:	pH <2 with HNO_3	cool 4 °C
Hold Time:	180 days	180 days

11.0 SAMPLE PREPARATION AND ANALYSIS

11.1 SIMAA

11.1.1 Turn spectrophotometer on. All necessary power up functions is carried out automatically by the instrument. On the computer screen double click on the SIMAA icon. A sequence of windows will open up. Call up the correct method from the method library. See Appendix A for recommended calibration concentrations.Note: All methods are stored in the method library section of the software. For individual furnace temperature profiles consult the stored program.

11.1.2 Now that the method is loaded, you will install all the EDL or hollow cathode lamps needed to carry out the analysis. Allow a full hour warm-up for EDL and 30 minutes for HCL. After warm-up, align and optimize each lamp with the adjustment wheels on the lamp cassette. Record the lamp reading in the lamp logbook.

11.1.3 Alignment of the furnace head is not necessary unless the contacts have been replaced since the last time the instrument was operated. If it does need alignment consult the operations manual.

11.1.4 Check alignment of the autosampler tip with respect to the graphite tube and the sample cups. See operations manual.

11.1.5 Inspect graphite tube. If worn replace before analysis. If tube is replaced, press "condition tube" on furnace control page.

11.1.6 Place modifier or modifiers, base std, blank, and rinse blank into the positions on the autosampler designated in the program.

11.1.7 Create a new sample info file. Input all sample ID's including LCS duplicates, etc. Designate which samples to auto-spike if there are

any. Save file with element symbol and today's date Ex) Pb030999. Print Autosampler loading list or sample info file.

11.1.8 Load autosampler, and on analysis page click on ANALYZE ALL-CALIBRATION and SAMPLES. Record the samples and sample info file in the SIMAA sample logbook.

11.1.9 After instrument has calibrated, record the characteristic mass of the element in the SIMAA run logbook. If chacteristic mass is not within 50-200% of the characteristic mass obtained during the MDL study, stop analysis and correct problem.

11.1.10 For Data Capture

11.1.10.1 When instrument is "idle" after running samples, open reformat data in AAWinLab by clicking on file and then reformat data

11.1.10.2 Click on open design and choose data capture

11.1.10.3 Choose the result data set by clicking on browse and choose the appropriate data set.

11.1.10.4 Name the file to be reformatted as the LIMS analytical run number

11.1.10.5 Click on save results.

11.1.10.6 Close reformat data section

12.0 INSTRUMENT MAINTENANCE AND TROUBLESHOOTING

12.1 Refer to Perkin Elmer operator manual for further troubleshooting information.

12.2 Daily Maintenance

12.2.1 Check and, if need be, replace the graphite tube.

12.2.2 Check and, if need be, clean or replace contact cylinders

12.2.3 Check sampler tip in tube. Check sampler tip alignment

12.2.4 Flush sampler

12.2.5 Change fume extractor water

12.2.6 Inspect fume extractor filter and replace if dirty

12.2.7 Check rinse reservoir and fill if needed

12.2.8 Empty waste reservoir if needed

12.2.9 Check argon gas tank to ensure there is suffient gas and that it is at the appropriate pressure.

13.0 DATA ACQUISITION, CALCULATIONS AND DATA REDUCTION

Sample Calculations:

Liquid Concentration (ug/L) = A x C

Solid Concentrations (mg/kg) = $\frac{A \times B \times C}{D \times E}$,

where A = instrument reading for sample (ug/L)

B = total volume of digestion (L)
C= analyst dilution factor, if necessary (ex. For a 1 to 10 dilution, C = 10)
D = amount of sample used in digestion (g)
E = percent solids/100, if necessary

$$\textit{Spike Recovery (\%)} = \frac{\text{(Spiked sample concentration – Sample concentration) x 100}}{\text{(Spike amount)}}$$

$$\%RSD = \frac{(MS - MSD) \times 100}{(MS + MSD)/2},$$

where MS = Matrix spike concentration
MSD = Matrix spike duplicate concentration

14.0 COMPUTER HARDWARE AND SOFTWARE

14.1 Computer with StarLIMS
14.2 Computer with Perkin Elmer AAWinLab

15.0 DATA MANAGEMENT AND RECORD MANAGEMENT

15.1 After data has been captured by LIMS, it is reviewed by the analyst for accuracy and completeness. See checklist for data review guidance.
15.2 Once analyst has reviewed and approved the data, it is given to a peer or supervisor for review.
15.3 After the second reviewer approves the data, the reviewer sends the data to "validated" status in LIMS.
15.4 The original data is filed by test in the file cabinet and periodically the contents of the file cabinet are archived.

16.0 QUALITY CONTROL AND QUALITY ASSURANCE

16.1 All calibrations are done within the linear range of the instrument. The acceptance criteria for linearity is a correlation coefficient of 0.995 or better. To ensure linearity all calibrations are made up of a blank and 5 standards. The highest standard used for each calibration is within the linear range for that element or combination of elements in the case of the SIMAA. Any sample measuring above the concentration of the highest standard is diluted until it is within range then reanalyzed.
16.2 Non-CLP (7000A, 200.9Modified):
16.2.1 ICV (initial calibration verification): Following instrument calibration, begin the analysis with the 'QC Standard'. ICV should be from a different source than the calibration standards. If recovery exceeds the following limits, terminate the run and correct the problem before proceeding.

SW846-method 7000A	SDWA- method 200.9Mod
90-100%	95-105%

ICB (initial calibration blank): Following the ICV, analyze a blank. The absolute value of the ICB must be below the MDL or reporting limit for the method or sample results must be less than MDL or greater than 20 times the blank for SDWA and below two times the MDL or reporting limit for the method or sample results must be less than MDL or greater than 20 times the blank for SW846.. If the result exceeds this, terminate the analysis and correct the problem before proceeding or qualify data.

16.2.2 LCS (laboratory control sample): Analyze an alternate source standard that has gone through the same preparation process as the samples. Use in-house control limits if available or use the default limits of 80-120% recovery for SW-846 and 90-110% for SDWA. If the recovery exceeds the limits, terminate the analysis and correct the problem before proceeding.

16.2.3 CCV (continuing calibration verification): Same standard used for the calibration standanrds but analyzed after every ten samples followed by a CCB. Must be also be run at the end of the analytical run. If the recovery exceeds the following limits, you must recalibrate and reanalyze all samples back to the last acceptable CCV or ICV.

SW846-method 7000A	SDWA-method 200.9Mod
80-120%	90-110%

16.2.4 CCB (continuing calibration blank): Analyze a blank following every CCV. The absolute value of the CCB must be below the MDL or reporting limit for the method or sample results must be less than MDL or greater than 20 times the blank for SDWA and below two times the MDL or reporting limit for the method or greater than 20 times the blank for SW846. If the result exceeds this, reanalyze all samples back to the last acceptable CCB or qualify data.

16.2.5 MS/MSD (Matrix spike/Matrix spike Duplicate): A MS/MSD is required every analytical run at a frequency of 5% per digestion batch for 7000 series or at a frequency of 10% per digestion batch for 200 series. For digested samples, appropriate samples are designated and spiked at the time of the digestion. For non-digested samples, a bench spike can be prepared with the Varian. The SIMAA will automatically dispense a predetermined amount into the designated samples. See operations manual.

16.2.5.1 The results from the MS-MSD are reviewed for both accuracy limits and precision limits. Acceptance criteria categorized by matrix found in the lab Quality Control Limits Sheet issued quarterly by Quality Assurance. These limits are applicable when the spike level is > 25% of the original analyte level in the sample (EPA 200.9Modified

and SW7000A). Failure to meet this criteria may be due to poor recovery during the preparation method or due to matrix interference within the digestate. To help determine the reason for the failure, a post-digestion spike is performed on failed samples to ascertain the role of the digestate matrix on the spike failure.

16.2.6 PDS (Post Digestion Spike) - When a matrix spike falls outside of the 25% acceptance range, a post digestion spike is used to determine if the sample digestate matrix is interfering with the analysis of the analyte. The sample is spiked at a level consistent with the matrix spike. Acceptable recovery is within 15% of the spike true value, indicating that the sample digestate matrix is not interfering with analysis. If the recovery is outside of that range, than the digestate matrix is causing interference with analysis and the PDS may be used as the single addition method of standard additions (MSA) to correct the sample result and to recalculate the MDL, as appropriate. **Note: For ACOE samples, a PDS will be performed at a rate of one per batch per matrix.**

16.2.7 Dilution Analysis – An SW846 sample digestate is diluted 1:5 with method blank solution and analyzed. The diluted digestate result and the undiluted digestate result should agree with less than 10% RPD, or a matrix effect is suspected. This is performed on one the MS/MSD sample for each batch of solid samples. **Note: For ACOE samples, a SD will be performed at a rate of one per batch per matrix.**

16.2.8 PB (preparation blank): From the digestion batch. If the result exceeds the CRDL and sample results are greater than the CRDL and less than 20 times the PB, re-digest all samples associated with the PB.

16.3 CLP-like Protocol

16.3.1 ICV (initial calibration verification): Following instrument calibration, begin the analysis with the 'QC Standard'. If the recovery exceeds the following limits, terminate the run and correct the problem before proceeding. ICV limit: 90-110%

16.3.2 ICB (initial calibration blank): Following the ICV, analyze a blank. The absolute value of the result for the ICB must be below the LOD for the method or below the level set by the client QAPP (1/2 the MRL for ACOE work). If the result exceeds this, terminate the analysis and correct the problem before proceeding.

16.3.3 CRDL/MRL standard: Analyze a standard at the CRDL or at a level set by the client. Limits are established by the client (70-130% for ACOE work)

16.3.4 PB (preparation blank): From the digestion batch. If the result exceeds the CRDL (1/2 the CRDL for ACOE work) and sample results are less than 20 times the PB and greater than the CRDL, re-digest all samples associated with the PB.

16.3.5 LCS (laboratory control sample): From the digestion batch. Analyze an alternate source reference sample. Use in-house control limits or client limits from QAPP if available or use the default limits of 80-120% recovery. If the recovery exceeds the limits, terminate the analysis and correct the problem before proceeding.

16.3.6 CCV (continuing calibration verification): Analyze the CCV following every ten samples, and at the end of the analysis. If the recovery exceeds the following limit, recalibrate and reanalyze all samples back to the last acceptable CCV. CCV Limit: 80-120% or as set by client QAPP.

16.3.7 CCB (continuing calibration blank): Analyze a blank following every CCV. The absolute value of the result for the CCB must be below the LOD for the method (less than ½ the MRL for ACOE work) or sample results bracketed by the CCB must be greater than 20 times the CCB or less than the LOD (or less than MRL for ACOE work). If the CCB result exceeds this, reanalyze all samples back to the last acceptable CCB.

16.3.8 Matrix Spike (MS): A matrix spike is required every for every sample delivery group of 20 samples or less or as required by the client QAPP. The matrix spike shall be prepared at the time of digestion. Use in-house conrol limits or client limits from QAPP if available or use the default limits of 75-125% recovery.

16.3.9 Duplicate: A duplicate is required for every sample delivery group of 20 samples or less or as required by client QAPP and is prepared at the time of digestion . For results exceeding five times the CRDL, use in-house control limits or client limits from QAPP if available or use the default limit of 20% RPD. For results that are less than five times the CRDL, the default control limit is +/- CRDL. If the recovery is outside this, see appropriate QAPP or ACOE "shell" document for corrective action.

16.3.10 Replicate injections: Replication injections for ACOE "Shell" work must have an RSD less than 10% for all standards except the blanks.

16.4 Any results that fall outside the limits established are flagged and noted in the Metals Data Review form attached to the data package.

16.5 For each run a "QC Bench Sheet" is completed, summarizing accuracy, precision, spike preparation, and calibration standard references. Data from these sheets are used to create quarterly control limits.

16.6 Data review is documented on the analysis data review checklist.

17.0 REFERENCES

17.1 *Test Methods for Evaluating Solid Waste*, EPA, 1986, SW-846, 3rd Edition, Rev 1 July 1992 Method 7000

17.2 *Methods for the Determination of Metals in Environmental Samples*, EPA/600/4-91/010. Rev 2.2 May 1994. Method 200.9.

17.3 USEPA Contract Laboratory Program. Statement of Work for Inorganic Analysis. ILM03.0.

17.4 Perkin Elmer Simultaneous Multielement AA Spectrophotometer Techniques- Operation and methods manuals

18.0 Tables

Pre-Digestion Matrix Spike Prep for (GFAA)

Element	Spike Amt. mL	Spike Soln.	Stock Conc. ug/L	Final Vol. mL	Expected Conc. ug/L
Antimony-GFAA	1.0	A	1000.0	50.0	20.0
Arsenic-GFAA	1.0	A	1000.0	50.0	20.0
Chromium-GFAA	1.0	A	1000.0	50.0	20.0
Lead-GFAA	1.0	A	1000.0	50.0	20.0
Selenium-GFAA	1.0	A	1000.0	50.0	20.0
Thallium-GFAA	1.0	A	1000.0	50.0	20.0
Silver-GFAA	1.0	A	150.0	50.0	3.00
Cadmium-GFAA	1.0	A	50.0	50.0	1.00
Tin-GFAA	0.1	B	10,000	50.0	20.0

Standard Source		
Supplier	Dilution	Solution
Inorg Ventures.-SPK1	1/100	A
VWR Sn std.	1/100	B

Analytical (non-digested) Spike Analysis (GFAA)

Element	Spike Vol. uL	Spike Solution	Stock Conc. ug/L	Final Volume uL	Expected Conc. ug/L
Antimony-GFAA	10.0	**GF-CAL**	50.0	25.0	20.0
Arsenic-GFAA	10.0	**GF-CAL**	50.0	25.0	20.0
Chromium-GFAA	10.0	**GF-CAL**	50.0	25.0	20.0
Lead-GFAA	10.0	**GF-CAL**	50.0	25.0	20.0
Selenium-GFAA	10.0	**GF-CAL**	50.0	25.0	20.0
Thallium-GFAA	10.0	**GF-CAL**	50.0	25.0	20.0
Silver-GFAA	10.0	**GF-CAL**	5.00	25.0	2.00
Cadmium-GFAA	10.0	**GF-CAL**	5.00	25.0	2.00
Tin-GFAA	10.0	**JT Baker Sn**	50.0	25.0	20.0

Supplier	Lot #	Prep Info
Inorg Vent.-GFCAL	11/1/2000	1/200 dil. of concentrate
JT Baker Sn Std.	4/2000	1/20000 of concentrate

Standard Quality Control Requirements and Corrective Action Guidelines

QC Type	Frequency	Conc. Level	*Acceptance Criteria*	*Corrective Action*
ICV	1 per calibration	20 ug/L	90-110%	Terminate run. Correct the problem before proceeding
ICB	Immediately after ICV	<MDL	SDWA: < MDL SW846: < MDL CLP:ABS<1/2 MRL or as stated in QAPP	Flag: Analyte detected in ICB or recalibrate
MB	1 per batch of 20 samples	<MDL	SDWA: < MDL SW846: < MDL CLP:ABS<1/2 MRL or as stated in QAPP	Flag: Analyte detected in Method Blank or reprep
LCS	1 per batch of 20 samples	mid cal. Range	In-house limits or, default 80-120% SDWA; 90-110%	Terminate analysis: correct problem before proceeding.
CCV	1 after every 10th sample	mid cal range	80-120%	Recalibrate and reanalyze all samples back to the last acceptable CCV or ICV
CCB	Immediately following each CCV	<MDL	SDWA: < MDL SW846: < MDL CLP:ABS<1/2 MRL or as stated in QAPP	Reanalyze all samples back to the last acceptable CCB or ICB or flag analyste detected
MS-MSD	5% (1 in 20) of samples per batch per matrix	See attached spike chart	In-house limits or, default of 75-125 when spike level is >25% of original analyte level	Perform PDS
Serial Dilution Analysis	1 per digestion batch per matrix	5 fold dilution of chosen sample	RPD within 10% of value of diluted and undiluted sample, but only if sample conc. >/= 50 X's LOD	Flag data only if sample conc. Is within range (>50X's LOD)

Post Digestion Spike (PDS)	Upon failure of MS and/or 1 per batch for ACOE work	Same level as MS	85-115%	Flag: Matrix interference or Method of Std. Additions

Appendix A
Recommend Calibration Curve Concentrations

Element	Concentrations (ug/L)
Antimony	0, 4, 10, 20, 30, 40
Arsenic	0, 4, 10, 20, 40, 50
Lead	0, 4, 10, 20, 40, 50
Selenium	0, 4, 20, 30, 40, 50
Silver	0, 0.9, 3, 4.5, 6, 7.5
Thallium	0, 4, 10, 20, 30, 40
Tin	0, 4, 20, 40, 80, 100

GFAA / FLAA / CVAA Data Review checklist			Method: 200.9 7000 series AA 245.1 7470/7471		
Instrumentation: PE SIMAA 6000 Varian Spec-20 Varian Spec-10					
Analysis Date:	Data File:		Date Review:		**Analyte:**_____
Cal Std ID:	LIMS # :	Analyst:	Reviewer:		Approved? Yes No
Calibration Parameters -		**YES**	**NO**	**YES**	**NO**	**Comments:**
1) Calibration linearity - r > 0.995					
2) ICV 90-110% 95-105%					
3) ICB ABS of LOD or RL					
6) CRA - (2X CRDL or LOD) 80-120%					
7) CCV1/CCB1- 90-110% / 80-120%					
8) CCV2/CCB2 ABS of LOD or RL					
9) CCV3/CCB3					
10) CCV4/CCB4					
11) CCV5/CCB5					
12) CCV6/CCB6					
Preparation Batch Parameters		**YES**	**NO**	**YES**	**NO**	**Comments:**
Prep Batch ID#:_____ Dig. Meth._____					
Prep. Blank - <LOD or RL					
LCS - generated limits;attached list					
Spiked samples in batch:					
a)_____ matrix = _____					
b)_____ matrix = _____					
c)_____ matrix = _____					
d)_____ matrix = _____					
e)_____ matrix = _____					
PDS 85-115% sample#_____					
MSA Performed? Yes No					
Prep Batch ID#:_____ Dig. Meth._____					
Prep. Blank - <LOD or RL					
LCS - generated limits;attached list					
Spiked samples in batch:					
a)_____ matrix = _____					
b)_____ matrix = _____					
c)_____ matrix = _____					
d)_____ matrix = _____					
e)_____ matrix = _____					
PDS 85-115% sample#_____					
MSA Performed? Yes No					

CT Laboratories
Baraboo Laboratory Divison

Title: **Inductively Coupled Plasma Emission—Trace 61E**

SOP Number: **6105B—Trace**

Prepared by: _____
Date

Technical Review by: _____
Date

Reviewed by: _____
Quality Assurance ***Date***

_____
Laboratory Director ***Date***

SOP Manual Control Number:_____

1.0 SCOPE AND APPLICATION

Metals in solution can be readily analyzed by atomic emission using an Inductively Coupled Plasma (ICP) spectrometer. This method is applicable to the determination of various metals in drinking water, surface water, groundwater, sludge, soils, and industrial wastes. All matrices, excluding filtered groundwater samples and drinking waters with a turbidity less than 1 NTU, will require a digestion prior to analysis.

2.0 METHOD SUMMARY

2.1 If necessary, prior to analysis, samples are digested using an approved method. See SOPs 6205B, 6225B, 6230B, M200.2, and M-soluble for further information on sample digestion.

2.2 This method describes multielement determinations using a TJA 61E Trace ICP. This instrument measures characteristic emission spectra by optical spectrometry. The samples are first nebulized using a glass nebulizer and transported to plasma. Element specific emission spectra are produced by the plasma. The spectra are dispersed by a diffraction grating and the intensity of the emission lines are monitored by photomuliplier dectors that contain individual exit slits for each wavelength being determined. Samples are routinely analyzed using an internal standard of Yttrium to eliminate certain interference problems.

2.3 The data is exported to the LIMS system and reviewed by the analyst. Following analyst review, the data is given to a qualified reviewer for complete data review. After the data has been reviewed and it is determined that it is valid data, the reviewer sends the data to the "validated" mode in the LIMS system.

3.0 DEFINITIONS -

3.1 Reagent Blank- A solution of de-ionized water, (containing in correct proportion, all reagents required by the method), used with the calibration standards to standardize the instrument, as a calibration blank, and for sample dilution.

3.2 Calibration Standards - A series of known standard solutions, which shall include the reagent blank, used for calibration of the instrument within the measurable linear range. Calibration standards shall contain, in correct proportion, all reagents required by the method. Acceptance of the calibration requires a correlation coefficient of 0.995 or better. No samples shall be analyzed without acceptable calibration.

3.3 Calibration Verification Standard-Initial (ICV) & Continuing (CCV) - A midpoint calibration standard which is analyzed at the beginning of the run (ICV), at a frequency of 1 per 10 samples during a run (CCV), and at the end of a run to verify calibration throughout the run. The ICV must be from a second source different than that of the calibration standards. **Note for method 200.7 that limits for ICV are tighter than those for CCV (see section 16).**

3.4 CB (Calibration Blanks- Initial and Continuing) - A reagent blank solution, which is analyzed immediately following the ICV (Initial Calibration Blank-ICB), at a frequency of 1 per 10 samples during a run (Continuing Calibration Blank-CCB), and at the end of a run to check for drifts in calibration, or possible analyte carry-over. Warning criteria include that the absolute value be less than or equal to the three times the IDL for a given analyte for SW-846 work or less than ½ the MRL for ACOE work. Control criteria consist of the absolute value being less than or equal to 2 times the MDL for a given analyte for SW-846 and is determined by the QAPP for ACOE work. If this range is exceeded, a new calibration will be necessary.

3.5 LCS (Laboratory Control Sample)- A mid-range standard, prepared from a source different from that used for calibration standards, that is carried through the entire preparation and analytical method. The LCS is used to verify the accuracy of the preparation method. A minimum of one LCS is prepared per batch and is analyzed at the beginning of an analytical batch.

3.6 MB (Method Blank) - A Reagent Blank (see 3.1) which is carried through the entire preparation and analytical method. The method blank is used to detect possible contamination that may occur prior to or during the sample preparation. A minimum of one MB is prepared per batch and is analyzed at the beginning of an analytical batch. Blank recovery should be less than 2x MDL for SW846, less than the MDL for SWDA samples and is determined by the QAPP for ACOE samples.

3.7 MS-MSD (Matrix Spike-Matrix Spike Duplicate): - Two separate sample aliquots to which a known concentration of analyte has been added which is carried through the entire preparation and analytical procedure. The purpose of a matrix spike is to reveal any matrix effect from the sample on the recovery of the analyte by the method being used. An MS-MSD pair is prepared for every 20 samples of a given matrix per day for 6010B and once for every 10 samples of a given matrix per day for 200.7. For ACOE work only an MS is prepared and a duplicate sample is prepared rather than an MSD. Failure to meet criteria may be due to poor recovery during the preparation method or due to matrix interference within the digestate. To be considered acceptable, MSD must meet both the same % recovery criteria as an MS, and the same % RPD as a duplicate sample.

3.8 Duplicate sample- A separate sample aliquot which is carried through the entire preparation and analytical procedure. A duplicate is prepared for every 20 samples for ACOE work.

3.9 Method Reporting Limit (MRL) or Contract Required Detection Limit (CRDL) Standard: Detection level standard at a level near the reporting limit, or at a level specified by client contract. When required, it is to be analyzed following the ICB, and prior to the last CCV standard in the run.

3.10 Interelement Correction Factors (IEC) – These correction factors are determined by analyzing a concentration range of known interferents (Al, Ca, Co, Cr, Cu, Fe, Mg, Mn, Ni, V and Zn) and examining all other lines for a significant linear response. A line is considered to be significantly affected when the correlation coefficient for the interference is 0.99 or better and the

correction factor multiplied by ten is greater than the MDL of the affected line. For interferents known to occur at high levels in environmental samples (Al, Ca, Cr, Cu, Fe, Mg and Zn) the interference will be considered to be significant when the correction factor multiplied by 100 is over the MDL of the affected line and the correlation coefficient in 0.99 or better. Interelement correction is used where applicable.

3.11 Linear Dynamic Range (LDR) – The upper limit of the linear dynamic range is established for each wavelength utilized by determining the signal responses from a minimum of three different concentration standards across the range. One of these will be near the upper limit of the range. The ranges used for the analysis of samples are judged by the analyst from the resulting data. The data and calculations are kept on file. The upper range limit is an observed signal no more than 10% below the level extrapolated from the lower standards. Determined analyte concentrations above the upper range limit are diluted and reanalyzed. **Note: for ACOE work, analyte concentrations above the upper calibration limit are diluted and reanalyzed.** New dynamic ranges are determined whenever there is a significant change in instrument response. For analytes that routinely approach the upper limit of the range, the range will be checked biannually. For analytes that are known interferents and exceed the dynamic range, the analyst will check that IEC's have been correctly applied.

3.12 ICS-A (Interelement Correction Standard-A): A standard containing the elements Al, Ca, and Mg at 500mg/L and Fe at 200mg/L for non-ACOE work and Al, Ca, Mg and Fe at 500mg/L for ACOE work. This standard is analyzed when using method 200.7 or performing ACOE work following the ICV at the beginning of the run to determine that interelement correction factors are correctly compensating for interference from these elements on other analyte lines. The ICSA may be required to be run before the last CCV of the run for ACOE work. Check the QAPP to determine if this is necessary. **For ACOE work, the ICSA should be within the absolute value of two times the MDL for all analytes except Al, Ca, Fe and Mg unless a different requirement is specified within the contract.**

3.13 ICS-AB (Interelement Correction Standard-AB): A standard containing the elements Al, Ca, Mg at 500mg/L, Fe at 200mg/L for non-ACOE work, Al, Ca, Mg and Fe at 500mg/L for ACOE work and all other elements at 500ug/L. This standard is analyzed following the ICV at the beginning of each run. It is analyzed to determine that the IEC are correctly preventing interference by these elements on the measurement of other analytes. The ICSAB may be required to be run before the last CCV of the run for ACOE work. Check the QAPP to determine if this is necessary

3.14 PDS (Post Digestion Spike): For CLP protocol, when a matrix spike falls outside of the acceptance limits a post digestion spike is used to determine if the sample digestion matrix is interfering with the analysis of the analyte. The sample is spiked at a level similar to that of the matrix spike. **For ACOE work, a PDS will be conducted at a minimum rate of one per prep batch per unique matrix.**

3.15 SD (Serial Dilution Analysis): A sample is diluted 1:5 with method blank solution and analyzed. The diluted result and the undiluted result should agree within a limit of precision defined by the program (SW846, CLP, 200.7) or client QAPP. **For ACOE work, a SD will be conducted at a minimum rate of one per prep batch per unique matrix.**

3.16 Batch- A batch consists of 20 samples of the same matrix analyzed on the same day or 20 samples of the same medium that have been prepared together.

4.0 HEALTH AND SAFETY

4.1 Gloves and protective clothing should be worn to protect against unnecessary exposure to hazardous chemicals and contaminants in samples. All activities performed while following this procedure should utilize appropriate laboratory safety systems.

4.2 Insure that waste collection vessels contain enough room to accommodate all wastes that will produced during the operation of the instrument.

5.0 CAUTIONS

5.1 Samples must be preserved and analyzed within holding times stated in chart.

	Aqueous	Solids
Preservative:	pH <2 with HNO_3	cool 4°C
Hold Time:	180 days	180 days

6.0 INTERFERENCES

6.1 Background emission and stray light are corrected using background correction. See TJA operator's manual for further instructions on background correction application.

6.2 Spectral overlaps are corrected for using interelement correction factors (IEC). When IEC are used, the interfering elements must be analyzed along with the elements of interest. The accuracy of IEC shall be verified daily by analyzing the ICSAB. All IEC factors shall be updated every six months or when an instrumentation change occurs, such as changing a torch, nebulizer, injector or plasma conditions.

6.3 Physical interferences such as viscosity are minimized by using an internal standard. Post digestion spike and serial dilutions help to determine if physical interferences are present.

6.4 Chemical interferences include molecular compound formation, ionization effects, and solute vaporization effects. Chemical interferences are not normally seen during ICP analysis and are highly matrix dependent.

6.5 Memory interferences occur when a sample of high analyte concentration does not thoroughly rinse prior to the analysis of the next sample. This causes elevated readings for that analyte in the subsequent sample. Memory effects can be minimized by rinsing at least 60 seconds between samples.

7.0 PERSONNEL QUALIFICATIONS

Personnel operating the ICP shall have background knowledge of the scientific principles used during this application. All operators shall perform an initial demonstration of capability (IDC) prior to analyzing any samples. It is preferable for the operator to have at least two semesters of college chemistry.

8.0 APPARATUS AND MATERIALS

8.1 Equipment and supplies

8.1.1 TJA Trace 61E ICP, autosampler, computer, printer.
8.1.2 Argon: liquid high purity or gaseous pre-purified grade.
8.1.3 Class A volumetric flasks and pipettes.
8.1.4 Disposable 15-mL polystyrene culture tubes.
8.1.5 100 uL eppendorf pipette.
8.1.6 10-mL oxford pipette.

8.2 Reagents

8.2.1 Mixed and single element stock metals standards. See Section 9 and Appendix A, B, C and D for instructions on making the working standards.
8.2.2 Nitric acid, conc. (Trace Metals grade)
8.2.3 Hydrochloric acid, (Trace Metals Grade)
8.2.4 Deionized water

9.0 INSTRUMENT CALIBRATION

The default calibration for routine work is a single-point calibration using a silver calibration standard, multi-element calibration standard and a calibration blank. See section 11.0 for further instructions on how to perform the calibration.

Note: For samples requiring a multipoint calibration use the ACOE-LCG method instead of the Yttrium internal standard method. See Appendix A for preparations of calibration standards and blank for the multipoint calibration. See Appendix B for the preparation of the calibration standards and blank for the "Shell" method. See Appendix C for the preparation of the calibration standards and blank for the Sodium and Potassium calibrations. See Appendix D for the preparation of the calibration standards and blank for the Boron calibration.

9.1 Multi-element calibration standard: (Called the High Std in the TJA method) Into a 1000mL volumetric flask, add 500mL of Milli-Q H2O, 10mL of conc. HNO3, and 10mL conc. HCl. Add 10mL each of SPEX QC-21 standard and SPEX QC-7, 2.4mL each of 10,000 mg/L Al, Ca, and Mg(ULTRA SCIENTIFIC or equivalent), 0.90mL of 10,000 mg/L Fe(ULTRA SCIENTIFIC or equivalent). Dilute to volume with Milli-Q H2O and mix
by inverting several times. Transfer to a clean 1L Nalgene bottle. Prepare every 6 months or as needed.
Concentration: 1000 ug/L
Analytes: Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Mo, Ni, Pb, Sb, Se, Tl, V, Zn

9.2 Silver Calibration Standard: (Called Standard #3 in the TJA method) Into a 1000mL volumetric flask, add 500mL of Milli-Q H2O, 10mL of conc. HNO3, and 10mL conc. HCl. Add 1mL of 1000 mg/L Ag Std(ULTRA SCIENTIFIC or equivalent). Dilute to volume with Milli-Q H2O and mix by inverting several times. Transfer to a clean 1L Nalgene bottle. Prepare every 6 months or as needed.
Concentration: 1000 ug/L
Analytes: Ag

9.3 Calibration Blank: Into a 1 L. volumetric flask, add 750 mL of Milli-Q water and 10mL of conc. HNO3 and 100mL HCl. Mix, dilute to volume with Milli-Q H2O. Transfer to a clean 1 L. nalgene bottle. Prepare every 6 months or as needed.

9.4 Yttrium Internal std : Into a 1000mL volumetric flask, add 500mL of Milli-Q H2O, 1mL 10,000 mg/L Yttrium std Dilute to volume with Milli-Q H2O and mix by inverting several times. Transfer to a clean 1L Nalgene bottle. Prepare every 6 months or as needed. **Note: for Na/K use the Lithium/Yttrium internal standard- see Appendix C for preparation instructions.**
Concentration: 10mg/L Yttrium solution.

9.5 Initial/Continuing Calibration Verification (ICV/CCV): Into a 1000mL volumetric flask, add 500mL of Milli-Q water, 10 mL of conc. HNO3 and 10mL HCl. Add the following:
10 mL SPEX Spike Sample Standard 1 or Equivalent
0.5mL Mo 1000mg/L
2mL Interferents-A-SPEX or equivalent
Dilute to volume with Milli-Q water, mix and transfer to a clean 1 L Nalgene bottle. Make new every 6 months or as needed.

Concentration:	Analyte:
50ug/L	Cd, Be
50ug/L	Ag
200ug/L	Cr
250ug/L	Cu
500ug/L	Co, Mn, Mo, Ni, Pb, Sb, V, Zn
2000ug/L	Ba, As, Tl, Se
5,000ug/L	Fe
10,000ug/L	Ca, Mg
12,000ug/L	Al

9.6 ACOE Initial/Continuing Calibration Verification (ACOE ICV/CCV): Into a 1000mL volumetric flask, add 250mL of Milli-Q water, 10 mL of conc. HNO3 and 10mL HCl. Add the following:
10 mL SPEX Spike Sample Standard 1 or Equivalent
0.5mL Mo 1000mg/L
50mL SPEX Interferent A solution or Equivalent
Dilute to volume with DI, mix and transfer to a clean 1 L Nalgene bottle. Make new every 6 months or as needed.

Concentration:	Analyte:

50ug/L	Cd, Be
50ug/L	Ag
200ug/L	Cr
250ug/L	Cu
500ug/L	Co, Mn, Mo, Ni, Pb, Sb, V, Zn
2000ug/L	Ba, As, Tl, Se
50,500ug/L	Fe
125000ug/L	Ca, Mg
126,000ug/L	Al

9.7 Interference Check Solution (ICSA): Into a 500 mL volumetric flask, add 300 mL of Milli-Q H2O, 5 mL of conc. HNO3 and 5mL conc. HCl. Add the following stock solutions in the volumes listed:
50 mL Spex Interferent A or equivalent
Dilute to volume with Milli-Q H2O and mix by inverting several times. Transfer to a clean 500 mL Nalgene bottle. Prepare every 6 months or as needed.

Concentration:	Analyte:
500,000 ug/L	Al, Ca, Mg
200,000 ug/L	Fe

9.8 Interference Check Solution (ICSAB): Into a 500 mL volumetric flask, add 300 mL of Milli-Q H2O, 5 mL of conc. HNO3 and 5 mL conc. HCl. Add the following stock solutions in the volumes listed:
50 mL Spex Interferent A or equivalent
2.5 mL Spex QC-21 or equivalent
0.25 mL Ultra Ag 1000 mg/L or equivalent
0.25 mL Ultra Ba 1000 mg/L or equivalent
Dilute to volume with Milli-Q H2O and mix by inverting several times. Transfer to a clean 500 mL Nalgene bottle. Prepare every 6 months or as needed.

Concentration:	Analyte:
500,000 ug/L	Al, Ca, Mg
200,000 ug/L	Fe
500 ug/L	Ag, As, Ba, Be Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Se, Sb, Tl, V, Zn

9.9 CLP/ACOE ICSA solution: Into a 500 mL volumetric flask, add 300 mL of Milli-Q H2O, 5 mL of conc. HNO3 and 5 mL conc. HCl. Add the following stock solutions in the volumes listed:
50 mL Spex Interferent A or equivalent
2.5 mL Spex QC-21 or equivalent
150mL Ultra Fe 10000mg/L or equivalent
Dilute to volume with Milli-Q H2O and mix by inverting several times. Transfer to a clean 500 mL Nalgene bottle.
Prepare every 6 months or as needed.

Concentration:	Analyte:
500,000 ug/L	Al, Ca, Fe, Mg

9.10 CLP/ACOE ICSAB solution: Into a 500 mL volumetric flask, add 300 mL of Milli-Q H2O, 5 mL of conc. HNO3 and 5 mL conc. HCl. Add the following stock solutions in the volumes listed:
50 mL Spex Interferent A or equivalent
2.5 mL Spex QC-21 or equivalent
150mL Ultra Fe 10000mg/L or equivalent
0.25 mL Ultra Ag 1000 mg/L or equivalent
0.25 mL Ultra Ba 1000 mg/L or equivalent
Dilute to volume with Milli-Q H2O and mix by inverting several times. Transfer to a clean 500 mL Nalgene bottle.
Prepare every 6 months or as needed.

Concentration:	Analyte:
500,000 ug/L	Al, Ca, Fe, Mg
500 ug/L	Ag, As, Ba, Be Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Se, Sb, Tl, V, Zn

9.11 CRI/CRDL/MRL solution: Concentrations needed depend on the CRDL/MRL of a given contract.

10.0 SAMPLE COLLECTION, HANDLING AND PRESERVATION

	Aqueous	Solids
Preservative:	pH <2 with HNO_3	cool 4°C
Hold Time:	180 days	180 days

11.0 SAMPLE ANALYSIS

11.1 Instrument start-up procedure:

11.1.1 Open valve at argon tank.

11.1.2 Inspect sample and rinse pump tubing and change if necessary.

11.1.3 Fill DI rinse reservoir with DI water.

11.1.4 Open up ThermoSpec software on the PC. Go to SETUP, then PLASMA CONTROL PANEL.

11.1.5 Plasma startup: Press STARTUP. The purge time should be set for 90 sec. The start up power should be set to the first value to be used in the analysis.

11.1.6 Press 'CONTINUE' to light the plasma.

11.1.7 Set the plasma conditions as follows:
RF power: 950
Nebulizer pressure: 0.70 L/Min
Pump speed: 130rpm

11.1.8 After a 30-minute warm-up period, perform a polychromator profile using a 2mg/L Arsenic Standard. The peak should be centered on zero. Record the resultant peak intensity. It should be greater than 700. Record this in the instrument run logbook.

11.1.8.1 Check the optics vacuum reading on front panel of instrument. Vacuum should be <20 millitor. If not, inspect vacuum pump oil reservoir and fill to halfway mark on inspection window if necessary.

11.1.8.2 Check condition of nebulizer: put pump tube into a 100mg/L Yttrium Std. With the lights off and after enough time has elapsed for the Yttrium standard to reach the plasma, a red cone should be noticeable in the center of the plasma. If the nebulizer is in good condition and the nebulizer gas flows are set properly, the red cone should project about ¼" beyond the coils. If not, check the settings, the pump tubes, and inspect the nebulizer under a microscope.

11.1.9 Create Autosampler Table:

11.1.9.1 Go to method; Choose method to analyze samples with.

11.1.9.2 Press AUTOSAMPLER ,then,

11.1.9.3 CREATE TABLESAMPLES

11.1.9.4 Press STANDARDS: Inputs the entire standard set into the table.

11.1.9.5 Add QC SAMPLES in order. The standard order is ICV, ICB, ICSA (if necessary, such as for ACOE work or SDWA samples. See section 16.0 for further information), and then ICAB

11.1.9.6 Add all samples, LCS, Blanks, MS-MSD, etc. in order.

11.1.9.7 Insert continuing QC into the table. A CCV followed by a CCB is placed after every 10 samples/batch QC samples and at the end of the run. The ICSA and ICSAB count as samples for ACOE work. For some ACOE work, a CRDL/MRL, an ICSA and an ICSAB may need to be analyzed prior to the last CCV, CCB- consult project QAPP for details.

11.1.9.8 All ICV, CCV, and ICSAB are compared to check tables constructed in the method. Make sure to designate these in the autosampler table so that they will be marked pass or fail as the analysis proceeds.

11.1.9.9 SAVE (F9), save 3 times in succession while exiting the screens to get back out to Analysis.

11.1.9.10 Print Autosampler Table: This will be used when preparing all samples and standards.

11.1.9.11 Using the printed autosampler table sheet, prepare all standards, QC samples, and samples in their designated positions in the autosampler. Prepare any bench spikes and place them in autosampler. Calibration standards, CCV, ICV, CCB, ICB and ICSAB all go into glass vials and are placed where designate by the table in the "L" rack portion of the autosampler. All others are poured into plastic vials

and go into the designated areas within the 48 position blocks.

11.2 Calibration and Analysis

Once all calibration standards have been placed in the autosampler, begin the calibration and prepare the remaining samples as the calibration is being carried out.

11.2.1 Press 'ANALYZE'.

11.2.2 Prepare a serial dilution for new or unusual matrices by performing a 1:5 dilution on the sample.

11.2.3 Arrange the standards on the autosampler according to the autosampler table positions.

11.3 Instrument shutdown

11.3.1 If run will not be finished during work hours, program the instrument to shutdown at the end of the analytical run. When setting up on the ANALYSIS page set the "end of analysis condition" to TERMINATE. This will shut off the plasma the argon and the pump.

11.3.2 For manual shutdown go to PLASMA STARTUP and select SHUTDOWN. After a 30 second cooling off period, the system will be in complete shutdown mode. Release the pump tube tensioners.

12.0 INSTRUMENT MAINTENANCE AND TROUBLESHOOTING

12.1 Pump tubing and rollers: Ensure that the pump rollers turn freely. Inspect pump tubing daily and replace when it starts failing to retain its shape.

12.2 Drain line: Spray chamber drain line must flow unimpeded directly down into the waste jug. Hose must be under water to maintain atmospheric pressure inside spray chamber. When emptying jug, always add back in about 6" of clean water for hose to be submerged in. Drain line for autosampler in separate jug. Make sure line is draining properly.

12.3 Spray Chamber: If the spray chamber becomes dirty, the sample waste may not drain properly. Remove and wash with hot soapy water, then rinse with DI H_2O.

12.4 Torch and O-rings: The O-rings surrounding the torch may need to be replaced if the plasma becomes unstable or internal standard emission counts fall off. See TJA manual for technique. Torch needs to be cleaned occasionally with aqua regia followed by sonication.

12.5 Vacuum system. Must maintain <20 millitorr vacuum. Change oil every 6 months. Pump needs a minor rebuild every 2 years (new gaskets, anti-suckback valve) or as needed, and a major rebuild every 4 years (gaskets, seals, anti-suckback valve, vanes, springs).

13.0 DATA ACQUISITION, CALCULATIONS, AND DATA REDUCTION

13.1 See SOP FO-DCICP for instructions on Data Capture

13.2 Sample Calculations:

Liquid Concentration (ug/L) = A x C

Solid Concentrations (mg/kg) = $\frac{A \times B \times C}{D \times E}$,

where A = instrument reading for sample (ug/L)
B = total volume of digestion (L)
C= analyst dilution factor, if necessary (ex. For a 1 to 10 dilution, C = 10)
D = amount of sample used in digestion (g)
E = percent solids/100, if necessary

Spike Recovery (%) = $\frac{\text{(Spiked sample concentration – Sample concentration)} \times 100}{\text{(Spike amount)}}$

%RSD = $\frac{(MS - MSD) \times 100}{(MS + MSD)/2}$,

where MS = Matrix spike concentration
MSD = Matrix spike duplicate concentration

14.0 COMPUTER HARDWARE AND SOFTWARE

14.1 Computer with StarLIMS
14.2 Computer with ThermoSPEC software

15.0 DATA MANGEMENT AND RECORD MANAGEMENT

15.1 After data is captured by LIMS, the data is reviewed by the analyst to insure data validity. See checklist for data review guidance.
15.2 After the analyst reviews data, it is given to a technical reviewer, usually the Inorganic Lab Supervisor, to review for validity of data. See checklist for data review guidance.
15.3 After data is deemed acceptable by both the analyst and the technical reviewer, it is sent to "validated" in LIMS.
15.4 Raw data, bench sheets and spreadsheets are stored in the file cabinet. Contents of the file cabinet are periodically archived to storage.

16.0 QUALITY CONTROL

16.1 For the routine analysis of groundwater, wastewater, leachate, surface water, soil, sludge, TCLP/SPLP extracts following method 6010B: Required QC following instrument calibration is as follows :

16.1.1 ICV (initial calibration verification); The ICV is prepared from an alternate source standard whose concentrations are within the linear working range of the instrument. The results of the ICV should agree within 10% of the expected value for a given analyte. The relative standard deviation (RSD) between the two replicate integrations should be <5%. If results are outside of this range, corrective action must be taken before samples can be analyzed.

This would include recalibration, repouring standard, or re-mixing standard.

16.1.2 ICB (initial calibration blank); analyze the calibration blank. The results of the initial calibration blank must be < 3x IDL for a given analyte. If the average of the two replicates is not < 3x IDL, terminate the analysis, correct the problem and recalibrate or appropriately qualify the data. If the blank is less than 1/10th the concentration of the action level of interest and no sample is within ten percent of the action limit, analyses need not be rerun and re-calibration is not necessary before continuing with the analysis.

16.1.3 ICSAB (interference check solution); analyze a solution containing 500 mg/L Al, Ca, Mg, 200 mg/L Fe and all other analytes of interest at 0.50 mg/L. Recovery for analytes of interest is +/- 20% true value. If recovery is outside this range, corrective action must be taken before samples can be analyzed. Check placement of background correction points and IECs as a place to start troubleshooting .

16.1.4 LCS (laboratory control sample); analyze an alternate source reference sample. Control limits are +/- 20% of true value or in-house limits, whichever is more restrictive, or as specified in a client QAPP.

16.1.5 MB (method blank); analyze a reagent blank. The method blank is a reagent blank that has been taken through the preparations steps along side the samples being analyzed. Control limits are ± the MDL. If the average of the two replicates is not < MDL, terminate the analysis, correct the problem and recalibrate or appropriately qualify the data that falls within the MDL and twenty times the concentration of the analyte in the method blank.

16.1.5 CCV (continuing calibration verification); analyze a check standard after every ten samples and following the last sample in the run. This standard should be at a level approximately mid-scale. Control limits are +/- 10% of true value. If values fall outside this range, all samples back to the last acceptable ICV or CCV must be repeated.

16.1.6 CCB (continuing calibration blank); The results of the continuing calibration blank must be < 3x IDL for a given analyte. If the result falls outside this, reanalyze all samples back to the last acceptable CCB or qualify all sample <20 times the blank and greater than the MDL.

16.1.7 MS/MSD (matrix spike/matrix spike duplicate); for non-digested samples, prepare a bench spike in duplicate at a frequency of 5% or per analytical batch, whichever is more frequent. Control limits are +/- 25% of true value, and 20% RPD, or use calculated limits, whichever is tighter. See Sec. 18.0 for bench spike preparation. For digested samples, see "Predigestion Spike" chart in section 18.0. For digested samples, analyze the MS/MSD samples as they apply

to each digestion set. Follow the above for control limits. For digested spikes with sample results greater than four times the digested spike level, prepare and analyze a PDS sample if the MS and/or MSD is outside the control limits. Prepare the PDS at a level approximately two times the sample level.

16.2 For SDWA analysis following method 200.7:
Required QC following instrument calibration is as follows :

16.2.1 ICV: Referred to in 200.7 as LPC (laboratory performance check); analyze the mid-cal standard. Control limits are +/- 5% of true value. If values fall outside this range, recalibrate for the affected analytes.

16.2.2 ICB (initial calibration blank); analyze the calibration blank. The absolute value of the result should be below the LOD for the analyte(s) of interest. If the blank result falls outside this, evaluate the effect on the sample results and/or recalibrate for the affected analytes. Samples with results >10x the associated blank value need not be reanalyzed.

16.2.3 ICSA (interference check solution: interference only) analyze a solution containing 500 mg/L Al, Ca, Mg, and 200 mg/L Fe. This sample must be analyzed at the beginning of the analytical run before the ICSAB. Recovery for interfering analytes is +/- 20% true value. All other analytes need to be ± 2X MDL. If recovery/result is outside the acceptable range, corrective action must be taken before samples can be analyzed. Check placement of background correction points and IECs as a place to start troubleshooting .

16.2.4 ICSAB (interference check solution); analyze a solution containing 500 mg/L Al, Ca, Mg, 200 mg/L Fe and all other analytes of interest at 0.50 mg/L. Recovery for analytes of interest is +/- 20% true value. If recovery is outside this range, corrective action must be taken before samples can be analyzed. Check placement of background correction points and IECs as a place to start troubleshooting .

16.2.5 LCS (laboratory control sample); analyze an alternate source reference sample per batch of 20 samples of the same matrix. Control limits are +/- 10% of true value, or manufacturer's limits, whichever is tighter.

16.2.6 MB (method blank); analyze a reagent blank per 20 samples of the same matrix. The method blank is a reagent blank that has been taken through the preparations steps along side the samples being analyzed. Control limits are ± the MDL. If the average of the two replicates is not < MDL, terminate the analysis, correct the problem and recalibrate or appropriately qualify the data that falls within the MDL and twenty times the concentration of the analyte in the method blank.

16.2.4 CCV: Referred to in 200.7 as LPC (laboratory performance check); analyze the mid-cal standard after every 10 samples. Control limits are +/- 10% of true value. If values fall outside this range, reanalyze all samples back to the last acceptable ICV or CCV.

16.2.5 CCB (continuing calibration blank); analyze the calibration blank immediately after each CCV. The absolute value of the result should be below the LOD for the analyte(s) of interest. If the result falls outside this, evaluate the effect on the sample results. Sample results >10x the associated blank value need not be reanalyzed. Otherwise, reanalyze all samples back to the last acceptable CCB or qualify data that is >LOD and <10x the associated blank.

16.2.6 MS/MSD (matrix spike/matrix spike duplicate); for non-digested samples, prepare a bench spike in duplicate at a frequency of 5% or per analytical batch, whichever is more frequent. Control limits are +/- 25% of true value, and 20% RPD, or use calculated limits, whichever is tighter. See Sec. 18.0 for bench spike preparation. For digested samples, see "Predigestion Spike" chart in section 18.0. For digested samples, analyze the MS/MSD samples as they apply to each digestion set. Follow the above for control limits. For digested spikes with sample results greater than four times the digested spike level, prepare and analyze a PDS sample if the MS and/or MSD is outside the control limits. Prepare the PDS at a level approximately two times the sample level.

16.3 For the CLP-like level 4 analysis of groundwater, surface water, wastewater and soil:

A default of three replicate exposures per sample should be used for ACOE work unless specified differently in QAPP.

Required QC following instrument calibration:

16.3.1 ICV (initial calibration verification): analyze the alternate source check standard immediately following calibration. Control limits +/- 10 % true value.

16.3.2 ICB (initial calibration blank): analyze the calibration blank. The absolute value of the result must be below the contract required detection limit (CRDL) or the limit stated within the QAPP for the project. If a result falls outside this, recalibrate for the affected analytes.

16.3.3 CRDL (contract required detection limit standard) or MRL (Method Required Limit): analyze a standard at a level two times the contract-required detection limits (CRDL) or at the level stated withing the QAPP for the project. Follow limits stated within the QAPP as there are no EPA specified control limits for this standard. This sample must be analyzed at the beginning and the end of the run.

16.3.4 ICSA (interference check solution: interference only) analyze a solution containing 500 mg/L Al, Ca, Mg, and Fe. This sample must be analyzed at the beginning of the analytical run prior to the

ICSAB. Refer to QAPP for acceptablility criteria. For ACOE work, the default criteria is the absolute value of two times the MDL for all analytes except Al, Ca, Mg and Fe which must have a recovery between 80-120%. Refer to QAPP to determine if the ICSA must also be analyzed at the end of the run.

16.3.5 ICSAB (interference check solution: interference plus analytes); analyze a solution containing 500 mg/L Al, Ca, Mg, and Fe, and all other analytes of interest at 0.50 mg/L. Recovery for analytes of interest is +/- 20% true value. If recovery is outside this range, corrective action must be taken before samples can be analyzed. Check placement of background correction points as a place to start troubleshooting. This sample must be analyzed at the beginning of the run. Refer to the QAPP to determine if the ICSAB must be analyzed at the end of the run.

16.3.6 Digested Sample set to include MB (S or W), LCS (S or W), MS, DUP.

16.3.7 Serial Dilution: Analyze a 1:5 dilution of a sample from the digestion set. For sample results > 50x the MDL, the %RSD between the serial dilution result and the sample result must be ≤ 10.

16.3.8 Post digestion spike addition (bench spike): An analyte spike added to a portion of a prepared sample, or its dilution, should be recovered to within +/- 25% of the known value or as specified by the client QAPP. The spike addition should produce a minimum level of 10 times the instrumental detection limit. If the spike recovery falls outside the limits, a matrix effect should be suspected.

16.3.9 CCV (continuing calibration verification): Analyze a mid-level standard after every ten samples. The CRDL/MRL, ICSA, ICSAB and batch QC all count as samples. Control limits are +/- 10% of true value. If any result falls outside this, all samples back to the last acceptable ICV/CCV must be reanalyzed.

16.3.10 CCB (continuing calibration blank); Analyze the calibration blank after the CCV. Refer to the QAPP for CCB acceptance limits. If any result falls outside the limits, all samples with results less 20 times the CCB must be reanalyzed back to the last acceptable CCB or appropriately qualified.

16.3.11 MS/DUP (matrix spike/matrix duplicate); for non-digested samples, prepare a bench spike and a duplicate at a frequency of 5% or per analytical batch, whichever is more frequent. Control limits are specified in client QAPP. See Sec. 18.0 for bench spike preparation. For digested samples, see "Predigestion Spike" chart in section 18.0. For digested samples, analyze the MS/DUP samples as they apply to each digestion set. Follow the above for control limits.

16.4 New or unusual matrices:

It is recommended that whenever a new or unusual sample matrix is encountered, a serial dilution and post digestion (bench) spike be performed prior to reporting results. These tests will ensure that neither positive nor negative interferences are affecting sample results.

Note: For ACOE work, a serial dilution and a post digestion spike will be performed at a rate of one per matrix with each prep batch.

16.4.1 Serial Dilution: If the analyte concentration is sufficiently high (minimally a factor of ten above the instrumental detection limit after dilution), an analysis of a 1:5 dilution should agree within +/- 10% of the original determination. If not, a chemical or physical interference effect should be suspected.

16.4.2 Post digestion spike addition (bench spike): An analyte spike added to a portion of a prepared sample, or its dilution, should be recovered to within +/- 25% of the known value. The spike addition should produce a minimum level of 10 times and a maximum of 100 times the instrumental detection limit. If the spike recovery falls outside these limits, a matrix effect should be suspected.

17.0 REFERENCES

17.1 *Test Methods for Evaluating Solid Waste*, EPA, SW-846, Method 6010B, 1996.

17.2 *Methods for the Determination of Metals in Environmental Samples*, EPA/600/4-91/010, Method 200.7 rev 4.4, 1991.

17.3 USEPA - Contract Laboratory Program, Statement of Work for Inorganic Analysis, ILM04.0.

17.4 *ICAP 61 Operator's Manual*, Thermo Jarrell Ash, January 1998 (part number 125791-01)

18.0 Tables

MS-MSD Preparation

SPIKE, LCS, & LFB ANALYSIS- ICP
Pre-digestion Spikes-LCS & LFB

Element	Spike Amt. mL of	Spike Stock A, B, C	Stock Conc. mg/L	Final Vol. mL	Expected Conc. ug/L
Aluminum	1	A	200	50	4000
Antimony	1	A	50	50	1000
Arsenic	1	A	200	50	4000
Barium	1	A	200	50	4000
Beryllium	1	A	5	50	100
Cadmium	1	A	5	50	100
Calcium	0.5	C	20,000	50	200000
Chromium	1	A	20	50	400
Cobalt	1	A	50	50	1000
Copper	1	A	25	50	500
Iron	1	A	100	50	2000
Lead	1	A	50	50	1000
Manganese	1	A	50	50	1000
Magnesium	0.5	C	10,000	50	100000
Molybdenum	0.1	B	1000	50	2000
Nickel	1	A	50	50	1000
Selenium	1	A	200	50	4000
Silver	1	A	5	50	100
Thallium	1	A	200	50	4000
Vanadium	1	A	50	50	1000
Zinc	1	A	50	50	1000

.Spike Solutions

Supplier	Lot #/ std	Stock
SPEX Certiprep	SPIKE 1-500	A
Molybdenum	1000 mg/L	B
Custom Std	SPEX	C

Bench Spike
SPIKE ANALYSIS-ICP

Post Digestion/ Bench Spikes

Element	Spike Amt. ML of	Spike Soln.	Stock Conc. mg/L	Final Vol. mL	Expected Conc. ug/L
Aluminum	0.2	A	200	10	4000
Antimony	0.2	A	50	10	1000
Arsenic	0.2	A	200	10	4000
Barium	0.2	A	200	10	4000
Beryllium	0.2	A	5	10	100
Cadmium	0.2	A	5	10	100
Calcium	0.2	B	20,000	10	400000
Chromium	0.2	A	20	10	400
Cobalt	0.2	A	50	10	1000
Copper	0.2	A	25	10	500
Iron	0.2	A	100	10	2000
Lead	0.2	A	50	10	1000
Manganese	0.2	A	50	10	1000
Magnesium	0.2	B	10,000	10	200000
Molybdenum	0.02	C*	1000	10	2000
Nickel	0.2	A	50	10	1000
Selenium	0.2	A	200	10	4000
Silver	0.2	A	5	10	10
Thallium	0.2	A	200	10	4000
Vanadium	0.2	A	50	10	1000
Zinc	0.2	A	50	10	1000

Standard Source	
Supplier	
SPEX	A
SPEX Custom Std	B
Molybdenum-1,000 mg/L Std	C*

C*: substock of 1,000 mg/L std.(1:10 dilution.)

Standard Quality Control Requirements and Corrective Action Guidelines

QC Type	Frequency	Conc. Level	*Acceptance Criteria*	*Corrective Action*
ICV	1 per calibration	Mid.Cal Range	SDWA: 95-105% SW846:90-110%	Terminate run. Correct the problem before proceeding
ICB	Immediately after the ICV	<MDL	SW846:ABSvalueof 3x IDL SDWA: ABS LOD CLP:ABS<1/2 MRL or as stated in QAPP.	Terminate analysis and correct the problem before proceeding.
MB	1 per batch of 20 samples	<MDL	SDWA: < MDL SW846: < 2x MDL CLP:ABS<1/2 MRL or as stated in QAPP	Flag: Analyte detected in Method Blank or reprep
LCS	1 per batch of 20 samples	mid cal. Range	In-house limits or, default 80-120% SDWA; 90-110%	Terminate analysis: correct problem before proceeding.
CCV	1 after every 10th sample	mid cal range	SW846: 90-110% SDWA: 90-110% CLP:90-110%	Recalibrate and reanalyze all samples back to the last acceptable CCV or ICV
CCB	Immediately following each CCV	<MDL	SW846:ABSvalueof 3x IDL SDWA: ABS LOD CLP:ABS<1/2 MRL or as stated in QAPP	Reanalyze all samples back to the last acceptable CCB or ICB or flag analyste detected
ICSA	Immediately After LCS (&before final CCV if required by QAPP)	500mg/L Al, CA, Mg 200mg/L Fe (non –ACOE) or 500mg/L Fe (ACOE)	80-120% for Interference Elements ABS of analytes not included must be < 2X MRL or as stated in QAPP	Terminate analysis, correct problem & reanalyze all samples back to last good ICSA/ICSAB
ICSAB	Immediately After ICSA (& before final CCVif required by QAPP)	500mg/L Al, CA, Mg 200mg/L Fe (non-ACOE) or 500 mg/L Fe (ACOE) Other elements 500ug/L	80-120% for All Elements	Terminate analysis, correct problem & reanalyze all samples back to last good ICSA/ICSAB

MS-MSD	5% (1 in 20) of samples per batch per matrix	See attached spike chart	In-house limits or, default of 75-125 when spike level is >25% of original analyte level	Perform PDS
Serial Dilution Analysis	1 per digestion batch per matrix	5 fold dilution of chosen sample	RPD within 10% of value of diluted and undiluted sample, but only if sample conc. >/= 50 X's LOD	Flag data only if sample conc. Is within range (>50X's LOD)
Post Digestion Spike (PDS)	Upon failure of MS and/or 1 per batch for ACOE work	Same level as MS	85-115%	Flag: Matrix interference or Method of Std. Additions

Appendix A.

Standard prep for multipoint calibration of ICP.

A1 Calibration Standard #1: Into a 100mL volumetric flask, add 50mL of Milli-Q H2O, 1mL of conc. HNO3 and 1mL conc. HCl. Add 1 mL of Calibration Standard #4. Dilute to volume with Milli-Q H2O and mix by inverting several times. Transfer to a clean Nalgene bottle. Prepare every 6 months or as needed. Concentration: 1ug/L

A2 Calibration Standard #2: Into a 100mL volumetric flask, add 50mL of Milli-Q H2O, 1mL of conc. HNO3 and 1mL conc. HCl. Add 10uL of SPEX Quality Control Standard 7 and 10uL of SPEX Quality Control Standard 21. Dilute to volume with Milli-Q H2O and mix by inverting several times. Transfer to a clean Nalgene bottle. Prepare every 6 months or as needed. Concentration: 10 ug/L

A3 Calibration Standard #3: Into a 100mL volumetric flask, add 50mL of Milli-Q H2O, 1mL of conc. HNO3 and 1mL conc. HCl. Add 50uL of SPEX Quality Control Standard 7 and 50uL of SPEX Quality Control Standard 21. Dilute to volume with Milli-Q H2O and mix by inverting several times. Transfer to a clean Nalgene bottle. Prepare every 6 months or as needed.Concentration: 50 ug/L

A4 Calibration Standard #4: Into a 100mL volumetric flask, add 50mL of Milli-Q H2O, 1mL of conc. HNO3 and 1mL conc. HCl. Add 100uL of SPEX Quality Control Standard 7 and 100uL of SPEX Quality Control Standard 21. Dilute to volume with Milli-Q H2O and mix by inverting several times. Transfer to a clean Nalgene bottle. Prepare every 6 months or as needed.Concentration: 100 ug/L

A5 Calibration Standard #5: Into a 100mL volumetric flask, add 50mL of Milli-Q H2O, 1mL of conc. HNO3 and 1mL conc. HCl. Add 0.5mL of SPEX Quality Control Standard 7 and 0.5mL of SPEX Quality Control Standard 21. Dilute to volume with Milli-Q H2O and mix by inverting several times. Transfer to a clean Nalgene bottle. Prepare every 6 months or as needed. Concentration: 500 ug/L

A6 Calibration Standard #6: Into a 100mL volumetric flask, add 50mL of Milli-Q H2O, 1mL of conc. HNO3 and 1mL conc. HCl. Add 1mL of SPEX Quality Control Standard 7 and 1mL of SPEX Quality Control Standard 21. Dilute to volume with Milli-Q H2O and mix by inverting several times. Transfer to a clean Nalgene bottle. Prepare every 6 months or as needed.Concentration: 1000 ug/L

A7 Calibration Standard #7: Into a 100mL volumetric flask, add 50mL of Milli-Q H2O, 1mL of conc. HNO3 and 1mL conc. HCl. Add 10mL of SPEX Quality Control Standard 7 and 10mL of SPEX Quality Control Standard 21. Dilute to volume with Milli-Q H2O and mix by inverting several times. Transfer to a clean Nalgene bottle. Prepare every 6 months or as needed.Concentration: 10000 ug/L

A8 Calibration Standard #8: Into a 100mL volumetric flask, add 50mL of Milli-Q H2O, 1mL of conc. HNO3 and 1mL of HCl. Add 1mL of 10,000 mg/L Al, 1mL of 10,000 mg/L Ca, 1mL of 10,000 mg/L Fe and 1mL of 10,000 mg/L Mg. Dilute to volume with Milli-Q H2O and mix by inverting several times. Transfer to a clean Nalgene bottle. Prepare every 6 months or as needed.Concentration: 100,000ug/L Al, Ca, Fe and Mg

A9 Calibration Standard #9: Into a 100mL volumetric flask, add 50mL of Milli-Q H2O, 1mL of conc. HNO3 and 1mL of HCl. Add 5mL of 10,000 mg/L Al, 5mL of 10,000 mg/L Ca, 5mL of 10,000 mg/L Fe and 5mL of 10,000 mg/L Mg. Dilute

to volume with Milli-Q H2O and mix by inverting several times. Transfer to a clean Nalgene bottle. Prepare every 6 months or as needed. Concentration: 500,000ug/L Al, Ca, Fe and Mg

A10 Calibration Blank: Into a 1 L. volumetric flask, add 750 mL of Milli-Q water and 10 mL of conc. HNO3 and 10mL HCl. Mix, dilute to volume with Milli-Q H2O. Transfer to a clean 1 L. nalgene bottle. Prepare every 6 months or as needed.

Appendix B
Standard Preparation for "Shell" Method

B1. Calibration Standard 1: Into a 100mL volumetric flask, add 50mL of Milli-Q H2O, 1mL of conc. HNO3 and 1mL conc. HCl. Add 10mL SPEX Quality Control 7 and 10mL of SPEX Quality Control 21. Dilute to volume with Milli-Q H2O and mix by inverting several times. Transfer to a clean Nalgene bottle. Prepare every 6 months or as needed. Concentration: 10,000ug/L
As, Be, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Mo, Ni, Pb, Sb, Se, Tl, V, Zn, Ag, Al, Ba

B2. Calibration Standard 2: Into a 100mL volumetric flask, add 50mL of Milli-Q H2O, 1mL of conc. HNO3 and 1mL conc. HCl. Add 5mL 10,000mg/L Ca, 5mL 10,000 Fe, 5mL 10,000 Al and 5mL 10,000 Mg. Dilute to volume with Milli-Q H2O and mix by inverting several times. Transfer to a clean Nalgene bottle. Prepare every 6 months or as needed. Concentration: 500,000 ug/L Al, Ca, Fe and Mg.

B3. Calibration Standard 3: Into a 100mL volumetric flask, add 50mL of Milli-Q H2O, 1mL of conc. HNO3 and 1mL conc. HCl. Add 1mL SPEX Quality Control 7 and 1mL of SPEX Quality Control 21. Dilute to volume with Milli-Q H2O and mix by inverting several times. Transfer to a clean Nalgene bottle. Prepare every 6 months or as needed. Concentration: 1,000ug/L
As, Be, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Mo, Ni, Pb, Sb, Se, Tl, V, Zn, Ag, Al, Ba

B4. Calibration Standard 4: Into a 100mL volumetric flask, add 50mL of Milli-Q H2O, 1 mL of conc. HNO3 and 1mL conc. HCL. Add 0.2mL of Ultra Zn 1000ug/L standard or equivalent. Dilute to volume with Milli-Q H2O and mix by inverting several times. Transfer to a clean Nalgene bottle. Prepare every 6 months or as needed. Concentration: 2000ug/L Zn.

Appendix C

Standard Prep for Sodium and Potassium analysis.

C1 Calibration Standard #1: Into a 200mL volumetric flask, add 100mL of Milli-Q H2O, 2mL of conc. HNO3 and 2mL conc. HCl. Add 0.2mL Sodium 1000mg/L and 0.2mL Potassium 1000mg/L. Dilute to volume with Milli-Q H2O and mix by inverting several times. Transfer to a clean Nalgene bottle. Prepare every 6 months or as needed. Concentration: 1 mg/L Na, K.

C2 Calibration Standard #2: Into a 200mL volumetric flask, add 100mL of Milli-Q H2O, 2mL of conc. HNO3 and 2mL conc. HCl. Add 1mL Sodium 1000mg/L and 1mL Potassium 1000mg/L. Dilute to volume with Milli-Q H2O and mix by inverting several times. Transfer to a clean Nalgene bottle. Prepare every 6 months or as needed. Concentration: 5 mg/L Na, K.

C3. Calibration Standard #3: Into a 200mL volumetric flask, add 100mL of Milli-Q H2O, 2mL of conc. HNO3 and 2mL conc. HCl. Add 2mL Sodium 1000mg/L and 2mL Potassium 1000mg/L. Dilute to volume with Milli-Q H2O and mix by inverting several times. Transfer to a clean Nalgene bottle. Prepare every 6 months or as needed. Concentration: 10 mg/L Na, K.

C4. Calibration Standard #4: Into a 200mL volumetric flask, add 100mL of Milli-Q H2O, 2mL of conc. HNO3 and 2mL conc. HCl. Add 5mL Sodium 1000mg/L and 5mL Potassium 1000mg/L. Dilute to volume with Milli-Q H2O and mix by inverting several times. Transfer to a clean Nalgene bottle. Prepare every 6 months or as needed. Concentration: 25 mg/L Na, K.

C5. Calibration Standard #5: Into a 200mL volumetric flask, add 100mL of Milli-Q H2O, 2mL of conc. HNO3 and 2mL conc. HCl. Add 10mL Sodium 1000mg/L and 10mL Potassium 1000mg/L. Dilute to volume with Milli-Q H2O and mix by inverting several times. Transfer to a clean Nalgene bottle. Prepare every 6 months or as needed. Concentration: 50 mg/L Na, K.

C6. Calibration Standard #6: Into a 200mL volumetric flask, add 100mL of Milli-Q H2O, 2mL of conc. HNO3 and 2mL conc. HCl. Add 20mL Sodium 1000mg/L and 20mL Potassium 1000mg/L. Dilute to volume with Milli-Q H2O and mix by inverting several times. Transfer to a clean Nalgene bottle. Prepare every 6 months or as needed. Concentration: 100 mg/L Na, K.

C7. ICV/CCV: Into a 200mL volumetric flask, add 100mL Milli-Q water, 2mL of conc. HNO3 and 2mL of conc. HCl. Add 1.0mL 10,000mg/L Na and 1.0mL 10,000 K. Dilute to volume with Milli-Q water and mix by inverting several times. Transfer to a clean Nalgene bottle. Prepare every 6 months or as needed. Concentration: 50 mg/L

C8. ICSAB: Into a 200mL volumetric flask, add 100mL Milli-Q water, 2mL of conc. HNO3 and 2mL of conc. HCl. Add 25 mL of SPEX Interferents A or equivalent,

2.0mL 10,000mg/L Na and 2.0mL 10,000 K. Dilute to volume with Milli-Q water and mix by inverting several times. Transfer to a clean Nalgene bottle. Prepare every 6 months or as needed. Concentration: 100mg/L Na and K, 500,000ug/L Al, Ca and Mg, 200mg/L Fe.

C9. Lithium/Yttrium internal standard: Into a 1L volumetric flask, add 500mL Milli-Q water, 1mL conc HCl and 4mL conc. HNO3. Add 1mL 10,000 mg/L Yttrium and 20g of Lithium Nitrate. Dilute to volume with Milli-Q water and mix until all Lithium Nitrate is dissolved. Transfer to a clean Nalgene bottle. Prepare every 6 months or as needed.

Appendix D

Standard Prep for Boron Analysis

D1. Calibration Standard #1: Into a 100mL **plastic** volumetric flask, add 50mL of Milli-Q H2O, 1mL of conc. HNO3 and 1mL conc. HCl. Add 0.2 mL 1000mg/L Boron. Dilute to volume with Milli-Q H2O and mix by inverting several times. Transfer to a clean Nalgene bottle. Prepare every 6 months or as needed.Concentration: 2000 ug/L

D2. Calibration Standard #2: Into a 100mL **plastic** volumetric flask, add 50mL of Milli-Q H2O, 1mL of conc. HNO3 and 1mL conc. HCl. Add 0.1 mL 1000mg/L Boron. Dilute to volume with Milli-Q H2O and mix by inverting several times. Transfer to a clean Nalgene bottle. Prepare every 6 months or as needed.Concentration: 1000 ug/L

D3. Calibration Standard #3: Into a 100mL **plastic** volumetric flask, add 50mL of Milli-Q H2O, 1mL of conc. HNO3 and 1mL conc. HCl. Add 0.02 mL 1000mg/L Boron. Dilute to volume with Milli-Q H2O and mix by inverting several times. Transfer to a clean Nalgene bottle. Prepare every 6 months or as needed.Concentration: 200 ug/L

D4. ICV/CCV: Into a 100mL **plastic** volumetric flask, add 50mL of Milli-Q water, 1 mL of conc HNO3 and 1mL conc. HCl. Add 0.1mL of 1000mg/L Boron (alternate source from calibration source). Dilute to volume with Milli-Q water and mix by inverting several times. Transfer to a clean Nalgene bottle. Prepare every 6 months or as needed. Concentration: 1000 ug/L.

D5. ICSAB: Into a 100mL **plastic** volumetric flask, add 50mL of Milli-Q water, 1 mL of conc HNO3 and 1mL conc. HCl. Add 0.05mL of 1000mg/L Boron and 10mL of SPEX Interferent A or equivalent. Dilute to volume with Milli-Q water and mix by inverting several times. Transfer to a clean Nalgene bottle. Prepare every 6 months or as needed. Concentration: 500 ug/L B, 500,000 ug/L Mg, Ca and Al, 200,000ug/L Fe.

Trace 61E ICAP Data Review Checklist	Analysis Date:			Data File:		Date review:
Cal Std ID: LIMS # :	Analyst:		Reviewer:		Approved?	Yes No
Calibration Parameters - 6010 200.7	**YES**	**NO**	**YES**	**NO**		**Comments:**
1) Calibration linearity - r > 0.995						
2) ICV 90-110% 95-105%						
3) ICB ABS 3X DL ABS DL						
4) ICSAB 80-120% True Value						
5) ICSA +/- 2X RL						
6) CRI - (2X CRDL or LOD) 50-150%						
7) CCV1/CCB1-90-110% / 3X DL ABS DL						
8) CCV2/CCB2						
9) CCV3/CCB3						
10) CCV4/CCB4						
11) CCV5/CCB5						
12) CCV6/CCB6						
13) CCV7/CCB7						
14) CCV8/CCB8						
15) CCV9/CCB9						
16) CCV10/CCB10						
Preparation Batch Parameters	**YES**	**NO**	**YES**	**NO**		**Comments:**
Prep Batch ID#:_____ Dig. Meth._____						
Prep. Blank - <LOD or RL						
LCS - generated limits;attached list						
Spiked samples in batch:						
a)_____ matrix = _____						
b)_____ matrix = _____						
c)_____ matrix = _____						
d)_____ matrix = _____						
e)_____ matrix = _____						
PDS 75-125% sample#_____						
Prep Batch ID#:_____ Dig. Meth._____						
Prep. Blank - <LOD or RL						
LCS - generated limits;attached list						
Spiked samples in batch:						
a)_____ matrix = _____						
b)_____ matrix = _____						
c)_____ matrix = _____						
d)_____ matrix = _____						
e)_____ matrix = _____						
PDS 75-125% sample#_____						
Prep Batch ID#:_____ Dig. Meth._____						
Prep. Blank - <LOD or RL						
LCS - generated limits;attached list						
Spiked samples in batch:						
a)_____ matrix = _____						
b)_____ matrix = _____						
c)_____ matrix = _____						
d)_____ matrix = _____						
e)_____ matrix = _____						
PDS 75-125% sample#						

Total Metals Sample Preparation for GFAA

Approved by: _____
Laboratory Director

Reviewed by: _____
Quality Assurance

Reviewed by: _____
Chemistry Section Manager

1.0 SCOPE AND APPLICATION

1.1 This digestion procedure is used for the preparation of aqueous samples, mobility-procedure extracts, and wastes that contain suspended solids for analysis by furnace atomic absorption spectroscopy (GFAA) for the metals listed below.

1.2 Samples prepared by this method may be analyzed by GFAA for the following metals:

Beryllium	Lead
Cadmium	Molybdenum
Chromium	Thallium
Cobalt	Vanadium

1.3

	Total Metals
Preservative	pH <2 HNO_3
Hold Time	180 days

2.0 REFERENCES

2.1 *Test Methods for Evaluating Solid Waste,* 1986, SW-846, 3rd Edition ,1992 Method 3020A.

3.0 DEFINITIONS

3.1 Batch - A batch consists of a maximum of 20 samples of similar matrix which are prepared and analyzed in the same manner. Each batch is given a unique prep batch number for tracking purposes.

3.2 Reagent Blank - A solution of de-ionized water, (containing in correct proportion, all reagents required by the method), used with the calibration standards to standardize the instrument, as a calibration blank, and for sample dilution.

3.3 LCS (Laboratory Control Sample)- A mid-range standard prepared from a source different from that used for calibration standards. The LCS is used to verify the accuracy of the calibration at the start of an analytical run, and is analyzed immediately after the initial CB (ICB).

3.4 PB or MB (Prep Blank or Method Blank)- A reagent blank (see 3.2) which is carried through the entire preparation and and analytical method. The method blank is used to detect possible contamination that may occur prior to or during the sample preparation process. A minimum of one MB is prepared per batch (see 3.1) and is analyzed at the beginning of an analytical batch.

3.5 MS-MSD (Matrix Spike-Matrix Spike Duplicate): - Two separate sample aliquots to which a known concentration of analyte has been added which is carried through the entire preparation and analytical procedure. The purpose of a matrix spike is to reveal any matrix effect from the sample on the recovery of the analyte by the method being used. An MS-MSD pair is prepared for every batch (see 3.1). Failure to meet criteria may be due to poor recovery during the preparation method or to matrix interference within the digestate. To be considered acceptable, MSD's must meet both the same % recovery criteria as an MS, and the same % RPD as a duplicate sample. MS/MSD %RPD and may be used as acceptance criteria for duplicate analysis.

3.5 Detection Limit (DL) or Contract Required Detection Limit (CRDL) Standard: Detection level standard at a level near the reporting limit, or at a level specified by client contract. When required, it is to be analyzed following the ICB, and prior to the last CCV standard in the run.

4.0 SAFETY

4.1 Gloves, protective eyewear, and protective clothing should be worn to protect against unnecessary exposure to hazardous chemicals and contaminants in samples. All activities performed while following this procedure should utilize appropriate laboratory safety systems.

5.0 METHOD

5.1 APPARATUS AND MATERIALS

5.1.1 Environmental Express Hotblock Digestion Apparatus: To maintain a temperature of 90-95C.

5.1.2 50 mL Graduated hotblock digestion tubes, with watch glasses and storage caps.

5.1.3 Qualitative filter paper and filter funnels.

5.1.4 Filtermate teflon digestion tube filters: Environmental Express

5.1.5 Thermometer: For monitoring temperature of the block at beginning and end of digestion process.

5.1.6 Acrylic digestion tube carriers. For suspending tubes in blocks and for cooling tubes on the counter.

5.1.7 Foam digestion tube racks for storage of prepped samples.

5.2 REAGENTS

5.2.1 ASTM Type II Water (ASTM D1193): Water should be monitored for impurities.

5.2.2 Concentrated Nitric Acid, trace metals grade (HNO_3): Acid is of sufficient purity and comes with a certificate of analysis. All metals levels are lower than our lowest detection limits for any given element. However, each acid lot is logged in and tracked to each individual bottle to help us identify when and if a bottle either becomes contaminated or arrives from out supplier with unacceptable levels of metals. If contamination is detected at any point and the problem is limited to a given bottle, the acid may be replaced with another bottle from the same lot. If the entire lot is a problem, then any remaining acid from the contaminated lot will be removed from the lab and a replacement acid from a different lot of sufficient purity shall be obtained.

5.3 PROCEDURE

5.3.1 Measure 50 mls of well-mixed sample into a clean, labeled hot-block digestion tube. For blanks use same amount of Type II water.

5.3.2 For samples to be spiked (MS, MSD, LFB/LCS), add the appropriate amount of spiking solution to sample (see Predigestion Spikes-LCS & LFB chart attached).

5.3.3 Add 1.5mL conc. Trace Metal Grade HNO3 from dispenser.

5.3.4 Cover with a plastic ribbed watch-glass for samples that may react strongly to acid or heat. Lower the tube racks into hot-block and heat at 90-95^0 C until the volume has been reduced to 5-7mls. Ensure that the sample does not boil and that no portion of the bottom of the tube is allowed to go dry. If this should occur, discard the sample and start over.

5.3.5 Remove tubes from block using rack. Cool tubes, then add another 1.5mL portion of conc. HNO3. Cover all tubes with watch-glasses. Reflux gently for one hour. At this point inspect the digestate. A complete digestion is indicated when the digestate becomes light in color or does not change in color or appearance with repeated refluxing. For those samples which are

not completely digested after the first reflux, continue to alternate additons of 1.5mL nitric with 30-60 minute reflux periods until they are completely digested.

5.3.6 For those digestions in which the color is stabilized, evaporate down to a low volume (3-5mL). If the remaining solution is clear and without suspended particles, cool and dilute to 50mL final volume. If not, then add 5mL of DI water to the tube and heat for an additonal 10-15 minutes to help solubilize the remaining residue.

5.3.7 Remove each tube from block using the tube racks provided and allow them to cool. Dilute to original volume and let sample sit to allow solids to settle out. If solids do not settle readily and remain suspended throughout sample, then it will be necessary to filter prior to analysis. Using the Environmental Express tube filters, push the filter down through the sample till it sits on the bottom. Alternately, filter through acid rinsed filter paper, rinsing at least 3 times into the funnel till filled to the line. When using the tube filter fill tube to the line first. If using filter and funnel, dilute to line after.

5.3.8 Cap sample, taking care not to touch underside of cap or inside of container. To minimize contamination and for safety purposes appropriate gloves must be worn at any point where sample solution is being transferred. If gloves become stained and dirty, discard and get a new pair as the surface of the gloves themselves may also transfer contaminants. When finished, cap all digestates and put into foam racks for storage until analysis.

6.0 QUALITY CONTROL

6.1 For each analytical batch of samples processed, a method blank (Type II water and reagents) should be carried throughout the entire sample preparation procedure.

6.2 Prepare one MS/MSD per matrix per 20 or fewer samples per digestion batch.

6.3 Prepare one LFB/ LCS (lab fortified blank/ lab control sample) for each digestion batch by spiking reagent water with the same amount of analyte used for the MS/MSD. The LFB/LCS is prepared from one or more commercially prepared reference standards but must be from a source different from that used to prepare the calibration standards for a given instrument. The LFB/LCS solution is carried through the entire digestion procedure. Prepare one LCS for every 20 samples on a given matrix per day.

6.4 Monitor block thermometer in one block location, record temperature in the sample prep book after 30 min, for the initial block temperature recording. Record again at the end of the digestion process.

7.0 MS-MSD, LFB/LCS Prep for GFAA

SPIKE, LCS & LFB ANALYSIS- ICP/FLAA Predigestion Spikes-LCS & LFB					
Element	**Spike Amt mL**	**Spike Stock**	**Stock Conc mg/L**	**Final Vol mL**	**Expected Conc. ug/L**
Antimony-GFAA	1.0	A	1000.0	50.0	20.0
Arsenic-GFAA	1.0	A	1000.0	50.0	20.0
Chromium-GFAA	1.0	A	1000.0	50.0	20.0
Lead-GFAA	1.0	A	1000.0	50.0	20.0
Selenium-GFAA	1.0	A	1000.0	50.0	20.0
Thallium-GFAA	1.0	A	1000.0	50.0	20.0

Standard Source		
Supplier	**Dilution**	**Solution**
Inorg Vent.-SPK1(multi-element std)	1/100	A

CT Laboratories
Baraboo Laboratory Divison

Title: **Total Metals Sample Preparation for FLAA and ICP**

SOP Number: **6225B**

Prepared by: _____
Date

Technical Review by: _____
Date

Reviewed by: _____
Quality Assurance ***Date***

_____
Laboratory Director ***Date***

SOP Manual Control Number:_____

1.0 SCOPE AND APPLICATION

1.1 This digestion procedure is used for the preparation of aqueous samples, EP and mobility-procedure extracts, and wastes that contain suspended solids for analysis, by ICP or FLAA, for the metals listed below. The procedure is used to determine total metals.

1.2 Samples prepared by this method may be analyzed by ICP or FLAA for the following:

Aluminum	Calcium	Lead
Potassium	Arsenic*	Chromium
Magnesium	Selenium*	Barium
Cobalt	Manganese	Sodium
Beryllium	Copper	Molybdenum
Thallium	Cadmium	Iron
Nickel	Vanadium	Zinc
Boron*		

*Analysis by ICP

1.3 This digestion procedure is not suitable for samples to be analyzed by graphite furnace atomic absorption spectroscopy because hydrochloric acid can cause interferences during furnace atomization.

2.0 METHOD SUMMARY

2.1 A mixture of nitric acid and the material to be analyzed is refluxed in a covered digestion tube. This step is repeated with additional portions of nitric acid. After the digestate has been brought to a low volume, it is refluxed with hydrochloric acid and brought up to volume. If sample should go to dryness, it must be discarded and the sample reprepared.

3.0 DEFINITIONS

3.1 Batch - A batch consists of a maximum of 20 samples of similar matrix which are prepared and analyzed in the same manner. Each batch is given a unique prep batch number for tracking purposes.

3.2 Reagent Blank - A solution of de-ionized water, (containing in correct proportion, all reagents required by the method), used with the calibration standards to standardize the instrument, as a calibration blank, and for sample dilution.

3.3 LCS (Laboratory Control Sample)- A mid-range standard prepared from a source different from that used for calibration standards. The LCS is used to verify the accuracy of the digestion process. A minimum of one LCS is prepared per batch and is analyzed at the beginning of an analytical batch.

3.4 PB or MB (Prep Blank or Method Blank)- A reagent blank which is carried through the entire preparation and and analytical method. The method blank is used to detect possible contamination that may occur prior to or during the sample preparation process. A minimum of one MB is prepared per batch and is analyzed at the beginning of an analytical batch.

3.5 MS-MSD (Matrix Spike-Matrix Spike Duplicate): - Two separate sample aliquots to which a known concentration of analyte has been added which is

carried through the entire preparation and analytical procedure. The purpose of a matrix spike is to reveal any matrix effect from the sample on the recovery of the analyte by the method being used. An MS-MSD pair is prepared for every batch of routine samples or an MS/DUP pair is prepared for every batch of ACOE samples. Failure to meet criteria may be due to poor recovery during the preparation method or to matrix interference within the digestate. To be considered acceptable, MSD's must meet both the same % recovery criteria as an MS, and the same % RPD as a duplicate sample. MS/MSD %RPD and may be used as acceptance criteria for duplicate analysis.

3.6 Detection Limit (DL) or Contract Required Detection Limit (CRDL) Standard: Detection level standard at a level near the reporting limit, or at a level specified by client contract. When required, it is to be analyzed following the ICB, and prior to the last CCV standard in the run.

3.7 Duplicate (DUP)- A separate aliquot of sample which has been carried through the entire preparation and analytical procedure the same as the original sample. One duplicate per batch is prepared for ACOE work.

4.0 HEALTH AND SAFETY

4.1 Gloves, protective eyewear, and protective clothing should be worn to protect against unnecessary exposure to hazardous chemicals and contaminants in samples. All activities performed while following this procedure should utilize appropriate laboratory safety systems

5.0 CAUTIONS

5.1 Do not allow samples to evaporate to dryness. If the samples do go to dryness, they must be reprepped.

5.2 Use caution when adding acid to hot samples. Sample can foam and splash when the acid is being added.

6.0 INTERFERENCES

6.1 This digestion procedure is not suitable for samples to be analyzed by graphite furnace atomic absorption spectroscopy because hydrochloric acid can cause interferences during furnace atomization.

7.0 PERSONNEL QUALIFICATIONS

7.1 All personnel performing this analysis should be instructed in the use of personal protective equipment prior to beginning analysis.

7.2 All personnel performing this analysis should have a valid IDC prior to performing preparation on samples.

8.0 APPARATUS AND MATERIALS

8.1 Environmental Express Hotblock Digestion Apparatus: To maintain a temperature of 90-95C.

8.2 50 mL Class A Graduated hotblock digestion tubes, with watch glasses and storage caps (Environmental Express p/n SC475 and SC505 or equivalent)

8.3 Qualitative filter paper and filter funnels.

8.4 Filtermate Teflon digestion tube filters: (Environmental Express p/n SC0401 or equivalent)

8.5 Thermometer: For monitoring temperature of the block at beginning and end of digestion process.

8.6 Acrylic digestion tube carriers. For suspending tubes in blocks and for cooling tubes on the counter.

8.7 Foam digestion tube racks for storage of prepped samples.

8.8 REAGENTS

8.8.1 ASTM Type II Water (ASTM D1193): Water should be monitored for impurities.

8.8.2 Concentrated Nitric Acid, trace metals grade (HNO_3): Acid is of sufficient purity and comes with a certificate of analysis. All metals levels are lower than our lowest detection limits for any given element. However, each acid lot is logged in and tracked to each individual bottle to identify potential contamination. If contamination is detected at any point and the problem is limited to a given bottle, the acid may be replaced with another bottle from the same lot. If the entire lot is contaminated, then any remaining acid from the lot will be removed from the lab and a replacement acid from a different lot of sufficient purity shall be obtained. All acid used to make standards is recorded in the log book when the standard is made.

8.8.3 Concentrated Hydrochloric Acid, trace metals grade (HCl): Acid is of sufficient purity and comes with a certificate of analysis. All metals levels are lower than our lowest detection limits for any given element. However, each acid lot is logged in and tracked to each individual bottle to identify potential contamination. If contamination is detected at any point and the problem is limited to a given bottle, the acid may be replaced with another bottle from the same lot. If the entire lot is contaminated, then any remaining acid from the lot will be removed from the lab and a replacement acid from a different lot of sufficient purity shall be obtained. All acid used to make standards is recorded in the log book when the standard is made.

8.8.4 Spike Standard Solution- SPEX cat # SPIKE-1-500

8.8.5 Molybdenum Standard- 1000 mg/L

8.8.6 Custom Standard- Ultra # ICUS 192- 20,000 mg/L Ca, 10,000 mg/L Mg and Na or equivalent

8.8.7 Potassium standard- 10,000 mg/L

8.8.8 Boron standard- 1,000 mg/L

9.0 INSTRUMENT OR METHOD CALIBRATION

9.1 There is no calibration necessary

10.0 SAMPLE COLLECTION, HANDLING AND PRESERVATION

	Total Metals
Preservative	pH <2 HNO_3
Hold Time	180 days

11.0 SAMPLE PREPARATION AND ANALYSIS

11.1 Turn on hot blocks by turning the silver timer switches, located on the right side of hood, clockwise. Allow hot blocks to come to temperature before placing samples into the blocks. Monitor temperature of the hot block by placing a thermometer immersed in water in a centrifuge tube and place it in the hot block. Temperature should be 90-95^{0}C for digestion. Move thermometer to various places on the block between digestion batches to insure that the the temperature is consistent throughout the block and that no "hot spots" have developed.

11.2 Measure 50 mls of well-mixed sample into a clean, labeled hot-block digestion tube. For blanks use same amount of Type II water.

11.3 For samples to be spiked (MS, MSD, LCS), add the appropriate amount of spiking solution to sample (see Predigestion Spikes-LCS & LFB chart attached).

11.4 Add 1.5 mL conc. Trace Metal Grade HNO3 from dispenser.

11.5 Cover with a plastic ribbed watch-glass for samples that may react strongly to acid or heat. Lower the tube racks into hot-block and heat at 90-95^0 C until the volume has been reduced to 5-10 mls. Do not allow sample to go dry. If this should occur, discard the sample and start over.

11.6 Remove tubes from block using rack. Add 1.5 mL conc. HNO3. Cover all tubes with watch-glasses. Place in block and reflux for one hour. Do not allow to go to dry. Continue addition of acid and heating until digestion is complete (usually indicated when the digestate is light colored or does not change in appearace while refluxing. Most samples will not require additional acid and heat cycles).

11.7 Remove tubes from block using rack. Add 2.5mL of Trace Metal Grade HCl. Cover tubes, and reflux for 15 minutes.

11.8 Remove each tube from block using the tube racks provided and allow them to cool.

11.9 Dilute to original volume inside tube. Hot block tubes are calibrated to volume $\pm$ 0.2mL. and let sample sit to allow solids to settle out. If solids do not settle readily and remain suspended throughout sample, then it will be necessary to filter prior to analysis. Using the Environmental Express filter-mates, push the filter down through the sample until it sits on the bottom. Alternately, filter through acid rinsed filter paper, rinsing at least 3 times into the funnel until filled to the 50 mL line. When using the tube filter fill tube to the 50 mL line first. If using filter and funnel, dilute to 50 mL line after.

11.10 Cap sample, taking care not to touch underside of cap or inside of container. To minimize contamination and for safety purposes appropriate gloves must be worn at any point where sample solution is being transferred. If gloves become stained and dirty, discard and replace as the surface of the gloves themselves may also transfer contaminants.

12.0 TROUBLESHOOTING AND MAINTENANCE

12.1 Refer to the Environmental Express maunal for troubleshooting directions.

13.0 DATA ACQUISITION, CALCULATIONS AND REDUCTION

13.1 There are no calculations associated with this procedure.

14.0 COMPUTER HARDWARE AND SOFTWARE

14.1 Computer with StarLIMS.

15.0 DATA MANAGEMENT AND RECORD MANAGEMENT

15.1 Data is recorded in the Metals digestion log.

15.2 Prep data is entered into LIMS, and then the batch sheet is given to the metals prep analyst.

16.0 QUALITY CONTROL AND QUALITY ASSURANCE

16.1 For each analytical batch of samples processed, a method blank (Type II water and reagents) should be carried throughout the entire sample preparation procedure.

16.2 Prepare one MS/MSD per matrix per 20 or fewer samples per digestion batch.

16.3 Prepare one LCS (lab control sample) for each digestion batch by spiking reagent water with the same amount of analyte used for the MS/MSD. The LCS is prepared from one or more commercially prepared reference standards but must be from a source different from that used to prepare the calibration standards for a given instrument. The LCS solution is carried through the entire digestion procedure. Prepare one LCS for every 20 samples on a given matrix per day.

16.4 Monitor block thermometer in one block location, record temperature in the sample prep book after 30 min, for the initial block temperature recording. Record again at the end of the digestion process.

17.0 REFERENCES

17.1 *Test Methods for Evaluating Solid Waste*. EPA, SW-846, 3rd Edition , 1992 Method 3010A.

SPIKE, LCS, & LFB ANALYSIS- ICP/FLAA Predigestion Spikes-LCS & LFB					
Element	**Spike Amt mL**	**Spike Stock**	**Stock Conc mg/L**	**Final Vol mL**	**Expected Conc ug/L**
Aluminum	1	**A**	200	50	4000
Antimony	1	**A**	50	50	1000
Arsenic	1	**A**	200	50	4000
Barium	1	**A**	200	50	4000
Beryllium	1	**A**	5	50	100
Boron	0.1	**D**	1,000	50	2000
Cadmium	1	**A**	5	50	100
Calcium	0.5	**C**	20,000	50	200000
Chromium	1	**A**	20	50	400
Cobalt	1	**A**	50	50	1000
Copper	1	**A**	25	50	500
Iron	1	**A**	100	50	2000
Lead	1	**A**	50	50	1000
Manganese	1	**A**	50	50	1000
Magnesium	0.5	**C**	10,000	50	100000
Molybdenum	0.1	**B**	1000	50	2000
Potassium	0.5	**E**	10,000	50	100000
Nickel	1	**A**	50	50	1000
Selenium	1	**A**	200	50	4000
Silver	1	**A**	5	50	100
Sodium	0.5	**C**	10,000	50	10,000
Thallium	1	**A**	200	50	4000
Vanadium	1	**A**	50	50	1000
Zinc	1	**A**	50	50	1000

Spike Solutions		
Supplier	**Lot #/ std**	**Stock**
SPEX Certiprep	SPIKE 1-500	**A**
Molybdenum	1000 mg/L	**B**
Ultra	ICUS 192	**C**
Boron	1000 mg/L	**D**
Potassium	10,000 mg/L	**E**

Analyst: **Metals Digestion Summary-CT Laboratories Baraboo** **Date:**

Prep Batch#	Sample ID#	Matrix*	Prep Method**	Sample Amt gms or mls	Final Volume, mLs	Blk	Dup	MS	MSD	Spike/LCS/ LFB info	Acid ID#

Method Temperature Verification					Review date/initials
					Digestion Tube Lot #
				Comments	

CT Laboratories
Baraboo Laboratory Divison

Title: **Acid Digestion of Solids and Semi-solids for Total Metals**

SOP Number: **6230B**

Prepared by: _____
Date

Technical Review by: _____
Date

Reviewed by: _____
Quality Assurance ***Date***

_____
Laboratory Director ***Date***

SOP Manual Control Number:_____

1.0 SCOPE AND APPLICATION

1.1 This method is an acid digestion procedure used to prepare soils, sediments, sludges, oils, paint chips, tissue samples, wipes and other solid waste samples for analysis by ICP, FLAA, or GFAA spectroscopy for the following metals:

Aluminum*	Calcium*	Magnesium*	Silver*
Antimony*	Chromium	Manganese*	Sodium*
Arsenic	Cobalt	Molybdenum	Strontium*
Barium*	Copper*	Nickel *	Thallium
Beryllium	Iron	Potassium*	Vanadium*
Cadmium	Lead	Selenium	Zinc*

* Cannot be used for GFAA for selected element

1.2 For analysis by ICP or FLAA both HCl and HNO_3 are used in the digestion procedure. For analysis by GFAA, HNO_3 only is used.

2.0 METHOD SUMMARY

2.1 For the digestion of samples, a representative 0.5 gram sample or 1-2g sample for ACOE work is digested with repeated additions of nitric acid and hydrogen peroxide

2.2 For GFAA analysis, the resultant digestate is reduced in volume while heating and then diluted to a final volume of 50 mL.

2.3 For ICP (trace) or FLAA analyses, hydrochloric acid (HCl) is added to the initial digestate and the sample is refluxed. The digestate is then diluted to a final volume of 50 mL.

3.0 DEFINITIONS

3.1 Batch - A batch consists of a maximum of 20 samples of similar matrix which are prepared and analyzed in the same manner. Each batch is given a unique prep batch number for tracking purposes.

3.2 Reagent Blank - A solution of de-ionized water, (containing in correct proportion, all reagents required by the method), used with the calibration standards to standardize the instrument, as a calibration blank, and for sample dilution.

3.3 LCS (Laboratory Control Sample)- A mid-range standard prepared from a source different from that used for calibration standards. The LCS is used to verify the accuracy of the digestion procedure and is analyzed at the beginning of the analytical batch .

3.4 MB (Method Blank)- A reagent blank which is carried through the entire preparation and analytical method. The method blank is used to detect possible contamination that may occur prior to or during the sample preparation process. A minimum of one MB is prepared per batch and is analyzed at the beginning of an analytical batch.

3.5 MS-MSD (Matrix Spike-Matrix Spike Duplicate): - Two separate sample aliquots to which a known concentration of analyte has been added which is carried through the entire preparation and analytical procedure. The purpose of a matrix spike is to reveal any matrix effect from the sample on the recovery of the analyte by the method being used. An MS-MSD pair is prepared for every batch (see 3.1) of routine samples. An MS and a DUP are prepared for every ACOE batch. Failure to meet criteria may be due to poor recovery during the preparation method or to matrix interference within the digestate. To be considered acceptable, MSD's must meet both the same % recovery criteria as an MS, and the same % RPD as a duplicate sample. MS/MSD %RPD may be used as acceptance criteria for duplicate analysis.

3.6 Duplicate (DUP)- A separate aliquot of sample which has been carried through the entire preparation and analytical procedure the same as the original sample. One duplicate per batch is prepared for ACOE work.

4.0 HEALTH AND SAFETY

4.1 Gloves, protective eyewear, and protective clothing should be worn to protect against unnecessary exposure to hazardous chemicals and contaminants in samples. All activities performed while following this procedure should utilize appropriate laboratory safety systems.

5.0 CAUTIONS

5.1 The extracts from GFAA and FLAA/ICP are not interchangeable and should only be used with the analytical determinations outlined.

5.2 This method is not a total digestion technique for most samples. It is a very strong acid digestion that will dissolve almost all elements that could become "environmentally available." By design, elements bound in silicate structures are not normally dissolved by this procedure as they are not usually mobile in the environment.

5.3 Reagent grade chemicals shall be used in all tests. The reagent blank must be less than the MDL in order to be used.

6.0 INTERFERENCES

6.1 Sludge samples can contain diverse matrix types, each of which may present its own analytical challenge. Spiked samples and any relevant standard reference material should be processed in accordance with the

quality control requirements to aid in determining whether Method 3050B is applicable to a given waste.

7.0 PERSONNEL QUALIFICATIONS

7.1 All personnel performing this analysis shall be instructed in the use of personal protective equipment prior to beginning analysis.

7.2 Personnel shall know how to read a meniscus and how to use a pipette correctly.

8.0 APPARATUS AND MATERIALS

8.1 Equipment Required

8.1.1 Environmental Express Hotblock Digestion Apparatus: To maintain a temperature of 90-95C.

8.1.2 50 mL Class A plastic hotblock digestion tubes, with watch glasses and storage caps. (Environmental Express p/n SC475 and SC505 or equivalent)

8.1.3 Qualitative filter paper and filter funnels.

8.1.4 Filtermate Teflon digestion tube filters: (Environmental Express p/n SC0401 or equivalent)

8.1.5 Thermometer: For monitoring temperature of the block at beginning and end of digestion process.

8.1.6 Balance: 0.01g capacity.

8.2 REAGENTS

8.2.1 ASTM Type II Water (ASTM D1193): Water should be monitored for impurities.

8.2.2 Concentrated Nitric Acid, trace metals grade (HNO_3): Acid is of sufficient purity and comes with a certificate of analysis. All metals levels are lower than our lowest detection limits for any given element. However, each acid lot is logged in and tracked to each individual bottle to identify potential contamination problems. If contamination is detected at any point and the problem is limited to a given bottle, the acid may be replaced with another bottle from the same lot. If the entire lot is a problem, then any remaining acid from the contaminated lot will be removed from the lab and a replacement acid from a different lot of sufficient purity shall be obtained. All acid used to make standards is recorded in the log book when the standard is made.

8.2.3 Concentrated Hydrochloric Acid, trace metals grade (HCl): Acid is of sufficient purity and comes with a certificate of analysis. All metals levels are lower than our lowest detection limits for any given element. However, each acid lot is logged in and tracked to each individual bottle to identify potential contamination problems. If contamination is detected at any point and the problem is limited to a given bottle, the acid may be replaced with

another bottle from the same lot. If the entire lot is a problem, then any remaining acid from the contaminated lot will be removed from the lab and a replacement acid from a different lot of sufficient purity shall be obtained. All acid used to make standards is recorded in the log book when the standard is made.

8.2.4 Hydrogen Peroxide, 30% (H_2O_2): Each peroxide lot is logged in and tracked to each individual bottle to identify potential contamination problems. If contamination is detected at any point and the problem is limited to a given bottle, the peroxide may be replaced with another bottle from the same lot. If the entire lot is a problem, then any remaining peroxide from the contaminated lot will be removed from the lab and a replacement hydrogen peroxide bottle from a different lot shall be obtained.

8.2.5 SPEX Certiprep Spike- SPEX catalog number SPIKE 1-500

8.2.6 Molybdenum- 1,000 mg/L standard SPEX PLMO9-2Y or equivalent

8.2.7 Potassium-10,000 mg/L standard PLK2-3X or equivalent

8.2.8 Ultra Custom Standard – Ultra Catalog numer ICUS192 or equivalent

8.2.9 Inorganic Venture Spike- Inorganic Venture catalog number SPK1 or equivalent

9.0 INSTRUMENT OR METHOD CALIBRATION

Please refer to the Hot Block operator manual for instrument temperature calibration.

10.0 SAMPLE COLLECTION, HANDLING AND PRESERVATION

10.1 All sample containers must be demonstrated to be free of contamination at or below the reporting limit. Plastic and glass containers are both suitable. Note: Environmental Express provides a certificate of analysis with each tube lot.

10.2 Samples shall be refrigerated upon receipt and analyzed within 180 days.

11.0 SAMPLE PREPARATION AND ANALYSIS

11.1 Turn on hot blocks to allow them to warm up. The switch is located on the right outer side of hood. Place a thermometer into a centrifuge tube of water and place it in the hot block to monitor the temperature of the hot block to insure the temperature is acceptable prior to use. The temperature should be 95 ± 5^0C for digestion.

11.2 Carefully weigh on a balance and then transfer a 0.5 g representative portion (for routine work) or for ACOE work 1-2g randomly of the sample to a tube, or use a known volume of a sludge sample based on the viscosity of the sample. Do not use metal spatulas. Refer to the subsampling SOP FO-10 for instructions on subsampling from the original sample. For some samples it is acceptable to use a larger sample size following the guidelines below:

Wet solids:	Up to 1.0 g.
Wipes:	The entire wipe is used.
Biological tissue:	Up to 2.0 g.
"liquidy" sludges	Up to 2.0 g

11.3 For samples to be spiked (MS, MSD, LCS), add the appropriate amount of spiking solution to sample (see Pre-digestion Spikes-LCS & LFB chart attached).

11.4 Add 5 mL 1:1 HNO_3 to routine samples or 10mL of 1:1 HNO_3 for ACOE samples, mix, and cover the tube with a watch glass. Do not handle the underside of the watch glass at any time, in order to prevent contamination. Place the tubes in the hotblock and heat the samples until they reflux for 10-15 minutes. For wipe samples, add DI water to wet the entire wipe if needed.

11.5 Add 2.5 mL concentrated HNO_3 to all routine samples and 5mL of concentrated HNO_3 to ACOE samples.

11.6 Place thermometer in one block location, record temperature in the sample prep book for the initial block temperature recording. Record again at the end of the digestion process in a different spot on the block. Rotate the placement of the thermometer between digestion batches to ensure that no "hot spots" develop on the block.

11.7 Return to the hotblock, and reflux the samples for 30 minutes. Do not allow the samples to go dry. If samples are still generating "brown" fumes, continue to add concentrated HNO_3 in 5mL increments until no more "brown" fumes are generated.

11.8 Allow the solution to evaporate to 2.5mL without boiling or heat at $95^0C \pm 5^0C$ without boiling for 2 hours. Do not allow samples to go to dryness.

11.9 Remove the samples from the hotblock and let cool to avoid excessive effervescence of hydrogen peroxide. Add 1mL of DI water to each tube. Add 1.5 mL of 30% hydrogen peroxide for routine samples and 3 mL 30% hydrogen peroxide for ACOE work (omit this step for Tin), return to hot block and heat gently until the effervescence subsides.

11.10 Repeat step 5.3.7 two times or until effervescence is minimal for routine samples using a maximum of 5mL of 30% hydrogen peroxide. For ACOE samples, add 30% hydrogen peroxide in 1mL increments, up to 10mL, until the sample effervescence is minimized or the sample consistency is unchanged. It will not be necessary to cool down the samples between additions if they do not react too strongly.

11.11 Return samples to hot block and heat until volume is reduced to 2.5mL or heat at $95^0C \pm 5^0C$ without boiling for 2 hours.

11.12 For samples to be analyzed by ICP or FLAA, add 5 mL concentrated HCl for routine samples or for ACOE samples add 10mL of concentrated HCl and reflux for an additional 15 minutes. Omit this step for samples to be analyzed by GFAA.

11.13 Remove each tube from block using the tube racks provided and allow them to cool. Dilute to exactly 50 mL using the guide on the digestion tube and let sample sit to allow solids to settle out. If solids do not settle readily and remain suspended throughout sample, then it will be necessary to filter prior to analysis. Using the Environmental Express tube filters, push the filter down through the sample till it sits on the bottom. The digestion tubes are calibrated to 50mL $\pm$ 0.2mL.

11.14 Cap sample, taking care not to touch underside of cap or inside of container. To minimize contamination and for safety purposes appropriate gloves must be worn at any point where sample solution is being transferred. If gloves become stained and dirty, discard and replace, as the surface of the gloves themselves may also transfer contaminants.

11.15 If the digestate is clear and without solids distributed throughout the liquid portion, sample aliquots may be decanted for analysis. If not, then filtration will be necessary prior to analysis. Follow instruction provided with filter-mate filters.

12.0 TROUBLESHOOTING

12.1 If method blank is higher than MDL, identify source of contamination. Contamination can come from many sources including the reagents used in the procedure and samples that were digested in the batch.

12.2 Over time, hot blocks can develop "hot spots". Monitor the temperature in different block spaces ensure that temperature is consistent throughout the hot block unit.

13.0 DATA ACQUISITION, CALCULATIONS AND DATA REDUCTION

There are no calculations for this method.

14.0 COMPUTER HARDWARE AND SOFTWARE

14.1 Computer with StarLIMS

15.0 DATA MANAGEMENT AND RECORD MANAGEMENT

15.1 Batch data information is recorded in the Digestion Log book.

15.2 Prep data is entered into LIMS, and then the batch sheet is given to the metals analyst.

16.0 QUALITY CONTROL

16.1 For each batch of samples processed, a method blank should be carried throughout the entire sample preparation procedure.

16.2 By matrix, prepare one MS/MSD for routine work or one MS/DUP for ACOE work per 20 or fewer samples per matrix per digestion batch.

16.3 Prepare one LCS (lab control sample) for each digestion batch. The LCS source is carried through the entire digestion procedure. Prepare one LCS for every 20 samples per medium per day.

17.0 REFERENCES

17.1 *Test Methods for Evaluating Solid Waste*. USEPA SW-846, Rev 2 Dec 1996, Method 3050B.

18.0 Prep Tables

18.1 ICP/FLAA Table

SPIKE & LFB ANALYSIS- ICP/FLAA Preparation Spikes-LCS & LFB					
Element	**Spike Amt mL**	**Spike Stock**	**Stock Conc mg/L**	**Final Vol: mL**	**Expected Conc. ug/L**
Aluminum	1	A	200	50	4000
Antimony	1	A	50	50	1000
Arsenic	1	A	200	50	4000
Barium	1	A	200	50	4000
Beryllium	1	A	5	50	100
Cadmium	1	A	5	50	100
Calcium	0.5	C	20,000	50	200000
Chromium	1	A	20	50	400
Cobalt	1	A	50	50	1000
Copper	1	A	25	50	500
Iron	1	A	100	50	2000
Lead	1	A	50	50	1000
Manganese	1	A	50	50	1000
Magnesium	0.5	C	10,000	50	100000
Molybdenum	0.1	B	1000	50	2000
Nickel	1	A	50	50	1000
Potassium	0.5	D	10,000	50	100000
Selenium	1	A	200	50	4000
Silver	1	A	5	50	100
Sodium	0.5	C	10,000	50	100000
Thallium	1	A	200	50	4000
Vanadium	1	A	50	50	1000
Zinc	1	A	50	50	1000

Spike Solutions		
Supplier	**Lot #/ std**	**Stock**
SPEX Certiprep	SPIKE 1-500	A
Molybdenum	1000 mg/L	B
Ultra	ICUS 192	C
Potassium	10,000	D

18.2 GFAA Table

Element	Spike Amt mL	Spike Stock	Stock Conc mg/L	[illegible]	[illegible]
Antimony-GFAA	1.0	A	1000.0	50.0	20.0
Arsenic-GFAA	1.0	A	1000.0	50.0	20.0
Lead-GFAA	1.0	A	1000.0	50.0	20.0
Selenium-GFAA	1.0	A	1000.0	50.0	20.0
Thallium-GFAA	1.0	A	1000.0	50.0	20.0

Standard Source		
Supplier	**Dilution**	**Solution**
Inorg Vent.-SPK1 (multi-element std)	1/100	A

Analyst: **Metals Digestion Summary-CT Laboratories Baraboo** Date:

Prep Batch#	Sample ID#	Matrix*	Prep Method**	Sample Amt gms or mls	Final Volume, mLs	Blk	Dup	MS	MSD	Spike/LCS/ LFB info	Acid ID#

Method Temperature Verification					Review date initials
Block Temp					Digestion Tube Lot #
Cell #				Comments.	

CT Laboratories
Baraboo Laboratory Division

Title: **Semi-Volatile PCB as Aroclor Analysis**

SOP Number: **8082**

Written by: _____

Technical Review by: _____

Approved by: _____
Quality Assurance Manager

Approved by: _____
Laboratory Director

SOP Manual Control Number: _____

1.0 SCOPE/APPLICATION

1.1 Method SW-846 8082 is used to determine the quantitation of polychlorinated biphenyls (PCBs) as Aroclors in extracts from solid and aqueous matrices. Capillary columns are employed with electron capture detectors (ECD). Target Aroclors determined by this method are listed in Table 1.0.

1.2 Aroclors are multi-component mixtures. When samples contain more than one Aroclor, a higher level of analyst expertise is required to attain acceptable levels of qualitative and quantitative analysis. Multiple Aroclors can be present, but due to peak sharing and pattern recognition, the most dominate Aroclor may be reported while the underlying Aroclor will be addressed in the client notes.

1.3 This method is a dual column analysis. Two analytical columns joined to a single injection port. The second gas chromatographic column can be used to confirm the measurements made with the primary column.

1.4 The procedures contained within this method are restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results.

Table 1.0
Aroclors and Retention Times

Aroclor Name	RT Peak#1	RT Peak#2	RT Peak#3	RT Peak#4	RT Peak#5
1016	3.32	4.73	5.83	6.07	7.97
1221	2.31	2.98	3.16	3.27	----
1232	3.32	4.72	5.83	6.07	10.10
1242	3.32	4.73	5.83	6.08	9.20
1248	4.24	5.83	6.07	7.97	10.14
1254	12.52	13.87	15.09	16.26	19.56
1260	13.80	15.04	16.25	19.55	21.10
Additional Aroclors					
1262	13.81	15.63	17.02	19.56	21.91
1268	18.10	19.77	19.88	20.58	21.07

2.0 SUMMARY OF METHOD

2.1 This method describes procedures for isolating organic compounds through sample preparation from aqueous and solid matrices (reference methods SW846-3510C and 3545), concentration techniques that are suitable for preparing the extract, and the quantitative/qualitative analysis for the determination of Aroclors by method SW846-8082.

2.2 A sample of a known volume or weight is extracted with solvent or diluted with solvent. Method applies for aqueous samples extracted by liquid-liquid separatory funnel (SW846-3510C). Method applies for soil/sediment, and solid waste samples extracted by standard solvent extraction methods utilizing pressurized extraction techniques as heated pressurized fluid extraction (SW846-3545). This method includes the extraction for waste dilution samples.

2.3 The resultant extract is chemically dried and concentrated in a Kuderna-Danish (K-D) apparatus in preparation for instrumental analysis.

2.4 Extracts for Aroclor analysis may be subjected to sulfuric acid, florisil, and/or sulfur cleanup designed specifically for these analytes. After cleanup, the extract is analyzed by injecting a known aliquot into a gas chromatograph equipped with dual capillary columns and ECD detectors.

2.5 The procedures contained within this method are restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results.

3.0 INTERFERENCES

3.1 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. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be necessary. Refer to each method for specific guidance on quality control procedures.

3.2 Phthalate esters contaminate many types of products commonly found in the laboratory. Plastics, in particular, must be avoided because phthalates are commonly used as plasticizers and are easily extracted from plastic materials

3.3 Soap residue (e.g. sodium dodecyl sulfate), which results in a basic pH on glassware surfaces, may cause degradation of certain analytes.

3.4 Interferences co-extracted from the samples will vary considerably from source to source. If analysis of an extracted sample is prevented due to interference, further cleanup of the sample may be necessary.

3.5 Elemental sulfur (S_8) is readily extracted from soil samples and may cause chromatographic interferences in the determination of Aroclors. Sulfur can be removed through cleanup procedures.

4.0 DEFINITIONS

4.1 Method Blank (MB): An analyte-free matrix to which all reagents are added in the same volumes or proportions as used in the sample processing. The method blank is carried through the complete sample preparation and analytical procedure. The method blank is used to document contamination resulting from the analytical process.

4.2 Laboratory Control Spike (LCS): Milli-Q water (for water) and Organic-Free Soil (for soil) is spiked with the target analytes and carried through the complete sample preparation and analytical procedure. The control spike is used to document the ability of an analyst to generate acceptable precision and bias to verify the analytical system performance, and to document method accuracy for each matrix.

4.3 Laboratory Control Spike Duplicate (LCSD): A duplicate Milli-Q water (for water) and Organic-Free Soil (for soil) is spiked with the target analytes and carried through the complete sample preparation and analytical procedure. The control spike duplicate is used to document the precision and bias of a method. This QC type is only performed when insufficient amount of sample is available for performing a matrix spike and matrix spike duplicate.

4.4 Matrix Spike (MS): An aliquot of sample spiked with a known concentration of target analytes. The spiking occurs prior to sample preparation and analysis. They are used to document the precision and bias of a method in a given sample matrix.

4.5 Matrix Spike Duplicate (MSD): Intra-laboratory split samples spiked with identical concentration of target analytes. The spiking occurs prior to sample preparation and analysis. They are used to document the precision and bias of a method in a given sample matrix.

4.6 Method Reporting Limit (MRL): The method reporting limit is a threshold value below which the laboratory reports a result as non-detect. The highest value reported for the method reporting limit is dependant upon project-specific action or decision levels. Method reporting limits are

adjusted based on the sample matrix and any sample dilution/concentrations when necessary.

4.7 Method Detection Limit (MDL): The method detection limit is the minimum concentration of a substance that can be measured and reported with 99 percent confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte. Depending on project specific MDLs may be in form of a MDL check standard or the MDL is subject to extraction procedures.

4.8 Surrogate (SSTD): An organic compound which is similar to the target analytes in chemical composition and behavior in the analytical process, but which is not normally found in environmental samples. Its use is to monitor the performance of the extraction, cleanup (as needed), the analytical system, and the effectiveness of the method. The surrogates are; 2,4,5,6-Tetrachloro-m-xylene and Decachlorobiphenyl.

4.9 Initial Calibration (ICAL): An analytical instrument is said to be calibrated when an instrumental response can be related to the concentration of Aroclors 1016/1260. This relationship may be depicted graphically, and referred to as a "calibration curve". Initial calibration curves must be established based upon the requisite number of standards identified within the method for each target analyte.

4.10 Initial Calibration Verification (ICV): The initial calibration verification standard (different lot # or manufacture from the initial calibration standard) shall verify the initial calibration curve. The initial calibration verification standard involves the analysis of all target analytes each time the initial calibration is performed.

4.11 Calibration Verification Standard (CCV): A standard solution that is used to check the validity of a calibration curve on a daily basis. It also provides information on satisfactory maintenance and adjustment of the instrument during sample analysis.

5.0 SAFETY

5.1 Protective clothing; safety glasses, gloves, apron and/or lab coat, long pants, and protective shoes, should be worn to protect against unnecessary exposure to hazardous chemicals and contaminants in samples. All activities performed while following this procedure should utilize appropriate laboratory safety systems.

5.2 The toxicity of chemicals used in this method has not been precisely defined. Each chemical should be treated as a potential health hazard, and exposure to these chemicals should be minimized.

6.0 APPARATUS & MATERIALS

Apparatus:

6.1 Gas Chromatograph- An analytical system complete with gas chromatograph suitable for split-splitless injection and all required accessories including syringes, analytical columns, electron capture detectors, auto sampler, electronic pressure control, and EZ Chrom Elite data acquiring system.

6.1.1 Carrier Gas: Nitrogen at 22.0 initial pressure
Make-up Gas: Nitrogen at 30 mL/minute
Injector: 220 °C
Detector (s): 300 °C
Oven: Initial – 165 °C (hold for 0.5 minute)
Ramp – 2 °C/minute
Final - 185 °C (hold for 1 minutes)
Ramp – 5 °C/minute
Final - 210 °C (hold for 0 minutes)
Ramp – 10 °C/minute
Final - 260 °C (hold for 0 minutes)

Note: Instrument operating parameters are subject to change to improve overall chromatography (changes are noted in the Instrument Maintenance Log Book).

6.2 Analytical column pair;

6.2.1 30m x 0.32 mm ID bonded with 5% phenyl polysiloxane / 95% dimethylsiloxane, 0.25 um. (ZB-5, part # 7HM-G002-11 or equivalent).

6.2.2 30m x 0.32 mm ID bonded with 14% Cyanopropylphenyl/86% dimethylplysiloxane, 0.25 um (ZB-1701, part # 7HM-G006-11 or equivalent).

6.3 Water bath- heated and capable of accepting a Kuderna-Danish apparatus.

6.4 Dionex ASE 200.

6.5 Organomation Nitrogen blow down concentrator.

6.6 Analytical balance capable of accurately weighing to the nearest 0.01 gram (for sample preparation).

6.7 Oven.

Glassware:

6.8 Separatory funnel - 2000 mL glass with Teflon stopcock.

6.9 Kuderna-Danish (K-D) apparatus:
- 6.9.1 Concentrator tube, 10.0 mL, graduated. (Fisher # K570051-1025).
- 6.9.2 Evaporation flask- 500 mL or 250 ml (Fisher # K570035-0250).
- 6.9.3 Synder column- Three-ball macro (Fisher # K503000-0121).
- 6.9.4 Springs or Teflon clamps to attach concentrator tube to evaporation.

6.10 Graduated cylinder (Class A) - 1000 mL. (Fisher 08-559G).

6.11 Beaker - 250 mL and 600 mL.

6.12 Vials - 2.0 mL and 60 mL screw cap vials with Teflon lined caps (Fisher # 03-377-10B).

6.13 Pasteur Pipets (Corning # 7095B-5X).

6.14 Funnels – glass.

6.15 Volumetric flask – (Class A) 10, 25, 50, and 100 mL.

6.16 Syringes 10 uL, 100 uL, 500 uL, and 1,000 uL.

Reagents:

6.17 Deionized water (Milli-Q processed).

6.18 Sodium sulfate (granular, anhydrous 60/120 mesh, Fisher # S415-212). Purify by heating to 400°C in a shallow glass tray, loosely covered with foil.

6.19 Silica sand- hydrocarbon free. Purify by heating to 400°C in a shallow glass tray, loosely covered with foil.

6.20 Methylene chloride, pesticide grade.

6.21 Acetone, pesticide grade.

6.22 Hexane, pesticide grade.

6.23 Isopropanol, pesticide grade.

6.24 Nitrogen (5.0 rating).

6.25 Sulfuric Acid (Certified ACS)/Deionzied Water-1:1(v/v)..

6.26 Sodium Hydroxide- 10 N (Certified ACS).

6.27 Diatomaceous earth (JT Baker # 1939-01).

Materials:

6.28 Boiling chips, carborundum, approximately 10/40 mesh (methylene chloride rinsed) (G. Frederick Smith Chemical Company, Catalog #198).

6.29 pH indicator paper- pH 0-14 (Whatman Catalog #2613991).

6.30 Dionex ASE Filters (Catalog #049458).

6.31 Filter- Glass Microfiber 12.5 cm GF/A (Whatman # 1827-125).

6.32 Aluminum foil.

6.33 Spatulas- stainless steel.

7.0 STANDARDS AND SPIKES

7.1 Preparation of standards is documented in the Pest/PCB standards logbook. Each standard is labeled by prep date to allow for tracking. Opened stock standards expire one year or sooner if comparison with quality control check samples indicated a problem. Leftover stock standards are saved in a capped vial in the original box in the freezer. Any subsequent dilutions made from the opened vial expire six months from the original opening. The cracking date of the stock standard vial will be recorded on the label along with the six month expiration date

7.2 Stock Standards -Stock Standards are purchased from vendors who provide certified solutions. Standards are stored at -10°C in a freezer reserved for standard solutions. Unopened standard shall have the manufactures suggested expiration date. Opened stock standards expire one year or sooner if comparison with quality control check samples indicated a problem (Not to exceed the manufactures expiration date).The following list of stock standards are commercially prepared standards, which are certified by the manufacturer, such as;

Aroclor 1016/1260: Restek Part # 32039 at 1000 ug/mL.
Aroclor 1016: Restek Part # 32006 at 1000 ug/ml.
Aroclor 1221: Restek Part # 32007 at 1000 ug/ml.
Aroclor 1232: Restek Part # 32008 at 1000 ug/ml.
Aroclor 1242: Restek Part # 32009 at 1000 ug/ml.
Aroclor 1248: Restek Part # 32010 at 1000 ug/ml.
Aroclor 1254: Restek Part # 32011 at 1000 ug/ml.
Aroclor 1260: Restek Part # 32012 at 1000 ug/ml.
Aroclor 1262: Restek Part # 32409 at 1000 ug/ml.
Aroclor 1268: Restek Part # 32410 at 1000 ug/ml.
Surrogate Mix: Restek Part # 32000 at 200 ug/ml.

7.3 Intermediate Stock Standards: These standards are diluted stock standards so that the concentration levels are manageable for the preparation of working standards. The Aroclor intermediate standards are prepared at an optimum level for the preparation of the working stock standard. Each Aroclor with surrogate are prepared at an optimum level for the intermediate stock standard. The concentration of each Aroclor is 10 ug/ml with surrogate concentrations at 1.0 ug/ml in hexane. The following is a list of each Aroclor.

Aroclor 1016	Aroclor 1254
Aroclor 1221	Aroclor 1260
Aroclor 1232	Aroclor 1262
Aroclor 1242	Aroclor 1268

Table 2.0
Intermediate Working Standard Concentration

Intermediate Standard	Stock Standard Concentration (ug/ml)	Standard Volume (ml)	Final Volume (ml)	Final Concentration (ug/ml)
Aroclor(s)	1000	0.100	10.0	10.0
Surrogate	200	0.050	10.0	1.0

*Note: The concentration of the Intermediate Stock standard and Intermediate ICV standard are prepared in the same manner.

7.4 Calibration standards: PCB are to be determined as Aroclors, external calibration techniques should be used. An initial calibration is performed using a minimum of a five point calibration curve for Aroclors 1016/1260. This standard mix will include many of the peaks represented in the other Aroclor mixtures. Such a standard may be used to demonstrate the

linearity of the detector and that a sample does not contain peaks that represent any one of the Aroclors. Standards for the other Aroclors are necessary for pattern recognition. These standards are also used to determine a single-point calibration factor (CF) for that specified Aroclor. The single-point calibration standard level is marked with an asterisk. (In situations where only a few Aroclors are of interest for a specific project, the analyst may employ a minimum of a five point initial calibration of each of the Aroclors of interest.)

Level 1	0.030 ug/ml
Level 2	0.100 ug/ml
Level 3	0.200 ug/ml
Level 4	0.400 ug/ml
Level 5 *	1.000 ug/ml
Level 6	1.600 ug/ml
Level 7	2.000 ug/ml

Table 2.1
Calibration Points for the Aroclor(s) Linearity

Linearity Points	Spike Concentration (ug/ml) Aroclor(s)	Standard Volume (ml)	Final Volume (ml)	Final Concentration (ug/ml) Aroclor(s)	Final Concentration (ug/ml) Surrogate**
1	10.0	0.030	10.0	0.03	0.003
2	10.0	0.100	10.0	0.10	0.010
3	10.0	0.200	10.0	0.20	0.020
4	10.0	0.400	10.0	0.40	0.040
5 *	10.0	1.000	10.0	1.00	0.100
6	10.0	1.600	10.0	1.60	0.160
7	10.0	2.000	10.0	2.00	0.200

7.5 Initial Calibration Verification (ICV): The initial calibration verification standard (different lot # or manufacture from the initial calibration standard) shall verify the initial calibration curve. The initial calibration verification standard involves the analysis of Aroclors 1016/1260 at a concentration of 1.0 ug/ml each time the initial calibration is performed. By taking known aliquots of the ICV intermediate standard and diluting them to volume in hexane. If the analyst uses a project specified Aroclor in Section 7.4, then the analyst must verify that Aroclor with an ICV.

Table 2.2
ICV Working Standard

Working ICV Standard	Intermediate Standard Concentration (ug/ml)	Standard Volume (ml)	Final Volume (ml)	Final Concentration (ug/ml)
Aroclor(s)	10.0	0.100	10.0	1.00
Surrogate	1.0	0.100	10.0	0.10

7.6 Calibration Verification Standard (CCV): A working standard solution for Aroclor 1016/1260 at a concentration of 1.0 ug/ml is used to check the validity of a calibration curve on a daily basis. If the analyst uses a project specified Aroclor in Section 7.4, then the analyst must use that Aroclor as a CCV. Standards for the other Aroclors are necessary for pattern recognition. These standards may be analyzed prior to same analysis for a single-point calibration factor (CF) for that specified Aroclor.

Table 2.3
CCV Working Standard

Working CCV Standard	Intermediate Standard Concentration (ug/ml)	Standard Volume (ml)	Final Volume (ml)	Final Concentration (ug/ml)
Aroclor(s)	10.0	0.100	10.0	1.00
Surrogate	1.0	0.100	10.0	0.10

7.7 Surrogate standard: A commercially prepared certified solution of 2,4,5,6-Tetrachloro-m-xylene and Decachlorobiphenyl is diluted in acetone to produce a working surrogate solution of 0.50 ug/mL. 1.0 mL is added to each sample. The surrogate concentration is normalized to 100% from the spiking solution in the initial calibration. This will provide percent recoveries that transfer directly to LIMS.

Table 2.4
Surrogate Spiking Solution

Surrogate Spiking Solution	Stock Standard Concentration (ug/ml)	Standard Volume (ml)	Final Volume (ml)	Final Concentration (ug/ml)
Surrogate	200	0.250	100.0	0.500

7.8 Spiking standards (matrix and control samples): Prepare a spiking solution in acetone that contains Aroclor 1016/1260 10.0 ug/mL for water

and sediment / soil samples. 1.0 ml is added to quality control and matrix spike samples. The concentration of the Aroclors should be five times higher for waste samples. If client request a specified Aroclor, a spiking solution will be altered to match the Aroclor of interest

Table 2.5
Aroclor Spiking Solution

Aroclor Spiking Solution	Stock Standard Concentration (ug/ml)	Standard Volume (ml)	Final Volume (ml)	Final Concentration (ug/ml)
Aroclor(s)	1000.0	0.500	50.0	10.00

NOTE: All standards are stored at -10°C. Opened stock standards expire one year or sooner if comparison with quality control check samples indicated a problem. Intermediate and working standards expire six months from the date made. A intermediate stock standard or working standard shall not exceed expiration date criteria. All subsequent standards made from the intermediate stock standards expire on the same date as the working stock standard. If more than one standard is added to a solution the expiration date will be the same as the stock standard with the earliest expiration date.

8.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

8.1 Aqueous samples are collected in 1-L amber glass containers with Teflon lined lids. Aqueous samples should be collected in duplicate. Solid samples are collected in 250-mL wide mouth glass containers with Teflon-lined lids. All samples are preserved by cooling to 4°C. The soil samples must be extracted within 14 days and water samples must be extracted in 7 days from the date of collection.

8.2 Sample extracts should be stored under refrigeration in the dark and analyzed within 40 days of extraction.

9.0 PREPARATION PROCEDURES

9.1 Water Extraction (Method SW-846, 3510)

9.1.1 Pre-rinse all glassware to be used in the extraction with methylene chloride (Pesticide Grade).

9.1.2 Mark the meniscus on the bottle for later determination of sample volume. From the glass sample collection jar, quantitatively transfer sample into a 2 liter separatory funnel.

9.1.3 One method blank and laboratory control spike must be prepared with each batch of 20 samples or less. Prepare by adding one liter of Milli-Q water to 2 liter separatory funnel.

9.1.4 One sample from each batch of 20 samples or less must be selected for use in the preparation of a matrix spike (MS) and matrix spike duplicate (MSD). Select the sample and from the glass sample collection bottle, quantitatively transfer half of the sample into a 2 liter separatory funnel and label MS, and transfer the other half of the sample into another 2 liter separatory funnel and label MSD. If there is no sample to perform a matrix spike/matrix spike duplicated a laboratory control spike duplicate must be performed.

9.1.5 Check and note the pH on the extraction bench sheet. Adjust the pH to between 5 and 9 with 10N sodium hydroxide and/or 1:1 sulfuric acid solution.

9.1.6 To the method blank, matrix spike/matrix spike duplicate, laboratory control spike, and all samples add 1.0 mL of the surrogate standard mix by using a 1.0 ml syringe. In addition, add 1.0 mL of the Aroclor 1016/1260 spiking solution to the matrix spike/matrix spike duplicate and laboratory control spike (laboratory control spike duplicate).

9.1.7 Add 60 mLs of methylene chloride to the sample bottle and rinse, pouring the methylene chloride into its respective separatory funnel. Extract the sample shaking vigorously for two minutes, venting frequently.

9.1.8 Allow the organic layer to separate from the water phase for a minimum of 10 minutes. Decant the lower layer into a 250 ml beaker. 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.

9.1.9 Repeat the extraction two more times using a fresh 60 mL portions of methylene chloride.

9.1.10 Determine the sample volume by filling the sample bottle to the mark (9.1.2) with water and transferring it to a "Class A" 1 liter graduated cylinder for measurement. Note all sample volumes on the extraction bench sheet.

9.1.11 Refer to section 9.4 for sample concentration.

9.2 Solid Extraction (Method SW-846, 3545)

9.2.1 Preparing the extraction cell for use: Pre-rinse extraction cell (tube and caps) with methylene chloride. Attach the screw fit tube cap of the soil extractor to the end of the tube without the serial number engraved on the side. Using the filter rod, push 1 Dionex filter through the open end of the tube until they reside flush on the bottom of the screwed end.

9.2.2 Decant and discard any water layer on a sediment sample. Mix sample thoroughly, especially composite samples. Discard any foreign objects such as sticks, leaves, and rocks.

9.2.3 Dry sediment/soil and dry waste samples amenable to grinding: Grind or otherwise reduce the particle size of the waste so that it either passes through a 1-mm sieve or can be extruded through a 1-mm hole. The addition of a drying agent (e.g. sodium sulfate or diatomaceous earth) can make sample more amenable to grinding.

9.2.4 Gummy, fibrous, or oily materials not amenable to grinding should be cut, shredded, or otherwise reduced in size to allow mixing and maximum exposure of the sample surfaces for the extraction. The addition of a drying agent (e.g. sodium sulfate or diatomaceous earth) can make sample easier to mix. Wipe samples can be placed directly into the cell.

9.2.5 (Refer to SOP FO-10 for subsampling guidance). Weigh approximately 10 g of sample to the nearest 0.1 g into a 250-mL beaker and record the final weight. Add 2.5 g of diatomaceous earth to the sample. Mix well. The samples should be a free flowing powder. If sample is not free flowing add more diatomaceous earth until the sample has a dry texture. This powder is so mixed that it will allow the sample to pass through a 2 mm sieve.

9.2.6 Transfer the ground sample, or wipe to an extraction cell of appropriate size for the aliquot.

9.2.7 One method blank and laboratory control spike must be prepared with each batch of 20 samples or less. Prepare by adding 10g of sand and 2.5g of diatomaceous earth to a clean 250 ml beaker. Transfer sample to extraction cell. For wipe samples transfer blank wipe to extraction cell

9.2.8 One sample from each batch of 20 samples or less must be selected for use in the preparation of a matrix spike (MS) and matrix spike duplicate (MSD). Select the sample and transfer approximately 40 grams to a 250 ml beaker. Mix well. Weigh three individual 10 grams aliquots of sample. Add drying agent. Transfer sample to extraction cell. If there is no sample available to perform a matrix spike/matrix spike duplicated a laboratory control spike duplicate must be performed. For wipe samples transfer a blank wipe directly to the cell.

9.2.9 Fill the void in each of the extraction cells with clean sand.

9.2.10 To the method blank, matrix spike/matrix spike duplicate, laboratory control spike, and all samples add 1.0 mL of the surrogate standard mix by using a 1.0 ml syringe. In addition, add 1.0 mL of the Aroclor 1016/1260 spiking solution to the matrix spike/matrix spike duplicate and laboratory control spike (laboratory control spike duplicate).

9.2.11 Attach the other cap to the extractor cell, making sure the tube is sitting flush on a hard surface so that no particulates get caught in the threads of the tube cap.

9.2.12 Place the extractor tube on the Dionex on a selected position with the serial number engraved end up on the top wheel. Place an empty 60 mL VOA collection vial on the matching position on the bottom wheel. Schedule the Dionex ASE 200 and begin the cycle.

9.2.13 The Dionex ASE 200 extraction cycle:

Oven temperature: 100 ° C Pressure: 1500 psi
Prepurge time: 0 minutes
Static time: 5 minutes
Heat: 5 minutes
Flush volume: 60%
Nitrogen purge: 60 sec. At 150 psi
Solvent A: 100%
Method rinse: ON
Static Cycles: 1
Extraction Fluid: (1:1) methylene chloride : acetone

9.2.13 Refer to section 9.4 for sample concentration

9.3 Waste Dilution Extraction (SW846-3580A)

9.3.1 (Refer to SOP FO-10 for subsampling guidance). Samples consisting of multiphase separations.

9.3.2 Pre-rinse "Class A" 10 ml volumetric with hexane.

9.3.3 One method blank and laboratory control spike must be prepared with each batch of 20 samples or less. One sample from each batch of 20 samples or less must be selected for use in the preparation of a matrix spike (MS) and matrix spike duplicate (MSD).

9.3.4 Place the 10 ml volumetric on analytical balance (capable of accurately recording weight to the 0.01 g). Using a Pasteur pipet, transfer 1.0 g (to the nearest 0.1 g) to the volumetric. Record the weight.

9.3.5 Fill the volumetric half way with hexane.

9.3.6 To the method blank, matrix spike/matrix spike duplicate, laboratory control spike, and all samples add 1.0 mL of the surrogate standard mix by using a 1.0 ml syringe. In addition, add 1.0 mL of the Aroclor 1016/1260 spiking solution to the matrix spike/matrix spike duplicate and laboratory control spike (laboratory control spike duplicate).

9.3.7 Bring samples up to volume with hexane and cap for storage.

9.3.8 Add 2.0 grams of conditioned sodium sulfate to a 15ml amber vial with a Teflon cap. Transfer sample from the 10 ml volumetric flask to the 15ml vial.

9.3.9 Shake sample for two minutes.

9.3.10 Loosely pack disposable Pasteur pipets with 2-3 cm glass wool plugs. Filter the extracts through the glass wool and collect 5ml of the extract in a tube or vial.

9.3.11 No concentration step is need for this extraction. Sample may require cleanup prior to analysis. Refer to attachment 1, 2, and 3 for sample cleanup options.

9.4 Sample Concentration

9.4.1 Place glass microfiber filter paper into a glass funnel. Fill the filter paper two-thirds of the depth with Na_2SO_4. Rinse filter paper Na_2SO_4, funnel, K-D apparatus, and concentrator tube with methylene chloride.

9.4.2 Quantitatively pour the extract through the filter and funnel seated on a 250mL Kuderna-Danish (K-D) apparatus complete with concentrator tube. Rinse the beaker three times with methylene chloride. Add these rinses through the filter and funnel into the K-D. Add a boiling chip to the K-D flask prior to placing it on the heated water bath. Wet a three ball Synder column with approximately 2 mL of methylene chloride. Attach the Synder column.

9.4.3 Place the K-D in the heated water bath so the concentrator tube is immersed in the water and the lower rounded surface of the K-D is bathed in steam. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood (set the knob of the temperature control to 5~6). It is critical that the analyst watch the extract as it concentrates. THE EXTRACT SHOULD NOT GO TO DRYNESS.

9.4.4 When the extract volume reaches approximately 5-7 mL, remove the K-D from the bath. Slightly tilt the apparatus and rotate to aid in solvent drainage from the Synder column. Allow it to cool completely.

9.4.5 Remove the Synder column and add 25 mL of hexane and replace Synder column. Turn the knob of the temperature control of water bath heater to 6~7. Mix the contents of the KD by slightly tilting and placing it upright several times using care so that the content does not spill out the Synder column. Concentrate the extract to approximately 4 mL. Remove the K-D apparatus from the bath. As above, slightly tilt the apparatus and rotate to aid in solvent drainage. Allow it to cool completely.

9.4.6 Remove the Synder column, rinse the ground glass joints with a small amount of hexane and then remove K-D flask. Add hexane to the concentrator tube so that the final volume is 10.0 mL. With a disposable Pasteur pipet draw up the extract and rinse the sides of the concentrator tube. Repeat this rinsing several times. (Note: If the sample extract appears highly colored or has a strong petroleum type odor a sulfuric acid clean-up may be required.) Transfer about 1 mL of the extract to a labeled screw-cap injection

vial, and the remainder into an amber storage vial. Record the final extract on the injection extraction bench sheet.

9.4.7 The sample extract is now ready for analysis. If samples are not analyzed immediately store the sample extract in a refrigerator.

9.4.8 Sample may require cleanup prior to analysis. Refer to attachment 1, 2, and 3 for sample cleanup options.

10.0 CALIBRATION

10.1 Calibration

10.1.1 The initial calibration for SW-846 chromatographic methods involves the analysis of standards containing the target compounds at a minimum of five different concentrations covering the working range of the instrument.

10.1.2 Quantitation is based upon indicator peaks in the Aroclor 1016/1260 mixture that are generally present in the Aroclors. The calibration factors (CF), generated Aroclors 1016/1260 from the initial calibration, are used to evaluate the linearity of the initial calibration. This involves the calculation of the mean calibration factor, the standard deviation , and the relative standard deviation (RSD) for each Aroclor peak. When the Aroclors 1016/1260 mixture is used to demonstrate the detector response, the calibration model (linear or non-linear models) chosen for this mixture must be applied to the other Aroclors for which only standards are analyzed. A minimum of five sets of calibration factors will be generated for the Aroclor 1016/1260 mixture, each set consisting of the calibration factors for each of the five (or more) peaks chosen for this mixture. If multi-point calibration is performed for individual Aroclors, use the calibration factors from those standards to evaluate the linearity.

10.1.3 The single point calibration standard will use a minimum of three to five peaks for each Aroclor. Choose peaks in the Aroclor standards that are at least 25% of the height of the largest Aroclor peak. For each Aroclor, the set of 3 to 5 peaks should include at least one peak that is unique to that Aroclor. The single standard for each of the other Aroclors will generate at least three calibration factors, one from each peak.

10.1.4 The identification of the multi-peaked analytes such as PCBs as Aroclors can be performed by a combination of pattern recognition

and retention time. Retention time widows are crucial to the identification of target compounds. Absolute retention times are used for the identification of PCBs as Aroclors. Retention time windows are established to compensate for minor shifts in absolute retention times as a result of sample loading and normal chromatographic variability. Each Aroclor should have one peak that is unique to its calibration. Refer to Table 1.0 for corresponding retention times for each Aroclor

10.1.5 Prepare the Aroclor 1016/1260 calibration standards (in table 2.1) at a minimum of five different concentrations by adding known volumes of the intermediate stock standard to a volumetric flask and diluting to volume with hexane.

10.1.6 The lowest concentration calibration standard, that is analyzed during an initial calibration curve, establishes the method's quantitation limit based on the finale volume of the sample extract described in the preparative method or employed by the laboratory.

10.1.7 External standard calibration involves comparison of instrument response from the target compounds in the calibration standards. Sample peak areas are compared to peak areas of the standards. The ratio of the detector response to the amount of analyte in the calibration standard is defined as the calibration factor (CF). Aroclors are a multi-component standard. For the initial calibration curve, five peaks (or more) will be selected from each Aroclor 1016/1260 and calibrated using the average %RSD of the peaks. If multi-point calibration is performed for individual Aroclors, use the calibration factors from those standards to evaluate the linearity.

10.1.8 Linear calibration using the average calibration factor. When calculating, both calibration factors and response factors are a measure of the slope of the calibration relationship and assume that the curve passed through the origin. The measured as the relative standard deviation (RSD), is less than or equal to 20%, the use of the linear model is generally appropriate, and the calibration curve can be assumed to be linear and to pass through the origin.

10.1.9 Linear calibration using a least squared regression. When the RSD of the calibration or response factors is greater than 20% over the calibration range, then linearity through the origin cannot be assumed. The approach is to employ a regression equation that does not pass through the origin. This approach may also be employed based on past experience of the instrument response.

10.1.10 Non-linear calibration. When using a calibration model for quantitation, the curve must be continuous, continuously differentiable and monotonic over the calibration range. The statistical considerations in using a non-linear calibration model require more data than the traditional linear approaches. A quadratic (second order) model required the use of six initial calibration points.

10.1.11 Directly inject the prepared calibration standards into the gas chromatograph. An external calibration technique is employed. One of the external standards should be at a concentration near, but above the method detection limit. If the RSD $\leq$ 20%, the correlation of 0.990, or $r^2 \geq 0.995$ is obtained then the calibration is deemed acceptable.

10.1.12 Check the validity of the calibration by analyzing a ICV. The variance of any given compound should not be more than +/- 15% difference when compared to the mean calibration factor. This standard must be prior to sample analysis. If an analyte meets the QC criteria; RSD $\leq$ 20%, linear requirement of 0.99, or $r^2 \geq 0.995$, but the best calibration fit is second order, then only one routine ICV need be analyzed. If an analyte exhibits unacceptable linear criteria, but meets criteria using a non-linear model, then two ICV standards must be performed, one at a point above and one at a point below the inflection point. In either case, if the percent drift or the percent difference criteria is not met then the subsequent sample analysis for that analyte is not acceptable.

10.1.13 Continuous checking the validity of the calibration by analyzing CCVs. The variance of the Aroclor 1016/1260 mixture should not be more than +/- 15% difference when compared to the mean calibration factor. This standard must be ran at the beginning, every ten samples or at every 12-hour interval, and at the end of the analysis run. The single-point standard for the other Aroclors should be analyzed before the analysis of any samples, and may be analyzed before or after the analysis of the five 1016/1260 initial calibration in Section 10.1.2.

10.2 Calibration Calculations

10.2.1 When determining PCBs as Aroclors by the external standard technique, calculate the calibration factor (CF) for each characteristic Aroclor peak in each of the initial calibration standards using the equation below

$$CF = \frac{\text{Peak Area (or Height) in the Standard}}{\text{Total Mass of the Standard Injected (in Nanograms)}}$$

10.2.2 Five sets of calibration factors will be generated for the Aroclor 1016/1260 mixture, each set consisting of the calibration factors for each of the five (or more) peaks chosen for this mixture. Each peak actually has a ratio concentration of the final concentration of that Aroclor, method sums the calculated values of the five target peaks, thus generates the correct final concentration.

10.2.3 The calibration factors from the initial calibration are used to evaluate the linearity of the initial calibration. This involves the calculation of the mean calibration factor, the standard deviation, and the relative standard deviation (RSD) for each Aroclor peak.

$$\text{Mean } CF = \overline{CF} = \frac{\sum_{i=1}^{n} CF_i}{n}$$

$$SD = \sqrt{\left(\frac{\sum_{I=1}^{n} (CF_I + \overline{CF})}{n-1} \right)}$$

$$RSD = \frac{SD}{\overline{CF}} \times 100$$

10.2.4 Linear Calibration: If the RSD of the calibration factor is greater than 20% over the calibration range, then linearity though the origin cannot be assumed. If this is the case, the analyst may employ a regression equation that does not pass through the origin. This approach may also be employed based on the past experience of the instrument response. The regression will produce the slope and intercept terms for a linear equation in the form:

$$y = mx + b$$

y = instrument response (peak area or height)
m = Slope of the line
x = Concentration of the calibration standard
b = The intercept

10.2.5 The analyst will not force the line through the origin, but have the intercept calculated from the five data points. The use of linear regression may not be used as a rationale for reporting results below the calibration range.

10.2.6 Non-Linear Calibration: In situations where the analyst knows that the instrument response does not follow a linear model over a sufficiently wide working range, or when the other approaches described here have not met the acceptance criteria, a non-linear calibration model may be employed. When using a calibration model for quantitation, the curve must be continuous, continuously differentiable and monotonic over the calibration range. The model chosen should have no more than four parameters, i.e., if the model is polynomial, it may be no more than third order as in the equation:

$$y = ax^3 + bx^2 + cx + d$$

10.2.7 The statistical considerations in developing a non-linear calibration model require more data that the more traditional linear approaches described above. Linear regression employ five calibration standards for the linear model, a quadratic model requires a minimum of six calibration standards.

10.2.8 The "goodness of fit" of the polynomial equation is evaluated by calculating

$$COD = \frac{\sum_{i=1}^{n} (y_{obs} - \bar{y})^2 - \left(\frac{n-1}{n-p}\right) \sum_{i=1}^{n} (y_{obs} - Y_i)^2}{\sum_{i=1}^{n} (y_{obs} - \bar{y})^2}$$

y_{obs} = Observed response (area) for each concentration of the calibration curve.

$\bar{y}$ = Mean observed response from the initial calibration
Y_I = Calculated response at each concentration from the initial calibrations.
n = Total number of calibration points (6 points for quadratic equation)
p = Number of adjustable parameters in the polynomial.

10.2.9 Under idea conditions, with a "perfect" fit of the model to the data, the coefficient of the determination will equal 1.0 In order to be an

acceptable non-linear calibration, the COD must be greater than or equal to 0.99.

11.0 SAMPLE ANALYSIS

11.1 Sample Sequence

11.1.1 Before initial calibration or sample analysis a priming standard must be injected at a level 2x the highest linearity point. A clean hexane blank must be analyzed to determine baseline characteristics. If the instrument has been in use within 24 hours prior to analysis, this step can be omitted.

11.1.2 Verify calibration each twelve hour shift by injecting a Continuing Calibration Verification standard (CCV), containing Aroclors 1016/1260, prior to conducting any sample analysis. A CCV must be injected at the beginning of the sequence and at intervals of not less than one per 10 sample injections or twelve hours (which ever comes first) and at the end of each sequence. The variance of any given Aroclor 1016/1260 should not be more than +/- 15% difference. If a different Aroclor is chosen for the continuing calibration verification, that CCV is subjected to the same QC criteria as the original CCV of Aroclors 1016/1260. The calibration verification process does not require analysis of the other Aroclor standards used for pattern recognition, but the analyst may desire to include a standard for one or all of these Aroclors after the 1016/1260 CCV for pattern reference.

11.1.3 Before sample analysis, inject a method blank to demonstrate that the instrument as well as the extraction procedure is free from contamination. All compounds must be below the method detection limit.

11.1.4 Samples can be directly injected after the successful analyses of the calibration curve, ICV, CCV and method blank. There can be up to 20 samples in an analytical batch. A matrix spike/matrix spike duplicate and laboratory control spike must be analyzed with every analytical batch. Recoveries must be within laboratory generated QC limits or client specified limits for all surrogate, matrix spike/matrix spike duplicate and laboratory control spike injections.

11.1.5 All detects in the associated sample must be confirmed with a second column. In this case, all detects are identified and quantitated on the Channel A detector. Results must be confirmed at +/- 40 % on Channel B.

11.1.6 Each sample analysis must be bracketed with passing continuing calibration verification standards. If the continuing calibration verification standard fail to meet QC criteria, all samples that were injected after the last standard which met QC criteria must be re-analyzed.

Note: The data acquisition software generates a ug/ml concentrations which can then be applied to the final calculation to give sample concentrations. Samples with results exceeding calibration range can be diluted accordingly in Hexane and reanalyzed.

11.2 Sample Calculations

11.2.1 The concentration of each analyte in the sample is determined by the computer software. It calculates the amount of compound from the peak area, using the specified calibration model (CF, Linear Regression, or Quadratic). Each peak actually is a ratio concentration of the final concentration of that Aroclor, method sums the calculated values of the five target peaks, thus generates the correct final concentration.

11.2.2 Calculation of the unknown sample by utilizing the CF is calculated as:

$$\text{Conc} = \frac{\text{Avg. Target Peak Areas}_{unk}}{\text{Avg. } \overline{\text{CF}}} \times \text{MF}$$

Conc. = the concentration of the unknown analytes of interest.
Amt_{unk} = the average sum of the uncorrected area of the unknown sample.
CF = Average sum of the Calibration Factors of the target peaks.
MF = multiplication factors (i.e. dilutions, percent moisture, etc.)

11.2.3 Using the slope (m) and the intercept (b) from this equation, the concentration of the sample (ug/ml) is calculated and appears on the report page following the chromatogram.

Water samples:

$$C_S = [(C_C)(V_E)(D)]/V_S$$

Soil samples:

$$C_S=[(C_c)(V_E)(D)]/[(W)(S)]$$

Wipe samples:

$$C=[(C_c)(V_E)(D)]$$

Where: C_S = Concentration of sample in ug/L for waters and mg/kg on a dry weight basis for soils

C_c = Concentration from the curve (ug/ml)

C = Concentration in total ug

V_E = Total volume of sample extract (after concentration) in ml

V_S= Volume of water sample in liters

D = Dilution factor if extract was diluted

W = Weight of wet soil sample in grams

S = Total percent solids, expressed as: percent total solids/100

12.0 QUALITY CONTROL

12.1 Method Performance

12.1.1 Certified standard solutions, properly maintained instrumentation, and analyst experience and expertise are critical elements in producing accurate results. Standards and instrument performance are continually checked by analyzing external performance test samples provided by the appropriately accredited agencies. Internal blind spikes are also utilized to check analyst performance.

12.1.2 Initial demonstration of capability (IDC) is another technique used to ensure acceptable method performance. An analyst must demonstrate initial precision and accuracy through the analysis of 4 laboratory control spikes for each matrix and sample type. After analysis, the analyst calculates the average recovery (x) in µg/L and the relative standard deviation (RSD) of the recovery Aroclors. In addition to each set of IDCs, a blind laboratory spike will be performed. In the absence of specific criteria found in the SW-846 methods or project specific limits, the default criteria of 70-130% recovery and 20 % RSD are used until internal limits are generated (Method 8000, sec. 8.4.9).

12.1.3 Creating and monitoring control charts is also important for maintaining and improving method performance. Currently all SSTD, MS, MSD, and LCS recoveries are monitored with the use of the LIMS system. The data collected is used to recognize trends in recovery performance, as well as for generating new in-house QC limits. Default accuracy limits of 70-130 % recovery and a

precision limit 20 % RSD are used until enough data points are generated to provide usable internal limits. Client and/or Project specific limits are also used frequently in sample analyses. The Quality Control Requirements chart (Table 3) also lists recovery limits specific to the method/project/program.

12.2 Data Assessment & Acceptance Criteria for QC Measures

12.2.1 If the initial analysis of a sample or a dilution of the sample has a concentration that exceeds the calibration range, the sample must be re-analyzed at a dilution.

12.2.2 The qualitative identification of PCBs as Aroclors are determined by this method is based on retention time and pattern recognition. This method employs a dual ECD detector with two dissimilar columns. There is a potential for many non-target compounds present in samples to interfere with this analysis, therefore sample extract may undergo cleanup procedures . The retention times are updated with each new calibration and is continually updated with the daily continuing calibration verification standards CCVs. A new method ID is provided for each new sequence with updated retention times or alteration to the operating initial calibration method. If an alteration occurs (other than daily retention time updates), project management and the QA officer will be notified. A description of the alteration will addressed in the client notes or case narrative.

12.2.3 The relative retention time (RRT) of the sample component is within +/- 0.01 RRT units of the RRT of the standard component.

12.3 Reporting Quantitative Analysis

12.3.1 When the analysis of an analytical batch or sequence has been completed, the data is processed and prepared for reporting. Once the standard retention times are compared to the sample retention times, the sample data can be reported.

12.3.2 When the analyst has finished processing the analytical batch, the results are electronically transferred to the LIMS system where weight to volume corrections, dilution factors and percent solids adjustments are made. Once the final results have been verified, a checklist (Table 4.) is filled out and signed confirming that all the data has been thoroughly scrutinized. At this point the data is turned over to another qualified analyst for final validation. The second analyst confirms the results and electronically marks them validated and signs the checklist. Finally, the validated results are made available to the client services personnel in order for the data to be given to the client or appropriate agencies.

12.3.3 A paper hard copy or electronic copy of the data is then filed or archived. The package includes the checklist, the sequence run log, a copy of the bench sheet, the LIMS run log, verification of calibration data. For each sample, the chromatogram. All the data is to be initialed and dated by the analyst. Each data file header should contain the Prep ID #, date prepped, Analytical ID #, and date of sequence.

12.4 Corrective Measures for Out-of-Control Data

12.4.1 When data is out of control, corrective actions are required. Certain situations will cause data deficiencies like; if the non-conformities involve failing QC within the analytical sequence batch, the reanalysis of samples may eliminate any out of control data. If the out of control data is the result of instrument malfunctions, then maintenance or repair of the downed instrument followed by reanalysis of affected data may correct the problem. If sample matrix affect or contamination is the reason for poor data, the instrument may need cleaning and decontamination, and the sample may need diluting or undergo sample clean-up procedures to reduce matrix affect. In all cases, when out of control data presents itself, the appropriate corrective measures need to be enacted to eliminate unusable data. The Quality Control Requirements chart can be used as a guide as to which corrective actions should be taken for different QC-type failures or non-conformities (Table 3.).

12.5 Contingencies for Handling Out-of-Control or Unacceptable Data

12.5.1 Due to limited sample volume, expiration of hold times, downed instrumentation, and analyst error, the sample data may be out of control or unacceptable to report. Since these potential instances can arise, contingency plans need to be in place to prevent and/or minimize their affect on data.

12.5.2 To avoid sample hold time issues, the analyst's first responsibility is to plan accordingly. The analyst is responsible for budgeting enough time for sample analysis, so if a problem arises re-analysis or re-extraction is an option

12.5.3 If a sample is extracted passed holding times, the analyst must notify client services immediately. Client services will inform the client and/or responsible parties. In some instances, more sample can be made available or re-sampling can occur. If the client still request sample analysis, the sample data is qualified for holding time violations.

12.5.4 If the non-conformities involve failing QC within the analytical sequence batch. The analyst must reanalyze the extract. This will ensure that the instrument was functioning properly. If the results are passing, the non-conformities were associated with the instrument. If data is still outside QC criteria, re-extraction of the all samples associated with the QC samples must be preformed (provide that there is sample available). If no sample is available for re-extraction, the samples are qualified accordingly.

12.5.5 If the out of control data is the result of instrument malfunctions, the analyst must evaluated and repair instrument prior to reanalysis of the affected data. After the instrument maintenance and repair of the downed instrument which caused data to be out of control must demonstrate corrective measures by analyzing a Continuing Calibration Verification (CCV) before continuing sample analysis. Any maintenance and repair must be noted in the instrument logbook.

12.5.6 If sample matrix affect or contamination is the reason for poor data. The analyst will use professional judgement for the reanalysis of the extract. The extract can be diluted and reanalyzed. The sample can be re-extracted confirming matrix interference. The analyst can report and qualify the sample data. The analyst must supply explanation for the qualified data in the narrative or client notes.

12.5.7 If the initial analyst makes an analysis error or inadvertently reports unacceptable data, the second analyst is responsible for finding and/or correcting those errors.

12.5.8 When out of control or unacceptable data is produced and it is too late for corrective measures, a number of actions can be taken. The first and foremost is alerting the client service personnel of the problem. Client services will inform the client and/or responsible parties. In some instances, more sample can be made available or re-sampling can occur, so it is important to alert the appropriate personnel as soon as possible.

12.5.8.1 If the out of control data affects only specific analytes, it is important to let the appropriate person(s) know in case his or her site assessment is based on a specific target analyte list.

12.5.8.2 In all instances, if results are reported from data that is out of control or unacceptable, that data is qualified accordingly. Once the client has been notified and he or she instructs us to

report the data, then flag the data indicating what type of nonconformity has occurred.

12.5.8.3 Out of control data is still retained by the laboratory and filed and archived along with acceptable data.

12.5.8.4 A non-conformance/corrective action report (CAR) form must be filled out whenever these types of events occur. The information on the report includes the problem encountered, planned corrective actions, and corrective action follow-up. The form is then discussed with and signed by the analyst, the client representative, the QA officer, and the laboratory manager. The purpose of the form is to document problems in order to eliminate the possibility of repeating nonconformance and to ensure that the proper corrective actions are employed.

13.0 WASTE MANAGEMENT

13.1 Samples are routinely held (refrigerated) for up to six weeks from analysis date before they enter the waste stream. Waste disposal of samples and standards follows the procedures documented in the Laboratory Waste Disposal SOP (Quality Assurance Section, SOP NO. FO-8, Rev. 4).

ATTACHMENT I
SULFUR CLEANUP
METHOD 3660B

1.0 SCOPE AND APPLICATION

This method covers the procedures used to eliminate sulfur interference from PCB extracts. Elemental sulfur is indicated by the presence of white crystals in the sample extract, or, upon analysis, a broadband interference from the solvent front.

2.0 REFERENCES

USEPA, SW-846, 3rd Ed. Method 3660B. December, 1996.

3.0 APPARATUS AND MATERIALS

1.1 Mechanical shaker or mixer

1.2 Pipets – disposable, Pasteur type

1.3 Disposable culture tubes – 25 mL with Teflon-lined screwcaps.

1.4 Tetrabutylammonium (TBA) – sulfite reagent

1.5 Sodium sulfate (granular, anhydrous 60/120 mesh, Fisher # S415-212).

4.0 PROCEDURE

4.1 Pipet 1.0 mL of PCB extract into a 25 mL culture tube.

4.2 Add 1.0 mL TBA – sulfite reagent and 2 mL iso-propanol to the tube and cap.

4.3 Shake for at least 1 minute. If the sample is colorless or if the initial color is unchanged, and if crystals are observed, sufficient sodium sulfite is present. If the precipitated sodium sulfite disappears, add more crystalline sodium sulfite in approximately 100 mg portions until a solid residue remains after repeated shaking.

4.4 Add 5 mL distilled water and shake for at least 5 minutes. Allow the sample to stand for 5-10 minutes. Transfer the hexane layer to injection vials and/or storage vials.

4.5 Analyze the extracts by gas chromatography.

4.6 Verify that the TBA-sulfite is free from contamination by shaking out 1.0 mL of TBA – sulfite with 10 mL of hexane and analyze.

4.7 Process all quality control samples (e.g., spikes, blanks and duplicates) along with any samples.

4.8 Verify that recoveries of PCB's are greater that 80% by processing a standard (CCV) through the procedure.

ATTACHMENT II
FLORISIL CARTRIDGE CLEANUP
METHOD 3620B

1.0 SCOPE AND APPLICATION

1.1 Florisil, a registered trade name of U. S. Silica Co., is a magnesium silicate with basic properties. It is used to separate analytes from interfering compounds prior to sample analysis by a chromatographic method.

1.2 Florisil has been used for the cleanup of pesticide residues and other chlorinated hydrocarbons; the separation of nitrogen compounds from hydrocarbons; the separation of aromatic compounds from aliphatic-aromatic mixtures; and similar applications for use with fats, oils, and waxes. Additionally, Florisil is considered good for separations with steroids, esters, ketones, glycerides, alkaloids, and some carbohydrates. Florisil cleanup may be accomplished using a glass chromatographic column packed with Florisil or using solid-phase extraction cartridges containing Florisil. This method includes procedures for cleanup of sample extracts containing the following analyte groups:

Chlorinated hydrocarbons
Organochlorine pesticides
Organophosphates
Organophosphorus pesticides
PCBs
Phthalate esters
Nitrosamines
Nitroaromatics
Haloethers
Aniline and aniline derivatives

2.0 SUMMARY OF METHOD

2.1 This method describes procedures for Florisil cleanup of solvent extracts of environmental samples using solid-phase extraction cartridges. The cartridge cleanup protocol uses solid-phase extraction cartridges containing 40 µm particles of Florisil (60 D pores). Each cartridge is washed with solvent immediately prior to use. The sample extract is loaded onto the cartridge which is then eluted with suitable solvent(s). A vacuum manifold is required to obtain reproducible results. The eluate may be further concentrated prior to gas chromatographic analysis.

3.0 INTERFERENCES

3.1 A reagent blank should be prepared and analyzed for the compounds of interest prior to the use of this method. The level of interferences must be below the method detection limit before this method is performed on actual samples. The procedures for reagent purification outlined here should be considered to be the minimum requirements for use of this method. More extensive procedures may be necessary to achieve acceptable levels of interferences for some analytes. However, during the evaluation of the cartridge clean-up procedure, phthalate esters were detected in the Florisil cartridge method blanks at concentrations up to 400 ng per cartridge. Therefore, complete removal of the phthalates esters from Florisil cartridges may not be possible.

4.0 APPARATUS AND MATERIALS

4.1 Vacuum manifold - VacElute Manifold SPS-24 (Analytichem International), Visiprep (Supelco, Inc.) or equivalent, consisting of glass vacuum basin, collection rack and funnel, collection vials, replaceable stainless steel delivery tips, built-in vacuum bleed valve and gauge. The system is connected to a vacuum pump or water aspirator through a vacuum trap made from a 500-mL sidearm flask fitted with a one-hole stopper and glass tubing. The manifold is required for use of the cartridge cleanup protocol.

5.0 REAGENTS

5.1 Eluting solvents - all solvents must be pesticide quality or equivalent.

5.2 Hexane, pesticide grade.

5.3 Methylene chloride, pesticide grade.

5.4 Acetone, pesticide grade.

5.5 Florisil cartridge phenol check solution (for the organochlorine pesticide technique) - Prepare a solution of 2,4,5-Trichlorophenol in acetone at a concentration of 0.1 g/L.

5.6 Florisil cartridge pesticide check solution - Prepare a solution containing the following analytes in hexane:

BHCs
Heptachlor
BHC
Endosulfan I
Dieldrin
Endrin
4,4'-DDD
4,4'-DDT
Methoxychlor
Tetrachloro-m-xylene
Decachlorobiphenyl

6.0 PROCEDURE

6.1.1 Whenever Florisil is used to fractionate groups of target compounds (rather than to simply remove potential interference) it is critical that the specific fractionation scheme be validated using spiked solutions or spiked sample extracts that contain most or all of the analytes of interest. This may be particularly important when the Florisil cartridge techniques are employed, as the differences between the various cartridge formats and manufacturers may affect the fractionation patterns. In addition, it may be useful to archive any fractions not originally intended for analysis, in the event that the fractionation scheme chosen does not yield the intended results. Once the determinative analysis has been performed and demonstrates that the fractionation has been successful, such archived fractions may be disposed of in an appropriate manner. However, if the fractionation did not perform as intended, the analytes of interest may be contained in the archived fractions, which may be able to be analyzed or combined with the other fraction(s) for reanalysis.

6.1.2 Following Florisil cleanup, extracts may require further concentration and/or solvent exchange.

6.2 Cartridge Evaluation

6.2.1 The efficiency of each lot of the solid-phase extraction cartridges must be verified. Only lots of cartridges from which the spiked analytes are quantitatively recovered may be used to process the samples. A check should also be performed at least once on each individual lot of cartridges and at least once for every 300 cartridges of a particular lot, whichever frequency is greater.

6.2.2 To check each new lot of Florisil cartridges before use, perform the following in duplicate.

6.2.3 Combine 0.5 ml of 2,4,5-Trichlorophenol solution in Section 5.5 and 0.5 ml of pesticide spiking solution in Section 5.6 in a two ml autosampler vial.

6.2.4 Arrange the cartridges on the manifold in the closed-valve position.

6.2.5 Turn on the vacuum pump and set the vacuum to 10 in (254 mm) of Hg. Do not exceed the manufacturer's recommendation for manifold vacuum. Flow rates may be controlled by opening and closing cartridge valves.

6.2.6 Condition the cartridges by adding 4 mL of hexane to each cartridge. Slowly open the cartridge valves to allow hexane to pass through the sorbent beds to the lower frits. Allow a few drops per cartridge to pass through the manifold to remove all air bubbles. Close the valves and allow the solvent to soak the entire sorbent bed for 5 minutes. Do not turn off the vacuum.

6.2.7 Slowly open cartridge valves to allow the hexane to pass through the cartridges.

6.2.8 Close the cartridge valves when there is still at least 1 mm of solvent above the sorbent bed.

6.2.9 Do not allow cartridges to become dry. If cartridges go dry, repeat the conditioning step.

6.2.10 Add the spiking solution in 6.2.3 to the Florisil cartridge.

6.2.11 Elute the cartridge with 9 ml of acetone/hexane (10/90, v/v). Collect the extraction in a 15 ml test tube.

6.2.12 Transfer extract to a concentrating thimble. Using the nitrogen blown apparatus, concentration the extract down to one ml and analyze by Method 8081A.

6.2.13 The lot of Florisil cartridges is acceptable if all pesticides are recovered at 80 to 110%, if the trichlorophenol is less than 5%, and if no peaks interfering with the target analytes are detected.

6.3 Handling sample extracts

6.3.1 Most sample extracts will have to be concentrated to a smaller volume prior to the use of Florisil cleanup. The extract volume is a function of the analytical sensitivity necessary to meet the project objectives. The extract volume will also affect the ability of the Florisil to separate target analytes from potential interferences where applying large extract volumes to the cartridges may cause poor results. Consult the appropriate extraction and determinative methods for the details on final extract volumes, extract concentration techniques, and solvent exchange procedures.

6.3.2 Reduce the sample extract volume to 10 mL prior to cleanup. The extract solvent should be hexane for these analytes. In most cases, given the sensitivity of the determinative methods, only 1 mL of the 10 mL extract needs to be subjected to the Florisil cleanup procedure. The remaining 9 mL should be archived for later use, if needed.

6.3.3 Place Florisil cartridges on manifold. Turn on the vacuum pump and adjust the pump pressure to 10 inches (254 mm) of Hg. Condition the cartridges by adding 4 ml of hexane. Slowly open the cartridge valve and collect the eluate into the collection vial. Allow a few drops of hexane to pass through the cartridge to remove any air bubbles. Close valve and allow solvent to soak the entire sorbent bed for five minutes. Do not turn off vacuum.

6.3.4 Slowly, open the valve to allow the hexane to pass through the cartridge. Close valve when about 1 mm of hexane is remaining above the sorbent bed.

6.3.5 Add 1 ml of extract to the Florisil cartridge. Allow the extract to pass through the cartridge at a rate about 2 ml per minute.

6.3.6 Before extract goes below the surface of the sorbent bed, add 9 ml of hexane/acetone (90/10, v/v) to the cartridge.

6.3.7 After extract has been collected, concentrate sample down to 1 ml. Refer to Section 9.5 for concentration techniques.

The following procedures are used to separate the organochlorine pesticides from the PCBs.

6.3.8 Add 3 mL of hexane to the cartridge. Turn on the vacuum pump and adjust the pump pressure to 10 inches (254 mm) of Hg. Allow the solvent to soak the sorbent bed for 1 minute or less. Slowly open the cartridge valve and collect the eluate into the collection

vial. This is Fraction 1 and it will contain the PCBs and a few of the organochlorine pesticides.

6.3.9 Close the cartridge valve, replace the collection vial, and add 5 mL of methylene chloride/hexane (26/74, v/v) to the cartridge. Slowly open the cartridge valve and collect the eluate into the collection vial. This is Fraction 2 and it will contain most of the pesticides.

6.3.10 Close the cartridge valve, replace collection vials, and add 5 mL of acetone/hexane (10/90, v/v) to the cartridge. Slowly open the cartridge valve and collect the eluate into the collection vial. This is Fraction 3 and it will contain the remaining pesticides.

6.3.11 As needed, perform a solvent exchange and adjust the final volume of the eluant to 1 ml.

7.0 QUALITY CONTROL

7.1 The analyst must demonstrate that the compounds of interest are being quantitatively recovered before applying this method to actual samples. A recovery check must be performed using standards of the target analytes at known concentration. The efficiency of each lot of the solid-phase extraction cartridges must be verified. Only lots of cartridges from which the spiked analytes are quantitatively recovered may be used to process the samples. A check should also be performed at least once on each individual lot of cartridges and at least once for every 300 cartridges of a particular lot, whichever frequency is greater.

7.2 Organochlorine pesticides - To check each new lot of Florisil cartridges before use, perform the following in duplicate. Combine 0.5 mL of the 2,4,5-trichlorophenol solution, 1.0 mL of the pesticide solution, and 0.5 mL of hexane in a vial. Condition the cartridge and then perform the cartridge cleanup Elute the cartridge with 9 mL of acetone/hexane (10/90, v/v) only. Reduce the volume to 1.0 mL and analyze. The lot of Florisil cartridges is acceptable if all pesticides are recovered at 80 to 110 %, if the recovery of trichlorophenol is less than 5 %, and if no peaks interfering with the target analytes are detected.

ATTACHMENT III
SULFURIC ACID CLEANUP
METHOD 3665A

1.0 SCOPE AND APPLICATION

1.1 This method is suitable for the rigorous cleanup of sample extracts prior to analysis for PCBs. This method should be used whenever elevated baselines or overly complex chromatograms prevent accurate quantitation of PCBs. This method cannot be used to cleanup extracts for other target analytes, as it will destroy most organic chemicals including pesticides.

1.2 This method is restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 An extract is solvent exchanged to hexane, then the hexane is sequentially treated with concentrated sulfuric acid.

2.2 Blanks and replicate analysis samples must be subjected to the same cleanup as the samples associated with them.

3.0 INTERFERENCES

3.1 This technique will not destroy chlorinated benzenes, chlorinated naphthalenes, and a number of chlorinated pesticides.

4.0 APPARATUS

4.1 Syringe or Class A volumetric pipet, glass; 1.0, 2.0, and 5.0 ml.

4.2 Vials – 1, 2, and 10 ml, glass with polytetrafluoroethylene (PTFE)-lined screw caps.

4.3 Vortex mixer

5.0 REAGENTS

5.1 Organic-free water (MilliQ-processed)

5.2 Sulfuric acid/water, H_2SO_4/H_2O (1:1, v/v)

5.3 Hexane, pesticide grade

6.0 PROCEDURE

6.1 Using a syringe or a volumetric pipet, transfer 1.0 or 2.0 ml of the hexane extract to a 10 ml vial and carefully add 5 ml of the 1:1 sulfuric acid/water solution. Mix well.

6.2 Allow the phased to separate for at least 1 minute. Examine the top hexane layer, it should not be highly colored nor should it have a visible emulsion or cloudiness. If clean hexane phase is not achieved repeat step one.

6.3 Transfer the hexane layer to a clean 5 ml vial.. Take care not to include any of the acid layer in this clean vial. Once the hexane layer is removed, perform a second "extraction" of the acid layer.

6.4 Add an additional 1 ml of hexane to the sulfuric acid layer, cap and mix well. This second extraction is done to ensure quantitative transfer of the PCBs or Toxaphene.

6.5 Remove the second hexane layer and combine with the clean extract

6.6 Reduce the volume of the combined hexane layers to the original volume (1 or 2 ml) using an appropriate concentration technique.

6.7 The extracts obtained may now be analyzed for the target analytes using the appropriate organic techniques. If analysis of the extract will not be performed immediately, transfer extract to a vial with a PTFE-line screw cap top.

Table 3
Summary of Method Objectives for Method 8082-PCBs by Aroclors

Quality Control Element	Frequency of Implementation	Acceptance Criteria	Corrective Action
Initial Calibration (Aroclors 1016/1260)		$r \geq 0.995$, RSD $\leq 20\%$, $r^2 \geq 0.990$, mean RSD $\leq 20\%$	Linearity must fit one of acceptance criteria, or the curve must be reanalyzed.
Initial Calibration Verification (ICV)	After initial calibration	85-115%	If ICV falls outside QC criteria, reanalysis must take place. If ICV still fails, it may be appropriate to repeat the initial calibration curve or to qualify the analyte with "A".
Continuing Calibration Verification (CCV)	Every twelve hours	D or mean $D \leq 15\%$ with a maximum $\%D \leq 30\%$	If CCV falls outside QC criteria, reanalysis must take place. If CCV still fails, it may be appropriate to repeat the initial calibration curve or to qualify the analyte with "A".
Retention Time Window (RTW)	Retention Times are updated upon the beginning CCV	Retention times are 3x Standard Deviation the absolute retention time, if the default standard deviation is employed, width of the window will be 0.03 minutes	

Table 3
Summary of Method Objectives for Method 8082-PCBs by Aroclors

Method Blank (MB)	1 per sample prep batch	Analytes <1/2 MRL	If sample is available and within holding times, sample associated with method blank needs to be reprepped. If no sample is available, qualify the data with a "B" to all associated positives when less than 5X blank concentration
Laboratory Control Sample (LCS)	1 per sample prep batch	In house limits or client specified	If LCS fails percent recoveries. Re-analyze the LCS. If LCS recoveries are still outside QC control limits, qualify the failing analytes with a "Q".
Matrix Spike (MS)	1 per sample prep batch	In house limits or client specified	No action is taken based on MS recovery alone, use of professional judgement. For recoveries outside QC criteria, qualify out lying compound with "M".
Matrix Spike Duplicate (MSD)	1 per sample prep batch	In house limits or client specified	No action is taken based on MSD results alone, use of professional judgement. If RPD is outside QC criteria, then qualify the out lying compounds with "Y".
Surrogates	Every sample and QC	In house limits or client specified	Rerun sample. If no apparent matrix interference noticed re-extract sample. If no sample is available, qualify the surrogate with "S".
Target Analyte Confirmation	Whenever a positive is detected on one column and confirmed on 2nd column.	RPD ≤40%	If the RPD ≥ 40%, qualify analyte with "P".

Table 4
8082 PCB Analysis Data Review Checklist

Sequence Date	Analyst / Data Interpreter	Independent Reviewer	Date of Review	Approved
				Yes or No

Instructions: Complete one checklist per *analytical run*. Enter the appropriate response for each question. Each "No" response requires an explanation in the Comments section, and may require the initiation of a Nonconformance Report.

Requirement:	Acceptance Criteria	Analyst Review		Independent Review		Comments: (indicate reference to an attachment if necessary)
		Yes	No	Yes	No	
1. INITIAL CALIBRATION (ICAL)						
a. Was the PCB initial calibration (all Aroclors) performed using a minimum of five varying standard concentration levels?	Lowest standard at or near MRL					
b. Is the variation between calibration response factors for all concentration levels <20% RSD, is r^2 >.990, or r > 0.995 for the regression line?	RSD <20%, r^2 >.990, r>0.995					
c. Was each ICAL uniquely identified (i.e. Standard Number)?						
d. Was an initial calibration blank (ICB) analyzed?						
2. INITIAL CALIBRATION VERIFICATION (ICV)						
a. Were there a second source ICVs for all Aroclors analyzed after the initial calibration and prior to analysis of any samples?	Second source					
b. If a quadratic curve was used for any Aroclor, were there two ICV injections preformed (one above and one below the inflection point)?	Quadratic Check					
b. Were the recoveries for the ICVs between 85% and 115%?	%R 85-115%					
c. Was the ICVs uniquely identified (i.e. Standard Number)?						
3. CONTINUING CALIBRATION VERIFICATION (CCV)						
a. Were CCVs (Aroclor 1016/1260) analyzed at the beginning of the sequence, after every 12 hours or every 10 samples (which ever comes first) and at the end of the analytical run?						
b. Were the recoveries for the CCVs between 85% and 115%?	%R 85-115%					
c. Were confirmed Aroclor detects processed using the appropriate Aroclor method?						
d. Was each CCV uniquely identified (i.e. Standard Number)?						

Table 4
8082 PCB Analysis Data Review Checklist Continued

Requirement:	Acceptance Criteria	Analyst Review		Independent Review		Comments:
		Yes	No	Yes	No	(Indicate reference to an attachment if necessary)
4. BLANKS						
a. Was method blank (MB) analyzed prior to the analysis of samples?						
b. Was the MB results <1/2 the reporting limit (RL)?	< ½ MRL					
c. Was a MB prepped and analyzed at a frequency of one per Prep Batch?	Batch < 20 samples					
5. LABORATORY CONTROL SAMPLE (LCS)						
a. Was a LCS analyzed at a frequency one per Prep Batch?	Batch < 20 samples					
b. Were the LCS recoveries in each LCS within the acceptance criteria?	In-house limits or client specified limits					
6. MATRIX SPIKES						
a. Was a matrix spiked (MS) sample analyzed at a frequency one per Prep Batch?	Batch < 20 samples					
b. Were MS recoveries in each MS within the acceptance criteria?	In-house limits or client specified limits					
7. LABORATORY CONTROL SPIKE / MATRIX SPIKE DUPLICATE						
a. Was a duplicate matrix spike or laboratory control spike sample analyzed at a frequency one per Prep Batch?	Batch < 20 samples					
b. Were MSD or LCSD recoveries within the acceptance criteria?	In-house limits or client specified limits					
c. Is the relative percent difference (RPD) between a matrix spike (MS) and its' duplicate (MSD) or laboratory control spike (LCS) and its' duplicate (LCSD) within the acceptance criteria?	In-house limits or client specified limits					

Table 4
8082 PCB Analysis Data Review Checklist Continued

Requirement:	Acceptance Criteria	Analyst Review		Independent Review		Comments: (indicate reference to an attachment if necessary)
		Yes	No	Yes	No	
8. SAMPLES (INCLUDING BLANKS, STANDARDS, AND QC SAMPLES)						
a. Are chromatogram characteristics, including peak shapes and areas, consistent with those of the CCV?						
b. Are surrogate recoveries for all samples, blanks, standards, and QC samples within acceptance criteria?						
c. Were all samples having analytes detected in amounts exceeding the calibration range diluted and reanalyzed?						
d. Were all samples extracted within holding times and analyzed within 40 days of extracting?	Analysis within 40 days of extraction					
e. Did the samples require additional cleanup steps? (i.e. acid treatment, florisil, and sulfur treatment)	Acid, Florisil, Sulfur Treatments					
f. Was there a hexane injection preformed prior to sample analysis?						
g. Was there a priming standard injected prior to sample analysis?						
9. RECORDS AND REPORTING						
a. Are Run, Prep Batch and Extraction sheets, Summary sheets, Sequence file, initial and rerun raw and process data present in the data file?						
b. Are all chromatograms dated and initialed?						
c. Are reported results whose amounts exceeded the acceptance criteria flagged with an appropriate qualifier and, if needed, a NCR completed?						
d. Do all values, dilution factors and qualifiers listed on the raw reports match the LIMS data?						
e. Is the ICAL method referenced on the Raw Data?						

CT Laboratories
Baraboo Laboratory Division

Title: **Semi-Volatile Organochlorine Pesticide Analysis**

SOP Number: **8081A**

Written by: _____

Technical Review by: _____

Approved by: _____
Quality Assurance Manager

Approved by: _____
Laboratory Director

SOP Manual Control Number: _____

1.0 SCOPE/APPLICATION

1.1 Method SW-846 8081A is used to determine the quantitation of various Organochlorine Pesticides in extracts from solid and aqueous matrices. Capillary columns are employed with electron capture detectors (ECD). Target analytes determined by this method are listed in Table 1.0.

1.2 Toxaphene and tech-Chlordane are multi-component mixtures. The identification of the multi-peaked analytes such as Toxaphene and tech-Chlordane can be performed by a combination of pattern recognition and retention time.

1.3 This method is a dual column analysis. Two analytical columns joined to a single injection port. The second gas chromatographic column that can be used to confirm the measurements made with the primary column.

1.4 The procedures contained within this method are restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results.

Table 1.0
Pesticides and Retention Times

Pesticide Name	Retention Time
alpha-BHC	4.17
beta-BHC	4.82
Lindane (gamma-BHC)	4.99
delta-BHC	5.65
Heptachlor	7.22
Aldrin	8.52
Heptachlor Epoxide (b)	10.33
gamma-Chlordane	11.52
Endosulfan I	12.12
alpha-Chlordane	12.33
Dieldrin	13.57
4,4'-DDE	13.85
Endrin	14.77
Endosulfan II	15.44
4,4'-DDD	16.57
Endrin Aldehyde	16.85
Endosulfan Sulfate	18.83
4,4'-DDT	19.67
Endrin Ketone	23.10
Methoxychlor	26.11

Table 1.1
Toxaphene and tech-Chlordane Retention Times

Compound Name	RT Peak#1	RT Peak#2	RT Peak#3	RT Peak#4	RT Peak#5
tech-Chlordane	5.03	5.60	9.43	10.17	10.43
Toxahene	14.03	16.92	17.26	17.62	17.89

2.0 SUMMARY OF METHOD

2.1 This method describes procedures for isolating organic compounds through sample preparation from aqueous and soil matrices (reference methods SW846-3510C and 3545), concentration techniques that are suitable for preparing the extract, and the quantitative/qualitative analysis for the determination of pesticides by method SW846-8081A.

2.2 A sample of a known volume or weight is extracted with solvent or diluted with solvent. Method applies for aqueous samples extracted by liquid-liquid separatory funnel (SW846-3510C). Method applies for soil/sediment, and solid waste samples extracted by standard solvent extraction methods utilizing pressurized extraction techniques as heated pressurized fluid extraction (SW846-3545).

2.3 The resultant extract is chemically dried and concentrated in a Kuderna-Danish (K-D) apparatus in preparation for instrumental analysis.

2.4 Extracts for pesticide analysis may be subjected to Florisil, and/or sulfur cleanup designed specifically for these analytes. After cleanup, the extract is analyzed by injecting a known aliquot into a gas chromatograph equipped with dual capillary columns and ECD detectors.

2.5 The procedures contained within this method are restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results.

3.0 INTERFERENCES

3.1 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. Specific selection of reagents and purification of solvents by distillation in all-glass systems mat be necessary. Refer to each method for specific guidance on quality control procedures.

3.2 Phthalate esters contaminate many types of products commonly found in the laboratory. Plastics, in particular, must be avoided because phthalates are commonly used as plasticizers and are easily extracted from plastic materials

3.3 Soap residue (e.g. sodium dodecyl sufate), which results in a basic pH on glassware surfaces, may cause degradation of certain analytes.

3.4 Interferences co-extracted from the samples will vary considerably from source to source. If analysis of an extracted sample is prevented due to interference, further cleanup of the sample may be necessary.

3.5 Elemental sulfur (S_8) is readily extracted from soil samples and may cause chromatographic interferences in the determination of Aroclors. Sulfur can be removed through cleanup procedures.

3.6 Other halogenated pesticides or industrial chemicals may interfere with the analysis of pesticides. Co-eluting chlorophenols may be eliminated by Florisil treatments. Aroclors may also interfere with analysis of Organochlorine pesticides. The biggest challenge is for the multi-component analytes such as tech-Chlordane and Toxaphene. If Aroclors are expected to occur in samples, the analyst should consult Methods 3620 (Florisil) and 3630 (silica gel) for techniques that may be used to separate the pesticides from the Aroclors.

4.0 DEFINITIONS

4.1 Method Blank (MB): An analyte-free matrix to which all reagents are added in the same volumes or proportions as used in the sample processing. The method blank is carried through the complete sample preparation and analytical procedure. The method blank is used to document contamination resulting from the analytical process.

4.2 Laboratory Control Spike (LCS): Milli-Q water (for water) and Organic-Free Soil (for soil) is spiked with the target analytes and carried through the complete sample preparation and analytical procedure. The control spike is used to document the ability of an analyst to generate acceptable precision and bias to verify the analytical system performance, and to document method accuracy for each matrix.

4.3 Laboratory Control Spike Duplicate (LCSD): A duplicate Milli-Q water (for water) and Organic-Free Soil (for soil) is spiked with the target analytes and carried through the complete sample preparation and analytical procedure. The control spike duplicate is used to document the precision and bias of a method. This QC type is only performed when insufficient amount of sample is available for performing a matrix spike and matrix spike duplicate.

4.4 Matrix Spike (MS): An aliquot of sample spiked with a known concentration of target analytes. The spiking occurs prior to sample preparation and analysis. They are used to document the precision and bias of a method in a given sample matrix.

4.5 Matrix Spike Duplicate (MSD): Intra-laboratory split samples spiked with identical concentration of target analytes. The spiking occurs prior to sample preparation and analysis. They are used to document the precision and bias of a method in a given sample matrix.

4.6 Method Reporting Limit (MRL): The method reporting limit is a threshold value below which the laboratory reports a result as non-detect. The highest value reported for the method reporting limit is dependant upon project-specific action or decision levels. Method reporting limits are adjusted based on the sample matrix and any sample dilution/concentrations when necessary.

4.7 Method Detection Limit (MDL): The method detection limit is the minimum concentration of a substance that can be measured and reported with 99 percent confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte. Depending on project specific MDLs may be in form of a MDL check standard or the MDL is subject to extraction procedures.

4.8 Surrogate (SSTD) An organic compound which is similar to the target analytes in chemical composition and behavior in the analytical process, but which is not normally found in environmental samples. Its use is to monitor the performance of the extraction, cleanup (as needed), the analytical system, and the effectiveness of the method. The surrogates are; 2,4,5,6-Tetrachloro-m-xylene and Decachlorobiphenyl.

4.9 Initial Calibration (ICAL): An analytical instrument is said to be calibrated when an instrumental response can be related to the concentration of an analyte. This relationship may be depicted graphically, and referred as to a "calibration curve". Initial calibration curves must be established based upon the requisite number of standards identified within the method for each target analyte.

4.10 Initial Calibration Verification (ICV): The initial calibration verification standard (different lot # or manufacture from the initial calibration standard) shall verify the initial calibration curve. The initial calibration verification standard involves the analysis of all target analytes each time the initial calibration is performed.

4.11 Calibration Verification Standard (CCV): A standard solution that is used to check the validity of a calibration curve on a daily basis. It also provides information on satisfactory maintenance and adjustment of the instrument during sample analysis.

4.12 Evaluation Verification Standard (EVAL): A standard solution that is used to determine injection port breakdown of DDT and Endrin. Injector ports that are contaminated, chemically active, or too hot can cause degradation ("breakdown"). Endrin and DDT breakdown to Endrin Aldehyde, Endrin Ketone, DDD, or DDE.

5.0 SAFETY

5.1 Protective clothing; safety glasses, gloves, apron and/or lab coat, long pants, and protective shoes, should be worn to protect against unnecessary exposure to hazardous chemicals and contaminants in samples. All activities performed while following this procedure should utilize appropriate laboratory safety systems.

5.2 The toxicity of chemicals used in this method has not been precisely defined. Each chemical should be treated as a potential health hazard, and exposure to these chemicals should be minimized.

6.0 APPARATUS & MATERIALS

Apparatus:

6.1 Gas Chromatograph- An analytical system complete with gas chromatograph suitable for split-splitless injection and all required accessories including syringes, analytical columns, electron capture detectors, auto sampler, electronic pressure control, and EZ Chrom Elite data acquiring system.

6.1.1 Carrier Gas: Nitrogen at 22.0 initial pressure
Make-up Gas: Nitrogen at 30 mL/minute
Injector: 220 °C (Splitless)
Detector (s): 300 °C
Oven: Initial – 165 °C (hold for 0.5 minute)
Ramp – 2 °C/minute
Final - 185 °C (hold for 1 minutes)
Ramp – 5 °C/minute
Final - 210 °C (hold for 0 minutes)
Ramp – 10 °C/minute
Final - 260 °C (hold for 0 minutes)

Note: Instrument operating parameters are subject to change to improve overall chromatography (changes are noted in the Instrument Maintenance Log Book).

6.2 Analytical column pair;

6.2.1 30m x 0.32 mm ID bonded with 5% phenyl polysiloxane / 95% dimethylsiloxane, 0.25 um. (ZB-5, part # 7HM-G002-11 or equivalent).

6.2.2 30m x 0.32 mm ID bonded with 14% Cyanopropylphenyl/86% dimethylplysiloxane, 0.25 um (ZB-1701, part # 7HM-G006-11 or equivalent).

6.3 Water bath- heated and capable of accepting a Kuderna-Danish apparatus.

6.4 Dionex ASE 200.

6.5 Organomation Nitrogen blow down concentrator.

6.6 Analytical balance capable of accurately weighing to the nearest 0.01 gram (for sample preparation).

6.7 Oven.

Glassware:

6.8 Separatory funnel - 2000 mL glass with Teflon stopcock.

6.9 Kuderna-Danish (K-D) apparatus:
6.9.1 Concentrator tube, 10.0 mL, graduated. (Fisher # K570051-1025).
6.9.2 Evaporation flask- 500 mL or 250 ml (Fisher # K570035-0250).
6.9.3 Synder column- Three-ball macro (Fisher # K503000-0121).
6.9.4 Springs or Teflon clamps to attach concentrator tube to evaporation.

6.10 Graduated cylinder (Class A) - 1000 mL. (Fisher 08-559G).

6.11 Beaker - 250 mL and 600 mL.

6.12 Vials - 2.0 mL and 60 mL screw cap vials with Teflon lined caps (Fisher # 03-377-10B).

6.13 Pasteur Pipets (Corning # 7095B-5X).

6.14 Funnels – glass.

6.15 Volumetric flask – (Class A) 10, 25, 50, and 100 mL.

6.16 Syringes 10 uL, 100 uL, 500 uL, and 1,000 uL.

Reagents:

6.17 Deionized water (Milli-Q processed).

6.18 Sodium sulfate (granular, anhydrous 60/120 mesh, Fisher # S415-212). Purify by heating to 400°C in a shallow glass tray, loosely covered with foil. Transferred to a clean glass container. Solvent rinsed prior to use.

6.19 Silica sand- hydrocarbon free. Purify by heating to 400°C in a shallow glass tray, loosely covered with foil. Transferred to a clean glass container. Solvent rinsed prior to use.

6.20 Methylene chloride, pesticide grade.

6.21 Acetone, pesticide grade.

6.22 Hexane, pesticide grade.

6.23 Isopropanol, pesticide grade.

6.24 Nitrogen (5.0 rating).

6.25 Sulfuric Acid-1:1(v/v).

6.26 Sodium Hydroxide- 10 N.

6.27 Diatomaceous earth (JT Baker # 1939-01). Purify by heating to 400°C in a shallow glass tray, loosely covered with foil.

Materials:

6.28 Boiling chips, carborundum, approximately 10/40 mesh (methylene chloride rinsed). (G. Frederick Smith Chemical Company, Catalog #198)

6.29 pH indicator paper- pH 0-14. (Whatman Catalog #2613991)

6.30 Dionex ASE Filters (Catalog #049458).

6.31 Filter- Glass Microfibre 12.5 cm GF/A, (Whatman # 1827-125).

6.32 Aluminum foil.

6.33 Spatulas- stainless steel.

7.0 STANDARDS AND SPIKES

7.1 Preparation of standards is documented in the Pest/PCB standards logbook. Each standard is labeled by prep date to allow for tracking. Opened stock standards expire one year or sooner if comparison with quality control check samples indicated a problem. Leftover stock standards are saved in a capped vial in the original box in the freezer. Any subsequent dilutions made from the opened vial expire six months from the original opening. The cracking date of the stock standard vial will be recorded on the label along with the six month expiration date.

7.2 Stock Standards -Stock Standards are purchased from vendors who provide certified solutions. Standards are stored at -10°C in a freezer reserved for standard solutions. Unopened standard shall have the manufactures suggested expiration date. Opened stock standards expire one year or sooner if comparison with quality control check samples indicated a problem (Not to exceed the manufactures expiration date).The following list of stock standards are commercially prepared standards, which are certified by the manufacturer, such as;

Organochlorine Pesticide Mix AB#1: Restek Part # 32291 at 200 ug/mL.
Toxaphene Pesticide Mix: Restek Part # 32005 at 1000 ug/ml.
tech-Chlordane Pesticide Mix: Restek Part # 32021 at 1000 ug/ml.
Pesticide Surrogate Mix: Restek Part # 32000 at 200 ug/ml.
Pesticide System Evaluation Mix: Supelco Part # 48282 at 500 ug/ml

7.3 Intermediate Stock Standards: These standards are diluted stock standards so that the concentration levels are manageable for the preparation of working standards. The pesticide intermediate standard is prepared at an optimum level for the preparation of the working stock standard. Each pesticide compound is at a concentration of 2.0 ug/ml with surrogate concentration at 2.0 ug/ml in hexane (Table 2.0). For the Toxaphene and tech-Chlordane, the multi-component compounds are at a concentration of 10.0 ug/ml with a surrogate concentration of 1.0 ug/ml (Table 2.1).

Table 2.0
Intermediate Standard Concentration

Intermediate Standard	Stock Standard Concentration (ug/ml)	Standard Volume (ml)	Final Volume (ml)	Final Concentration (ug/ml)
Pesticide Mix AB	200	0.100	10.0	2.0
Surrogate	200	0.100	10.0	2.0

*Note: The concentration of the Intermediate Working standard and Intermediate ICV standard are prepared the same manner.

Table 2.1
Intermediate Standard Concentration

Intermediate Standard	Stock Standard Concentration (ug/ml)	Standard Volume (ml)	Final Volume (ml)	Final Concentration (ug/ml)
Toxaphene	1000	0.100	10.0	10.0
tech-Chlordane	1000	0.100	10.0	10.0
Surrogate	200	0.05	10.0	1.0

7.4 Calibration standards: An initial calibration of the listed pesticides in Table 1.0 is performed using a minimum of 5 points. The following concentrations correspond to the expected range of concentrations found in real samples and should bracket the linear range of the detector. By taking known aliquots of the intermediate standard and diluting them to volume in hexane. The following levels are repeated across all pesticide compounds:

Organochlorine Pesticides:

Level 1	0.001 ug/ml
Level 2	0.002 ug/ml
Level 3	0.008 ug/ml
Level 4	0.020 ug/ml
Level 5	0.040 ug/ml
Level 6	0.080 ug/ml

Table 2.2
Calibration Points for the Pesticide Linearity

Linearity Points	Spike Concentration (ug/ml) Pesticides	Standard Volume (ml)	Final Volume (ml)	Final Concentration (ug/ml) Pesticides	Final Concentration (ug/ml) Surrogate**
1	2.0	0.005	10.0	0.001	0.001
2	2.0	0.010	10.0	0.002	0.002
3	2.0	0.040	10.0	0.008	0.008
4	2.0	0.100	10.0	0.020	0.020
5	2.0	0.200	10.0	0.040	0.040
7	2.0	0.400	10.0	0.080	0.080

7.5 Calibration standards: Standards for the tech-Chlordane and Toxaphene are necessary for pattern recognition. These standards are also used to determine a single-point calibration factor (CF) for that specified

compounds. (In situations where only analyzing for Toxaphene or tech-Chlordane for a specific project, the analyst may employ a minimum of a five point initial calibration of each of the compound of interest.).

7.6 An initial calibration of the listed multi-component pesticides in Table 1.1 is performed using a single point RF or a minimum of a five point calibration curve. These concentrations correspond to the expected range of concentrations found in real samples and should bracket the linear range of the detector. By taking known aliquots of the intermediate standard and diluting them to volume in hexane.

Toxaphene and tech-Chlordane:

Level 1	0.05 ug/ml
Level 2	0.10 ug/ml
Level 3	0.20 ug/ml
Level 4	0.40 ug/ml
Level 5	0.80 ug/ml
Level 6	1.60 ug/ml

Table 2.3
Multiple Point Calibration

Linearity Points	Spike Concentration (ug/ml)	Standard Volume (ml)	Final Volume (ml)	Final Concentration (ug/ml)	Final Concentration (ug/ml) Surrogate**
1	10.0	0.05	10.0	0.05	0.005
2	10.0	0.10	10.0	0.10	0.010
3	10.0	0.20	10.0	0.20	0.020
4	10.0	0.20	5.0	0.40	0.040
5	10.0	0.40	5.0	0.80	0.080
6	10.0	0.80	5.0	1.60	0.160

Table 2.4
Single Point Calibration

Linearity Points	Spike Concentration (ug/ml)	Standard Volume (ml)	Final Volume (ml)	Final Concentration (ug/ml)	Final Concentration (ug/ml) Surrogate**
1	10.0	0.800	10.0	0.800	0.08

7.7 Initial Calibration Verification (ICV): The initial calibration verification standard (different lot # or manufacture from the initial calibration standard) shall verify the initial calibration curve. The initial calibration verification standard involves the analysis of target pesticides in table 1.0 at 0.040 ug/ml. By taking known aliquots of the ICV intermediate standard and diluting them to volume in hexane.

Table 2.5
ICV Working Pesticide Standard

Working ICV Standard	Intermediate Standard Concentration (ug/ml)	Standard Volume (ml)	Final Volume (ml)	Final Concentration (ug/ml)
Pesticides	2.0	0.200	10.0	0.040
Surrogate	2.0	0.200	10.0	0.040

7.8 Calibration Verification Standard (CCV): A working standard solution for Organochlorine pesticides at a concentration of 0.040 ug/L is used to check the validity of a calibration curve on a daily basis. By taking known aliquots of the intermediate standard and diluting them to volume in hexane. Standards for the other Toxaphene and tech-Chlordane are necessary for pattern recognition. These standards may be analyzed prior to sample analysis for a single-point calibration factor (CF) for that compound.

Table 2.6
CCV Working Pesticide Standard

Working CCV Standard	Intermediate Standard Concentration (ug/ml)	Standard Volume (ml)	Final Volume (ml)	Final Concentration (ug/ml)
Pesticide	2.0	0.200	10	0.040
Surrogate	2.0	0.200	10	0.040

7.9 Surrogate standard: A commercially prepared certified solution of 2,4,5,6-Tetrachloro-m-xylene and Decachlorobiphenyl is diluted in acetone to produce a working surrogate solution of 0.50 ug/mL. 1.0 mL is added to each sample. The surrogate concentration is normalized to 100% from the spiking solution in the initial calibration. This will provide percent recoveries that transfer directly to LIMS.

Table 2.7
Surrogate Spiking Solution

Surrogate Spiking Solution	Stock Standard Concentration (ug/ml)	Standard Volume (ml)	Final Volume (ml)	Final Concentration (ug/ml)
Surrogate	200	0.250	100.0	0.500

7.10 Spiking standards (matrix and control samples): Prepare a spiking solution in acetone that contains pesticides and concentration of 0.400 ug/ml and Toxaphene and tech-Chlordane at 8.0 ug/mL for water and sediment / soil samples. 1.0 ml is added to quality control and matrix spike samples. The concentration of these compounds should be five times higher for waste samples. If other compounds of interest are to be monitored they can be added at an appropriate level and noted in the standard preparation log. If client request a specified pesticide, a spiking solution will altered to match the pesticide of interest.

Table 2.8
Pesticide Spiking Solution

Spiking Solution	Stock Standard Concentration (ug/ml)	Standard Volume (ml)	Final Volume (ml)	Final Concentration (ug/ml)
Pesticide	100	0.100	50.0	0.400

Table 2.9
Toxaphene and tech-Chlordane Spiking Solution

Spiking Solution	Stock Standard Concentration (ug/ml)	Standard Volume (ml)	Final Volume (ml)	Final Concentration (ug/ml)
Tox/Chlor	1000.0	0.400	50.0	8.00

NOTE: All standards are stored at -10°C. Opened stock standards expire one year or sooner if comparison with quality control check samples indicated a problem. Intermediate and working standards expire six months from the date made. A intermediate stock standard or working standard shall not exceed expiration date criteria. All subsequent standards made from the intermediate stock standards expire on the same date as the working stock standard. If more than one standard

is added to a solution the expiration date will be the same as the stock standard with the earliest expiration date.

8.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

8.1 Aqueous samples are collected in 1-L amber glass containers with Teflon lined lids. Aqueous samples should be collected in duplicate. Solid samples are collected in 250-mL wide mouth glass containers with Teflon-lined lids. All samples are preserved by cooling to 4°C. The soil samples must be extracted within 14 days and water samples must be extracted in 7 days, from the date of collection.

8.2 Sample extracts should be stored under refrigeration in the dark and analyzed within 40 days of extraction.

9.0 PROCEDURE

9.1 Water Extraction (Method SW-846, 3510C)

9.1.1 Pre-rinse all glassware to be used in the extraction with methylene chloride (Pesticide Grade).

9.1.2 Mark the meniscus on the bottle for later determination of sample volume. From the glass sample collection bottle, quantitatively transfer sample into a 2 liter separatory funnel.

9.1.3 One method blank and laboratory control spike must be prepared with each batch of 20 samples or less. Prepare by adding one liter of Milli-Q water to 2 liter separatory funnel.

9.1.4 One sample from each batch of 20 samples or less must be selected for use in the preparation of a matrix spike (MS) and matrix spike duplicate (MSD). Select the sample and from the glass sample collection bottle, quantitatively transfer half of the sample into a 2 liter separatory funnel and label MS, and transfer the other half of the sample into another 2 liter separatory funnel and label MSD. If there is no sample to perform a matrix spike/matrix spike duplicated a laboratory control spike duplicate must be performed. Provided that there is sample available, the analyst may perform a sample duplicate per a batch up to 20 samples.

9.1.5 Check and note the pH on the extraction bench sheet. Adjust the pH to between 5 and 9 with 10N sodium hydroxide and/or 1:1 sulfuric acid solution.

9.1.6 *To the method blank, matrix spike/matrix spike duplicate, laboratory* control spike, and all samples add 1.0 mL of the surrogate standard mix by using a 1.0 ml syringe. In addition, add 1.0 mL of the pesticide spiking solution to the matrix spike/matrix spike duplicate and laboratory control spike (laboratory control spike duplicate). A separate laboratory control spike for Toxaphene and tech-Chlordane may be extracted with each pesticide analysis (provided that these multi-component compounds are requested). Add 1.0 of spiking solution of Toxaphene and tech-Chlordane and 1.0 ml of surrogate solution to the TOX/CHLOR laboratory control sample.

9.1.7 Add 60 mLs of methylene chloride to the sample bottle and rinse, pouring the methylene chloride into its respective separatory funnel. Extract the sample shaking vigorously for two minutes, venting frequently.

9.1.8 Allow the organic layer to separate from the water phase for a minimum of 10 minutes. Decant the lower layer into a 250 ml beaker. 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.

9.1.9 Repeat the extraction two more times using a fresh 60 mL portions of methylene chloride.

9.1.10 Determine the sample volume by filling the sample bottle to the mark (9.1.2) with water and transferring it to a "Class A" 1 liter graduated cylinder for measurement. Note all sample volumes on the extraction bench sheet.

9.1.11 Refer to section 9.3 for sample concentration.

9.2 Soil Extraction (Method SW-846, 3545)

9.2.1 Preparing the extraction cell for use: Pre-rinse extraction cell (tube and caps) with methylene chloride. Attach the screw fit tube cap of the soil extractor to the end of the tube without the serial number engraved on the side. Using the filter rod, push 1 filter through the open end of the tube until they reside flush on the bottom of the screwed end.

9.2.2 Decant and discard any water layer on a sediment sample. Mix sample thoroughly, especially composite samples. Discard any

foreign objects such as sticks, leaves, and rocks. Refer to SOP FO:10 for subsampling guidance.

9.2.3 Dry sediment/soil and dry waste samples amenable to grinding: Grind or otherwise reduce the particle size of the waste so that it either passes through a 1-mm sieve or can be extruded through a 1-mm hole. The addition of a drying agent (e.g. sodium sulfate or diatomaceous earth) can make sample more amenable to grinding.

9.2.4 Gummy, fibrous, or oily materials not amenable to grinding should be cut, shredded, or otherwise reduced in size to allow mixing and maximum exposure of the sample surfaces for the extraction. The addition of a drying agent (e.g. sodium sulfate or diatomaceous earth) can make sample easier to mix.

9.2.5 (Refer to SOP FO-10 for subsampling guidance). Weigh approximately 10 g of sample to the nearest 0.1 g into a 250-mL beaker and record the final weight. Add 2.5 g of diatomaceous earth to the sample. Mix well. The samples should be a free flowing powder. If sample is not free flowing add more diatomaceous earth until the sample has a dry texture. This powder is so mixed that it will allow the sample to pass through a 2 mm sieve.

9.2.6 Transfer the ground sample to an extraction cell of appropriate size for the aliquot.

9.2.7 One method blank and laboratory control spike must be prepared with each batch of 20 samples or less. Prepare by adding 10g of sand and 2.5g of diatomaceous earth to a clean 250 ml beaker. Transfer sample to extraction cell. A separate laboratory control spike for Toxaphene and tech-Chlordane must be extracted with each pesticide analysis (provided that these multi-component compounds are requested).

9.2.8 One sample from each batch of 20 samples or less must be selected for use in the preparation of a matrix spike (MS) and matrix spike duplicate (MSD). Select the sample and transfer approximately 40 grams to a 250 ml beaker. Mix well. Weigh three individual 10 grams aliquots of sample. Add drying agent. Transfer sample to extraction cell. If there is no sample available to perform a matrix spike/matrix spike duplicated a laboratory control spike duplicate must be performed.

9.2.9 Fill the void in each of the extraction cells with clean sand.

9.2.10 To the method blank, matrix spike/matrix spike duplicate, laboratory control spike, and all samples add 1.0 mL of the surrogate standard mix by using a 1.0 ml syringe. In addition, add 1.0 mL pesticide spiking solution to the matrix spike/matrix spike duplicate and laboratory control spike (laboratory control spike duplicate). A separate laboratory control spike for Toxaphene and tech-Chlordane may be extracted with each pesticide analysis (provided that these multi-component compounds are requested). Add 1.0 of spiking solution of Toxaphene and tech-Chlordane and 1.0 ml of surrogate solution to the TOX/CHLOR laboratory control sample.

9.2.11 Attach the other cap to the extractor cell, making sure the tube is sitting flush on a hard surface so that no particulates get caught in the threads of the tube cap.

9.2.12 Place the extractor tube on the Dionex on a selected position with the serial number engraved end up on the top wheel. Place an empty 60 mL VOA collection vial on the matching position on the bottom wheel. Schedule the Dionex ASE 200 and begin the cycle.

9.2.13 The Dionex ASE 200 extraction cycle:

Oven temperature: 100 ° C Pressure: 1500 psi
Prepurge time: 0 minutes
Static time: 5 minutes
Heat: 5 minutes
Flush volume: 60%
Nitrogen purge: 60 sec. At 150 psi
Solvent A: 100%
Method rinse: ON
Static Cycles: 1
Extraction Fluid: (1:1) methylene chloride : acetone

9.2.13 Refer to section 9.3 for sample concentration.

9.3 Sample Concentration

9.3.1 Place glass microfiber filter paper into a glass funnel. Fill the filter paper two-thirds of the depth with Na_2SO_4. Rinse filter paper Na_2SO_4, funnel, K-D apparatus, and concentrator tube with methylene chloride.

9.3.2 Quantitatively pour the extract through the filter and funnel seated on a 250mL Kuderna-Danish (K-D) apparatus complete with concentrator tube. Rinse the beaker three times with methylene chloride. Add these rinses through the filter and funnel into the K-

D. Add a boiling chip to the K-D flask prior to placing it on the heated water bath. Wet a three ball Snyder column with approximately 2 mL of methylene chloride. Attach the Snyder column.

9.3.3 Place the K-D in the heated water bath so the concentrator tube is immersed in the water and the lower rounded surface of the K-D is bathed in steam. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood (set the knob of the temperature control to 5~6). It is critical that the analyst watch the extract as it distills. THE EXTRACT SHOULD NOT GO TO DRYNESS.

9.3.4 When the extract volume reaches approximately 5-7 mL, remove the K-D from the bath. Slightly tilt the apparatus and rotate to aid in solvent drainage from the Snyder column. Allow it to cool completely.

9.3.5 Remove the Snyder column and add 25 mL of hexane and replace Snyder column. Turn the knob of the temperature control of water bath heater to 6~7. Mix the contents of the KD by slightly tilting and placing it upright several times using care so that the content does not spill out the Snyder column. Concentrate the extract to approximately 4 mL. Remove the K-D apparatus from the bath. As above, slightly tilt the apparatus and rotate to aid in solvent drainage. Allow it to cool completely.

9.3.6 Remove the Snyder column, rinse the ground glass joints with a small amount of hexane and then remove K-D flask. Add hexane to the concentrator tube so that the final volume is 10.0 mL. With a disposable Pasteur pipet draw up the extract and rinse the sides of the concentrator tube. Repeat this rinsing several times. (Note: If the sample extract appears highly colored or has a strong petroleum type odor a sulfuric acid clean-up may be required.) Transfer about 1 mL of the extract to a labeled screw-cap injection vial, and the remainder into an amber storage vial. Record the final extract on the injection extraction bench sheet.

9.3.7 The sample extract is now ready for analysis. If samples are not analyzed immediately store the sample extract in a refrigerator.

9.3.8 Sample may require cleanup prior to analysis. Refer to attachment 1 and 2 for sample cleanup options.

10.0 Calibration

10.1 Calibration

10.1.1 The initial calibration for SW-846 chromatographic methods involves the analysis of standards containing the target compounds at a minimum of five different concentrations covering the working range of the instrument.

10.1.2 For each pesticide compound (in table 1.0) and surrogate of interest, prepared calibration standards at a minimum of five different concentrations by adding volumes of one or more stock standards to a volumetric flask and diluting to volume with hexane.

10.1.3 The lowest concentration calibration standard, that is analyzed during an initial calibration curve, establishes the method's quantitation limit based on the finale volume of the sample extract described in the preparative method or employed by the laboratory.

10.1.4 The single point calibration standard will use a minimum of four to five peaks for Toxaphene and tech-Chlordane. Choose peaks in the Toxaphene and tech-Chlordane standards that are at least 25% of the height of the largest peak in that compound. The single-point standard for each of the other these compounds will generate at least four calibration factors, one from each peak

10.1.5 External standard calibration involves comparison of instrument response from the target compounds in the calibration standards. Sample peak areas are compared to peak areas of the standards. The ratio of the detector response to the amount of analyte in the calibration standard is defined as the calibration factor (CF). Toxaphene and tech-Chlordane are a multi-component standard. Four to five peaks will be selected from compound and calibrated using the average calibration factors (CF) for those peaks.

10.1.6 Linear calibration using the average calibration or response factor. When calculating, both calibration factors and response factors are a measure of the slope of the calibration relationship and assume that the curve passed through the origin. The measured as the relative standard deviation (RSD), is less than or equal to 20%, the use of the linear model is generally appropriate, and the calibration curve can be assumed to be linear and to pass through the origin.

10.1.7 Linear calibration using a least squared regression. When the RSD of the calibration or response factors is greater than 20% over the calibration range, then linearity through the origin cannot be assumed. The approach is to employ a regression equation that

does not pass through the origin. This approach may also be employed based on past experience of the instrument response.

10.1.8 Non-linear calibration. When using a calibration model for quantitation, the curve must be continuous, continuously differentiable and monotonic over the calibration range. The statistical considerations in using a non-linear calibration model require more data than the traditional linear approaches. A quadratic (second order) model required the use of six initial calibration points.

10.1.9 Retention time widows are crucial to the identification of target compounds. Absolute retention times are used for the identification of pesticides. Retention time windows are established to compensate for minor shifts in absolute retention times as a result of sample loading and normal chromatographic variability.

10.1.10 Directly inject the prepared calibration standards into the gas chromatograph. An external calibration technique is employed. One of the external standards should be at a concentration near, but above the method detection limit. If a correlation of 0.990 or better is obtained then the calibration is deemed acceptable.

10.1.11 Check the validity of the calibration by analyzing a ICV. The variance of any given compound should not be more than +/- 15% difference. This standard must be prior to sample analysis. If an analyte meets the linear requirement of 0.99, but the best calibration fit is second order, then only one routine ICV need be analyzed. If an analyte exhibits unacceptable linear criteria, but meets criteria using a non-linear model, then two ICV standards must be performed, one at a point above and one at a point below the inflection point. In either case, if the percent drift or the percent difference criteria is not met then the subsequent sample analysis for that analyte is not acceptable.

10.1.12 Continuous checking the validity of the calibration by analyzing CCVs. The variance of any given compound should not be more than +/- 15% difference. This standard must be ran at the beginning, every ten samples or every 12-hour interval, and at the end of the analysis run. Standards for the other Toxaphene and tech-Chlordane are necessary for pattern recognition. These standards may be analyzed prior to sample analysis for a single-point calibration factor (CF) for that compound

10.2 Calibration Calculations

10.2.1 When determining Organochlorine Pesticides, Toxahene and tech-Chlordane by the external standard technique, calculate the calibration factor (CF) for each peak in each of the initial calibration standards using the equation below. The single point calibration standard will use a minimum of four to five peaks for Toxaphene and tech-Chlordane. Choose peaks in the Toxaphene and tech-Chlordane standards that are at least 25% of the height of the largest peak in that compound. The single-point standard for each of the other these compounds will generate at least four calibration factors, one from each peak

$$CF = \frac{\text{Peak Area (or Height) in the Standard}}{\text{Total Mass of the Standard Injected (in Nanograms)}}$$

10.2.2 The calibration factors from the initial calibration are used to evaluate the linearity of the initial calibration. This involves the calculation of the mean calibration factor, the standard deviation, and the relative standard deviation (RSD) for each multi-component peak.

$$\text{Mean } CF = \overline{CF} = \frac{\sum_{i=1}^{n} CF_i}{n}$$

$$SD = \sqrt{\left(\frac{\sum_{I=1}^{n} (CF_I + \overline{CF})}{n-1} \right)}$$

$$RSD = \frac{SD}{\overline{CF}} \times 100$$

10.1.3 Linear Calibration: If the RSD of the calibration factor is greater than 20% over the calibration range, then linearity though the origin cannot be assumed. If this is the case, the analyst may employ a regression equation that does not pass through the origin. This approach may also be employed based on the past experience of the instrument response. The regression will produce the slope and intercept terms for a linear equation in the form:

$$y = mx + b$$

y = instrument response (peak area or height)
m = Slope of the line
x = Concentration of the calibration standard
b = The intercept

10.1.4 The analyst will not force the line through the origin, but have the intercept calculated from the five data points. The use of origin (0,0) as a calibration point. The use of linear regression may not be used as a rationale for reporting results below the calibration range.

10.1.5 Non-Linear Calibration: In situations where the analyst knows that the instrument response does not follow a linear model over a sufficiently wide working range, or when the other approaches described here have not met the acceptance criteria, a non-linear calibration model may be employed. When using a calibration model for quantitation, the curve must be continuous, continuously differentiable and monotonic over the calibration range. The model chosen should have no more than four parameters, i.e., if the model is polynomial, it may be no more than third order as in the equation:

$$y = ax^3 + bx^2 + cx + d$$

10.1.6 The statistical considerations in developing a non-linear calibration model require more data that the more traditional linear approaches described above. Linear regression employ five calibration standards for the linear model, a quadratic model requires a minimum of six calibration standards.

10.1.7 The "goodness of fit" of the polynomial equation is evaluated by calculating;

$$COD = \frac{\sum_{i=1}^{n} (y_{obs} - \bar{y})^2 - \left(\frac{n-1}{n-p}\right) \sum_{i=1}^{n} (y_{obs} - Y_i)^2}{\sum_{i=1}^{n} (y_{obs} - \bar{y})^2}$$

y_{obs} = Observed response (area) for each concentration of the calibration curve.

$\bar{y}$ = Mean observed response from the initial calibration

Y_I = Calculated response at each concentration from the initial calibrations.
n = Total number of calibration points (6 points for quadratic equation)
p = Number of adjustable parameters in the polynomial.

10.1.8 Under idea conditions, with a "perfect" fit of the model to the data, the coefficient of the determination will equal 1.0 In order to be an acceptable non-linear calibration, the COD must be greater than or *equal to 0.99.*

11.0 Sample Analysis

11.1 Sample Sequence

11.1.1 Before initial calibration or sample analysis, an Evaluation standard must be performed. This standard will determine the break-down potential for the instrument. The compounds of interest are; Endrin, Endrin Aldehyde, Endrin Ketone, 4,4'-DDT, 4,4'-DDD, and 4,4'-DDE. This standard must be analyzed and at the beginning of the each analytical run and every twelve hours. The EVAL must pass QC requirements before analysis of standards or samples. The break-down of the parent compounds; Endrin and 4,4'-DDT must be less than 15%.

Calculate Percent Breakdown:

$$\%\text{Breakdown of DDT} = \frac{\text{sum of degradation peak areas (DDD + DDE)}}{\text{sum of all peaks (DDT + DDD + DDE)}} \times 100$$

$$\%\text{Breakdown of Endrin} = \frac{\text{sum of degradation peak areas (Endr. Ald., Endr. Ket.)}}{\text{sum of all peak areas (Endrin, Endr. Ald., Endr. Ket.)}} \times 100$$

11.1.2 Before initial calibration or sample analysis, a clean hexane blank must be analyzed to determine baseline characteristics.

11.1.3 Verify calibration each twelve hour shift by injecting a Continuing Calibration Verification standard (CCV), containing Organochlorine Pesticides, prior to conducting any sample analysis. A CCV must be injected at the being of the sequence and at intervals of not less than one per 10 sample injections or twelve hours (which comes first) and at the end of each sequence. The variance of any given pesticide should not be more than +/- 15% difference. The calibration verification process does not require analysis of Toxaphene or tech-Chlordane standards for continuing

calibration use, but the analyst may desire to include these standards for Toxpahene or tech-Chlordane after the pesticide CCV for pattern reference.

11.1.4 Before sample analysis, inject a method blank to demonstrate that the instrument as well as the extraction procedure is free from contamination. All compounds must be below the method detection limit.

11.1.5 Samples can be directly injected after the successful analyses of the calibration curve, CCV and method blank. There can be up to 20 samples in an analytical batch. A matrix spike/matrix spike duplicate and laboratory control spike must be analyzed with every analytical batch. Recoveries must be within laboratory generated QC limits or client specified limits for all surrogate, matrix spike/matrix spike duplicate and laboratory control spike injections. If the sample shows interference's after analysis; such as sulfur or hydrocarbon contamination, cleanup may be required. Refer to attachment 1 and 2 for sample cleanup options.

11.1.6 All detects in the associated sample must be confirmed with a second column. In this case, all detects are identified and quantitated on the Channel A detector. Results must be confirmed at +/- 40 % on Channel B.

11.1.7 Each sample analysis must be bracketed with passing continuing calibration verification standards. If the continuing calibration verification standard fail to meet QC criteria, all samples that were injected after the last standard which met QC criteria must be re-analyzed.

Note: The data acquisition software generates a ug/ml concentrations which can then be applied to the final calculation to give sample concentrations. Samples with results exceeding calibration range can be diluted accordingly in Hexane and reanalyzed.

11.2 Sample Calculations

11.2.1 The concentration of each analyte in the sample is determined by the computer software. It calculates the amount of compound from the peak area, using the specified calibration model (CF, Linear Regression, or Quadratic).

11.2.2 Calculation of the unknown sample by utilizing the CF is calculated as:

$$\text{Conc} = \frac{\text{Target Peak Areas}_{unk}}{\overline{CF}} \times MF$$

Conc. = the concentration of the unknown anlytes of interest.
Amt_{unk} = the average sum of the uncorrected area of the unknown sample.
CF = Average sum of the Calibration Factors of the target peaks.
MF = multiplication factors (i.e. dilutions, percent moisture, etc.)

For Toxaphene and tech-Chlordane Single-Point Calibration Factor;

$$\text{Conc} = \frac{\text{Avg. Target Peak Areas}_{unk}}{\text{Avg. } \overline{CF}} \times MF$$

Conc. = the concentration of the unknown anlytes of interest.
Amt_{unk} = the average sum of the uncorrected area of the unknown sample.
CF = Average sum of the Calibration Factors of the target peaks.
MF = multiplication factors (i.e. dilutions, percent moisture, etc.)

11.2.3 The concentration of each analyte in the sample is determined by the computer software. It calculates the amount of compound from the peak area, using the calibration curve. Linear regression of standard responses (R) against their known concentration (C in ug/ml), derives the following equation:

$$C = mR + b$$

11.2.4 Using the slope (m) and the intercept (b) from this equation, the concentration of the sample (ug/ml) is calculated and appears on the report page following the chromatogram.

Water samples:
$C_S = [(C_C)(V_E)(D)]/V_S$
Soil samples:
$C_S=[(C_c)(V_E)(D)]/[(W)(S)]$
Wipe samples:
$C=[(C_c)(V_E)(D)]$
Where: C_S = Concentration of sample in ug/L for waters and mg/kg on a dry weight basis for soils

C_c = Concentration from the curve (ug/ml)

C = Concentration in total ug

V_E = Total volume of sample extract (after concentration) in ml

V_S= Volume of water sample in liters

D = Dilution factor if extract was diluted

W = Weight of wet soil sample in grams

S = Total percent solids, expressed as: percent total solids/100

12.0 Quality Control

12.1 Method Performance

12.1.1 Certified standard solutions, properly maintained instrumentation, and analyst experience and expertise are critical elements in producing accurate results. Standards and instrument performance are continually checked by analyzing external performance test samples provided by the appropriately accredited agencies. Internal blind spikes are also utilized to check analyst performance.

12.1.2 Initial demonstration of capability (IDC) is another technique used to ensure acceptable method performance. An analyst must demonstrate initial precision and accuracy through the analysis of 4 laboratory control spikes for each matrix and sample type. After analysis, the analyst calculates the average recovery (x) in µg/L and the relative standard deviation (RSD) of the recovery of target pesticides. In addition to each set of IDCs, a blind laboratory spike will be performed. In the absence of specific criteria found in the SW-846 methods or project specific limits, the default criteria of 70-130% recovery and 20 % RSD are used until internal limits are generated (Method 8000, sec. 8.4.9).

12.1.3 Creating and monitoring control charts is also important for maintaining and improving method performance. Currently all SSTD, MS, MSD, and LCS recoveries are monitored with the use of the LIMS system. The data collected is used to recognize trends in

recovery performance, as well as for generating new in-house QC limits. Default accuracy limits of 70-130 % recovery and a precision limit 20 % RSD are used until enough data points are generated to provide usable internal limits. Client and/or Project specific limits are also used frequently in sample analyses. The Quality Control Requirements chart (Table 3) also lists recovery limits specific to the method/project/program.

12.2 Data Assessment & Acceptance Criteria for QC Measures

12.2.1 If the initial analysis of a sample or a dilution of the sample has a concentration that exceeds the calibration range, the sample must be re-analyzed at a dilution.

12.2.2 The qualitative identification of Organochlorine Pesticides are determined by this method is based on retention time. This method employs a dual ECD detector with two dissimilar columns. There is a potential for many non-target compounds present in samples to interfere with this analysis, therefore sample extract may undergo cleanup procedures . The retention time is updated with each new calibration and is continually updated with the continuing calibration verification standards CCVs. A new method ID is provided for each new sequence with updated retention times or alteration to the operating initial calibration method. If an alteration occurs (other than daily retention time updates), project management and the QA officer will be notified. A description of the alteration will addressed in the client notes or case narrative.

12.2.3 The relative retention time (RRT) of the sample component is within +/- 0.01 RRT units of the RRT of the standard component.

12.3 Reporting Quantitative Analysis

12.3.1 When the analysis of an analytical batch or sequence has been completed, the data is processed and prepared for reporting. Once the standard retention times are compared to the sample retention times, the sample data can be reported.

12.3.2 When the analyst has finished processing the analytical batch, the results are electronically transferred to the LIMS system where weight to volume corrections, dilution factors and percent solids adjustments are made. Once the final results have been verified, a checklist (Table 4.) is filled out and signed confirming that all the data has been thorough scrutinized. At this point the data is turned over to another qualified analyst for final validation. The second analyst confirms the results and electronically marks them validated

and signs the checklist. Finally, the validated results are made available to the client services personnel in order for the data to be given to the client or appropriate agencies.

12.3.3 A paper hard copy or electronic copy of the data is then filed or archived. The package includes the checklist, the sequence run log, a copy of the bench sheet, the LIMS run log, verification of calibration data. For each sample, the chromatogram. All the data is to be initialed and dated by the analyst. Each data file header should contain the Prep ID #, date prepped, Analytical ID #, and date of sequence.

12.4 Corrective Measures for Out-of-Control Data

12.4.1 When data is out of control, corrective actions are required. Certain situations will cause data deficiencies like; if the non-conformities involve failing QC within the analytical sequence batch, the reanalysis of samples may eliminate any out of control data. If the out of control data is the result of instrument malfunctions, then maintenance or repair of the downed instrument followed by reanalysis of affected data may correct the problem. If sample matrix affect or contamination is the reason for poor data, the instrument may need cleaning and decontamination, and the sample may need diluting or undergo sample clean-up procedures to reduce matrix affect. In all cases, when out of control data presents itself, the appropriate corrective measures need to be enacted to eliminate unusable data. The Quality Control Requirements chart can be used as a guide as to which corrective actions should be taken for different QC-type failures or non-conformities (Table 3.).

12.5 Contingencies for Handling Out-of-Control or Unacceptable Data

12.5.1 Due to limited sample volume, expiration of hold times, downed instrumentation, and analyst error, the sample data may be out of control or unacceptable to report. Since these potential instances can arise, contingency plans need to be in place to prevent and/or minimize their affect on data.

12.5.2 To avoid sample hold time issues, the analyst's first responsibility is to plan accordingly. The analyst is responsible for budgeting enough time for sample analysis, so if a problem arises re-analysis or re-extraction is an option

12.5.3 If a sample is extracted passed holding times, the analyst must notify client services immediately. Client services will inform the client and/or responsible parties. In some instances, more sample can be

made available or re-sampling can occur. If the client still request sample analysis, the sample data is qualified for holding time violations.

12.5.4 If the non-conformities involve failing QC within the analytical sequence batch. The analyst must reanalyze the extract. This will ensure that the instrument was functioning properly. If the results are passing, the non-conformities were associated with the instrument. If data is still outside QC criteria, re-extraction of the all samples associated with the QC samples must be preformed (provide that there is sample available). If no sample is available for re-extraction, the samples are qualified accordingly.

12.5.5 If the out of control data is the result of instrument malfunctions, the analyst must evaluated and repair instrument prior to reanalysis of the affected data. After the instrument maintenance and repair of the downed instrument which caused data to be out of control must demonstrate corrective measures by analyzing a Continuing Calibration Verification (CCV) before continuing sample analysis. Any maintenance and repair must be noted in the instrument logbook.

12.5.6 If sample matrix affect or contamination is the reason for poor data. The analyst will use professional judgement for the reanalysis of the extract. The extract can be diluted and reanalyzed. The sample can be re-extracted confirming matrix interference. The analyst can report and qualify the sample data. The analyst must supply explanation for the qualified data in the narrative or client notes.

12.5.7 If the initial analyst makes an analysis error or inadvertently reports unacceptable data, the second analyst is responsible for finding and/or correcting those errors.

12.5.8 When out of control or unacceptable data is produced and it is too late for corrective measures, a number of actions can be taken. The first and foremost is alerting the client service personnel of the problem. Client services will inform the client and/or responsible parties. In some instances, more sample can be made available or re-sampling can occur, so it is important to alert the appropriate personnel as soon as possible.

12.5.8.1 If the out of control data affects only specific analytes, it is important to let the appropriate person(s) know in case his or her site assessment is based on a specific target analyte list.

12.5.8.2 In all instances, if results are reported from data that is out of control or unacceptable, that data is qualified accordingly. Once the client has been notified and he or she instructs us to report the data, then flag the data indicating what type of nonconformity has occurred.

12.5.8.3 Out of control data is still retained by the laboratory and filed and archived along with acceptable data.

12.5.8.4 A non-conformance/corrective action report (CAR) form must be filled out whenever these types of events occur. The information on the report includes the problem encountered, planned corrective actions, and corrective action follow-up. The form is then discussed with and signed by the analyst, the client representative, the QA officer, and the laboratory manager. The purpose of the form is to document problems in order to eliminate the possibility of repeating nonconformance and to ensure that the proper corrective actions are employed.

13.0 Waste Management

13.1 Sample are routinely held (refrigerated) for up to six weeks from analysis date before they enter the waste stream. Waste disposal of samples and standards follows the procedures documented in the Laboratory Waste Disposal SOP (Quality Assurance Section, SOP NO. FO-8, Rev. 4).20.1

ATTACHMENT I
SULFUR CLEANUP
METHOD 3660B

1.0 SCOPE AND APPLICATION

This method covers the procedures used to eliminate sulfur interference from Pesticide extracts. Elemental sulfur is indicated by the presence of white crystals in the sample extract, or, upon analysis, a broad band interference from the solvent front.

2.0 REFERENCES

USEPA, SW-846, 3rd Ed. Method 3660B. December, 1996.

3.0 APPARATUS AND MATERIALS

1.1 Mechanical shaker or mixer.

1.2 Pipets – disposable, pasteur type.

1.3 Disposable culture tubes – 25 mL with Teflon-lined screwcaps.

1.4 Tetrabutylammonium (TBA) – sulfite reagent.

1.5 Sodium sulfate (granular, anhydrous 60/120 mesh, Fisher # S415-212)

4.0 PROCEDURE

4.1 Pipet 1.0 mL of PCB extract into a 25 mL culture tube.

4.2 Add 1.0 mL TBA – sulfite reagent and 2 mL iso-propanol to the tube and cap.

4.3 Shake for at least 1 minute. If the sample is colorless or if the initial color is unchanged, and if crystals are observed, sufficient sodium sulfite is present. If the precipitated sodium sulfite disappears, add more crystalline sodium sulfite in approximately 100 mg portions until a solid residue remains after repeated shaking.

4.4 Add 5 mL distilled water and shake for at least 5 minutes. Allow the sample to stand for 5-10 minutes. Transfer the hexane layer to injection vials and/or storage vials.

4.5 Analyze the extracts by gas chromatography.

4.6 Verify that the TBA-sulfite is free from contamination by shaking out 1.0 mL of TBA – sulfite with 10 mL of hexane and analyze.

4.7 Process all quality control samples (e.g., spikes, blanks and duplicates) along with any samples.

4.8 Verify that recoveries of pesticides's are greater that 85% by processing a standard (CCV) through the procedure.

ATTACHMENT II
FLORISIL CARTRIDGE CLEANUP
METHOD 3620B

1.0 SCOPE AND APPLICATION

1.1 Florisil, a registered trade name of U. S. Silica Co., is a magnesium silicate with basic properties. It is used to separate analytes from interfering compounds prior to sample analysis by a chromatographic method.

1.2 Florisil has been used for the cleanup of pesticide residues and other chlorinated hydrocarbons; the separation of nitrogen compounds from hydrocarbons; the separation of aromatic compounds from aliphatic-aromatic mixtures; and similar applications for use with fats, oils, and waxes. Additionally, Florisil is considered good for separations with steroids, esters, ketones, glycerides, alkaloids, and some carbohydrates. Florisil cleanup may be accomplished using a glass chromatographic column packed with Florisil or using solid-phase extraction cartridges containing Florisil. This method includes procedures for cleanup of sample extracts containing the following analyte groups:

Chlorinated hydrocarbons
Organochlorine pesticides
Organophosphates
Organophosphorus pesticides
PCBs
Phthalate esters
Nitrosamines
Nitroaromatics
Haloethers
Aniline and aniline derivatives

2.0 SUMMARY OF METHOD

2.1 This method describes procedures for Florisil cleanup of solvent extracts of environmental samples using solid-phase extraction cartridges. The cartridge cleanup protocol uses solid-phase extraction cartridges containing 40 µm particles of Florisil (60 D pores). Each cartridge is washed with solvent immediately prior to use. The sample extract is loaded onto the cartridge which is then eluted with suitable solvent(s). A vacuum manifold is required to obtain reproducible results. The eluate may be further concentrated prior to gas chromatographic analysis.

3.0 INTERFERENCES

3.1 A reagent blank should be prepared and analyzed for the compounds of interest prior to the use of this method. The level of interferences must be below the method detection limit before this method is performed on actual samples. The procedures for reagent purification outlined here should be considered to be the minimum requirements for use of this method. More extensive procedures may be necessary to achieve acceptable levels of interferences for some analytes. However, during the evaluation of the cartridge clean-up procedure, phthalate esters were detected in the Florisil cartridge method blanks at concentrations up to 400 ng per cartridge. Therefore, complete removal of the phthalates esters from Florisil cartridges may not be possible.

4.0 APPARATUS AND MATERIALS

4.1 Vacuum manifold - VacElute Manifold SPS-24 (Analytichem International), Visiprep (Supelco, Inc.) or equivalent, consisting of glass vacuum basin, collection rack and funnel, collection vials, replaceable stainless steel delivery tips, built-in vacuum bleed valve and gauge. The system is connected to a vacuum pump or water aspirator through a vacuum trap made from a 500-mL sidearm flask fitted with a one-hole stopper and glass tubing. The manifold is required for use of the cartridge cleanup protocol.

5.0 REAGENTS

5.1 Eluting solvents - all solvents must be pesticide quality or equivalent.

5.2 Hexane, pesticide grade.

5.3 Methylene chloride, pesticide grade.

5.4 Acetone, pesticide grade.

5.5 Florisil cartridge phenol check solution (for the Organochlorine pesticide technique) - Prepare a solution of 2,4,5-Trichlorophenol in acetone at a concentration of 0.1 g/L.

5.6 Florisil cartridge pesticide check solution - Prepare a solution containing the following analytes at a concentration of 0.1 ug/ml in hexane:

BHCs
Heptachlor
BHC
Endosulfan I
Dieldrin
Endrin
4,4'-DDD
4,4'-DDT
Methoxychlor
Tetrachloro-m-xylene
Decachlorobiphenyl

6.0 PROCEDURE

6.1.1 Whenever Florisil is used to fractionate groups of target compounds (rather than to simply remove potential interference) it is critical that the specific fractionation scheme be validated using spiked solutions or spiked sample extracts that contain most or all of the analytes of interest. This may be particularly important when the Florisil cartridge techniques are employed, as the differences between the various cartridge formats and manufacturers may affect the fractionation patterns. In addition, it may be useful to archive any fractions not originally intended for analysis, in the event that the fractionation scheme chosen does not yield the intended results. Once the determinative analysis has been performed and demonstrates that the fractionation has been successful, such archived fractions may be disposed of in an appropriate manner. However, if the fractionation did not perform as intended, the analytes of interest may be contained in the archived fractions which may be able to be analyzed or combined with the other fraction(s) for reanalysis.

6.1.2 Following Florisil cleanup, extracts may require further concentration and/or solvent exchange.

6.2 Cartridge Evaluation

6.2.1 The efficiency of each lot of the solid-phase extraction cartridges must be verified. Only lots of cartridges from which the spiked analytes are quantitatively recovered may be used to process the samples. A check should also be performed at least once on each

individual lot of cartridges and at least once for every 300 cartridges of a particular lot, which ever frequency is greater.

6.2.2 To check each new lot of Florisil cartridges before use, perform the following in duplicate.

6.2.3 Combine 0.5 ml of 2,4,5-Trichlorophenol solution in Section 5.5 and 0.5 ml of pesticide spiking solution in Section 5.6 in a two ml autosampler vial.

6.2.4 Arrange the cartridges on the manifold in the closed-valve position.

6.2.5 Turn on the vacuum pump and set the vacuum to 10 in (254 mm) of Hg. Do not exceed the manufacturer's recommendation for manifold vacuum. Flow rates may be controlled by opening and closing cartridge valves.

6.2.6 Condition the cartridges by adding 4 mL of hexane to each cartridge. Slowly open the cartridge valves to allow hexane to pass through the sorbent beds to the lower frits. Allow a few drops per cartridge to pass through the manifold to remove all air bubbles. Close the valves and allow the solvent to soak the entire sorbent bed for 5 minutes. Do not turn off the vacuum.

6.2.7 Slowly open cartridge valves to allow the hexane to pass through the cartridges.

6.2.8 Close the cartridge valves when there is still at least 1 mm of solvent above the sorbent bed.

6.2.9 Do not allow cartridges to become dry. If cartridges go dry, repeat the conditioning step.

6.2.10 Add the spiking solution in 6.2.3 to the Florisil cartridge.

6.2.11 Elute the cartridge with 9 ml of acetone/hexane (10/90, v/v). Collect the extraction in a 15 ml test tube.

6.2.12 Transfer extract to a concentrating thimble. Using the nitrogen blown apparatus, concentration the extract down to one ml and analyze by Method 8081A.

6.2.13 The lot of Florisil cartridges is acceptable if all pesticides are recovered at 80 to 110%, if the trichlorophenol is less than 5%, and if no peaks interfering with the target analytes are detected.

6.3 Handling sample extracts

6.3.1 Most sample extracts will have to be concentrated to a smaller volume prior to the use of Florisil cleanup. The extract volume is a function of the analytical sensitivity necessary to meet the project objectives. The extract volume will also affect the ability of the Florisil to separate target analytes from potential interferences where applying large extract volumes to the cartridges may cause poor results. Consult the appropriate extraction and determinative methods for the details on final extract volumes, extract concentration techniques, and solvent exchange procedures.

6.3.2 Reduce the sample extract volume to 10 mL prior to cleanup. The extract solvent should be hexane for these analytes. In most cases, given the sensitivity of the determinative methods, only 1 mL of the 10 mL extract needs to be subjected to the Florisil cleanup procedure. The remaining 9 mL should be archived for later use, if needed.

6.3.3 Place Florisil cartridges on manifold. Turn on the vacuum pump and adjust the pump pressure to 10 inches (254 mm) of Hg. Condition the cartridges by adding 4 ml of hexane. Slowly open the cartridge valve and collect the eluate into the collection vial. Allow a few drops of hexane to pass through the cartridge to remove any air bubbles. Close valve and allow solvent to soak the entire sorbent bed for five minutes. Do not turn off vacuum.

6.3.4 Slowly, open the valve to allow the hexane to pass through the cartridge. Close valve when about 1 mm of hexane is remaining above the sorbent bed.

6.3.5 Add 1 ml of extract to the Florisil cartridge. Allow the extract to pass through the cartridge at a rate about 2 ml per minute.

6.3.6 Before extract goes below the surface of the sorbent bed, add 9 ml of hexane/acetone (90/10, v/v) to the cartridge.

6.3.7 After extract has been collected, concentrate sample down to 1 ml. Refer to Section 9.5 for concentration techniques.

The following procedures are used to separate the Organochlorine Pesticides from the PCBs.

6.3.8 Add 3 mL of hexane to the cartridge. Turn on the vacuum pump and adjust the pump pressure to 10 inches (254 mm) of Hg. Allow the solvent to soak the sorbent bed for 1 minute or less. Slowly

open the cartridge valve and collect the elute into the collection vial. This is Fraction 1 and it will contain the PCBs and a few of the Organochlorine pesticides.

6.3.9 Close the cartridge valve, replace the collection vial, and add 5 mL of methylene chloride/hexane (26/74, v/v) to the cartridge. Slowly open the cartridge valve and collect the eluate into the collection vial. This is Fraction 2 and it will contain most of the pesticides.

6.3.10 Close the cartridge valve, replace collection vials, and add 5 mL of acetone/hexane (10/90, v/v) to the cartridge. Slowly open the cartridge valve and collect the eluate into the collection vial. This is Fraction 3 and it will contain the remaining pesticides.

6.3.11 As needed, perform a solvent exchange and adjust the final volume of the eluant to 1 ml.

7.0 QUALITY CONTROL

7.1 The analyst must demonstrate that the compounds of interest are being quantitatively recovered before applying this method to actual samples. A recovery check must be performed using standards of the target analytes at known concentration. The efficiency of each lot of the solid-phase extraction cartridges must be verified. Only lots of cartridges from which the spiked analytes are quantitatively recovered may be used to process the samples. A check should also be performed at least once on each individual lot of cartridges and at least once for every 300 cartridges of a particular lot, whichever frequency is greater.

Table 3
Summary of Method Objectives for Method 8081A-Pesticides

Quality Control Element	Frequency of Implementation	Acceptance Criteria	Corrective Action
Initial Calibration		$r \geq 0.995$, RSD $\leq$20%, $r^2 \geq 0.990$, mean RSD $\leq$20%	Linearity must fit one of acceptance criteria, or the curve must be reanalyzed.
Initial Calibration Verification (ICV)	After initial calibration	85-115%	If ICV falls outside QC criteria, reanalysis must take place. If ICV still fails, it may be appropriate to repeat the initial calibration curve or to qualify the analyte with "A".
Continuing Calibration Verification (CCV)	CCVs are analyzed at the beginning of the sequence, after every 12 hours or every 10 samples (which ever comes first) and at the end of the analytical run.	D or mean D$\leq$15% with a maximum %D$\leq$30%	If CCV falls outside QC criteria, reanalysis must take place. If CCV still fails, it may be appropriate to repeat the initial calibration curve or to qualify the analyte with "A".
Retention Time Window (RTW)	Retention Times are updated upon the beginning CCV	Retention times are 3x Standard Deviation the absolute retention time, if the default standard deviation is employed, width of the window will be 0.03 minutes	

Table 3
Summary of Method Objectives for Method 8081A-Pesticides

Quality Control Element	Frequency of Implementation	Acceptance Criteria	Corrective Action
Evaluation Standard (EVAL)	Beginning of a analytical sequence and every twelve hours	Breakdown for Endrin and 4,4'-DDT must be <15%	Correct problem and repeat.
Method Blank (MB)	1 per sample prep batch	Analytes < MRL	If sample is available and within holding times, sample associated with method blank needs to be reprepped. If no sample is available, qualify the data with a "B" to all associated positives when less than 5X blank concentration
Laboratory Control Sample (LCS)	1 per sample prep batch	In house limits or client specified.	If LCS fails percent recoveries. Re-analyze the LCS. If LCS recoveries are still outside QC control limits, qualify the failing analytes with a "Q".
Matrix Spike (MS)	1 per sample prep batch	In house limits or client specified.	No action is taken based on MS recovery alone, use of professional judgement. For recoveries outside QC criteria, qualify out lying compound with "M".
Matrix Spike Duplicate (MSD)	1 per sample prep batch	In house limits or client specified.	No action is taken based on MSD results alone, use of professional judgement. If RPD is outside QC criteria, then qualify the out lying compounds with "Y".
Surrogates	Every sample and QC	In house limits or client specified.	Rerun sample. If no apparent matrix interference noticed re-extract sample. If no sample is available, qualify the surrogate with "S".
Target Analyte Confirmation	Whenever a positive is detected on one column and confirmed on 2nd column.	RPD ≤40%	If the RPD ≥ 40%, qualify analyte with "P".

Table 4
8081A Pesticide Analysis Data Review Checklist

Sequence Date	Analyst / Data Interpreter	Independent Reviewer	Date of Review	Approved
				Yes or No

Instructions: Complete one checklist per *analytical run*. Enter the appropriate response for each question. Each "No" response requires an explanation in the Comments section, and may require the initiation of a Nonconformance Report.

Requirement:	Acceptance Criteria	Analyst Review		Independent Review		Comments:
		Yes	No	Yes	No	(indicate reference to an attachment if necessary)
1. INITIAL CALIBRATION (ICAL)						
a. Were the Pesticide initial calibration performed using a minimum of five varying standard concentration levels?	Lowest standard at or near MRL					
b. Is the variation between calibration response factors for all concentration levels <20% RSD, is r^2 >.990, or r > 0.995 for the regression line?	RSD <20%, r^2 >.990, r>0.995					
c. Was each ICAL uniquely identified (i.e. Standard Number)?						
d. Was an initial calibration blank (ICB) analyzed?						
e. Was there an Evaluation standard injected prior to initial calibration?	Breakdown <15%					
2. INITIAL CALIBRATION VERIFICATION (ICV)						
a. Were there a second source ICVs for all target analytes analyzed after the initial calibration and prior to analysis of any samples?	Second source					
b. If target analytes are using a quadric model, were there two ICV injections preformed (one above and one below the inflection point?)	Quadratic Check					
c. Were the recoveries for the ICVs between 85% and 115%?	%R 85-115%					
d. Was the ICVs uniquely identified (i.e. Standard Number)?						
3. CONTINUING CALIBRATION VERIFICATION (CCV)						
a. Were CCVs analyzed at the beginning of the sequence, after every 12 hours or every 10 samples (which ever comes first) and at the end of the analytical run?						
b. Were the recoveries for the CCVs between 85% and 115%?	%R 85-115%					
c. Was each CCV uniquely identified (i.e. Standard Number)?						

Table 4
8081A Pesticide Analysis Data Review Checklist Continued

Requirement:	Acceptance Criteria	Analyst Review		Independent Review		Comments:
		Yes	No	Yes	No	(indicate reference to an attachment if necessary)
4. BLANKS						
a. Was method blank (MB) analyzed prior to the analysis of samples?						
b. Was the MB result less than the reporting limit (RL)?	< ½ MRL					
c. Was a MB prepped and analyzed at a frequency of one per Prep Batch?	Batch <20 samples					
5. LABORATORY CONTROL SAMPLE (LCS)						
a. Was a LCS analyzed at a frequency one per Prep Batch?	Batch <20 samples					
b. Were the LCS recoveries in each LCS within the acceptance criteria?	In-house limits or client specified limits					
6. MATRIX SPIKES						
a. Was a matrix spiked (MS) sample analyzed at a frequency one per Prep Batch?	Batch <20 samples					
b. Were MS recoveries in each MS within the acceptance criteria?	In-house limits or client specified limits					
7. LABORATORY CONTROL SPIKE / MATRIX SPIKE DUPLICATE						
a. Was a duplicate matrix spike or laboratory control spike sample analyzed at a frequency one per Prep Batch?	Batch <20 samples					
b. Were MSD or LCSD recoveries within the acceptance criteria?	In-house limits or client specified limits					
c. Is the relative percent difference (RPD) between a matrix spike (MS) and its' duplicate (MSD) or laboratory control spike (LCS) and its' duplicate (LCSD) within the acceptance criteria?	In-house limits or client specified limits					

Table 4
8081A Pesticide Analysis Data Review Checklist Continued

Requirement:	Acceptance Criteria	Analyst Review		Independent Review		Comments:
		Yes	No	Yes	No	(indicate reference to an attachment if necessary)
8. SAMPLES (INCLUDING BLANKS, STANDARDS, AND QC SAMPLES)						
a. Are chromatogram characteristics, including peak shapes and areas, consistent with those of the CCV?						
b. Are surrogate recoveries for all samples, blanks, standards, and QC samples within acceptance criteria?						
c. Were all samples having analytes detected in amounts exceeding the calibration range diluted and reanalyzed?						
d. Were all samples extracted within holding times and analyzed within 40 days of extracting?	Analysis within 40 days of extraction					
e. Did the samples require additional cleanup steps? (i.e. Florisil, and sulfur treatment)	Florisil and/or Sulfur Treatments					
f. Was there a hexane injection preformed prior to sample analysis?						
g. Was there an Eval standard injected prior to sample analysis and every twelve hours?	Breakdown <15%					
9. RECORDS AND REPORTING						
a. Are Run, Prep Batch and Extraction sheets, Summary sheets, Sequence file, initial and rerun raw and process data present in the data file?						
b. Are all chromatograms dated and initialed?						
c. Are reported results whose amounts exceeded the acceptance criteria flagged with an appropriate qualifier and, if needed, a NCR completed?						
d. Do all values, dilution factors and qualifiers listed on the raw reports match the LIMS data?						
e. Is the ICAL method referenced on the Raw Data?						

CT Laboratories
Baraboo Laboratory Division

Title: **Sulfide, Titrimetric Method**

SOP Number: **CC-32**

Prepared by: _____
Date

Technical Review by: _____
Date

Reviewed by: _____
Quality Assurance ***Date***

_____
Laboratory Director ***Date***

SOP Manual Control Number:

1.0 SCOPE AND APPLICATION

1.1 This method is applicable to the measurement of total and dissolved sulfides in drinking waters, surface and saline waters, domestic and industrial wastes.

1.2 Acid insoluble sulfides are not measured by the use of this test. (Copper sulfide is the only common sulfide in this class).

1.3 This method is suitable for the measurement of sulfide in concentrations above 1mg/L.

2.0 METHOD SUMMARY

2.1 Excess iodine is added toa sample which may or may not have been treated with zinc acetate to produce zinc sulfide. The iodine oxidizes the sulfide to sulfur under acidic conditions. The excess iodine is backtitrated with phenylarsine oxide.

3.0 DEFINITIONS

3.1 Duplicate Analysis: Two aliquots of a given sample are analyzed. The relative percent difference (RPD) is then determined from the two results and compared to the lab control limits for that particular matrix.

4.0 HEALTH AND SAFETY

4.1 Gloves and protective clothing should be worn to protect against unnecessary exposure to possibly hazardous chemicals and contaminants in samples. All activities performed while following this procedure should utilize appropriate laboratory safety systems (see CTI Health and Safety Manual).

5.0 CAUTIONS

There are no cautions

6.0 INTERFERENCES

6.1 Reduced sulfur compounds, such as sulfite, thiosulfate and hydrosulfite, which decompose in acid, may yield erratic results. Also, volatile iodine-consuming substances will give high results.

6.2 Samples must be taken with a minimum of aeration. Sulfide may be volatilized by aeration and any oxygen inadvertently added to the sample may convert the sulfide to an unmeasurable form.

6.3 If the sample is not preserved with zinc acetate and NaOH, the analysis must be started immediately.

7.0 PERSONNEL QUALIFICATIONS

7.1 All personnel need to demonstrate capability by completing a valid IDC, initial demonstration of capability. study prior to performing analyses on actual samples

8.0 APPARATUS AND MATERIALS

8.1 25 ml buret, borosilicate glass, with 0.1 ml or 0.01 ml graduations
8.2 Stir plate, magnetic with teflon stir bar.
8.3 Oxford pipet, 10 ml capacity.
8.4 Oxford pipet, 5 ml capacity.
8.5 500 – 1000 mL glass bottles with stoppers: For use in the analysis of dissolved sulfide.
8.6 **REAGENTS**
8.6.1 Zinc Acetate Preservative (2N): Dissolve 220 gm of $Zn(C_2H_3O_2)_2$ - H_2O in 870 mL of DI water. Dilute to 1000 mL.
8.6.2 Hydrochloric acid, HCl, 6 N: Prepare by adding 10 mls of concentrated HCl to 10 mls of DI water.
8.6.3 Standard iodine solution, 0.0250 N: Commercially available
8.6.4 Phenylarsine oxide 0.0250 N: Commercially available
8.6.5 Starch indicator: Commercially available.
8.6.6 Sodium hydroxide solution, NaOH, 6N: into a 500 ml volumetric, dissolve 120 g of NaOH pellets and bring up to vol with DI water.
8.6.7 Aluminum chloride solution: Commercially available

9.0 INSTRUMENT OR METHOD CALIBRATION

There is no calibration for this method.

10.0 SAMPLE COLLECTION, HANDLING AND PRESERVATION

10.1 Collect at a minimum 500 mL of sample and preserve with zinc acetate plus sodium hydroxide to pH >9. Keep refrigerated at 4 C. Hold time 7 days.
10.2 Keep aeration of sample to a minimum.

11.0 SAMPLE PREPARATION AND ANALYSIS

11.1 Total sulfides:
11.1.1 Place a known amount of standard iodine solution into a 500 ml flask. The amount should be estimated to be in excess of the amount of sulfide expected.
11.1.2 Add distilled water, if necessary, to bring the volume to approximately 20 ml.
11.1.3 Add 2 ml of 6 N HCl.
11.1.4 Pipet 200 ml of sample into the flask, keeping the tip of the pipet below the surface of the sample.
11.1.5 If the iodine color disappears, add more iodine until the color remains. Record the total number of milliliters of standard iodine used in performing steps 11.1.1 and 11.1.5.
11.1.6 Titrate with 0.0250 N phenylarsine oxide solution using a starch indicator until the blue color disappears. Record the number of milliliters used.
11.2 Dissolved Sulfides:
11.2.1 Unless the sample is entirely free from suspended solids, (dissolved sulfide equals total sulfide), to measure dissolved

sulfide first remove insoluble matter. This can be done by producing an aluminum hydroxide floc that is settled, leaving a clear supernatant for analysis.

11.2.2 To a 100-mL glass bottle add 0.2 mL (4 drops) 6*N* NaOH. Fill bottle with sample and add 0.2 mL (4 drops) $AlCl_3$ solution. Stopper bottle with no air under stopper. Rotate back and forth about a transverse axis vigorously for 1 min or longer to flocculate contents. Vary volumes of these chemicals to get good clarification without using excessively large amounts and to produce a pH of 6 to 9. If a 500 or 1000 mL bottle is used, add proportionally larger amounts of reagents.

11.2.3 Let settle until reasonably clear supernatant can be drawn off. With proper flocculation, this may take 5 to 15 min. Do not wait longer than necessary.

11.2.4 Perform steps 11.1.1 through 11.1.6.

12.0 INSTRUMENT MAINTENANCE AND TROUBLESHOOTING

There is no maintenance or troubleshooting for this method.

13.0 DATA ACQUISITION, CALCULATION AND REDUCTION

13.1 One ml of 0.0250 N standard iodine solution (5.2) reacts with 0.4 mg of sulfide present in the titration vessel.

13.2 Use the formula:

$$\text{mg/L sulfide} = \frac{400\,(A - B)}{\text{ml sample}}$$

where: A = ml of 0.0250 N standard iodine solution
B = ml of 0.0250 N standard reducing phenylarsine oxide solution

14.0 COMPUTER HARDWARE AND SOFTWARE

14.1 Computer with StarLIMS

15.0 DATA MANAGEMENT AND RECORD MANAGEMENT

15.1 After data has been entered into LIMS, it is reviewed by the analyst for accuracy and completeness. See checklist for data review guidance.

15.2 Once analyst has reviewed and approved the data, it is given to a peer or supervisor for review.

15.3 After the second reviewer approves the data, the reviewer sends the data to "validated" status in LIMS.

15.4 The original data is filed by test in the file cabinet and periodically the contents of the file cabinet are archived.

16.0 QUALITY CONTROL AND QUALITY ASSURANCE

16.1 A blank should be titrated with each run to verify the absence of reagent contamination and to confirm the possible presence or absence of sample matrix interference. Blanks should measure less than the limit of detection (0.2 mg/L).

16.2 Duplicate analyses are done every 20 samples. The relative percent difference between the two sample results should be no more than 20%.

17.0 REFERENCES

17.1 Methods for Chemical Analyses of Water and Wastes, EPA - 1983. EPA-600/4-79-020, Method 376.1.

17.2 *Standard Methods for the Examination of Water and Wastewater*, 18th Edition. 1992, APHA-AWWA--WPCF. Method 4500-S^{2-}.

Procedure	Frequency of Procedure	Acceptance Criteria	Corrective Action if Unacceptable
Sample duplicate (DUP)	One (1) per analytical batch per matrix	In-house derived limits Default: RPD $\leq$ 20% if analytes > RL	Investigate problem, if system precision in control qualify results, if system precision out of control reanalyze entire batch
Method Blank (MB)	One (1) per analytical batch	Analytes < RL	Clean analytical system, repeat until MBs are in control

Commonwealth Technology, Inc.

Data Validation Checklist

LIMS #:	Method: Sulfide EPA 376.1			
Analysis Date	**Analyst / Data Interpreter**	**Independent Reviewer**	**Date of Review**	**Approved**
				Yes ... No

Instructions: Complete one checklist per *analytical run*. Enter the appropriate response for each question. Each "No" response requires an explanation in the Comments section, and may require the initiation of a Nonconformance Report.

Requirement:	Acceptance Criteria	**Analyst Review**		**Independent Review**		Comments: (indicate reference to an attachment if necessary)
		Yes	No	Yes	No	
1. Does a titration bench sheet accompany the run?	---					
2. Were the samples analyzed within hold time?	7 days					
3. Was a blank titrated along with the samples?	---					
4. Was the blank result acceptable?	< LOD					
5. Were duplicates analyzed at the required frequency?	1 per 20 samples of the same matrix					
6. Was the RPD of the duplicates acceptable?	Within in house QC limits					
7. Are all samples on the job lists accounted for?	---					

CT Laboratories.
Baraboo Laboratory Division

Title: **Analysis of Semivolatile Organic Compounds by GC/MS**

SOP Number: **5260**

Written by: _____

Technical Review by: _____
Quality Assurance Manager

Approved by: _____
Laboratory Director

SOP Manual Control Number: _____

Analysis of Semivolatile Organic Compounds by GC/MS

1.0 Scope & Application

This method is used for the determination of solvent-extractable semivolatile organic compounds in many types of solid waste matrices, soils, and groundwater. Most neutral, acidic, and basic organic compounds which can be soluble in methylene chloride and capable of being eluted in a gas chromatograph without derivatization can be quantitated. Target compounds determined by this method are listed in Table 1.

The reporting limits (RL) for determining an individual compound by this method are approximately 2.0 ug/L for ground water samples, 0.2 mg/kg for soil/sediment/solid samples, and 20 mg/kg for wastes (dependent on matrix and method of preparation). The reporting limit will be higher for sample extracts that require dilution to avoid saturation of the detector and contamination of the chromatographic column.

Table 1. EPA SW-846 8270

Codes (Tables 1A, 1B):

I = IntStd
T = Target
C = CCC compound
QIon = quantitation ion
RL_RT = relative retention time
S = Surrogate
M = Matrix Spike
P = SPCC compound
Exp_RT = typical retention time (minutes)

PK#	Code	Compound Name	QIon	Exp_RT	Rel_RT
1	I	1,4-Dichlorobenzene-d4	152	10.53	1.000
2	TM	N-Nitrosodimethylamine	74	5.23	0.497
3	TM	Pyridine	79	5.21	0.495
4	S	2-Fluorophenol	112	8.00	0.760
5	TM	Aniline	93	9.90	0.941
6	TM	bis(2-chloroethyl)ether	93	10.04	0.953
7	S	Phenol-d5	99	9.82	0.933
8	CTM	Phenol	94	9.85	0.935
9	TM	2-Chlorophenol	128	10.11	0.960
10	TM	1,3-Dichlorobenzene	146	10.41	0.989
11	CTM	1,4-Dichlorobenzene	146	10.56	1.003
12	TM	1,2-Dichlorobenzene	146	10.85	1.030

Table 1 – Continued

PK#	Code	Compound Name	QIon	Exp_RT	Rel_RT
13	TM	Benzyl alcohol	108	10.81	1.026
14	TM	bis(2-Chloroisopropyl)ether	45	11.08	1.053
15	TM	2-Methylphenol	108	11.02	1.046
16	TM	N-Nitrosopyrrolidine	100	11.31	1.075
17	TM	Acetophenone	105	11.34	1.077
18	TM	Hexachloroethane	117	11.51	1.093
19	PTM	N-Nitroso-di-n-propylamine	70	11.36	1.079
20	TM	3-Methylphenol & 4-Methylphenol	108	11.33	1.076
21	I	Naphthalene-d8	136	13.06	1.000
22	S	Nitrobenzene-d5	82	11.62	0.890
23	TM	Nitrobenzene	77	11.67	0.893
24	TM	Isophorone	82	12.15	0.930
25	TM	2-Nitrophenol	139	12.29	0.941
26	TM	2,4-Dimethylphenol	107	12.38	0.948
27	TM	bis(2-Chloroethoxy)methane	93	12.59	0.964
28	TM	2,4-Dichlorophenol	162	12.77	0.978
29	TM	1,2,4-Trichlorobenzene	180	12.94	0.991
30	TM	Benzoic acid	105	12.59	0.964
31	TM	Naphthalene	128	13.10	1.003
32	TM	4-Chloraniline	127	13.22	1.012
33	TM	2,6-Dichlorophenol	162	13.22	1.012
34	TM	Hexachloropropene	213	13.27	1.016
35	TM	Hexachlorobutadiene	225	13.34	1.022
36	CTM	4-Chloro-3-methylphenol	107	14.18	1.086
37	TM	2-Methylnaphthalene	142	14.50	1.110
38	I	Acenaphthene-d10	164	16.64	1.000
39	TM	Hexachlorocyclopentadiene	237	14.81	0.890
40	TM	1.2.4.5-Tetrachlorobenzene	216	14.83	0.892
41	TM	2,4.6-Trichlorophenol	196	15.06	0.906
42	TM	2,4.5-Trichlorophenol	196	15.13	0.910

Table 1 – Continued

PK#	Code	Compound Name	QIon	Exp_RT	Rel_RT
43	S	2-Fluorobiphenyl	172	15.26	0.917
44	TM	2-Chloronaphthalene	162	15.49	0.931
45	TM	2-Nitroaniline	65	15.71	0.944
46	TM	Acenaphthylene	152	16.34	0.982
47	TM	Dimethylphthalate	163	16.10	0.968
48	TM	2,6-Dinitrotoluene	165	16.22	0.975
49	TM	Acenaphthene	153	16.69	1.004
50	TM	3-Nitroaniline	138	16.55	0.995
51	TM	2,4-Dinitrophenol	184	16.76	1.007
52	TM	Dibenzofuran	168	17.05	1.025
53	MT	2,4-Dinitrotoluene	165	17.04	1.024
54	PTM	4-Nitrophenol	109	16.89	1.015
55	TM	2-Naphthylamine	143	17.37	1.044
56	TM	Fluorene	166	17.75	1.067
57	TM	4-Chlorophenyl-phenylether	204	17.76	1.067
58	TM	Diethylphthalate	149	17.55	1.055
59	TM	4-Nitroaniline	138	17.81	1.070
60	I	Phenanthrene-d10	188	19.68	1.000
61	TM	4,6-Dinitro-2-methylphenol	198	17.86	0.908
62	TM	N-Nitrosodiphenylamine & Diphenylamine	169	18.01	0.915
63	TM	Azobenzene & 1,2-Diphenylhydrazine	182	18.09	0.919
64	TM	2,4,6-Tribromophenol	330	18.24	0.927
65	TM	4-Bromophenyl-phenylether	248	18.76	0.953
66	TM	Hexachlorobenzene	284	18.86	0.958
67	CTM	Pentachlorophenol	266	19.27	0.979
68	TM	Phenanthrene	178	19.73	1.002
69	TM	Anthracene	178	19.82	1.007
70	TM	Carbazole	167	20.16	1.024
71	TM	Di-n-butylphthalate	149	20.91	1.062
72	TM	Fluoranthene	202	22.15	1.126

Table 1 – Continued

PK#	Code	Compound Name	QIon	Exp_RT	Rel_RT
73	I	Chrysene-d12	240	25.11	1.000
74	TM	Benzidine	184	22.44	0.894
75	TM	Pyrene	202	22.62	0.901
76	S	Terphenyl-d14	244	22.95	0.914
77	TM	Butylbenzylphthalate	149	23.98	0.955
78	TM	3,3'-Dichlorobenzidine	252	25.04	0.997
79	TM	Benzo[a]anthracene	228	25.07	0.999
80	TM	Chrysene	228	25.15	1.002
81	TM	bis(2-Ethylhexyl)phthalate	149	25.16	1.002
82	I	Perylene-d12	264	28.02	1.000
83	TM	Di-n-octylphthalate	149	26.42	0.943
84	TM	Benzo[b]fluoranthene	252	27.16	0.969
85	TM	Benzo[k]fluoranthene	252	27.23	0.972
86	TM	Benzo[a]pyrene	252	27.87	0.995
87	TM	Indeno[1,2,3-cd]pyrene	276	30.90	1.103
88	TM	Dibenz[a,h]anthracene	278	30.97	1.105
89	TM	Benzo[g,h,i]perylene	276	31.80	1.135

2.0 Method Summary

The samples for analysis are prepared using the appropriate extraction method for the sample matrix. This involves extraction into methylene chloride and concentration of the extract.

Internal spiking compounds for quantitation of the results are added to the extract before analysis by gas chromatography/mass spectrometry (GC/MS). Some of the sample containing semivolatile compounds are drawn into a syringe, and injected into a gas chromatograph (GC) with a narrow-bore fused-silica capillary column. An inert gas flow and a ramped temperature program separates the analytes, which are then detected with a mass spectrometer (MS) directly connected to the gas chromatograph.

Software enables identification of the analytes by comparing the mass spectra of the target analytes to the electron impact mass spectra of calibration standards prepared from certified commercially-prepared stock standards. Quantitation is accomplished by comparing the response of a representative major ion relative to an internal standard using at least a five-point calibration

curve.

3.0 Definitions

3.1 DFTPP: Decafluorotriphenylphosphine
3.2 EICP: Extracted Ion Current Profile
3.3 GC-MS: Gas Chromatograph-Mass Spectrometer system
3.4 ICAL: Initial CALibration standard
3.5 CCV: Continuing Calibration Verification
3.6 CCC: Calibration Check Compounds
3.7 SPCC: System Performance Check Compounds
3.8 LCS: Laboratory Control Spike
3.9 MS: Matrix Spike
3.10 MSD: Matrix Spike Duplicate
3.11 MDL: Method Detection Limit
3.12 RF: Response Factor
3.13 RRT: Relative Retention Time
3.14 ISTD: Internal StanDard
3.15 MB: Method Blank
3.16 IB: Instrument Blank

4.0 Health & Safety

Safety glasses, gloves, and protective clothing: long pants, leather shoes and lab coat or apron should be worn to protect against unnecessary exposure to hazardous chemicals and contaminants in samples. All activities performed while following this procedure should utilize appropriate laboratory safety systems. Follow all items in the in-house Chemical Hygiene Plan and Health and Safety Manual.

5.0 Caution

5.1 Benzidine, 3,3'-dichlorobenzidine, and 4-chloroaniline are subject to oxidative losses during sample concentration.

5.2 2-Naphylamine is observed to degrade easily, has poor extraction efficiency and has erratic chromatographic behavior, especially if the GC system is contaminated with high boiling material.

5.3 Hexachlorocylcopentadiene is subject to thermal decomposition in the inlet of the gas chromatograph, chemical reaction in acetone solution, photochemical decomposition, poor extraction efficiency, and poor chromatographic behavior.

5.4 N-nitrosodiphenylamine decomposes in the gas chromatograph and cannot be separated or differentiated from diphenylamine. Both analytes are reported as a pair.

5.5 1,2-Diphenylhydrazine decomposes in the gas chromatograph and cannot be separated or differentiated from azobenzene. Both analytes are reported as a pair.

5.6 3-Methylphenol (m-cresol) and 4-Methylphenol (p-cresol) coelute. Both analytes are reported as an isomeric pair.

5.7 Pentachlorophenol, 2-methylphenol, 3&4-methylphenol, 2,4-dinitrophenol, 4-nitrophenol, benzoic acid, 4,6-dinitro-2-methylphenol, 4-chloro-3-methylphenol, aniline, 2-nitroaniline, 3-nitroaniline, 4-chloroaniline, benzidine and benzyl alcohol are subject to erratic chromatographic behavior, especially if the GC system is contaminated with high boiling material, poor extraction efficiency, and have a tendency to decompose.

5.8 N-nitrosodiphenylamine and pyridine is difficult to separate from the solvent front under the chromatographic conditions described.

6.0 Interferences

6.1 Raw GC/MS data from all blanks, samples, spikes must be evaluated for interferences. Determine if the source of the interference is from sample preparation or contamination of the chromatographic system and take corrective action. Before sample analysis, inject and analyze an instrument blank containing only solvent and internal standards to verify the chromatographic system is interference free.

6.2 An instrument blank should also be analyzed after an unusually concentrated sample or whenever carryover is suspected. Reanalyze any samples suspected of carryover.

7.0 Personnel Qualifications

The GC/MS analyst should have at a minimum one year of experience in operating and maintaining GC/MS with a bachelor's degree in chemistry or in any related scientific/engineering discipline, or in place of a bachelor's degree, three years of experience in operating and maintaining the GC/MS and interpreting GC/MS data.

8.0 Apparatus & Materials

8.1 Gas Chromatograph/Mass Spectrometer

8.1.1 GC-MS system - Hewlett Packard 6890 GC/7683 autosampler/5973 MSD.

8.1.2 Column - 30m x 0.25mm ID x 0.50 um film thickness capillary column (DB5-MS or equivalent).

8.1.3 Helium carrier gas, 5.0 grade

8.2 Data system - Hewlett Packard (HP) Kayak XA, 400 MHz with HP EnviroQuant Chemstation.

8.3 Syringes - 10 uL, Hamilton syringe # 701, 26s gauge

- 500 uL, Hamilton syringe #1750, 22 gauge, PTFE –coated plunger

- 1.0 mL, Hamilton syringe #1001, 22 gauge, PTFE –coated plunger

8.4 Volumetric flasks, Class A - 10 mL , Pyrex brand with stopper No. 9, Corning number 5640-10.

- 25 mL, Kimax brand, red stripe with stopper No. 9, Kimble number 28013-25

8.5 Balance - Ohaus AP250D, capacity 210g x 0.1 mg

8.6 Bottles - 2 ounce amber glass with polytetrafluoroethylene (PTFE)-lined screw caps, level 6 prcleaned, QEC item no. 6122-0002T.

8.7 Vials - 2.0 mL autosampler screwcap vials with teflon lined septa, National Scientific Company, Target DP brand, National Scientific number C4000-53R.

- 2.0 mL amber crimp-top glass autosampler with mark on spot, 12 x 32 mm with 11 mm crimp caps and PTFE lined septa, Fisher number HP-5181-3376.

- 8 mL amber screw thread glass sample vials with attached PTFE closure, Kimble number 60940A-8.

- 12 mL amber screw thread glass sample vials with attached PTFE closure, Kimble number 60940A-12.

8.8 Spatulas - micro-spoon, stainless steel, glazed finish, 9 " , VWR number 57952-253.

- micro, stainless steel, mirrored finish, 6.5" , VWR number 57949-044.

8.9 Beakers - 250 mL Pyrex Brand, Corning number 1000-250.

8.10 Pasteur Pipet Bulbs - Latex, 2 mL, VWR number 56311-062.

8.11 Pasteur Pipets - Pyrex brand, disposable, 5 ¾", VWR number 53283-911.

8.12 Reagents

8.12.1 Solvents (pesticide grade, GC/MS grade, or equivalent)

8.12.1.1 Dichloromethane - 4 L, CAS 75-09-2, Burdick & Jackson number 300-4

8.12.1.2 Hexane - 4 L, CAS 110-54-3, EM Science number HX0296-1

8.12.1.3 Acetone - 4 L, CAS 67-64-1, EM Science number AX0116-1

8.12.1.4 Methanol - 4 L, CAS 67-56-1, Burdick & Jackson number AH230-4

8.12.2 Standards

8.12.2.1 Standards are purchased from vendors who provide certified solutions. Standards are stored in a freezer reserved for standard solutions.

8.12.2.2 Preparation of standards is documented in the GC-MS standards logbook. Each standard is labeled by prep date to allow for tracking. Standards expire six months from the prep date. Leftover stock standards are saved in a capped vial in the original box in the freezer and expire six months from the opening of the standard vial. Any subsequent dilutions made from the opened vial expire six months from the original opening. The cracking date of the stock standard vial will be recorded on the label along with the six month expiration date. The semivolatiles continuing calibration verification standard will be prepared weekly. Any standards prepared for sample spiking will be verified by analysis prior to use.

a. GC-MS tuning standard: DFTPP, benzidine, pentachlorophenol and DDT:

Ultra Scientific GCM-150 (1,000 ug/mL).

A 1:40 dilution is made from the stock standard to provide for 25.0 ng/uL when 2.0 uL is directly injected onto the column via the autosampler.

b. Initial calibration (ICAL) standards: all targets of interest, plus surrogates and internal standards.

Surrogates: Ultra Scientific, 4,000 ug/mL, catalog number ISM-331

Target analytes:

Absolute Standards, 2,000 ug/mL, catalog numbers 10001, 10002, 10004, 10005, 10006, 10007, 10018, 82501, and 82705.

Absolute Standards 1,000 ug/mL, catalog numbers 70414 and 70451.

ISTD: Ultra Scientific, 4000 ug/mL, catalog number US-108N.

10.0 uL of ISTD are added directly to each 1.0 mL of calibration standard (40.0 ug/mL). Preparation procedures for the calibration standards are given in Table 2.

c. Initial calibration verification (ICV) standards: all analytes listed in the calibration method.

Surrogates: Ultra Scientific, 4000 ug/mL, catalog number ISM-331.

Target analytes:

Ultra Scientific, 1000 ug/mL, catalog numbers SVM-8270-1 and SVM-8271-1.

Ultra Scientific 2000 ug/mL, catalog numbers US-105N and US-120 ANS.

Ultra Scientific, 95-99%, catalog number RCC-174.

ISTD: Ultra Scientific, 4000 ug/mL, catalog number US-108N.

10.0 uL of ISTD are added directly to each 1.0 mL of calibration standard (40.0 ug/mL).

Table 2. EPA SW-846 8270 Standard Solutions

A 100 μg/mL stock 8270 solution containing all target compounds is made by accurately measuring 0.5 mL of each of the 2000 μg/mL mixes and surrogates* to a 10.0 mL Volumetric flask. The solution is brought to volume with $MeCl_2$. A 10.0 ug/mL standard is made by measuring 1.0 mL of the 100 ug/mL working stock standard into a 10.0 mL volumetric flask and bringing up to volume with $MeCl_2$. Dilutions will be made from these working stock standards. 10.0 uL of internal standard(4,000 ug/mL) is added to each vial.

FINAL STANDARD CONCENTRATION	VOLUME OF STOCK/ FINAL VOLUME	DILUTION FACTOR
60 ug/mL	600 μL/1.0 mL $MeCl_2$	1:1.67
40 ug/mL	400 μL/1.0 mL $MeCl_2$	1:2.5
20 ug/mL	200 μL/1.0 mL $MeCl_2$	1:5
10 ug/mL	1.0 mL of 10.0 ug/mL	
5 ug/mL	500 μL/1.0 mL $MeCl_2$	1:2
2 ug/mL	200 μL/1.0 mL $MeCl_2$	1:5

*Alternative mixes may be used, with dilution to achieve the same and final concentration.

9.0 Instrument or Method Calibration

9.1 Tune/system performance check (DFTPP)

Before analysis of any samples or standards can begin, the GC/MS system must be hardware tuned so a 50 ng injection of Decafluorotriphenylphosphine (DFTPP) passes the tuning criteria listed in Table 3. These criteria must be demonstrated each 12-hour

shift during which samples are analyzed.

Table 3. DFTPP Key Ions and Ion Abundance Criteria

DFTPP mass spectrum must meet EPA criteria described below.

51	30-60% of mass 198
68	<2% of mass 69
69	<100% of mass 198
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	> 1.0% of mass 198
441	Present but less than mass 443
442	> 40% of mass 198
443	17-23% of mass 442

To acquire the mass spectrum of DFTPP , three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction to eliminate column bleed or instrument background noise is accomplished using a single scan acquired no more than 20 scans prior to the elution of DFTPP.

The DFTPP standard must also contain pentachlorophenol, benzidine, and DDT to assess GC column performance and injection port inertness. Degradation of DDT to DDE and DDD should not exceed 20%. Benzidine and pentachlorophenol should be present at their normal responses and peak tailing should be evaluated. Benzidine should have a tailing factor less than 3, and pentachlorophenol should have a tailing factor less than 5.

9.2 Initial Calibration and Instrument Performance

The following steps are taken to create an initial calibration:

a. - standard preparation
b. - analysis of standards
c. - verify quantitation

d. - create/update calibration curve
e. - verify ICAL criteria
f. - ICV quantitation

9.2.1 Calibration criteria:

Method 8270: A minimum 5 point curve (usually a six or seven point curve is used), CCCs must have <30% RSD, RF for SPCCs >= 0.050, r^2 >= 0.990.

SPCCs: N-nitroso-di-n-propylamine
Hexachlorocyclopentadiene
2,4-dinitrophenol
4-nitrophenol

CCCs:

Base/Neutral Fraction	Acid Fraction
Acenaphthene	4-chloro-3-methylphenol
1,4-Dichlorobenzene	2,4-Dichlorophenol
Hexachlorobutadiene	2-Nitrophenol
Diphenylamine	Phenol
Di-n-octylphthalate	Pentachlorophenol
Fluoranthene	2,4,6-Trichlorophenol
Benzo(a)pyrene	

The relative retention time (RRT) of each compound in each calibration standard should agree within 0.06 RRT units. Late-eluting compounds usually have much better agreement.

Linearity - If the RSD of any compound is 15% or less, then the relative response factor is assumed to be constant over the calibration range, and the average relative response factor may be used for quantitation. If the RSD of any compound is greater than 15% a different curve fit should be applied. To determine the goodness of fit of the line, the coefficient of determination (r^2, the squared correlation coefficient) should be equal to or greater than 0.99.

When the RSD exceeds 15%, the plotting and visual inspection of a calibration curve can be a useful diagnostic tool. The inspection may indicate analytical problems, including errors in standard preparation, the presence of active sites in the chromatographic system, analytes that exhibit poor chromatographic behavior, etc. The creation of a new calibration curve may be required. If a quadratic curve fit is applied, a minimum of six levels must be included.

9.2.2 Initial Calibration Verification

Each time an initial calibration is performed and before analyses of samples, an initial calibration verification (ICV) standard containing each target analyte must be analyzed. The analytes are at the middle of the concentration range. Percent recovery of each analyte must be 70% to 130% with up to five compounds allowed at 50% to 150% as sporadic marginal failures (SMF). When only a subset of the analytes are required, the percent recovery of the ICV is allowed up to one

base/neutral SMF and one acid SMF.

10.0 Sample Collection, Handling & Preservation

10.1 Sample Collection

MATRIX	HOLDING TIME	PRESERVATIVE
Water, No Residual Chlorine Present	Extracted within 7 days and extracts analyzed within 40 days.	Cool, 4°C
Water, Residual Chlorine Present	Extracted within 7 days and extracts analyzed within 40 days.	3 mL 10% sodium thiosulfate solution per gallon. Cool, 4°C
Soil/Sediments and Sludges	Extracted within 14 days and extracts analyzed within 40 days.	Cool, 4°C
Concentrated Waste	Extracted within 14 days and extracts analyzed within 40 days.	None

10.2 The sample extracts should be protected from light, and stored at –10 °C in a sealed, PTFE-*septa lined, screw cap or crimptop vials.*

11.0 Sample Preparation and Analysis

11.1 Sample Preparation – a separate in-house sample preparation method exists for semivolatiles by GC/MS analysis.

11.2 Extracts may contain high boiling interferents that may saturate the detector or precipitates that may clog the syringe, injection port components, or the analytical column. A resonable attempt to correct for any matrix interference encountered would include

transfering the precipitate free extract to a second sample vial, dilution of the extract, or utilizing a cleanup method. If a cleanup method such as GPC is used, all samples in the analytical batch must undergo cleanup using identical conditions.

11.3 Analysis

Establish the GC/MS operating conditions using the following parameters,

Hewlett Packard Instrument Setup Parameters

Tune file	DFTPP.U
Solvent delay	4.50 min.
SCAN	35-500 3.2 scans/sec. (0.31 sec/scan)
Column Flow	1.5 mL/min (12.07 psi @ 40°C) Constant flow, Pressure program. Vacuum Compensation ON
Injector B	250°C
Detector B	280°C
Oven	40°C (hold 4.0 min) 12°C/min. to 310°C (hold 9.0 min)
A/S Inject	2 µL Pulsed splitless injection
Injection pulse pressure	25.0 psi until 0.60 min
Purge flow to split vent	50.0 mL/min at 1.00 min

11.3.1 General/Daily Operation

11.3.1.1 Fill the solvent reservoir with fresh solvent, check the autoinjector syringe for free movement of the plunger in the barrel, and inspect the injection port liner for residue of discoloration. Inject 50 ng DFTPP to begin a GC/MS tune evaluation. If the DFTPP standard mix criteria are met, continue analysis by injecting a continuing calibration verification standard. The CCV must meet all the CCC and SPCC criteria. For analytes requiring a linear or quadratic calibration curve, an evaluation of percent drift must be reported. If the CCV passes all requirements for continuing calibration, inject an instrument blank to verify that the gas chromatograph column and injection port are free from contaminants. Only after the instrument blank is found to be clean should an autosampler sequence begin.

11.3.1.2 For instrument QC purposes, the working period of the GC/MS is divided into 12 hour segments. To meet method criteria, each sequence of sample injections is set up so that the last injection of the sequence group is made within 12 hours of the beginning DFTPP injection. Each vial contains 1.0 mL of final extract to which 10.0 uL of 4000 ug/mL ISTD is added. A typical sequence is set up in the following order:

Tune/system performance check ('DFTPP')

Criteria:

DFTPP - to meet ion abundance criteria (Table 3)
benzidine - tailing factor < 3
pentachlorophenol - tailing factor < 5
DDT - decomposition <=20%

Continuing calibration verification

Criteria:

Standard containing each compound of interest, CCC compounds <20% difference from ICAL, SPCCs>0.050 RF, ISTD 50% to 100% relative to last daily calibration check, retention times within 30s.

Instrument blank

Criteria:

No hits present or less than reporting limit for all compounds of interest.

Method blank

Criteria:

No hits present or less than reporting limit for all compounds of interest.

Samples

Criteria:

ISTD 50% less to 100% more relative to CCV. Surrogates within established limits. Compounds not exceeding calibration range.

Spikes(Matrix and LCS).

Criteria:

Recoveries within established limits.

The data analysis software should be configured to use an audit trail for a record of changes to either the analytical method or the data file results.

11.3.1.2 Allow the sample extract to reach room temperature before analysis.

12.0 Troubleshooting

12.1 If the response of the primary ion used for quantitation exceeds the calibration range of the initial calibration, the sample extract must be diluted and reanalyzed. Additional internal standard must be added to maintain a final concentration of 40 ug/mL.

12.2 If the DFTPP tuning criteria cannot be met after repeated attempts, the mass spectrometer source may require cleaning.

12.3 Periodic replacement of the gas chromatograph injection port liner and/or seal, and the clipping of the analytical column may be required to remove residue of higher boiling

compounds.

13.0 Data Acquisition, Calculations & Data Reduction

13.1 Data Acquisition

Software control of the GC/MS hardware allows scanning from 35 to 500 amu three times a second using 70 volts (nominal) electron energy in the electron impact ionization mode. Continuous acquisition and storage of machine readable media of all mass spectra enables the identification of target analytes. Ions of a specific mass can be plotted as ion abundances versus time or scan number. The ion abundances within a specified time limit are integrated and compared to the ion abundances in the initial calibration curve to quantitate an analyte.

13.2 Calculations

Once the target components of the extract have been identified and quantitated, the "as-analyzed" value is converted to the "as-received" concentration as follows:

Water Matrix:

$$\frac{(ng/\mu L\ injected)\ x\ (mL\ extract\ final\ volume) x (dilution factor)}{(volume\ of\ sample\ extracted, in\ L)} = \mu g/L$$

Soil Matrix:

$$\frac{(ng/\mu L\ injected)\ x\ (mL\ extract\ final\ volume) x (dilution factor)}{(weight\ of\ sample\ extracted, in\ g)} = mg/Kg$$

Matrix spike samples are also calculated and reported on a µg/L or mg/Kg basis, along with the true (spike reference) value converted to the same units.

$$\frac{Quantitated\ Amount\ (\mu g/L)}{True\ Amount\ (\mu g/L)}\ x\ 100 = \%\ Recovery$$

13.3 Data Reduction

13.3.1 Qualitative Analysis

Compounds detected in the sample must meet retention time and mass spectral quality criteria.

- From the EICP for the quantitation ions, the target compound must be within 0.06 RRT units of the reference standard.
- All ions present in the standard spectrum at >10% must be present in the sample spectrum.
- The relative intensity of these ions must agree +/-20% (abs) between reference and sample spectra.

Reference spectra, generated from standards run on the individual instrument, are stored in the individual method. The instrument mass spectral reference library is updated with each new CCV.

Edit each analyte and delete the false positives or add false negative detections. Regenerate the quantitation report.

13.3.2 Quantitative Analysis

Once a compound has been identified, the quantitation is based on the integrated abundance from the EICP of the characteristic quantitation ion relative to that of the internal standard with the nearest retention time:

$$Quantitated\ Amount\ (ng/\mu L) = \frac{A_X}{A_{IS}} \times \frac{I_{IS}}{RF}$$

where:

A_X = Area of characteristic ion for compound being measured in the sample.
I_S = Amount of internal standard injected (ng).
A_{IS} = Area of characteristic ion for the internal standard.
RF = Response factor for compound being measured.
and where:

$$RF = \frac{(A_s C_{IS})}{(A_{IS} C_s)}$$

where:
A_s = Area of the characteristic ion for the compound being measured in the calibration standard.
A_{IS}= Area of the characteristic ion for the specific internal standard.

C_{IS}= Concentration of the specific internal standard.
C_s = Concentration of the compound being measured in the calibration standard or from the calibration curve generated by EnviroQuant.

13.3.3 Final Data Package

The data package includes extraction bench sheet, sequence log, verification of tuning and system performance, verification of calibration, and for each sample, the chromatogram, quantitation and library spectra for all positive targets. Printouts and explainations of any quantitation edits requiring manual integration. All are to be initialed and dated by the analyst. The data package should also include a report comparing the initial calibration internal standard areas and retention times to the internal standards of continuing calibrations , a CLP Internal Standard QA Summary report, and a CLP Surrogate QA Summary report. If applicable, the final data package should include a LCS Blank Spike Summary report, a Matrix Spike/Duplicate Recovery report, and a LSC report for Tentatively Identified Compounds

14.0 Computer Hardware & Software

14.1 Computer hardware - Hewlett Packard (HP) Kayak XA PC Workstation, X86 Family 6, Model 5, Stepping 2, AT/AT compatible, Pentium 400 MHz, with 98MB RAM.

14.2 Computer software - Hewlett Packard (HP) G1034C MS Chemstation, HP G1032C EnviroQuant Target Compound Software, Prolab Resources Inc., ProLab's Extend, version 1.4, and Microsoft Windows NT, version 4.00.

15.0 Data Management & Record Management

15.1 Data Management - An in-house method exists to follow guidelines from EPA's Good Automated Laboratory Practices (GALP).

15.2 Record Management - An in-house method covers the retaining of all raw data, documentation, and records. Archives exist for storage and retrieval of all raw data, documentation, and records for the retention period given by requirements.

16.0 Quality Control and Quality Assurances

16.1 Initial Demonstration of Capabilities

Before the analysis of samples, the analyst must demonstrates initial proficiency by generating data of acceptable precision and accuracy of the target analytes for the extraction and determinative method being used. Using a clean matrix (organic free silica sand or water) the analyst makes four replicate spikes and a blind. The replicates are spiked at 20.0 ug/L and taken through the same process as samples. The average recovery, X, and the standard deviation of the recovery, s, are compared with the acceptance ranges.

16.2 Detection Limits

Method detection limits are determined by the analysis of at least 7 low-level replicate spikes. Refer to the proper analytical procedure for determining the MDL (40 CFR Part 136, Appendix B). The MDL created is instrument specific.

16.3 On-going QC

Method blank - should be free of contamination, relative to the reporting limit. Phthalate esters should be less than 5 times the reporting limit.

Matrix Spike/Matrix Spike Duplicate - Prepared/analyzed per batch of twenty samples. Recovery should meet criteria determined in-house.

LCS – An LCS must be analyzed per batch of twenty samples and pass recovery criteria determined in-house. A LCS is prepared using organic free water or soil and spiked at the same level as the matrix spikes.

Surrogate recovery acceptance criteria are in-house determined criteria from the analysis of 15-20 field samples. Surrogate amounts are typically spiked at 20.0 ug/mL.

MDL Check Sample – A sample spiked at 2 x MDL must be analyzed quarterly for a continuing demonstration of capabilities. Analysis must be repeated until all analytes are detected.

16.4 Corrective action based on QC criteria – see Table 6.

17.0 References

17.1 USEPA "SW-846 Test Methods for Evaluating Solid Waste," Third Edition, Method 8270C, Revision 3, December 1996

17.2 USEPA "SW-846 Test Methods for Evaluating Solid Waste," Third Edition, Method 8000B, Revision 2, December 1996

17.3 USEPA, EPA-600/4-79-020, Revised March 1983, Method 625.

17.4 "Shell for Analytical Chemistry Requirements", U.S. Army Corps of Engineers (USACE), Version 1.0, November 2, 1998.

17.5 USEPA Contract Laboratory Program "Statement of Work for Organics Analysis," Multi-Media, Multi-Concentration, OLM03.0, Revision OLM03.1, August 1994.

17.6 "Independent Data Review Checklist," CT Laboratories, Inc., Revision 0, March 2000.

18.0 Checklists

18.1 Independent Data Review Checklist

18.1.1 A checklist must be completed per analytical run to be reviewed by the analyst and an independent reviewer.

18.1.2 The checklist includes criteria for flagging results and covers DFTPP tune check, initial calibration, continuing calibration verification, blanks, laboratory control samples (LCS), matrix spikes/matrix spike duplicates, samples, blanks, standards, QC samples, records, and reporting.

Table 6

Semivolatile Organic Compounds - SW846 Method 8270B
Quality Control Requirements

Quality Control Item	Frequency	Acceptance Criteria	Corrective Action
Tune Check (50ng DFTPP)	Every 12 hours.	Ensure correct mass assignment. DFTPP % Relative abundance criteria as specified in Table 3.	Retune. Do not proceed with analysis until DFTPP spectrum meets criteria.
Initial Calibration	1. Upon initial instrument set-up and when CCCs ad SPCCs in the calibration do not meet criteria. 2. Established initially at six concentration levels - low standard at or below project required quantitiation limit (PRRL).	1. Average RRF for each SPCC $\geq$ 0.050. 2. %RSD for RRFs for each CCC < 30%. 3. %RSD for RRFs for all compounds < 15% or linear or quadratic regression with a coefficient of determination R^2 >= 0.990. 4. If quadratic curve is applied a minimum of six levels must be included.	1. Correct system and recalibrate. Criteria must be met before sample analysis may begin. 2. If any compound > 15% RSD, generate a new calibration curve or use regression curve.
Continuing Calibration	Every 12 hours. Must be at or near the midpoint calibration range for all target compounds, SPCCws, CCCs, and surrogates.	1. RRF for each SPCC > 0.050. 2. %D for RRFs of each CCC < 20%, for non-CCC - <25% - except four must be <40%. 3. All project specified analytes %Drift <20% or %D <20%.	Correct system, if necessary, and recalibrate. Criteria must be met before sample analysis may begin.
Internal Standards	Added to all blanks, standards, and samples.	1. Peak area within -50% to +100% of area in associated continuing calibration standard. 2. Retention time (RT) within 30 sec of RT for associated continuing calibration standard.	1. Inspect instrument for malfunctions, then reanalyze samples. 2. If no instrument malfunction identified proceed as follows: * Reanalyze sample. * If reanalysis is out, report both sets of data to section manager. If in, report only second set.
Method Blank	One per extraction batch of 20 or fewer samples/matrix. Must undergo all sample preparative procedures. Must be run on each instrument used for sample analysis.	1. Target phthalate esters <5xPRRL. All other target compounds <PRRL. 2. Must meet internal standard criteria. 3. Must meet surrogate criteria.	Reanalyze to determine if instrument contamination was the cause. If the method blank is still non-compliant, reextract and reanalyze all samples in the prep batch unless > 10x the blank, or there are no positive results.

Semivolatile Organic Compounds - SW846 Method 8270B
Quality Control Requirements
(Continued)

Quality Control Item	Frequency	Acceptance Criteria	Corrective Action
Laboratory Control Sample (LCS)	One per matrix/per extraction batch (if applicable)/per set of 20 samples. Must undergo all sample preparative procedures. Must be from second source and contain all target compounds specified in Table 4B at concentrations at the midpoint of the calibration range.	% Recoveries (and RPDs, if applicable) within the acceptance criteria in Table 4B.	Reanalyze the LCS to determine if instrumental conditions or analytical preparation was the cause. If still out reprep and reanalyze associated samples and LCS. Exception: If lCS recovery is higha dn no associated positive results are reported, then address the issue in the Case Narrative and no further action is needed.
Matrix Spike/Matrix Spike Duplicate	One per matrix/per extraction batch (if applicable) per set of 20 samples. Must undergo all sample preparative procedures. Must be spiked with the target compounds specified in the Table 4B at concentrations at or near the mid-point of the calibration range.	1. % Recoveries within acceptance criteria in Table 4B. 2. RPDs within Table 4B.	If LCS is acceptable, then report in the Case Narrative that there was probably matrix interference.
Initial Calibration Verification	Upon initial calibration	1. Recovery for each analyte 70 –130% or 50 –150% for up to five SMFs. 2. Recovery for subset of analytes 70 – 130% or 50 –150% for one base neutral and one acid.	Reanalyze the ICV to determine if instrumental conditions or analytical preparation was the cause. If still out, correct the system and recalibrate.
Qualitative/Quantitative Issues	If instrument level of any compound in a sample exceeds the highest standard, the sample must be diluted to approximately mid-level of the calibration range and reanalyzed.	The instrument level of all compounds must be within the calibration range for all samples.	Dilute the sample to bring the level of the highest concentration of target compounds within the calibration range.

Semivolatile Organic Compounds - SW846 Method 8270B
Quality Control Requirements
(Continued)

Quality Control Item	Frequency	Acceptance Criteria	Corrective Action
Surrogate	1. Calibrated as target compounds. 2. Added to all blanks, samples, and QC samples.	1. All surrogate recoveries must be within limits specified in Table 5.	If recovery acceptance criteria are not within limits: 1. Check to be sure that there are no errors in calculations, surrogate solutions, and internal standards. Also, check instrument performance. 2. If no problem is found, re-prep and re-analyze the sample. 3. If the reanalysis is within limits, report only the reanalysis. 4. If the reanalysis is within limits, but out of hold, report both sets of data. 5. If the reanalysis is still out of limits, report both sets of data. 6. No reanalysis is required if the MS and/or MSD are outside limits, but the RPDs are within acceptance ranges.

CT Laboratories
Baraboo Laboratory Divison

Title: **TCLP and SPLP Extraction for Non-Volatile Parameters**

SOP Number: **CL-8B**

Prepared by: _____
Date

Technical Review by: _____
Date

Reviewed by: _____
Quality Assurance ***Date***

_____
Laboratory Director ***Date***

SOP Manual Control Number:_____

1.0 SCOPE AND APPLICATION

1.1 The Toxicity Characteristic Leaching Procedure (TCLP) and Synthetic Precipitation Leaching Procedure (SPLP) are designed to determine the mobility of both organic and inorganic analytes present in liquid, solid, and multiphasic wastes.

1.2 The following procedure will be used for performing the metals and semi-volatile extraction.

2.0 METHOD SUMMARY

2.1 TCLP

2.1.1 For liquid wastes (i.e., those containing less than 0.5% dry solid material), the waste, after filtration through a 0.6 to 0.8 µm glass fiber filter, is defined as the TCLP extract.

2.1.2 For wastes containing greater than or equal to 0.5% solids, the liquid, if any, is separated from the solid phase and stored for later analysis; the particle size of the 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. The extraction fluid employed is a function of the alkalinity of the solid phase of the waste. Following extraction, the liquid extract is separated from the solid phase by filtration through a 0.6 to 0.8 µm glass fiber filter.

2.1.3 If compatible (i.e., multiple phases will not form on combination), the initial liquid phase of the waste is added to the liquid extract, and these are analyzed together. If incompatible, the liquids are analyzed separately and the results are mathematically combined to yield a volume-weighted average concentration.

2.2 SPLP

2.2.1 For liquid samples (i.e., those containing less than 0.5 % dry solid material), the sample, after filtration through a 0.6 to 0.8 µm glass fiber filter, is defined as the SPLP extract.

2.2.2 For samples containing greater than 0.5 % solids, the liquid phase, if any, is separated from the solid phase and stored for later analysis; the particle size of the 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. 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. Following extraction, the liquid extract is separated from the solid phase by filtration through a 0.6 to 0.8 µm glass fiber filter.

2.2.3 If compatible (i.e., multiple phases will not form on combination), the initial liquid phase of the waste is added to the liquid extract, and these are analyzed together. If incompatible, the liquids are

analyzed separately and the results are mathematically combined to yield a volume-weighted average concentration.

3.0 DEFINITIONS

3.1 Batch - A batch consists of a maximum of 20 samples of similar matrix which are prepared and analyzed in the same manner. Each batch is given a unique prep batch number for tracking purposes.

3.2 PB or MB (Prep Blank/ Method Blank) - A Reagent Blank which is carried through the entire preparation and analytical method. The method blank is used to detect possible contamination that may occur prior to or during the sample preparation. A minimum of one MB is prepared per batch, and is analyzed at the beginning of an analytical batch.

3.3 MS (Matrix Spike): - A separate sample aliquot to which a known concentration of analyte has been added which is carried through the entire preparation and analytical procedure. The purpose of a matrix spike is to reveal any matrix effect from the sample on the recovery of the analyte by the method being used. One MS is prepared for each waste type in a given batch of samples. Failure to meet criteria may be due to poor recovery during the preparation method or due to matrix interference within the sample.

4.0 HEALTH AND SAFETY

4.1 Gloves and protective clothing should be worn to protect against unnecessary exposure to hazardous chemicals and contaminants in samples. All activities performed while following this procedure should utilize appropriate laboratory safety systems.

5.0 CAUTIONS

There are no cautions

6.0 INTERFERENCES

Refer to the sample analytical methods for interferences.

7.0 PERSONNEL QUALIFICATIONS

7.1 All personnel performing this analysis should be instructed in the use of personal protective equipment prior to beginning analysis.

7.2 Personnel should know how to read a meniscus and how to use a balance correctly.

8.0 APPARATUS AND MATERIALS

8.1 Rotator apparatus capable of turning at 30 +/- 2 rpm.

8.2 2 liter glass extraction jars.

8.3 2 liter polyethylene extraction containers.

8.4 Millipore pressure filtration apparatus. Note: The interior surface of the pressure filtration apparatus should be free smooth and free of scratches. Clean using only a very soft bristled brush if necessary. Also, the screen

on which the filter is placed should be clean of debris. If any of the holes are clogged they can be cleaned by sonicating for 15 minutes.

8.5 Glass fiber filters 0.7 micron: Environmental Express TCLP filters or equivalent.

8.6 Ceramic filtration funnel, 15 cm.

8.7 2 liter filtration flask.

8.8 pH meter.

8.9 Top-loading balance, 0.01 g capacity.

8.10 Hotplate.

8.11 Magnetic stirrer.

8.12 100 mL graduated cylinder.

8.13 5 mL oxford pipette.

8.14 Thermometer, 100^0C.

8.15 Reagents:

8.15.1 De-ionized water: Milli-Q type II

8.15.2 Hydrochloric acid 1N: Prepare in hood. Into a 1 liter volumetric flask, add 900 mL of D.I. H2O. Carefully add 83 mL ACS reagent grade conc. HCl. Dilute to volume with D.I. H2O and mix well.

8.15.3 Glacial acetic acid, conc. ACS reagent grade.

8.15.4 Sodium Hydroxide 10N: Into a 1 liter volumetric flask, add 500 mL of D.I. H2O. Dissolve 400g. ACS reagent grade NaOH pellets (caution: mixture will become very hot). When cool, dilute to volume with D.I. H2O and mix well.

8.15.5 SPLP extraction fluid acid mixture: To a 100 mL volumetric flask, add 50 mL D.I. H2O. Carefully add 6 g. Conc. H2SO4 and 4 g. Conc. HNO3. Mix by swirling and dilute to volume with D.I. H2O.

8.16 EXTRACTION FLIUDS

8.16.1 TCLP extraction fluid #1: (To prepare a 20 liter quantity): Fill a 20 L carboy with 19 L Of D.I. H_2O. Add 114 mL glacial acetic acid and 128.6 mL 10N NaOH. Dilute to 20 L With D.I. H_2O and mix by stirring. When correctly prepared, the pH of this fluid will be 4.93 +/- 0.05.

8.16.2 TCLP extraction fluid #2: (To prepare a 20 liter quantity): Fill a 20 L Carboy with 19 L of D.I. H_2O. Add 114 mL glacial acetic acid. Dilute to 20 L and mix by stirring. When correctly prepared, the pH of this fluid will be 2.88 +/- .05.

8.16.3 SPLP extraction fluid #1: To be used for sites that are east of the Mississippi River. Prepare a sufficient quantity of extraction fluid by adding the SPLP acid mixture (see step 8.15.5 of this SOP) to D.I. H_2O to obtain a pH of 4.20 +/- 0.05. Note: solutions are unbuffered and the exact pH may not be obtained.

8.16.4 SPLP extraction fluid #2: To be used for sites that are west of the Mississippi River. Prepare a sufficient quantity of extraction fluid by adding the SPLP acid mixture (see step 8.15.5 of this SOP) to

D.I. H_2O to obtain a pH of 5.00 +/- 0.05. Note: solutions are unbuffered and the exact pH may not be obtained.

9.0 INSTRUMENT OR METHOD CALIBRATION

No calibration is necessary.

10.0 SAMPLE COLLECTION, HANDLING AND PRESERVATION

10.1 Preservatives shall not be added to samples before extraction. Extracts to be analyzed for metals shall be preserved following filtration with conc. HNO_3. Extracts to be analyzed for Semivolatile organic compounds (SVOCs) shall not be preserved following filtration. Extracts to be analyzed for Phenolics shall be preserved following filtration with conc. sulfuric acid.

10.2 Sample hold times are as follows (days):

	SVOCs	Mercury	Metals	Phenolics
From sample date to TCLP extraction:	14	28	180	28
From TCLP extraction to preparative extraction:	7	n/a	n/a	n/a
From preparative extraction to analysis:	40	28	180	28

See TCLP method 1311 sec. 6.0 and SPLP method 1312 sec. 6.0 for a detailed description of sample handling.

11.0 SAMPLE PREPARATION AND ANALYSIS

11.1 See appropriate SOP for sample analysis following extraction with this mehod.

11.2 DETERMINE SAMPLE % SOLIDS

11.2.1 For solid samples which contain no free liquids, proceed to sec. 11.3.2.

11.2.2 For samples which are liquid, contain free liquids, or are multi-phasic, filtration or liquid/solid separation is required as follows:

11.2.2.1 Preweigh a GFF filter and record the weight.

11.2.2.2 Preweigh a receiving beaker and record the weight.

11.2.2.3 Preweigh a transfer beaker and record the weight.

11.2.2.4 Assemble the pressure filtration device with the GFF filter, and place the receiving beaker beneath the outlet.

11.2.2.5 Weigh out a subsample of the waste (100g. minimum) and record the weight. An additional minimum 100g. will be needed for the extraction.

11.2.2.6 Transfer the waste to the filtration device and secure the top.

11.2.2.7 Re-weigh the empty transfer beaker and record the weight.

11.2.2.8 Slowly apply air pressure to the filtration device in 10 psi increments up to 50 psi. or until air passes through

the filter. Hold at each increment for 2 minutes before proceeding to the next higher increment.
*Note: Some wastes, such as oily wastes and some paint wastes will contain material that appears to be a liquid. Even after applying pressure to 50 psi, this material may not filter. In this case, the material in the filter holder is defined as the solid phase and is carried through the extraction as a solid. Proceed to sec. 11.4.

11.2.2.9 Weigh the receiving beaker and record the weight.

11.2.2.10 The material in the filter holder is defined as the solid phase of the waste, and the material in the receiving beaker is defined as the liquid phase.
*Note: This subsample is not to be used for the extraction procedure.

11.2.2.11 Determine and record the weight of the liquid phase.

11.2.2.12 Determine the weight of the solid phase by subtracting the weight of the liquid phase from the total weight of the waste.

11.2.2.13 Calculate the % solids as follows:

$$\% \text{ solids} = \frac{\text{weight of solid phase}}{\text{total weight of waste}} \times 100$$

11.3 EVALUATION OF % SOLIDS

11.3.1 If the % solids is <0.5%, the filtrate is defined as the TCLP extract. Proceed to section 11.5 to prepare the extract for analysis.

11.3.2 If the % solids is significantly >0.5%, the solid portion must have a particle size which is smaller than 1cm. or have a surface area >3.1 cm^2 /g. (paper, cloth, etc.).If the above is not met, the material must be reduced to particles of the appropriate size by cutting, crushing, or grinding.

11.3.3 If the % solids is ≥0.5% or is very close, and it is noticed that the solid material is entrained in the filter, dry the filter at 80-120C until two successive weighings agree within +/- 1%. Determine the % dry solids. If the % dry solids is <0.5%, the filtrate is defined as the TCLP extract. Proceed to section 11.5 . If the % dry solids is >0.5%, see note below.
*Note: there must be a significant level of % solids such that a minimum of 25-50g of solids can be generated for the extraction. This minimum amount of solids will yield 500-1000 mL of extract.

11.4 DETERMINE THE APPROPRIATE EXTRACTION FLUID

11.4.1 TCLP

11.4.1.1 Transfer 5.0 g. of a representative subsample of the waste to a clean 250 mL beaker.

11.4.1.2 Add 96.5 mL D.I. H2O and cover with a

watchglass.

11.4.1.3 Stir vigorously for 5 min.

11.4.1.4 Measure and record the pH.

*Note: Accurate pH measurement is critical; calibrate the pH meter daily with fresh buffer solutions.

11.4.1.5 If the pH is <5.0, use extraction fluid #1.

11.4.1.6 If the pH is >5.0, add 3.5 mL of 1N HCl, cover with a watchglass, and heat on a hotplate to 50^0 C. Hold at 50^0 C for 10 min. Cool to room temperature, measure and record the pH. If the pH is < 5.0, use extraction fluid #1. If the pH is > 5.0, use extraction fluid #2.

11.4.2 SPLP

11.4.2.1 For samples collected from sites east of the Mississippi River, use extraction fluid #1.

11.4.2.2 For samples collected from sites west of the Mississippi River, use extraction fluid #2.

11.5 EXTRACTION PREPARATION

11.5.1 For samples that are 100% total solids

11.5.1.1 Perform particle size reduction if necessary.

11.5.1.2 Weigh **at least** 100 g of sample directly into the extraction vessel and record the weight. (For SVOC and phenolics analysis, a glass container must be used. For metals analysis, a glass or plastic container may be used.)

11.5.1.3 Record the number of the vessel being used and also check it off on the vessel usage sheet in front of the TCLP extraction log. A blank must be run on each container at a minimum of every 20th use.

11.5.1.4 Determine the amount of extraction fluid to add to the extraction container as follows:
Volume of extraction Fluid (mL) = 20 x mass of sample (g)

11.5.1.5 Measure and record the pH of the extraction fluid immediately prior to use.

11.5.1.6 Add the appropriate amount of extraction fluid.

11.5.1.7 Measure and record the initial pH.

11.5.1.8 Tightly cap the extraction container. The sample is now ready for extraction. Proceed to sec. 11.6.

11.5.2 For samples which are liquid, contain free liquids, or are multi-phasic, filtration or liquid/solid separation is required on a new portion of the waste:

11.5.2.1 Preweigh a GFF filter and record the weight. Filters should be prewashed with 1N HNO_3 followed by D.I. H_2O if metals are to be analyzed.

11.5.2.2 Preweigh a receiving beaker and record the weight.

11.5.2.3 Preweigh a transfer beaker and record the weight.

11.5.2.4 Assemble the pressure filtration device with the GFF filter, and place the receiving beaker underneath.

11.5.2.5 Weigh out at least 100 g of waste and record the weight. Ideally, enough sample should be filtered to allow for 100 g of solids to remain.

11.5.2.6 Transfer the waste to the filtration device and secure the top.

11.5.2.7 Re-weigh the empty transfer beaker and record the weight.

11.5.2.8 Slowly apply air pressure to the filtration device in 10 psi increments up to 50 psi. or until air passes through the filter. Hold at each increment for 2 minutes before proceeding to the next higher increment.

11.5.2.9 Weigh the receiving beaker and record the weight.

11.5.2.10 The material in the filter holder is defined as the solid phase of the waste, and the material in the receiving beaker is defined as the liquid phase.

11.5.2.11 Measure and record the weight and volume of the liquid phase.

11.5.2.12 Using a transfer pipette and a small beaker, add a few drops of the liquid phase to a small quantity of D.I. H_2O.

11.5.2.13 If the two phases are miscible, save the liquid phase for addition back to the filtered TCLP or SPLP extract. Store at 4^0 C in an appropriate container until the extraction is complete. If the two phases do not mix, the liquid phase will need to be analyzed separately and the results mathematically combined with the results from the extract.

Calculation:

Final analyte concentration = $\frac{(V1)(C1) + (V2)(C2)}{V1 + V2}$

V1 = volume of the first phase liquid
C1 = concentration of the first phase in mg/L
V2 = volume of the second phase liquid
C2 = concentration of the second phase in mg/L

11.5.2.14 Disassemble the filtration apparatus and carefully remove the filter and waste. Perform particle size reduction if necessary. Quantitatively transfer the filter and waste into the appropriate extraction container.

11.5.2.15 Determine the amount of extraction fluid to add to the extraction container as follows:

Volume of extraction Fluid (mL) = 20 x mass of sample (g)

11.5.2.16 Add the appropriate amount of extraction fluid.

11.5.2.17 Measure and record the initial pH.

11.5.2.18 Tightly cap the extraction container. The sample is now ready for extraction.

11.6 EXTRACTION

11.6.1 Secure the samples in the rotation apparatus which is located in the BOD incubator

11.6.2 Rotate for 18 +/- 2 hours. A room temperature of 23 +/- 2^{0}C must be maintained during the extraction period. This can be checked in the electronic temperature data logger.

11.6.3 Begin rotating. Record the time.

11.7 FILTRATION FOLLOWING EXTRACTION

11.7.1 Record the time and temperature at the end of the extraction period, as well as the minimum and maximum temperatures.

11.7.2 Following the rotation period, measure and record the pH of each bottle

11.7.3 Assemble the 2 L vacuum flask and ceramic filtration funnel.

11.7.4 Obtain the necessary sample containers and pH paper.

11.7.5 Place a 0.7 micron glass fiber filter (Environmental Express TCLP filters) in the filtration funnel. Record the lot # of filter that is used.

11.7.6 Filter the extract.

11.7.7 Transfer a suitable quantity of the filtrate to the appropriate sample containers:

Metals: 250 mL in polyethylene with HNO_3 preservative.
Semi-volatiles and phenolics: 1 L in amber glass jar.

11.7.8 For metals analysis, preserve the sample to pH <2 with conc. HNO_3.

11.7.9 For semi-volatile analysis, preservative is not added. Store at 4 °C.

11.7.10 For phenolics analysis, preserve the sample to pH<2 with conc. H_2SO_4.

12.0 TROUBLESHOOTING AND MAINTENANCE

12.1 There is no troubleshooting or maintenance for this method.

13.0 DATA ACQUISITION, CALCULATION AND REDUCTION

13.1 See section 11.0 for any applicable calcuations.

14.0 COMPUTER HARDWARE AND SOFTWARE

14.1 Computer with StarLIMS

15.0 DATA MANAGEMENT AND RECORD MANAGEMENT

15.1 Data is recorded in the TCLP/SPLP extraction log.

15.2 Prep data is entered into LIMS, and then the batch sheet is given to the metals prep analyst or the semi-volatile prep analyst.

16.0 QUALITY CONTROL/QUALITY ASSURANCE

16.1 A minimum of one blank, using the same extraction fluid as used for the samples, is required for every extraction batch. Also, a blank must be performed every 20th time an extractions is performed in a particular container to check for contamination.

16.2 A matrix spike is required for each waste type, with a minimum of one matrix spike per extraction batch. Matrix spikes are prepared at the time of digestion/analysis.

17.0 REFERENCES

17.1 *Test Methods for Evaluating Solid Waste*,. EPA-SW-846. September, 1994. Method 1311.

17.2 *Test Methods for Evaluating Solid Waste*,. EPA-SW-846. September, 1994. Method 1312.

CT Laboratories
Baraboo Laboratory Divison

Title: TCLP and SPLP Extraction for Volatile Organic Compounds

SOP Number: CL-8A

Prepared by: _____
Date

Technical Review by: _____
Date

Reviewed by: _____
Quality Assurance *Date*

_____
Laboratory Director *Date*

SOP Manual Control Number:_____

1.0 SCOPE AND APPLICATION

1.1 The Toxicity Characteristic Leaching Procedure (TCLP) and Synthetic Precipitation Leaching Procedure (SPLP) are designed to determine the mobility of both organic and inorganic analytes present in liquid, solid, and multiphasic wastes.The following procedure will be used for performing the volatile organic ZHE procedure.

2.0 METHOD SUMMARY

2.1 TCLP

2.1.1 For liquid wastes (i.e., those containing less than 0.5% dry solid material), the waste, after filtration through a 0.6 to 0.8 µm glass fiber filter, is defined as the TCLP extract.

2.1.2 For wastes containing greater than or equal to 0.5% solids, the liquid, if any, is separated from the solid phase and stored for later analysis; the particle size of the 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. A special extractor vessel is used when testing for volatile analytes. Following extraction, the liquid extract is separated from the solid phase by filtration through a 0.6 to 0.8 µm glass fiber filter.

2.1.3 If compatible (i.e., multiple phases will not form on combination), the initial liquid phase of the waste is added to the liquid extract, and these are analyzed together. If incompatible, the liquids are analyzed separately and the results are mathematically combined to yield a volume-weighted average concentration.

2.2 SPLP

2.2.1 For liquid samples (i.e., those containing less than 0.5 % dry solid material), the sample, after filtration through a 0.6 to 0.8 µm glass fiber filter, is defined as the SPLP extract.

2.2.2 For samples containing greater than 0.5 % solids, the liquid phase,if any, is separated from the solid phase and stored for later analysis; the particle size of the 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. 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. A special extractor vessel is used when testing for volatile analytes. Following extraction, the liquid extract is separated from the solid phase by filtration through a 0.6 to 0.8 µm glass fiber filter.

2.2.3 If compatible (i.e., multiple phases will not form on combination), the initial liquid phase of the waste is added to the liquid extract, and these are analyzed together. If incompatible, the liquids are analyzed separately and the results are mathematically combined to yield a volume-weighted average concentration.

3.0 DEFINITIONS

3.1 Batch - A batch consists of a maximum of 20 samples of similar matrix which are prepared and analyzed in the same manner. Each batch is given a unique prep batch number for tracking purposes.

3.2 PB or MB (Prep Blank/ Method Blank) - A Reagent Blank which is carried through the entire preparation and analytical method. The method blank is used to detect possible contamination that may occur prior to or during the sample preparation. A minimum of one MB is prepared per batch, and is analyzed at the beginning of an analytical batch.

3.3 MS (Matrix Spike): - A separate sample aliquot to which a known concentration of analyte has been added which is carried through the entire preparation and analytical procedure. The purpose of a matrix spike is to reveal any matrix effect from the sample on the recovery of the analyte by the method being used. One MS is prepared for each waste type in a given batch of samples. Failure to meet criteria may be due to poor recovery during the preparation method or due to matrix interference within the sample.

4.0 HEALTH AND SAFETY

4.1 Gloves and protective clothing should be worn to protect against unnecessary exposure to hazardous chemicals and contaminants in samples. All activities performed while following this procedure should utilize appropriate laboratory safety systems.

5.0 CAUTIONS

5.1 For the ZHE to be acceptable for use, the piston within the ZHE should be able to be moved with approximately 15 psig or less. If it takes more pressure to move the piston, the O-rings in the device should be replaced.

5.2 The ZHE should be checked for leaks after every extraction. If the device contains a built-in pressure gauge, pressurize the device to 50 psig, allow it to stand unattended for 1 hour, and recheck the pressure. If the device does not have a built-in pressure gauge, pressurize the device to 50 psig, submerge it in water, and check for the presence of air bubbles escaping from any of the fittings. If pressure is lost, check all fittings and inspect and replace O-rings, if necessary. Retest the device.

6.0 INTERFERENCES

6.1 Potential interferences that may be encountered during analysis are discussed in the individual analytical methods.

7.0 PERSONNEL QUALIFICATIONS

7.1 All personnel performing this analysis should be instructed in the use of personal protective equipment prior to beginning analysis.

7.2 Personnel should know how to read a meniscus and how to use a balance correctly.

8.0 APPARATUS AND MATERIALS

8.1 Rotator apparatus capable of turning at 30 +/- 2 rpm.
8.2 ZHE extraction devices.
8.3 Millipore pressure filtration apparatus.
8.4 Glass fiber filters 0.6-0.8 micron 11.0 cm. (Whatman GFF or equivalent).
8.5 Glass fiber filters 0.6-0.8 micron: 15.0 cm. (Whatman GFF or equivalent).
8.6 Fluid pump.
8.7 Gas pressure/vacuum pump.
8.8 250 mL and 500 mL beakers.
8.9 100mL glass gas tight syringe.
8.10 Tedlar bags.
8.11 40 mL VOA vials.
8.12 Top-loading balance.
8.13 TCLP/SPLP prep log.
8.14 Reagents
8.14.1 De-ionized water: Milli-Q type II
8.14.2 Extraction fluids:
8.14.2.1 **TCLP extraction fluid 'A'**: (To prepare a 20 liter quantity):
Fill a 20 L. Carboy with 19 L. Of D.I. H2O. Add 114 mL 1N glacial acetic acid and 128.6 mL 10N NaOH. Dilute to 20L. With D.I. H2O and mix by stirring. Adjust the pH with acetic acid or NaOH to obtain 4.93 +/- 0.05.
8.14.2.2 **SPLP extraction fluid**: reagent water

9.0 INSTRUMENT OR METHOD CALIBRATION

There is no calibration for this method.

10.0 SAMPLE COLLECTION, HANDLING AND PRESERVATION

10.1 Preservatives shall not be added to samples before extraction.
10.2 Care shall 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 and stored at 4C. Samples should be opened only immediately prior to extraction). Extracts or portions of extracts for organic analyte determinations shall not be allowed to come into contact with the atmosphere (i.e., no headspace) to prevent losses.
10.3 Volatiles have 14 days from the date of collection to be extracted.
10.4 Volatiles have 14 days from the date of extraction to be analyzed.

11.0 SAMPLE PREPARATION AND ANALYSIS

11.1 **Determine sample % solids:**
11.1.1 For solid samples which contain no free liquids, proceed to sec. 11.3.

11.1.2 For samples which are liquid, contain free liquids, or are multi-phasic, filtration or liquid/solid separation is required as follows:

11.1.2.1 Preweigh a GFF filter and record the weight.

11.1.2.2 Preweigh a receiving beaker and record the weight.

11.1.2.3 Preweigh a transfer beaker and record the weight.

11.1.2.4 Assemble the pressure filtration device with the GFF filter, and place the receiving beaker underneath.

11.1.2.5 Weigh out a subsample of the waste (100g. minimum) and record the weight. An additional minimum 25g. will be needed for the extraction. For low volume samples, consult your supervisor.

11.1.2.6 Transfer the waste to the filtration device and secure the top.

11.1.2.7 Re-weigh the empty transfer beaker and record the weight.

11.1.2.8 Slowly apply air pressure to the filtration device in 10 psi increments up to 50 psi. or until air passes through the filter. Hold at each increment for 2 minutes before proceeding to the next higher increment.

*Note: Some wastes, such as oily wastes and some paint wastes will contain material that appears to be a liquid. Even after applying pressure to 50 psi, this material may not filter. In this case, for the non-volatile extraction, the material in the filter holder is defined as the solid phase and is carried through the extraction procedure as a solid.However, since the volatile procedure requires utilizing the ZHE device to filter the sample following rotation, the ZHE filter may become plugged and filtration of the extract from the ZHE device may not be possible.

11.1.2.9Weigh the receiving beaker and record the weight.

11.1.2.10 The material in the filter holder is defined as the solid phase of the waste, and the material in the receiving beaker is defined as the liquid phase.

11.1.2.11 Determine and record the weight of the liquid phase.

11.1.2.12. Determine the weight of the solid phase by subtracting the weight of the liquid phase from the total weight of the waste.

11.1.2.13. Calculate the % solids as follows:

$$\% \text{ solids} = \frac{\text{weight of solid phase}}{\text{total weight of waste}} \times 100$$

11.2 Evaluation of % solids:

11.2.1 If the % solids are <0.5%, a fresh portion of the waste will be filtered through the ZHE device and collected in a Tedlar bag or a 100 mL syringe. This filtrate will be defined as the TCLP extract. Proceed to sec.11.3, then 11.4.4

11.2.2 If the % solids are significantly >0.5%, proceed to section 11.3, then 11.4.1. or 11.4.2.

11.2.3 If the % solids are ≥0.5% or are very close, and it is noticed that the solid material is entrained in the filter, dry the filter at 80-120C until two successive weighings agree within +/- 1%. Determine the % dry solids. If the % dry solids are <0.5%, follow 11.2.1. If the % dry solids are >0.5%, see note below.
*Note: there must be a significant level of % solids such that a minimum of 5-10g of solids can be generated for the extraction. This minimum amount of solids will yield 100-200 mL of extract.

11.3 ZHE device preparation:

11.3.1 Assemble the ZHE device as follows:

11.3.1.1 Place two O-rings on the piston.

11.3.1.2 Place an O-ring in the ZHE base.

11.3.1.3 Wet the O-rings of the piston and place the piston inside the ZHE body. Depress the piston into the ZHE body only far enough to allow room for the sample.

11.3.1.4 With the piston installed, place the ZHE body into the base.

11.3.1.5 Place an O-ring on the top of the ZHE body.

11.3.1.6 Place a 11.0 cm. GFF filter between the two filter screens and set aside.

11.3.1.7 The ZHE device is now ready to receive a sample.

11.4 Adding sample to the ZHE device:

11.4.1 For samples that are 100% total solids:

11.4.1.1 Weigh out 25.0g. of sample into a beaker or other suitable container and record the weight. If particle size reduction if required, chill the sample and reduction equipment to 4^0C to reduce the loss of volatile compounds. Proceed to chop, crush, or grind the sample to a minimum $1 cm^2$ size. Minimize exposure to the atmosphere.

11.4.1.2 Transfer the waste material to the ZHE device and secure the top.

11.4.1.3 Attach the air line from the pressure pump to the lower valve. Open the upper and lower valves.

11.4.1.4 Slowly pressurize the ZHE device to 50 psi to force the piston to the top of the ZHE body, thereby removing any headspace. Remove the air line.

11.4.1.5 Determine the amount of extraction fluid to add follows: amount of fluid added = 20 x's the weight of the sample

11.4.1.6 Proceed to sec. 11.5

11.4.2 For samples >5% but <100% total solids:

11.4.2.1 Determine the amount of sample to add to the ZHE as follows:

Weight of sample to use = _____25_____ x 100

% total solids (sec. 11.1)

11.4.2.2 Proceed to sec. 11.4.3, using the amount of sample determined above.

11.4.3 For samples that are between 0.5% - 5% total solids:

11.4.3.1 Weigh a 500 mL beaker and record the weight.

11.4.3.2 Into the beaker, weigh out 500 g. of sample and record the weight.

11.4.3.3 Transfer the waste to the ZHE device and secure the top.

11.4.3.4 Connect the air line to the lower valve. Open upper and lower valves.

11.4.3.5 Slowly pressurize the ZHE to expel any air. Close the top valve when liquid appears.

11.4.3.6 Pre-weigh a Tedlar bag and record the weight.

11.4.3.7 Slowly pressurize the ZHE to expel the liquid into the bag. Do not exceed 50 psi.

11.4.3.8 Close the valves. Remove the bag, weigh the bag and it's contents, and record the weight.

11.4.3.9 Determine the amount of extraction fluid to add follows:

$$\text{weight of extraction fluid} = \frac{20 \times \text{weight of sample waste} \times \%\ \text{solids}}{100}$$

11.4.3.10 Proceed to sec. 11.5

11.4.4 For samples that are <0.5% total solids:

11.4.4.1 The liquid portion of the waste, after filtration is defined as the TCLP extract. The ZHE device will be used to filter the sample.

11.4.4.2 Add an appropriate amount of sample to the ZHE device to complete the requested analyses.

11.4.4.3 Secure the top, connect the air line to the lower valve. Open upper and lower valves.

11.4.4.4 Slowly pressurize the ZHE to expel any air. Close the top valve when liquid appears.

11.4.4.5 Connect a 100 mL syringe or evacuated Tedlar bag to the top valve. Slowly pressurize the ZHE to force the liquid into the syringe or bag. If collecting the liquid with a syringe, carefully transfer, (after discarding the first 5 mL) with headspace, to 40 mL VOA vials. If using a bag, allow the liquid to flow into the bag until a sufficient quantity has been collected for analysis. Store the extract at 4^0C until analysis.

11.5 Adding extraction fluid to the ZHE device:

11.5.1 Transfer the appropriate amount and type of extraction fluid to a 500 mL beaker.

11.5.2 Using the fluid pump, place the intake line into the beaker of extraction fluid. Turn on the pump, and allow the fluid to enter the

pump. Stop the pump when the fluid appears at the end of the outlet line.

11.5.3 Connect the outlet line to the ZHE top valve. Turn on the pump, and allow the pump to charge the ZHE with the entire contents of the beaker. Stop the pump before any air reaches the ZHE. Close the top and bottom valves, and remove the inlet line. Manually rotate the ZHE device in an end over end fashion 2 or 3 times. *Note: while the ZHE is filling, check for fluid leaking out of the bottom valve. If this happens, stop the pump and use a different ZHE device with a fresh sample.

11.5.4 Attach the air line to the bottom valve. Open the top valve, and while holding a paper towel at the valve, slowly pressurize the ZHE to expel any remaining air. Close the valve at the first sign of fluid at the valve.

11.5.5 With the air line still attached, re-pressurize the ZHE device to 10 psi. Check for leaks. The ZHE is now ready for the 18 +/- 2 hr. rotation. Proceed to sec. 11.6.

11.6 Extraction:

11.6.1 Secure the samples in the rotation apparatus.

11.6.2 Rotation time is 18 +/- 2 hours at 30 +/- 2 rpm. A room temperature of 23 +/- 2^{0}C must be maintained during the extraction period. A min/max thermometer shall be used to monitor the temperature.

11.6.3 Begin rotating. Record the time and room temperature.

11.6.4 Following the rotation period, record the end time of rotation. Proceed to sec 11.7 for filtering the extract.

11.7 Filtration following extraction:

11.7.1 Following the rotation period, check the ZHE pressure gauge to ensure that the device did not leak. If pressure was not maintained, the sample must be re-extracted with a new portion of waste.

11.7.2 If pressure has been maintained, the material in the ZHE device is separated into liquid and solid phases.

11.7.3 For samples with no initial liquid phase:

11.7.3.1 Attach the 100 mL gastight syringe to the ZHE outlet valve. Open the valve and carefully withdraw the extract into the syringe. Do not allow air bubbles into the syringe. Pressurizing the ZHE to 10 psi may help in withdrawing the extract.

11.7.3.2 Discard the first 5 mL out of the syringe, then transfer the remaining extract to 40 mL VOA vials (without headspace). Store at 4^{0}C until analysis.

11.7.4 For samples containing an initial liquid phase:

11.7.4.1 If an initial liquid phase was collected, determine if the ZHE liquid extract will mix with the initial liquid phase:

11.7.4.1.1 Using a transfer pipette and a small beaker, add a few drops of the liquid phase to a small quantity of D.I. water. Observe to see if the two liquids are miscible, or if they separate into layers.

11.7.4.1.2 If the two phases are miscible, combine the filtered extract with the initial liquid phase and analyze as one sample. Attach the Tedlar bag containing the initial liquid phase to the outlet valve of the ZHE device. Gradually apply pressure to the lower valve and slowly filter all of the extract into the Tedlar bag. Store at 4^0C until analysis.

11.7.4.1.3 If the two phases do not mix, the initial liquid phase and the filtered extract will need to be collected and analyzed separately. Collect all of the extract in a separate Tedlar bag.

11.7.4.2 Calculate the results as follows:

$$\text{Final analyte concentration} = \frac{(V1)(C1) + (V2)(C2)}{V1 + V2}$$

V1 = volume of the first phase liquid
C1 = concentration of the first phase in mg/L
V2 = volume of the second phase liquid
C2 = concentration of the second phase in mg/L

12.0 INSTRUMENT MAINTENANCE AND TROUBLESHOOTING

13.0 DATA ACQUISITION, CALCULATION AND REDUCTION

13.1 Refer to section 11 for necessary calculations

14.0 COMPUTER HARDWARE AND SOFTWARE

14.1 Computer with StarLIMS

15.0 DATA MANAGEMENT AND RECORD MANAGEMENT

15.1 Data is recorded in the TCLP/SPLP extraction log.

15.2 Prep data is entered into LIMS, and then the batch sheet is given to the metals prep analyst or the semi-volatile prep analyst.

16.0 QUALITY CONTROL/QUALITY ASSURANCE

16.1 A minimum of one blank, using the same extraction fluid as used for the samples, is required for every extraction batch. Also, a blank must be performed every 20th time an extractions is performed in a particular container to check for contamination.

16.2 A matrix spike is required for each waste type, with a minimum of one matrix spike per extraction batch. Matrix spikes are prepared at the time of digestion/analysis.

17.0 REFERENCES

17.1 *Test Methods for Evaluating Solid Waste*,. EPA-SW-846. September, 1994. Method 1311.

17.2 *Test Methods for Evaluating Solid Waste*,. EPA-SW-846. September, 1994. Method 1312.

CT Laboratories
Baraboo Laboratory Division

Title: Total Organic Carbon in Solids

SOP Number:

Prepared by: _____
Date

Technical Review by: _____
Date

Reviewed by: _____
Quality Assurance *Date*

_____
Laboratory Director *Date*

SOP Manual Control Number:_____

1.0 SCOPE AND APPLICATION

1.1 This SOP is used to determine the concentration of organic carbon in soils, sludge, sediments, wastes, and other solid matrices.

1.2 The detection limit for this method (determined annually) is approximately 100 mg/kg.

2.0 METHOD SUMMARY

2.1 Organic carbon is measured using a carbonaceous analyzer. The instrument converts the organic carbon in a sample to carbon dioxide (CO_2) by catalytic combustion. The CO_2 formed is then directly by an infrared detector. The amount of CO_2 in a sample is directly proportional to the concentration of carbonaceous material in the sample.

2.2 Carbonate and bicarbonate are inorganic forms of carbon and must be separated from the total organic carbon value. The carbonate and bicarbonate are removed by treatment with phosphoric acid prior to combustion.

3.0 DEFINITIONS

3.1 Initial Calibration Verification (ICV): A midrange check standard analyzed after the calibration has been completed, to evaluate calibration curve and or instrument performance. The ICV is from a different source than the calibration standards.

3.2 Continuing Calibration Verification (CCV): A check standard analyzed after every fifteen samples and at the end of the analytical run, to evaluate instrument performance. The CCV can be from the same source as the calibration curve.

3.3 Calibration Blank (ICB or CCB): A blank standard analyzed after every ICV or CCV to evaluate instrument contamination or carry over.

3.4 Matrix Replicate (DUP): A separate aliquot of a given sample that is analyzed in quadruplicate and is taken through all steps of preparation and analysis, exactly like the original sample. The precision of the method is determined by calculating the Relative Standard Deviation (RSD) in percent of the original sample and the 3 matrix replicates.

3.5 Table 1 lists the frequency, accuracy, and precision limits as well notes corrective action and/or qualification requirements.

4.0 HEALTH AND SAFETY

4.1 The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonable achievable.

4.2 Gloves and protective clothing should be worn to protect against unnecessary exposure to hazardous chemicals and contaminants in samples. All activities performed while following this procedure should utilize appropriate laboratory safety systems.

4.3 The furnace is at 900^{0}C. Use caution when inserting and removing boats from the furnace and when doing any maintenance on the instrument.

4.4 Always use clean forceps to handle sample boats to avoid contaminating boats.

4.5 Add the phosphoric acid (dropwise) to the sample slowly. The samples can react with the acid and bubble out of the boat if the acid is not added slowly. The acid is added until the effervescence stops.

5.0 INTERFERENCES

5.1 Carbonate and bicarbonate carbon represents an interference under the terms of this test and must be removed by adding phosphoric acid to the sample prior to analysis.

6.0 APPARATUS AND MATERIALS

6.1 Equipment and Supplies

- 6.1.1 Shimadzu TOC-5000A
- 6.1.2 TOC Catalyst- Shimadzu part number 638-92069-01
- 6.1.3 Cobalt Oxide Catalyst – Shimadzu part number 630-00566-00 or equivalent
- 6.1.4 Mixed catalyst- Mix 2 containers of Cobalt Oxide Catalyst (7.1.3) with 1 container of TOC Catalyst (7.1.2). Make sure this is well homogenized. Use 45g of the mixed catalyst to fill the combustion tube.
- 6.1.5 Quartz Wool- Shimadzu part number 630-00557 or equivalent
- 6.1.6 Metal screen for catalyst- Shimadzu part number 638-58102
- 6.1.7 Ceramic fiber- Shimadzu part number 638-60074 or equivalent
- 6.1.8 Combustion tube- Shimadzu part number 638-41325-01
- 6.1.9 Shimadzu SSM-5000
- 6.1.10 Analytical Balance-Ohaus, Model AP 2500 or equivalent
- 6.1.11 Drying Oven-Lab Line, L-C Oven or equivalent

6.2 Reagents and Materials

- 6.2.1 Milli-Q water
- 6.2.2 25% Phosphoric Acid- Into a 1L volumetric flask, add 250 ml concentrated Phosphoric Acid (Fisher catalog number A242SK-212 or equivalent) and dilute to volume with Milli-Q water. Store on shelf.
- 6.2.3 Dextrose- Fisher (Cat. #D16-500 or equivalent).
- 6.2.4 Potassium Hydrogen Phthalate or an alternate source of Dextrose-E.M. Science (Cat. # DX0145-11).

7.0 INSTRUMENT OR METHOD CALIBRATION

7.1 Turn on oxygen to the instrument. Set pressure to 60psi.

7.2 Turn on the SSM module. Power button is located on the right side of the SSM.

7.3 Turn on instrument. Power button is located on the left side of the instrument.

7.4 Check to verify that the carrier gas flow rate is 0.5 L/min. Gas flow regulator is located on the right front of the SSM. Open door and adjust to 0.5 ml/min if necessary.

7.5 Check to verify that the pressure is 300 kPa. The pressure regulator is located on the right front of the SSM. Open the door and adjust to 300 kPa if necessary.

7.6 Once the screen powers up, press F1 to go to the main menu.

7.7 Using the arrow keys on the front of the instrument, arrow down to 3 (General Conditions) and press enter. This will take you to the general conditions screen.

7.7.1 Under general conditions, make sure the following options are set (for each condition press the enter button after value entry):

7.7.1.1 TC Catalyst should be 1 (normal)
7.7.1.2 Syringe size should be 1 (250ul)
7.7.1.3 Number of Washes should be 4
7.7.1.4 Unit of concentration should be 1 (ppm)
7.7.1.5 Auto ranging and injection volume should be 1 (off)
7.7.1.6 Regeneration of IC solution should be 1 (on)
7.7.1.7 Auto printout should be 1 (data only)
7.7.1.8 Furnace on/off should be 3 (TOC and SSM) if you plan on running waters the same day or 4 (SSM) if you only plan on running soils
7.7.1.9 Buzzer should be 2 (not used)
7.7.1.10 Injection speed should be 3 (0.8mm)
7.7.1.11 ESU option should be 2 (not used)
7.7.1.12 Bubble Removal should be 2 (off)
7.7.1.13 Syringe wash should be 1 (std)
7.7.1.14 Cell length should be 1 (std)
7.7.1.15 TOC or SSM should be 2 (SSM)
7.7.1.16 Printer device should be 2 (Internal-New)
7.7.1.17 Page length should have an *
7.7.1.18 Calibration curve form should be 2 (least squares)
7.7.1.19 POC option is 1 (not used)
7.7.1.20 Press F1 to go to the next screen
7.7.1.21 Set measurement interval for TOC/NPOC to 480s
7.7.1.22 Set measurement interval for IC/POC to 360s
7.7.1.23 Press F2 to return to the main menu

8.8 Press 1 on the main menu then press enter. A calibration curve screen will appear.

8.8.1 Type in the curve file name. The instrument will default to the next available number.

8.8.2 Next to the first standard type in 0 for the mg and 40000 for the concentration

8.8.3 Type in the mg used (should be around 10 mg) for the second standard and 40000 for the concentration.

8.8.4 Type in mg used for the third standard (should be around 25-30mg) and 40000 for the concentration
8.8.5 Type in mg used for the fourth standard (should be around 50-60mg) and 40000 for the concentration
8.8.6 Type in 30 for the range
8.8.7 Press F1 next.
8.8.8 Insert a clean sample boat for your zero point of the curve and close the cover.
8.8.9 Press Start.
8.8.10 Push the sample boat into the furnace when the instrument tells you to.
8.8.11 When instructed, pull the boat to the cooling position, about halfway out of the furnace.
8.8.12 When the instrument says the analysis is complete, pull the boat back completely out of the furnace.
8.8.13 Press F1 next to go to the next standard.
8.8.14 Repeat steps 8.8.9-8.8.14 with the boats containing your dextrose standards.
8.8.16 When analyses are complete, press F1 to return to main menu.

8.9 Choose 4- Calibration curve file list
8.9.1 Highlight the calibration curve number you assigned and press enter to display the curve.
8.9.2 Press F5 to print curve.
8.9.3 Confirm R-value displayed is >0.995. If it is not, fix problem and repeat calibration.
8.9.4 Press F1 to return to the Calibration curve list.
8.9.5 Press F2 to return to the main menu.

8.0 SAMPLE COLLECTION, HANDLING AND PRESERVATION

8.1 Sampling and storage of samples in glass bottles is preferable but plastic is allowable if it does not contribute to TOC content of sample.
8.2 Samples should be stored at 4^0C until analysis.
8.3 Hold time for samples is 14 days.

9.0 SAMPLE PREPARATION AND ANALYSIS

9.1 Place approximately 500 mg of sample in a clean sample boat. Add phosphoric acid (see sec. 5.3) and heat to 75°C for 20 minutes.
9.2 After calibration is completed choose 2 (Sample Measurement) from the main menu screen.
9.2.1 Enter 1 for sample #.
9.2.2 Enter the current curve reference number for Cal Curve #.
9.2.3 Enter 30 for Range.
9.2.4 Enter sample weight (in mg).
9.2.5 Enter 1 for Density
9.2.6 Sample volume should default to number entered for sample weight.

9.2.7 Units should be 1 (mg), may default to setting in General Conditions (*).

9.3 Press next and place sample boat in SSM for analysis.

9.3.1 Press Start and follow instrument instructions.

9.3.2 Push the sample boat into the furnace when the instrument tells you to.

9.3.3 When instructed, pull the boat to the cooling position, about halfway out of the furnace.

9.3.4 When the instrument says the analysis is complete, pull the boat back completely out of the furnace.

9.3.5 Press F1 next to start the 2nd sample (sample #2).

9.3.6 Repeat steps 9.3.1-9.3.5 with the boats containing your remaining samples.

10.4 When analyses are complete, press F1 to return to main menu.

10.4.1 If all analyses are acceptable the instrument can be shut down at this time.

10.0 TROUBLESHOOTING AND MAINTENANCE

10.1 Refer to the Shimadzu TOC 5000-A and TOC SSM-500 instruction manuals for maintenance instructions.

11.0 DATA ACQUISITION, CALCULATIONS AND DATA REDUCTION

Dry weight Concentration (mg/kg) = A/B

Where A = instrument reading for sample (ppm)
B= % solids as a decimal

%RSD = Percent Relative Standard Deviation (%RSD):

$$\%RSD = \frac{SD \times 100}{Mean}$$

12.0 COMPUTER HARDWARE AND SOFTWARE

12.1 Computer with StarLIMS

12.2 Final Dry weight determination is completed in LIMS when the % solids values are entered and validated.

13.0 DATA MANAGEMENT AND RECORD MANAGEMENT

13.1 After data has been entered into LIMS, it is reviewed by the analyst for accuracy and completeness. See checklist for data review guidance (Table 2).

13.2 Once analyst has reviewed and approved the data, the analyst sends the data to "validated" status in LIMS.

13.3 A secondary reviewer, either a supervisor or a qualified peer reviews 10% of the data.

13.4 The original data is filed by test in the file cabinet and periodically the contents of the file cabinet are archived.

14.0 QUALITY CONTROL AND QUALITY ASSURANCE

14.1 The analyst must show an initial demonstration of capability (IDC) to generated acceptable data, by successfully analyzing four replicates of a known standard and having acceptable results for a blind sample.

14.2 ICV (Initial Calibration Verification): This mid range second- source check standard is analyzed after calibration. Control limits are +/- 10% of the true value. If the recovery is outside of this range, terminate the run and correct the problem before proceeding.

14.3 ICB (Initial Calibration Blank): Analyzed immediately after the ICV. The value of the ICB must be below the method LOD. If not, terminate the analysis and correct the problem before proceeding or qualify results less than 20 times the ICB with a 'B' flag.

14.4 CCV (Continuing Calibration Verification: Analyze a CCV following every fifteen samples and at the end of the analysis. Control limits are +/- 10% of the true value. If recovery is outside these limits, recalibrate and reanalyze all samples back to the last acceptable CCV or ICV.

14.5 CCB (Continuing Calibration Blank): Analyzed immediately after the CCV. The value of the CCB must be below the method LOD. If CCB is outside these limits, recalibrate and reanalyze all samples back to the last acceptable CCB or ICB or qualify results less than 20 times the CCB with a 'B' flag.

14.6 Matrix Replicates/Duplicates. Analyze a sample in quadruplicate for every 20 samples. The precision of the method is determined by calculating the Relative Standard Deviation (RSD) of the original sample and the 3 matrix replicates Refer to the control limits for acceptance criteria for precision. *If the RSD is outside of the acceptable range, flag the sample with a* 'Y' qualifier.

14.7 Contract Specific Sample Analysis: For certain samples, limits are specified by the QAPP (Quality Assurance Project Plan) associated with a given project. For these samples follow the limits specified in the QAPP for that project.

15.0 REFERENCES

17.1 *Determination of Total Organic Carbon in Sediment (Lloyd Kahn Method),* USEPA, July 27, 1988.

17.3 Shimadzu Instruction Manual Total Organic Carbon Analyzer Model TOC- 5000A.

17.4 Shimadzu Solid Sample Module SSM-5000 for TOC-5000/5050 Total Organic Carbon Analyzer Instruction Manual. 1993.

Table 1.
SUMMARY OF QUALITY CONTROL REQUIREMENTS

Procedure	Frequency of Procedure	Acceptance Criteria	Corrective Action if Unacceptable
4 point curve (3 standards and a blank)	Initially and as needed	$r \geq 0.995$ for each regression line	Repeat until acceptable
Initial calibration verification (ICV)	Second source standard run after each ICAL and daily prior to sample analysis	%R: 90-110%	Reanalyze ICV standard, if still unacceptable repeat ICAL
Initial calibration blank (ICB)	After each ICV, prior to sample analysis	< RL	Remake and reanalyze CB once, if still unacceptable investigate and correct problem or flag results less than 20 X's the ICB with a 'B' qualifier
Continuing calibration verification (CCV)	Daily, prior to sample analysis, after every 10 analyses, and at end of run	%R: 90-110%	Remake and reanalyze CCV, if still unacceptable investigate and correct problem. Reanalyze all samples after last acceptable CCV.
Continuing calibration blank (CCB)	After each CCV	<RL or <20 times less than the lowest sample result	Remake and reanalyze CB once, if still unacceptable investigate and correct problem then reanalyze all samples after the last acceptable CCB or flag results less than 20 X's the CCB with a 'B' qualifier
Matrix Replicate (DUP)	Every 20 samples per solids matrix	% RSD within in house limits (Default ±30%)	Qualify results with 'Y' flag
Capability demonstration sample (IDC)	Four (4) prepared samples analyzed one time prior to any sample analyses and one blind sample	80-120% Recovery ±20% RSD	Repeat until acceptable

Table 2.

Data Validation Checklist (TOC Solids)

LIMS #:	Method: Total Organic Carbon: Lloyd Khan Method			
Analysis Date	Analyst / Data Interpreter	Independent Reviewer	Date of Review	Approved
				Yes ... No

Instructions: Complete one checklist per *analytical run*. Enter the appropriate response for each question. Each "No" response requires an explanation in the Comments section, and may require the initiation of a Nonconformance Report.

Requirement:	Acceptance Criteria	Analyst Review		Independent Review		Comments: (indicate reference to an attachment if necessary)
		Yes	No	Yes	No	
1. Were the samples acidified prior to analysis?	No effervescence					
2. Was a calibration curve performed using the required number of standards?	3 standard levels and 1 blank					
3. Was the correlation coefficient acceptable?	>= 0.995					
4. Was the ICV standard run at the beginning of the run prior to sample analysis?	---					
5. Was the ICV recovery acceptable?	90 – 110 %					
6. Was the ICB result acceptable?	< Detection limit					
7. Were the CCV's and the CCB's analyzed at the required frequency?	1 per 10 analyses					
8. Were the CCV recoveries acceptable?	90 – 110 %					
9. Were the CCB results acceptable?	< Detection Limit					
10. Were all standards used before the indicated expiration date?	---					
11. Were all positive results that were reported within the calibration's range?	---					
12. Were the appropriate numbers of samples analyzed in quadruplicate?	1 per 20 samples					
13. Was the %RSD on the replicated sample acceptable?	±30 %					

CT Laboratories
Baraboo Laboratory Division

Title: Total Organic Carbon in Water

SOP Number: CC-TOC H2O

Prepared by: _____
Date

Technical Review by: _____
Date

Reviewed by: _____
Quality Assurance *Date*

_____
Laboratory Director *Date*

SOP Manual Control Number:_____

1.0 SCOPE AND APPLICATION

1.1 This SOP is used to determine the concentration of organic carbon in ground water, surface and saline waters, and domestic and industrial wastes.

1.2 The detection limit for this method is approximately 1 mg/L.

2.0 METHOD SUMMARY

2.1 Organic carbon is measured using a carbonaceous analyzer. The instrument converts the organic carbon in a sample to carbon dioxide (CO_2) by catalytic combustion. The CO_2 formed is then directly detected by an infrared detector. The amount of CO_2 in a sample is directly proportional to the concentration of carbonaceous material in the sample.

2.2 Carbonate and bicarbonate are inorganic forms of carbon and must be separated from the total organic carbon value. The carbonate and bicarbonate are removed by converting them to CO_2 with degassing prior to analysis.

3.0 DEFINITIONS

3.1 Initial Calibration Verification (ICV): A midrange check standard analyzed after the calibration has been completed, to evaluate calibration curve and or instrument performance. The ICV is from a different source than the calibration standards.

3.2 Lab Control Sample (LCS): A known concentration obtained from a second source.

3.3 Continuing Calibration Verification (CCV): A check standard analyzed after every ten samples and at the end of the analytical run, to evaluate instrument performance.

3.4 Matrix spike-matrix spike duplicate (MS-MSD): To two of three aliquots of a given sample a known amount of spike solution is added. Matrix spikes and matrix spike duplicates are taken through all steps of analysis, exactly like a sample. The amount of spike recovered helps to assess the effect of the sample matrix on the analysis. The precision of the method is also determined, by calculating the relative percent difference (RPD) of the two spiked aliquots. An MS-MSD should be prepared for every 10 samples in each matrix.

3.5 Calibration Blank (ICB or CCB): A blank standard analyzed after every ICV or CCV to evaluate instrument contamination or carry over.

4.0 HEALTH AND SAFETY

4.1 The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonable achievable.

4.2 Gloves and protective clothing should be worn to protect against unnecessary exposure to hazardous chemicals and contaminants in samples.

All activities performed while following this procedure should utilize appropriate laboratory safety systems.

5.0 CAUTIONS

5.1 Use Milli-Q water for doing all dilutions and reagents.

5.2 Samples must be analyzed in quadruplicate.

6.0 INTERFERENCES

6.1 Carbonate and bicarbonate carbon represent an interference under the terms of this test and must be removed or accounted for in the final calculation.

6.2 This procedure is applicable only to homogeneous samples which can be injected into the apparatus reproducibly by means of a microliter syringe. The opening of the syringe limits the maximum size of particle which may be included in the sample.

6.3 Removal of carbonate and bicarbonate by acidification and purging with nitrogen, or other inert gas, can result in the loss of volatile organic substances.

7.0 APPARATUS AND MATERIALS

7.1 Equipment and Supplies

7.1.1 Shimadzu TOC-5000A

7.1.2 TOC Catalyst- Shimadzu part number 638-92069-01

7.1.3 Combustion tube- Shimadzu part number 638-41323

7.1.4 Shimadzu ASI -5000A

7.1.5 Analytical Balance

7.1.6 Eppendorf micropipettors or equivalent- various sizes

7.1.7 Class A volumetric flasks- various sizes

7.2 Reagents and Materials

7.2.1 Milli-Q water

7.2.2 25% Phosphoric Acid- Into a 1L volumetric flask, add 250 mL concentrated Phosphoric Acid (Fisher catalog number A242SK-212 or equivalent) and dilute to volume with Milli-Q water. Store on shelf.

7.2.3 2N Hydrochloric Acid- Into a 1L volumetric flask, add 167mL concentrated HCl (Fisher catalog number A508SK212 or equivalent) and dilute to volume with Milli-Q water. Store on shelf.

7.2.4 Calibration Curve, Stock Standard: Into a 100 mL volumetric flask, dissolve 0.2128g of Potassium Hydrogen Phthalate (Fisher catalog number AC424061000 or equivalent) and dilute to volume with Milli-Q water. True Value is 1000 mg/L TOC. Store at 4^0C. Stock standard expires after one year.

7.2.5 Calibration Curve : Into 4-25mL volumetric flasks add the following:

mLs Stock (7.2.4)	mLs Milli-Q Water	True Value (mg/L)

0	25	0
0.25	24.75	10
1.25	23.75	50
2.5	22.5	100

Calibration standards should be stored at at 4^0C and standards expire after 28 days.

7.2.6 LCS, Stock Standard: Into a 100 mL volumetric flask, dissolve 0.2128g of Potassium Hydrogen Phthalate (Fisher catalog number P243-100 or equivalent) from a source secondary to the calibration standards and dilute to volume with Milli-Q water. True Value is 1000 mg/L TOC. Store at 4^0C. Stock standard expires after one year.

7.2.7 LCS : Into a 100mL volumetric flask, add 5mL of LCS stock standard (7.2.6) and dilute to volume with Milli-Q water. True Value is 50 mg/L. LCS should be stored at at 4^0C and standards expire after 28 days.

8.0 INSTRUMENT OR METHOD CALIBRATION

8.1 Turn on compressed air to the instrument. Set pressure to 40psi.

8.2 Turn on instrument. Power button is located on the left side of the instrument.

8.3 Check to verify that the carrier gas flow rate is 150 mL/min. Gas flow regulator is located on the upper left portion of the front of the instrument. Open door and adjust to 150 mL/min if necessary.

8.4 Check the water levels in the IC pot and the humidifier. Add water to the humidifier if necessary. See manual for how to adjust water level in IC pot.

8.5 Once the screen powers up, press F5 to initialize the autosampler. If this option is not available, go to 8.6.

8.6 Press F1 to go to the main menu.

8.7 Using the arrow keys on the front of the instrument, arrow down to 3 (General Conditions) and press enter. This will take you to the general conditions screen.

8.7.1 Under general conditions, make sure the following options are set:

8.7.1.1 TC Catalyst should be 1 (normal)
8.7.1.2 Syringe size should be 1 (250ul)
8.7.1.3 Number of Washes should be 4
8.7.1.4 Unit of concentration should be 3 (mg/L)
8.7.1.5 Auto ranging and injection volume should be 1 (on)
8.7.1.6 Autoregeneration of IC solution should be 1 (on)
8.7.1.7 Auto printout should be 1 (data only)
8.7.1.8 Furnace on/off should be 1 (on)
8.7.1.9 Buzzer should be 2 (not used)
8.7.1.10 Injection speed should be 3 (0.8mm)
8.7.1.11 ESU option should be 2 (not used)
8.7.1.12 Bubble Removal should be 1 (on)

8.7.1.13 Syringe wash should be 1 (std)
8.7.1.14 Cell length should be 1 (std)
8.7.1.15 TOC or SSM should be 1 (TOC)
8.7.1.16 Printer device should be 2 (Internal-New)
8.7.1.17 Page length should have an *
8.7.1.18 Calibration curve form should be 2 (least squares)
8.7.1.19 POC option is 1 (not used)
8.7.1.20 Press F1 to go to the next screen
8.7.1.21 Set measurement interval for TOC/NPOC to 480s
8.7.1.22 Set measurement interval for IC/POC to 360s
8.7.1.23 Press F2 to return to the main menu

8.8 Press 9 and enter to go to the autosampler screen.

8.8.1 On the screen next to the number 1, highlight the TC. Choose 4 (NPOC) and press enter

8.8.2 Arrow over to the IS column, press 1 and enter.

8.8.3 Arrow over to the FS column, press 1 or your last vial number if you are analyzing samples and enter.

8.8.4 Place an autosampler vial with Milli-Q water in autosampler position 1 or place your samples in the autosampler in the appropriate order. Cover vials with parafilm.This will be analyzed after the calibration curve is run.

8.8.5 Arrow over to the C1 column, press 1 and enter. A calibration curve screen will appear.

8.8.5.1 Choose 1 for TC
8.8.5.2 Type in 0 for the first standard concentration and S1 for the tube number
8.8.5.3 Type in 10 for the second standard concentration and S2 for the tube number
8.8.5.4 Type in 50 for the third standard concentration and S3 for the tube number
8.8.5.5 Type in 100 for the fourth standard concentration and S4 for the tube number
8.8.5.6 Set the range to x5
8.8.5.7 Set the injection volume to 50uL
8.8.5.8 Set the number of injections to 4
8.8.5.9 Set the maximum number of injections to 6.
8.8.5.10 Accept the default numbers for the SD and CV.
8.8.5.11 Set the sparge time to 10 min.
8.8.5.12 Set shift to origin to 2 (off)
8.8.5.13 Set acid addition to 1 (on)
8.8.5.14 Press F2 to return to the autosampler screen.

8.8.6 Arrow over to the RG column. Enter 5 under that column if necessary.

8.8.7 Arrow over to the VOL column. Enter 50 under that column.

8.8.8 Arrow over to the NO column. Enter 4 under that column.

8.8.9 Arrow over to the W colume. Enter 4 under that column.

8.8.10 Arrow over to the MAX column. Enter 5 under that column.
8.8.11 Arrow over to the SP column. Enter 10 under that column.
8.8.12 Press F1 to go to the next screen. The ASI Condition screen will appear.
8.8.12.1 Set the rinse to 1 (rinse)
8.8.12.2 Set the No of needle washes to 2
8.8.12.3 Set the Flow line washes to 2
8.8.12.4 Set Calibrate before to 1 (All Sample Groups)
8.8.12.5 Set Print Information to 3 (Cal and Data)
8.8.12.6 Set Auto addition of acid to 1 (on)
8.8.12.7 Set Acid volume to 50
8.8.12.8 Set Rinse after addition to 1 (rinse)
8.8.12.9 Set Key Lock to 2 (unlock)
8.8.12.10 Set Finish or Running to 3 (no change)
8.8.13 Press F1 to go to the next screen.

8.9 Fill autosampler vials with standards and place 2N HCl (7.2.3) in large vial in position S8. Cover vials with parafilm. Place standards in appropriate vial positions.

8.10 Make sure rinse water vessel is full with Milli-Q water.

8.11 Press Start.

8.12 When analysis is complete, press F2 to return to main menu.

8.13 Choose 4- Calibration curve file list

8.13.1 Highlight the calibration curve and press enter to display the curve.
8.13.1.1 Press F to print curve.
8.13.1.2 Confirm R value displayed is >0.995. If it is not, fix problem and repeat calibration.
8.13.1.3 Press F1 to return to the Calibration curve list.

9.0 SAMPLE COLLECTION, HANDLING AND PRESERVATION

9.1 Sampling and storage of samples in glass bottles is preferable but plastic is allowable if it does not contribute to TOC content of sample.

9.2 The sample should be acidified (pH < 2) with HCl or H_2SO_4.

9.3 Samples should be stored at 4^0C until analysis.

9.4 Hold time for preserved samples is 28 days.

10.0 SAMPLE PREPARATION AND ANALYSIS

10.1 Turn on compressed air to the instrument. Set pressure to 40psi.

10.2 Turn on instrument. Power button is located on the left side of the instrument.

10.3 Check to verify that the carrier gas flow rate is 150 mL/min. Gas flow regulator is located on the upper left portion of the front of the instrument. Open door and adjust to 150 mL/min if necessary.

10.4 Check the water levels in the IC pot and the humidifier. Add water to the humidifier if necessary. See manual for how to adjust water level in IC pot.

10.5 Once the screen powers up, press F5 to initialize the autosampler. If this *option is not available, go to next step.*

10.6 Press F1 to go to the main menu.

10.7 Using the arrow keys on the front of the instrument, arrow down to 3 (General Conditions) and press enter. This will take you to the general conditions screen.

10.7.1 Under general conditions, make sure the following options are set:

10.7.1.1 TC Catalyst should be 1 (normal)
10.7.1.2 Syringe size should be 1 (250ul)
10.7.1.3 Number of Washes should be 4
10.7.1.4 Unit of concentration should be 3 (mg/L)
10.7.1.5 Auto ranging and injection volume should be 1 (on)
10.7.1.6 Autoregeneration of IC solution should be 1 (on)
10.7.1.7 Auto printout should be 1 (data only)
10.7.1.8 Furnace on/off should be 1 (on)
10.7.1.9 Buzzer should be 2 (not used)
10.7.1.10 Injection speed should be 3 (0.8mm)
10.7.1.11 ESU option should be 2 (not used)
10.7.1.12 Bubble Removal should be 1 (on)
10.7.1.13 Syringe wash should be 1 (std)
10.7.1.14 Cell length should be 1 (std)
10.7.1.15 TOC or SSM should be 1 (TOC)
10.7.1.16 Printer device should be 2 (Internal-New)
10.7.1.17 Page length should have an *
10.7.1.18 Calibration curve form should be 2 (least squares)
10.7.1.19 POC option is 1 (not used)
10.7.1.20 Press F1 to go to the next screen
10.7.1.21 Set measurement interval for TOC/NPOC to 300s
10.7.1.22 Set measurement interval for IC/POC to 300s
10.7.1.23 Press F2 to return to the main menu

10.8 Press 9 to go to the autosampler screen.

10.8.1 On the screen next to the number 1, highlight the TC. Choose 4 (NPOC) and press enter

10.8.2 Arrow over to the IS column, type in the position of the first tube for your run and press enter.

10.8.3 Arrow over to the FS column, type in the position of the last tube of the run and press enter.

10.8.4 Fill vials with appropriate samples and cover with a small piece of parafilm. Place filled vials in autosampler. For MS and MSD, use 0.25 mL of stock standard (7.2.4) and 4.75mL of sample. True value is 50 mg/L.

10.8.5 Arrow over to the F1 column, press 1 (or the appropriate cal curve number) and enter.

10.8.6 Arrow over to the RG column. Enter 5 under that column if necessary.

10.8.7 Arrow over to the VOL column. Enter 50 under that column.

10.8.8 Arrow over to the NO column. Enter 4 under that column.
10.8.9 Arrow over to the W column. Enter 4 under that column.
10.8.10 Arrow over to the MAX column. Enter 5 under that column.
10.8.11 Arrow over to the SP column. Enter 10 under that column.
10.8.12 Press F1 to go to the next screen. The ASI Condition screen will appear.
- **10.8.12.1** Set the rinse to 1 (rinse)
- **10.8.12.2** Set the No of needle washes to 2
- **10.8.12.3** Set the Flow line washes to 2
- **10.8.12.4** Set Calibrate before to 1 (All Sample Groups)
- **10.8.12.5** Set Print Information to 3 (Cal and Data)
- **10.8.12.6** Set Auto addition of acid to 1 (on)
- **10.8.12.7** Set Acid volume to 50
- **10.8.12.8** Set Rinse after addition to 1 (rinse)
- **10.8.12.9** Set Key Lock to 2 (unlock)
- **10.8.12.10** Set Finish or Running to 3 (no change)

10.8.13 Press F1 to go to the next screen.

10.9 Place 2N HCL in vial position S8. Cover vial with parafilm.
10.10 Make sure rinse water vessel is full with Milli-Q water.
10.11 Press Start.
10.12 When analysis is complete, press F2 to return to main menu.
10.13 Shut instrument down by turning off power button and compressed air supply.

11.0 TROUBLESHOOTING AND MAINTENANCE

11.1 Refer to the Shimadzu TOC 5000-A instruction manual for maintenance instructions.

12.0 DATA ACQUISITION, CALCULATIONS AND DATA REDUCTION

Liquid Concentration (mg/L) = A x B

where A = instrument reading for sample (mg/L)
B= analyst dilution factor, if necessary (ex. For a 1 to 10 dilution, B = 10)

$$\textit{Spike Recovery (\%)} = \frac{\text{(Spiked sample concentration} - \text{Sample concentration)} \times 100}{\text{(Spike amount)}}$$

$$\%RPD = \frac{(MS - MSD) \times 100}{(MS + MSD)/2}$$

where MS = Matrix spike concentration
MSD = Matrix spike duplicate concentration

13.0 COMPUTER HARDWARE AND SOFTWARE

13.1 Computer with StarLIMS

14.0 DATA MANAGEMENT AND RECORD MANAGEMENT

14.1 After data has been entered into LIMS, it is reviewed and validated by the analyst for accuracy and completeness. See checklist for data review guidance.

14.2 Once analyst has reviewed and validated the data, it is given to a peer or supervisor for review on 10% or more of the data.

14.3 The original data is filed by test in the file cabinet and periodically the contents of the file cabinet are archived.

15.0 QUALITY CONTROL AND QUALITY ASSURANCE

15.1 The analyst must show an initial demonstration of capability (IDC) to generated acceptable data, by successfully analyzing four replicates of a known standard and having acceptable results for a blind sample.

15.2 ICV/LCS (initial calibration verification/Laboratory control standard): This mid range second- source check standard is analyzed after calibration.. ICV/LCS is at the mid-point of the calibration curve. Control limits are +/- 10% of the true value. If the recovery is outside of this range, terminate the run and correct the problem before proceeding.

15.3 ICB (initial calibration blank): Analyzed immediately after the ICV. The value of the ICB must be below the method LOD. If not, terminate the analysis and correct the problem before proceeding or qualify results less than 20 times the ICB with a 'B' flag.

15.4 CCV/LCS (continuing calibration verification/laboratory control standard): Analyze a CCV/LCS following every ten samples and at the end of the analysis. CCV/LCS is at the mid-point of the calibration curve. Control limits are +/- 10% of the true value. If recovery is outside these limits, recalibrate and reanalyze all samples back to the last acceptable CCV or ICV.

15.5 CCB (continuing calibration blank): Analyzed immediately after the CCV. The value of the CCB must be below the method LOD. If not, terminate the analysis and correct the problem before proceeding. If CCB is outside these limits, recalibrate and reanalyze all samples back to the last acceptable CCB or ICB or qualify results less than 20 times the CCB with a 'B' flag.

15.6 MS-MSD (matrix spike-matrix spike duplicate):A MS-MSD is required every analytical run at a frequency of 10% (1 for every 10 samples) per matrix type. Refer to the control limits for acceptance criteria for both accuracy and precision. Unless otherwise specified in a contract if recovery is outside of acceptable range, flag the sample with an 'M' qualifer. If the RPD is outside of the acceptable range, flag the sample with a 'Y' qualifier.

15.7 Contract Specific Sample Analysis: For certain samples, limits are specified by the QAPP (Quality Assurance Project Plan) associated with a given project. For these samples follow the limits specified in the QAPP for that project.

16.0 REFERENCES

17.1 *Methods for the Determination of Inorganic Substances in Environmental Samples*, 1974, Method 415.1.

17.2 *Standard Methods for the Examination of Water and Wastewater*, 18th Edition, 1992, APHA-AWWA-WEF, Method 5310B.

17.3 *SW 846*, 3rd Edition, Update III, 1997 Method 9060.

17.4 Shimadzu Instruction Manual Total Oranic Carbon Analyzer Model TOC-5000A.

17.5 Shimadzu Autosampler ASI-5000A for Total Organic Carbon Analyzer TOC 5000(A)/5050(A) Instruction Manual., 1994.

SUMMARY OF QUALITY CONTROL REQUIREMENTS

Procedure	Frequency of Procedure	Acceptance Criteria	Corrective Action if Unacceptable
Six-point initial calibration plus blank (ICAL)- two different 4 point curves	*Initially and as needed*	$r \geq 0.995$ for each regression line	Repeat until acceptable
Initial calibration verification (ICV)	Second source standard run after each ICAL and daily prior to sample analysis	%R: 90-110% for all analytes	Remake and reanalyze ICV standard, if still unacceptable repeat ICAL
Laboratory Control Standard (LCS)	Standard run after every 20 samples	Within in house limits Default: 80-120%	Remake and reanalyze CCV, if still unacceptable investigate and correct problem. Reanalyze all samples after last acceptable LCS.
Initial calibration blank (ICB)	After each ICV, prior to sample analysis	< RL	Remake and reanalyze CB once, if still unacceptable investigate and correct problem or flag results less than 20 X's the ICB with a 'B' qualifier
Continuing calibration verification (CCV)	Daily, prior to sample analysis, after every 10 samples, and at end of run	%R: 90-110% for all analytes	Remake and reanalyze CCV, if still unacceptable investigate and correct problem. Reanalyze all samples after last acceptable CCV.
Continuing calibration blank (CCB)	After each CCV	<RL or <20 times less than the lowest sample result	Remake and reanalyze CB once, if still unacceptable investigate and correct problem then reanalyze all samples after the last acceptable CCB or flag results *less than 20 X's the CCB with a* 'B' qualifier
Method Blank (MB)	After each LCS	<RL or <20 times less than the lowest sample result	Remake and reanalyze MB once, if still unacceptable investigate and correct problem then reanalyze all samples after the last acceptable MB or flag results less than 20 X's the MB with a 'B' qualifier
Capability demonstration sample (IDC)	Four (4) prepared samples analyzed one time prior to any sample analyses and one blind sample	80-120% Recovery $\leq$20% RPD	Repeat until acceptable
Matrix Spike Duplicate (MSD)	One (1) per 10 samples per matrix	In-house derived limits Default = 80-120% 20% RPD	Investigate problem, if LCS in control qualify results. Qualify results with a 'M' or 'Y' flag if necessary
Matrix spike sample (MS)	One (1) per 10 samples per matrix	In-house derived limits Default = 80-120%	Investigate problem, if LCS in control qualify results. Qualify results with a 'M' flag if necessary

Data Validation Checklist

LIMS #:	Method: Total Organic Carbon Method 415.1/9060			
Analysis Date	**Analyst / Data Interpreter**	**Independent Reviewer**	**Date of Review**	**Approved**
				Yes ... No

Instructions: Complete one checklist per *analytical run*. Enter the appropriate response for each question. Each "No" response requires an explanation in the Comments section, and m require the initiation of a Nonconformance Report.

Requirement:	Acceptance Criteria	Analyst Review		Independent Review		Comments: (indicate reference to an attachment if necessary)
		Yes	No	Yes	No	
1. Were the samples preserved prior to analysis?	pH <2					
2. Was the calibration curve performed using the required number of standards?	3 standards and a blank					
3. Is the standard prep log number noted on the analytical report?	---					
3. Was the correlation coefficient acceptable?	>= 0.995					
4. Was LCS standard run at the beginning of the run prior to sample analysis?	---					
5. Was the LCS recovery acceptable?	90 – 110 %					
6. Was the ICB result acceptable?	< LOD					
7. Were the CCV/LCS's and the CCB's analyzed at the required frequency?	1per 10 samples					
8. Were the CCV/LCS recoveries acceptable?	90 – 110 %					
9. Were the CCB results acceptable?	< LOD					
10. Was the LCS used before the indicated expiration date?	---					
11. Were all positive results that were reported within the calibration curve?	---					
12. Were matrix spike and matrix spike duplicate samples run at the required frequency?	1 per 10 of the same matrix					
13. Was the matrix spike and matrix spike duplicate recovery acceptable?	Within in house QC limits					
14. Was the RPD of the matrix spike and matrix spike duplicate acceptable?	Within in house QC limits					
15. Were all samples and QC analyzed in quadruplicate?	---					
16. Are all samples on the job lists accounted for?	---					

CT Laboratories .
Baraboo Laboratory Division

Title: ***Analysis of Volatile Organic Compounds by GC/MS***

SOP Number: **5280B**

Prepared by: _____
Date

Technical Review by: _____
Date

Reviewed by: _____
Quality Assurance ***Date***

_____
Laboratory Director ***Date***

SOP Manual Control Number:_____

1.0 Method

1.1 This method is designed to follow procedures and QC requirements found in EPA SW-846 methods 5030, 5035, 8000 and 8260 in order to determine quantities of volatile organic compounds found in a variety of different sample matrices.

2.0 Applicable Matrix or Matrices

2.1 Volatile organic compounds are quantitated from a variety of matrices. This method is applicable to nearly all types of samples regardless of water content, including ground water, surface water, wastewater, soils and sediments, as well as other matrices noted in SW-846 method 8260B.

3.0 Detection Limits

1.1 Method detection limits (MDLs) are determined annually and results vary from compound to compound. Water MDLs typically fall in the range of 0.10 to 10 ug/L (5.0 mL purge) or 0.02 to 2.0 ug/L (25 mL purge). Soil MDLs are usually found to be between 0.0001 to 0.005 mg/kg (low-level soils) or 0.005 to 0.50 mg/kg (methanol preserved). Procedures for conducting MDL studies can be found in CT Laboratories Initial Method Performance and Reporting SOP.

4.0 Scope and Application

4.1 This method is used to quantify Volatile Organic Compounds (VOCs) with boiling points below 200° Celsius (°C) in water and soils. See Table 1 for typical target analyte list (TAL).

4.2 Examples of other compounds which have been analyzed by this method include: Iodomethane, 2,3-Dichloro-1-propene, 1-Chlorohexane, Acrolein, Acrylonitrile, and 2-Chloroethylvinyl ether. SW-846, method 8260B notes a number of other compounds amenable to this test.

5.0 Method Summary

5.1 A Purge & Trap system (including autosampler), a Gas Chromatograph (GC), and a Mass Spectrometer (MS) are utilized for the detection of VOCs. The autosampler introduces the sample to the purge and trap concentrator. The concentrator then removes the volatile constituents by purging the sample with an inert gas (Helium). The constituents are then collected onto an adsorption trap. The trap is then rapidly heated and the volatilized compounds are introduced to the GC. The GC is temperature programmed to facilitate separation of the individual organic compounds. Finally the separated compounds enter the MS (which is interfaced with the GC) for quantitative and qualitative analyses.

5.2 Utilizing computer software, identification of target analytes is accomplished by comparing the mass spectra of the sample constituent with that of commercially purchased standards. Quantitation is achieved by comparing the response of a quantitation ion relative to an

internal standard using a five point (minimum) calibration curve.

6.0 Definitions

6.1 4-Bromofluorobenzene (BFB), is used to verify that the GC/MS is properly tuned and ready for calibration and sample analyses. BFB is directly injected at 25-50 ng and precedes all other analyses. A twelve hour analysis time window is used before another BFB injection is required.

6.2 An initial calibration verification standard (ICV) is analyzed before the analysis of samples as a check on the calibration curve. The ICV should be of a second source, meaning a separate vendor and/or lot # should be used to prepare this standard. A second source is needed to validate the integrity and concentration of the standards used for calibration.

6.3 An initial calibration blank (ICB) is also analyzed before samples to confirm that the deionized water (DI H2O) used for standards, blanks, and dilutions is free from contamination. An ICB for soil samples also includes organic free sand and/or methanol used for standard and QC preparation, as well as sample dilutions and volume adjustments; the control sand and methanol must also be documented as free from contamination.

6.4 A calibration check verification standard (CCV) is analyzed at the beginning of each sequence (following the BFB injection) shift and every 12 hour shift thereafter. A CCV is made up from the same standards used for calibration and is used to ensure that the calibration and retention times are stable.

6.5 An analytical batch is defined as a group of samples (not to exceed 20 samples) analyzed per sequential run. Depending on client or program requirements, an analytical batch may or may not include matrix spikes as part of the 20 samples.

6.6 Internal standards (ISTD) are added to each sample, blank, spike, and check standard. The ISTDs used are Fluorobenzene, Chlorobenzene-d_5, and 1,4-Dichlorobenzene-d_4. The ISTD is used for internal calibration as a reference peak and to check purging efficiency.

6.7 Surrogate standards (SSTD) are also added to each sample, blank, spike, and check standard. The SSTDs used are Toluene-d_4, 4-Bromofluorobenzene, 1,2-Dichloroethane-d_4, and Dibromofluoromethane. The SSTD is used as matrix interference and as a method control check.

6.8 A method blank (MBW = water, MBS = soil) is analyzed with every batch of samples to ensure the instrument is free from contamination. Method blanks are also used to demonstrate that the DI H2O, organic free sand, and methanol used in sample preparation is also free from contamination.

6.9 A continuing calibration blank (CCB) is analyzed every 12 hour shift after the MB has been analyzed and before sample reanalyses to ensure the system is still free from contamination.

6.10 Instrument blanks (IB) are analyzed whenever instrument contamination is a suspected possibility. The purpose of an IB is to prevent carry over from a standard, spike, or contaminated sample into another sample or blank. The acceptance criteria for an IB is the same as for a MB or CCB (for example: if an IB contains detections above acceptance criteria and a MB and/or sample following the IB exhibit the same contamination above

acceptance criteria, then the instrument should be considered contaminated). The samples and/or MBs should be reanalyzed after the instrument is confirmed free from contamination.

6.11 A matrix spike and matrix spike duplicate (MS/MSD) are analyzed with every batch of samples as a matrix interference and control check.

6.12 A laboratory control spike (LCS) is analyzed with every sample batch as a system control and method control check.

7.0 Interferences

7.1 Volatile materials in the laboratory and impurities in the purging gas and sorbent trap can cause significant amounts of background contamination. Improper tubing such as certain plastics and rubber should not be used. The analysis of IBs and MBs should indicate as to whether or not this type of contamination is present. Since subtraction on background contamination is not allowed, care should be taken to eliminate this type of contamination.

7.2 Carry over contamination is a problem when a highly contaminated sample is followed by a clean sample. Rinsing the autosampler and concentrator and adequate baking of the trap can greatly reduce contamination from carry over.

7.3 Some samples contain a lot of water soluble materials, suspended solids, compounds with high boiling points, or target analytes with very high concentrations which may contaminate some or all of the analytical system. Removing components of the system for cleaning or cleaning of the entire system may be required to eliminate the interferences.

7.4 Compounds with poor purging efficiencies may remain in the purge system, particularly with 25 ml purges. Ensuring adequate rinsing and increased line temperatures will help reduce this problem.

7.5 All chromatography gas/purge lines should be stainless steel or copper to prevent permeation from possible background contaminants (i.e. Methylene chloride). Background levels of Methylene chloride are possible so care should be taken to reduce this possibility. Analyst clothing previously exposed to Methylene chloride should not be worn and isolating the instruments from possible airborne contamination is essential in reducing Methylene chloride background contamination.

7.6 A trip blank normally accompanies sample in shipment and storage as a check on possible contamination from volatile organics by diffusion through the septum seal in sample vials/containers.

7.7 Mass spectrometer sensitivity, column degradation, and contamination can also contribute to background interferences. Proper maintenance procedures on instrumentation is essential to continually producing quality data. Maintenance manuals are provided with each piece of equipment and are essential for proper instrument care. The manuals used are as follows: Autosampler (Archon Purge and Trap Autosampler System Operator' Manual, Varian Model 5100;4552), Concentrator (LCS 2000 User Manual Tekmar and Purge & Trap Concentrator, Tekmar 3000), Gas Chromatograph--HP 5890 Series II Operating Manual, and Mass Spectrometer--HP 5972A MSD Hardware Manual). The presence of semi-volatile hydrocarbons should also be taken into consideration, so appropriate post analysis bake out

times should be incorporated.

8.0 SAFETY

8.1 Gloves and protective clothing should be worn to protect against unnecessary exposure to hazardous chemicals and contaminants in samples. All activities performed while following this procedure should utilize appropriate laboratory safety systems.

8.2 The toxicity and carcinogenicity of the chemicals used in this method are not precisely defined. Each chemical and sample should be treated as a potential health hazard, so care should be taken to prevent undue or extensive exposure.

9.0 Equipment and Supplies

9.1 40 mL screw cap "VOA" vials-borosilicate glass with a Teflon faced silicone septum (QEC or equivalent).

9.2 2 oz., 4 oz., or 60- mL Teflon lined screw top sample jars (QEC or equivalent).

9.3 5 g or 25 g samplers for low level soils (Encore)

9.4 Top loading balance sensitive to 0.01 g (Mettler-Toledo, BD202).

9.5 pH paper to confirm water sample preservation(Color pHast, EM Reagents)

9.6 Stainless steel spatulas

9.7 10, 25, 50, 100, 500, and 1000 uL gas tight syringes for sample dilutions and standard preparation (Hamilton or equivalent).

9.8 5.0, 10.0, 25.0, 50.0 mL syringes with luer-lok tips for methanol preserved soil sample preparation and sample dilutions (Hamilton/SGE or equivalents).

9.9 10, 50 100, 200, 1000, and 2000 mL Volumetric flask for sample dilutions and standard preparation (Class A, Pyrex/Kimble or equivalents).

9.10 Auto pipetter – 2.5 to 25.0 ml – for dispensing methanol (Dispensette).

9.11 Sonicator used for methanol-preserved soil sample extraction (Fisher, FS-28).

9.12 Auto sampler used for sample introduction to the Purge and Trap (EST, Archon).

9.13 Purge and Trap concentrator (Tekmar, 2000/3000)

9.13.1 The glass purging tubes are of 5 mL or 25mL size. The all-glass purging device should be designed to accept 5 or 25 mL samples with a water column at least 5 cm deep. The smaller (5 mL) purging device is recommended if the GC/MS system has adequate sensitivity to obtain the method detection limits required for a specific project or program.

9.13.2 The trap currently used is Supelco Type K. As required by SW-846 methods, the trap must be at least 25 cm long and have an inside diameter of at least 0.105 inches. Starting from the inlet, the trap should contain 1.0 cm of methyl silicone coated packing and the following amounts of adsorbents: 33% of 2,6-diphenylene oxide polymer, 33% of silica gel, and 33% of coconut charcoal.

9.14 Gas Chromatograph/Mass Spectrometer/Data System (GC/MS)

9.14.1 Hewlett Packard Series II Gas Chromatograph

9.14.1.1 Column, Supelco (SPB-624), 30 Meter x 0.25 mm ID, 1.4 um film thickness

9.14.2 Hewlett Packard 5972 Mass Spectrometer

9.14.3 Hewlett Packard Chemstation Data Management System (version G1701AA v. A.03.02) with Enviroquant and Prolab data processing software.

10.0 Reagents and Materials

10.1 Purge and trap grade methanol: (Fisher, Purge & Trap grade or equivalent), stored in laboratory warehouse.

10.2 Reagent grade water, organic free (Milipore, 18 megaohm quality).

10.3 Certified Calibration Standards: (VOC Mix--2000 ug/mL, Accustandard--#M-502-10X; Additions--1000/10,000 ug/mL, Protocol--#XCTIVOA-Rev or equivalents), stored in VOC Standards Freezer in Volatiles laboratory at ≤ -10 °C.

10.3.1 A 100 ug/mL[1] Continuing Calibration Verification (CCV) working standard is prepared by adding 150 uL of the VOC mix and 300 uL of the Additions mix to 2550 uL of methanol in a 3 mL Mininert vial.

10.4 Certified Calibration Check Standards: (VOC Mix--2000 ug/mL, Ultra Scientific--#DWM-588; Additions--1000/10,000 ug/mL, Protocol--#XCTIVOA-Rev or equivalents), stored in VOC Standards Freezer in Volatiles laboratory at ≤ -10 °C.

10.4.1 A 100 ug/mL[1] Initial Calibration Verification (ICV) working standard is prepared by adding 150 uL of the VOC mix and 300 uL of the Additions mix to 2550 uL of methanol in a 3 mL Mininert vial.

10.5 Certified Internal Standards: (ISTD Mix--2500 ug/mL, Restek--#30241 or equivalent), stored in VOC Standards Freezer in Volatiles laboratory at ≤ -10 °C.

10.5.1 An 80 ug/mL ISTD working standard is prepared by adding 320 of the ISTD mix to a 10 ml volumetric flask and brought to volume with methanol.

10.6 Certified Surrogate Standards: (SSTD Mix, Restek--#30240; 1,2-DCA-d_4 Ultra Scientific--

#STS210, or equivalents[2]), stored in VOC Standards Freezer in Volatiles laboratory at ≤ -10 °C.

10.6.1 A 100 ug/mL SSTD working standard is prepared by adding 120 uL of the SSTD mix and 150 uL of 1,2-DCA-d_4 to 2730 mL of methanol in a 3 mL mininert vial.

10.6.2 An 80 ug/mL ISTD/SSTD working standard is prepared by adding 320 uL of the ISTD Mix (sec. 10.5), 320 uL of the SSTD Mix (sec. 10.6), and 400 uL of 1,2-DCA-d_4 (sec. 10.6) to a 10 mL volumetric flask and brought to volume with methanol.

10.7 Certified Tuning Standard: 4- bromofluorobenzene {BFB} (Ultra Scientific—2000 ug/mL, #STS-110N or equivalent), stored in VOC Standards Freezer in Volatiles laboratory at ≤ -10 °C.

10.7.1 A 50 ug/mL working standard is prepared by adding 75 uL of the Certified standard to 2925 mL of methanol in a 3 mL mininert vial.

10.8 Sodium bisulfate (JT Baker--#3534-01 or equivalent), stored in cabinet in Volatiles laboratory.

10.9 All certified stock standards use the expiration date provided by the manufacturer/supplier. The subsequent working standards expire one week after preparation. When standards used for calibration are prepared from freshly open stock standard vials, the expiration of working standards used from that point on can be extended. They can be extended if the integrity of those standards can be confirmed and documented. For example, if an ISTD/SSTD or a CCV/ICV standard continues to produce acceptable results after one week from preparation, it can be assumed still valid. The integrity of the stock standards (once opened) must also be confirmed and documented; otherwise it also expires in one week.

[1] Due to lower response or purging efficiencies, a number of compounds are purchased and prepared at concentrations greater than 100 ug/mL . Those compounds and concentrations are noted on the calibration curve.
[2] This compound is needed for Method 524.2 and is not used for this method.

11.0 Sample Preservation and Storage

11.1 Water samples are stored at 4° C (+/- 2°). The sample storage area must be free of organic solvent vapors and direct or intense light. Samples are stored in the Volatiles lab in a double door refrigerator (separate from analytical standards).

11.1.1 Analyze properly preserved samples (pH <2) samples within 14 days of collection. Samples not analyzed within this period must be discarded and recollected. If samples are not preserved then they must be analyzed within 7 days.

11.1.2 Samples analyzed for Acrolein and Acrylonitrile should be preserved at a pH of 4-5 and analyzed within 14 days (3 days if unpreserved).

11.1.3 If reactive compounds such as 2-Chloroethyl vinyl ether are target compounds than

no preservatives are added and the sample should be analyzed as soon as possible.

11.1.4 Samples containing residual chlorine require alternative preservation (ascorbic acid or sodium thiosulfate) to reduce the chlorine. These sample should be analyzed within 7 days unless they were reduced to a pH of <2 (using HCL or $NaHSO_4$), then 14 day is the hold time.

11.2 Soil samples are stored at 4° C (+/- 2°). The sample storage area must be free of organic solvent vapors and direct or intense light Samples are stored in a double door refrigerator located in the laboratory warehouse.

11.2.1 Samples received for low level analysis in Encore samplers must be preserved within 48 hours from time of collection. To preserve a sample, weigh it into a 40 mL VOA vial, record the weight, then add 0.2 grams of sodium bisulfate per 1.0 gram of sample. Finally add 5.0 mL of DI H2O. Analyze all samples within 14 days of collection. Samples not analyzed within this period must be discarded and recollected.

11.2.2 Samples received in filled 2 oz. or 4 oz. jars can be weighed and prepared for low level analysis as described in section 11.2.1. or they can be weighed into a VOA vial and preserved at a 1:1 ratio with methanol for medium/high- level analysis. Analyze all samples within 14 days of collection. Samples not analyzed within this period must be discarded and recollected.

11.2.3 Samples collected and preserved with methanol in the field in preweighed 60-ml jars are weighed as is. The preweighed jar weight, as well as the methanol weight (19.8 grams for 25 mL of methanol) is subtracted from the total weight of the jar to determine sample weight. If the weight to volume ratio is more than 1:1 then methanol is added using the auto pippetter to correct the ratio to 1:1. Unless instructed by the client to do otherwise, the maximum acceptable weight for volume correction is 35 grams. If samples are being analyzed for the Wisconsin LUST program then the hold time is 21 days from collection. Otherwise hold time should be considered 14 days.

11.2.4 All soil sample are weighed on the top loading balance which is connected to a computer so that all weights can be automatically entered onto an Excel spread sheet. The Excel spreadsheet is set up to record the weights as well as calculate the methanol to weight adjustments. The spreadsheets are saved so the data can be transferred electronically to the LIMS system.

11.3 Most samples received are accompanied with a Trip Blank (TB). In most cases the TBs are prepared by the lab and are sent along with the vials used for sample collection. The intent of the trip blank is to accompany the sample vials through all collection, preservation, shipping, and storage procedures. The infusion of outside contamination in the trip blank is not common, but can be an indicator of incorrect preparation/sampling procedures or inadequate sample storage.

12.0 Quality Control

12.1 This SOP is designed to follow a variety of different projects and programs requirements. Table 2. is designed to illustrate the control steps and provisions required to adequately

producing acceptable data.

13.0 Calibration and Standardization

13.1 To facilitate appropriate separation and provide adequate sensitivity, the entire operating system must be correctly set up and maintained before calibration and analyses can occur. Proper settings and programming of the GC/MS volatile system greatly increase the likelihood that calibrations will be acceptable. Generating and reproducing results will also be affected favorably in a well-maintained system.

13.1.1 The following tables provide instrument settings for the daily use of the Archon/Tekmar Purge and Trap Systems. Any modifications are noted in the specific instrument's maintenance log:

PARAMETER SETTINGS FOR TEKMAR 2000/3000	
Standby	30° C
Preheat	40° C (low level soils only)
Purge	11.00 minutes
Dry Purge	2.0 minutes
Desorb Preheat	245° C
Desorb	2.00 minutes at 250° C
Bake	12.00 minutes at 260 ° C
Auto Drain	Off
Valve	150 ° C
Line	150 ° C
Mount	40 ° C
Gas	Helium
Flow	35 ml/minute

13.1.2 An example of the GC temperature program for the SPB-624 column used for the analysis of samples is as follows:

Start temp	End temp	Rate	Time

°C	°C	°C/minute	minutes
32	32	0.0	3.0
32	155	5.0	0.00
155	200	15.0	0.00

13.1.3 The injector is a split/splitless injector operated in split mode ranging from 1:10 to 1:60. The injector temperature is 200 °C.

13.1.4 The MS detector parameters are subject to change to achieve optimum chromatography. See instrument maintenance logbook for recent changes regarding source maintenance, as well as filament and multiplier replacements. Current tune values and EM voltage settings are documented and can be found in the appropriate instrument's tuning logbook.

13.1.5 4-Bromofluorobenzene (BFB) Standard - A standard solution containing 50 ug/mL is used for the daily tune check. The BFB is directly injected onto the column in 25 to 50 ng injections (0.5 to 1.0 uL).

13.1.5.1 The GC/MS system tune must be verified at the beginning of any calibration or a sequence run and verified every 12 hours thereafter. The tuning compound is BFB which is injected directly onto the GC column The software is set up to check the tune by using the mean of three scans across the apex. Background subtraction is performed using a single scan no more than 20 scans prior to the elution of BFB. Manual scans can be checked by taking an average of scans across the BFB peak. The tuning acceptance criteria are listed below (m/z range 35-260):

Mass (m/z)	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	<2% of mass 174.
174	>50% of mass 95.
175	5 to 9% of mass 174.
176	>95% but <101% of mass 174.
177	5 to 9% of mass 176.

13.1.6 The preparation of working standards is routinely performed each week unless integrity is shown to be intact. All standards are assigned a unique identification number and preparations are documented in a Standards Logbook.

13.1.6.1 Calibration Standards - Calibration standards are prepared at a minimum of five concentration levels (in most instances, seven levels are currently used) and are prepared from the working standard dilutions of stock standards. One of the concentration levels should be at a concentration near, but above, the detection limit and at or below the reporting limit. The remaining concentration levels should correspond to the expected range of concentrations found in real samples and should contain each analyte for detection by this method. For low-level soil calibrations, sodium bisulfate is added at a 0.2 g/1.0 g sample to the water to match sample matrix /acidity if the samples were collected and preserved with sodium bisulfate. Med/high-level soil calibrations have MeOH added at a 0.1 ml /5.0 ml H2O to match sample matrix/preservation. All final concentrations are brought to volume with DI water. The following tables outline the preparation of a seven level calibration curve for water and soil samples (all calibration standards are transferred into 40 mL VOA vials for placement on the autosampler):

1) Waters Curve (5.0 mL Purge)

Concentration (ug/L)	Amount added of the 100 ug/mL CCV and SSTD (in uL)	Final Volume (mL) (Volumetric flask)
1.0	1.0	100
2.0	2.0	100
5.0	5.0	100
10.0	10.0	100
20.0	20.0	100
30.0	30.0	100
40.0	40.0	100

2)Waters Curve (25.0 mL Purge)

Concentration (ug/L)	Amount added of the 100 ug/mL CCV and SSTD (in uL)	Final Volume (mL) (Volumetric flask)
0.2	1.0	500
0.4	2.0	500
1.0	1.0	100
2.0	2.0	100
4.0	4.0	100
6.0	6.0	100
8.0	8.0	100

3) Low Level Soils Curve

Concentration (mg/kg)	Amount added of the 100 ug/mL CCV and SSTD (in uL)	Grams of sodium bisulfate added (if needed)	Final Volume (mL) (Volumetric flask)
0.001	1.0	1.0	100
0.002	2.0	1.0	100
0.005	5.0	1.0	100
0.010	10.0	1.0	100
0.020	20.0	1.0	100
0.030	30.0	1.0	100
0.040	40.0	1.0	100

4) Medium/High Soils Curve

Concentration (mg/kg)	Amount added of the 100 ug/mL CCV and SSTD (in uL)	uL of MeOH added	Final Volume (mL) (Volumetric flask)
0.050	1.0	998	100
0.100	2.0	996	100
0.250	5.0	990	100
0.500	10.0	980	100
1.000	20.0	960	100
1.500	30.0	940	100
2.000	40.0	920	100

13.1.6.2 Internal Standards - The internal standards used are Chlorobenzene-d_5, 1,4-Difluorobenzene, 1,2-Dichloroethane-d_4 and Fluorobenzene. Other compounds may be used as internal standards as long as they have retention times similar to the compounds being detected by GC/MS. The Archon autosampler automatically adds approximately 1 uL of the 80 ug/mL-working standard (exact amounts are determined and recorded in the maintenance logbook) to each sample/standard purged.

13.1.6.3 Surrogate Standards - The surrogate standards used are Toluene-d_8, 1,2-Dichloroethane-d_4, 4-Bromofluorobenzene, and Dibromofluoromethane. Other compounds may be used as surrogates, depending upon the analysis requirements. The 100 ug/mL-working standard is used for calibration and is added at the same concentrations as the target compounds (see above).

13.1.6.4 *ISTD/SSTD* Combined Standard - A combination of internal standard and surrogate standard at 80 ug/mL is automatically added by the autosampler to all samples, blanks, CCVs and spikes used for any given sequence after calibration. Limits are generated internally or project/program limits are used.

13.1.6.5 Calibration curves are prepared fresh from newly made working standards to ensure accurate concentrations are maintained.

13.1.6.6 Secondary dilution standards (when necessary) - secondary dilution standards containing the compounds of interest (usually at 10.0/100 ug/mL) for low level and MDL analyses should be prepared in methanol and must be stored with minimal headspace and should be checked frequently for degradation. They should be stored for one week only.

13.1.6.7 Preparation of standards is documented in the Volatile standards logbook. Each standard solution is documented with the standard name, concentration, preparation date, expiration date and a unique number given to that standard for future traceability.

13.2 The curve is generated using the relative response factor (RRF or RF). The data system tabulates the area response of the characteristic ions against the concentration of each compound and each internal standard. Calculate response factors for each compound relative to one of the internal standards. The internal standard selected for the calculation for the RF for a compound should be the internal standard that has a retention time closest to the compound being measured. The RF is calculated by the data system as follows:

$$RF = \frac{A_S \times C_{IS}}{A_{IS} \times C_S}$$

where:

A_s = Area of the characteristic ion for the compound being measured in the calibration standard.

A_{IS} = Area of the characteristic ion for the specific internal standard.

C_{IS} = Concentration of the specific internal standard.

C_s = Concentration of the compound being measured in the calibration standard.

13.2.1 The average response factor (ARF) for all calibration levels is used when determining sample concentration and is calculated (along with the standard deviation) to evaluate the linearity of the curve (SW-846 Method 8000. Sec. 7.5.1).

13.3 When ARFs are not acceptable, results are sometimes calculated using linear (1st order) regression curves and/or quadratic (2nd order) curves. Internal standard quantitation is also used when generating linear and non-linear calibrations. All equations and acceptance criteria follow the examples in SW-846, Method 8000 (sec. 7.5.2 and sec. 7.5.3).

13.4 A system performance check should be made before the calibration curve is used. Five compounds (the System Performance Check Compounds, or SPCCs) are used for system performance check. These compounds are used to check compound instability and check for degradation caused by contaminated lines or active sites in the system. Examples of these occurrences are as follows (Method 8260B sec. 7.3.5):

	Minimum RF	Comment
Chloromethane	>0.10	This compound is the most likely compound to be lost if the purge flow is too fast.
Bromoform	>0.10	This compound is one of the compounds most likely to purge poorly if the purge flow is too slow. Cold spots and/or active sites in the transfer lines may adversely affect response. Response of the quantitation ion (m/z 173) is directly affected by the tuning of BFB at ions m/z 174/176. Increasing the m/z 174/176 ratio relative to m/z 95 may improve bromoform response.
Chlorobenzene	>0.30	
1,1,2,2 Tetrachloroethane	>0.30	The response of this compound is degraded by contaminated transfer lines in purge and trap systems and/or active sites in trapping materials.
1,1 Dichloroethane	>0.10	The response of this compound is also degraded by contaminated transfer lines in purge and trap systems and/or active sites in trapping materials.

13.5 The RSD for the RFs for each individual calibration check compound (CCC) must be less than 30%. For the calibration to be valid, this criterion must be met for each CCC compound even if it is not a target compound for the project of concern or for the samples being analyzed. The CCC compounds are Vinyl chloride, 1,1-Dichloroethene, Chloroform, 1,2-Dichloropropane, Toluene, and Ethylbenzene. If the RSD of any CCC is greater than 30%, then corrective action must be taken and the system re-calibrated.

13.5.1 If the RSD of the RFs is less than 15%, then the RF is assumed to be constant over the calibration range, and the average response factor may be used for quantitation. If the RSD of any analyte or surrogate mean RF exceeds 15% but is less that 30% than linear regression or second order curves may be used for quantitation. If the RSD of the RFs is greater than 30%, either analyze additional aliquots of appropriate calibration solutions to obtain an acceptable RSD of RFs over the entire concentration range, or take action to improve GC/MS performance. Surrogate compounds are present at the same concentration on every sample, CCV, LCS, MS, MSD and all types of blanks.

13.6 All calibrations are confirmed by the analysis of a "second source" Initial Calibration Verification (ICV) standard before daily checks and analyses are performed. The criteria for the SPCCs is the same as stated above (sec.13.3), but the CCCs must be ≤ 20 % RSD. If these criteria are not met and a reanalysis of the ICV confirms the nonconformities, then corrective actions must be taken and the instrument recalibrated. The RSD limit for all other target compounds is also 20%. Any outliers suggest a problem and poor performers should be addressed. The concentrations of the ICV should be near the mid point of the curve (10/100 ug/L for water-5 mL purge, 2.0/20 ug/L for water-25 mL purge, 0.010/0.10 mg/kg for low level soils, and 0.50/5.0 mg/kg for MeOH preserved soils). The preparation of ICVs are as follows:

Water (5 mL purge)--Spike 50 mL of DI water(volumetric flask) with 5.0 uL of the 100/1000 ug/mL ICV standard, invert three times and transfer to a VOA vial for analysis.

Water (25 mL purge)-- Spike 50 mL of DI water(volumetric flask) with 1.0 uL of the 100/1000 ug/mL ICV standard, invert three times and transfer into a VOA vial for analysis.

Low-level Soils--Spike 50 mL of DI water(volumetric flask) with 5.0 uL of the 100/1000 ug/mL ICV standard, invert three times and transfer 5.0 ml into a VOA vial (containing and a stir bar) for analysis. As an alternative, prepare a 10.0/100 ug/mL working standard, then add 5.0 uL of this to 5.0 mL of DI water and transfer into a VOA (containing and a stir bar) for analysis.

Med/high-level soils-- Spike 49 mL of DI water (volumetric flask) with 1.0 mL of MeOH and 5.0 uL of the 100/1000 ug/mL ICV standard, invert three times and transfer into a VOA vial for analysis.

13.6 Finally an Initial Calibration Blank (ICB) is analyzed to confirm that the instrument is free from contamination. Any detects in the ICB should be less than the method detection limit and/or less than ½ the program/project limits. Any detects above MDL or program limits must be addressed before sample analyses begins. To prepare an ICB fill a 40 mL VOA vial preserved with 5% HCL with DI water.

13.7 Demonstration and documentation of an acceptable initial calibration is required before any samples are analyzed. Refer to EPA SW-846, Method 8000B, Section 7, for a detailed discussion of calibration procedures.

14.0 Procedure

14.1 Prior to sample anlaysis a GC/MS tune and calibration check must made. Verify the MS tune and initial calibration at the beginning of each 12-hour work shift during which analyses are performed.

14.1.1 Introduce into the GC (by direct injection) 25 to 50 ng of BFB and acquire a mass spectrum that includes data for m/z 35-260. If the spectrum does not meet all criteria, the MS must be retuned and adjusted to meet all criteria before proceeding with the continuing calibration check.

14.1.2 The calibration curve integrity for each analyte must be confirmed with the use of a CCV standard once every 12 hours of analysis time. The calibration check verification standard should be at concentrations near the midpoint of the calibration curves (10/100 ug/L for water-5 mL purge, 2.0/20 ug/L for water-25 mL purge, 0.010/0.10 mg/kg for low level soils, and 0.50/5.0 mg/kg for MeOH preserved soils). The CCV is placed on the autosampler in the same manner as the samples (sec. 14.2.3). The SPCC and CCC criteria must be met before the calibration is considered still valid. Preparation of CCVs is as follows:

Water (5 mL purge)--Spike 50 mL of DI water(volumetric flask) with 5.0 uL of the 100/1000 ug/mL CCV standard, invert three times and transfer to a VOA vial for analysis.

Water (25 mL purge)-- Spike 50 mL of DI water(volumetric flask) with 1.0 uL of the 100/1000 ug/mL CCV standard, invert three times and transfer into a VOA vial for analysis.

Low-level Soils--Spike 50 mL of DI water(volumetric flask) with 5.0 uL of the 100/1000 ug/mL CCV standard, invert three times and transfer 5.0 ml into a VOA vial (containing and a stir bar) for analysis. As an alternative, prepare a 10.0/100 ug/mL working standard, then add 5.0 uL of this to 5.0 mL of DI water and transfer into a VOA vial (containing and a stir bar) for analysis.

Med/high-level soils-- Spike 49 mL of DI water (volumetric flask) with 1.0 mL of MeOH and 5.0 uL of the 100/1000 ug/mL CCV standard, invert three times and transfer into a VOA vial for analysis.

14.1.2.1 System Performance Check Compounds (SPCCs) - A system performance check must be made each 12 hour shift. If the SPCC criteria are met, a comparison of response factors is made for all compounds. This is the same check that is applied during the initial calibration (sec. 13.3). 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.

14.1.2.2 Calibration Check Compounds (CCCs) - After the system performance check is met, CCCs are used to check the validity of the initial calibration. If the percent difference for any compound is greater than 20%, the laboratory should consider this a warning limit (SMFs need to be checked, as well as program/project criteria met before analysis continues). If the percent deviation for each CCC is less than 20%, the initial calibration is assumed to be valid. If the criterion is not met (> 20% D.) for any one CCC, corrective action must be taken. Problems similar to those listed under SPCCs could affect this criterion. If no source of the problem can be determined after corrective action has been taken, a new calibration must be generated. This criterion must be met before quantitative sample analysis begins. If the CCCs are not required analytes by the permit, then all required analytes must meet the 20% difference criteria.

14.1.2.3 The internal standard responses and retention times in the CCV standard must be evaluated immediately after or during data acquisition. If the retention time for any internal standard changes by more than 30 seconds from the last check calibration (12 hours), the chromatographic system

must be inspected for malfunctions and corrections must be made, as required. If the EICP area for any of the internal standards changes by a more than a factor of two (-50% to +100%), when compared to the average from the calibration, then the mass spectrometer must be inspected for malfunctions and corrections must be made. Reanalysis of CCVs and associated samples while the system was malfunctioning is necessary.

14.2 Sample Introduction and Purging

14.2.1 BFB tuning criteria and daily GC/MS calibration criteria must be met before analyzing samples. Currently 18-19 purged samples including QC can be analyzed within 12 hours of the BFB injection. The Archon autosampler can be programmed to accommodate the number of samples needed per analytical shift.

14.2.2 After the continuing calibration is verified, the system must be proven to be free of contamination by analyzing a Method Blank (MB). The MB should not contain detects above the detection limits for any given compound. Some programs allow detects up to but not exceeding one half the Method Reporting Limits (MRLs). If the method blank contains detects above the detection limits or MRLs, then corrective actions must be performed to ensure the system is free from contamination; all affected samples should also be reanalyzed. The MBs are also placed on the autosampler in the same manner as the samples (sec. 14.2.3).

14.2.3 Analysis of samples begins by allowing the sample to come to ambient temperature prior to analysis. The VOA vials containing the water samples are placed on the autosampler where a 5.0 to 25.0 mL aliquot is withdrawn from the vial and added into the appropriate purge vessel. The same procedure is followed for methanol preserved soils (1.0 mL of soil extract/50.0 mL DI H2O is prepared and added into a 40 ml VOA vial prior to adding the samples to the autosampler). Low level soils are prepared by adding the VOA vial containing a magnetic stir bar and ≈5 g sample/5.0 mL DI H2O to the autosampler (2-5 grams of sample required for low-level analysis). The autosampler then adds an additional 5.0-mL of H2O containing the ISTD/SSTD mixture. The sample is heated to 40°C and purged in the VOA vial while being stirred, and the volatiles are collected onto the trap.

14.2.3.1 The ISTD/SSTD is added automatically by the Archon autosampler as the sample is transferred from the 40 mL sample vial to the sparge tube; the exception is for low level soils as noted above (sec.14.2.3).

14.2.3.2 The sample is purged for 11 minutes at ambient temperature (40°C for low-level soils) using helium with a flow of 35 mL/min at a 20 psi purge pressure.

14.2.3.3 During the 11-minute purge time, the purgeable volatile organics are adsorbed onto the Supelco Carbosieve K trap.

14.2.3.4 During desorbtion the trapped materials are rapidly heated while back-flushing the trap with helium at 35 mL/min. for 2 minutes at 250°C and introduced in the GC/MS. After the valve to the GC is closed the trap is

then baked and back flushed with helium for ≈12 minutes at 260°C.

14.2.3.5 The GC is temperature programmed at 32°C for 3 minutes, then ramped to 155°C at 5°C/min, and finally ramped to 200°C at 15°C/min. The column flow is set at 1 mL/min. constant flow using helium as the carrier gas.

14.2.3.6 The transfer line to the MS is maintained at 250°C and the ion source is maintained at ≈260°C while under constant vacuum. The GC injector is set at 200°C.

14.2.4 For each sample batch a matrix spike (MS), matrix spike duplicate (MSD), and laboratory control spike (LCS) is prepared and analyzed. The concentrations for water spikes are 10.0/100 ug/L for 5 mL purge and 1.0/10.0 ug/L for 25 mL purge. The spiked concentrations for soil samples are ≈0.010/0.10 mg/kg for low level and ≈0.50/5.0 mg/kg for MeOH preserved depending on sample weights and percent solids. One exception is for the analysis of field collected MeOH preserved soils. These samples are analyzed with a laboratory control spike and a laboratory control spike duplicate (LCSD). All spikes are transferred into 40 mL VOA vials and added to the autosampler. The spike concentrations may vary depending on program/project specific criteria, but the preparation volumes are constant and only the spiking amount changes. 14.2.4.1 lists examples of spike preparation based on the concentrations above.

14.2.4.1 The preparation of the matrix spikes is performed as follows:

Water (5 mL purge)--Spike 40 mL of sample with 4.0 uL of the 100/1000 ug/mL ICV standard, invert three times and transfer to a VOA vial for analysis. When adequate sample amounts are not provided, one 40 mL aliquot of sample is spiked and split into two separate VOA vials containing 15 mL glass inserts.

Water (25 mL purge)-- Spike 50 mL of sample with 1.0 uL of the 100/1000 ug/mL ICV standard, invert three times and transfer into a VOA vial for analysis.

Low-level Soils--Spike 50 mL of DI water(volumetric flask) with 5.0 uL of the 100/100 ug/mL ICV standard, invert three times and transfer 5.0 mL into a VOA vial containing ≈5 g of sample and a stir bar for analysis. As an alternative, prepare a 10.0/100 ug/mL working standard, then add 5.0 uL of this to 5.0 mL of DI water and transfer into a VOA vial containing ≈5 g of sample and a stir bar for analysis.

Med/high-level soils--Spike ≈10 g of sample contained in a VOA vial with 50 uL of the 100/1000 ug/mL ICV standard. Add 9.95 mL of methanol to the spiked sample and sonicate for 20 minutes. Add 1.0 mL of methanol extract to 49.0 mL DI water in a 50 mL syringe and then transfer into a VOA vial for analysis.

14.2.4.2 The preparation of laboratory control spikes is performed as follows:

Water (5 mL purge)--Spike 50 mL of DI water(volumetric flask) with 5.0 uL of the 100/1000 ug/mL ICV standard, invert three times and transfer to a VOA vial for analysis.

Water (25 mL purge)-- Spike 50 mL of DI water (volumetric flask) with 1.0 uL of the 100/1000 ug/mL ICV standard, invert three times and transfer into a VOA vial for analysis.

Low-level Soils--Spike 50 mL of DI water(volumetric flask) with 5.0 uL of the 100/1000 ug/mL ICV standard, invert three times and transfer 5.0 ml into a VOA vial containing 5 g of control and a stir bar for analysis. As an alternative, prepare a 10.0/100 ug/mL working standard, then add 5.0 uL of this to 5.0 mL of DI water and transfer into a VOA vial containing 5 g of control sand and a stir bar for analysis.

Med/high-level soils--Spike 10 g of control sand contained in a VOA vial with 50 uL of the 100/1000 ug/mL ICV standard. Add 9.95 mL of methanol to the spiked sand and sonicate for 20 minutes. Add 1.0 mL of methanol extract to 49.0 mL DI water in a 50 mL syringe and then transfer into a VOA vial for analysis.

14.2.5 The data is collected by the Chemstation software using the response factors (or linear/second order regressions when necessary), and results are calculated using the internal standard method of quantitation. Response factors for each detected compound are compared with that obtained in calibration, and based on those comparisons, results are generated. Software manuals define the procedures for creating and understanding a specific method (Understanding Your Chemstation, Hewlett Packard, G2070-90100, October, 1994, Environmental Forms Software, Hewlett Packard, G1032-90021, November, 1992, and Productivity Enhancement Software for HP Chemstation, Prolab Resources Inc., XMS01A-002, Rev. G, 2001).

15.0 Calculations

15.1 Using the following equations, the Chemstation software (used with the GC/MS system) calculates the concentration of target analytes:

Waters

$$\text{Initial concentration } (\mu g/L) = \frac{A_X \times I_{IS}}{A_{IS} \times RF}$$

Where:

A_X = Area of characteristic ion for compound being measured in the sample.
I_{IS} = Amount of internal standard injected (ug/L). Typical concentrations used are 20.0 ug/L for 5.0 mL purge, and 4.0 ug/L for 25.0 ml purge
A_{IS}= Area of characteristic ion for the internal standard.
RF = Response factor for compound being measured.

Soils

$$A_X \times I_{IS}$$

$$\text{Initial concentration (mg/kg)} = \frac{\quad}{A_{IS} \times RF}$$

Where:

A_X = Area of characteristic ion for compound being measured in the sample.
I_{IS} = Amount of internal standard injected (mg/kg). Typical concentrations used are 0.020 mg/kg for low-level soils and 1.0 mg/kg for med/high-level soils.
A_{IS}= Area of characteristic ion for the internal standard.
RF = Response factor for compound being measured.

15.2 The initial concentration results are then transferred to the laboratory's LIMS system where the final concentrations are calculated.

15.2.1 The final concentration for water samples is calculated as follows:

Final concentration (ug/L) = Initial concentration x DF

Where:
DF = Dilution Factor

15.2.2 The final concentrations for low-level and med/high-level soils are calculated by the following equation:

$$\text{Final concentration (mg/Kg)} = \frac{\text{Initial concentration x Sample volume x DF}}{\text{Sample weight x Percent solids}}$$

Where:

Sample volume = 5.0 mL for low-level soils, or volume of MeOH used for med/high-level soils preservation.

Sample weight = grams of sample place in VOA vial for low-level soils, or total grams of sample preserved for med/high-level soils.

Percent solids = fraction equivalent (e.g. 97.1 % = 0.971)

DF = Dilution factor (applicable for MeOH preserved soils).

15.3 The spike percent recoveries (%R) and relative percent differences (RPD) are calculated in LIMS as follows:

Water--concentration (conc.) of spike added =

$$\text{ug/L} = \frac{\text{mL of spike added x conc. spiking std..}}{\text{mL of sample (or DI H2O) spiked}} \times 100$$

Soil--concentration of spike added =

$$\text{mg/kg} = \frac{\text{mL of spike added x conc.spiking std..}}{\text{grams of sample (or control sand) spiked.}}$$

$$\text{MS/MSD \%R} = \frac{(\text{conc. spike} + \text{conc. sample} - \text{conc. sample})}{\text{conc. spike added}} \times 100$$

$$\text{MS/MSD RPD} = \frac{[\text{conc. MS} - \text{conc. MSD}]}{(\{\text{conc. MS} + \text{conc. MSD}\}/2)} \times 100$$

$$\text{LCS \% R} = \frac{\text{conc. spike}}{\text{conc. spike added}} \times 100$$

Notes:
--Concentrations (conc.) of samples, MS/MSD, and LCS spikes are obtained directly from calibration curve.
--Soil spike concentrations and recoveries are calculated on a dry weight basis.
--[ ] Signifies absolute values.

16.0 Method Performance

16.1 Certified standard solutions, properly maintained instrumentation, and analyst experience and expertise are critical elements in producing accurate results. Standards and instrument performance are continually checked by analyzing external performance test samples provided by the appropriately accredited agencies. Internal blind spikes are also utilized to check analyst performance.

16.2 Initial demonstration of capability (IDC) is another technique used to ensure acceptable method performance. An analyst must demonstrate initial precision and accuracy through the analysis of 4-5 laboratory control spikes for each matrix and sample type. After analysis, the analyst calculates the average recovery (x) in µg/L and the relative standard deviation (RSD) of the recoveries for each analyte. In the absence of specific criteria found in the SW-846 methods or project specific limits, the default criteria of 70-130% recovery and 20 % RSD are used until internal limits are generated (Method 8000B, sec. 8.4.9).

16.2.1 Examples of the preparation of IDCs are as follows:

Water (5 mL purge)--Spike 50 mL of DI water(volumetric flask) with 5.0 uL of the 100/1000 ug/mL ICV standard, invert three times and transfer to a VOA vial for analysis.

Water (25 mL purge)-- Spike 50 mL of DI water(volumetric flask) with 1.0 uL of the 100/1000 ug/mL ICV standard, invert three times and transfer into a VOA vial for analysis.

Low-level Soils--Spike 50 mL of DI water(volumetric flask) with 5.0 uL of the 100/1000 ug/mL ICV standard, invert three times and transfer 5.0 ml into a VOA vial containing 5 g of control and a stir bar for analysis. As an alternative, prepare a 10.0/100 ug/mL working standard, then add 5.0 uL of this to 5.0 mL of DI water and transfer into a VOA vial containing 5 g of control sand and a stir bar for analysis.

Med/high-level soils--Spike 10 g of control sand contained in a VOA vial with 50.0 uL of the 100/1000 ug/mL ICV standard. Add 9.95 mL of methanol to the spiked sand and sonicate for 20 minutes. Add 1.0 mL of methanol extract to 49.0 mL DI water in a 50 mL syringe and then transfer into a VOA vial for analysis.

16.3 Many program (i.e. USACOE) require the analysis of method reporting limit (MRL) standards and method detection limit (MDL) check samples as another means of checking method performance. The MRLs are analyzed at the beginning and end of each 12 hour shift and are typically prepared at concentrations equal to the lowest standard on the calibration curve. Recovery limits are program specific but are usually set at 70-130%. The MDL check sample is usually spiked at approximately 2x the method detection limit. The MDL check sample is analyzed quarterly (as a minimum) to confirm instrument sensitivity (e.g. to verify that the method detection limits are still achievable). The MDL check samples are taken through all preparation and extraction steps used for actual samples (e.g. spiking/preserving control sand for soil samples). In most instances, a method detection limit check sample is analyzed at the end of each sequence requiring an MRL standard. The recovery criteria for MDL check samples is the ability to detect all compounds. If any given compound is not detected, the MDL check is spiked at a higher level and analyzed again. Detection limits for those compounds not detected on the initial MDL check analysis need to be raised to match the MDL check analysis at which they were detected.

16.4 Creating and monitoring control charts is also important for maintaining and improving method performance. Currently all SSTD, MS, MSD, and LCS recoveries are monitored with the use of the LIMS system. The data collected is used to recognize trends in recovery performance, as well as for generating new in-house QC limits. Default accuracy limits of 70-130 % recovery and a precision limit 20 % RSD are used until enough data points are generated to provide usable internal limits. Other programs such as the Shell Document for the USACOE use default LCS limits of 80-120 % recovery for water samples and 75-125 % for soil samples (SMF 60-140%). The Shell also uses default MS/MSD recovery limits for water and soils of 70-130% (SMF 60-140 %), and default precision limits of 30% for water samples (SMF 40%, no RPD limits for soils). The WI UST program uses default accuracy and precision limits for surrogates and spikes of 80-120/20 %. Client and/or Project specific limits are also used frequently in sample analyses. The Quality Control Requirements chart (Table 2.) also lists recovery limits specific to the method/project/program.

17.0 Data Assessment & Acceptance Criteria for QC Measures

17.1 If the initial analysis of a sample or a dilution of the sample has a concentration of an

particular analyte that exceeds the calibration range, the sample must be reanalyzed at a dilution. Secondary ion quantitation is allowed only when there are sample interferences with the primary ion. When a sample is analyzed that has saturated ions from a compound, this analysis must be followed by a blank water analysis. If the blank analysis is not free of interferences, the system must be decontaminated. Sample analyses can not resume until a blank can be analyzed that is free of interferences.

17.2 After the analyses of water samples, the pH should be taken to verify proper field preservation. pH strips are used to verify the pH which is then documented in the bench sheet logbook.

17.3 Qualitative Analysis (Method 8260B, sec. 7.6)

17.3.1 The qualitative identification of compounds determined by this method is based on retention time and on comparison of the sample mass spectrum (ion scans) after background correction with characteristic ions in a reference mass spectrum. The reference mass spectrum must be generated (by the laboratory) using the conditions of this method. The mass spectral library is updated with each new calibration and is continually updated with the mass spectra from CCVs.

17.3.2 The characteristic ions from the reference mass spectrum are defined to be the three ions of greatest relative intensity or any ions over 30% relative intensity if fewer than three such ions occur in the reference spectrum. Table 3 lists compounds along with the Primary Ion (Quantitation ion) used for calculating results, and the Secondary Ions (Qualitative ions) used for qualitatively matching sample spectrums with reference spectrums for positive identifications. Compounds should be identified as present when the criteria below are met.

17.3.2.1 The intensities of the characteristic ions of a compound maximize in the same scan or within one scan of each other. Selection of a peak by a data system target compound search routine where the search is based on the presence of a target chromatographic peak containing ions specific for the target compound at a compound-specific retention time will be accepted as meeting this criterion.

17.3.2.2 The relative retention time (RRT) of the sample component is within +/- 0.06 RRT units of the RRT of the standard component.

17.3.2.3 The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum. (Example: For an ion with an abundance of 50% in the reference spectrum, the corresponding abundance in a sample spectrum can range between 20% and 80%).

17.3.2.4 Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

17.3.2.5 Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When gas chromatographic peaks obviously represent more than one sample component (i.e., a broadened peak with shoulder(s) or a valley between two or more maxima), appropriate selection of analyte spectra and background spectra are important. Examination of extracted ion current profiles of appropriate ions can aid in the selection of spectra and in qualitative identification of compounds. When analytes coelute (i.e., only one chromatographic peak is apparent), the identification criteria can be met, but each analyte spectrum will contain extraneous ions contributed by the coeluting compound.

17.3.3 For samples containing compounds that are not a part of the normal target list, a library search may be required for the purpose of tentative identification. Tentative identified compounds (TICs) are needed only when requested or required by a particular project or program. Data system library search routines should not use normalization routines that would misrepresent the library of unknown spectra when compared to each other. Use the following a guidance for reporting TICs (Method 8260B, sec. 7.6.6):

1) Relative intensities of major ions in the reference spectrum (ions greater than 10% of the most abundant ion) should be present in the sample spectrum

2) The relative intensities of the major ions agree within ± 20%.

3) Molecular ions present in the reference spectrum should be present in the sample spectrum.

4) Ions present in the sample spectrum but not in the reference spectrum should be checked for possible background contamination. They should also be reviewed for possible coelution with another compound.

5) Ions present in the reference spectrum but not in the sample spectrum should be check against the possibility of subtraction from the sample spectrum due to background contamination or co-eluting peaks. Some data reduction programs can create these discrepancies.

17.4 Quantitative Analysis (Method 8260B, sec. 7.7)

17.4.1 When a compound has been identified, the quantitation of that compound will be based on the integrated abundance from the EICP of the primary characteristic ion. Quantitation is performed by the data system using the internal standard technique. The internal standard used shall be the one nearest the retention time of that of a given analyte. Quantitation is performed using the RF averages from the initial (i.e. 7 pt) calibration, and not the continuing calibration check (ICV).

17.5 When the analysis of an analytical batch or sequence has been completed, the data is processed and prepared for reporting. Once the reference spectrums are compared and

the sample spectrums and identifications have been made, the sample data can be reported. Assessments of all spiked and calibration control samples and standards should also be finalized before reporting the data.

17.5.1 When the analyst has finished processing the analytical batch, the results are electronically transferred to the LIMS system where weight to volume corrections, dilution factors and percent solids adjustments are made. Once the final results have been verified, a checklist (Table 4.) is filled out and signed confirming that all the data has been thorough scrutinized. At this point the data is turned over to another qualified analyst for final validation. The second analyst confirms the results and electronically marks them validated and signs his or her portion of the checklist (an example of the checklist is included in this SOP). Finally, the validated results are made available to the client services personnel in order for the data to be given to the client or appropriate agencies.

17.5.2 A paper hard copy of the data is then filed or archived. The package includes the checklist, the sequence run log, a copy of the bench sheet, the LIMS run log, verification of tuning and system performance data, and verification of calibration data. For each sample, the chromatogram, quantitation and library spectra (ion scans) for all positive target compounds are also included. All the data is to be initialed and dated by the analyst. Each data file header should contain the sample ID # and the date and time acquired.

18.0 Corrective Measures for Out-of-Control Data

18.1 When data is out of control, a number of corrective actions may need implementing. If the nonconformities involve failing QC within the analytical sequence batch, then reanalysis of samples may eliminate any out of control data. If the out of control data is the result of instrument malfunctions, then maintenance or repair of the downed instrument followed by reanalysis of affected data may correct the problem. If sample matrix affect or contamination is the reason for poor data, the instrument may need cleaning and decontamination, and the sample may need diluting to reduce matrix affect. In all cases, when out of control data presents itself, the appropriate corrective measures need to be enacted to eliminate unusable data. The Quality Control Requirements chart can be used as a guide as to which corrective actions should be taken for different QC-type failures or nonconformities (Table 2.).

19.0 Contingencies for Handling Out-of-Control or Unacceptable Data

19.1 Due to limited sample volume, expiration of hold times, downed instrumentation, and analyst error, the sample data may be out of control or unacceptable to report. Since these potential instances can arise, contingency plans need to be in place to prevent and/or minimize their affect on data.

19.1.1 The first thing addressed is prevention of producing unacceptable data. When limited sample volume is the issue, the analyst should determine if splitting the sample into lesser volumes or weights is an option. To avoid sample hold time issues, the analyst's first responsibility is to plan accordingly. The analyst is responsible for budgeting enough time for sample analysis, so if a problem arises reanalysis is an option. Loss of data due to downed or malfunctioning instrumentation can be addressed with the use of backup instrumentation. If an

instrument becomes unusable, the samples should be analyzed on a different instrument system. Analyst error is prevented by second analyst confirmation and validation. If the initial analyst makes an analysis error or inadvertently reports unacceptable data, the second analyst is responsible for finding and/or correcting those errors.

19.1.2 When out of control or unacceptable data is produced and it is too late for corrective measures, a number of actions can be taken. The first and foremost is alerting the client service personnel of the problem. Client services will inform the client and/or responsible parties. In some instances, more sample can be made available or re-sampling can occur, so it is important to alert the appropriate personnel as soon as possible.

19.1.2.1 If the out of control data affects only specific analytes, it is important to let the appropriate person(s) know in case his or her site assessment is based on a specific target analyte list.

19.1.2.2 In all instances, if results are reported from data that is out of control or unacceptable, that data should be qualified accordingly. Once the client has been notified and he or she instructs us to report the data, then flag the data indicating what type of nonconformity has occurred.

19.1.2.3 Out of control data is still retained by the laboratory and filed and archived along with acceptable data. The file folder should be labeled as such, indicating that the data is out of control.

19.1.2.4 A non-conformance/corrective action report (CAR) form must be filled out whenever these types of events occur. The information on the report includes the problem encountered, planned corrective actions, and corrective action follow-up. The form is then discussed with and signed by the analyst, the client representative, the QA officer, and the laboratory manager. The purpose of the form is to document problems in order to eliminate the possibility of repeating nonconformance and to ensure that the proper corrective actions are employed.

20.0 Waste Management

20.1 Sample are routinely held (refrigerated) for up to six weeks from analysis date before they enter the waste stream. Waste disposal of samples and standards follows the procedures documented in the Laboratory Waste Disposal SOP (Quality Assurance Section, SOP NO. FO-8, Rev. 4).

21.0 References

21.1 USEPA, SW-846 Methods 8000B, Rev. 2, December, 1996
21.2 USEPA, SW_846 Method 8260B, Rev. 2, December, 1996
21.3 USEPA, SW-846 Methods 5030B, Rev. 2, December, 1996
21.4 USEPA ,SW-846 Methods 5035 (inc. App. A), Rev. 0, December, 1996
21.5 National Environmental Laboratory Accreditation Program (NELAP), Quality Systems, Chapter 5, June, 2000
21.6 USACOE , Shell for Analytical Chemistry Requirements,

EM 200-1-3, February, 2001
21.7 USEPA, Method 603, Acrolein and Acrylonitrile, July, 1982

Table 1.
Analyte List

Analyte	Analyte
Acetone	2,2-Dichloropropane
Benzene	1,1-Dichloropropene
Bromobenzene	cis-1,3-Dichlropropene
Bromochloromethane	trans-1,3-Dichloropropene
Bromodichloromethane	Diisopropyl ether
Bromoform	Ethylbenzene
Bromomethane	Hexachlorobutadiene
2-Butanone	2-Hexanone
n-Butylbenzene	Isopropylbenzene
sec-Butylbenzene	p-Isopropyltoluene
tert-Butylbenzene	Methylene chloride
Carbon disulfide	4-Methyl-2-pentanone
Carbon tetrachloride	Methyl tert butyl ether
Chlorobenzene	Naphthalene
Chloroethane	n-Propylbenzene
2-Chloroethylvinyl ether	Styrene
Chloroform	1,1,1,2-Tetrachloroethane
Chloromethane	1,1,2,2-Tetrachloroethane
2-Chlorotoluene	Tetrachloroethene
4-Chlorotoluene	Tetrahydrofuran
Dibromochloromethane	Toluene
1,2-Dibromo-3-chloropropane	1,2,3-Trichlorobenzene
1,2-Dibromoethane	1,2,4-Trichlorobenzene
Dibromomethane	1,1,1-Trichloroethane
1,2-Dichlorobenzene	1,1,2-Trichloroethane
1,3-Dichlorobenzene	Trichloroethene
1,4-Dichlorobenzene	Trichlorofluoromethane
Dichlorodifluoromethane	1,2,3-Trichloropropane
1,1-Dichloroethane	1,2,4-Trimethylbenzene
1,2-Dichloroethane	1,3,5-Trimethylbenzene
1,1-Dichloroethene	Vinyl chloride
cis-1,2-Dichloroethene	Vinyl acetate
trans-1,2-Dichloroethene	o-Xylene
1,2-Dichloropropane	m/p-Xylene
1,3-Dichloropropane	

Table 2.
Volatile Organic Compounds by GC/MS
Quality Control Requirements

Quality Control Item	Frequency	Acceptance Criteria	Corrective Action
Tune Check (BFB)	Every 12 hours.	Ensure correct mass assignment. BFB % Relative abundance criteria as specified in method 8260 or use program/project specific criteria.	Retune. Do not proceed with analysis until tune meets criteria.
Initial Calibration (IC)	Each time the instrument is set up and when CCCs and SPCCs in the continuing calibration verification (CCV) do not meet criteria. Established initially at minimum five concentration levels (six concentration levels if a second order {quadratic} curve is used) - low standard at or below project required reporting limit (PRRL), near but above method detection limits (MDL). Heated purge for low-level soils.	1. Average relative response factors (RRFs) for SPCCs Chloromethane, 1,1-Dichloroethane, and Bromoform ≥0.10 and for SPCCs Chlorobenzene and 1,1,2,2-Tetrachloroethane ≥ 0.30. 2. % RSD for RRFs for each CCC ≤30%. 3. % RSD for RRFs for all target compounds ≤15%. IF RF % RSD >15% use linear curve, r =.995, r2 = .990. 4. ACOE, NELAC, or other programs/agencies may require different criteria than stated here. Program and/or project specific criteria should be followed as stated in their documents. ACOE maximum allowable limits for %RSD = 30%	Correct system and recalibrate. Criteria must be met before sample analysis may begin. Any samples reported from data not meeting these criteria must be qualified (Z).

Initial Calibration Verification standards (ICV)	Every 12 hours. Should be at or near the mid-point of calibration range for all target compounds, CCCs, SPCCs and surrogates and should also be prepared from second source standards. Typically use 10/100 ppb for H2O and Low Level Soils, 0.5/5.0 mg/kg for MeOH preserved soils. ICVs analyzed for compounds using second order (quadratic) curves need to be analyzed at levels above and below the inflection point. Heated purges for low-level soils.	1. RRF for SPCCs Chloromethane, 1, 1-Dichloroethane, and Bromoform ≥0.10 and for SPCCs Chlorobenzene and 1,1,2,2-Tetrachloroethane ≥0.30. 2. % Deviation. for RRFs of each CCC <20%. 3. Non-CCCs - <20% Deviation for RRFs, <20 % Drift for linear curve and non linear curves- Sporadic marginal failure of up to 10 % of target compounds = 40% RSD. 4. ACOE, NELAC, or other programs/agencies may require different criteria than stated here. Program and/or project specific criteria should be followed as stated in their documents.	Correct system and recalibrate. Criteria must be met before sample analysis may begin. IF % relative standard deviation (RSD) >20%, then system must be inspected and problem corrected before sample analysis. If >20% RSD then confirm the integrity of the second source standard by reanalysis, and/or determine if it's a sporadic problem involving compounds that are typically poor performers. ACOE allows no tolerances for % D. Problem compounds need to be addressed on a project to project basis.
Continuing Calibration Verification standards(CCV)	Every 12 hours. Should be at or near the mid-point of calibration range for all target compounds, CCCs, SPCCs and surrogates and is prepared from standards used for calibration. Typically use 10/100 ppb for H2O and Low Level Soils, 0.5/5.0 mg/kg for MeOH preserved soils. Heated purges for low-level soils..	1. RRF for SPCCs Chloromethane, 1, 1-Dichloroethane, and Bromoform ≥0.10 and for SPCCs Chlorobenzene and 1,1,2,2-Tetrachloroethane ≥0.30. 2. % Deviation for RRFs of each CCC <20%. 3. Non-CCCs - <20% Deviation for RRFs, <20 % Drift for linear curve and non linear curves- Sporadic marginal failure of up to 10 % of target compounds = 40% RSD. 4. ACOE, NELAC, or other programs/agencies may require different criteria than stated here. Program and/or project specific criteria should be follow as stated in their documents.	Correct system and recalibrate. Criteria must be met before sample analysis may begin. IF % RSD >20%, then system must be inspected and problem corrected before sample analyses. If >20% RSD correct problem if determinable then reanalyze, and/or determine if it's a sporadic problem involving compounds that are typically poor performers. In any case sample results reported that have %D failures must be qualified (A). ACOE allows no tolerance for % D. Problem compounds need to be addressed on a project to project basis

Internal Standards (ISTD)	Added to all blanks, standards, and samples.	1. Peak area within -50% to +100% of area in associated CCV standard. 2. Retention time (RT) within 30 sec of RT for associated CCV standard. 3. ACOE, NELAC, or other programs/agencies may require different criteria than stated here. Program and/or project specific criteria should be follow as stated in their documents.	Inspect instrument for malfunctions; correct identified malfunctions, then reanalyze samples. *If no instrument malfunction identified proceed* as follows: * Reanalyze sample. * If reanalysis is outside limits the data should be qualified (S). Follow specified criteria as stated in Shell or other documentation.
Method Blank (MB)	One per medium/20 samples per matrix. The MB is used to document contamination resulting in the analytical process and should be carried through the complete sample preparation and analytical procedure.	1. Concentration of analytes of concern should be less than the highest of either : *Method Detection Limit *Five percent of the regulatory limit for that analyte or. *Five percent of the measured concentration in the sample. 2. ACOE ≤ ½ MRL 3. Follow criteria according to specific program/agency.	Reanalyze to determine if instrument or laboratory background contamination was the cause. If the method blank is still non-compliant, re-prepare and reanalyze blank and samples.* For ACOE data if less than ½ MRL no action required.* *If reanalysis of blank still contains contamination above specified limits, affected data should be flagged (B).
Laboratory Control Sample (LCS)	One per medium/per 20 samples/matrix. Must undergo all sample preparation procedures. Should be from a second source and contain target compounds with concentrations at or near the mid-point of the calibration range.	1. % Recoveries (and RPDs, if applicable) within in-house generated limits. Default 70-130% (20% RPD). Sporadic marginal failure (SMF) of up to 10 % of target compounds = 60-140 % rec. 2. ACOE Limits: H2O 80-120 % rec., Soils- 75-125% rec. Sporadic Marginal Failures (five percent of target compounds) = 60-140%. 3. Use Project Specific/Client limits when applicable.	If LCS recoveries are within control limits or within SMF frequency and limits then no action is required. If the LCS exceeds control limits, as well as SMF criteria the reanalyze the LCS to confirm proper preparation procedure. If still exceeding limits then reanalyze associated samples with a new LCS.. If sample data is reported with LCS failures then that data must be qualified (Q). Exception: If the LCS recoveries are high with no associated positives then no further action is taken.

Matrix Spike/Matrix Spike Duplicate	One per set of 20 samples per matrix. Must undergo all sample preparation procedures. Must be spiked with target compounds with concentrations at or near the mid-point of the calibration range.	1. % Recoveries and RPDs within in-house generated limits. Default 70-130 / 20%RPD. 2. ACOE limits = 70-130% rec. RPD = 30% for water. No limits for soils. Sporadic Marginal Failures (five percent of target compounds) = 60-140% rec. 40% RPD for water. 3. Use Project Specific/Client limits when applicable.	If LCS is acceptable, then report probable matrix interference. Qualify non detects if the recoveries are low (M), and detects if the recoveries are low and the sample amount + the true spiked amount should be within calibration range. Qualify detects if recoveries are high and the detects + the true spiked amount should be within calibration range. If recoveries are high and there are no detects in the unspiked sample then that data does not require flagging. If spiked amount + sample amount for any given compound exceeds calibration range than the spike is considered invalid for that compound. Qualify data for RPD failures (Y) when there is a detect for the failing compounds (non-detected compounds are not qualified). Exception: If a compound is already qualified for a LCS failure then no RPD qualifier is applied.
Qualitative/Quantitative Issues	1. If detection level of any compound in a sample exceeds the detection level of that compound in the highest level standard, the sample must be diluted to approximately mid-level of the calibration range and reanalyzed. 2. If the concentration of the target analyte (that exceeded the calibration range) is present in the sample following the high level sample and is greater than the RL but ≤5x RL, then that sample must be reanalyzed to determine if carryover occurred.	1. The instrument level of all compounds must be within the calibration range for all samples. 2. The sample analyzed immediately after a high-level sample must display concentrations of the high level target compounds less than the RL or greater than 5x RL.	Dilute the sample to bring the level of the highest concentration of target compounds within the calibration range. If any data is reported with any results over range then those results should be flagged (X). A sample displaying concentrations of target compounds between the RL and 5x the RL that was analyzed immediately after a high-level sample must be reanalyzed. If the results do not agree within the RL, report only the second analysis.

Surrogate	1. Calibrated as target compounds. 2. Added to all blanks, samples, and QC samples, as a part of the internal standard-surrogate spiking mixture.	1. All % Recoveries within in-house generated limits. Default 70-130%. 2. ACOE: Interference free matrix = 80-120% for water, 75-125% for solids. Project sample matrix = 70-130% 3. Use Project Specific/Client limits when applicable.	If recoveries are not within limits: Check to be sure that there are no errors in calculations, surrogate solutions, or internal standards. Also, check instrument performance. If no problem is found, re-prepare and reanalyze the sample. If the reanalysis is within limits, report only the reanalysis. If the reanalysis is still out of limits the sample should be qualified (S). Due to matrix affect, no reanalysis is required if the MS and/or MSD are outside limits.

Table 3.
Characteristic ions

Analyte	Primary Ion	Secondary Ion(s)	Analyte	Primary Ion	Secondary Ion(s)
Acetone	43	58	2,2-Dichloropropane	77	97,79
Benzene	78	51,77	1,1-Dichloropropene	110	77,75
Bromobenzene	156	77,158	cis-1,3-Dichlropropene	75	110
Bromochloromethane	128	49,130	trans-1,3-Dichloropropene	75	77,110
Bromodichloromethane	83	85,129	Diisopropyl ether	45	87,43
Bromoform	173	175,171	Ethylbenzene	91	106
Bromomethane	94	96	Hexachlorobutadiene	225	223,227
2-Butanone	43	72,57	2-Hexanone	43	58,57
n-Butylbenzene	91	92,134	Isopropylbenzene	105	120
sec-Butylbenzene	105	134	p-Isopropyltoluene	119	134,91
tert-Butylbenzene	119	91,134	Methylene chloride	84	86,49
Carbon disulfide	76	78	4-Methyl-2-pentanone	43	58,57
Carbon tetrachloride	119	121	Methyl tert butyl ether	73	57,43
Chlorobenzene	112	77,114	Naphthalene	128	51,129
Chloroethane	64	66	n-Propylbenzene	91	120
2-Chloroethylvinyl ether	63	65,106	Styrene	104	78
Chloroform	83	85	1,1,1,2-Tetrachloroethane	131	133,119
Chloromethane	50	52	1,1,2,2-Tetrachloroethane	83	85
2-Chlorotoluene	91	126	Tetrachloroethene	166	168,129
4-Chlorotoluene	91	126	Tetrahydrofuran	42	72,71
Dibromochloromethane	129	127,131	Toluene	92	91
1,2-Dibromo-3-chloropropane	157	155	1,2,3-Trichlorobenzene	180	182,145
1,2-Dibromoethane	107	109	1,2,4-Trichlorobenzene	180	182,145
Dibromomethane	93	95,174	1,1,1-Trichloroethane	97	99,61
1,2-Dichlorobenzene	146	111,148	1,1,2-Trichloroethane	83	97,85,99
1,3-Dichlorobenzene	146	111,148	Trichloroethene	95	130,132
1,4-Dichlorobenzene	146	111,148	Trichlorofluoromethane	101	103,105
Dichlorodifluoromethane	85	87	1,2,3-Trichloropropane	75	110
1,1-Dichloroethane	63	65,83	1,2,4-Trimethylbenzene	105	120
1,2-Dichloroethane	62	98,64	1,3,5-Trimethylbenzene	105	120
1,1-Dichloroethene	96	61,63	Vinyl chloride	62	64
cis-1,2-Dichloroethene	96	61,98	Vinyl acetate	43	86
trans-1,2-Dichloroethene	96	61,98	o-Xylene	106	91
1,2-Dichloropropane	63	76,112	m/p-Xylene	106	91
1,3-Dichloropropane	76	78			
ISTD			**SSTD**		
Fluorobenzene	96	77	Dibromofluoromethane	113	111,192
Chlorobenzene-d_5	117		1,2-Dichloroethane-d_4	102	104
1,4-Dichlorobenzene-d_4	152		Toluene-d_8	98	100
			4-Bromofluorobenzene	95	174,176

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Table 4.

INDEPENDENT DATA REVIEW CHECKLIST			Method: GCMS (EPA SW-846 8260)		
Analysis Date	Analyst/Data Interpreter	Independent Reviewer	Date or Review	Approved?	
				Yes	No

Instructions: Complete one checklist per analytical run. Enter the appropriate response for each question. Each "No" response requires an explanation in the Comments section and may require the initiation of a Nonconformance Report.

Requirement:	Acceptance Criteria	Analyst Review		Independent Review		Comments:
		Yes	No	Yes	No	
I. BFB Tune Check						
BFB tune check analyzed?	Relative abundance criteria met?					
II. Initial Calibration						
Was initial calibration performed using a minimum of five standard concentratrion levels?	Lowest standard at or near MDL/LOD?					
Were SPCC compounds acceptable?	Avg. RRF> 0.1; 0.3?					
Were CCC RF's less than 15% ? (Or alternatively no greater than 30% if generating results using linear regression?)						
Was Initial Calibration Blank analyzed?						
Were the ICB results for all target analytes less than the limit of detection (LOD).	<LOD or < project/program specific limits					
III. Continuing Calibration Verification (CCV)						
Was a BFB tune check run at the beginning of every twelve hour shift?	Relative abundance criteria met?					
Was a CCV analyzed after every 12 hour tune check?						
Were SPCC compounds acceptable?	Avg. RRF> 0.1; 0.3?					
Were CCC compounds acceptable?	%D < 20%					
Were all other compounds acceptable? If yes, then continue run.	%D < 20%					
If No, did number of failures exceed sporatic marginal failure limits?	<10% failing or see program limits					If yes, samples reanalyzed
Were detects for outlying compounds qualified?						

Requirement:	AcceptanceCriteria	AnalystReview		Independent Review		Comments:
		Yes	No	Yes	No	
IV. Blanks						
Was method blank (MB) analyzed prior to analysis of samples?						
Were the MB results for all target analytes less than the limit of detection (LOD)?	*All target analytes <LOD or < project/program specific limits					*see SOP for more detailed criteria
If analytes were detected in the MB with no associated positives in the samples, no further action is needed. If analyte detects are greater than the acceptance criteria with associated positives in the samples, flag associated positives with "B".						
V. Laboratory Control Sample						
Was a LCS analyzed at a frequency of one per 20 samples (or program specified frequency)?						
Were the LCS recoveries for all analytes within acceptance criteria?	Default 70-130%, or see internally generated limits, or client/program specified limits.					
If no, were detects (and non-detects for low recoveries) qualified?						
Was the LCS a second source to the initial calibration standards?						
VI. Laboratory Control Spike Duplicate (LCSD) [illegible]						
Was a LCSD analyzed at a frequency of one per 20 samples (or program specified frequency)?						
Were the LCSD recoveries for all analytes within acceptance criteria?	Default 70-130%, or see internally generated limits, or client/program specified limits.					
If no, were detects (and non-detects for low recoveries) flagged "Q"?						
Is the relative percent difference (RPD) for each analyte between duplicate samples acceptable?	Default 20%, or see internally generated limits, or client/program specified limits.					
If No, were detects in samples flagged "Y"?						
VII. Matrix Spike/Matrix Spike Duplicate (MS/MSD)						
Was a MS and a MSD analyzed at a frequency of one each per 20 samples (or program specified frequency)?						
Were the MS/MSD recoveries for all analytes within acceptance criteria?	Default 70-130%, or see internally generated program limits, or client specified limits.					

Requirement:	Acceptance Criteria	AnalystReview		Independent Review		Comments:
		Yes	No	Yes	No	
If No, were nondetects for analytes with low MS/MSD recoveries and detects < 1x spiked amount flagged "M"?						
Is the relative percent difference (RPD) for each analyte between duplicate samples acceptable?	Default 20%, or see internally generated limits, or client specific limits.					
If No, were detects in samples <1x the spiked amount flagged "Y"?						
VIII. Sample Analysis						
Are chromatogram characteristics, including peak shapes and areas, consistent with those of the CCV?						
Were surrogate recoveries for all samples and QC within acceptance criteria?	Default 70-130%, or see internally generated program limits, or client specified limits.					
If no, was the sample reanalyzed and/or flagged "S"?						
Were all samples having analytes detected in amounts exceeding the calibration range diluted and reanalyzed?	Target upper middle range of calibration curve.					
Did all samples meet hold time and preservation criteria as defined by method/program.						
Was a sample with detects between LOD and 5x LOD reanalyzed if following a sample with high level detects exceeding calibration range?	Detects are not attributed to carryover					
Were all samples and QC injected within 12 hours of BFB tune check?						
Were internal standard recoveries acceptable relevant to associated CCV?	Response = -50 to +200%; Ret. time = +/- 30 sec.					
IX. Records and Reporting						
Is sequence file / injection log present in the data package?						
Were all data, calculations, and values verified in LIMS upon completion of data capture?						
Were reported results with amounts exceeding acceptance criteria flagged with appropriate qualifier and, if needed, a NCR completed?						
Was the integrity of the sample kept intact? If not, was a NCR completed?						

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CT Laboratories.
Baraboo Laboratory Division

Title ***Laboratory Waste Disposal***

SOP Number: FO-8

Prepared by: _____
Date

Reviewed by: _____
Quality Assurance ***Date***

_____
Laboratory Director ***Date***

SOP Manual Control Number:_____

1.0 Introduction

CT Laboratories generates waste while performing the tasks normally associated with the business of testing. All of the wastes we generate are regulated in some form or another. Wastes that can be managed by municipal services are done so following guidelines issued by that provider. Other waste must be handled in a different manner by CT Laboratories personnel or their contractors. These other waste can be divided into two groups, hazardous and nonhazardous. Due to the variability of nonhazardous waste, these are not fully addressed in this procedure. Below are outlined procedures addressing the handling of mainly hazardous and other lab waste.

2.0 Scope

As noted in the Introduction, this procedure focuses on manageable wastes generated CT Laboratories at 1230 Lange Ct., Baraboo WI. Municipal waste handling is addressed in a municipal pamphlet and is under the direction of lab management. Hazardous waste management from CT Laboratories lab operations are addressed below.

3.0 Definitions and Explanations

Municipal Waste -
For the purposes of this procedure the term *municipal waste* is any waste handled by the City of Baraboo. The *Garbage Recycling Guidelines,* issued by the city, identifies the wastes the city will handle. It includes recycling paper, plastic and glass as well as general garbage. It does not include "household hazardous wastes" or any other program designed specifically for normal residential homeowners.

Hazardous Waste -
A hazardous waste is defined two ways: either it is specifically listed or it is not listed but exhibits a hazardous characteristic. Listed hazardous waste can be found in Wisconsin Administrative Code NR 605.08 or .09. Wastes not specifically listed may be hazardous if they exhibit a hazardous characteristic, such as ignitability, corrosive, reactive or EP Toxic.

Nonhazardous / Non-municipal Waste -
This term is used to describe wastes that the city will not dispose of and are not hazardous by definition. Although these types of waste arise occasionally, they are not covered in this policy. These types of waste are the responsibility of CT Laboratories to properly dispose of. They may include such things as building materials, drums and office furniture.

4.0 Procedures

4.1 Municipal waste

4.1.1. Non-hazardous waste that can be disposed of or recycled by the municipal program is handled under the direction of the laboratory office manager.

Procedures involving CT Laboratories's municipal waste removal are referred to the office manager.

4.1.2. A current guide provided by the city of Baraboo describes their program. Every effort should be made to recycle or dispose of waste through this program. The laboratory office manager has a copy of the municipal program and its requirements.

4.1.3. *Materials and containers that were considered hazardous and are made non-hazardous by* acceptable means are allowed into this program.

4.2 Hazardous Waste

4.2.1 Reduction

The most important portion of hazardous waste management is the prevention and reduction of wastes that would be considered hazardous. The type and amount of hazardous waste generated by our laboratory operations can be minimized through daily attention to the chemicals we use. Outlined below are some steps to be taken but they may not be the only ones. Through constant awareness of this potential or real problem all employees may find additional ways to reduce the wastes we generate.

4.2.2 If testing allows for choices in the methods or chemicals used try to select the one that generates the least acute, quantity or additional category of hazardous waste. Check with the supervisor or Safety Officer for assistance.

4.2.3 Purchase only the quantity of chemical that can be used within its'shelf life. Excessive quantity and outdated chemicals are both costly and may be dangerous to dispose of.

4.2.4 Containers that held hazardous chemicals are themselves considered hazardous waste if they are not cleaned before disposal. Listed below are two methods of disposal for containers that held chemicals, one for acutely hazardous and one for containers that did not contain acutely hazardous chemicals. If it is unclear if the chemical that was in the container was acutely hazardous or not then it should be treated as hazardous.

4.2.5 Containers that held hazardous waste can be disposed of with the municipal waste if they are completely empty and triple rinsed.

4.2.6 Containers that held non-acute chemicals can be directly disposed of if ;

4.2.6.1 no more material can be removed from the container by normal means (pouring or pumping).
4.2.6.2 containers have no more than one inch of waste remaining.
4.2.6.3 containers have no more than 3 % by weight of waste remaining.

4.2.7 Labels on containers are altered so as not to misidentify contents (example: methanol solvent can, emptied and triple rinsed with tap water should have the labels covered or

scratched out, then put into the dumpster).

5.0 Determination of Hazardous Wastes

5.1 Determine if the material waste is hazardous according to NR 605.09. The MSDS may be useful in this determination. The Safety Officer has a copy of this rule.

5.2 If the material is listed, then the material and the container the material is directly contained in are considered a HAZARDOUS MATERIAL. Contact the Safety officer for proper disposal. Provide the name, type hazard (number and/or class) and quantity of material to be disposed of in writing to the Safety Officer.

5.3 If it is not clear if the material is hazardous, contact the Safety Officer and/or the area supervisor for further investigation. The material can be tested for hazardous characteristics (NR 605.08) at CT Laboratories or subcontracted to another lab.

5.4 If the chemical is not listed as a hazardous waste it may be disposed of by other means. Reference books such as *Flinn Chemical Catalog & Reference, Aldrich Chemical or Baker Chemical* are sources providing guidance on disposal.

6.0 Known Wastes and Established Procedures

6.1 Samples, Solvents and Solutions

6.1.1 Water samples may contain known and suspected hazards in them such as acid preservatives, bacteria and industrial contaminants. To date, all of the waters CT Laboratories receives can be disposed of through the municipal sewer system. When water samples are released from sample storage, they can be directly disposed of by discharge into the sink drain, never a storm water drain. Samples from some sources may emit noxious odors and therefore dictate a sink drain in a hood. The bottles should be rinsed and disposed of in the municipal recycling program

6.1.2 Wastes containing potential pathogens (i.e., spent media, bacteria solutions, culture plates, etc.) Are autoclaved for a minimum of 30 minutes at 121° C/15 PSI prior to placement in the Municipal waste.

6.1.3 Pretreatment - Solid samples vary in disposal process depending on the type of solid and the effects of testing on the sample. We split solid samples into two groups, sludge and soils Sludge is disposed of in the same manner as water samples due to their origin from wastewater treatment facilities. Soils are all disposed of in different waste streams, and may be pretreated to reduce the effects from testing. Listed below are the pretreatments performed.

6.1.3.1 Non-RCRA soil samples, not used in testing or never come in contact with testing chemicals do not require pretreatment. The soil may be removed from the sample

container, placed in the soil disposal drum and the sample container recycled with the municipal wastes, or the sample and container placed in the disposal drum. Other sample containers that did not contain acutely toxic chemicals and can be recycled with the municipal waste.

6.1.3.2 RCRA soils, and sample containers with solvent and soil, are disposed of into the appropriate hazardous (RCRA) soil waste stream, either PCB containing or reagent exposed.

6.1.3.3 Instrumental testing byproducts, such as extracts and eluents, require special attention in some instances. Wastes from the Lachat Autoanalyzer and the AA Spectrometers are discarded to the municipal wastewater system. Extracts from organic testing are disposed of by removing the liquid extracts from the containers and adding them to the flammable waste stream. The current exceptions to this are extracts that contain carbon disulfide, an acutely hazardous chemical. The small quantity of carbon disulfide used in testing (< 50 mL a month) is exempt from current laboratory emissions. The carbon disulfide is decanted from the vials into a beaker in a hood and allowed to evaporate.

6.1.3.4 Waste solvents not recycled are presently split into three hazardous waste streams. These are listed below along with a general description of the hazard. Any waste not listed must not be added to these waste streams without prior authorization of the Safety Officer. To do so may change the waste stream into a different classification and make CT Laboratories noncompliant under regulations. Before transferring these wastes into the storage barrels check and wear proper personal protection equipment.

6.1.3.4.1 Flammable Liquid waste, such as hexane from testing, extracts and recycling are combined into one stream. A drum properly marked is used to combine these types of wastes.

6.1.3.4.2 Halogenated Liquid wastes, such as methylene chloride and freon mixtures from testing, extracts and recycling are combined into another waste stream. A drum properly marked is used to combine these types of wastes.

6.1.3.4.3 Corrosive - Oxidizer Liquid wastes from COD, Phosphorus and TKN testing comprise the last of the liquid waste streams we have. A drum properly marked is used to combine these wastes. Special care must be exercised when transferring these wastes into the storage drum as not to mistakenly add these to the flammable waste. This could produce a potentially explosive mixture.

6.2 Disposal (Hazardous waste)

6.2.1 Waste Disposed of Off-site

CT Laboratories contracts with licensed hazardous waste handlers to dispose of the laboratory waste streams. The current hazardous waste (RCRA) contract is held by Safety Kleen. The contracted hazardous waste hauler must be contacted for a pick-up every 180 days or less. There are a total of five waste streams that are approved for disposal at Safety Kleen. These waste streams include the following; 1) 6950299-Flammable solvents, this waste stream consists of the solvent waste from various testing, 2) 6950303-Reagent soils, this waste stream is made up of soil samples brought to the laboratory preserved or come into contact with extraction solvents during the testing process, 3) 6950301-COD/TKN/Metals Standards waste, this waste stream consists of digested COD solution , digested and undigested TKN solution along with old standard from the metals group, 4) 6950302-Halogenated solvents, this waste stream consists of Methylene chloride from PAH testing, 5) (Unassigned number)- PCB liquids, this waste streams consists of all liquid wastes that are known to contain PCBs. 5) (Unassigned number)- PCB solids, this waste streams consists of all solid wastes that are known to contain PCBs. The current special soil waste (NON-RCRA) contract is held by Leach Environmental Services.

The following table describes the disposal methods used for each particular waste stream:

Profile No.	Waste Stream Name	Disposal Method
6950299	Flammable solvents	Incineration
6950303	Reagent Soils	Incineration
6950301	COD/TKN	Chemical Fixation or Incineration
6950302	Halogenated solvents	Resource Recovery
Unassigned	PCB	Incineration
Non-RCRA Soils	Special soils	License Landfill

The following table describes the proper containers for each specific waste stream:

Waste Stream Name	Container Description	Container Size
Flammable Solvents	Black Steel Drum	30 or 55 gallon
Reagent Soils	Black Open Head Steel Drum	55 gallon
COD/TKN Waste Metal Standards	Poly (Plastic) Closed Head Drum	30 or 55 gallon
Halogenated Solvents	Black Steel Drum	30 or 55 gallon
PCB	Black Steel Drum	30 gallon
Non-RCRA Soils	Black Steel Drum	55 gallon

6.2.2 The hazardous waste storage area is located in the brown shed on the west side of the building. This storage is for hazardous waste only and any hazardous waste supplies such as extra drums, vermiculite, etc,.

6.2.3 All bulking of laboratory waste receptacles into the proper labeled drums must be done in the storage shed and over the safety pallets to ensure that nothing is spilled onto the concrete pad or the ground. Each time a new drum is starting to be filled the accumulation start date is noted on the drum. This notation can be marked on the side of the drum or a hazardous waste label can be used and the accumulation start date area filled in.

The following is a table which describes the packing and labeling requirements for each waste stream:

Waste Steam Name	Packing Requirements	Labeling Requirements
Flammable Solvents	Fill with liquid only, leave last 4 inches free of liquid.	Requires Flammable Liquid label
RCRA Solids	Fill with RCRA solids only. Leave 3 inches of headspace.	Hazardous Waste Label
COD/TKN	Fill with liquid only. Leave last 3 inches free of liquid.	Corrosive Liquid label
Halogenated Solvent	Fill only with liquids. Leave last 3 inches free of liquid.	Hazardous Waste Liquid Label
PCB	Fill with liquid and solids. Leave last 3 inches free.	PCB & Hazardous Waste Liquid Label
Non-RCRA Soils	Fill with special soils only. Leave 3 inches of headspace.	NON-RCRA Blue Label

6.2.4 All of the above waste streams require a waste label. The pacing requirements are straight forward and follow common sense practices. Never combine two waste streams into one drum. This could lead to a serious reaction inside the drum. Also, the waste streams are accepted by the waste disposal company as they are now categorized. If a mutual change is made by both CT Laboratories and the waste disposal company the new agreement would supersede the current agreement.

6.2.5 The non-RCRA waste stream requires a blue NON-RCRA waste label.

CT Laboratories
Baraboo Laboratory

Title: **Restrictive Sample Handling and Documentation**

SOP Number: **SS-4**

Written by: _____

Technical Review by: _____
Quality Assurance Manager

Approved by: _____
Laboratory Director

SOP Manual Control Number: _____

1.0 SCOPE AND APPLICATION

1.1 The following procedure applied to samples submitted for analysis or subcontracted to another laboratory that require restrictive handling. Samples that normally require this handling are EPA Superfund and Superfund level, samples having high probability of legal proceedings or are sensitive in nature. The procedure and accompanying forms should meet most needs that are not specifically addressed in other documents.

1.2 Upon prior notification, all samples requiring restrictive handling, whether analyzed at this laboratory or subcontracted, will be handled in a prescribed manner and documented.

1.3 Due to the legal nature of enforcement driven investigations, possession of samples must be traced from time of collection until introduced as evidence in a legal proceeding or destroyed. To maintain and document sample possession, restrictive internal procedures are followed. The following operating procedure outlines the steps that must be followed to meet these requirements.

2.0 DEFINITIONS

2.1 A sample is in your **custody** if;
- 2.1.1 it is in your possession, or
- 2.1.2 it is in your view, after being in your possession, or
- 2.1.3 it was in your possession and you returned it, or
- 2.1.4 it is in a designated secure area.

2.2 LIMS – Laboratory Information Management System

3.0 PROCEDURES

3.1 Field Custody

3.1.1 The field sampler or designated field person is personally responsible for the proper care and custody of the field samples until they are properly transferred or dispatched to the laboratory.

3.1.2 Sample labels or tags must be completed for each sample and any subsample that would make up a sample. At a minimum, the labels or tags should contain the sampling location, date, time and samplers name.

3.1.3 Although not common practice, sample containers or shipping containers can be secured with a custody seal. If used, the seal must be made in such a manner that visually shows a break, destruction or change in nature if the seal is tampered with.

3.1.4 All samples must be accompanied by proper documentation in the form of a *CHAIN OF CUSTODY* record. This document must clearly identify the samples and/or subsamples, the designation of the intended testing to be done on each sample, the sampler, who is the responsible person relinquishing the custody of the samples, who the samples are relinquished to and the dates/time of the events.

3.2 Transfer of Custody and Transport/Shipment

3.2.1 Samples must be properly packaged for shipment. For samples requiring temperature preservation, sufficient ice should surround samples to assure ice is present when the samples reach the lab. Internal packaging should be in place to assure container integrity and comply with shipping requirements.

3.2.2 A Chain of Custody record must accompany all samples. If the samples are shipped via common carriers (UPS, FedEx, Airborne, etc.) the mode of shipping should be noted in the "Remarks" section of the form. The person relinquishing the samples can sign, date and note the time in the first "Relinquished by" portion on the form. The shipping document (Air Bill, etc.) will serve as documentation of custody possession. The *Chain of Custody* should accompany the samples by placing it in a waterproof container and placing it directly in the shipping container.

3.2.3 Courier transferred samples should have the person relinquishing the samples can sign, date and note the time in the first "Relinquished by" portion on the form. The courier should take possession of the samples and immediately sign the "Received by" portion of the corresponding line on the form.

3.2.4 The original Chain of Custody will accompany the samples. Each shipping container should be accompanied by a Chain of Custody form. A copy of the form should be retained by the field personnel.

3.3 Sample Receipt

3.3.1 Upon receipt by the laboratory Sample Entry will take possession of the sample by one or more of the following;

3.3.1.1 Samples shipped by common carrier, and signed for by Sample Entry Technician, will have the carrier's paperwork retained and attached to the back of the *Chain of Custody.*

3.3.1.2 Samples in the possession of couriers will have the courier transfer possession to Sample Entry Technician by signing the Chain of Custody in the next available "Relinquished by" line on the form.

3.3.1.3 Once the samples are in the possession of sample entry the Chain of Custody is

signed, dated and time noted in the "Received by Laboratory" portion of the form.

3.3.2 The Sample Entry Technician will observe condition of Shipping container, accompaning paperwork and samples to record in the sample condition function of LIMS.

3.3.2.1 Examine the shipping container and record the following;

- CT Laboratories cooler tracking number
- Date and time cooler was received
- Sample Entry Technician who received cooler
- Presence or absence of a custody seal on the shipping container
- The condition of the seal (intact, damaged, open, etc.)
- Shipping method and tracking number of shipping container
- Obvious damage or leaking shipping containers

3.3.2.2 Open the shipping container, remove the enclosed accompanying documents and record;

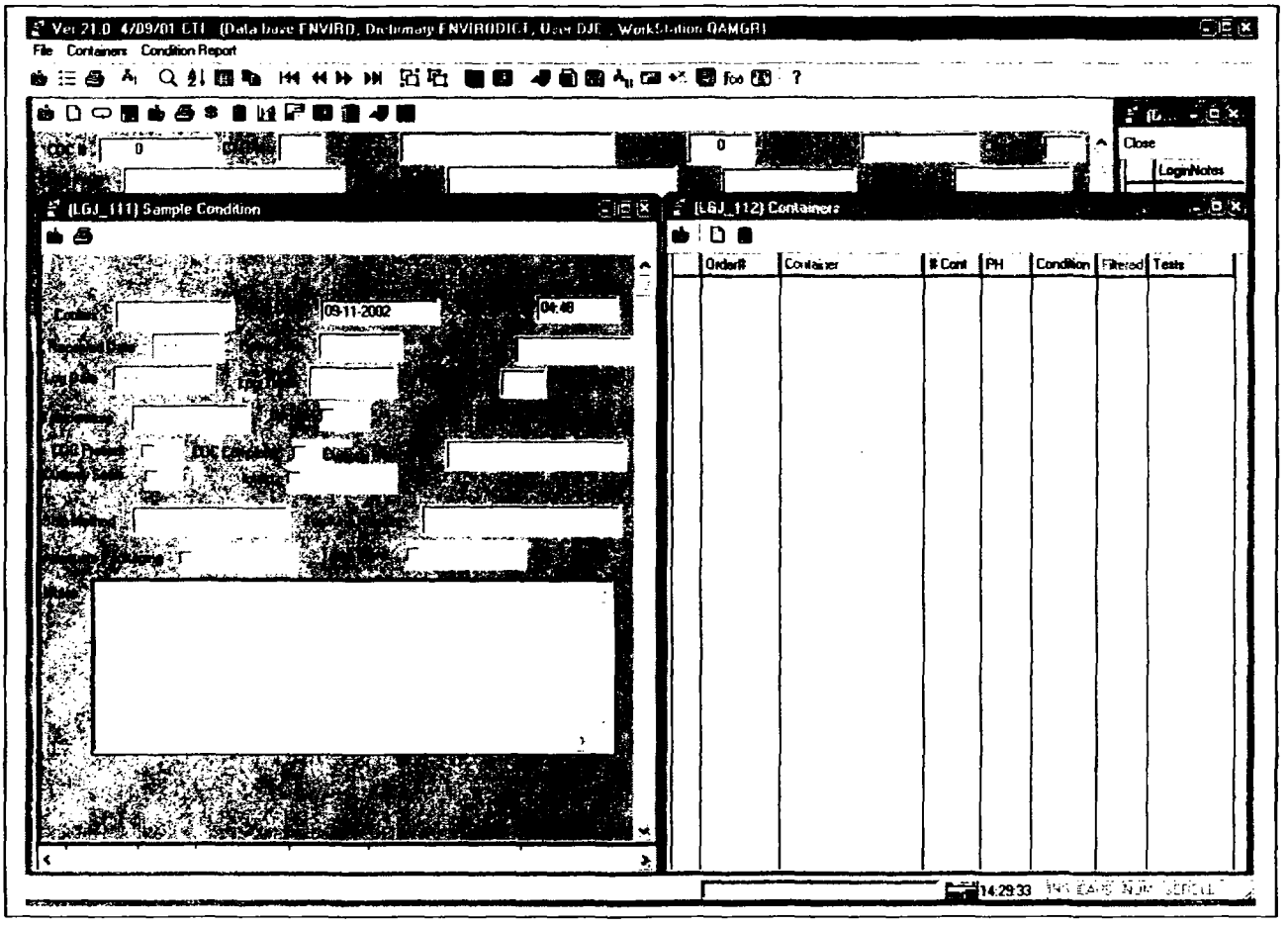
- The presence or absence of a *Chain of Custody*
- The *Chain of Custody* must be complete

3.3.2.3 Remove the sample from the shipping container and record the following;

- The temperature of temperature blank or melt water temperature
- Ice present or absent, or melt water
- Adequate packaging of samples
- Condition of each sample, subsample or container by the following codes
  - (1) Intact
  - (2) Too Many Containers
  - (3) Broken Container
  - (5) Missing Bottle
  - (7) Wrong Container
  - (8) Past Hold Time
  - (9) Incorrectly Preserved
  - (10) Insufficient Volumne
  - (11) Lables Missing/Unreadable
  - (12) Air bubbles in VOA vials

3.3.2.4 Compare documents to verify agreement between;

- Chain of Custody records
- Sample tags or labels
- Air Bills or Bills of Lading



3.3.2.5 Sample condition function in LIMs will be sent to the Project Manager via internal e-mail

3.4 Sample LIMS Log-in

3.4.1 Samples are processed through the routine log-in procedure. With the exception of distribution noted below.

3.5 Restrictive Sample Storage

3.5.1 Samples will be stored in a secured area, appropriately designated and conditions required for proper preservation.

3.5.2 Damaged samples will be disposed of appropriately and the method of disposal documented.

3.5.3 The laboratory and sample storage areas are secure with strict limited access by laboratory personnel.

3.5.4 When ever samples are removed / returned from storage that fact will be documented on an *Internal Chain of Custody.*

3.5.5 The location of stored sample extracts will be appropriately recorded.

3.5.6 VOC samples will be stored separately from other samples, extracts, standards or any source of possible contamination.

3.5.7 Standards will be stored separately from samples and extracts.

3.5.8 After completion of analysis, samples and extracts will be stored in compliance with the contract or until otherwise instructed by the appropriate authority.

3.6 Sample Security

3.6.1 Samples will be stored in a secure area within the laboratory.

3.6.2 Access to the laboratory is through locked doors.

3.6.3 Visitors will be escorted at all times while in the laboratory.

3.6.4 Samples will remain in secure sample storage until removed for analytical preparation or analysis. All transfers of samples into and out of storage will be documented on an *Internal Chain of Custody* form.

3.6.5 When samples are removed from secure storage by the analyst, the analyst is responsible for the custody of the sample. The analyst will return the sample to secure storage before the end of the work day.

3.6.6 Internal Chain of Custody forms will be retained in the associated sample file.

3.7 Internal Chain of Custody Procedures

3.7.1 VOC samples requiring temperature preservation will be stored in the VOC refrigerator. Non-VOC samples will be stored in the Semi-Volatile refrigerator.

3.7.2 The refrigerators will remain secure during periods restrictive samples are present.

3.7.3 Restrictive samples will remain in the secured areas until removed for sample preparation or analysis.

3.7.4 All transfers of restrictive samples into and out of secure storage will be documented on an *Internal Chain of Custody*. These records are maintained by the Sample Entry

Technician.

3.7.5 When a sample is removed from secure storage the analyst taking custody of it will document the action on the Internal Chain of Custody. The sample will remain in the custody of that analyst until it is returned to the secured area. If the contents of the sample container are completely used, this fact will be documented on the *Internal Chain of Custody*. If the contents of a sample container are used by more than one analysis (multiple tests) this fact will be documented on the *Internal Chain of Custody*.

3.7.6 All restrictive samples will be returned to secure storage at or before the end of the work day.

3.7.7 When sample analysis is completed by the laboratory or after three months time, which ever is longer, the unused portion of the sample will be disposed of properly. All forms data sheets and records will be retained as permanent documentation as directed by the contract or regulations.

4.0 REFERENCES

4.1 NEIC Policies and Procedures, May 1978 (Rev. March 1986)

4.2 EPA-330/9-78-001-R

4.3 EPA Central Regional Laboratory (communications)

4.4 US ACOE – EM 200-1-3

Sample Condition Report

Folder #: 29071 Coolers: 12345 Date: 9/12/2002 Time: 09:23
Client: CT Laboratories Received Date/Time: 9/12/2002 0930 Received By: DJE
Project Name: 2002 PT Log-In Date/Time: 9/12/2002 0945 Logged By: DJE
Project #: WP-92 PM: PML

Temperature: 2.0 C On Ice: Y COC Present: Y Complete: Y
Custody Seals Present: Y Intact: Y Numbers: 123456789
Ship Method: FedEx Tracking Number: 123456789
Adequate Packaging: Y Temp Blank Enclosed: Y
Notes: One of three VOC vials broke in shipping. Client contacted by DJE at 0940 on 09/12/02.

Sample ID/Description	Condition	Container	#	Cont Code	Filtered	Tests
148568	574	AMBER GL	1	1	Y	HG
148569	580	HNO3	1	11	Y	ICP
148570	582	AMBER HCL	1	9	N	O&G
148572	586	HNO3	1	7	Y	ICP
148573	830	VOA HCL	3	3	N	VOC

1 Sample Received OK
3 Broken Container
7 Wrong Container
9 Incorrectly Preserved
11 Label Missing/Unreadable

CT Laboratories

Title: ***Chemistry & Microbiology Sample Receiving and Processing***

SOP Number: **SS-5**

Prepared by: _____
Date

Reviewed by: _____
Quality Assurance ***Date***

_____
Laboratory Director ***Date***

SOP Manual Control Number:_____

1.0 SCOPE/APPLICATION

1.1 To provide consistency when receiving and logging samples for the analytical laboratory, this document will provide guidance and serve as a resource for information when logging samples.

1.2 This procedure should only be used for the receiving and logging of samples analyzed in the Chemistry and Microbiology laboratory. This procedure should be used as a resource along with pertinent supplement information to log samples into the LIMS.

2.0 SAFETY

2.1 Gloves, safety glasses, and protective clothing should be worn to protect against unnecessary or accidental exposure to hazardous chemicals and contaminants in samples. All activities performed while following this procedure should utilize appropriate laboratory safety systems. All applicable sections of CT Laboratories Chemical Hygiene Plan are followed.

3.0 PROCEDURE

3.1 Sample Arrival

3.1.1 Samples are received at the west side of the building inside the third door.

3.1.2 Samples will be accepted during our normal working hours of 8:00 am - 5:00 pm, Monday through Friday.

3.1.3 Samples may arrive via UPS, Federal Express, US Mail, privately contracted delivery services, and/or by the client.

3.1.4 Sample coolers arriving will require a signature of the individual receiving the coolers. This signature will verify the number of packages delivered and accepted.
***When handling samples, gloves and safety glasses must be worn.**

3.1.5 Paperwork should accompany the samples. This paperwork may be in the form of a chain of custody (COC), and/or purchase order. If there is no paperwork accompanying the samples, the project manager should be contacted and apprised of the situation and is recorded on the Sample Condition report and e-mailed to the Project Manager. Exercise caution when opening coolers. Some may contain samples of unknown origin and may be hazardous to health. If unsure of the type of samples being

delivered carefully open the cooler in a hood or well-ventilated area.

3.1.6 The COC must be checked to insure that it is properly filled out.
- Filled out in pen
- Project # on COC (where it applies)
- Desired tests are marked.
- Check sample dates to ensure they are within hold time
- Signatures of sampler and anyone who took possession of the samples
- Sample descriptions filled out
- Any special instructions, billing information, or turnaround requests

3.1.7 Record the preservation temperature of samples on the COC when they arrive. The following steps should be taken to determine the temperature:
- *If there is a temperature blank associated with the samples (one per* cooler), take the temperature of the temp. blank.
- If the samples are received on ice, note "on ice" (circle "yes" or "no").
- If the samples are submitted directly within 4 hours, note "direct" next to the temperature.
- If the samples were previously on ice but it has completely melted, take the temperature of the melt water.
- If there is no temperature blank, record the temperature from a sample.

3.1.8 Remove samples from the cooler matching the sample with the chain of custody. Verify that all samples arrived undamaged and all samples listed on chain of custody are present. Any damaged containers and/or discrepancies in the chain of custody and samples should be reported to the appropriate Project Manager. Any problems encountered while unpacking samples must also be documented on a Sample Condition Report and e-mailed to the Project Manager.

3.1.9 Verify sample preservation by checking that the client supplied their sample in the proper bottles and supplied accurate sample quanitity. Air bubbles in VOC vials must also be documented on the Sample Condition Report. If all vials for a particular sample contain bubbles, notify the appropriate Project Manger.

3.2 Log-in using LIMS

3.2.1 Double Click on the Lims Icon on your Desktop
The Login Screen appears
Enter your User Name and Password
Select OK

3.2.2 After the Lims Main screen appears select Login
Select Sample Login
Select ADD NEW in the client section of the window
Select Client from list of Clients available
Select project name or number from the List of Projects

3.2.3 Fill in the project name, project number, report and invoice contacts, and name of sampler (in Iowa).

3.2.4 Fill in sample date, sample time, matrix, and sample description. Change lab due date if applicable (ie. Rush).

3.2.5 Choose the "add tests" folder. Scroll through the tests to locate the requested test and double click to select. When all tests for a sample have been selected, and all samples have been logged in, commit the folder and record the folder and sample numbers on the chain of custody.

3.2.6 Print container labels and affix each label to the appropriate container.

3.3 Post Log-in

3.3.1 Numbered samples must now be transferred from the sample receiving area to the appropriate refrigerator.
- VOC Waters will be transferred to the double door in the Volatiles Lab
- VOC Soils will be trasferred to the double door in the storage area.
- Semi Volatiles will be transferred to the first "Organic" walk-in.
- Inorganics will be transferred to the second "Wetchem" walk-in.
- Metals will be transferred to the shelving located in the storage area.

The chemists can refer you to the appropriate shelves in a particular refrigerator.

3.3.2 When all samples are logged in for a given day, login confirmation sheets can be printed. Login confirmation sheets list summaries of all the information entered regarding each project including the tests assigned to each particular sample and are subsequently used to check for log-in errors by comparing the original chain of custody with the submission coversheet.

3.4 Handling Sample Log-In Problems

3.4.1 If log-in has encountered any problems during the log-in procedure, proper documentation and notification must be performed. Examples of problems include, but are not limited to: received above proper temperature, broken containers, incomplete chain of custodies, missing samples, samples received past hold times, samples without proper preservation, inadequate volume to perform test. For any situation that may warrant that the Project Manager is notified, proper documentation must be in place to resolve the problem.

3.4.2 Log-In personnel must fill in the electronic "Sample Condition" form whenever there is any question or problem with samples within our custody. Once the proper information is gathered, the form goes immediately to the Project Manager for that folder number. The Project Manager will then contact the client for direction on how the problem should be handled. The Project Manager documents what action will be taken with the samples in question. The form is kept with the original chain of custody and mailed out with the final report to the client. Sample Condition forms are kept within the electronic file folder and are saved electronically for future reference.

QUALITY ASSURANCE PROJECT PLAN

OMC PLANT 2
Waukegan, Illinois

Remedial Investigation

WA No. 237-RICO-0528 / Contract No. 68-W6-0025

January 2005

SUPPLEMENT TO APPENDIX A

Appendix A (continued)

Analytical Standard Operating Procedures
STL SOPs

STANDARD OPERTING PROCEDURE
VOLATILE ORGANIC COMPOUNDS (VOCs) IN AIR BY (GC/MS)
EPA Compendium Method TO-14 / EPA Compendium Method TO-15

Applicable Matrix: Air

Standard Compound List and Reporting Limits: See Table 1

Approvals and Signatures

Laboratory Director:	Michael F. Wheeler, Ph.D.	Date: 11/15/04
QA Manager:	Kirstin L. McCracken	Date: 11-15-04
Department Manager	Bryce E. Stearns	Date: 11/15/04

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1.0 SCOPE AND APPLICATION

1.1 This SOP describes the laboratory procedure for analysis of polar and non-polar volatile organic compounds (VOCs) in ambient air. The procedure is applicable to those VOCs that have been evaluated by the laboratory for their consistent performance in meeting the control criteria put forth in Compendium Method TO-15. While the compendium method is specifically written for the analysis of samples collected in leak-free passivated stainless steel canisters, it may be applied to the analysis of samples that have employed the use of other collection devices such as Tedlar bags and solid absorbents.

1.2 *The target compound list(s) are given in Table 1 along with the reporting limit (RL).*

2.0 SUMMARY OF METHOD

2.1 A sample submitted for analysis is directed from the sample container through a series of solid sorbent bed traps, which also reduces the water content of the sample. The sample is thermally desorbed and the VOCs are carried onto a gas chromatographic column coupled to a mass spectrometer. Compounds are identified by comparison of the mass spectra for individual peaks in the total ion chromatogram to the fragmentation patterns of ions corresponding to VOCs including the intensity of primary and secondary ions as well as the patterns of stored spectra taken under similar conditions. The concentration of the target compound is calculated by internal standard technique using the average response factor of that compound as determined by the initial calibration.

2.2 This procedure is based on Compendium Methods TO-14 and TO-15, Determination of *Volatile Organic Compounds (VOCs) in Air Collected in Specially-Prepared Canisters* and Analyzed by Gas Chromatography/Mass Spectrometry (GC/MS). USEPA Office of Research and Development, Cincinnati OH, January 1999.

3.0 DEFINITIONS

Absolute Pressure-pressure measured with reference to absolute zero pressure (as opposed to atmospheric pressure), usually expressed as kPa, mm Hg, or psia.

Cryogen-a *refrigerant used to obtain very low temperatures* in the cryogenic trap of the analytical system. A typical cryogen is liquid nitrogen (bp –195.8°C) or liquid argon (bp –185.7°C).

Internal Standards (IS)-Non-target analyte compounds that are similar to the target analytes but are not expected to be found in environmental media (generally, isotopically labeled target analytes are used for this purpose) and are added to every standard, quality control sample, and field sample at a known concentration prior to analysis. IS responses are used as the basis for quantitation of target analytes.

Stock solutions-A concentrated solution containing one or more method analytes prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source.

Calibration Standard (CAL)-A solution prepared from the primary dilution standard solution or stock standard solutions and the internal standards and surrogate analytes. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

Continuing Calibration Verification (CCV)-An analytical standard solution containing all target analytes and internal standard compounds that is used to evaluate the performance of the instrument system with respect to a defined set of method criteria.

Method Blank-A canister of ambient air or other blank matrix that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, and internal standards that are used with other samples. The ABLK is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

Laboratory Control Sample (LCS)-The LCS consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. Its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements. When the results of the matrix spike analysis indicates a potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix.

Initial Calibration Verification (ICV)-An analytical standard solution containing all target analytes and internal standard compounds that are prepared from a source external to the laboratory and independent from the source of the initial calibration standards. The purpose of the ICV is to verify that the initial calibration is in control.

4.0 INTERFERENCES

4.1 Contamination may occur in the sampling system if canisters are not properly cleaned before use. Additionally, all other sampling equipment (e.g., pump and flow controllers) should be thoroughly cleaned to ensure that the filling apparatus does not contaminate samples.

5.0 SAFETY

Employees must abide by the policies and procedures in the Corporate Safety Manual and this document.

5.1 Specific Safety Concerns or Requirements

The analytical system contains zones with elevated or depressed temperatures that are capable of causing injury upon direct contact. The analyst needs to be aware of the

locations of those zones, and allow them to return to room temperature prior to maintenance activities or take measures to avoid contact with hot and/or cold surfaces.

There are areas of high voltage in the analytical system. Depending on the type of work involved, either turn the power to the instrument off, or disconnect it from its source of power.

Liquid nitrogen (LN2) is used for cryogenic purposes. In addition to avoiding contact with LN2 cooled surfaces, analysts must be aware of the potential for oxygen depletion in a confined space in the event of an unexpected large release of the product. Users should evacuate a confined space in which large amounts of LN2 have been released.

Sample canisters are occasionally pressurized for cleaning or sample dilution purposes. Lab systems are designed to ensure that the cans are not pressurized above 32 psi. Eye protection must be worn when cans are pressurized in the event of a canister failure.

5.2 Primary Materials Used

The materials used in this method are generally commercially prepared gas phase standards. On rare occasions, gas phase standards may be formulated from neat materials. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

6.0 EQUIPMENT AND SUPPLIES

6.1 Sample Canisters

SUMMA® Leak-Free Passivated Stainless Steel Canisters, 1 and 6 Liter, Restek Catalog #555656 or equivalent.

Vacuum Pressure Gauges / Flow Controllers, Restek Catalog #24239 or equivalent.

Note: The catalog numbers listed in this SOP are subject to change.

6.2 Analytical System

VOC Autosampler, Entech 7016CA or equivalent.

Cryogenic Concentrator equipped with an electronic mass flow controller that maintains a constant flow for carrier gas and sample over a range of 0-200 cc/min. Entech 7100A or equivalent.

Multisorbent Bed Cryotrap capable of effectively removing water and CO_2 while trapping polar and non-polar compounds.

Gas Chromatograph: Agilent 6890 or equivalent

Mass Spectrometer: Agilent 5973 or 5972 MSD or equivalent

Primary Column: Fused silica capillary column, Restek RTX-624 60m x 0.32 mm x 1.8 µm or equivalent

Vacuum Pumps

Syringes-1.0 mL - 1.0 L gas tight syringes with Luer-Lok tip

Data System: PC software for Entech instrumentation. Hewlett-Packard ChemStation data acquisition software and Hewlett-Packard ChemServer, Target 3.5 data processing software

Canister Cleaning System: Entech auto-canister cleaning system, Model 3000 or 3100 or equivalent.

Vacuum Pump: Capable of evacuating sample canisters to a vacuum of -29.9" Hg.

Manifold: Equipped with stainless steel and Teflon transfer lines and connections for cleaning up to eight canisters simultaneously.

Vacuum Gauge: Capable of measuring vacuum in the manifold to an absolute pressure of 0.05-mm Hg or less.

Heating Manifolds: Individually thermal-stated heating manifolds used to heat canisters during the cleaning cycle.

Tedlar Bag

7.0 REAGENTS AND STANDARDS

7.1 Standards

Unless otherwise noted gaseous standards are stored at room temperature and assigned an expiration date of three months.

4-Bromofluorobenzene (BFB) Working Standard (100 ppbv): Spectra Gases or equivalent.

Gaseous Stock Standard 1: A commercially purchased gaseous stock standard that includes all target compounds except for naphthalene at a concentration of 1.0 ppmv. Spectra Gases or equivalent.

Gaseous Stock Standard 2: A commercially purchased standard that includes naphthalene at a concentration of 1.0 ppmv and bromoform at a concentration of 3.0 ppmv. Spectra Gases or equivalent.

Intermediate Standards: Prepare intermediate standards by adding a known amount of the stock standard(s) into a SUMMA canister and pressurizing the canister with humidified (relative humidity >20 percent) zero air to achieve the concentrations given in the following table:

Intermediate Standard	Component(s)	Volume Added (mL)	Final Concentration (ppbv)
1	Stock Standard 1	495	40
2	Stock Standard 1	125	10
3	Intermediate Standard 1	495	0.5
4	Stock Standard 1, Stock Standard2	495	40
5	Stock Standard 1, Stock Standard 2	125	10
6	Intermediate Standard 4	495	0.5

Internal standards: (Bromochloromethane, 1,4-Difluorobenzene, and Chlorobenzene-d5) are purchased from Spectra Gases at a concentration of 1 ppmv. 20 mL of each internal standard is introduced directly to the concentrator to volumes sufficient to achieve a final concentration of 10 ppbv in sample.

Laboratory Control Sample: A multi-component stock standard purchased from commercial vendor, Spectra Gases. Prepare the working LCS standard by adding 125 mL to a canister and then pressurizing the canister with humidified zero air to achieve the target concentration, which is at or near the midpoint of the calibration curve.

8.0 SAMPLE COLLECTION, PRESERVATION & STORAGE

8.1 The laboratory recommends that samples be collected in passivated stainless steel canisters that have been cleaned and tested prior to sampling. The ability to collect a representative sample, particularly for the higher boiling compounds, is highly dependent on such factors as the length of the sampling train and the materials of construction, the temperature and relative humidity at which sampling occurs, and the sampling flow rate. Because the laboratory does not perform sample collection, specific sampling procedures are not provided in this SOP. Guidance for sample collection may be found in the published reference methods for Compendium Methods TO-14 and TO-15. After collection samples may be stored at ambient temperature until analysis.

8.2 The analytical holding time for samples collected in passivated stainless steel canisters is 30 days from the date of collection.

8.3 Unless otherwise specified by client or regulatory program, after analysis sample canisters are cleaned in accordance with the procedure given in Section 11.1.

9.0 QUALITY CONTROL

This section provides a brief description of the QC check samples analyzed with this method. The minimum frequency requirements, acceptance criteria and recommended corrective action for all QC samples are summarized in Section 17.0, Table 3.

The following QC samples are analyzed with each analytical batch: a Method Blank (MB), Laboratory Control Sample (LCS), and Laboratory Control Sample Duplicate (LCSD). Sample duplicates are performed per client request.

Internal standards are added to all calibration standards, samples, and blanks to verify that the analytical system is in control.

10.0 CALIBRATION AND STANDARDIZATION

10.1 Instrument Performance Check (BFB)

Every 24 hours, prior to the acquisition of a calibration curve or the analysis of samples, analyze a BFB standard following the procedure given in section 11.2. The results of the BFB analysis must meet the mass spectral ion abundance criteria given in Table 2. If the acceptance criteria are not met, perform instrument maintenance and reanalyze the tune standard.

10.2 Initial Calibration

After the criteria for the tune standard are met, calibrate the instrument with a minimum of five calibration standards for each target analyte at concentrations that span the working range of the system. The recommended concentrations for the calibration standards are 0.2, 0.5, 5, 10, 15, 20, and 40 ppbv. The 15 ppbv calibration point is specific to acetone, isopropyl alcohol, tertiarybutyl alcohol, tetrahydrofuran, and 1,4-dioxane. These compounds are not included in either the 0.2 ppbv or the 0.5 ppbv calibration points. Additionally, naphthalene is not included in the 0.2ppbv standard. The standard for naphthalene is formulated with one and possibly more of the other target analytes. For this reason there is a separate 0.5 ppbv acquisition specific to naphthalene. This provides for the low calibration point for napthalene without affecting the concentration of each of the target analytes at the 0.5 ppbv concentration level. The remaining calibration points (5, 10, 20, and 40 ppbv) are acquired with the inclusion of the naphthalene standard, and the concentration of co-formulated compounds needs to be included in developing the response factors for these compounds. For ease of reference, each calibration standard is assigned one of the following calibration group identifiers: A, B, C, D, E, which can be cross-referenced to the target analytes listed in Table 1 in order to determine which calibration level is used.

The working calibration standards are introduced to the GC/MS by injecting the appropriate volume(s) of the intermediate standards directly into the sample concentrator following the procedure that begins in Section 11.3. The injection volume and final concentration for each calibration level is provided in the following table but is

subject to change if the composition or concentration for any parent component standard should change or if the working range of the calibration should be adjusted.

Calibration Level	Intermediate Standard	Calibration Group Identification	Volume Injected (mL)	Final Concentration (ppbv)
1	Standard 3	A, E	80	0.2
2	Standard 3	E	200	0.5
3	Standard 6	A, B, D, E	200	0.5
4	Standard 5	A, B, C, D, E	100	5.0
5	Standard 5	A, B, C, D, E	200	10.0
6	Standard 4	C	75	15.0
7	Standard 4	A, B, C, D	100	20.0
8	Standard 4	A, B, C, D	200	40.0

The data system calculates a relative response factor (RRF) for each analyte and/or isomer pair for each calibration standard using the appropriate internal standard. (See Table 1 for internal standard assignments). The data system then calculates a mean relative response factor, percent relative standard deviation, relative retention time (RRT) and the mean RRT. The %RSD for each compound must be < 30%, **with at most two exceptions up to a limit of 40%*.** The RRT for each target compound at each calibration level must be within 0.06 RRT units of the mean RRT for the compound. The retention time shift for each of the internal standards at each calibration level must be within 20 seconds of the mean retention time over the initial calibration range for each internal standard. If these criteria are not met, inspect the system for problems and recalibrate.

**This exception may not be applicable to project specific compounds.*

Perform initial calibration prior to any sample analysis (initial method set-up), whenever a new column is installed, when significant instrument maintenance has been performed, and when the CCV standard does not meet acceptance criteria.

10.3 Initial Calibration Verification

Immediately following an acceptable initial calibration, verify the accuracy of the calibration with a second source standard (ICV). For this procedure the laboratory control sample serves as the ICV. The procedures for the preparation and analysis of the ICV/LCS are provided in Section 11.3. The percent recovery of the ICV/LCS should be within 70-130%. If criteria are not met, correct the problem and reanalyze the ICV/LCS. If the reanalysis fails, remake the calibration standards and recalibrate.

10.4 Daily Calibration Check

Analyze a continuing calibration verification (CCV) standard each day prior to sample analysis, to ensure the instrument is reliable and has not changed significantly from the current initial calibration curve. The CCV should include all target analytes and the

concentration of the CCV standard should be at or below the middle of the calibration range and varied within the calibration range. Analyze the CCV following the procedure that begins in Section 11.3.

The data system calculates a response factor for each analyte along with the percent difference of the RRF to the mean RRF in the most recent initial calibration. The %D for each target compound must be within ±30%. If this criterion is not met, correct the problem prior to further analysis.

11.0 PROCEDURE

11.1 Canister Cleaning & Certification Procedure

Each canister must be certified clean prior to its initial use for sample collection. Thereafter one canister from each cleaning batch is analyzed to verify that the cleaning procedure was effective for all canisters in the cleaning batch. The canister chosen for analysis should always be the canister that had the highest target/TIC concentration from the previous sample analysis. If no targets are detected in the "certification" canister analyzed, then it is presumed the cleaning procedure was effective and all other canisters cleaned within the same cleaning batch are certified as clean.

Procedure:

Connect the canister(s) to the manifold. Open the vent shut-off valve and the canister valve(s) to release any remaining pressure in the canister(s). Attach the heating band(s) to the canister(s) and turn on the current, allowing the bands to heat to 100 °C. Establish the number of cycles (≥3 for 6 L canisters and ≥6 for 1 L canisters) on the cleaning system and depress the "Auto" button.

After the evacuation/pressurization cycles are complete, pressurize the certification canister to 10 psig with humidified zero air and analyze this canister using the procedure that begins in Section 11.3. No analytes should be detected in this canister above the RL. If this criterion is not met, repeat the cleaning procedure.

After an acceptable certifying analysis, re-attach the canister to the cleaning manifold and evacuate the canister to <-29.5" Hg. Close the canister valve and remove the canister from the cleaning apparatus. Cap the canister with a swagelock fitting and initial and date the canister identification tag. Complete the Canister Certification Report, attach supporting data to the report and retain on file.

Prior to shipment of canisters to the client, perform a leak test on each canister by evacuating the canister to approximately -29.5"Hg. Measure the initial vacuum, close the valve then recheck the vacuum after at least 24 hours has elapsed. The vacuum should not vary more than 0.5"Hg over the time period for the leak test to be considered acceptable. If there is a loss of more than 0.5" Hg, the canister is to be removed from service.

11.2 Instrument Operating Conditions

Optimize the GC and MS conditions for compound separation and sensitivity. The recommended operating conditions are as follows:

Carrier Gas:	Helium, Ultra High Purity
Cyrogenic Focusing Gas:	Liquid Nitrogen
Flow Rate:	~1.5mL/min
Temperature Program:	Initial Temperature: 40°C
	Initial Hold Time: 4 minutes
	Ramp1 Rate: 20°C/min. to 200°C.
	Ramp 2 Rate: 40°C/min. to 220°C
	Final Temperature: 220°C
	Final Hold Time: 6.5 minutes
Electron Energy:	70 electron volts
Mass Range:	35-265amu
Scan Time:	≥ 1 scan per second

These operating conditions may be changed but once the operating conditions are established the same conditions must be used for both calibration and analysis of field samples.

11.2 Sample Preparation

Inspect the condition of each sample container on receipt and notify the laboratory Project Manager of any signs of damage. Check the pressure of each sample canister by attaching a pressure gauge to the canister inlet and briefly opening the canister valve to obtain the pressure reading. Notify the laboratory Project Manager if the residual vacuum is greater than -10.0" Hg (- 5.0" Hg for 1 L canisters), or when there is no residual vacuum. Adjust the pressure of canisters received at a vacuum of greater than –10.0" Hg with zero grade air to ensure that sample volume can be withdrawn for analysis. Record the final pressure and calculate and record the dilution factor, using the "Canister Dilution Worksheet".

11.3 Sample Analysis

Set up the analytical run in the following sequence:

BFB Tune
Initial Multi-Point Calibration or Daily Calibration Check
ICV/LCS
LCSD
Method Blank
Field Samples

Set the MS system so that it scans the atomic mass range from 35 to 265 amu with acquisition of at least 1 scan per second. Introduce the BFB standard directly to the

instrument concentrator, and thermally desorb into the GC/MS system. Acquire the data for the BFB tune and evaluate the results against the criteria given in Table 2. If the acceptance criteria are not met, perform corrective action prior to further analysis.

Introduce each calibration standard directly to the instrument concentrator, with the addition of internal standards equivalent to 10 ppbv. Analyze the standards in a sequence from lowest to highest concentration. Thermally desorb into the GC/MS system, and acquire the data. Evaluate the results against the criteria given in Table 3, Section 17.0. If the acceptance criteria are not met perform corrective action prior to further analysis.

Analyze the CCV, alternating the concentration of the CCV between 10 ppbv and 20 ppbv. Acquire the data and evaluate the results against the criteria given in Table 3, Section 17.0. If the acceptance criteria are not met perform corrective action prior to further analysis.

If time remains in the 24-hour period immediately following an initial calibration, samples may be analyzed without analysis of the daily calibration standard. Otherwise, an instrument performance check (BFB) and daily calibration check must be analyzed prior to samples.

Prepare the laboratory control sample(s) (ICV/LCS, LCSD) according to the procedure given in Section 7.2. Attach the canister to an autosampler inlet and introduce 200 mL of volume to the instrument concentrator for a 6 L canister (20 mL for a 1 L canister), with the addition of internal standards equivalent to 10 ppbv. Thermally desorb into the GC/MS system.

Analyze the method blank by introducing 200 mL of humidified zero air, with the addition of internal standards equivalent to 10 ppbv, to the concentrator. Thermally desorb into the GC/MS system.

Analyze field samples in a consistent manner by introducing 200 mL of volume (20 mL of volume for 1 L canisters) to the instrument concentrator. Thermally desorb the sample into the GC/MS system.

Acquire the data and evaluate the results (See Section 13.0). The data system identifies target analytes by comparison of the mass spectrum (after background subtraction) to a reference spectrum in the user created database and calculates the concentration of target analytes in ppbv using the equation given in Section 12.0. If the on-column concentration of any sample exceeds the range of calibration (40 ppbv), reanalyze an aliquot of the original sample at an appropriate dilution.

When the aliquot to be analyzed is less than 20 milliliters, prepare the dilution by pressurizing the canister, and document the dilution using the canister dilution worksheet. The maximum pressurization set by the laboratory is 30 psig. This, with the smaller sample aliquot, provides for dilutions of up to 30-fold on the base method, or the ability to provide for constituent concentrations of nominally 1000 ppbv. Samples

requiring a greater dilution are considered to be outside the scope of the TO-15 method. If these samples are to be analyzed with the quantification of responses within the calibrated range, perform a secondary dilution into a Tedlar bag, using a gas-tight syringe and humidified air. In performing this type of dilution, prepare and analyze a method blank and a laboratory control sample using the same technique and materials that are used in the preparation of the sample(s).

Samples containing carbon dioxide and/or methane approximating 1 percent by volume may significantly affect analytical performance when a 200 mL sample volume is analyzed. Such samples are to be diluted for analysis, the reason for the dilution noted on the analytical run-log, and the Project Manager notified of the situation.

The application of the method to the analysis of samples collected in Tedlar bags is outside the scope of the TO-15 method, however certain project work may employ the use of this collection device. If samples are to be analyzed from Tedlar bags, prepare and analyze a method blank and a laboratory control sample using the same technique and materials that are used in the preparation of the sample(s).

11.4 Data Reporting

Report the results with target concentrations less than the RL as RL "U". Report the results above the RL as the target concentration. Adjust the reporting limit (RL) for sample dilution/concentration and apply data qualifiers as appropriate. The laboratory's RL for each target analyte is provided in Table 1.

Report the result of samples collected in Tedlar bags, or diluted in Tedlar bags, using the RL from Table 1 adjusted for sample dilution and associate the samples results with the Tedlar bag blank and Tedlar bag LCS.

Some projects may require MDL↔RL reporting, when this is the case, report the values between the MDL and the RL as estimated indicating that in this region (MDL↔RL) the analyte can be qualitatively detected by not accurately quantified. Flag all results reported between the MDL and RL with a "J" data qualifier.

Some project may require RLs that are less than the laboratory's routine RL. Sample results may be reported to the project RL if the project RL is greater than the quantitation limit (QL). In this context, the QL is defined as the concentration of the low calibration standard. If the project RL is less than the QL, all values less than the QL must be reported as estimated and qualified with a "J".

Further guidance on the application and use of method detection limits (MDLs), reporting limits (RLs) and quantitation limits (QL) for the reporting analytical data is provided in laboratory SOP LP-LB-009 *Determination of Method Detection Limits.*

12.0 CALCULATIONS

12.1 Equation 1: Dilution Factor

$$DF = \frac{V_2}{V_1} x \frac{V_4}{V_3}$$

Where:
V_1 = Canister gas volume before dilution
V_2 = Canister gas volume after dilution
V_3 = gas volume analyzed
V_4 = gas volume basis of the analysis (200mL)
V_5 = gas volume used in secondary dilution
V_6 = final volume of secondary dilution

12.2 Equation 2: Relative Response Factor (RRF)

$$RRF = \frac{(A_x)(Q_{is})}{(A_{is})(Q_x)}$$

Where:
A_x = area of the quantitation ion of the analyte
A_{is} = area of the quantitation ion of the internal standard
Q_x = quantity of analyte purged in nanograms or concentration units
Q_{is} = quantity of internal standard purged in ng or concentration units

12.3 Equation 3: Percent Relative Standard Deviation (%RSD)

$$\%RSD = \frac{SD}{Mean} x100$$

Where:
SD = standard deviation individual response factors
Mean = average of initial calibration response factors

12.4 Equation 4: Sample Concentration

$$C_x = \frac{(A_x)(C_{IS})}{(A_{IS})(\overline{RRF})}(DF)$$

Where:
C_x = Compound concentration, (ppbv)
C_{IS} = Concentration of associated internal standard (ppbv).
A_{IS} = Area of quantitation ion for associated internal standard
A_x = Area of quantitation ion for compound
DF = Dilution Factor

Mean RRF = Average Relative Response Factor from initial calibration.

12.8 Equation 8: Percent Recovery (%R)

$$\%R = \frac{C_s - C_u}{C_n}(100)$$

Where:
C_s = Concentration of the spiked sample
C_u = Concentration of the unspiked sample
C_n = Nominal concentration of spike added

12.9 Equation 9: Precision (%RPD)

$$RPD = \frac{(C_1 - C_2)}{\left(\frac{C_1 + C_2}{2}\right)}(100)$$

Where:
C_1 = Measured concentration of the first sample
C_2 = Measured concentration of the second sample

13.0 DATA ASSESSMENT, CRITERIA AND CORRECTIVE ACTION

13.1. Data Review and Corrective Action

Review the samples, standards and QC samples against the acceptance criteria given in Table 3*. If the results do not fall within the established limits perform the recommended corrective action. If corrective action is not taken or is unsuccessful, document the situation with a nonconformance report and qualify the data using an appropriate data qualifier (See Appendix C for data qualifier definitions). For additional guidance regarding the laboratory's protocol and required elements for each level of data review (primary, secondary, and tertiary) refer to laboratory SOP LP-LB-003 *Data Review*.

14.0 METHOD PERFORMANCE

14.1. A demonstration of capability (IDOC) is required prior to use of this SOP and any time there is a significant change in instrument type, personnel or test method. IDOC procedures are further described in laboratory SOP LP-QA-011, *Employee Training*.

14.2. A Method Detection Limit (MDL) Study is performed at initial method set-up and subsequently once per 12 month period and when there is a significant change to the analytical system. The procedure and acceptance criteria for MDL studies are given in laboratory SOP LP-LB-009 Method Detection Limits. The laboratory considers an MDL

study based on the performance defined by the analysis from a 6 L canister as having a direct application to the analysis from a 1 L canister, with a scalar relationship of the established MDL to the volume analyzed. The application of the method to the analysis of samples collected in Tedlar bags is outside the scope of the TO-15 method, and MDL studies specific to this collection device are not routinely performed by the laboratory.

15.0 POLLUTION PREVENTION & WASTE MANAGEMENT

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

15.2 Waste Streams Produced by this Method

The following waste stream is produced when this procedure is performed:

- Expired Standards; these standards are returned to the vendor for disposal.

16.0 REFERENCES

16.1 Compendium Method TO-15, "Determination of Volatile Organic Compounds in Ambient Air using Specially Prepared Canisters and Analyzed by Gas Chromatography/Mass Spectrometry", US EPA, January, 1999.

16.2 Compendium Method TO-14, "Determination of Volatile Organic Compounds in Ambient Air using Specially Prepared Canisters and Analyzed by Gas Chromatography/Mass Spectrometry", US EPA, January, 1999.

17.0 TABLES, DIAGRAMS & FLOWCHARTS

17.1 Table 1: *Target Analyte List*
17.2 Table 2: *Ion Abundance Criteria*
17.3 Table 3: *QC Summary and Recommended Corrective Action*

Table 1: Target Analyte List, RL, Quantitation Ions, Internal Standard and Calibration Goup Assignments

**Denotes TO-14 Target Analyte List*

[1] TO-15 Target Analyte List

TO-14	Analyte[1]	CAS No.	6L RL (ppbv)	1L RL (ppbv)	Quant Mass	Qualifier Mass	Qualifier Mass	ISTD Group	Cal Group
•	Dichlorodifluoromethane	75-71-8	0.5	5	85	87		1	B
•	1,2-Dichlorotetrafluoroethane	76-14-2	0.2	2	85	135	87	1	A
•	Chloromethane	74-87-3	0.5	5	50	52		1	B
•	Vinyl Chloride	75-01-4	0.2	2	62	64		1	A
	1,3-Butadiene	106-99-0	0.2	2	54	0		1	A
•	Bromomethane	74-83-9	0.2	2	94	96		1	A
•	Chloroethane	75-00-3	0.2	2	64	66		1	A
	Bromoethene	593-60-2	0.2	2	106	108	81	1	A
•	Trichlorofluoromethane	75-69-4	0.2	2	101	103		1	A
•	Freon TF	76-13-1	0.2	2	101	151	103	1	A
•	1,1-Dichloroethene	75-35-4	0.2	2	96	61	63	1	A
	Acetone	67-64-1	5	50	43	58		1	C
	Isopropyl Alcohol	67-63-0	5	50	45	43		1	C
	Carbon Disulfide	75-15-0	0.5	5	76			1	B
	3-Chloropropene	107-05-1	0.2	2	41	76		1	A
•	Methylene Chloride	75-09-2	0.5	5	49	84	86	1	B
	tert-Butyl Alcohol	75-65-0	5	50	59	41	43	1	C
	Methyl tert-Butyl Ether	1634-04-4	0.5	5	73	43		1	B
	trans-1,2-Dichloroethene	156-60-5	0.2	2	61	96		1	A
	n-Hexane	110-54-3	0.2	2	57	86		1	A
•	1,1-Dichloroethane	75-34-3	0.2	2	63	65	83	1	A
	1,2-Dichloroethene (total)	540-59-0	0.2	2	61	96		1	A
	Methyl Ethyl Ketone	78-93-3	0.5	5	43	72		1	B
•	cis-1,2-Dichloroethene	156-59-2	0.2	2	96	98		1	A
•	Chloroform	67-66-3	0.2	2	83	85		1	A
	Tetrahydrofuran	109-99-9	5	50	42	72		2	C
•	1,1,1-Trichloroethane	71-55-6	0.2	2	97	99	61	2	A
	Cyclohexane	110-82-7	0.2	2	84	56		2	A
•	Carbon Tetrachloride	56-23-5	0.2	2	117	119		2	A
	2,2,4-Trimethylpentane	540-84-1	0.2	2	57	41	43	2	A
•	Benzene	71-43-2	0.2	2	78	77		2	A
•	1,2-Dichloroethane	107-06-2	0.2	2	62	98		2	A
	n-Heptane	142-82-5	0.2	2	43	71		2	A
•	Trichloroethene	79-01-6	0.2	2	95	130	132	2	A
	Methyl Methacrylate	80-62-6	0.5	5	69	41	39	2	B
•	1,2-Dichloropropane	78-87-5	0.2	2	63	41		2	A
	1,4-Dioxane	123-91-1	5	50	88	58		2	C
	Bromodichloromethane	75-27-4	0.2	2	83	85		2	A
•	cis-1,3-Dichloropropene	10061-01-5	0.2	2	75	110		2	A
	Methyl Isobutyl Ketone	108-10-1	0.5	5	43	58		2	B
•	Toluene	108-88-3	0.2	2	92	91		3	A
•	trans-1,3-Dichloropropene	10061-02-6	0.2	2	75	110		2	A
•	1,1,2-Trichloroethane	79-00-5	0.2	2	83	97	85	3	A
•	Tetrachloroethene	127-18-4	0.2	2	166	168	129	3	A

Table 1 Continued

TO-14	Analyte[1]	CAS No.	6L RL (ppbv)	1L RL (ppbv)	Quant Mass	Qualifier Mass	Qualifier Mass	ISTD Group	Cal Group
	Methyl Butyl Ketone	591-78-6	0.5	5	43	58		3	B
	Dibromochloromethane	124-48-1	0.2	2	129	127		3	A
•	1,2-Dibromoethane	106-93-4	0.2	2	107	109		3	A
•	Chlorobenzene	108-90-7	0.2	2	112	77	114	3	A
•	Ethylbenzene	100-41-4	0.2	2	91	106		3	A
•	Xylene (m,p)	1330-20-7	0.2	2	106	91		3	A
•	Xylene (o)	95-47-6	0.2	2	106	91		3	A
•	Styrene	100-42-5	0.2	2	104	78		3	A
	Xylene (total)	1330-20-7	0.2	2	106	91		3	A
	Bromoform	75-25-2	0.2	2	173	175	171	3	E
•	1,1,2,2-Tetrachloroethane	79-34-5	0.2	2	83	131	85	3	A
	4-Ethyltoluene	622-96-8	0.2	2	105	120		3	A
•	1,3,5-Trimethylbenzene	108-67-8	0.2	2	105	120		3	A
	2-Chlorotoluene	95-49-8	0.2	2	91	63		3	A
•	1,2,4-Trimethylbenzene	95-63-6	0.2	2	105	120		3	A
•	1,3-Dichlorobenzene	541-73-1	0.2	2	146	111	148	3	A
•	1,4-Dichlorobenzene	106-46-7	0.2	2	146	111	148	3	A
•	1,2-Dichlorobenzene	95-50-1	0.2	2	146	111	148	3	A
•	1,2,4-Trichlorobenzene	120-82-1	0.5	5	180	182		3	B
•	Hexachlorobutadiene	87-68-3	0.2	2	225	223		3	A
	Naphthalene	91-20-3	0.5	5	128			3	D
	Internal Standards								
•	Bromochloromethane	74-97-5	NA	NA	128	49	130	1	NA
•	1,4-Difluorobenzene	540-36-3	NA	NA	114			2	NA
•	Chlorobenzene-d5	3114-55-4	NA	NA	117			3	NA

Table 2: BFB Tune Criteria

BFB Key Ions and Ion Abundance Criteria	
Mass	**Ion Abundance Criteria**
50	8.0 to 40.0 percent of mass 95
75	30.0 to 66.0 percent of mass 95
95	Base Peak, 100 percent relative abundance
96	5.0 to 9.0 percent of mass 95
173	Less than 2.0 percent of mass 174
174	50.0 to 120.0 percent of mass 95
175	4.0 to 9.0 percent of mass 174
176	93.0 to 101.0 percent of mass 174
177	5.0 to 9.0 percent of mass 176

Table 3: QC Summary and Recommended Corrective Action (EPA TO-15, EPA TO-14)

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action
BFB Tune	Prior to calibration and every 24 hours during sample analysis	See Table 2	Correct problem, reanalyze
ICAL	As Needed	%RSD for each target analyte ≤ 30% with at most two exceptions up to 40%*	Correct problem, repeat calibration.
ICV/LCS	ICV: After each ICAL LCS: Per analytical batch or every 20 samples, whichever is more frequent	%R (70-130)	ICV: Correct problem, reverify second source standard. If that fails, repeat calibration. LCS: Correct problem, reanalyze LCS and all samples in associated batch. Flag data.
LCSD	Per analytical batch or every 20 samples, whichever is more frequent	%R (70-130) RPD ≤ 25	Correct problem, reanalyze LCSD and all samples in associated batch. Flag data.
CCV	Daily, before sample analysis	%D for each target analyte ≤ 30%	Correct problem, reanalyze, repeat initial calibration.
Method Blank	One per analytical batch or every 20 samples, whichever is more frequent	No analytes > RL DoD: ½ RL	Reanalyze all samples associated with method blank; Flag data.
Internal Standards	Added to every calibration standard and field and QC check sample.	± 40% area response from last acceptable calibration RT± .33min (20 seconds) from last acceptable calibration.	Reanalyze

STANDARD OPERATING PROCEDURE
SAMPLE MANAGEMENT

APPROVAL SIGNATURES

Laboratory Director: Michael F. Wheeler, Ph.D. Date: 9-10-03 KLM for Mike Wheeler

QA Manager: Kirstin L. McCracken Date: 9-10-03

Customer Service Manager: Christopher J. Anderson Date: 9-10-03

Department Supervisor: Peter E. Bowser Date: 9/10/03

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1.0 SCOPE AND APPLICATION

1.1. This SOP describes the routine laboratory procedures for sample container requests, sample receipt, storage, tracking, and scheduling the disposal of field samples received in the laboratory. The procedure is applicable to all samples received in the laboratory but project specific protocol may replace or supplement sections of this SOP as warranted. This SOP also describes the laboratory procedure for work initiation and project log in via the Laboratory Information Management System (LIMS).

2.0 SUMMARY

2.1. The laboratory's sample acceptance policy outlines the circumstances under which samples are accepted. Any comprised samples, nonconformance, abnormality or departure from the laboratory sample acceptance policy is documented, the client is contacted for resolution and/or the situation is noted in the project narrative.

On receipt the condition of the cooler is inspected and the temperature of the sample containers in each cooler is checked with an infrared (IR) thermometer. The cooler is unpacked and the contents are checked for agreement between the chain-of-custody and the sample container labels. Each sample is assigned a unique laboratory identification (LAB ID) that is unequivocally linked to the client's sample identification (ID). Individual sample containers with the same sample ID are subsequently assigned a unique bottle code used to track individual containers. A preservation (pH) check is performed for samples submitted for inorganic tests that require chemical preservation. The preservation of samples for volatile and extractable organics is checked in the respective analytical department prior to sample preparation or analysis. The samples are placed in designated storage areas that are temperature controlled and monitored.

Samples are logged into the Sample Registry Logbook and the Laboratory Management Information System (LIMS). After log in is complete, an Environmental Test Request (ETR) and department worksheets are created. The ETR and associated sample receipt paperwork are forwarded to the assigned Project Manager and the worksheets are placed in designated work folders for each laboratory section.

Unless otherwise specified by client or regulation, samples, digestates, and extracts are retained for 30 days after the date the report was sent to the client and then disposed of in accordance with Federal, State and local regulations following procedures described in the laboratory SOP LB-0010 *Hazardous Waste Disposal.*

3.0 DEFINITIONS

3.1. A list of general laboratory terms and definitions is given in Appendix A.

4.0 RESPONSIBILITIES

4.1. It is the responsibility of the department supervisor to implement the procedures given in this SOP and to ensure that employees are trained on and adhere to the procedures given in this SOP.

4.2. It is the responsibility of every employee to adhere to the procedures given in this SOP.

5.0 SAFETY

5.1. The toxicity or carcinogenicity of each chemical and/or sample encountered in the laboratory has not been fully established. Each chemical and/or sample should be regarded as a potential health hazard and exposure should be minimized as reasonably possible. Material Safety Data Sheets (MSDS) for reagents and chemical are available to all personnel. The MSDS for routine chemicals and reagents handled in sample management must be read prior to performing this procedure.

5.2. Safety glasses, latex gloves and protective clothing (lab coat) should be worn while performing tasks outlined in this SOP.

5.3. All laboratory personnel must be familiar with the laboratory environmental health and safety plan described in the STL Corporate Safety Manual.

5.4. Coolers that exhibit a strong odor or are suspected to contain highly contaminates samples are opened in a fume hood. Any samples exhibiting such characteristics are stored in the negative pressure room located in the sample receipt area.

6.0 PROCEDURE

6.1. Sample Container Requests

The laboratory will provide certified clean sample containers upon client request. At the time of request the following information is required: the date the sample containers are needed, site identification, number of samples per test method and matrix including trip blanks, equipment blanks, matrix spikes and sample duplicates. The laboratory can also provide ice packs, and extra packing materials as well as STL Chain of Custody forms, and custody seals. For all bottle requests, an advance notification of five business days is preferred to ensure sufficient time to process the order and delivery by ground transportation, but the laboratory will try to accommodate requests for expedited delivery when possible.

Requests for sample containers should be directed to the laboratory project manager (PM). When the container request is received, the PM will initiate a Sample Container Request Form and forward the request to a designated sample custodian who will check, compile, pack and arrange for shipment of the sample containers to the designated location.

The containers provided by the laboratory are purchased pre-cleaned and certified by a commercial vendor. A chemical preservative is added to the sampling containers by the commercial vendor. In some instance the chemical preservative may be supplied as a separate solution or neat material for addition after sampling in order to preserve the integrity of the sample. Unless thermal preservation is not required, all samples should be iced at the time of collection to a temperature of 0-6°C, with no frozen samples, unless freezing is the recommended thermal preservation technique.

The routine container and minimum volume or weight of sample needed is determined by the procedure. The laboratory must receive sufficient volume of sample to perform the test and analyze matrix related quality control samples such as sample duplicates and matrix spikes when mandated by regulatory program and/or a site specific quality manual or project plan. If insufficient volume is supplied, the data may be qualified by the laboratory in accordance with quality system requirements for laboratory accreditation (DOD, NELAC).

Tables that list the test method, routine container, chemical preservative, hold time (preparation and analytical), and minimum volume or weight of sample required to complete the analysis are provided in Appendix B.

6.2. Sample Acceptance Policy

The sample management department is staffed Monday-Friday from 7-5:30PM and from 9-3:00PM on Saturday to ensure that a sample custodian is available to accept delivery from commercial carriers (FED EX, UPS) and/or courier service. The laboratory can make arrangements to accommodate sample delivery outside this time schedule provided that sufficient advance notification is given. Samples received after normal business hours are received by designated personnel and placed in a refrigerated storage area in order to maintain thermal preservation.

The receipt of samples is acknowledged on the chain of custody (COC) form with the signature and date/time of the sample custodian. The condition of samples is recorded using a Cooler Receipt Checklist and the Sample Log In Form (DC-1). Any deficiencies identified during sample receipt are documented and communicated to the laboratory project manager (PM), who will attempt to contact the client and fully document any decision to proceed with analysis in the project record. Any consultation with the client should be immediate and timely (next business day or as specified in the project plan). Correspondence records and/or records of conversations concerning the decision to proceed with analysis and/or the disposition of rejected samples is maintained in the project record. All data associated with samples that did not meet the sample acceptance criteria are qualified and/or noted in the project narrative that accompanies the final test report.

Sample receipt is considered deficient when the following conditions are observed:

- Shipping cooler and/or samples are received outside the temperature specification
- Sample bottles are received broken or leaking
- Samples are received beyond holding time
- Samples are received without the appropriate preservation
- Samples were not received in appropriate containers
- Chain of Custody does not match the samples received
- Chain of Custody was not received or is incomplete*
- Custody seals are broken
- Evidence of tampering with the cooler and/or samples
- Headspace in VOA vials
- Seepage of extraneous water or other material into the samples
- Inadequate sample volume

- Illegible, impermanent, or non-unique sample labeling
- One or more cooler missing from a multi parcel shipment
- Shipping container is damaged

**Complete documentation shall include sample identification, the location date/time of collection, collector's name, preservation type, sample type and any special remarks concerning the sample.*

The laboratory uses a Sample Registry Logbook and the LIMS database to maintain a permanent chronological record that documents receipt of samples. The Sample Registry records the range of laboratory Ids associated with a set of samples along with the date and ETR number. The date and time of sample receipt is documented on the chain-of-custody form and linked to the laboratory ID on the Sample Log In Form that is provided in each data package report. A copy of this form is also retained in the project record. The client sample identification (field code) is linked to the laboratory ID code in the LIMS along with the matrix, date/time of sample collection, requested analyses and any comments or other concerns related to the project samples.

6.3. Sample Tracking, Storage & Security

6.3.1. Laboratory ID Assignment

Each sample is assigned a unique laboratory ID. The laboratory ID is a six-digit sequential number that is pre-printed on a durable label with indelible ink and affixed to each sample container. The laboratory ID is also used to identify subsequent extracts and/or digestates and is the link that associates the sample with laboratory activities. When multiple containers with the same sample ID are received, the label of each container is uniquely identified with a bottle code that corresponds to the bottle type and/or preservation and assigned a subsequent numeric designation. To identify the container that was used for each test method, the laboratory ID and bottle code is documented on the sample preparation log or the instrument run log for samples that do not require preparation.

Bottle codes are assigned as follows:

Bottle Code	Analysis/Preservation	Bottle Code	Analysis/Preservation
A	HCL VOA Vials	K	RSK-175 VOA Vials
B	H_2SO_4 Preserved	L	CO_2 VOA Vials
C	HNO_3 Preserved	M	MeOH VOA Vials
D	None Preserved	N	$NaHSO_4$ Preserved
E	Extraction Water /Amber	S	Soil
F	NaOH Preserved	T	TOC Analysis
G	DOC Analysis	R	Tissue
H	EPH Water	Z	Sulfide
I	HCl Preserved	P	Air
J	504.1 Analysis		

For example, if two 1L amber containers are received for field ID: MW-1 and test methods 8270C and 8081A are requested on the COC for analysis, the laboratory would assign a laboratory ID code to field sample MW-1 and affix a laboratory ID label on each container. To uniquely identify each container, the laboratory ID label for the first bottle would be appended with bottle code and numeric identifier "E1" and the laboratory ID label for the second container would be appended with bottle code and numeric identifier "E2".

6.3.2. Sample Storage Conditions

Unless otherwise specified by client or regulatory program, samples are stored according to the conditions specified in the test method. Inorganic, metals, air and geotechnical samples/digestates are stored at ambient temperature. Organic samples and extracts are stored under refrigeration at a temperature of 4±2°C or frozen at a temperature of -15±5°C. All samples are stored away from standards, reagents, or other potentially contaminating sources and samples designated for volatile organic analysis (VOA) are segregated from other samples. Samples that are or are suspected of high concentration are segregated in a negative pressure room in order to prevent cross contamination. A storage blank is maintained with VOA samples and routinely analyzed to verify that no cross contamination has occurred.

An automated electronic temperature monitoring system continuously checks and records the temperature of all refrigerated/frozen sample storage areas 7 days per week. The results of these checks are acquired and recorded in a database using Lab Tech's Notebook Pr v10.1 for Windows 95/98. Temperature measurements are recorded every 2 minutes. The data software is linked to a pager that alerts the department supervisor, or designee, when two consecutive temperature readings over a 2-hour time period are outside criteria. The temperature measurements for refrigerators are taken by thermistors and the freezer measurements are taken by thermocouples manufactured by Omega. The temperature readings from the thermistors and thermocouples is checked annually by the QA Department against an NIST traceable thermometer following the procedure given laboratory SOP LP-LB-0004 *Calibration of Thermometers.*

6.3.3. Sample Integrity

For most projects, a secure facility and monitored access to the laboratory is sufficient to ensure the integrity of samples. Access to the laboratory is controlled by measures that include locked doors, electronic access codes and a staffed reception area. All visitors must sign in to the visitor registry and while in the facility, they are escorted by laboratory personnel. When required by project specific scope of work or agency, a continuous record of sample and extract/digestate chain-of-custody within the laboratory will be maintained. To initiate internal chain-of-custody (ICOC) protocol, the PM must note the requirement for ICOC on the Sample Login Checklist.

6.4. Sample Receipt Protocol

On receipt the condition of the cooler/samples, including those items listed in 6.3 is checked and the results are recorded on laboratory forms designated for this purpose.

Procedure:

1) Examine the cooler and record the presence/absence of custody seals and if present, their condition (intact, broken) and serial number.

2) Screen each cooler for radioactivity with a Geiger counter. Hold the Geiger counter ¼ inch away from the cooler and sweep the outer surface of the cooler at a rate of 2 inches per second. If the reading is >0.05 mr/hr, immediately stop work, evacuate the work area, and notify the Project Manager and the EHS Coordinator. The laboratory does not accept samples that are known or suspected to be radioactive and the client must be contacted for resolution.

3) Check the temperature of the sample containers using the infrared thermometer.

   Unless otherwise specified by client project plan or regulatory program, the arrival temperature is considered acceptable if it is within 0-6°C. Samples that are hand delivered to the laboratory immediately following collection may not meet the criteria. In those cases, the thermal preservation of the samples is considered acceptable if there is evidence that the chilling process has begun, such as arrival on ice.

4) Open the cooler and inspect the sample containers. If any sample bottles are broken or if an odor is detected, immediately close the cooler and transport the cooler to an available fume hood.

5) Remove the samples from the cooler. Check to ensure that all samples listed on the chain-of-custody (COC) were received. Arrange the samples in the order provided on the COC and verify that the sample labels match the client description given on the COC. Record the presence/absence of sample tags on the Sample Log-in Form (DC-1) and if present, record the sample tag number(s).

6) Dispose of the packing materials and dry the inside of the shipping cooler. If the cooler has an odor or otherwise appears dirty, wash the cooler with warm water and Liqui-Nox Detergent diluted 1:100 with reagent water. Thoroughly rinse and dry the cooler. If washing does not seem effective, notify the department manager who will determine if the shipping cooler should be disposed.

7) Check the COC against the LIMS Quotation and the Sample Log In Checklist that was prepared by the PM (See Section 6.6). If these forms are not available, notify the PM of sample arrival and request that he/she generate these forms for the project. The test methods requested for analysis on the COC should agree with those listed on the Quotation. If they do not, contact the PM for resolution.

8) Assign a laboratory ID number to each sample and affix the laboratory ID label to each sample container. Assign bottle codes and numeric designations to the samples for which multiple containers were received.

9) Check the chemical preservation of each aqueous inorganic sample container for which the following test methods are requested: AVS, ammonia-N, COD, cyanide, ferrous iron, metals, mercury, hardness, nitrate/nitrite-N, oil & grease, phenols, total phosphorus, orthophosphorus, sulfide, TKN, TOC and TPH.

Invert the sample to mix and remove the sample container cap. Using a clean disposable pipette, transfer a drop of sample from the container to a narrow range pH indicator strip. Compare the color change on the indicator strip to the pH chart and record the pH reading on the Sample Preservation Form. Compare the ample pH against the requirement given in the tables provided in Appendix B. If the pH is not within specification, notify the PM for further instruction. If instructed by the client via the PM, add preservative to the samples with inadequate preservation. Record any pH adjustments made on the Preservation Check Form along with the date of preservation, your initials and the lot number of the preservative added.

Note: Samples designated for metals analysis should not be digested within 16 hours of preservation. If a pH adjustment is performed, sample management staff must flag the samples with the time of preservation or otherwise notify the metals department that a pH adjustment was performed.

10) Document all instances of comprised sample receipt and contact the PM for further instruction. To ensure thermal preservation is maintained, place samples in refrigerated/frozen storage within 2 hours of removal from the shipping cooler and/or keep them remain packed in ice during the log in procedure.

6.5. Sample Log In Procedure

Prior to the receipt of samples, the PM prepares a log in template in the LIMS database that is referred to as a 'Quotation' The quotation lists the preparation and analysis codes applicable to the project along with any additional project information. Additional project requirements such as project number, SDG assignment, job number, matrix spike requirements, sample disposal requirements, client contact information and subcontracting instructions and/or other contractual requirements including internal chain of custody is noted using a Sample Log In Checklist. When project samples are received, sample custodians log the samples into the LIMS database and the project quotation along with information provided on the Sample Log In Checklist is converted to an Environmental Test Request (ETR) that is used to initiate, schedule and track work for that project.

After an ETR is created it is reviewed for correctness and if no errors are found, analytical worksheets are created and placed in department work folders. The sample custodian generates the Sample Log In Form (CLP DC-1) from the LIMS database and forwards the original sample receipt documents to the PM along with Sample Log-In Form and the Sample Acceptance Policy & ETR Review Checklist for secondary review. Any errors identified during PM review are corrected and communicated to the laboratory in a timely manner.

All documents related to sample receipt and log in are retained in the project file or submitted to the client as part of the final data report.

6.6. Sample Disposal

Unless otherwise specified by project or regulation, samples, extracts and digestates are retained for 30 days from the date of invoice and then disposed by authorized personnel following the procedures given in laboratory SOP LB-0010 *Hazardous Waste Disposal.*

7.0 REFERENCES

7.1. *Constitution, Bylaws, and Standards National* Environmental Laboratory Accreditation Conference, May 2001. USEPA Office of Research and Development.

7.2. *Department of Defense Quality System Manual for Environmental Laboratories, Final Version 2,* June 2002, DOD Environmental Data Quality Workgroup.

7.3. *Shell for Analytical Chemistry Requirements*, February 2001, USACE EM 200-1-3.

8.0 TABLES, DIAGRAMS, FLOWCHARTS

8.1. Appendix A: *List of Terms & Definitions*

8.2. Appendix B: *Recommended Sample Containers, Preservation and Hold Times*

8.3. Appendix C: *Example Forms/Checklists*

REVISIONS FROM PREVIOUS SOP VERSION:

The name of the SOP was changed from Sample Receipt to Sample Management. The approval signatures were updated to identify current management team and the format and content of the SOP were updated to adhere to relevant requirements. This SOP replaces SOPs LP-SM-002 *Sample Handling*, LP-SM-003 *Preservation Check*, LP-SM-004 *Sampling Considerations*, LP-SM-005 *Sample Storage Temperature Monitoring*.

Appendix A

Terms & Definitions

The following definitions are used in the text of quality systems and laboratory operations. In preparing this list, the following definition references were used: STL Quality Management Plan, STL Burlington Laboratory Quality Manual, definitions developed by NELAC and those published in the DOD Quality Systems Manual which are taken from ISO 8402, ANSI/ASQC, EPA's Quality Assurance Division of Glossary and Terms, and definitions develop by NELAC. The source of each definition unless otherwise identified, is from STL documents.

Acceptance Criteria: Specified limits placed on characteristics of an item, process, or service defined in required documents. (DOD / ASQC)

Chain of Custody Form: a record that documents the possession of samples from the time of collection to receipt in the laboratory. This record generally includes: the number and types of containers; the mode of collection, collector, time of collection and requested analyses (NELAC).

Client: The party that has agreed to pay the bill for services rendered by the laboratory and with whom the laboratory has a contractual relationship for the project (DOD).

Comprised Sample: Those samples which are improperly sampled, insufficiently documented (chain of custody and other sample records and/or labels), improperly preserved, collected in improper containers or exceeding holding times when delivered to the laboratory. (NELAC)

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

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

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

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

Method Blank (MB): a blank matrix processed simultaneously with and under the same conditions as samples through all steps of the procedure. Also known as the preparation blank (PB).

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

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

Appendix B

Insert Spreadsheet of Recommended Sample Containers, Preservation and Hold Times

STL BURLINGTON COLLECTION AND RESERVATION REQUIREMENTS

Volatile Organic Compounds

Volatile Organics		Analytical	Contain[illegible]	[illegible]	Max Hold	[illegible]	[illegible]		
Parameter	Matrix	Method	Size (ml)	Sample	[illegible]	Amt	[illegible]	[illegible]	
Volatile Organics	Water	502.2	G/3X44 ml VOA	44 ml	14d	0.2 ml	1:1 HCL	4C	Add 25 mg ascorbic acid if residual chlorine is suspected
EDB/DBCP	Water	504	[illegible]	[illegible]	28d(ext)	75 ul	40 mg/L Sodium Thiosulfate	4C	
Volatile Organics	Water	524.2 Rev.4	G/3X44 ml VOA	44 ml	14d	0.2 ml	1:1 HCL	4C	Add 25 mg ascorbic acid if residual chlorine is suspected
Volatile Organics	Water	601/602	G/3X44 ml [illegible]	[illegible]	[illegible]	NA	NA	4C	
Volatile Organics	Soil	601/602	G/1X2 oz WM	30 g	14d	NA	NA	4C	
Volatile Organics	Water	624	G/3X[illegible]	[illegible]	[illegible]	0.2 ml	[illegible]	[illegible]	
Volatile Organics	Sediment	1624	G/1X2 oz WM	25 g	14d	NA	NA	-20C	
[illegible]	[illegible]	1624	G/1X2 oz WM	10 g	[illegible]	NA	[illegible]	[illegible]	
Volatile Organics	Water	5030B/8260B	G/3X44 ml VOA	44 ml	14d	0.2 ml	1:1 HCL	4C	
Volatile Organics	Soil	5035/8260B	G/1X2 oz WM G/3X44 ml [illegible] bisulfate preserved	[illegible]	[illegible]	20%	Sodium Bisulfate	[illegible]	See footnote 2 for other options.
Volatile Organics	Water	8021	G/3X44 ml VOA	44 ml	14d	0.2 ml	1:1 HCL	4C	
Volatile Organics	Soil	8021	G/1X2 oz WM	[illegible]	[illegible]	NA	NA	4C	
Volatile Organics	Water	OLC02.1	G/3X44 ml VOA	44 ml	10d VTSR	0.2 ml	1:1 HCL	4C	
Volatile Organics	Soil	OLMLLS	G/1X2 oz WM	25 g	10d VTSR	NA	NA	4C	
Volatile Organics	Water	OLM03	G/3X44 ml VOA	44 ml	10d VTSR	0.2 ml	1:1 HCL	4C	
Volatile Organics	Soil	OLM03	G/1X2 oz WM	25 g	10d VTSR	NA	NA	4C	

STL BURLINGTON COLLECTION AND PRESERVATION REQUIREMENTS

Volatile Organic Compounds - cont'd

Petroleum Organics Parameter	Matrix	Analytical Method	Container Type/ Size(ml)	Min. Sample	Max Hold Time	[illegible]	Preservation Type	Temp	Notes
Volatile Organics	Air	ASTM D1946	Summa Cannister	200 ml	20d	NA	NA	NA	
Volatile Organics	[illegible]	ASTM D1946	[illegible]	200 ml	[illegible]	[illegible]	[illegible]	NA	
Voaltile Organics	Air	TO14/TO15	Tedlar Bags	200 ml	3d	NA	NA	NA	
Volatile Organics	Air	TO14/TO15	Summa Canister	200 ml	20d	NA	NA	[illegible]	
Voaltile Organics	Air	RSK-175	G/1X44 ml VOA	44 ml	14d	0.2 ml	1:1 HCL	4C	No HCL if CO2 required!
Total Petroleum Hydrocarbons (TPH) as Gasoline	Water	California Luft	G/3X40 ml VOA	44 ml	14d	2 ml	1:1 HCL	[illegible]	
Total Petroleum Hydrocarbons (TPH) as Gasoline	Soil	California Luft	G/1X2 oz WM	25 g	14d	NA	NA	4C	
Volatile Petroleum Hydrocabons	Water	MADEP VPH	G/3X40 ml VOA	[illegible]	14d	[illegible]	[illegible]	4C	
Volatile Petroleum Hydrocabons	Soil	MADEP VPH	G/1X44 ml VOA	25 g	28d	25 ml	Methanol	4C	

STL BURLINGTON COLLECTION AND PRESERVATION REQUIREMENTS

Semivolatile Organic Compounds

Semivolatile Organics Parameter	Matrix	Analytical Method	Container Type Size (ml)	Min Sample	Max Hold Time	Preservation Amt	Preservation Type	Temp	Notes
Nitrogen / Phosphorous Pesticides	Water	EPA 507	G/2X1000 ml	1000 ml	7d(ext) / 14d analy	NA	NA	4C	
Chlorinated Pesticides	Water	EPA 508	G/2X1000 ml	1000 ml	7d(ext) / 14d analy	NA		4C	
Chlorinated Acids	Water	EPA 515	G/2X1000 ml	1000 ml	14d(ext) / 28d analy	NA	NA	4C	
Organochlorine PCBs	Water	EPA 508	G/2X1000 ml	1000 ml	7d(ext) / 40d analy	NA		4C	
Polynuclear Aromatic Hydrodcarbons	Water	EPA 610	G/2X1000 ml	1000 ml	7d(ext) / 40d analy	NA	NA	4C	
Chlorinated Herbicides	Water	EPA 615	G/2X1000 ml	1000 ml	7d(ext) / 40d analy	NA	NA	4C	
Triazine Pesticides	Water	EPA 619	G/2X1000 ml	1000 ml	7d(ext) / 40d analy	NA	NA	4C	
Carbamate and Urea Pesticides	Water	EPA 632	G/2X1000 ml	1000 ml	7d(ext) / 40d analy	NA	NA	4C	
Semivolatile Organics	Sediment	1625	G/1X2 oz WM	250 g	180d(ext) / 40d analy	NA	NA	-20C	
Semivolatile Organics	Tissue	1625	G/1X2 oz WM	250 g	10d VTSR analy	NA	NA	-20C	
Semivolatile Organics	Water	1625	G/2X1000 ml	1000 ml	10d VTSR (ext) / 40d analy	NA	NA	4C	

STL BURLINGTON COLLECTION AND PRESERVATION REQUIREMENTS

Semivolatile Organic Compounds - cont'd

Semivolatile Organics								
Parameter	Matrix	Analytical Method	Container Type Size (ml)	Min Sample Volume	Max Hold Time	Preservation Type		Temp	Notes
Organochlorine Pesticides	Water	EPA 8081A	G/2X1000 ml	1000 ml	7d(ext) / 40d analy	NA	NA	4C	
Organochlorine Pesticides	Soil	EPA 8081A	G/1X8 oz WM	100 G	14d(ext) / 40d analy	NA	NA	4C	
Polychlorinated Biphenyls	Water	EPA 8082	G/2X1000 ml	1000 ml	7d(ext) / 40d analy	NA	NA	4C	
Polychlorinated Biphenyls	Soil	EPA 8082	G/1X8 oz WM	100 G	14d(ext) / 40d analy	NA	NA	4C	
Organophosphorous Pesticides	Water	EPA 8141A	G/2X1000 ml	1000 ml	7d(ext) / 40d analy	NA	NA	4C	
Organophosphorous Pesticides	Soil	EPA 8141A	G/1X8 oz WM	100 G	14d(ext) / 40d analy	NA	NA	4C	
Chlorinated Herbicides	Water	EPA 8151A	G/2X1000 ml	1000 ml	7d(ext) / 40d analy	NA	NA	4C	
Chlorinated Herbicides	Soil	EPA 8151A	G/1X8 oz WM	100 G	14d(ext) / 40d analy	NA	NA	4C	
Semivolatile Organics	Water	EPA 8270C	G/2X1000 ml	1000 ml	7d(ext) / 40d analy	NA	NA	4C	
Semivolatile Organics	Soil	EPA 8270C	G/1X8 oz WM	100 G	14d(ext) / 40d analy	NA	NA	4C	
Polynuclear Aromatic Hydrodcarbons	Water	EPA 8310	G/2X1000 ml	1000 ml	7d(ext) / 40d analy	NA	NA	4C	
Polynuclear Aromatic Hydrodcarbons	Soil	EPA 8310	G/1X8 oz WM	100 G	14d(ext) / 40d analy	NA	NA	4C	

STL BURLINGTON COLLECTION AND PRESERVATION REQUIREMENTS

Semivolatile Organic Compounds - cont'd

Semivolatile Organics		Analytical	Container Type/	Min.	Max Hold	Preservation			
Parameter	Matrix	Method	Size (ml)	Sample	Time	Amt	Type	Temp	Notes
Formaldehyde	Water	EPA 8315A	G/2X250 ml	100 ml	7d(ext) / 40d analy	NA	NA	4C	
Formaldehyde	Soil	EPA 8315A	G/1X4 oz WM	5 g	14d(ext) / 40d analy	NA	NA	4C	
N-Methylcarbamates	Water	EPA 8318	G/2X1000 ml	1000 ml	7d(ext) / 40d analy	NA	NA	4C	
Nitroaromatics and Nitramines	Water	EPA 8330	G/2X1000 ml	1000 ml	7d(ext) / 40d analy	NA	NA	4C	
Semivolatile Organics	Water	CLP OLM03	G/2X1000 ml	1000 ml	5d VTSR (ext) / 40d analy	NA	NA	4C	
Semivolatile Organics	Soil	CLP OLM03	G/1X8 oz WM	100 g	10d VTSR (ext) / 40d analy	NA	NA	4C	
Organochlorine Pesticides and PCBs	Water	CLP OLM03	G/2X1000 ml	1000 ml	5d VTSR (ext) / 40d analy	NA	NA	4C	
Organochlorine Pesticides and PCBs	Soil	CLP OLM03	G/1X8 oz WM	100 g	10d VTSR (ext) / 40d analy	NA	NA	4C	
Chlorinated Pesticides and Polychlorinated Biphenyl Cogeners	Water	SATPPCB	G/2X1000 ml	1000 ml	7d(ext) / 40d analy	NA	NA	4C	
Chlorinated Pesticides and Polychlorinated Biphenyl Cogeners	Soil	SATPPCB	G/1X8 oz WM	100 g	10d(ext) / 40d analy	NA	NA	4C	

STL BURLINGTON COLLECTION AND PRESERVATION REQUIREMENTS

Petroleum Organics

Parameter	Matrix	Analytical Method	Container Type/ Size (ml)	Min Sample	Max Hold Time	Preservation Type	Preservation Type	Temp	Notes
Total Petroleum Hydrocarbons (TPH) as Diesel	Water	California Luft	G/2X1000 ml	1000 ml	7d(ext) / 40d analy	NA	NA	4C	
Total Petroleum Hydrocarbons (TPH) as Diesel	Soil	California Luft	G/2X4 oz WM	100 g	14d(ext) / 40d analy	NA	NA	4C	
Extractable Petroleum Hydrocabons	Water	MADEP EPH	G/2X1000 ml	1000 ml	14d(ext) / 40d analy	NA	NA	4C	
Extractable Petroleum Hydrocabons	Soil	MADEP EPH	G/2X4 oz WM	100 g	14d(ext) / 40d analy	NA	NA	4C	

STL BURLINGTON COLLECTION AND PRESERVATION REQUIREMENTS

Inorganic Analytes

Metals

Parameter	Matrix	Analytical Method	Container Type/ Size (ml)	Min. Sample	Max Hold Time	Preservatives Amt	Type	Temp	Notes
TAL Metals	Water	CLP ILM04	P/1X500 ml	100 ml	180d	3 ml/L	1:1 HNO3	Ambient	
TAL Metals	Soil	CLP ILM04	G/1X4 oz WM	10 g	180d	NA	NA	4C	
Mercury	Water	CLP ILM04	P/1X500 ml	100 ml	26d	3 ml/L	1:1 HNO3	Ambient	
Mercury	Soil	CLP ILM04	G/1X4 oz WM	10 g	26d	NA	NA	4C	
TAL Metals	Water	EPA 6010B	P/1X500 ml	100 ml	180d	3 ml/L	1:1 HNO3	Ambient	
TAL Metals	Water	EPA 6010B	[illegible]	[illegible] ml	180d	[illegible]	[illegible]	Ambient	
TAL Metals	Soil	EPA 6010B	G/1X4 oz WM	10 g	180d	NA	NA	4C	
TAL Metals	Water	EPA 200.8	P/1X500 ml	100 ml	180d	3 ml/L	1:1 HNO3	Ambient	
Mercury	Water	EPA 200.8	P/1X500 ml	100 ml	28d	3 ml/L	1:1 HNO3	Ambient	
Mercury	Water	EPA [illegible]	[illegible]	[illegible] ml	28d	[illegible]	[illegible]	Ambient	
Mercury	Soil	EPA 7471	G/1X4 oz WM	10 g	28d	NA	NA	4C	

STL BURLINGTON COLLECTION AND PRESERVATION REQUIREMENTS

General Chemistry

Parameter	Matrix	Analytical Method	Container SP[illegible]	Sample	Max Hold Time	Preservation Amt	Preservation Type	Temp	Notes
Acid Volatile Sulfide	Water	QSIA	P,G/2X500 ml	500 ml	14d	2 ml / 2 pellets	ZnAc / NaOH	4C	
[illegible]olatile Sulfide	[illegible]	QSIA	[illegible]X4 oz W[illegible]		14d	NA	[illegible]		
AVS w/ SEM	Water	QSIA	P,G/2X500 ml	500 ml	14d	NA	NA	4C	
AVS w/ SEM	[illegible]	QSIA	[illegible]X4 o[illegible]		[illegible]	NA	N[illegible]		
Acidity	Water	305.2	P,G/1X500 ml	100 ml	14d	NA	NA	4C	
Alkalinity	[illegible]	310.1	P,G/1X5[illegible]		14d	NA	[illegible]		
Alkalinity	Water	SM2320B	P,G/1X500 ml	100 ml	14d	NA	NA	4C	
Ammonia	[illegible]	350.2	P,G/[illegible] ml	500 ml	[illegible]	[illegible]	70	4C	
Ammonia-N	Soil	350.2	G/1X4 oz WM	10 g	28d	NA	NA	4C	
BOD(5-day)	Water	405.1	P,G/1[illegible] ml	1000 ml	48hrs	NA	NA	4C	*VT required 24hr HT.
Bromide by IC	Water	300.0	P,G/1X500 ml	10 ml	28d	NA	NA	4C	

STL BURLINGTON COLLECTION AND PRESERVATION REQUIREMENTS

General Chemistry - cont'd

Parameter	Matrix	Analytical Method	Container Type/ Size (ml)	Min Sample	Max Hold Time	[illegible]	[illegible]	Temp	Note
Chloride by IC	Water	300.0	P,G/1X500 ml	10 ml	28d	NA	NA	4C	
Chloride	Water	325.2/9250	P,G/1X500 ml	[illegible]	[illegible]	[illegible]	[illegible]	4C	
Chloride	Soil	9250	G/1X4 oz WM	50 g	28d	NA	NA	4C	
COD	Water	[illegible]	P,G/1X500 ml	[illegible]	[illegible]	[illegible]	70% H2SO4	4C	
COD	Soil	410.1	G/1X4 oz WM	2 g	28d	NA	NA	4C	
Color	Water	SM2120B	Container Type/	50 ml	48hrs	NA	NA	4C	
Conductivity	Water	120.1/9050	P,G/1X500 ml	100 ml	28d	NA	NA	4C	
Conductivity	Water	SM2510B	P,G/1X500 ml	100 ml	28d	NA	NA	4C	
Cyanide	Water	335.2/9010	P,G/2X500 ml	[illegible]	[illegible]	[illegible]	NaOH / Ascorbic Acid	[illegible]	
Cyanide	Water	ILM04	P,G/2X500 ml	500 ml	14d	5 pellets / 1g	NaOH / Ascorbic Acid	4C	
Cyanide, Total	Water	SM4500CNE	P,G/2X500 ml	[illegible]	[illegible]	[illegible]	NaOH / Ascorbic Acid	[illegible]	

STL BURLINGTON COLLECTION AND PRESERVATION REQUIREMENTS

General Chemistry - cont'd

Parameter	Matrix	Analytical Method	Container Size (ml)	Min Sample	Max Hold Time	Preservation Amt	Preservation Type	Temp	Notes
Cyanide, Amenable to Chloride	Water	SM4500CNG	P,G/2X500 ml	500 ml	14d	5 pellets / 1g	NaOH / Ascorbic Acid	4C	
Cyanide	[illegible]	[illegible]	G/1X4 oz WM	5 g	14d	[illegible]	NA	[illegible]	
Disolved Oxygen	Water	360.2	P,G/1X500 ml	300 ml	immediately	BOD bottle	NA	4C	
EDTA	Water	[illegible]	P,G/1X500 ml	250 ml	[illegible]	[illegible]	NA	4C	
Fluoride	Water	340.2	P/1X500 ml	20 ml	28d	NA	NA	4C	
Fluoride	Water	[illegible]	P/1X500 ml	20 ml	28d	[illegible]	NA	4C	
Fluoride	Soil / Effluent	340.1	P/1X500 ml	50 g	28d	NA	NA	4C	
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
Hardness (Total)	Water	130.2	P,G/1X500 ml	100 ml	28d	3 ml/L	1:1 HNO3	4C	
Heating	Soil / [illegible]	ASTM D23	P,G/1X500 ml	[illegible]	[illegible]	NA	NA	4C	
Hex. Chromium	Water	7196	P,G/1X500 ml	100 ml	24hr	NA	NA	4C	
Hex. Chromium	Soil	[illegible]	G/1X4 oz WM	[illegible]	3d ext / [illegible]	[illegible]	NA	4C	

STL BURLINGTON COLLECTION AND PRESERVATION REQUIREMENTS

General Chemistry - cont'd

Parameter	Matrix	Analytical Method	Container Size	Min. Sample	Max Hold Time	Preservation Type	Preservation Temp	Notes
Ignitability	Water / Soil	1010	G/1X500 ml	250 ml	14d	NA	NA	4C
Nitrate-N by IC	Water	[illegible]	P,G/1X500 ml	[illegible]	[illegible]	[illegible]	[illegible]	4C
Nitrate/Nitrite-N	Water	353.2	P,G/1X500 ml	10 ml	28d	3 ml/L	70% H2SO4	4C
Nitrate/Nitrite-N	Soil	353.2	G/1X4 oz WM	[illegible]	[illegible]	[illegible]	[illegible]	4C
Nitrite Nitrogen	Water	SM4500N02B	P,G/1X500 ml	100 ml	48hr	NA	NA	4C
Nitrite Nitrogen	Water	354.1	P,G/1X500 ml	[illegible] ml	[illegible]	[illegible]	NA	[illegible]
Nitrite Nitrogen	Soil	354.1	G/1X4 oz WM	100g	48hr	NA	NA	4C
Oil and Grease	Water	[illegible]	G/1X500 ml	[illegible] ml	28d	5 ml	1:1 HCl	4C
Oil and Grease	Soil	413.1	G/1X4 oz WM	50 g	28d	NA	NA	4C
Oil and Grease	Water	413.2	G/1X500 ml	1000 ml	28d	5 ml	1:1 HCl	4C
Oil and Grease	Soil	413.2	G/1X4 oz WM	50 g	28d	NA	NA	4C
Orthophosphate as P	Water	SM4500PE	P,G/1X500 ml	[illegible] ml	48hr	NA	NA	4C

STL BURLINGTON COLLECTION AND PRESERVATION REQUIREMENTS

General Chemistry
cont'd

Parameter	Matrix	Analytical Method	Container Type (Size/ml)	Min. Sample	Max Hold Time	Preservation Amt	Preservation Type	Preservation Temp	Notes
Orthophosphate as P	Water	365.2	P,G/1X500 ml	50 ml	48hr	NA	NA	4C	
Orthophosphate as P	Water	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
Orthophosphate as P	Water	300.0	P,G/1X500 ml	10 ml	48hr	NA	NA	4C	
pH	Water	150.1 / 9040	P,G/[illegible]	50 ml	[illegible]	[illegible]	[illegible]	[illegible]	
pH	Soil	9045.0	G/1X4 oz WM	10 g	immediately	NA	NA	4C	
Phenol (Total)	Water	420.1 / 9065	G/1X[illegible]	500 ml	[illegible]	[illegible]	[illegible]	[illegible]	
Phenol (Total)	Soil	420.1 / 9065	G/1X4 oz WM	5 g	28d	NA	NA	4C	
Phosphate-P (Total)	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
Phosphate-P (Total)	Soil	365.2	G/1X4 oz WM	10 g	28d	NA	NA	4C	
Reactive Cyanide	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
Reactive Cyanide	Soil	9014M	G/1X4 oz WM	50 g	7d	NA	NA	4C	
Reactive Sulfide	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	

STL BURLINGTON COLLECTION AND PRESERVATION REQUIREMENTS

General Chemistry
cont'd

Parameter	Matrix	Analytical Method	Container Type/ Size (ml)	Min. Sample	Max Hold Time[1]	Preservative Amt	Preservative Type	Temp	Notes
Reactive Sulfide	Soil	9034M	G/1X4 oz WM	50 g	7d	NA	NA	4C	
[illegible]	[illegible]	330.4	Amber,G/1X500 ml	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
Percent Solids	Soil	IN623	G/1X4 oz WM	10 g	28 d	NA	NA	4C	
Total Dissolved Solids	Water	SM2540C	P,G/1X500 ml	100 ml	7d	NA	NA	4C	
Total Suspended Solids	Water	SM2540D	P,G/1X1000 ml	[illegible]	[illegible]	NA	[illegible]	[illegible]	
Total Solids	Water	SM2540B	P,G/1X500 ml	100 ml	7d	NA	NA	4C	
Volatile Solids	Water	SM2540E	P,G/1X500 ml	[illegible]	[illegible]	NA	[illegible]	[illegible]	
Settleable Solids	Water	SM2540F	P,G/1X1000 ml	1000 ml	48 hr	NA	NA	4C	
Specific Gravity	Water	QSIA	P,G/1X500 ml	100 ml	28 d	NA	[illegible]	[illegible]	
Specific Gravity	Soil	QSIA	G/1X4 oz WM	50 g	28 d	NA	NA	4C	
Sulfate	Water	375.4	P,G/1X500 ml	100 ml	28 d	NA	NA	[illegible]	
Sulfate	Water	9036	P,G/1X500 ml	100 ml	28 d	NA	NA	4C	

STL BURLINGTON COLLECTION AND PRESERVATION REQUIREMENTS

General Chemistry
cont'd

Parameter	Matrix	Analytical Method	Container Type Size	Min. Sample	Max. Time	[illegible]	[illegible]	Temp	Notes
Sulfate	Water	300	P,G/1X500 ml	10 ml	28 d	NA	NA	4C	
Sulfate	Soil	9036	[illegible]	[illegible]	28 [illegible]	[illegible]	[illegible]	[illegible]	
Sulfide	Water	376.2	P,G/1X500 ml	250 ml	7 d	2 ml/L / 2 pellets	zinc acetate / NaOH	4C	
Sulfide	Water	9030	P,G/1X500 ml	500 ml	7 d	[illegible]	zinc acetate / NaOH	4C	
Sulfide	Soil	IN715	G/1X4 oz WM	50 g	7 d	NA	NA	4C	
Sulfite	Water	[illegible]	P,G/1X500 ml	250 ml	ASAP	[illegible]	NA	4C	
Surfactant (MBAS)	Water	425.1	P,G/1X500 ml	100 ml	48 hr	NA	NA	4C	
TKN	Water	351.3	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
TKN	Soil	351.3	G/1X4 oz WM	10 g	28 d	NA	NA	4C	
TOC	Water	[illegible]	G/2X44 ml VOA	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
TOC	Water	9060	G/4X44 ml VOA	44 ml	28 d	0.2 ml	70% H2SO4	4C	
[illegible]	Soil	IN847	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	

STL BURLINGTON COLLECTION AND PRESERVATION REQUIREMENTS

General Chemistry
cont'd

Parameter	Matrix	Analytical Method	Container Size	Min Sample	Max Hold Time	Amount	Preservation	Temp	Notes
TOX	Water	450.1	Amber G/1X500 ml	100 ml	28 d	0.2 ml	70% H2SO4	4C	
TOX	Soil	IN899	[illegible]	[illegible]	28 d	[illegible]	[illegible]	[illegible]	
TPH	Water	418.1	G/1X1000 ml	1000 ml	28 d	5 ml/L	1:1 HCL	4C	
TPH	Soil	IN670	[illegible] oz WM	[illegible]	28 d	NA	NA	[illegible]	
Turbidity	Water	180.1	P,G/1X500 ml	100 ml	48 hr	NA	NA	4C	

1 Individual state holding times may differ from the Federally mandated minimum requirements. Please review comments and methods to determine if alternate holding times are applicable.

2 EPA Region 9 accepts the following preservation options for VOCs:

1) A VOA vial with 5 mL of water without preservative and approximately 5 g of sample. Which must be analyzed within 48 hours of collection by closed system purge and trap.
2) A VOA vial with approximately 5 g of sample. Water must be introduced through the septa at time of analysis by closed system purge and trap. Sample must be analyzed within 48 hours of collection if stored at 4±2°C or 7 days if frozen. (This alternative must be approved on a project specific basis.)
3) An En Core™ sampler which is analyzed or preserved within 48 hours of collection if stored at 4±2°C or analyzed within 7 days if frozen. (This alternative must be approved on a project specific basis.)

SAMPLE HOLDING TIMES, RECOMMENDED DIGESTION VOLUMES AND RECOMMENDED COLLECTION VOLUMES FOR INORGANIC SAMPLE CONTAINERS, PRESERVATION, TECHNIQUES, AND HOLDING TIMES

VOLATILE ORGANICS			
Sample Matrix	Container	Preservative	Holding Time
Concentrated Waste Samples	Method 5035: 40-mL vials with stirring bar. Method 5021: See method. Methods 5031 & 5032: 125-mL widemouth glass container. Use Teflon-lined lids for all procedures.	Cool to 4 C.	14 days
Aqueous Samples With No Residual Chlorine Present	Methods 5030, 5031, & 5032: 2 X 40-mL vials with Teflon-lined septum caps	Cool to 4 C and adjust pH to less than 2 with H_2SO_4, HCl, or solid $NaHSO_4$.	14 days
Aqueous Samples WITH Residual Chlorine Present	Methods 5030, 5031, & 5032: 2 X 40-mL vials with Teflon-lined septum caps	Collect sample in a 125-mL container which has been pre-preserved with 4 drops of 10% sodium thiosulfate solution. Gently swirl to mix sample and transfer to a 40-mL VOA vial. Cool to 4 C and adjust pH to less than 2 with H_2SO_4, HCl, or solid $NaHSO_4$.	14 days
Acrolein and Acrylonitrile in Aqueous Sample	Methods 5030, 5031, & 5032: 2 X 40-mL vials with Teflon-lined septum caps	Adjust to pH 4-5. Cool to 4 C.	14 days
Solid Samples (e.g. soils, sediments, sludges, ash)	Method 5035: 40-mL vials with septum and stirring bar. Method 5021: See method. Methods 5031 & 5032: 125-mL widemouth glass container with Teflon-lined lids.	See the individual methods.	14 days

			until analyzed
<u>Mercury</u>:			
Aqueous			
Total	100	400	HNO_3 to pH <2 28 days
Dissolved	100	400	Filter; HNO_3 to pH <2 28 days
Solid			
Total	0.2 g	200 g	28 days Store at 4°± 2°C until analyzed

[a] Unless stated otherwise.
[b] Either glass or plastic containers may be used.
[c] Any sample volume reduction from the reference method's instructions must be made in the exact proportion as described in the method and representative sampling must be maintained.

(EPA SW846 Preservation Requirements)

(EPA SW846 Preservation Requirements)

SEMIVOLATILE ORGANICS/ORGANOCHLORINE PESTICIDES/PCBs AND HERBICIDES			
Sample Matrix	Container	Preservative	Holding Time
Concentrated Waste Samples	125-mL widemouth glass with Teflon-lined lid	None	Samples extracted within 14 days and extracts analyzed within 40 days following extraction.
Aqueous Samples With No Residual Chlorine Present	1-gal., 2 x 0.5-gal., or 4 x 1-L amber glass container with Teflon-lined lid	Cool to 4 C	Samples extracted within 7 days and extracts analyzed within 40 days following extraction.
Aqueous Samples WITH Residual Chlorine Present	1-gal., 2 x 0.5-gal., or 4 x 1-L, amber glass container with Teflon-lined lid.	Add 3-mL 10% sodium thiosulfate solution per gallon (or 0.008%). Addition of sodium thiosulfate solution to sample container may be performed in the laboratory prior to field use. Cool to 4 C.	Samples extracted within 7 days and extracts analyzed within 40 days following extraction.
Solid Samples (e.g. soils, sediments, sludges, ash)	250-mL widemouth glass container with Teflon-lined lid	Cool to 4 C	Samples extracted within 14 days and extracts analyzed within 40 days following extraction.

Wastewater (40CFR136) REQUIRED CONTAINERS, PRESERVATION TECHNIQUES, AND HOLDING TIMES

Parameter No./name	Container [1]	Preservation [2,3]	Maximum holding time [4]
Table IA—Bacteria Tests:			
1–4 Coliform, fecal and total	P,G	Cool, 4C, 0.008% $Na_2S_2O_3$ [5]	6 hours.
5 Fecal streptococci	P,G	Cool, 4C, 0.008% $Na_2S_2O_3$ [5]	6 hours.
Table IA—Aquatic Toxicity Tests:			
6–10 Toxicity, acute and chronic	P,G	Cool, 4 °C [10]	36 hours.
Table IB—Inorganic Tests.			
1. Acidity	P, G	Cool, 4°C	14 days.
2. Alkalinity	P, G	do	Do.
4. Ammonia	P, G	Cool, 4°C, H_2SO_4 to pH<2	28 days.
9. Biochemical oxygen demand	P, G	Cool, 4°C	48 hours.
10. Boron	P, PFTE, or Quartz.	HNO_3 TO pH<2	6 months.
11. Bromide	P, G	None required	28 days.
14. Biochemical oxygen demand, carbonaceous	P, G	Cool, 4°C	48 hours.
15. Chemical oxygen demand	P, G	Cool, 4°C, H_2SO_4 to pH<2	28 days.
16. Chloride	P, G	None required	Do.
17. Chlorine, total residual	P, G	do	Analyze immediately.
21. Color	P, G	Cool, 4°C	48 hours.
23–24. Cyanide, total and amenable to chlorination.	P, G	Cool, 4°C, NaOH to pH>12, 0.6g ascorbic acid [5].	14 days.[6]
25. Fluoride	P	None required	28 days.
27. Hardness	P, G	HNO_3 to pH<2, H_2SO_4 to pH<2	6 months.
28. Hydrogen ion (pH)	P, G	None required	Analyze immediately.
31, 43. Kieldahl and organic nitrogen	P, G	Cool, 4°C, H_2SO_4 to pH<2	28 days.
Table IC—Organic Tests [8]			
13, 18–20, 22, 24–28, 34–37, 39–43, 45–47, 56, 76, 104, 105, 108–111, 113. Purgeable Halocarbons.	G, Teflon-lined septum.	Cool, 4 °C, 0.008% $Na_2S_2O_3$ [5].	14 days.
6, 57, 106. Purgeable aromatic hydrocarbons	do	Cool, 4 °C, 0.008% $Na_2S_2O_3$,[5] HCl to pH2[9].	Do.
3, 4. Acrolein and acrylonitrile	do	Cool, 4 °C, 0.008% $Na_2S_2O_3$,[5] adjust pH to 4–5[10].	Do.
23, 30, 44, 49, 53, 77, 80, 81, 98, 100, 112. Phenols [11].	G, Teflon-lined cap..	Cool, 4 °C, 0.008% $Na_2S_2O_3$ [5]	7 days until extraction. 40 days after extraction.
7, 38. Benzidines [11]	do	do	7 days until extraction.[13]
14, 17, 48, 50–52. Phthalate esters [11]	do	Cool, 4 °C	7 days until extraction; 40 days after extraction.
82–84. Nitrosamines [11 14]	do	Cool, 4 °C, 0.008% $Na_2S_2O_3$,[5] store in dark.	Do.
88–94. PCBs [11]	do	Cool, 4 °C	Do.
54, 55, 75, 79. Nitroaromatics and isophorone [11]	do	Cool, 4 °C, 0.008% $Na_2S_2O_3$,[5] store in dark.	Do.
1, 2, 5, 8–12, 32, 33, 58, 59, 74, 78, 99, 101. Polynuclear aromatic hydrocarbons [11].	do	do	Do.
15, 16, 21, 31, 87. Haloethers [11]	do	Cool, 4 °C, 0.008% $Na_2S_2O_3$ [5]	Do.
29, 35–37, 63–65, 73, 107. Chlorinated hydrocarbons [11].	do	Cool, 4 °C	Do.
60–62, 66–72, 85, 86, 95–97, 102, 103. CDDs/CDFs [11].			
aqueous: field and lab preservation.	G	Cool, 0–4 °C, pH<9, 0.008% $Na_2S_2O_3$ [5].	1 year.
Solids, mixed phase, and tissue, field preservation..	do	Cool, <4 °C	7 days.
Solids, mixed phase, and tissue, lab preservation	do	Freeze, < – 10 °C	1 year.
Table ID—Pesticides Tests:			
1–70. Pesticides [11]	do	Cool, 4°C, pH 5–9 [15]	Do.
Table IE—Radiological Tests:			
1–5. Alpha, beta and radium	P, G	HNO_3 to pH<2	6 months.

Table II Notes

[1] Polyethylene (P) or glass (G). For microbiology, plastic sample containers must be made of sterilizable materials (polypropylene or other autoclavable plastic).

[2] Sample preservation should be performed immediately upon sample collection. For composite chemical samples each aliquot should be preserved at the time of collection. When use of an automated sampler makes it impossible to preserve each aliquot, then chemical samples may be preserved by maintaining at 4°C until compositing and sample splitting is completed.

[3] When any sample is to be shipped by common carrier or sent through the United States Mails, it must comply with the Department of Transportation Hazardous Materials Regulations (49 CFR part 172). The person offering such material for transportation is responsible for ensuring such compliance. For the preservation requirements of Table II, the Office of Hazardous Materials, Materials Transportation Bureau, Department of Transportation has determined that the Hazardous Materials Regulations do not apply to the following materials: Hydrochloric acid (HCl) in water solutions at concentrations of 0.04% by weight or less (pH about 1.96 or greater); Nitric acid (HNO_3) in water solutions at concentrations of 0.15% by weight or less (pH about 1.62 or greater); Sulfuric acid (H_2SO_4) in water solutions at concentrations of 0.35% by weight or less (pH about 1.15 or greater); and

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[4] Samples should be analyzed as soon as possible after collection. The times listed are the maximum times that samples may be held before analysis and still be considered valid. Samples may be held for longer periods only if the permittee, or monitoring laboratory, has data on file to show that for the specific types of samples under study, the analytes are stable for the longer time, and has received a variance from the Regional Administrator under § 136.3(e). Some samples may not be stable for the maximum time period given in the table. A permittee, or monitoring laboratory, is obligated to hold the sample for a shorter time if knowledge exists to show that this is necessary to maintain sample stability. See § 136.3(e) for details. The term "analyze immediately" usually means within 15 minutes or less of sample collection.

[5] Should only be used in the presence of residual chlorine.

[6] Maximum holding time is 24 hours when sulfide is present. Optionally all samples may be tested with lead acetate paper before pH adjustments in order to determine if sulfide is present. If sulfide is present, it can be removed by the addition of cadmium nitrate powder until a negative spot test is obtained. The sample is filtered and then NaOH is added to pH 12.

[7] Samples should be filtered immediately on-site before adding preservative for dissolved metals.

[8] Guidance applies to samples to be analyzed by GC, LC, or GC/MS for specific compounds.

[9] Sample receiving no pH adjustment must be analyzed within seven days of sampling.

[10] The pH adjustment is not required if acrolein will not be measured. Samples for acrolein receiving no pH adjustment must be analyzed within 3 days of sampling.

[11] When the extractable analytes of concern fall within a single chemical category, the specified preservative and maximum holding times should be observed for optimum safeguard of sample integrity. When the analytes of concern fall within two or more chemical categories, the sample may be preserved by cooling to 4°C, reducing residual chlorine with 0.008% sodium thiosulfate, storing in the dark, and adjusting the pH to 6–9; samples preserved in this manner may be held for seven days before extraction and for forty days after extraction. Exceptions to this optional preservation and holding time procedure are noted in footnote 5 (re the requirement for thiosulfate reduction of residual chlorine), and footnotes 12, 13 (re the analysis of benzidine).

[12] If 1,2-diphenylhydrazine is likely to be present, adjust the pH of the sample to 4.0±0.2 to prevent rearrangement to benzidine.

[13] Extracts may be stored up to 7 days before analysis if storage is conducted under an inert (oxidant-free) atmosphere.

[14] For the analysis of diphenylnitrosamine, add 0.008% $Na_2S_2O_3$ and adjust pH to 7–10 with NaOH within 24 hours of sampling.

[15] The pH adjustment may be performed upon receipt at the laboratory and may be omitted if the samples are extracted within 72 hours of collection. For the analysis of aldrin, add 0.008% $Na_2S_2O_3$.

[16] Sufficient ice should be placed with the samples in the shipping container to ensure that ice is still present when the samples arrive at the laboratory. However, even if ice is present when the samples arrive, it is necessary to immediately measure the temperature of the samples and confirm that the 4C temperature maximum has not been exceeded. In the isolated cases where it can be documented that this holding temperature can not be met, the permittee can be given the option of on-site testing or can request a variance. The request for a variance should include supportive data which show that the toxicity of the effluent samples is not reduced because of the increased holding temperature.

Drinking water (40CFR141) REQUIRED CONTAINERS, PRESERVATION TECHNIQUES, AND HOLDING TIMES

Contaminant	Preservative [1]	Container [2]	Time [3]
Antimony	Conc HNO_3 to pH <2	P or G	6 months.
Asbestos	Cool, 4° C	P or G	
Barium	Conc HNO_3 to pH <2	P or G	6 months.
Beryllium	Conc HNO_3 to pH <2	P or G	6 months.
Cadmium	Conc HNO_3 to pH <2	P or G	6 months
Chromium	Conc HNO_3 to pH <2	P or G	6 months.
Cyanide	Cool, 4 °C, NaOH to pH>12 [3]	P or G	14 days
Fluoride	None	P or G	1 month.
Mercury	Conc HNO_3 to pH <2	P or G	28 days.
Nickel	Conc HNO_3 to pH <2	P or G	6 months.
Nitrate			
Chlorinated	Cool, 4° C	P or G	28 days.
Non-chlorinated	Conc H_2SO_4 to pH <2	P or G	14 days.
Nitrite	Cool, 4° C	P or G	48 hours.
Selenium	Conc HNO_3 to pH <2	P or G	6 months.
Thallium	Conc HNO_3 to pH <2	P or G	6 months.

[1] P=plastic, hard or soft; G=glass, hard or soft.
[2] In all cases, samples should be analyzed as soon after collection as possible.
[3] See method(s) for the information for preservation.

Appendix C

Insert Example Forms & Checklists

Sample Container Request Form
Cooler Receipt Checklist
Preservation Check Form
Sample Acceptance Policy and ETR Review Checklist

LIMS Quotation
Sample Log In Checklist
Sample Log In Form (DC-1)
Environmental Test Request (ETR)

- Extraction Worksheet
- Analysis Worksheet
- Subcontracting Worksheet

SAMPLE CONTAINER REQUEST FORM

CLIENT CODE:	DATE NEEDED BY CLIENT:	SHIP TO:
PROJECT#:	DATE REQUESTED:	
SITE:	REQUESTED BY:	

SEND FOR CLIENT USE (yes or no):	FOR SAMPLE MANAGEMENT USE ONLY Coolers: # Sent # Returned	SHIPPING
CUSTODY SEALS:	Small:	CARRIER (FEDEX or UPS): FOR SAMPLE MANAGEMENT USE ONLY
CHAIN OF CUSTODY FORMS:	Medium:	CHARGE FOR SHIPPING? Charge: $
EXTRA PACKING MATERIAL:	Large:	CHARGE FOR BOTTLES? Charge: $

SPECIAL INSTRUCTIONS:

		Container													Water						
Quantity	Parameter Preservation Type: A=HC1 B=H2SO4 C=NaOH+Ascorbic Acid D=HNO3 E=NaOH+ZnAcetate F=Sodium Thiosulfate G=Other (Specify)	Preservative Required	40ml vial clear glass	250ml NM amber glass	250ml WM amber glass	500ml WM amber glass	1L NM amber glass	2L amber jug glass	500ml NM poly	1L NM poly	125ml WM jar glass	60m. WM jar glass	2 oz. Jars	250mL poly	40ml vial VOA Free	250ml amber VOA Free	1L amber Analyte Free	2L amber Analyte Free	1L poly Analyte Free	500ml poly Analyte Free	

STL Burlington
COOLER RECEIPT CHECKLIST

Date Received: _____ **Sample Custodian:** _____

Time Received: _____ **ETR/SDG:** _____

RADIATION SCREEN: <0.05 MR/HR YES NO

If yes, stop work and alert the Supervisor and the PM.

CUSTODY SEALS PRESENT: YES NO

If yes, were the custody seals signed? YES NO

If yes, are custody seal numbers present? YES NO

List custody seal numbers: _____

_____

TEMPERATURE CHECK: _____ **(°C)**

Acceptance Criteria (0-6°C) except air samples, which should be shipped at ambient temperature and/or biota/tissue samples, which may be frozen on receipt. The thermal preservation of samples that are hand delivered immediately following collection is considered acceptable if there is evidence that the chilling process has begun.

Thermal Preservation Type: ICE ICE PACK NONE

CONDITION OF SAMPLE CONTAINERS: INTACT BROKEN

If broken, list the client ID for each broken container:

_____

_____

Were any samples received with a short hold time* remaining?

** <7 Days*

WET CHEMISTRY	**YES**	**NO**
METALS	**YES**	**NO**
ORGANIC EXTRACTABLES	**YES**	**NO**
VOLATILE (received unpreserved)	**YES**	**NO**

If yes, expedite sample log in procedure and alert the appropriate Department Manager.

Date:_____ Client Code:_____

ETR:_____ Performed By:_____

Preservation Check Form

Tests Requested on COC:

CONTAINER ID	Initial pH	Ammonia pH<2	AVS pH<2	COD pH<2	Cyanide pH>12	Ferrous Iron pH<2	Hardness pH<2	Metals pH<2 *	Mercury pH<2	Nitrate-Nitrite pH<2	Orthophosphorus pH<2	Phenols pH<2	Phosphorus pH<2	Sulfide pH>10	TKN pH<2	TOC pH<2	TOX pH<2	TPH pH<2	O&G pH<2	Final pH	Preservative Type

pH Adjustment Performed By:_____

pH Adjustment Authorized By:_____

Metals DM Notified: Date_____ Initials_____

(1) H_2SO_4 = Sulfuric Acid (70%): Lot #_____

(2) HCl = Hydrochloric Acid (50%): Lot #_____

(3) H_2NO_3 = Nitric Acid (50%): Lot #_____

(4) NaOH = Sodium Hydroxide: Lot #_____

(5) Zinc Acetate: Lot #_____

FSM003:09.09.03:0

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Sample Acceptance Policy & ETR Review Checklist

Client: _____ **ETR/SDG:** _____

Date: _____ **ETR Reviewed By:** _____

Sample Acceptance Policy	Yes	No	NA	Comment
Was the temperature of each cooler received within acceptance criteria?				
Were any coolers missing from a multi-cooler shipment?				
Were any sample containers received broken or leaking?				
Was there evidence that the coolers or samples had been tampered with?				
If cooler/sample custody seals present, are they intact?				
Was there evidence of water or other material seepage into the samples?				
If cooler/sample custody seals present, are they intact?				
Were any samples received with inappropriate containers?				
Were any discrepancies between the COC and samples received?				
Were any samples received outside of holding time? ***If yes, NCR Report Required.***				
Was adequate sample volume provided for tests requested, and MS/MSD?				
Were any sample received without proper preservation?				
Was headspace present in any VOA Vial?				
Did the radiation screen pass for all coolers?				

List all instances of comprised sample receipt and attach supporting documentation, as necessary:

_____

_____

_____

_____

_____

Sample Receipt / Project Log In / ETR Review	Yes	No	NA	Comment
Are the COC(s) & Air Bills signed by the sample custodian that acknowledged receipt of samples?				
Was the preservation check performed for aqueous inorganic samples?				
Is project information correct? (Client, SDG, Project Number, PM)				
Are all samples listed on COC present on the ETR?				
Does the ETR sample description and date/time of collection correspond to COC?				
Does each sample have a unique lab ID and is each sample container uniquely identified?				
Are all analysis for the test methods requested on the COC logged in?				
If soils were received, was method code BITLAB Method IN623 logged in to initiate percent solids determination?				
Was a worksheet generated for every prep/analytical test listed on ETR?				
Are additional instructions, compounds lists or similar information attached to the worksheets, if required?				

Correct any errors found and ensure the ETR and associated worksheets are re-generated and/or notify the Department Manager(s) of any changes required.

PM Review: _____

STL Burlington
SAMPLE LOGIN INFORMATION CHECKLIST

Client Information:

Client Contact: _____ Company: _____

Phone Number: _____ FAX Number: _____

Email address: _____ Other: _____

Should sample receipt /log in information be faxed to client? : □Yes □No
If yes, □COC □ETR □Other _____

Additional Instructions: _____

SDG Construction:

SDG Designation: _____ Is the W Field Required? _____

Close SDG : □Weekly □Biweekly □Every 20 samples □20 tests □Ask PM

Should Field QC samples be included in count of field samples? □Yes □No

Is an MS/MSD or Matrix Duplicate required per SDG? □Yes □No □Ask PM

If yes, are these samples to be assigned by client? □Yes □No

If yes, notify the PM if additional sample was not received? □Yes □No

Should the client be invoiced for MS/MSD/MD analysis? □Yes □No

Is Internal Chain of Custody required? □Yes □No

Are soil results to be reported on a dry weight basis? □Yes □No
If yes, ensure BIT Lab Method Code IN623 is listed on Quote

Attach instructions/compound lists to the analytical worksheets? □Yes □No

Can samples be disposed of under normal protocol*? □Yes □No
If no, specify sample retention _____
**30 days from date of invoice, except DOD, CLP Contract, which require that the laboratory retain samples for 60 days from date of invoice prior to disposal.*

Subcontracting Information: *See Subcontracting Form for Additional Information*

Test Method(s) _____ PO# _____

Subcontract Lab Address: Instructions:

_____ _____

_____ _____

_____ _____

_____ _____

QUOTATION

Client	: JOESMO Prepay	Date Printed	: 09/19/03 Time 11:50:12
PO Number	: N893L21G64	Quote No	: 66809
Results To CC	: Johnny Validator	Page	: 1
Joe's Environmental Services		Prepared By	: Christopher Anderson
123 Prospect Lane		Project No	: 23000
		Project Name	: Acme Industry RI/FS
Anywhere, VT 05655-001		Project Dir	: Christopher Anderson
		Turnaround	: 19 Days
Attention	: Jane Doe	Est Arr Date	: 09/18/03
Phone No.	: 555-555-1234	No Samples	: 100 ONGOING

Comments/Special Instructions

See CJA with questions, x 137. Site: Acme Industries, Nowhere, NJ
GC/MS VOCs: Please preserve Encores 1:1 with sodium bisulfate to meet site action limits for Benzene.
Air results to be reported in ug/m3, the client will provide air volume
Document Control: 2 copies of full CLP data package to JES w/ EDD.
Accounts Rec: Please reference PO # on invoice and include the COC.

Method No.		Parameter	Quantity	P.L.	Price	P.F.	Ext.
5030_8260B	:W	Analysis, VOA Water	10.00	4	115.00*	1.00	1150.00
5035_8260B	:S	Analysis, VOA Soil Closed	50.00	4	165.00*	1.00	8250.00
3550_8270C		Sonication, SVOA	50.00	4	*	1.00	
8270C		Analysis, SVOA	50.00	4	265.00*	1.00	13250.00
3550_8082		Sonication, PCBs	50.00	4	*	1.00	
8082		Analysis, PCBs	50.00	4	95.00*	1.00	4750.00
TO-4		Analysis, Pesticide	10.00	4	180.00	1.00	1800.00
TO-13A		Analysis, PAHs	10.00	4	250.00	1.00	2500.00
PM10		Particulate Matter	10.00	4	30.00	1.00	300.00
3050	:1T	Digestion, ICP Soil	50.00	4	*	1.00	
6010B	:TAL	ICP TAL Metals	50.00	4	140.00*	1.00	7000.00
6020	:TL	Thallium, Total	50.00	4	45.00*	1.00	2250.00
DISKETTE		Enhanced ERPIMS 4.0	1.00	4		1.00	
TOTAL							41250.00

Accepted On : Approved By : STL Burlington

Quote Valid Until 12/31/04

STL Burlington

Prepay

ENVIRONMENTAL
TEST REQUEST

ETR NO : 96209

Printed : 09/30/03 14:42:29 19 Days Page 1

Client id : JOESMO	Date Due : 10/19/03
Results to :	
Joe's Environmental Services	Samples Arr'd : 09/30/03
123 Prospect Lane	No. Samples : 3
	Quote no. : 66809
Anywhere, VT 05655-001	Project no. : 23000
	Project Name : Acme Industry RI/FS
	Project Dir. : Christopher Anderson
Attention : Jane Doe	Operator id : CJA
Phone no. : 555-555-1234	P.O. Number : N893L21G64
CC Results to : Johnny Validator	

Date Completed	Date Transmitted	Date Invoiced	Invoice Number

COMMENTS/SPECIAL INSTRUCTIONS

See CJA with questions, x 137. Site: Acme Industries, Nowhere, NJ
GC/MS VOCs: Please preserve Encores 1:1 with sodium bisulfate to meet site action limits for Benzene.
Air results to be reported in ug/m3, the client will provide air volume
Document Control: 2 copies of full CLP data package to JES w/ EDD.
Accounts Rec: Please reference PO # on invoice and include the COC.
Received 2 x 40mL vials preserved with sodium bisulfate, 1x 40mL P w/
(Continued on Next Page)

Method No.		Parameter	P.L.	Price	P.F.	Kit	St.
543626	SB-01-092903 10-12'	:[ ]09/30/03 @1104(Soil)					
035_8260B	:S	Analysis, VOA Soil Closed	4	165.00*	1.00		
3550_8270C	:	Sonication, SVOA	4	*	1.00		
270C	:	Analysis, SVOA	4	265.00*	1.00		
550_8082	:	Sonication, PCBs	4	*	1.00		
3082	:	Analysis, PCBs	4	95.00*	1.00		
3050	:1T	Digestion, ICP Soil	4	*	1.00		
010B	:TAL	ICP TAL Metals	4	140.00*	1.00		
020	:TL	Thallium, Total	4	45.00*	1.00		
543626a	MW-1A DBR	:[ ]09/30/03 @0800(Water)					
030_8260B	:W	Analysis, VOA Water	4	115.00*	1.00		
543626B	AQS01	:[ ]09/30/03 @0700(PUF)					

STL Burlington

Prepay

ENVIRONMENTAL
TEST REQUEST

ETR NO : 96209

Printed : 09/30/03 14:42:29 19 Days

COMMENTS/SPECIAL INSTRUCTIONS

MeOH, 2x 250mL WM ambers and 1x 60mL WM clear jar for 543626.
This is the first set of samples for this SDG.

Method No.		Parameter	P.L.	Price	P.F.	Kit	St.
TO-4	:	Analysis, Pesticide	4	180.00	1.00		
TO-13A	:	Analysis, PAHs	4	250.00	1.00		
PM10	:	Particulate Matter	4	30.00	1.00		

Item Number		Item Description	P.L.	Price	P.F.	Kit	St.
DISKETTE	:	Enhanced ERPIMS 4.0	4		1.00		

STL Burlington

PRINTED : 09/30/03 METHOD NO : 5030_8260B :W ETR NO : 96209
IME : 14:42:48 PAGE NO : 1

| LEVEL 4 | TURNAROUND 19 DAYS | SECTION 1MCIV |

ARAMETER : Analysis, VOA Water
DATE DUE : 10/19/03
ATE REC'D : 09/30/03
LIENT : JOESMO
PROJECT : 23000

RANSCRIPTION BY :
HECKED BY :
WORKSHEET & DATA FILED :

TECH	DATE	TIME	INST	DATE	TIME

COMMENTS/SPECIAL INSTRUCTIONS

See CJA with questions, x 137. Site: Acme Industries, Nowhere, NJ
GC/MS VOCs: Please preserve Encores 1:1 with sodium bisulfate to meet site action limits for Benzene.
Air results to be reported in ug/m3, the client will provide air volume
(Continued on Next Page)

LAB NO.	NOTES AND CALCULATIONS	RESULTS
43626a		

LAB NO.	LAB SAMPLE DESCRIPTION
43626a	MW-1A DBR :[ ]09/30/03 @0800(Water)

STL Burlington

PRINTED : 09/30/03 METHOD NO : 5030_8260B :W ETR NO : 96209
TIME : 14:42:48 PAGE NO : 2

| LEVEL 4 | TURNAROUND 19 DAYS SECTION 1MCIV |

PARAMETER : Analysis, VOA Water
DATE DUE : 10/19/03
DATE REC'D : 09/30/03
CLIENT : JOESMO
PROJECT : 23000

TRANSCRIPTION BY :
CHECKED BY :
WORKSHEET & DATA FILED :

TECH	DATE	TIME	INST	DATE	TIME

COMMENTS/SPECIAL INSTRUCTIONS

Document Control: 2 copies of full CLP data package to JES w/ EDD.
Accounts Rec: Please reference PO # on invoice and include the COC.
Received 2 x 40mL vials preserved with sodium bisulfate, 1x 40mL P w/ MeOH, 2x 250mL WM ambers and 1x 60mL WM clear jar for 543626.
This is the first set of samples for this SDG.

STL Burlington

PRINTED : 09/30/03 METHOD NO : 5035_8260B :S ETR NO : 96209
IME : 14:42:48 PAGE NO : 1

| LEVEL 4 | TURNAROUND 19 DAYS | SECTION 1MCIV |

ARAMETER : Analysis, VOA Soil Closed
DATE DUE : 10/19/03
ATE REC'D : 09/30/03
LIENT : JOESMO
PROJECT : 23000

RANSCRIPTION BY :
HECKED BY :
WORKSHEET & DATA FILED :

TECH	DATE	TIME	INST	DATE	TIME

COMMENTS/SPECIAL INSTRUCTIONS

See CJA with questions, x 137. Site: Acme Industries, Nowhere, NJ
GC/MS VOCs: Please preserve Encores 1:1 with sodium bisulfate to meet site action limits for Benzene.
Air results to be reported in ug/m3, the client will provide air volume
(Continued on Next Page)

LAB NO.	NOTES AND CALCULATIONS	RESULTS
43626		

LAB NO.	LAB SAMPLE DESCRIPTION
43626	SB-01-092903 10-12' :[ ]09/30/03 @1104(Soil)

STL Burlington

PRINTED : 09/30/03 METHOD NO : 5035_8260B :S ETR NO : 96209
TIME : 14:42:48 PAGE NO : 2

| LEVEL 4 | TURNAROUND 19 DAYS | SECTION 1MCIV |

PARAMETER : Analysis, VOA Soil Closed
DATE DUE : 10/19/03
DATE REC'D : 09/30/03
CLIENT : JOESMO
PROJECT : 23000

TRANSCRIPTION BY :
CHECKED BY :
WORKSHEET & DATA FILED :

TECH	DATE	TIME	INST	DATE	TIME

COMMENTS/SPECIAL INSTRUCTIONS

Document Control: 2 copies of full CLP data package to JES w/ EDD.
Accounts Rec: Please reference PO # on invoice and include the COC.
Received 2 x 40mL vials preserved with sodium bisulfate, 1x 40mL P w/ MeOH, 2x 250mL WM ambers and 1x 60mL WM clear jar for 543626.
This is the first set of samples for this SDG.

STL Burlington

PRINTED : 09/30/03 METHOD NO : 3550_8270C ETR NO : 96209
IME : 14:42:48 PAGE NO : 1

| LEVEL 4 | TURNAROUND 19 DAYS | SECTION 1GCPE |

PARAMETER : Sonication, SVOA
DATE DUE : 10/19/03
ATE REC'D : 09/30/03
LIENT : JOESMO
PROJECT : 23000

RANSCRIPTION BY :
HECKED BY :
WORKSHEET & DATA FILED :

TECH	DATE	TIME	INST	DATE	TIME

COMMENTS/SPECIAL INSTRUCTIONS

See CJA with questions, x 137. Site: Acme Industries, Nowhere, NJ
GC/MS VOCs: Please preserve Encores 1:1 with sodium bisulfate to meet site action limits for Benzene.
Air results to be reported in ug/m3, the client will provide air volume
(Continued on Next Page)

LAB NO.	NOTES AND CALCULATIONS	RESULTS
43626		

LAB NO.	LAB SAMPLE DESCRIPTION
43626	SB-01-092903 10-12' :[ ]09/30/03 @1104(Soil)

STL Burlington

PRINTED : 09/30/03 METHOD NO : 3550_8270C ETR NO : 96209
TIME : 14:42:48 PAGE NO : 2

| LEVEL 4 | TURNAROUND 19 DAYS SECTION 1GCPE |

PARAMETER : Sonication, SVOA
DATE DUE : 10/19/03
DATE REC'D : 09/30/03
CLIENT : JOESMO
PROJECT : 23000

TRANSCRIPTION BY :
CHECKED BY :
WORKSHEET & DATA FILED :

TECH	DATE	TIME	INST	DATE	TIME

COMMENTS/SPECIAL INSTRUCTIONS

Document Control: 2 copies of full CLP data package to JES w/ EDD.
Accounts Rec: Please reference PO # on invoice and include the COC.
Received 2 x 40mL vials preserved with sodium bisulfate, 1x 40mL P w/ MeOH, 2x 250mL WM ambers and 1x 60mL WM clear jar for 543626.
This is the first set of samples for this SDG.

STL Burlington

PRINTED : 09/30/03 METHOD NO : 8270C ETR NO : 96209
IME : 14:42:48 PAGE NO : 1

| LEVEL 4 | TURNAROUND 19 DAYS SECTION 1MCIS |

ARAMETER : Analysis, SVOA
DATE DUE : 10/19/03
ATE REC'D : 09/30/03
LIENT : JOESMO
PROJECT : 23000

RANSCRIPTION BY :
HECKED BY :
WORKSHEET & DATA FILED :

TECH	DATE	TIME	INST	DATE	TIME

COMMENTS/SPECIAL INSTRUCTIONS

See CJA with questions, x 137. Site: Acme Industries, Nowhere, NJ
GC/MS VOCs: Please preserve Encores 1:1 with sodium bisulfate to meet site action limits for Benzene.
Air results to be reported in ug/m3, the client will provide air volume
(Continued on Next Page)

LAB NO.	NOTES AND CALCULATIONS	RESULTS
43626		

LAB NO.	LAB SAMPLE DESCRIPTION
43626	SB-01-092903 10-12' :[ ]09/30/03 @1104(Soil)

STL Burlington

PRINTED : 09/30/03 METHOD NO : 8270C ETR NO : 96209
TIME : 14:42:48 PAGE NO : 2

| LEVEL 4 | TURNAROUND 19 DAYS SECTION 1MCIS |

PARAMETER : Analysis, SVOA
DATE DUE : 10/19/03
DATE REC'D : 09/30/03
CLIENT : JOESMO
PROJECT : 23000

TRANSCRIPTION BY :
CHECKED BY :
WORKSHEET & DATA FILED :

TECH	DATE	TIME	INST	DATE	TIME

COMMENTS/SPECIAL INSTRUCTIONS

Document Control: 2 copies of full CLP data package to JES w/ EDD.
Accounts Rec: Please reference PO # on invoice and include the COC.
Received 2 x 40mL vials preserved with sodium bisulfate, 1x 40mL P w/ MeOH, 2x 250mL WM ambers and 1x 60mL WM clear jar for 543626.
This is the first set of samples for this SDG.

STL Burlington

PRINTED : 09/30/03 METHOD NO : 3550_8082 ETR NO : 96209
IME : 14:42:48 PAGE NO : 1

| LEVEL 4 | TURNAROUND 19 DAYS | SECTION 1GCPE |

ARAMETER : Sonication, PCBs
DATE DUE : 10/19/03
ATE REC'D : 09/30/03
LIENT : JOESMO
PROJECT : 23000

RANSCRIPTION BY :
HECKED BY :
WORKSHEET & DATA FILED :

TECH	DATE	TIME	INST	DATE	TIME

COMMENTS/SPECIAL INSTRUCTIONS

See CJA with questions, x 137. Site: Acme Industries, Nowhere, NJ
GC/MS VOCs: Please preserve Encores 1:1 with sodium bisulfate to meet site action limits for Benzene.
Air results to be reported in ug/m3, the client will provide air volume
(Continued on Next Page)

LAB NO.	NOTES AND CALCULATIONS	RESULTS
543626		

LAB NO.	LAB SAMPLE DESCRIPTION
543626	SB-01-092903 10-12' :[ ]09/30/03 @1104(Soil)

STL Burlington

PRINTED : 09/30/03 METHOD NO : 3550_8082 ETR NO : 96209
TIME : 14:42:48 PAGE NO : 2

| LEVEL 4 | TURNAROUND 19 DAYS SECTION 1GCPE |

PARAMETER : Sonication, PCBs
DATE DUE : 10/19/03
DATE REC'D : 09/30/03
CLIENT : JOESMO
PROJECT : 23000

TRANSCRIPTION BY :
CHECKED BY :
WORKSHEET & DATA FILED :

TECH	DATE	TIME	INST	DATE	TIME

COMMENTS/SPECIAL INSTRUCTIONS

Document Control: 2 copies of full CLP data package to JES w/ EDD.
Accounts Rec: Please reference PO # on invoice and include the COC.
Received 2 x 40mL vials preserved with sodium bisulfate, 1x 40mL P w/ MeOH, 2x 250mL WM ambers and 1x 60mL WM clear jar for 543626.
This is the first set of samples for this SDG.

STL Burlington

PRINTED : 09/30/03 METHOD NO : 8082 ETR NO : 96209
IME : 14:42:48 PAGE NO : 1

| LEVEL 4 | TURNAROUND 19 DAYS | SECTION 1GCIP |

.ARAMETER : Analysis, PCBs
DATE DUE : 10/19/03
ATE REC'D : 09/30/03
LIENT : JOESMO
PROJECT : 23000

RANSCRIPTION BY :
HECKED BY :
WORKSHEET & DATA FILED :

TECH	DATE	TIME	INST	DATE	TIME

COMMENTS/SPECIAL INSTRUCTIONS

See CJA with questions, x 137. Site: Acme Industries, Nowhere, NJ
GC/MS VOCs: Please preserve Encores 1:1 with sodium bisulfate to meet site action limits for Benzene.
Air results to be reported in ug/m3, the client will provide air volume
(Continued on Next Page)

LAB NO.	NOTES AND CALCULATIONS	RESULTS
43626		

LAB NO.	LAB SAMPLE DESCRIPTION
43626	SB-01-092903 10-12' :[ ]09/30/03 @1104(Soil)

STL Burlington

PRINTED : 09/30/03 METHOD NO : 8082 ETR NO : 96209
TIME : 14:42:48 PAGE NO : 2

| LEVEL 4 | TURNAROUND 19 DAYS SECTION 1GCIP |

PARAMETER : Analysis, PCBs
DATE DUE : 10/19/03
DATE REC'D : 09/30/03
CLIENT : JOESMO
PROJECT : 23000

TRANSCRIPTION BY :
CHECKED BY :
WORKSHEET & DATA FILED :

TECH	DATE	TIME	INST	DATE	TIME

COMMENTS/SPECIAL INSTRUCTIONS

Document Control: 2 copies of full CLP data package to JES w/ EDD.
Accounts Rec: Please reference PO # on invoice and include the COC.
Received 2 x 40mL vials preserved with sodium bisulfate, 1x 40mL P w/ MeOH, 2x 250mL WM ambers and 1x 60mL WM clear jar for 543626.
This is the first set of samples for this SDG.

STL Burlington

PRINTED : 09/30/03 METHOD NO : TO-4 ETR NO : 96209
'IME : 14:42:48 PAGE NO : 1

| LEVEL 4 | TURNAROUND 19 DAYS SECTION 1GCIP |

.ARAMETER : Analysis, Pesticide
DATE DUE : 10/19/03
ᐧATE REC'D : 09/30/03
LIENT : JOESMO
PROJECT : 23000

RANSCRIPTION BY :
HECKED BY :
WORKSHEET & DATA FILED :

TECH	DATE	TIME	INST	DATE	TIME

COMMENTS/SPECIAL INSTRUCTIONS

See CJA with questions, x 137. Site: Acme Industries, Nowhere, NJ
GC/MS VOCs: Please preserve Encores 1:1 with sodium bisulfate to meet site action limits for Benzene.
Air results to be reported in ug/m3, the client will provide air volume
(Continued on Next Page)

LAB NO.	NOTES AND CALCULATIONS	RESULTS
ᐧ43626B		

LAB NO.	LAB SAMPLE DESCRIPTION
543626B	AQS01 :[ ]09/30/03 @0700(PUF)

STL Burlington

PRINTED : 09/30/03 METHOD NO : TO-4 ETR NO : 96209
TIME : 14:42:48 PAGE NO : 2

| LEVEL 4 | TURNAROUND 19 DAYS SECTION 1GCIP |

PARAMETER : Analysis, Pesticide
DATE DUE : 10/19/03
DATE REC'D : 09/30/03
CLIENT : JOESMO
PROJECT : 23000

TRANSCRIPTION BY :
CHECKED BY :
WORKSHEET & DATA FILED :

TECH	DATE	TIME	INST	DATE	TIME

COMMENTS/SPECIAL INSTRUCTIONS

Document Control: 2 copies of full CLP data package to JES w/ EDD.
Accounts Rec: Please reference PO # on invoice and include the COC.
Received 2 x 40mL vials preserved with sodium bisulfate, 1x 40mL P w/ MeOH, 2x 250mL WM ambers and 1x 60mL WM clear jar for 543626.
This is the first set of samples for this SDG.

STL Burlington

PRINTED : 09/30/03 METHOD NO : TO-13A ETR NO : 96209
TIME : 14:42:48 PAGE NO : 1

| LEVEL 4 | TURNAROUND 19 DAYS | SECTION 1MCIS |

PARAMETER : Analysis, PAHs
DATE DUE : 10/19/03
DATE REC'D : 09/30/03
CLIENT : JOESMO
PROJECT : 23000

TRANSCRIPTION BY :
CHECKED BY :
WORKSHEET & DATA FILED :

TECH	DATE	TIME	INST	DATE	TIME

COMMENTS/SPECIAL INSTRUCTIONS

See CJA with questions, x 137. Site: Acme Industries, Nowhere, NJ
GC/MS VOCs: Please preserve Encores 1:1 with sodium bisulfate to meet site action limits for Benzene.
Air results to be reported in ug/m3, the client will provide air volume
(Continued on Next Page)

LAB NO.	NOTES AND CALCULATIONS	RESULTS
543626B		

LAB NO.	LAB SAMPLE DESCRIPTION
543626B	AQS01 :[ ]09/30/03 @0700(PUF)

STL Burlington

PRINTED : 09/30/03 METHOD NO : TO-13A ETR NO : 96209
TIME : 14:42:48 PAGE NO : 2

| LEVEL 4 | TURNAROUND 19 DAYS | SECTION 1MCIS |

PARAMETER : Analysis, PAHs
DATE DUE : 10/19/03
DATE REC'D : 09/30/03
CLIENT : JOESMO
PROJECT : 23000

TRANSCRIPTION BY :
CHECKED BY :
WORKSHEET & DATA FILED :

TECH	DATE	TIME	INST	DATE	TIME

COMMENTS/SPECIAL INSTRUCTIONS

Document Control: 2 copies of full CLP data package to JES w/ EDD.
Accounts Rec: Please reference PO # on invoice and include the COC.
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This is the first set of samples for this SDG.

STL Burlington

PRINTED : 09/30/03 METHOD NO : PM10 ETR NO : 96209
IME : 14:42:48 PAGE NO : 1

| LEVEL 4 | TURNAROUND 19 DAYS SECTION 3ENV |

ARAMETER : Particulate Matter
DATE DUE : 10/19/03
ATE REC'D : 09/30/03
LIENT : JOESMO
PROJECT : 23000

RANSCRIPTION BY :
HECKED BY :
WORKSHEET & DATA FILED :

TECH	DATE	TIME	INST	DATE	TIME

COMMENTS/SPECIAL INSTRUCTIONS

See CJA with questions, x 137. Site: Acme Industries, Nowhere, NJ
GC/MS VOCs: Please preserve Encores 1:1 with sodium bisulfate to meet site action limits for Benzene.
Air results to be reported in ug/m3, the client will provide air volume
(Continued on Next Page)

LAB NO.	NOTES AND CALCULATIONS	RESULTS
43626B		

LAB NO.	LAB SAMPLE DESCRIPTION
43626B	AQS01 :[ ]09/30/03 @0700(PUF)

STL Burlington

PRINTED : 09/30/03 METHOD NO : PM10 ETR NO : 96209
TIME : 14:42:48 PAGE NO : 2

| LEVEL 4 | TURNAROUND 19 DAYS SECTION 3ENV |

PARAMETER : Particulate Matter
DATE DUE : 10/19/03
DATE REC'D : 09/30/03
CLIENT : JOESMO
PROJECT : 23000

TRANSCRIPTION BY :
CHECKED BY :
WORKSHEET & DATA FILED :

TECH	DATE	TIME	INST	DATE	TIME

COMMENTS/SPECIAL INSTRUCTIONS

Document Control: 2 copies of full CLP data package to JES w/ EDD.
Accounts Rec: Please reference PO # on invoice and include the COC.
Received 2 x 40mL vials preserved with sodium bisulfate, 1x 40mL P w/ MeOH, 2x 250mL WM ambers and 1x 60mL WM clear jar for 543626.
This is the first set of samples for this SDG.

STL Burlington

PRINTED : 09/30/03 METHOD NO : 3050 :1T ETR NO : 96209
IME : 14:42:48 PAGE NO : 1

| LEVEL 4 | TURNAROUND 19 DAYS SECTION 1MTP |

	TECH	DATE	TIME	INST	DATE	TIME
ARAMETER : Digestion, ICP Soil						
DATE DUE : 10/19/03						
ATE REC'D : 09/30/03						
LIENT : JOESMO						
PROJECT : 23000						
RANSCRIPTION BY :						
HECKED BY :						
WORKSHEET & DATA FILED :						

COMMENTS/SPECIAL INSTRUCTIONS

See CJA with questions, x 137. Site: Acme Industries, Nowhere, NJ
GC/MS VOCs: Please preserve Encores 1:1 with sodium bisulfate to meet site action limits for Benzene.
Air results to be reported in ug/m3, the client will provide air volume
(Continued on Next Page)

LAB NO.	NOTES AND CALCULATIONS	RESULTS
43626		

LAB NO.	LAB SAMPLE DESCRIPTION
543626	SB-01-092903 10-12' :[ ]09/30/03 @1104(Soil)

STL Burlington

PRINTED : 09/30/03 METHOD NO : 3050 :1T ETR NO : 96209
TIME : 14:42:48 PAGE NO : 2

| LEVEL 4 | TURNAROUND 19 DAYS SECTION 1MTP |

PARAMETER : Digestion, ICP Soil
DATE DUE : 10/19/03
DATE REC'D : 09/30/03
CLIENT : JOESMO
PROJECT : 23000

TRANSCRIPTION BY :
CHECKED BY :
WORKSHEET & DATA FILED :

TECH	DATE	TIME	INST	DATE	TIME

COMMENTS/SPECIAL INSTRUCTIONS

Document Control: 2 copies of full CLP data package to JES w/ EDD.
Accounts Rec: Please reference PO # on invoice and include the COC.
Received 2 x 40mL vials preserved with sodium bisulfate, 1x 40mL P w/ MeOH, 2x 250mL WM ambers and 1x 60mL WM clear jar for 543626.
This is the first set of samples for this SDG.

STL Burlington

PRINTED : 09/30/03 METHOD NO : 6010B :TAL ETR NO : 96209
IME : 14:42:48 PAGE NO : 1

| LEVEL 4 | TURNAROUND 19 DAYS SECTION 1MTIP |

ARAMETER : ICP TAL Metals
DATE DUE : 10/19/03
ATE REC'D : 09/30/03
LIENT : JOESMO
PROJECT : 23000

RANSCRIPTION BY :
HECKED BY :
WORKSHEET & DATA FILED :

TECH	DATE	TIME	INST	DATE	TIME

COMMENTS/SPECIAL INSTRUCTIONS

See CJA with questions, x 137. Site: Acme Industries, Nowhere, NJ
GC/MS VOCs: Please preserve Encores 1:1 with sodium bisulfate to meet site action limits for Benzene.
Air results to be reported in ug/m3, the client will provide air volume
(Continued on Next Page)

LAB NO.	NOTES AND CALCULATIONS	RESULTS
43626		

LAB NO.	LAB SAMPLE DESCRIPTION
43626	SB-01-092903 10-12' :[ ]09/30/03 @1104(Soil)

STL Burlington

PRINTED : 09/30/03 METHOD NO : 6010B :TAL ETR NO : 96209
TIME : 14:42:48 PAGE NO : 2

| LEVEL 4 | TURNAROUND 19 DAYS | SECTION 1MTIP |

PARAMETER : ICP TAL Metals
DATE DUE : 10/19/03
DATE REC'D : 09/30/03
CLIENT : JOESMO
PROJECT : 23000

TRANSCRIPTION BY :
CHECKED BY :
WORKSHEET & DATA FILED :

TECH	DATE	TIME	INST	DATE	TIME

COMMENTS/SPECIAL INSTRUCTIONS

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STL Burlington

PRINTED : 09/30/03 METHOD NO : 6020 :TL ETR NO : 96209
'IME : 14:42:48 PAGE NO : 1

| LEVEL 4 | TURNAROUND 19 DAYS | SECTION 1MTIP |

:ARAMETER : Thallium, Total
DATE DUE : 10/19/03
'ATE REC'D : 09/30/03
LIENT : JOESMO
PROJECT : 23000

'RANSCRIPTION BY :
:HECKED BY :
WORKSHEET & DATA FILED :

TECH	DATE	TIME	INST	DATE	TIME

COMMENTS/SPECIAL INSTRUCTIONS

See CJA with questions, x 137. Site: Acme Industries, Nowhere, NJ
GC/MS VOCs: Please preserve Encores 1:1 with sodium bisulfate to meet site action limits for Benzene.
Air results to be reported in ug/m3, the client will provide air volume
(Continued on Next Page)

LAB NO.	NOTES AND CALCULATIONS	RESULTS
543626		

LAB NO.	LAB SAMPLE DESCRIPTION
543626	SB-01-092903 10-12' :[ ]09/30/03 @1104(Soil)

STL Burlington

PRINTED : 09/30/03 METHOD NO : 6020 :TL ETR NO : 96209
TIME : 14:42:48 PAGE NO : 2

| LEVEL 4 | TURNAROUND 19 DAYS SECTION 1MTIP |

PARAMETER : Thallium, Total
DATE DUE : 10/19/03
DATE REC'D : 09/30/03
CLIENT : JOESMO
PROJECT : 23000

TRANSCRIPTION BY :
CHECKED BY :
WORKSHEET & DATA FILED :

TECH	DATE	TIME	INST	DATE	TIME

COMMENTS/SPECIAL INSTRUCTIONS

Document Control: 2 copies of full CLP data package to JES w/ EDD.
Accounts Rec: Please reference PO # on invoice and include the COC.
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