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QUALITY ASSURANCE PROJECT PLAN

FOR THE REMEDIAL DESIGN/REMEDIAL ACTION PRP-LEAD PROJECT AT THE AMERICAN CHEMICAL SERVICE, INC. NPL SITE GRIFFITH, INDIANA

NOVEMBER 2001

REVISION 0

Prepared For:
American Chemical Service NPL Site
Griffith, Indiana

• • •

Prepared By:
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Project No. 2090603.030401

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Appendix A Laboratory SOPs
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LIST OF ACRONYMS

AALA	American Association of Laboratory Accreditation
ACS	American Chemical Service
amsl	Above mean sea level
BWES	Barrier Wall Extraction System
°C	Degrees Celsius
CCV	Continuing calibration verification
COC	Chain of Custody
CRADA	Cooperative Research and Development Agreement
DQO	Data Quality Objective
FSP	Field sampling plan
GC/MS	Gas Chromatography/Mass Spectroscopy
GWTP	Groundwater Treatment Plant
ICAL	Initial calibration standard
IDEM	Indiana Department of Environmental Management
ISVE	In-Situ Soil Vapor Extraction
K-P	Kapica-Pazmey
LCS	Laboratory control sample
LIMS	Laboratory Information Management Systems
MCL	Maximum Contaminant Level
MDLs	Method Detection Limits
MS	Matrix Spike
MSD	Matrix Spike Duplicate
MWH	Montgomery Watson Harza
NIST	National Institute of Standards and Technology
NPL	National Priorities List
OFCA	Off-Site Containment Area
ONCA	On-Site Containment Area
ORC®	Oxygen Release Compound®
PARCC	Precision, accuracy, representativeness, completeness, and comparability
PGCS	Perimeter Groundwater Containment System
PQLs	Practical Quantitation Limits
ppm	Part per million
PRPs	Potentially Responsible Parties
PCB	Polychlorinated Biphenyl
PSVP	Performance Standard Verification Plan
QA	Quality Assurance
QAO	Quality Assurance Officer
QAPP	Quality Assurance Project Plan
QC	Quality Control

LIST OF ACRONYMS

RCRA	Resource Conservation and Recovery Act
RD/RA	Remedial Design/Remedial Action
RI/FS	Remedial Investigation/Feasibility Study
ROD	Record of Decision
RCRA	Resource Conservation and Recovery Act
RD/RA	Remedial Design/Remedial Action
RI/FS	Remedial Investigation/Feasibility Study
ROD	Record of Decision
RPD	Relative Percent Difference
SBP Area	Still Bottoms Pond Area
SOPs	Standard Operating Procedures
SRM	Standard Reference Material
SVOCs	Semivolatile Organic Compounds
U.S. EPA	United States Environmental Protection Agency
VOCs	Volatile Organic Compounds

DISTRIBUTION LIST

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1.0 INTRODUCTION

This Quality Assurance Project Plan (QAPP) presents the project organization, objectives, functional activities, and the project-specific quality assurance (QA) and quality control (QC) procedures for remedial design/remedial action (RD/RA) site activities at the American Chemical Service, Inc. National Priority List (NPL) Site (ACS) in Griffith, Indiana.

This QAPP covers all sampling and analytical work for groundwater monitoring activities (including private wells), groundwater treatment plant effluent compliance sampling and off-gas compliance sampling for the groundwater treatment plant and in-situ soil vapor extraction (ISVE) System (to be installed in 2001 and 2002), and confirmation sampling for excavation of polychlorinated biphenyl (PCB)-impacted soils. This QAPP supercedes previous Agency-approved QAPPs that cover these specific site activities.

The objectives of this QAPP are to define the project data quality objectives (DQOs) and the field and analytical procedures which will ensure that the resulting data are of sufficient quality to support the end use of the data.

All procedures presented in this QAPP are in accordance with applicable professional technical standards, United States Environmental Protection Agency (U.S. EPA) Region V requirements, Indiana Department of Environmental Management (IDEM) requirements, and the project-specific DQOs. This QAPP was prepared by Montgomery Watson Harza, (MWH) in accordance with the *EPA Requirements for Quality Assurance Project Plans QA/R-5* (November, 1999a). The analytical protocol described in this QAPP is based on the *EPA Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW-846),* (U.S. EPA Third edition, Final Update III, December 1996), the *Compendium of Methods for Determination of Toxic Organic Compounds in Ambient Air* (EPA/600/4-89/017, June 1988), and *EPA Methods for Chemical Analysis of Water and Wastes and the EPA Manual 600/4-79-020* (U.S. EPA, 1983).

2.0 PROJECT DESCRIPTION

The history of the ACS Site is well documented. Thorough investigations of the Site, including both the upper and lower aquifers, have established the contaminants of concern and the extent of contamination. In groundwater, benzene and chloroethane are the main contaminants of concern. In soils, PCBs are the contaminants of concern in portions of the wetland area in the western part of the Site.

2.1 SITE DESCRIPTION

The ACS Site is located at 420 South Colfax Avenue in Griffith, Indiana (Figure 2-1). The Site is bordered on the east and northeast by Colfax Avenue. An abandoned section of the Chesapeake and Ohio Railway, now owned by ACS, bisects the Site in an east-west direction. This separates the fenced On-Site Area to the north and the Off-Site Area (also fenced) to the south. South of the former Chesapeake and Ohio Railway, the Site is bordered on the southwest by the Griffith Municipal Landfill. North of the former Chesapeake and Ohio Railway, the Site is bordered on the west by wetlands. The Grand Trunk Railway forms the northern boundary of the Site.

The Site comprises approximately 30 acres of land including the On-Site Containment Area (ONCA), the Still Bottoms Pond/Treatment Lagoon (SBP Area), the Off-Site Containment Area (OFCA), and the Kapica/Pazmey (K-P) Area[1]. The Griffith Municipal Landfill is also located within the boundaries of the Site as defined by U.S. EPA. However, the remedial design and remedial action activities do not address the landfill. The landfill operated from the 1950's to the 1990's. It is currently is going through closure by the owner, the Town of Griffith.

The Site is relatively flat, ranging in elevation from about 630 to 650 feet above mean sea level (amsl). The highest area is near the intersection of Colfax and Reder Road (650 feet), and the wetlands to the west are the lowest topography, between 625 and 630 feet amsl.

Site geology has been well described in previous investigations. The local geology can be divided into an upper aquifer, a clay-confining unit, and a lower aquifer. The soils of the upper aquifer are generally classified as fine to coarse sand, with trace to some silt and clay, and trace to little, fine to coarse gravel. The upper aquifer thickness ranges from 13 to 32 feet. The clay-confining unit ranges in thickness across the site from approximately 3 to 30

[1] The terms On-Site and Off-Site are used to denote particular portions of the ACS Site; both areas are within the NPL Site. The Off-Site Containment Area was designated as "Off-Site" only because ACS, Inc. considered it off the facility, rather than within the boundaries of the property where ACS conducts its chemical formulation operations. However, ACS owns the property and as noted, for CERCLA purposes, both of these areas are considered part of the site.

feet thick. The clay is described as gray silty clay with trace to some fine to medium sand and trace fine to coarse gravel. The lower aquifer consists of a brown to dark gray fine to coarse sand with trace silt and gravel.

The regional gradient in the upper aquifer is generally east to west. Groundwater flow in the upper aquifer has been altered in the vicinity of the Site by the installation of the Barrier Wall Extraction System (BWES) and the Perimeter Groundwater Containment System (PGCS). Flow is now directed to the north and south around the barrier wall. Groundwater flow in the lower aquifer is consistently northward at a gradient of about 0.004.

2.2 SITE HISTORY AND BACKGROUND INFORMATION

The ACS facility began operation in May 1955 as a solvent recovery facility. Solvent recovery remained the primary on-site operation until the late 1960s, when operations changed to the manufacture of small quantities of specialty chemicals. These manufacturing operations included treating rope with fungicide, bromination, and treating ski lift cable.

In 1961, ACS sold a two-acre parcel to Mr. John Kapica, and in 1962 Mr. Kapica began operating a drum reclaiming and reconditioning business at the location. Residual wastes and rinse waters from the Kapica-Pazmey (K-P) drum reconditioning operation were discharged to the ground in the K-P Area. Kapica Drum was sold to Pazmey Corporation in February 1980. K-P operated from 1980 to 1987. The Pazmey Corporation property was sold to Darija Djurovic in March 1987.

ACS' solvent operations included recovery of spent solvent mixtures containing alcohols, ketones, esters, chlorinated solvents, aromatics, aliphatics, and glycols. In the early years of operation, spent solvents were stored in 55-gallon drums at various locations at the Site. Solvent was recovered in batch evaporation units, which were charged by pumping material directly from 55-gallon drums into the evaporation vessels. Still bottoms from the evaporation vessels were disposed in the Still Bottom Pond, prior to the installation of incinerators at the facility. During the mid-1960s, an estimated 400 drums of sludge and semi-solids were landfilled in the ONCA. In 1972, the pond and lagoons were drained, and were used to landfill drums partially filled with sludge materials. ACS installed its first incinerator in 1966 and installed a second incinerator in 1969. The incinerators were used to burn still bottoms and non-reclaimable materials generated at the Site, and wastes from off site. The incinerator units were dismantled in 1977.

The OFCA was used to landfill wastes including materials excavated from the Still Bottoms/Treatment Lagoon between 1958 and 1975. The waste types disposed in the OFCA over the course of ACS' operations also included general refuse, non-intact drums,

still bottoms, and incinerator ash. According to the ACS, Inc. owner/operator, drums placed in the OFCA were crushed or punctured as part of the disposal process.

From 1970 to 1975, an increasing percentage of solvent shipments were received at the Site in bulk tanker trucks. In addition, the batch manufacturing processes were expanded during this period. A lard oil process, utilizing tallow and animal rendering, was used in the manufacture of a lubricant product. In 1971, the additive manufacturing area was built to produce various detergents, lubricants, and chemical additives, as well as soldering flux, various amines, methanol, formaldehyde, sodium hydroxide, and maleic anhydride. An epoxidation plant was constructed in 1974, and a bromination operation using hexane was added in 1975. At various times until 1990, the epoxidation plant used toluene or benzene as a reaction carrier. The lard oil and soldering flux operations were discontinued prior to 1990.

Between 1975 and 1990, the solvent distillation units were replaced with new units, although the types of solvent wastes reclaimed remained essentially the same. Spent and reclaimed solvent recovery tank farms were constructed during this period, and the majority of the spent solvent waste streams were shipped in bulk tanker trucks, although drummed wastes were still processed. A hazardous waste drum unloading dock and storage area was built in the early 1970s, with spill containment curbing and a sump area added at a later date. In September 1990, ACS ceased accepting hazardous waste shipments and filed for closure. On March 31, 1993 ACS completed closure and terminated its interim Resource Conservation and Recovery Act (RCRA) status.

ACS currently operates a chemical production facility at the Site. The operations include chemical reaction processes, custom blending, and product distribution. The facility encompasses 15 acres with a process building, tank farms, loading and unloading areas, a laboratory, offices, and support utility buildings. The company operates 24 hours per day, five to six days per week. The operating production facility is secured by a continuous fence with one main access gate.

2.3 HISTORICAL AND CURRENT ENVIRONMENTAL INVESTIGATIVE AND REMEDIAL ACTIVITIES

In February 1980, the U.S. EPA performed a Preliminary Assessment of the ACS Site, and in May 1980 collected samples in the Off-Site Containment Area and at the Griffith Municipal Landfill. The U.S. EPA performed a site inspection on September 9, 1980. In July 1982, U.S. EPA contractors installed four monitoring wells near the OFCA and the Griffith Landfill. Based on information developed during these investigations, U.S. EPA assigned a hazard ranking system score of 34.98 to the ACS Site in June 1983.

In 1986, a group of approximately 125 Potentially Responsible Parties (PRPs) formed a Steering Committee to conduct the Remedial Investigation/Feasibility Study (RI/FS) pursuant to an agreement with the U.S. EPA. In June 1988, the PRPs signed a Consent Order to perform the RI/FS. Following U.S. EPA approval of the RI/FS Work Plan, the field investigation for Phase I of the RI began in July 1989. Phase II RI field work began in March 1990, and the Phase III RI field work was initiated in December 1990,. The RI report was completed in June 1991. Warzyn (now MWH) completed the FS report in June 1992.

In June 1992, the U.S. EPA published notice of its Proposed Plan for Remedial Action for the ACS Site. The remedy presented in that Proposed Plan was described by U.S. EPA as a modification of Remedial Alternative 6B from the FS. The U.S. EPA issued the Record of Decision (ROD) for the Site in September 1992, which described the remedial action to be implemented on the site.

In 1996, a preliminary investigation was conducted in the wetlands to the west of the ACS facility to determine the extent of impact from facility operation on the wetlands. Analytical samples collected during this investigation indicated that certain localized sediments in the wetlands area were contaminated with PCBs greater than 1 part per million (ppm). These PCBs likely were transported from the facility via surface water runoff from the facility which drained into the wetlands areas.

In February 1997, as part of the expedited interim remedial measures, a groundwater pumping system, the PGCS, was installed in the wetland area. This pumping system provides containment for a groundwater plume in the northwest portion of the Site. In addition, a groundwater treatment plant (GWTP) was constructed to treat groundwater from the PGCS; the GWTP treated groundwater using phase separation, biological degradation, metals precipitation, filtration, air stripping, and carbon adsorption methods.

In 1997, a continuous barrier wall was installed around the ONCA, the ACS operating facility, the OFCA, and the K-P Area to contain the contamination source areas. The barrier wall encloses the delineated source areas and buried waste at the Site. A groundwater extraction system inside the barrier wall, comprised of eight 100-foot long extraction trenches, was installed to maintain a hydraulic capture zone within the barrier wall, and is referred to as the BWES. Groundwater from the BWES is also treated at the GWTP.

The PGCS has been operated since March of 1997, and the BWES was started-up in May 1997. Groundwater from these systems continues to be treated through the GWTP and is discharged to the wetlands in accordance with standards established by the U.S. EPA and IDEM. Based on the GWTP effluent data and groundwater levels collected from within the barrier wall, these interim systems have successfully isolated the source areas of the Site. They prevent further off-site groundwater contamination from occurring, and provide active

treatment of groundwater from within the barrier wall. The PGCS also prevents further off-site migration to the north and northwest portion of the Site.

During 1999 and 2000, a Pilot Study was conducted in the north area of the Site to test the effectiveness of Oxygen Releasing Compound® (ORC®) in reducing benzene concentrations in the groundwater. ORC® adds oxygen to the groundwater, and thus enhances the natural biodegredation of organic compounds in the subsurface soil. Monitoring wells were installed near the Pilot Study, and the groundwater was collected monthly and analyzed.

Also during 1999 and 2000, the GWTP was upgraded to treat larger volumes of water. An activated sludge biological treatment unit was added to reduce the volatile and semi-volatile organic compounds (VOCs and SVOCs, respectively) in the collected groundwater. The treated effluent from the treatment system is discharged to the nearby wetlands, and in accordance with Agency approvals, regular effluent compliance samples are collected from the GWTP. Annual sediment samples are also collected from the wetland area near the GWTP discharge point and analyzed for PCBs. The GWTP treatment process also includes an aeration tank that releases off-gas to the atmosphere, and this off-gas is monitored for compliance. A catalytic oxidizer has been put in place to be available to treat the off-gas as necessary.

During late 2001 and 2002, MWH plans to install and operate two ISVE Systems on the site, one in the Off-Site Area and one in the On-Site Area. A thermal oxidizer will be installed to treat the off-gas generated by the ISVE Systems.

MWH plans to excavate PCB-impacted sediment from portions of the wetland area during 2001. Post-excavation sampling of the soil will be conducted to confirm the removal of soil impacted at PCB concentrations greater than 1 ppm.

From 1997 to 2000, a Groundwater Monitoring Program has been conducted with a monitoring network consisting of 44 upper and lower aquifer monitoring wells, as well as five private residential wells. A Long-Term Groundwater Monitoring Plan is being developed on the basis of the groundwater data collected from this program.

2.4 PROJECT OBJECTIVES AND SCOPE

This QAPP addresses three parts of future investigative and compliance work to be completed at ACS: 1) Long-Term Groundwater Monitoring, 2) Treatment Plant Effluent and Off-Gas sampling, and 3) PCB-Impacted Soils Excavation. Future site activities not included in those described herein will either be submitted for approval under this existing QAPP or will be submitted with a separate QAPP.

2.4.1 Long-Term Groundwater Monitoring Plan

The Long-Term Groundwater Monitoring Plan (July 1998) was designed to detect changes in water quality and concentrations of hazardous substances or pollutants in groundwater at and beyond the point of compliance. The specific water level elevation monitoring points, the monitoring and residential wells to be sampled, and the analytical and sample frequency are currently being revised, and will be outlined in the upcoming revised monitoring plan. This revised monitoring plan will also include the Field Sampling Plan, and will be submitted under separate cover. This QAPP addresses the analytical and field parameters, quality control sample frequency, sample volumes, and required containers for the revised monitoring plan. The approximate number of analytical samples, field parameters, and quality control samples are presented on Table 2-1.

2.4.2 Effluent and Off-Gas Sampling

The GWTP was designed to treat groundwater collected from the PGCS and BWES. The treated effluent from the system is then discharged to the nearby wetlands. A catalytic oxidizer treats off-gas from the GWTP process. The ISVE system collects soil vapor removed from the On-Site Area and Off-Site Area, and a thermal oxidizer treats off-gas from the ISVE process[2]. The effluent and off-gas are then sampled at regular intervals to comply with permit requirements. The analytical and quality control samples to be collected are included on Table 2-1.

2.4.3 PCB-Impacted Soils Excavation

MWH plans to excavate PCB-impacted sediment from portions of the wetland area during 2001. Post-excavation sampling of the soil will be conducted to confirm the removal of all impacted soil. Groundwater sampling for PCB analysis may also be conducted and is included in this section. Analytical samples, field parameters, and quality control samples are included on Table 2-1.

2.5 SAMPLE NETWORK DESIGN AND RATIONALE

The sampling network design and rationale for the three site activities described in this QAPP are presented in their respective work plans. A brief summary is provided here.

For groundwater monitoring activities at the ACS Site, the Long-Term Groundwater Monitoring Plan is being revised to reflect the current needs for monitoring at the ACS Site. Many years of groundwater monitoring outside of the BWES has shown that VOCs, specifically benzene and chloroethane, are the main concern in groundwater in areas surrounding the Site. The revised monitoring plan has been developed to monitor source areas, as well as upgradient, transgradient, and downgradient locations. Several nearby private wells are also sampled once a year for VOCs, SVOCs, PCBs, pesticides, and

[2] The ISVE system is not yet installed. As soon as this system is operational, the off-gas air samples will be collected.

inorganics. The analytical program described in this QAPP will allow for comparison to U.S. EPA MCLs.

The sampling network design for the Effluent and Off-gas has been determined and is described in the U.S. EPA-approved Performance Standard Verification Plan (PSVP) for the groundwater collection (PGCS and BWES) and treatment systems (July 1997). Since the treatment plant treats groundwater from within the BWES, the analytical program was developed to monitor for several contaminants of concern known at the Site. The analytical program described in this QAPP will allow for comparison to effluent standards.

The sampling network design for the PCB-impacted soils sampling is described in the U.S. EPA-approved PCB-Impacted Soils Excavation Work Plan (April 1999). After soil excavation, confirmation soil samples will be collected from the edges of the excavation to ensure that all soils with PCB concentrations greater than 1 ppm are removed. The analytical program described in this QAPP will ensure that detection limits are sufficient to document that no soils with concentrations greater than 1 ppm remain.

2.6 PARAMETERS TO BE TESTED AND FREQUENCY

The list of target parameters, method detection limits (MDLs), practical quantitation limits (PQLs), the U.S. EPA maximum contaminant levels (MCLs), and effluent discharge limits for each project are included in Table 2-2. The target parameters have been chosen based on past data collection activities at the ACS Site. For groundwater, the compounds of concern are VOCs, specifically, benzene and chloroethane. For the groundwater treatment effluent, the compounds of concern are VOCs, SVOCs, metals and inorganics, PCBs, BOD, TSS, and pH (a parameter of concern). VOCs and SVOCs are the compounds of concern for off-gas monitoring. For the PCB-impacted soil removal activities, PCBs in soil are the compound of concern.

2.7 DATA QUALITY OBJECTIVES

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

- Clarify the study objective
- Define the most appropriate type of data to collect
- Determine the most appropriate conditions from which to collect the data.

The DQOs are used to develop a scientific and resource-effective sampling design.

The DQO process allows decision-makers to define their data requirements and acceptable levels of decision during planning before any data are collected. Sample collection and associated DQOs for sample collection activities at ACS are based on the seven-step DQO process (EPA QA/G-4, August 2000). Table 2-3 provides the DQO process for the specific tasks in this QAPP..

2.8 SCHEDULE OF WORK

The three projects described in this QAPP will operate on independent schedules. The ongoing groundwater monitoring program will continue with periodic sampling events, as defined in the approved Long-Term Groundwater Monitoring Plan. The effluent and off-gas sampling is currently scheduled to be conducted quarterly. Some effluent analytes may be monitoring more frequently, based on the guidelines in the PSVP. The one-time PCB-impacted soils removal is scheduled to occur during the Summer of 2001. Table 2-4 summarizes the anticipated schedule of work.

3.0 PROJECT ORGANIZATION AND RESPONSIBILITY

At the direction of the ACS RD/RA Executive Committee and the approval of the U.S. EPA, MWH has overall responsibility for the implementation and analysis of the RD/RA sampling at ACS. MWH's responsibilities include preparing the QAPP. Under the direction of the ACS PRP Executive Committee, MWH also is responsible for project management. The various quality assurance and management responsibilities of key project personnel are defined below. A site-specific project organization chart is provided as Figure 3-1.

3.1 MANAGEMENT RESPONSIBILITIES

U.S. EPA Region V is the lead agency and is responsible for providing oversight of the ACS remediation. The U.S. EPA Remedial Project Manager has overall responsibility for the ACS site projects and also is responsible for coordinating communication between the U.S. EPA, IDEM, the ACS RD/RA Committee, and MWH.

The IDEM Project Manager is responsible for ensuring that the State of Indiana's environmental requirements are met.

The ACS RD/RA Committee is responsible for implementing the project and has the authority to obtain the resources necessary to meet the project objectives and requirements.

The MWH Project Manager has overall responsibility for ensuring that the U.S. EPA project objectives and MWH's quality standards are met. In addition, this person is responsible for technical quality control and project oversight, and provides the ACS RD/RA Committee with access to corporate management. Responsibilities of the Project Manager include:

- Defining project objectives and developing a detailed Work Plan schedule.
- Establishing project policy and procedures to address the specific needs of the project as a whole, as well as the objectives of each task.
- Acquiring and applying technical and corporate resources as needed to ensure performance within budget and schedule constraints
- Orienting all field leaders and support staff concerning the project's special considerations.
- Monitoring and directing the field leaders.

- Developing and meeting ongoing project and/or task staffing requirements, including mechanisms to review and evaluate each task product.
- Reviewing work performed on each task to ensure its quality, responsiveness, and timeliness.
- Reviewing and analyzing overall task performance with respect to planned requirements and authorizations.
- Approving all external reports (deliverables) before their submittal to the client and U.S. EPA.
- Preparing and ensuring the quality of design and construction submittals.
- Representing the project team at meetings and public hearings.

3.2 QUALITY ASSURANCE RESPONSIBILITIES

The U.S. EPA Region V Quality Assurance Coordinator has the responsibility to review and approve this QAPP. Additional project responsibilities include conducting external performance and system audits of the laboratories and field activities, and evaluating analytical field and laboratory procedures.

The MWH Quality Assurance Officer (QAO) will remain independent of direct project involvement and day-to-day operations. Specific QA responsibilities of the QAO include conducting internal and external performance and system audits, reviewing and approving QA plans and procedures, and providing technical assistance to project staff for QA issues. The QAO is responsible for ensuring that the QA program defined in this QAPP is implemented.

Data validation and data assessment will be conducted by either MWH chemists or by an outside validation subcontractor.

3.3 FIELD RESPONSIBILITIES

The MWH Field Team Leader supports the MWH Project Manager and is responsible for leading and coordinating the day-to-day activities of the project staff under his supervision. Responsibilities include:

- Day-to-day coordination with the project manager on technical issues in specific areas of expertise.
- Development and implementation of field-related Work Plans, assurance of schedule compliance, and adherence to management-developed study requirement.
- Coordination and management of field staff.
- Implementation of QC for technical data provided by the field staff including field measurement data.
- Adherence to work schedules provided by the project manager.
- Generation, review, and approval of text and graphics required for field team efforts.
- Coordination and oversight of technical efforts of subcontractors.
- Identification of problems at the field-team level, discussion of resolutions with the project manager, and communication between the field team and upper management.
- Participation in the preparation of project reports.

The Technical staff for the projects included in this QAPP will be selected from MWH's pool of corporate resources. The technical staff will gather and analyze data, and prepare various task reports and support materials. All of the designated technical staff will be experienced professionals who possess the degree of specialization, training, and technical competence required to effectively and efficiently perform the required work.

3.4 LABORATORY RESPONSIBILITIES

CompuChem, A Division of Liberty Analytical Corporation, of Cary, North Carolina; Air Toxics, LTD., of Fulsom, California; or Severn Trent Laboratories of University Park, Illinois will provide analytical services for the specific tasks included is this QAPP. CompuChem will serve as the primary analytical laboratory for analysis of all groundwater and soil samples. Severn Trent will serve as the backup analytical laboratory to CompuChem. Severn Trent will either serve as the quality assurance laboratory or provide analytical support in the event CompuChem capacity becomes an issue. Air Toxics will serve as the primary analytical laboratory for analysis of all air samples. See Table 2-2 for a list of all parameters and matrices to be analyzed by each laboratory.

Analysis will be conducted in accordance with *EPA Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW-846),* (U.S. EPA Third edition, Final Update III, December 1996); *EPA Methods for Chemical Analysis of Water and Wastes and the EPA Manual 600/4-79-020* (U.S. EPA, 1983); or the *Compendium of Methods for Determination of Toxic Organic Compounds in Ambient Air* (EPA/600/4-89/017, June 1988). Any other laboratory used in subsequently named activities will fully follow this QAPP, their standard operating procedures (SOPs) and procedures specified by the analytical method.

3.4.1 Laboratory Project Manager

Each laboratory will assign a specific individual to assume Project Management responsibilities for the projects included in this QAPP. This individual will be the primary contact for MWH and will be responsible for ensuring that the project requirements as they relate to the laboratory are met. This individual will be responsible for scheduling sample analysis and ensuring that the data are generated in accordance with the specifications presented in this QAPP. This person will also be responsible for monitoring the progress and timeliness of the work, reviewing work orders and laboratory reports, and processing any changes in the scope of work. This individual will also be responsible for ensuring that project-specific corrective action is taken when necessary to address problems identified by the QC sample results or QA audit results and for approving final analytical reports prior to submission to MWH.

3.4.2 Laboratory Project Quality Assurance Officer

Each laboratory quality assurance officer will be responsible for ensuring that the laboratory QA/QC activities are performed in accordance with the requirements specified in both this QAPP, the laboratory's internal QAPP, and the laboratory-specific SOPs. Responsibilities will include (but not be limited to) preparing QA documents that define QA/QC procedures, reviewing and approving laboratory QC procedures, and oversight of inter-laboratory testing programs and laboratory certifications. These individuals will also be responsible for monitoring method operation through periodic data reviews and technical system audits. Unacceptable findings will be reported to the appropriate individuals for corrective action. These individuals will be responsible for signing the title page of this QAPP.

3.4.3 Laboratory Sample Custodian

Each laboratory sample custodian will report directly to the Laboratory Manager and will be responsible for:

- Receiving and inspecting samples.
- Recording information regarding sample condition on and signing the appropriate forms.

- Verifying the chain-of-custody and documenting any discrepancies.
- Notifying the Laboratory Project Manager or other appropriate laboratory personnel of sample receipt and inspection.
- Assigning a unique identification number and customer number to each sample and logging it into the sample receiving log book and laboratory information management system (LIMS).
- Transferring samples to the appropriate laboratory sections
- Controlling and monitoring access and storage of samples and extracts.

3.4.4 Laboratory Technical Staff

All laboratory staff involved with sample preparation and analysis will consist of experienced professionals who possess the degree of specialization and technical competence required to effectively and efficiently perform the required work.

3.5 TRAINING RESPONSIBILITIES

All MWH and laboratory staff associated with the projects included in this QAPP will have sufficient training to safely, effectively, and efficiently perform their assigned tasks as documented in the Site Safety Plan (Montgomery Watson, 1996) and Site Safety Plan Addendum (June 1999a), and the laboratories' internal QAPP, respectively. Training records will be reviewed by MWH prior to initiation of field activities to ensure technical competency. The MWH Project Manager will maintain documentation of this training in the project files.

4.0 QUALITY ASSURANCE OBJECTIVES FOR MEASUREMENT DATA

Data quality refers to the reliability associated with a particular data set or data point. The data quality associated with environmental measurement data is a function of the sampling plan rationale, the sample collection procedures, and the analytical methods and instrumentation used in making the measurements. The overall QA objective for the projects included in this QAPP is to develop and implement procedures for field sampling, chain-of-custody, laboratory analysis, and data reporting that will provide data that meet the task-specific DQOs and that are legally defensible. The remainder of this section describes the type of data that will be collected and the precision, accuracy, representativeness, comparability, and completeness criteria for projects included in this QAPP.

4.1 DATA TYPES

The data types required for the projects included in this QAPP are based on the type of investigation, the project-specific DQOs, the end use of the analytical data, and the level of documentation. Screening and definitive data will be collected for those tasks included in this QAPP. Whether data are considered screening or definitive is based on the method of sample collection, preparation, and analysis. Screening data include data that are collected using non-standard sampling methodology or collected using rapid, less precise methods of analysis with less rigorous sample preparation or quality control as compared to analytical methods from which definitive data are generated. Definitive data include data that are collected using standard sampling methodology and analytical methodology of known precision and accuracy.

4.2 DATA QUALITY DEFINITION AND MEASUREMENT

To determine the overall quality of definitive data, the results of QC sample analysis will be evaluated in terms of precision, accuracy, representativeness, completeness, and comparability (PARCC). The QC samples that will be used to assess the quality of both the field and laboratory data (prepared both in the laboratory and in the field) are described later in this section. A summary of the chemical data quality control evaluation program in terms of the PARCC parameters is presented in Table 4-1. Method specific quality control procedures, QC sample analysis frequency and acceptance criteria, and laboratory corrective action procedures that will be followed for this project are presented in Tables 4-2 through 4-21. Failure of the laboratories to follow this guidance will result in resampling (if applicable) and reanalysis at the laboratories cost. The guidance presented in this QAPP is based on the analytical method and current industry standards. The specific QC acceptance criteria for accuracy and precision that will be used by laboratory providing screening level data will be based on the historical performance of the laboratory (as specified by the analytical methods).

The project-specific Practical Quantitation Limits (PQLs) and Method Detection Limits (MDLs) for every parameter are listed in Table 2-2. Standard and Low-Level PQLs for soil and groundwater are listed for all organic parameters. Only Standard PQLs are listed for inorganic parameters; the PQLs listed will be required for all soil or groundwater analyses for metals.

In most cases, laboratory PQLs are equal to or less than the U.S. EPA MCLs. However, there are twelve parameters for which the PQL is greater than the MCL (vinyl chloride, benzo(a)pyrene, bis(2-chloroethyl)ether, bis(2-ethylhexyl)phthalate, hexachlorobenzene, pentachlorophenol, antimony, arsenic, beryllium, cadmium, mercury, thallium). For these parameters, the sample data will be reported to the MDL. Sample results greater than the MDL but lower than the PQL will be reported as estimated concentrations (flagged as estimated), and all non-detections will be reported as less than the MDL.

4.2.1 Precision

Definition. Precision is the reproducibility of measurements under a given set of conditions. For large data sets, precision is expressed as the variability of a group of measurements compared to their average value (i.e., standard deviation). For duplicate or replicate measurements, precision is expressed as the relative percent difference (RPD) of a data pair and is calculated using the following equation:

$$RPD = \frac{|A - B|}{\frac{(A + B)}{2}} \times 100$$

Where A and B are the reported concentrations for duplicate sample analyses.

Field Precision. For the projects included in this QAPP, field precision will be assessed through the collection and analysis of field replicate soil or field duplicate water samples.

Laboratory Precision. Analytical laboratory precision will be assessed using the calculated RPD between the following data:

- Matrix spike and matrix spike duplicate (MS/MSD) sample data.
- Investigative and associated field duplicate or replicate sample data.
- Laboratory precision will also be assessed for three or more replicated samples (e.g., response factors for calibration standards).

4.2.2 Accuracy

Definition. Accuracy is the degree of agreement of a measurement or an average of measurements with an accepted reference or "true" value, and is a measure of bias in the system. The accuracy of a measurement system is affected by the sample matrix or by errors introduced during sample collection, preservation, handling, preparation, and analysis. Accuracy will be evaluated using the percent recovery calculated using the following equation:

$$\text{Percent Recovery} = \frac{|A - B|}{C} \times 100$$

Where: A is the target analyte concentration determined analytically from the spiked sample.

B is the background level determined by a separate analysis of the unspiked sample.

C is the concentration of spike added.

Field Accuracy. Although accuracy of the field program cannot be assessed quantitatively, a qualitative accuracy assessment for the projects included in this QAPP will be conducted by reviewing the sample collection, preservation, handling, and shipping procedures for compliance with the specifications presented in this QAPP and through analysis of equipment rinseate and trip blanks.

Laboratory Accuracy Objectives. Laboratory accuracy will be assessed quantitatively through the analysis of MS/MSD samples and standard reference materials (SRM), which include surrogate spikes (organic analysis only), laboratory control samples (LCS), response factors for calibration standards, and internal standard recoveries.

4.2.3 Representativeness

Definition. Representativeness is a qualitative expression of the degree to which sample data accurately and precisely represent a characteristic of a population, a sampling point, or an environmental condition. Representativeness is maximized by ensuring that, for a given project, the number and location of sampling points and the sample collection and analysis techniques are appropriate for the specific investigation, and that the sampling and analysis program provides information that reflects "true" site conditions.

Field Data. Representativeness of field data is dependent upon the proper design of the data collection procedures. The sampling and field measurement procedures to be used for the tasks included in this QAPP are based on site knowledge, the physical setting, past land use, and operations history. Representativeness of the field data will be evaluated by assessing whether the sampling procedures defined in this QAPP and the project-specific

Field Sampling Plan (FSP) or Work Plan were followed during sample collection. In addition, the analytical results from trip and equipment rinseate blank samples and field duplicate or replicate samples also will be used to evaluate the representativeness of field sampling procedures.

Laboratory Data. Laboratory data will be evaluated for representativeness by assessing whether the laboratory followed the specified analytical criteria in this QAPP and their SOPs, assessing compliance with holding time criteria, and the results of method, instrument, trip, and equipment rinseate blank samples and field replicate or duplicate samples.

4.2.4 Comparability

Definition. Comparability is a qualitative parameter that expresses the confidence with which one data set may be compared to another. Comparability is dependent on similar QA objectives and is achieved through the use of standardized methods for sample collection and analysis, the use of standardized units of measure, normalizing results to standard conditions, and the use of standard and comprehensive reporting formats as defined by this QAPP.

Field Data. Field data comparability is dependent on the use of similar and standard sampling and analytical methodology and the use of standard units of measure between different projects at a site. For the projects included in this QAPP, field data will be collected using standard sampling and measurement procedures. All field data will be recorded in the field logbook or on the applicable field forms (i.e., sample log forms or chain of custody). Comparability of field data will be evaluated by reviewing the field documentation to determine whether the field data collection procedures and sample collection, handling, and shipping protocols specified in this QAPP and the task specific FSP or Work Plan were followed.

Laboratory Data. Like field data, laboratory data comparability is dependent on the use of similar sampling and analytical methodology and standard units of measure between different projects at a specific site. For this investigation, standard sampling and analytical methodologies that are similar to those utilized for previous sampling activities will be followed (to the extent possible). Laboratory data comparability will be assessed by comparing data collected during this investigation to historical data (as available), QC sample results (field duplicates or replicates), and assessing whether the analytical methodology presented in this QAPP was followed.

4.2.5 Completeness

Definition. Completeness is a measure of the amount of valid data obtained from a measurement system relative to the amount of data scheduled for collection under correct, normal conditions. Completeness measures the effectiveness of the overall investigation in

collecting the required samples, completing the required analyses, and producing valid results. Completeness will be calculated using the following equation:

$$\text{Completeness} = \frac{\text{Number of valid data points}}{\text{Total number of measurements}} \times 100$$

where: the number of valid data points is the total number of valid analytical measurements based on the precision, accuracy, and holding time evaluation.

Field Data. Field completeness is a quantitative measure of the actual number of samples collected compared to those samples scheduled for collection. The field data completeness goal for data collected under this QAPP is 95 percent.
Laboratory Data. Laboratory data completeness is a quantitative measure of the percentage of valid data for all analytical data as determined by the precision, accuracy, and holding time criteria evaluation. Completeness will be calculated using the completeness equation by dividing the total number of valid data points by the total number of data points. The laboratory completeness goal for data collected under this QAPP is 95 percent.

If the 95% completeness goal is not met for field or laboratory data, the U.S. EPA and IDEM will be immediately notified. The determination regarding the need for corrective action will be based upon how critical the data are to the project DQOs and will be made by MWA in conjunction with U.S. EPA.

4.3 QUALITY CONTROL SAMPLES

The following paragraphs describe the QC samples and holding time criteria that will be used to assess data quality. These include QC samples prepared both in the field and by the laboratory. As noted previously, QC samples will not be collected or analyzed for screening level data. A summary of QC sample evaluations in relation to the PARCC parameters is presented in Table 4-1, and a description summary of the QC samples is provided in Table 4-22. Method specific quality control procedures, frequency of QC sample analysis, acceptance criteria (control limits), and corrective actions are included in Tables 4-2 through 4-21.

4.3.1 Field Program

For field sampling, quality control samples are used to assess sample collection techniques and to assess environmental conditions during sample collection and transport. Quality control samples will be collected for the groundwater monitoring activities and the PCB-Impacted Soils Excavation activities. QC samples will not be collected for effluent or off-gas samples. Quality control samples will include temperature blanks, equipment rinseate blanks, field duplicates for water samples, and field replicates for soil samples (submitted blind to the laboratory).

Temperature Blanks and Cooler Temperature. Temperature blanks and the internal temperature of the cooler will be used to evaluate representativeness by assessing whether the sample temperature criterion of 4 degrees Celsius (°C) ± 2°C was met during sample shipment. The temperature of the blank and the internal temperature of the cooler are measured at the time the samples are received by the laboratory and recorded on the chain of custody. Temperatures that exceed the temperature criterion indicate that the samples may not have been handled or transported properly.

Equipment Rinseate Blanks. Equipment rinseate blanks (equipment blanks) will be used to evaluate representativeness and will be prepared in the field (after decontamination of sampling equipment is complete) by collecting the final rinse water into the appropriate sample container. Equipment blanks will be collected at a frequency of one per every ten groundwater samples collected.

Trip Blanks. Trip blanks will be submitted with water samples, and analyzed for VOCs to detect any potential cross-contamination of samples that may occur from sample containers, during sample transport to the laboratory, or during sample storage at the laboratory. Trip blanks will be prepared by the laboratory and consist of 40 milliliter glass vials filled with acidified reagent-grade water and then sealed with a cap with a Teflon septum. The trip blank samples will accompany the empty sample bottles from the laboratory to the site. One set of trip blank samples will be placed in the sample cooler at the start of each day of sampling and remain in the cooler throughout the day. The trip blanks will then be shipped with the samples to the laboratory. One set of trip blanks will accompany each cooler containing samples to be analyzed for VOCs.

Duplicate Samples. Duplicate water samples (submitted blind to the laboratory) will be used to assess variability in the sample media and to assess sampling and analytical precision. A duplicate sample pair is a single grab sample that is split into two samples during collection. For each duplicate sample pair, one of the samples is labeled with the correct sample identification and the other is labeled with a fictitious sample identification. This sample pair will then be submitted to the same laboratory as two separate samples. Duplicate samples will be collected at a frequency of one per every ten water samples collected.

Replicate Samples. Replicate soil samples (submitted blind to the laboratory) will be used to assess variability in the sample media and to assess sampling and analytical precision. A replicate sample pair is a single grab sample that is split into two samples during collection. For each replicate sample pair, one of the samples is labeled with the correct sample identification and the other is labeled with a fictitious sample name. This sample pair is then submitted to the same laboratory as two separate samples. Replicate samples will be collected at a frequency of one per every ten soil samples collected.

4.3.2 Laboratory Program

The laboratory will, at a minimum, analyze internal QC samples at the frequency specified by the analytical method, their SOPs, and this QAPP. Method-specific quality control procedures, frequency of QC sample analysis, acceptance criteria (control limits), and corrective actions are provided in Tables 4-2 through 4-21. The following paragraphs discuss holding time and the QC samples that the laboratory will use to assess data quality.

Sample Holding Time. Sample holding time reflects the length of time that a sample or sample extract remains representative of environmental conditions. For methods that do not require sample extraction, one holding time will be evaluated, the length of time from sample collection to analysis. For methods that require sample extraction prior to analysis two holding times will be evaluated; the length of time from sample collection until sample extraction, and the length of time from sample extraction to sample analysis. These holding times will be compared to the holding times specified by the analytical method. The holding times are presented in Section 4.0 for each analytical method.

Method Blanks. Method blanks will be used to monitor the laboratory preparation and analytical systems for interferences and contamination from glassware, reagents, sample manipulations, and the general laboratory environment. The method blank is an analyte-free matrix (reagent grade water or laboratory grade sand) to which all reagents will be added in the same volumes or proportions as used in sample processing. Method blanks will be taken through the entire sample preparation/extraction and analytical process. Method blanks will be prepared and analyzed with each analytical or preparation batch of environmental samples up to a maximum of 20 samples of a similar matrix.

Internal Standards. Internal standards are compounds that behave similarly to the target analytes during analysis and will be used to assess accuracy for gas chromatography/mass spectroscopy (GC/MS) analysis. Internal standards will be prepared and added to the initial calibration standard (ICAL), the continuing calibration verification standard (CCV), and all samples (field and QC) prior to analysis. Internal standard data will be reviewed for compliance with the analytical method or laboratory's SOPs acceptance (Appendix A).

Surrogate Spikes. Surrogate spikes will be used to evaluate the accuracy of analytical instrument performance for all organic analysis. Surrogate spikes will be added to each sample for organic compound analysis, including QC samples, prior to extraction as specified in the Laboratory's SOP. The percent recovery of each surrogate spike will be calculated and compared to the project acceptance criteria (Tables 4-2 through 4-21).

Laboratory Control Samples. The LCS will be used to measure laboratory accuracy in the absence of matrix interference. Laboratory control samples are prepared in the laboratory and consist of samples of a known matrix (reagent grade water or laboratory grade sand) spiked with a known quantity of specific target analytes in accordance with the

laboratory SOPs. These samples are taken through the entire sample preparation and analytical process. LCSs will be prepared and analyzed with each analytical or preparation batch of environmental samples up to a maximum of 20 samples of a similar matrix.

Matrix Spikes and Matrix Spike Duplicates. Matrix spikes measure matrix-specific method performance and will be used to assess accuracy and precision. Unlike LCSs, MS/MSD samples will be used to assess the influence of the sample media (media interference) on the analysis. Samples for MS/MSD analysis will be site specific and analyzed at a frequency of five percent of the total number of samples for each analysis, or one MS/MSD sample per every 20 samples collected. Each MS/MSD sample will be spiked with the compounds specified by the analytical method prior to sample extraction or analysis in accordance with the Laboratory's SOPs (Appendix A).

Field Duplicates. As discussed previously, field duplicates (water samples) will be used to assess both sampling and analytical precision. The purpose of submitting samples "blind" to the laboratory is to assess the consistency or precision of the laboratory's analytical system. Precision will be evaluated by calculating the RPD between the field duplicate samples.

Field Replicates. As discussed previously, field replicates (soil samples) will be used to assess both sampling and analytical precision. The purpose of submitting samples "blind" to the laboratory is to assess the consistency or precision of the laboratory's analytical system. Precision will be evaluated by calculating the RPD between the field replicate samples.

4.4 LABORATORY BATCH QUALITY CONTROL LOGIC

The frequency of instrument calibration and QC sample analysis for the analytical methods will be batch controlled. All site sample data for the projects included in this QAPP will be associated with sample batch QC samples that were extracted concurrently with the site samples and analyzed in the same analytical batch (analyzed on the same instrument relative to the primary sample results). The following paragraphs define sample and instrument batches.

For the projects included in this QAPP, a sample batch is a group of twenty or less environmental samples of the same matrix which are extracted within the same time period (concurrently) or in limited continuous sequential time periods. Keeping batches "open" for more than two hours will not be accepted; samples and their associated QC samples (method blank, LCS, and MS/MSD) will be prepared in a continuous process. The sample batch will be analyzed sequentially on a single instrument (as practicable).

The instrument batch is a group of 20 or less environmental samples which are analyzed together within the same analytical run sequence as defined by the method calibration criteria or in continuous sequential time periods. Samples in each batch will be of similar matrix (e.g., soil and sediment or liquid waste and water), will be treated in a similar manner, and will use the same reagents.

5.0 SAMPLING PROCEDURES

5.1 SAMPLING PROCEDURES

The procedures that will be followed for sample collection for the projects included in this QAPP are described in their respective FSP or Work Plan. Procedures for the groundwater sampling will be included in the Long-Term Groundwater Monitoring Plan. Procedures for the treatment plant effluent are provided in the PSVP (July 1997) and an addendum to the PSVP (June 1999b), and procedures for off-gas sampling are provided in the Field Sampling Plan Addendum (June 1999c). Procedures for the sample collection of PCB-impacted soils are provided in the PCB-Impacted Soils Excavation Work Plan (April 1999). The following sections describe sample collection order, the types of sample containers, required sample preservation, and sample holding times.

5.2 SAMPLE COLLECTION ORDER, CONTAINERS, PRESERVATION, AND HOLDING TIME

5.2.1 Sample Collection Order

In general, sample containers will be filled in order of compound volatility or stability. The procedures for sample collection order in the project-specific FSP or Work Plan will be followed. For groundwater sampling, inorganic samples may be collected immediately after VOCs, to ensure that low turbidity samples are collected.

5.2.2 Sample Containers, Preservation, and Holding Time

All samples will be placed in contaminant-free containers as specified in the *U.S. EPA Specifications and Guidance for Obtaining Contaminant-Free Sample Containers* (U.S. EPA, 1992). The analytical laboratories will provide the required containers for sample collection. Containers will be stored in clean areas to prevent exposure to fuels, solvents, and other contaminants. The containers that will be used for sample collection and the required sample volume, preservation, and holding times are listed Table 5-1.

6.0 SAMPLE HANDLING AND CUSTODY

This section outlines procedures which ensure that samples are collected, transferred, stored and analyzed by authorized personnel, that sample integrity is maintained at all times, and that an accurate written record is maintained of sample handling and treatment from the time of collection through disposal. Field sampling personnel will be responsible for ensuring that proper documentation and custody procedures are initiated at the time of sample collection, and that individual samples can be tracked from the time of sample collection until custody of the samples is transferred to the laboratory. The laboratory will be responsible for maintaining sample custody and documentation from the time the laboratory receives the samples until final sample disposition.

To minimize common problems such as labeling errors, chain of custody errors, transcription errors, preservation failures, etc., detailed procedures for properly recording sample information and analytical requests on chain of custody records, for preserving samples as appropriate, and for sample packaging and shipment are described below. Field sampling personnel will be required to become familiar with the project-specific FSP or Work Plan and this QAPP, prior to initiating fieldwork.

6.1 SAMPLING HANDLING

Proper field sampling documentation and laboratory analytical documentation help ensure that sample authenticity and data integrity is maintained.

Where applicable, the respective FSP will describe the order of analytical parameter sample fraction collection. In general, VOCs will be collected first. The project-specific FSP will also describe the sample label scheme to be used for each site activity. In general, the sample label will be completed and attached to the sample containers at the time each sample is collected. The following information will be included on the sample label:

- Company's name
- Project name
- Sample location
- Field sample identification
- Sample type
- Date and time of sample collection
- Type of analyses to be performed
- Preservative (if applicable)
- Sampler's initials.

All soil and groundwater samples will be packaged and shipped in accordance with the

project-specific FSP or Work Plan to the laboratory the same day of sample collection via a commercial carrier. Samples requiring ice preservation will be sent via overnight carrier. The following provides a general description of the sample shipping procedures that will be followed:

- Sample labels will be completed and attached to sample containers as described previously.
- The samples will be placed upright in a waterproof metal (or equivalent strength plastic) ice chest or cooler.
- Wet ice in double Ziploc™ bags (to prevent leakage) will be placed around, among, and on top of the sample bottles. Enough ice will be used so that the samples will be chilled and maintained at 4°C ± 2°C during transport to the laboratory.
- To prevent the sample containers from shifting inside the cooler, the remaining space in cooler will be filled with inert cushioning material, such as shipping peanuts, additional bubble pack, or cardboard dividers.
- The original copy of the completed Chain-of-Custody (COC) Form will be placed in a waterproof plastic bag and taped to the inside of the cooler lid.
- The lid will be secured by wrapping strapping tape completely around the cooler in two locations.
- "This Side Up" labels will be placed on two sides of the cooler.
- Custody seals will be placed in two locations (the front right and back left of the cooler) across the cooler closure to ensure that any tampering is detected. The date and initials of the sampler will be written on the custody seal.
- A copy of the COC record and the signed air bill will be retained for the project files.

Treatment plant off-gas samples will be collected in Summa Canisters and will be shipped to the laboratory in the same containers in which the Summa Canisters were received by MWH. There are no special shipping requirements for Summa Canisters. Samples will be arranged by the laboratory into Sample Delivery Groups (SDGs). An SDG will be a group of 20 or fewer samples.

6.2 SAMPLING CUSTODY

COC is defined as the sequence of persons who have the item in custody. By a combination of field and laboratory records, these COC procedures will provide an accurate written record of the possession of each sample from the time it is collected in the field through Laboratory analysis and disposal. A sample is considered in custody if one of the following applies:

- It is in an authorized person's immediate possession
- It is in view of an authorized person after being in physical possession
- It is in a secure area after having been in an authorized person's physical possession
- It is in a designated secure area, restricted to authorized personnel only.

6.2.1 Field Custody Procedures

Sample custody and documentation procedures will be initiated at the time each sample is collected. The field sampler has ultimate responsibility for the samples until they are submitted to the laboratory for analysis. If a commercial carrier is used to transport the samples to the laboratory, the field sampler's responsibility ends when the carrier assumes responsibility for the samples. Sample identification numbers are defined in the project-specific FSP or Work Plan and will be assigned prior to sample collection. Sample collection details will be documented on the appropriate field forms including the COC form and the field logbook. All entries will be made using indelible ink. Any errors will be corrected by drawing a single line through the incorrect entry, entering the correct information, and then initialing and dating the change.

Field logbooks will be bound, field survey books or notebooks and will be assigned to the field sampling team. Information to be entered in the logbook will include:

- The date
- Personnel on Site (including visitors)
- Weather conditions
- The type of field equipment used
- Field equipment calibration methods
- Sampling methodology (if not recorded on a project-specific field form)
- Sample depths (if not recorded on a project-specific field form)
- Samples submitted to the laboratory for analysis (if not recorded on a project-specific field form)
- Sample type (e.g., field duplicates) (if not recorded on a project-specific field form)
- Sample destinations and how they were transported (e.g., name of laboratory and shipping agent) (if not recorded on a project-specific field form)
- Photograph numbers and descriptions (if applicable)
- Description of decontamination activities
- Schematic drawings of sample locations (if not done on field forms)

- Problems and corrective actions
- Any deviations from the task specific FSP or Work Plan or this QAPP
- Any other observations that may be relevant to the specific field program.

Sample tags and sample labels will be used to properly identify individual sample aliquot, and will minimize the possibilities that sample containers and/or tags can be switched.

Each COC form will be completed properly to ensure that sample custody is documented, appropriate sample fractions have been collected, and scheduled analyses are properly assigned. As described previously, all entries will be made using indelible ink. Any errors will be corrected by drawing a single line through the incorrect entry, entering the correct information, and then initialing and dating the change.

Unused portions of the COC form will be crossed out and initialed. A completed COC record will be included with each sample cooler. Shipping cooler custody seals will be placed on cooler to determine whether coolers may have been tampered with.

All samples will be transported via a commercial carrier (e.g., Federal Express Priority Service or Airborne Express Service). The air bill number will be recorded on the COC record and in the field book. The signed air bills will serve as evidence of custody transfer between the field sampler and carrier, and the carrier and laboratory. The sampler will retain and file copies of the COC record and the air-bill after the samples are shipped. The carrier will relinquish samples to the laboratory upon arrival, and the laboratory personnel will then complete the COC.

6.2.2 Laboratory Custody Procedures

Upon receipt by the laboratory, the integrity of the shipping container will be checked by verifying that the custody seals are not broken. The cooler will be opened and examined for evidence of proper cooling, and the presence of trip blanks and temperature blanks (as appropriate). The individual sample containers will be checked for breakage, damage, or leakage. The contents of the shipping container will then be verified against the COC. If any problems are found, they will be documented on the sample custody form(s) and the MWH Project Manager will be notified immediately. The shipping receipts will be placed with the COC records and stored in the project file.

If the samples and documentation are acceptable, each sample container will be assigned a unique laboratory identification number and entered into the laboratory's sample tracking system. Sample tracking will be documented in the laboratory LIMS, or other appropriate tracking system. Other information that will be recorded includes date and time of sampling, sample description, due dates, and required analytical tests.

When sample log-in has been completed, the samples will be transferred to limited-access temperature controlled storage areas. The sample storage areas (coolers, refrigerators) will

be kept at 4°C ± 2°C and their temperatures will be recorded daily with thermometers calibrated against National Institute of Standards and Technology (NIST) thermometers. Storage blanks will be used to assess the cleanliness of sample storage areas. Separate refrigerators will be used for samples suspected of containing high concentrations of organic compounds. Samples for VOC analysis will be stored separately from other samples, standards, and sample extracts.

The laboratory will follow its standard operating procedures for sample log-in, storage, tracking, and control. These procedures will be documented and available for review.

Sample custody will be maintained within the laboratory's secure facility until the samples are disposed. The laboratory will be responsible for sample disposal, which will be conducted in accordance with all applicable local, state, and federal regulations. All sample disposals will be documented and the records will be maintained by the laboratory in the project file.

6.2.3 Final Evidence File

All sample handling and custody information, such as field logbooks, COC forms, air bills and other shipping information will be stored in the Final Evidence File. The Final Evidence File for the project-specific tasks described in this QAPP may be held at different locations. The files will be maintained either at the MWH field office at the ACS Site, or at the MWH office in Warrenville, Illinois. All files are secure and have limited access. The files will be maintained for 10 years.

7.0 CALIBRATION PROCEDURES AND FREQUENCY

7.1 FIELD INSTRUMENT CALIBRATION

Field equipment or instruments will be calibrated in accordance with the manufacturer's directions and expected field conditions, and calibrated with sufficient frequency and in such a manner that accuracy and reproducibility of resulting data can be assessed. Field equipment calibration is specific to the type of instruments or equipment that will be used for the tasks included in this QAPP and is detailed in the task-specific FSP or Work Plan. The following paragraphs provide general guidance that will be followed for calibration for equipment used for groundwater elevation measurements and water quality parameter measurements.

Each field instrument or piece of equipment used to collect field data will be examined prior to use to ensure that it is in good working order. This includes reviewing and understanding the manufacturer's operation manual for each instrument and ensuring that all maintenance requirements are followed.

Field equipment or instruments will be calibrated on a daily basis prior to use. Calibration will also be checked periodically while equipment or instruments are in use. In addition, a calibration check will be performed at the conclusion of each day of use in order to evaluate instrument performance. Instruments or equipment will not be adjusted before the final calibration check has been performed and recorded. Calibration gases or reference solutions will not be used past their expiration date.

Electronic Water-Level Meter. The electric water-level meter will be checked before the beginning of field activities to ensure that it is in good working order. The meter will be checked for overall appearance (cleanliness, cuts in the tape) and the meter probe will be submerged in water to check for operation. If the water-level meter's measurements are suspect, then the instrument will be calibrated against a steel surveyor's tape. This calibration check will also be recorded in the field book or appropriate field form. Since water level meters are usually rented, annual calibrations of the water-level meter are not feasible.

Groundwater Quality Parameter Measurements. A water quality parameter meter with a flow-cell will be utilized for measurements of pH, dissolved oxygen, oxidation-reduction potential, temperature, specific conductivity, and turbidity during groundwater sampling. Although the meter is factory calibrated, the meter will be calibrated daily prior to field use, and whenever instrument drift is suspected. All calibrations will be recorded in the field book. Instrument calibration will be completed by following the manufacturer's recommended calibration methods. The Horiba U-22 series, commonly used for groundwater sampling at the ACS Site, has a special "Auto-Cal" solution that provides an

easy calibration of all its functions. The calibration procedures for this instrument are included in Appendix B.

7.2 LABORATORY INSTRUMENT CALIBRATION PROCEDURES

Instrument calibration is necessary to ensure that the analytical system is operating correctly and functioning at the proper sensitivity to meet the project-specific practical reporting limits (i.e., practical quantitation limits). Calibration establishes the dynamic range of an instrument, establishes response factors to be used for quantitation, and demonstrates instrument sensitivity. Criteria for calibration are specific to the instrument and the analytical method. The following paragraphs provide a general description of laboratory instrument calibration procedures. Specific procedures are described in the laboratories' SOPs in Appendix A, and specific variances to these SOPs are outlined in Section 7.2.3 of this QAPP.

7.2.1 Calibration Standard Preparation

Standard/Reagent Preparation. All instruments will be calibrated in accordance with the laboratories' SOPs (Appendix A) and the specific variances outlined in Section 7.2.3. To ensure the highest quality standard, primary reference standards will be used by the laboratory and will be obtained from the NIST, EPA Cooperative Research and Development Agreement (CRADA) vendors, American Association of Laboratory Accreditation (AALA) vendors, or other reliable commercial sources. When standards are received at the laboratory, the date received, supplier, lot number, purity, concentration, and expiration date will be recorded in a standards logbook. Vendor certifications for the standards will be retained in the files and made available upon request.

Standards will be obtained in their pure form or in a stock or working standard solution. Dilutions will be made from the vendor standards. All records regarding standards will unambiguously trace their preparation, use in calibration, expiration dates, and quantitation of sample results. All standards will be given a standard identification number, and the following information recorded in the appropriate file (standards logbook): source of standard, the initial concentration of the standard, the final concentration of the standard, the volume of the standard that was diluted, the solvent and the source and lot number of the solvent used for standard preparation, the expiration date of the standard, and the preparer's initials. All standards will be verified prior to use.

After preparation and before routine use, the identity and concentration of the standards will be verified. Verification procedures include a check for chromatographic purity (if applicable) and verification of the standard's concentration by comparing its response to a standard of the same analyte prepared or obtained from a different source. Reagent purity will be assessed by analyzing an aliquot of the reagent lot using the analytical method in which it will be used; for example, every lot of dichloromethane (for organic extractables)

will be analyzed for undesirable contaminants prior to use in the laboratory. Standards will be routinely checked for signs of deterioration (e.g., discoloration, formation of precipitates, and changes in concentration), and will be discarded if deterioration is suspected or the expiration date has passed. Expiration dates may be taken from the vendor recommendation, the analytical methods, or from internal research, whichever is most restrictive.

7.2.2 Instrument Calibration

Criteria for calibration are specific to the instrument and the analytical method. Each instrument will be calibrated according to the analytical methods following manufacturer's guidelines and using standard solutions appropriate to the type of instrument and the linear range established for the method. All reported analytes will be present in both initial and continuing calibrations, which must meet the acceptance criteria specified in the method and summarized in Attachment A. The instrument calibration will be from lowest to the highest calibration standard and the lowest calibration standard concentration will be equal to or less than the PQL for each target analyte. Either calibration curves or response factors will be used to determine analyte concentrations. The following paragraph describes the general requirements for instrument calibration, and standards preparation and traceability.

All instrument calibration information will be documented, and at a minimum include the equipment to be calibrated, the reference standards used for calibration, the calibration techniques, actions, acceptable performance tolerances, frequency of calibration, and calibration documentation format. The laboratory will maintain records of standard preparation and instrument calibration. Calibration records will include daily checks using standards prepared independently of the calibration standards, and instrument response will be evaluated against established criteria. The analysis logbook, maintained for each analytical instrument, will include at a minimum the date and time of calibration, the initials of the person performing instrument calibration, and the calibrator reference number and concentration. The calibration procedures are presented with the laboratory SOPs in Appendix A, and the corrective actions and QC acceptance limits are provided in Tables 4-2 through 4-21.

7.2.3 Variances to Calibration Procedures

The following variances to the laboratory SOPs included in Appendix A are to be followed:

AIR TOXICS, LTD. SOP #6 – Analysis of volatile organic compounds in Summa polished canisters – EPA Methods TO-14/TO-14A/TO-15

- (page 2) Table 1 - The internal standard retention time criteria for the daily CCV will be ± 0.33 minutes, instead of ± 0.5 minutes as stated in the SOP.
- (page 4) Section 7.1 - The tuning check will be done every 12 hours.
- (page 5) Section 7.4 - The CCV will be run every 12 hours.
- (page 6) Section 7.8 - A humidified blank will be analyzed after the CCV at the beginning of every 12 hours of instrument operation.

- (page 8) Section 9.2 – The 24-hour periods will be changed to 12-hour periods for both cases.

AIR TOXICS, LTD. SOP #10 – Analysis of semi-volatile organic compounds collected on PUF cartridges by GS/MS full scan & selective ion monitoring (SIM) – Modified EPA Methods TO-13

- (page 1) Table 1 – Initial calibration: The 20 percent criteria for %RSD for initial and continuing calibration will be used for all PAH analytes listed in method TO-13. The 30 percent criteria will be used for all other semi-volatile organic analytes.
- (page 1) Table 1 – Daily check standard: The 20 percent criteria for %D for initial and continuing calibration will be used for all PAH analytes listed in method TO-13. The 30 percent criteria will be used for all other semi-volatile organic analytes.
- (page 2) Table 1 – Surrogate recovery limits: The surrogate recovery acceptance criteria of 80 to 120 percent will be used.

8.0 ANALYTICAL PROCEDURES

This section describes the analytical procedures that will be used for the acquisition of chemical data for the ACS projects included in this QAPP and includes the relevant aspects of field and laboratory procedures (sample preparation and extraction procedures, instrumentation, MDLs, and PQLs. Analytical quality control requirements, evaluation criteria, acceptance criteria, calibration procedures, preventive maintenance, and corrective actions are discussed in Sections 4.0, 7.0, 12.0, and 14.0, respectively.

8.1 FIELD ANALYTICAL PROCEDURES

Groundwater Sample Analysis. Oxidation-reduction potential, dissolved oxygen, pH, temperature, specific conductivity, and turbidity will be measured in the field using field meters. These measurements will be collected in accordance with the field meter's manufacturer's directions and as specified in the task-specific FSP or Work Plan.

8.2 LABORATORY ANALYTICAL PROCEDURES

8.2.1 Analytical Methodology

Analytical services for the projects included in this QAPP will be provided by CompuChem, A Division of Liberty Analytical Corporation, of Cary, North Carolina; Air Toxics, LTD., of Fulsom, California; or Severn Trent Laboratories, of University Park, Illinois. CompuChem will serve as the primary analytical laboratory for analysis of all groundwater and soil samples. Severn Trent will serve as the backup analytical laboratory to CompuChem. Severn Trent will either serve as the quality assurance laboratory or provide analytical support in the event CompuChem capacity becomes an issue. Air Toxics will serve as the primary analytical laboratory for analysis of all air samples. See Table 2-2 for a list of all parameters and matrices to be analyzed by each laboratory.

All soil and groundwater analyses will be conducted in accordance with *EPA Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW-846),* (U.S. EPA Third edition, Final Update III, December 1996) or *EPA Methods for Chemical Analysis of Water and Wastes and the EPA Manual 600/4-79-020* (U.S. EPA, 1983). All treatment plant off-gas samples will be analyzed in accordance with the *Compendium of Methods for Determination of Toxic Organic Compounds in Ambient Air* (EPA/600/4-89/017, June 1988).

The methods included in this QAPP are presented and briefly described in Table 8-1. All samples will be prepared and analyzed in accordance with the referenced analytical method and in accordance with the laboratories' SOPs.

8.2.2 Method Detection Limits and Practical Quantitation Limits

Method Detection Limits. The MDL is an empirically derived value that is used to estimate the lowest concentration a method can detect in a matrix-free environment. The MDL is defined as the minimum concentration of a substance that can be measured and reported with 99 percent confidence that the analyte concentration is greater than zero. MDLs will be updated as scheduled in the laboratory's SOPs following guidance in 40 CFR 136 Attachment A. The MDLs for each method listed in this QAPP are presented in Table 2-2.

Practical Quantitation Limits. The PQL is the lowest concentration that can be reliably achieved within limits of precision and accuracy during routine operating conditions and is based on the MDL for each analyte. The PQLs for the analytical methods included in this QAPP are presented in Table 2-2. The lowest calibration standard concentration will be at the PQL or below the PQL for each target analyte.

8.2.3 Reporting Requirements

The following criteria for reporting data apply for all samples, except method blanks:

- All target analyte non-detections will be reported (at a minimum) as less than the PQL.
- If target analytes are detected at or above the PQL, they will be reported as quantified.
- Detections below the PQL and above the MDL will be reported and flagged with a "T" qualifier to indicate that the reported concentration is an estimate. Please refer to Table 10-1 for a summary of laboratory data qualifiers.
- Non-detections in method blanks will be reported as less than the MDL or PQL.

Table 2-2 lists all PQLs, as provided by Compuchem. Also, Table 2-2 lists example remediation/compliance objectives for the three projects addressed by this QAPP, i.e., the groundwater monitoring project, the effluent and off-gas sampling, and the PCB-impacted soils excavation project.

The groundwater monitoring plan was developed to detect changes in the concentrations of constituents in the groundwater surrounding the Site. Therefore, the MCLs listed in Table 2-2 are given to illustrate that the project-specific reporting limits are acceptable. Sample results from the private wells are compared to the MCLs for drinking water standards.

Project-specific compliance objectives have been established for the effluent and off-gas monitoring program. These objectives are listed in Table 2-2 to facilitate comparison to the project PQLs.

The remediation objective for PCBs in soil for the PCB-impacted soils excavation project is 1 part per million (ppm), as established by the U.S. EPA-approved April 1999 PCB-Impacted Soils Excavation Work Plan.

8.2.4 Additional Reporting Requirements for Definitive Data.

If a sample must be diluted and reanalyzed for the concentration of a single compound of interest to be within the linear calibration range of the instrument, and this results in non-detect values for other originally detected target analytes, the data for both the initial and reanalysis will be reported with the appropriate notations in the case narrative. The MWH Project Manager will be notified immediately regarding the failure of target analytes to meet PQLs to assess potential corrective action. The decision to implement corrective action will be based on whether there are any analytical alternatives or clean up steps that would improve the detection limits and whether the elevated detection limits will adversely affect data use. Any data that do not meet the PQLs due to sample dilution will be included in the case narrative and the supporting documentation (chromatograms) will be included in the data packages.

9.0 INTERNAL QUALITY CONTROL CHECKS

Internal quality control checks are used to evaluate whether field measurements and sampling procedures and laboratory analytical method performance is within acceptable limits of precision and accuracy. The following sections describe the internal QC that will be followed for both field and laboratory activities.

9.1 SAMPLE COLLECTION

Projects included in this QAPP include collection of water quality parameters. The quality control measures that will be used to assess the accuracy and precision of the field measurements, include obtaining multiple readings on a single grab sample, performing replicate sample analysis, and calibrating field instruments as described in the task-specific FSP or Work Plan and this QAPP.

The accuracy and precision of the field procedures will be assessed as described in Section 4.0 of this QAPP. Sample representativeness will be assessed by the analysis of field duplicate, field replicate, trip blank, equipment rinseate blank, and source water samples. These samples are described in Section 4.0.

9.2 LABORATORY ANALYSIS

The general objectives of the internal laboratory QC program are to:

- Ensure that all procedures are documented, including any changes in administrative and/or technical procedures.
- Ensure that all analytical procedures are validated and conducted according to method guidelines and laboratory SOPs.
- Monitor the performance of the laboratory using a systematic inspection program.
- Ensure that all data are properly reported and archived.

The laboratories will conduct internal quality control checks for analytical methods in accordance with their SOPs (Appendix A), the individual method requirements, and this QAPP. The laboratories will notify the MWH Project Manager in writing before making significant changes resulting from corrective actions to the project-specific FSP or Work Plan, this QAPP, or analytical methodology.

Laboratory quality control consists of two distinct components, a laboratory component and a matrix component. The laboratory component measures the performance of the laboratory analytical process during sample analyses, while the matrix component measures the effects of a specific media on the method performance. The QC samples that will be used to assess the laboratory component include:

- Method blank samples
- Reagent/preparation blanks (organic analysis only)
- Instrument blanks
- Instrument calibration
- MS/MSD sample results
- Surrogate spike recoveries
- Laboratory control samples
- Internal standard areas (gas chromatography/mass spectroscopy analysis only [GC/MS])
- Interference check standards(metals only)
- Mass tune standard results (GC/MS only).

The media and laboratory components of analysis are described in detail in Section 4.0 of this QAPP. The criteria against which the QC data will be evaluated are listed in Tables 4-2 through 4-21. Corrective actions for instrument calibration or QC sample data out of compliance are listed in the corrective action summary tables, also included in Tables 4-2 through 4-21.

10.0 DATA REDUCTION, REPORTING, AND VALIDATION

10.1 DATA REDUCTION

10.1.1 Field Data Reduction

Field data will be used as reported from the direct read instruments.

10.1.2 Laboratory Data Reduction

The laboratories will reduce all analytical data in accordance with their SOPs, analytical method guidance, and the guidance presented in Sections 4.0 and 7.0 of this QAPP. Refer to Section 4.0 of this QAPP for equations that will be used by the laboratory to assess precision and accuracy, and refer to Section 7.0 and Appendix A regarding instrument calibration and target analyte quantitation.

10.2 DATA REVIEW

10.2.1 Field Data Review

Prior to use, the MWH QAO or its designee will review all field data. The data will be reviewed to assess whether the procedures specified in the task-specific FSP or Work Plan and this QAPP were followed and to identify inconsistencies and/or anomalous values. Any inconsistencies will be resolved immediately, if possible, by seeking clarification from those personnel responsible for data collection. At a minimum, the information contained in boring logs, field notes, field-sampling forms, and chain of custody records, as applicable, will be included in the review process. All changes or corrections to this field documentation will also be reviewed. A narrative will be prepared that describes any deviations from the procedures, explains any qualifications regarding the data quality, and describes any significant problem identified during the review process.

10.2.2 Laboratory Data Review

The laboratory will perform in-house data review under the direction of the laboratory Project Manager and/or the QAO and will prepare and retain full analytical and QC documentation. Both screening and definitive data will be reviewed prior to release by the laboratory. In general, the laboratory data review will be conducted as described in the following paragraphs:

The bench analyst will conduct the initial data review based on established protocols specified in laboratory SOPs, analytical method protocol, and project-specific data quality objectives. At a minimum this review will include the following:

- An assessment of sample preparation procedures and documentation for accuracy and completeness.

- An assessment of sample analysis procedures and documentation for accuracy and completeness.
- Assessments of whether the appropriate SOPs were followed.
- An assessment of analytical results for accuracy and completeness.
- An assessment of whether QC samples are within the project established control limits presented in Section 4.0 of this QAPP and method blank data are acceptable.
- An assessment of whether documentation is complete (e.g., all anomalies in the preparation and analysis have been documented, out-of-control forms, if required, are complete, holding times are documented, etc.).

The calculations that will be used to evaluate precision and accuracy, the project-specific acceptance criteria for calibration, precision, and accuracy assessment, and the corrective action summaries are provided in Section 4.0 of this QAPP.

When an analysis of a QC sample (blank, spike, internal standard, or similar sample) indicates that the analysis of that batch of samples is not in control, the analyst will immediately bring the matter to the attention of the appropriate designated QC staff (QAO, Project Manager, Section Leader, etc.). This individual will determine whether the analysis can proceed, or if selected samples should be rerun, or specific corrective action needs to be taken before analyzing additional samples. Out-of-control analyses and information justifying accuracy or precision outside acceptance criteria will be documented. A Nonconformance Report will be prepared for all laboratory analysis out of control events that require documentation. The MWH Project Chemist or Project Manager will be notified as soon as feasibly possible to determine appropriate corrective action for out-of-control events resulting in unacceptable data.

After this review is complete, the analyst will sign the applicable control documentation associated with the analytical batch and forward to the appropriate reviewer. This reviewer (department manager, QAO, etc.) will be responsible for review and approval of the analytical control documentation associated with each analytical batch, as well as any corrective action explanations provided by the analyst. This individual will also be responsible for determining whether the analytical data meet quality control criteria established by the analytical methods and by this QAPP and for identifying QC problems that require further resolution. A permanent record of any corrective actions will be maintained in the laboratory files.

The laboratory Project Manager will provide the final review and approval of the analytical data that have been approved by the analyst and other designated reviewer. The Project Manager will also be responsible for reviewing all final data reports for proper format and

reporting consistency prior to releasing the reports to MWH. This review will include the following as a minimum:

- Laboratory name and address.
- Sample information (includes unique sample identification, sample collection date and time, date of sample receipt, and date(s) of sample preparation and analysis).
- Analytical results reported with an appropriate number of significant figures.
- Reporting limits reflecting dilutions, interferences, and corrections for dry weight as applicable.
- Method references.
- Appropriate QC results and correlations for sample batch traceability and documentation.
- Data qualifiers with appropriate references and narrative on the quality of results.
- Confirmation that project-specific requirements have been met.

The laboratory Project Manager and/or the laboratory QAO will also be responsible for qualifying any data that may be unreliable. Data qualifications will be based on the laboratory SOPs, the analytical method, and the principles outlined in the *Contract Laboratory Program National Functional Guidelines for Organic and Inorganic Data Review* (Functional Guidelines; EPA, 1999b). The flags that will be used by the laboratory for data qualification are listed in Table 10-1.

10.3 DATA REPORTING

10.3.1 Field Data

Field data will be reported as described in Table 10-2 and presented in a format that will facilitate data review and evaluation. Tables, graphs, or figures will be used to present the data in associated project reports.

10.3.2 Laboratory Data

The analytical data will be reported in a format organized to facilitate data validation. The information that will be included in the laboratory data packages is listed in Table 10-2.

10.4 DATA VALIDATION

As described in Section 4.0, the validity of the field and analytical data will be evaluated using the PARCC parameters, which are quantitative and qualitative statements that describe data quality. The PARCC parameters will be used to determine whether the DQOs of this investigation have been met by comparing QC sample results and standard procedures with acceptance criteria established for the tasks included in this QAPP. For the projects included in this QAPP, all definitive data will be validated by MWH based on the principles outlined in the *Contract Laboratory Program National Functional Guidelines for Organic and Inorganic Data Review* (Functional Guidelines; EPA, 1999b). A Level III data validation will be conducted for all definitive data and a Level IV data validation will be performed for 10 percent of the definitive data. The Level III validation will consist of a systematic evaluation of all calibration data, QC sample results (both field and laboratory), and sample holding times as listed in Figures 10-1A/B and 10-2A/B (organic and inorganic data validation forms). The criteria that will be used for data validation are presented in Section 4.0. The Level IV validation will include all Level III evaluation criteria and a review of all instrument output (raw data) and calculations. If significant problems are identified during the Level IV data validation, additional data will be validated using Level IV procedures until data problems are resolved.

10.4.1 Field Data

The MWH QAO or designee will assess the quality of field data. Because there are no formal quantitative procedures for validation of screening data, which includes field data, field data will be quantitatively evaluated in terms of the PARCC parameters as described in Section 4.0.

10.4.2 Laboratory Data Validation

The MWH Project Chemist or an outside subcontractor will perform the data validation. As discussed previously, there are no formal data validation requirements for screening data. The following discussions regarding data validation are specific to definitive data; screening data will not be included in this process.

The objective of the definitive data validation is to provide a data review that verifies the laboratory QC results. This validation will be based on the principles outlined in the *Contract Laboratory Program National Functional Guidelines for Organic and Inorganic Data Review* (U.S. EPA, 1999b) and structured to assess whether the acceptance criteria for instrument calibration and QC sample analysis have been met. PARCC parameters will be used to validate the quality of analytical data and determine whether the DQOs of the project have been met. Table 4-1 depicts how the QC samples will be used to assess PARCC parameters. The calculations that will be used to assess data quality are presented in Sections 4.0 and 13.0 and the criteria that will be used to assess data quality are described in Section 14.0.

Data validation techniques include accepting, rejecting, or qualifying the data on the basis of acceptance criteria defined in Section 4.0. Data qualifiers that will be used for validation are listed in Table 10-3.

The data validation will be documented on the data validation forms. An example of the type of forms that will be used are shown in Figures 10-1A and B and 10-2A and B. These forms also require the signature of the reviewer and the date of the validation. Data will not be released for use prior to completion of the data validation.

10.5 DATA MANAGEMENT

The individuals responsible for data management include all personnel responsible for identifying, reporting, and documenting activities affecting data quality. In general, the qualifications of the individuals associated with data management activities will be commensurate with the level of expertise necessary to ensure the intended level of evaluation.

The laboratory will maintain a project specific file such that the data management and analytical process can be completely reconstructed. The laboratory will preserve all information regarding sample analyses (correspondence, sample custody forms, raw data [hard copies], results, calibration records, etc.) in the project file. Data and storage and documentation will be maintained using logbooks and data sheets that will be included in the project file. Computer acquired data will also be stored on magnetic tape, disks, or other media, that can be accessed using industry-standard hardware and software for data processing, retrieval, or reporting. The laboratory will maintain all data collected for the projects included in this QAPP a minimum of ten years following submission of the data reports.

11.0 PERFORMANCE AND SYSTEM AUDITS

Independent technical systems and performance audits of field and laboratory activities will be conducted to assess whether sampling and analysis protocols conform to the criteria specified in the task-specific FSP or Work Plan and this QAPP. The systems audit is a qualitative review of the overall sampling or measurement system, while the performance audit is a quantitative assessment of a measurement system, and includes both internal and external audits. These audits will be used to assess whether the resulting data meet the project-specific DQOs, to assess whether the data comply with QC criteria, and to identify the need for corrective action. Definitive data validation is also a quantitative check of the analytical process, where documentation and calculations are evaluated and verified. Data validation is discussed in Section 9.0. Internal audits will be conducted by MWH or the laboratory's QAO. U.S. EPA Region V or IDEM will perform external audits.

11.1 FIELD PERFORMANCE AND SYSTEM AUDITS

Oversight of field procedures will be the direct responsibility of the MWH Project Manager, who will review all elements of the project-specific FSP and this QAPP to ensure that the objectives of the project are met. In addition to an initial review, the sampling procedures will be reviewed as the field work progresses so that any necessary modifications are implemented.

MWH's QAO or designee will conduct internal audits of field activities (sampling and measurements) to assess the performance and effectiveness of the existing quality management systems in accordance with this QAPP. The intent of these audits is to identify, correct, and prevent management problems that hinder the achievement of the project DQOs.

The audits will include examining field equipment calibration and documentation records; field instrument operation records; field measurement records; field sampling records including log books and field sampling forms; sample collection, handling, storage, and transportation procedures including organization and minimization of potential contamination sources; and chain-of-custody records and procedures. Field activities will be audited at the beginning of the project to verify that all of the procedures outlined in the task-specific FSP or Work Plan and this QAPP are followed.

After the internal audit is completed, a debriefing session will be held for all participants to discuss the preliminary audit results. The auditor will prepare an audit evaluation report that includes observations of any deficiencies and the necessary recommendations for corrective actions. Compliance with the specifications presented in the task-specific FSP or Work Plan and this QAPP will be noted and noncompliance or deviations will be

addressed in writing by MWH. This information will be forwarded to appropriate management (as defined in Section 3.0 of this QAPP) with corrective actions and a time frame for implementation of the corrective actions. Follow-up audits will be performed prior to completion of the project to ensure corrective actions have been implemented.

External field audits are the responsibility of U.S. EPA Region V or IDEM. Field audits may be conducted at any time during the field operations and will be based upon the information presented in the task-specific FSP or Work Plan and this QAPP. The audits may or may not be announced, at the discretion of the auditing agency.

11.2 LABORATORY PERFORMANCE AND SYSTEMS AUDITS

In-house and regulatory agency audits of laboratory systems and performance will be a regular part of the laboratory's QA program. Internal audits will be conducted by the laboratory's QAO or designee, and consist of a review of the entire laboratory system and at a minimum include: examination of sample receiving, log-in, storage, and chain-of-custody documentation procedures; sample preparation and analysis; and instrumentation procedures.

An internal audit of the laboratory may be performed by MWH within six months of project start up and will include a review of laboratory agency audit or performance evaluation results and review of the following items:

- Sample custody procedures
- Calibration procedures and documentation
- Completeness of data forms, notebooks, and other reporting requirements
- Data review and validation procedures
- Data storage, filing, and record keeping procedures
- QC procedures, tolerances, and documentation
- Operating conditions of facilities and equipment
- Documentation of training and maintenance activities
- Systems and operations overview
- Security of laboratory automated systems.

MWH will forward audit results to appropriate management (as defined in Section 3.0). Deficiencies and corrective action procedures will be clearly documented in the audit report.

To verify proper implementation of laboratory procedures and adherence to this QAPP, U.S. EPA Region V or IDEM prior to or during a project may perform external audits. These audits may or may not be announced and are conducted at the discretion of agency. External audits will include (but not be limited to) review of laboratory analytical

procedures, laboratory on-site audits, and/or submission of performance evaluation samples to the laboratory for analysis.

12.0 PREVENTIVE MAINTENANCE PROCEDURES

A preventive maintenance program is necessary for the timely and effective completion of a measurement effort for either field or laboratory programs. The preventive maintenance program for the ACS tasks included in this QAPP will be designed to minimize the downtime of crucial sampling and/or analytical equipment due to unexpected component failure. In implementing this program, efforts will be focused on establishment of maintenance responsibilities, establishment of maintenance schedules for major and/or critical instrumentation and apparatus, and establishment of an adequate inventory of critical spare parts and equipment.

12.1 FIELD EQUIPMENT/INSTRUMENTS

The field equipment that will be used for the ACS project will be maintained and used according to the manufacturers' directions and as specified in the task-specific FSP or Work Plan and Section 7.0 of this QAPP. It is the responsibility of the field team leader to ensure that each piece of equipment is operational and is inspected on a regular basis. Any preventive maintenance or repair conducted in the field will be recorded in the field logbook or other appropriate field forms. Backup instruments and equipment will be available on-site or within short turnaround time to avoid field schedule delays. A description of typical maintenance for field equipment is presented in Table 12-1.

Field instruments will be checked and calibrated before they are shipped or carried to the field, and will be checked and calibrated daily before use. Calibration check procedures are specified in Section 7.0 of this QAPP and will be performed in accordance with the manufacturer's directions.

In addition to scheduled maintenance activities, an adequate inventory of spare parts will be maintained by MWH to minimize equipment downtime. The inventory includes those parts (and supplies) that are subject to frequent failure, have limited useful lifetimes, or cannot be obtained in a timely manner should failure occur.

12.2 LABORATORY EQUIPMENT

Preventive maintenance of all laboratory equipment and instruments is essential to ensure the quality of the analytical data produced. The objective of preventive maintenance is to ensure instrument operation is appropriate for both project and method DQOs. The laboratory will have a routine preventive maintenance program to minimize the occurrence of instrument failure and other system malfunctions and will have designated individuals who perform routine scheduled maintenance for each instrument system and required

support activity. The following paragraphs focus on maintenance responsibilities, maintenance schedules, record keeping, and inventory of spare parts and equipment.

Maintenance Responsibilities. Maintenance responsibilities for laboratory equipment will be assigned to designated personnel. These individuals will establish maintenance procedures and schedules for each major equipment item. The instrument manufacturer service engineers will perform instrument maintenance and repair, as scheduled/needed. The analysts will perform other routine preventive maintenance tasks. Only qualified individuals will perform any maintenance activities.

Maintenance Schedules. Maintenance schedules are based on the manufacturers' recommendations and/or sample load. Typical maintenance and maintenance schedules for the type of laboratory instrumentation that will used is described in Table 12-2. Maintenance activities for each instrument will be documented in a maintenance logbook, as described below.

Record Keeping. All instrument maintenance will be documented in instrument-specific bound logbooks, which are kept with the instrument. The date, initials of the individual performing the maintenance and the type of maintenance will be recorded in this logbook. Receipts from routine maintenance performed by the manufacturer's representative will be filed in the appropriate laboratory department (e.g., GC/MS maintenance receipts are stored in the organic section). This logbook will serve as a permanent record that documents any routine preventive maintenance performed, as well as any service performed by external individuals such as manufacturers' service representatives. In addition, all receipts from routine maintenance performed by manufacturers' representatives will be maintained in the laboratory's file. These records will be made available upon request during external audits.

Spare Parts. An adequate inventory of spare parts will be maintained to minimize equipment down time. This inventory will include those parts (and supplies) which are subject to frequent failure, have limited useful lifetimes, or cannot be obtained in a timely manner.

Contingency Plan. In the event of instrument failure, every effort will be made to analyze samples by an equivalent alternate means within holding times. If the redundancy in equivalent instrumentation is insufficient to handle the affected samples, MWH will be immediately notified and the corrective action to be taken will be determined by the MWH Project Manager and the laboratory.

13.0 SPECIFIC ROUTINE PROCEDURES USED TO EVALUATE DATA PRECISION, ACCURACY, AND COMPLETENESS

The purpose of this section is to define the methods by which the data will be evaluated for compliance with the project specific DQOs. As discussed in Section 4.0 the data will be evaluated in terms of precision, accuracy, and completeness. The remainder of this section describes how this assessment will be conducted.

13.1 ACCURACY ASSESSMENT

As discussed in Section 4.0, laboratory accuracy will be assessed quantitatively through the analysis of MS/MSD samples and SRMs, which include surrogate spikes (organic analysis only), LCS, response factors for calibration standards, and internal standard recoveries. Accuracy for definitive data will be calculated using the following equation:

$$\text{Percent Recovery} = \frac{|A - B|}{C} \times 100$$

Where: A is the target analyte concentration determined analytically from the spiked sample.

B is the background level determined by a separate analysis of the unspiked sample.

C is the concentration of spike added.

13.2 PRECISION ASSESSMENT

As discussed in Section 4.0, precision is the reproducibility of measurements under a given set of conditions. For large data sets, precision is expressed as the variability of a group of measurements compared to their average value (i.e., standard deviation). For duplicate replicate measurements, precision is expressed as the RPD of a data pair and is calculated using the following equation:

$$\text{RPD} = \frac{|A - B|}{\frac{(A + B)}{2}} \times 100$$

Where A and B are the reported concentrations for duplicate sample analyses.

Analytical laboratory precision for definitive data will be assessed using the calculated RPD between the following data:

- MS/MSD sample data.
- Investigative and associated field duplicate or replicate sample data.
- Laboratory precision will also be assessed for three or more replicated samples (e.g., response factors for calibration standards).

13.3 DATA COMPLETENESS ASSESSMENT

Completeness is a measure of the amount of valid data obtained from a measurement system relative to the amount of data scheduled for collection under correct, normal conditions. Completeness measures the effectiveness of the overall investigation in collecting the required samples, completing the required analyses, and producing valid results. Completeness will be calculated using the following equation:

$$\text{Completeness} = \frac{\text{Number of valid data points}}{\text{Total number of measurements}} \times 100$$

where: the number of valid data points is the total number of valid analytical measurements based on the precision, accuracy, and holding time evaluation.

Laboratory definitive data completeness is a quantitative measure of the percentage of valid data for all analytical data as determined by the precision, accuracy, and holding time criteria evaluation. Completeness will be calculated using the completeness equation by dividing the total number of valid data points by the total number of data points. The laboratory completeness goal for data collected under this QAPP is 95 percent.

13.4 DATA ASSESSMENT

The QC results associated with each analytical parameter for each matrix will be compared to the objectives presented in Sections 2.0 and 4.0 of this QAPP. Only data generated in association with QC results meeting these objectives will be considered usable for decision-making purposes.

In addition, the data obtained will be both qualitatively and quantitatively assessed on a project-wide, matrix-specific, parameter-specific, and unit-specific basis. This assessment will be performed by the MWH Project Manager (or designee), and the results presented

and discussed in detail in the task-specific report. Factors that will be considered during this evaluation will include, but not be limited to the following:

- Were all samples collecting using the methodologies included in this QAPP and the task specifiec FSP or Work Plan?
- Were all proposed analysis performed in accordance with this QAPP and the laboratory's SOPs?
- Were the PQLs elevated and what impact if any to data usability occurred?
- Were samples obtained from all proposed sampling locations and depths?
- Do any data exhibit elevated detection limits due to matrix interference or contaminants present at high concentrations?
- Were any analytes not expected to be present at this site identified as target parameters?
- Were all field and laboratory data validated in accordance with the validation protocols, including the project-specific QC objectives specified in this QAPP?
- Which data sets were found to be unusable ("R" qualified) based on the data validation results?
- Which data sets were found to be usable for limited purposes ("J" qualified) based on the data validation?
- What affect do qualified data have on the ability to implement the project decision rules?
- Can valid conclusions be drawn for all matrices at each unit and/or area under investigation?

14.0 CORRECTIVE ACTION

14.1 CORRECTIVE ACTION REQUIREMENTS

Corrective action is the process of identifying, recommending, approving, and implementing measures to counter unacceptable procedures or out of quality control performance that may affect data quality. All proposed and implemented corrective action will be documented in a quality assurance report to the appropriate project management as defined in Section 3.0 of this QAPP. Corrective action will be implemented only after approval by the U.S. EPA Region V, IDEM, the ACS RD/RA Committee, and the MWH Project Manager. If immediate corrective action is required, approvals secured by telephone from the MWH Project Manager will be documented in an additional memorandum.

For each incidence of noncompliance, a formal corrective action program will be established and implemented at the time the problem is identified. The individual who identifies the problem will be responsible for notifying the MWH Project Manager, who in turn will notify other project managers (as defined in Section 3.0). Implementation of corrective action will be confirmed in writing as described previously.

Any nonconformance with the established QC procedures specified in the task-specific FSP or Work Plan and this QAPP will be identified and corrected in accordance with the QAPP. Corrective actions will be implemented and documented in the field logbook. No staff member will initiate corrective action without prior communication of findings through the proper channels.

14.1.1 Field Corrective Action

During any field activity, the field staff will be responsible for documenting and reporting all suspected technical and QA nonconformances, and suspected deficiencies. The nonconformances and/or deficiencies will be documented in the field logbook and reported to the MWH Project Manager. If the problem is associated with field measurements or sampling equipment, the field staff will take the appropriate steps to correct the problem. Typical field procedures to correct problems include the following:

- Repeating the measurement to check for error
- Making sure the meters or instruments are adjusted properly for ambient conditions, such as temperature
- Checking or replacing batteries
- Recharging batteries

- Recalibrating the instruments
- Replacing the meters or instruments used to measure field parameters
- Stopping work (if necessary) until the problem is corrected.

If a nonconformance or problem requires a major adjustment to the field procedures outlined in the task specific FSP or Work Plan or this QAPP (e.g., changing sampling methodology or sampling schedule), the MWH Project Manager, in conjunction with the ACS RD/RA Committee, will be responsible for initiating corrective actions and notifying U.S. EPA Region V and IDEM. The MWH Project Manager will be responsible for:

- Evaluating the reported nonconformance.
- Controlling additional work on nonconforming items.
- Determining the appropriate corrective actions in conjunction with appropriate project managers and U.S. EPA Region V and IDEM.
- Maintaining a log of all nonconformances and corrective actions.
- Approving all changes in writing or verbally prior to field implementation, if feasible. If deemed unacceptable, the action taken during the period of non-conformance will be evaluated to determine the significance of any departure from established program practices.
- Ensuring that explanation of nonconformances and corrective actions is included in an appendix to the report scheduled for this investigation.
- Ensuring that no additional work that is dependent on the nonconforming activity is performed until the appropriate corrective actions are completed.
- Ensuring nonconformance reports are included in the final site documentation in the project files.
- Reporting all changes to all affected parties, including U.S. EPA Region V and IDEM.

14.1.2 Laboratory Corrective Action

Corrective actions are required whenever unreliable analytical results prevent the quality control criteria from being met, as specified by the analytical method; the laboratory's SOPs, or this QAPP. The corrective action taken depends on the analysis and the nonconformance. The corrective actions that will be undertaken for problems associated with specific laboratory analyses is provided in the SOPs in Appendix A and Section 4.0 of this QAPP.

Corrective action will be undertaken if one of the following occurs:

- Blanks consistently contain target analytes above acceptance levels.
- Undesirable trends are detected in spike recoveries, spike recoveries are outside the QC limits, or RPDs between duplicate analyses are consistently outside QC limits.
- There are unusual changes in detection limits.
- Deficiencies are detected during either internal or external QA audits.
- Inquiries concerning data quality are received from MWH's Project Chemist.

The analyst who reviews the sample preparation or extraction procedures, and performs the instrument calibration and analysis will handle corrective actions at the bench level (primarily). If the problem persists or its cause cannot be identified, the matter will be referred to the department supervisor or QA department for further investigation. Once resolved, full documentation of the corrective action procedure will be filed with the appropriate laboratory QA department. A summary of the corrective actions will be included in the data reports.

14.1.3 Data Validation Corrective Actions

Corrective action may be initiated during data validation or data assessment. Potential types of corrective action include resampling by the field team or reanalysis of samples by the laboratory.

Corrective actions that will be taken are dependent upon the ability to mobilize the field team, how critical the data are to the project DQOs, and whether the samples are still within holding time criteria. When a corrective action situation is identified by the validating party, the MWH Project Manager and the ACS RD/RA Committee will be notified, and will have the final responsibility for authorizing the implementation of the corrective action, including resampling and documenting the corrective action and notifying U.S. EPA Region V and IDEM.

15.0 REFERENCES

Montgomery Watson, January 1996. *Site Safety Plan.*

Montgomery Watson, July 1997. *Operations and Maintenance Manual for the Perimeter Ground Water Containment System and the Barrier Wall and Associated Extraction System. Vol 2 Performance Standard Verification Plans.*

Montgomery Watson, April 1999. *PCB-Impacted Soils Excavation Work Plan.*

Montgomery Watson, June 1999a. *Site Safety Plan Addendum.*

Montgomery Watson, June 1999b. *Performance Standard Verification Plan [Addendum].*

Montgomery Watson, June 1999c. *Field Sampling Plan Addendum.*

U.S. EPA, 1983. *Methods for Chemical Analysis of Water and Wastes*, EPA Manual, 600/4-79-020 (U.S. EPA, 1983, with additions).

U.S. Environmental Protection Agency, 1998. *Compendium of Methods for Determination of Toxic Organic Compounds in Ambient Air* (EPA/600/4-89/017, June 1988).

U.S. Environmental Protection Agency, 1992. *U.S. EPA Specifications and Guidance for obtaining Contaminant-Free Sample Containers.*

U.S. Environmental Protection Agency, 1994. *Data Quality Objectives Process for Superfund Interim Final Guidance,* EPA QA/G-4.

U.S. Environmental Protection Agency, 1996. *EPA Test Methods for Evaluating Solid Waste, Physical/Chemical Methods,* SW-846, 3rd Edition, Final Update III, December 1996.

U.S. Environmental Protection Agency,1999a. *EPA Requirements for Quality Assurance Project Plans* (QA/R-5).

U.S. Environmental Protection Agency, 1999b. *U.S. EPA Contract Laboratory Program National Functional Guidelines For Organic and Inorganic Data Review.*

TABLES

Table 2-1
Proposed Groundwater, Effluent and Off-Gas, and PCB Soil Samples
American Chemical Service, Griffith, Indiana

Parameter Group	Reporting Units	Approximate Number of Samples[a]	Approximate Number of Field Duplicates[b]	Approximate Number of Equipment Blanks[c]	Approximate Number of MS/MSDs[b]	Approximate Number of Trip Blanks[b]	Total Number of Samples
Long-Term Groundwater Monitoring[d]							
Upper and Lower Aquifer Wells							
Indicator[f] VOCs	µg/l	28	3	3	2	3	39
Volatile Organic Compounds	µg/l	28	3	3	2	3	39
Semi-Volatile Organic Compounds	µg/l	28	3	3	2	NS	36
Pestcides/Polychlorinated biphenyls	µg/l	28	3	3	2	NS	36
Metals[e]	µg/l	28	3	3	2	NS	36
Cyanide	µg/l	28	3	3	2	NS	36
Residential Wells							
Volatile Organic Compounds (low level)	µg/l	5	1	NS	1	1	8
Semi-Volatile Organic Compounds (low level)	µg/l	5	1	NS	1	NS	7
Pesticides/PCBs (low level)	µg/l	5	1	NS	1	NS	7
Metals[e]	µg/l	5	1	NS	1	NS	7
Cyanide	µg/l	5	1	NS	1	NS	7
Effluent and Off-gas Sampling							
Treatment Plant Effluent[g]							
Volatile Organic Compounds	µg/l	1	NS	NS	NS	NS	1
Semi-Volatile Organic Compounds	µg/l	1	NS	NS	NS	NS	1
Polychlorinated biphenyls	µg/l	1	NS	NS	NS	NS	1
Metals	µg/l	1	NS	NS	NS	NS	1
Biological Oxygen Demand-5	µg/l	1	NS	NS	NS	NS	1
Total Suspended Solids	µg/l	1	NS	NS	NS	NS	1
pH	µg/l	1	NS	NS	NS	NS	1
Treatment Plant Off-Gas							
Volatile Organic Compounds	ppb/vol	2	1	NS	NS	NS	3
Semi-Volatile Organic Compounds	µg/sample	2	1	NS	NS	NS	3
ISVE System Off-Gas							
Volatile Organic Compounds	ppb/vol	2	1	NS	NS	NS	3
Semi-Volatile Organic Compounds	µg/sample	2	1	NS	NS	NS	3
PCB Remedial Actions							
Soil PCB	µg/kg	TBD	1 per 10	1 per 10	1 per 20	NS	TBD

Notes:
EPA Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, (U.S. EPA Third edition, Final Update III, December 1996).
EPA 600 Series - Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater (U.S. EPA, CFR Title 40, Part 136, Appendix A, July 1996).
EPA 100-400 Series - Methods for the Determination of Inorganic Substances in Environmental Samples (EPA/600R-93/100, August 1993).
Compendium of Methods for Determination of Toxic Organic Compounds in Ambient Air (EPA/600/4-89/017, June 1988).

Table 2-1
Proposed Groundwater, Effluent and Off-Gas, and PCB Soil Samples
American Chemical Service, Griffith, Indiana

Notes (cont.)

[a] All sample numbers are approximate. The actual number of samples and their sampling frequency will be presented in the Long-Term Groundwater Monitoring Plan or respective task-specific field sampling or work plan.

[b] QC Sample freqencies are: 1 field duplicate for every 10 samples, 1 equipment blank for every 10 samples, and 1 MS/MSD for every 20 samples. A trip blank will be shipped with every cooler containing VOC water samples.

[c] Equipment blanks will be collected by sampling de-ionized or distilled water through the sampling equipment.

[d] pH, temperature, oxidation-reduction potential, dissolved oxygen, specific conductivity, and turbidity data will be collected at each well sampled.

[e] Metals include the Contract Laboratory Program list.

[f] Indicator parameters for VOCs include: tetrachloroethene, trichloroethene, trans- and cis-1,2-dichloroethene, 1,1-dichloroethene, 1,1-dichloroethane, 1,2-dichloroethene, vinyl chloride, chloroethane, and benzene.

[g] Volatile organic compounds include benzene, acetone, 2-butanone, chloromethane, 1,4-dichlorobenzene, 1,1-dichloroethane, cis-1,2-dichloroethene, ethylbenzene, methylene chloride, tetrachloroethene, trichloroethene, vinyl chloride. Semi-volatile organic compuonds include 4-methyl-2-pentanone, bis (2-chloroethyl) ether, bis (2-ethylhexyl) phthalate, 4-methylphenol, isophorone, pentachlorophenol. Metals include arsenic, beryllium, cadmium, magnanese, mercury, selenium, thallium, zinc.

µg/l	microgram/liter
µg/kg	microgram/kilogram
ppb/vol	parts per billion by volume
NS	not sampled
TBD	to be determined
ISVE	In-Situ Soil Vapor Extraction

Table 2-2
Analytes, Practical Reporting Limits, and Maximum Contaminant Levels
American Chemical Service, Griffith, Indiana

Groundwater					
	Compuchem				
	Standard	Low Level			
Target Parameter	PQL (µg/L)	PQL (µg/L)	MDL (µg/L)	U.S. EPA MCL (µg/L)	Effluent Discharge Limits (µg/L)
VOCs by SW8260B					
1,1,1-Trichloroethane	5.0	0.5	0.25	200	N/A
1,1,2,2-Tetrachloroethane	5.0	0.5	0.39	NE	N/A
1,1,2-Trichloroethane	5.0	0.5	0.17	5.0	N/A
1,1-Dichloroethane	5.0	0.5	0.25	NE	NE
1,1-Dichloroethene	5.0	0.5	0.29	7.0	N/A
1,2-Dichloroethane	5.0	0.5	0.16	5.0	N/A
1,2-Dichloropropane	5.0	0.5	0.17	5.0	N/A
2-Butanone (MEK)	12.5	2.5	1.11	NE	210
2-Hexanone	12.5	2.5	1.03	NE	N/A
4-Methyl-2-pentanone (MIBK)	12.5	2.5	1.22	NE	15
Acetone	12.5	10.0	4.28	NE	6800
Benzene	5.0	0.5	0.19	5.0	5.0
Bromodichloromethane	5.0	0.5	0.17	80[1]	N/A
Bromoform	5.0	0.5	0.13	80[1]	N/A
Bromomethane	5.0	0.5	0.29	NE	N/A
Carbon Disulfide	5.0	0.5	0.24	NE	N/A
Carbon Tetrachloride	5.0	0.5	0.22	5.0	N/A
Chlorobenzene	5.0	0.5	0.19	NE	N/A
Chloroethane	5.0	0.5	0.27	NE	N/A
Chloroform	5.0	0.5	0.20	80[1]	N/A
Chloromethane	5.0	0.5	0.20	NE	NE
cis-1,2-Dichloroethene	5.0	0.5	0.24	70	70
cis-1,3-Dichloropropene	5.0	0.5	0.15	NE	N/A
Dibromochloromethane	5.0	0.5	0.14	80	N/A
Ethylbenzene	5.0	0.5	0.26	700	34
Methylene chloride	5.0	10.0	2.12	5.0	5.0
Styrene	5.0	0.5	0.22	100	N/A
Tetrachloroethene	5.0	0.5	0.28	5.0	5.0
Toluene	5.0	0.5	0.17	1000	N/A
trans-1,2-Dichloroethene	5.0	0.5	0.27	100	N/A
trans-1,3-Dichloropropene	5.0	0.5	0.16	NE	N/A
Trichloroethene	5.0	0.5	0.22	5.0	5.0
Vinyl chloride[3]	5.0	0.5	0.28	2.0	2.0
Xylenes (total)	5.0	1.0	0.47	10,000	N/A
1,2,4-Trichlorobenzene	10.0	0.5	0.13	70	N/A
1,2-Dichlorobenzene	10.0	0.5	0.15	600	N/A
1,3-Dichlorobenzene	10.0	0.5	0.18	NE	N/A
1,4-Dichlorobenzene	10.0	0.5	0.17	75	NE

Table 2-2
Analytes, Practical Reporting Limits, and Maximum Contaminant Levels
American Chemical Service, Griffith, Indiana

Groundwater					
	Compuchem				
	Standard	Low Level			
Target Parameter	PQL (µg/L)	PQL (µg/L)	MDL (µg/L)	U.S. EPA MCL (µg/L)	Effluent Discharge Limits (µg/L)
SVOCs by SW8270C					
2,2'-oxybis(1-Chloropropane)	10.0	5	1.61	NE	N/A
2,4,5-Trichlorophenol	10.0	20	2.31	NE	N/A
2,4,6-Trichlorophenol	10.0	5	2.33	NE	N/A
2,4-Dichlorophenol	10.0	5	0.69	NE	N/A
2,4-Dimethylphenol	10.0	5	0.88	NE	N/A
2,4-Dinitrophenol	50.0	50	26.32	NE	N/A
2,4-Dinitrotoluene	10.0	5	1.54	NE	N/A
2,6-Dinitrotoluene	10.0	5	1.25	NE	N/A
2-Chloronaphthalene	10.0	5	1.37	NE	N/A
2-Chlorophenol	10.0	5	1.31	NE	N/A
2-methyl-4,6-Dinitrophenol	20.0	20	2.34	NE	N/A
2-Methylnaphthalene	10.0	5	1.35	NE	N/A
2-Methylphenol (o-Cresol)	10.0	5	1.10	NE	N/A
2-Nitroaniline	20.0	20	2.32	NE	N/A
2-Nitrophenol	10.0	5	1.25	NE	N/A
3,3'-Dichlorobenzidine	10.0	5	2.99	NE	N/A
3/4-Methylphenol (m-and p-Cresol)	10.0	5	1.68	NE	34
3-Nitroaniline	20.0	20	3.35	NE	N/A
4-Bromophenylphenylether	10.0	5	1.41	NE	N/A
4-Chloro-3-methylphenol	10.0	5	1.10	NE	N/A
4-Chloroaniline	10.0	5	1.06	NE	N/A
4-Chlorophenylphenylether	10.0	5	1.61	NE	N/A
4-Nitroaniline	20.0	20	3.81	NE	N/A
4-Nitrophenol	20.0	5	3.33	NE	N/A
Acenaphthene	10.0	5	0.96	NE	N/A
Acenaphthylene	10.0	5	1.15	NE	N/A
Anthracene	10.0	5	0.98	NE	N/A
Benzo(a)anthracene	10.0	5	1.02	NE	N/A
Benzo(a)pyrene(3)	10.0	5	0.98	0.2	N/A
Benzo(b)fluoranthene	10.0	5	1.41	NE	N/A
Benzo(g,h,i)perylene	10.0	5	0.93	NE	N/A
Benzo(k)fluoranthene	10.0	5	0.96	NE	N/A
Bis(2-chloroethoxy)methane	10.0	5	1.44	NE	N/A
Bis(2-chloroethyl)ether(3)	10.0	5	1.43	NE	9.6
Bis(2-ethlyhexyl)phthalate(3)	10.0	5	1.08	6.0	6.0
Butylbenzylphthalate	10.0	5	1.91	NE	N/A
Carbazole	10.0	5	1.29	NE	N/A
Chrysene	10.0	5	0.91	NE	N/A
Dibenzo(a,h)anthracene	10.0	5	1.10	NE	N/A
Dibenzofuran	10.0	5	1.38	NE	N/A

Table 2-2
Analytes, Practical Reporting Limits, and Maximum Contaminant Levels
American Chemical Service, Griffith, Indiana

Groundwater					
	Compuchem				
	Standard	Low Level			
Target Parameter	PQL (µg/L)	PQL (µg/L)	MDL (µg/L)	U.S. EPA MCL (µg/L)	Effluent Discharge Limits (µg/L)
SVOCs by SW8270C (Continued)					
Diethylphthalate	10.0	5	2.03	NE	N/A
Dimethylphthalate	10.0	5	2.67	NE	N/A
Di-n-butylphthalate	10.0	5	1.24	NE	N/A
Di-n-octylphthalate	10.0	5	0.92	NE	N/A
Fluoranthene	10.0	5	1.04	NE	N/A
Fluorene	10.0	5	1.09	NE	N/A
Hexachlorobenzene[3]	10.0	5	1.20	1.0	N/A
Hexachlorobutadiene	10.0	5	1.54	NE	N/A
Hexachlorocyclopentadiene	10.0	5	1.38	50	N/A
Hexachloroethane	10.0	5	1.55	NE	N/A
Indeno(1,2,3-c,d)pyrene	10.0	5	0.96	NE	N/A
Isophorone	10.0	5	1.35	NE	50
Naphthalene	10.0	5	1.19	NE	N/A
Nitrobenzene	10.0	5	1.97	NE	N/A
N-Nitrosodi-n-propylamine	10.0	5	1.05	NE	N/A
N-Nitrosodiphenylamine	10.0	5	1.09	NE	N/A
Pentachlorophenol[3]	10.0	20	2.36	1.0	1.0
Phenanthrene	10.0	5	0.76	NE	N/A
Phenol	10.0	5	1.00	NE	N/A
Pyrene	10.0	5	0.94	NE	N/A
Pesticides by SW8081A					
4,4'-DDD	0.10	0.02	N/A	NE	N/A
4,4'-DDE	0.05	0.02	N/A	NE	N/A
4,4'-DDT	0.15	0.02	N/A	NE	N/A
Aldrin	0.025	0.01	N/A	NE	N/A
alpha-BHC	0.025	0.01	N/A	NE	N/A
alpha-Chlordane	0.05	0.01	N/A	2.0	N/A
beta-BHC	0.05	0.01	N/A	NE	N/A
delta-BHC	0.025	0.01	N/A	NE	N/A
Dieldrin	0.05	0.02	N/A	NE	N/A
Endosulfan I	0.05	0.01	N/A	NE	N/A
Endosulfan II	0.10	0.02	N/A	NE	N/A
Endosulfan Sulfate	0.10	0.02	N/A	NE	N/A
Endrin	0.10	0.02	N/A	2.0	N/A
Endrin aldehyde	0.10	0.02	N/A	NE	N/A
Endrin ketone	0.25	0.02	N/A	NE	N/A
gamma-BHC (Lindane)	0.025	0.01	N/A	NE	N/A
gamma-Chlordane	0.025	0.01	N/A	2.0	N/A
Heptachlor	0.025	0.01	N/A	0.4	N/A
Heptachlor epoxide	0.025	0.01	N/A	0.2	N/A
Methoxychlor	0.25	0.10	N/A	40	N/A
Toxaphene	2.5	1.0	N/A	3.0	N/A

Table 2-2
Analytes, Practical Reporting Limits, and Maximum Contaminant Levels
American Chemical Service, Griffith, Indiana

Groundwater and Soil					
	Compuchem				
	Standard	Low Level			
Target Parameter	Water PQL (µg/L)	Water PQL (µg/L)	Soil PQL (µg/kg)	Soil Cleanup Standard (µg/kg)	Effluent Discharge Limits[2] (µg/L)
Polychlorinate Biphenyls (PCBs) by SW8082					
Arochlor-1016	2.0	0.2	63.0	1000	0.1 to 0.9
Arochlor-1221	3.0	0.4	83.0	1000	0.1 to 0.9
Arochlor-1232	2.0	0.2	63.0	1000	0.1 to 0.9
Arochlor-1242	2.0	0.2	42.0	1000	0.1 to 0.9
Arochlor-1248	2.0	0.2	42.0	1000	0.1 to 0.9
Arochlor-1254	2.0	0.2	42.0	1000	0.1 to 0.9
Arochlor-1260	2.0	0.2	63.0	1000	0.1 to 0.9

The U.S. EPA MCL for PCBs is 0.5 ug/L.

Table 2-2
Analytes, Practical Reporting Limits, and Maximum Contaminant Levels
American Chemical Service, Griffith, Indiana

Groundwater					
	Compuchem				
	Standard	Low Level			
Target Parameter	PQL (µg/L)	PQL (µg/L)	MDL (µg/L)	U.S. EPA MCL (µg/L)	Effluent Discharge Limits (µg/L)
Metals by SW6010B/7471A					
Aluminum	100.0	N/A	19.92	NE	N/A
Antimony(3)	10.0	N/A	6.66	6.0	N/A
Arsenic(3)	10.0	N/A	1.88	5.0	50
Barium	10.0	N/A	1.31	2000	N/A
Beryllium(3)	5.0	N/A	0.10	4.0	NE
Cadmium(3)	5.0	N/A	0.24	5.0	4.1
Calcium	1000.0	N/A	12.34	NE	N/A
Chromium (Total)	5.0	N/A	0.52	100	N/A
Cobalt	5.0	N/A	0.36	NE	N/A
Copper	5.0	N/A	0.48	1300	N/A
Iron (Total)	100.0	N/A	12.24	NE	N/A
Lead	3.0	N/A	1.45	15	N/A
Magnesium	1000.0	N/A	3.92	NE	N/A
Manganese	10.0	N/A	1.75	NE	NE
Mercury(3)	0.2	N/A	0.044	2.0	0.02
Nickel	5.0	N/A	0.52	NE	N/A
Potassium	1000.0	N/A	26.90	NE	N/A
Selenium	5.0	N/A	2.47	50	8.2
Silver	0.5	N/A	0.47	NE	N/A
Sodium	2000.0	N/A	154.0	NE	N/A
Thallium(3)	10.0	N/A	2.34	2.0	NE
Vanadium	20.0	N/A	0.31	NE	N/A
Zinc	20.0	N/A	2.20	NE	411
Wet Chemistry Prameters					
pH	N/A	N/A	N/A	N/A	6 to 9
Cyanide	N/A	10.0	1.51	N/A	N/A
Total Suspended Solids	1000.0	N/A	N/A	N/A	30,000
Biological Oxygen Demand	5000.0	N/A	N/A	N/A	30,000

Table 2-2
Analytes, Practical Reporting Limits, and Maximum Contaminant Levels
American Chemical Service, Griffith, Indiana

Air				
	Air Toxics Standard			
Target Parameter	PQL (ppbv)	MDL (ppbv)	U.S. EPA MCL	Effluent Discharge Limits
VOCs by TO-14				
1,1,1-Trichloroethane	0.5	0.11	N/A	N/A
1,1,2,2-Tetrachloroethane	0.5	0.09	N/A	N/A
1,1,2-Trichloroethane	0.5	0.16	N/A	N/A
1,1-Dichloroethane	0.5	0.05	N/A	N/A
1,1-Dichloroethene	0.5	0.09	N/A	N/A
1,2-Dichloroethane	0.5	0.19	N/A	N/A
1,2-Dichloropropane	0.5	0.11	N/A	N/A
2-Butanone (MEK)	2.0	0.26	N/A	N/A
2-Hexanone	2.0	0.50	N/A	N/A
4-Methyl-2-pentanone (MIBK)	2.0	0.42	N/A	N/A
Acetone	2.0	0.28	N/A	N/A
Benzene	0.5	0.08	N/A	N/A
Bromodichloromethane	2.0	0.56	N/A	N/A
Bromoform	2.0	0.31	N/A	N/A
Bromomethane	0.5	0.11	N/A	N/A
Carbon Disulfide	2.0	0.35	N/A	N/A
Carbon Tetrachloride	0.5	0.10	N/A	N/A
Chlorobenzene	0.5	0.10	N/A	N/A
Chloroethane	0.5	0.16	N/A	N/A
Chloroform	0.5	0.10	N/A	N/A
Chloromethane	0.5	0.19	N/A	N/A
cis-1,2-Dichloroethene	0.5	0.07	N/A	N/A
cis-1,3-Dichloropropene	0.5	0.12	N/A	N/A
Dibromochloromethane	2.0	0.51	N/A	N/A
Ethylbenzene	0.5	0.20	N/A	N/A
Methylene chloride	0.5	0.05	N/A	N/A
Styrene	0.5	0.14	N/A	N/A
Tetrachloroethene	0.5	0.11	N/A	N/A
Toluene	0.5	0.19	N/A	N/A
trans-1,2-Dichloroethene	2.0	0.42	N/A	N/A
trans-1,3-Dichloropropene	0.5	0.14	N/A	N/A
Trichloroethene	0.5	0.13	N/A	N/A
Vinyl chloride	0.5	0.09	N/A	N/A
Xylenes (total)	0.5	0.21	N/A	N/A
SVOCs by TO-13				
1,2,4-Trichlorobenzene	1.0	0.83	N/A	N/A
1,2-Dichlorobenzene	1.0	0.88	N/A	N/A
1,3-Dichlorobenzene	1.0	0.76	N/A	N/A
1,4-Dichlorobenzene	1.0	0.74	N/A	N/A
2,2'-oxybis(1-Chloropropane)			N/A	N/A
2,4,5-Trichlorophenol	5.0	4.34	N/A	N/A

Table 2-2
Analytes, Practical Reporting Limits, and Maximum Contaminant Levels
American Chemical Service, Griffith, Indiana

Air				
	Air Toxics Standard			
Target Parameter	PQL (ppbv)	MDL (ppbv)	U.S. EPA MCL	Effluent Discharge Limits
SVOCs by TO-13 (Continued)				
2,4,6-Trichlorophenol	5.0	4.71	N/A	N/A
2,4-Dichlorophenol	5.0	3.77	N/A	N/A
2,4-Dimethylphenol	5.0	2.06	N/A	N/A
2,4-Dinitrophenol	20	0.8	N/A	N/A
2,4-Dinitrotoluene	5.0	0.88	N/A	N/A
2,6-Dinitrotoluene	5.0	0.95	N/A	N/A
2-Chloronaphthalene	1.0	0.89	N/A	N/A
2-Chlorophenol	5.0	3.96	N/A	N/A
2-methyl-4,6-Dinitrophenol	10	3.43	N/A	N/A
2-Methylnaphthalene	1.0	0.81	N/A	N/A
2-Methylphenol (o-Cresol)	5.0	3.74	N/A	N/A
2-Nitroaniline	10	7.54	N/A	N/A
2-Nitrophenol	5.0	3.99	N/A	N/A
3,3'-Dichlorobenzidine	20	0.77	N/A	N/A
3/4-Methylphenol (m-and p-Cresol)	5.0	5.1	N/A	N/A
3-Nitroaniline	10	2.04	N/A	N/A
4-Bromophenylphenylether	1.0	0.73	N/A	N/A
4-Chloro-3-methylphenol	5.0	3.77	N/A	N/A
4-Chloroaniline	10	3.38	N/A	N/A
4-Chlorophenylphenylether	1.0	0.98	N/A	N/A
4-Nitroaniline	10	1.9	N/A	N/A
4-Nitrophenol	20	4.03	N/A	N/A
Acenaphthene	1.0	0.86	N/A	N/A
Acenaphthylene	1.0	0.91	N/A	N/A
Anthracene	1.0	0.57	N/A	N/A
Benzo(a)anthracene	1.0	0.47	N/A	N/A
Benzo(a)pyrene	1.0	0.53	N/A	N/A
Benzo(b)fluoranthene	1.0	0.76	N/A	N/A
Benzo(g,h,i)perylene	1.0	0.71	N/A	N/A
Benzo(k)fluoranthene	1.0	0.53	N/A	N/A
Bis(2-chloroethoxy)methane	1.0	0.85	N/A	N/A
Bis(2-chloroethyl)ether	1.0	0.88	N/A	N/A
Bis(2-ethlyhexyl)phthalate	5.0	0.55	N/A	N/A
Butylbenzylphthalate	5.0	0.72	N/A	N/A
Carbazole			N/A	N/A
Chrysene	1.0	0.59	N/A	N/A
Dibenzo(a,h)anthracene	1.0	0.71	N/A	N/A
Dibenzofuran	1.0	0.8	N/A	N/A
Diethylphthalate	5.0	0.82	N/A	N/A
Dimethylphthalate	5.0	0.85	N/A	N/A
Di-n-butylphthalate	5.0	0.48	N/A	N/A
Di-n-octylphthalate	5.0	0.93	N/A	N/A

Table 2-2
Analytes, Practical Reporting Limits, and Maximum Contaminant Levels
American Chemical Service, Griffith, Indiana

Air				
	Air Toxics Standard			
Target Parameter	PQL (ppbv)	MDL (ppbv)	U.S. EPA MCL	Effluent Discharge Limits
SVOCs by TO-13 (Continued)				
Fluoranthene	1.0	0.45	N/A	N/A
Fluorene	1.0	0.88	N/A	N/A
Hexachlorobenzene	1.0	0.68	N/A	N/A
Hexachlorobutadiene	1.0	0.72	N/A	N/A
Hexachlorocyclopentadiene	20		N/A	N/A
Hexachloroethane	1.0	1.00	N/A	N/A
Indeno(1,2,3-c,d)pyrene	1.0	0.78	N/A	N/A
Isophorone	1.0	0.86	N/A	N/A
Naphthalene	1.0	0.76	N/A	N/A
Nitrobenzene	1.0	0.87	N/A	N/A
N-Nitrosodi-n-propylamine	1.0	1.14	N/A	N/A
N-Nitrosodiphenylamine	10	0.78	N/A	N/A
Pentachlorophenol	20	4.21	N/A	N/A
Phenanthrene	1.0	0.61	N/A	N/A
Phenol	5.0	3.26	N/A	N/A
Pyrene	1.0	0.47	N/A	N/A

Notes:
Analyte list is derived from CLP criteria
PQL Practical Quantiation Limits from Compuchem and Air Toxics
MDL Method Detection Limits from Compuchem and Air Toxics
U.S. EPA United States Environmental Protection Agency
N/A Not Applicable
NE Not Established
A 25ml purge will be used for all VOC water samples to meet the project reporting limits.
(1) Total sum of trihalomethanes may not exceed 80 μg/l
(2) Effluent limit for PCBs is actually 0.00056, but analytical results showing less than the MDL listed will be considered in compliance. The MDL for each PCB is different for each isomer.
(3) The PQLs for these parameters are greater than the MCLs. For these parameters, the sample data will be reported to the MDL. Sample results greater than the MDL but lower than the PQL will be reported as estimated concentrations (flagged), and all non-detections will be reported as less than the MDL.

TABLE 2-3
DATA QUALITY OBJECTIVES
AMERICAN CHEMICAL SERVICE, GRIFFITH, INDIANA

LONG-TERM GROUNDWATER MONITORING

Step 1 - State the Problem	Step 2 - Identify the Decisions	Step 3 - Identify inputs to the decisions	Step 4 - Define study Boundaries	Step 5 - Develop Decision Rules	Step 6 - Specifiy Limits on Decision Errors	Step 7 - Optimize Sampling Design
VOCs, SVOCs, and Metals have been detected in groundwater samples at concentrations greater than USEPA MCLs at the ACS Site. A barrier wall has been installed to contain the source, so the Long-Term Groundwater Monitoring Plan will monitor the exterior areas for contaminant migration and reduction.	Do groundwater samples exceed historical groundwater concentrations? Are downgradient groundwater concentrations increasing or decreasing? Are groundwater concentrations at wells within the plume decreasing? Are upgradient groundwater concentrations changing in such a way as to affect the interior groundwater concentrations? Are concentrations at private wells detected above U.S. EPA MCLs?	Validated defensible chemical data from the upper and lower aquifer monitoring wells located upgradient, downgradient, and within the plume. Validated defensible chemical data from the residential wells that supply drinking water to the houses. Previous, validated groundwater data collected from past several years at the Site.	Groundwater from the upper and lower aquifers will be sampled and analyzed. The upper and lower aquifers are separated by a clay confining unit. Groundwater samples will be collected from previously existing site wells that provide upgradient, sidegradient, and downgradient locations. Groundwater samples will collected and analyzed for residential wells annually.	If concentrations in groundwater samples from downgradient or interior wells are decreasing, then the barrier wall and perimeter groundwater collection system are operating properly. If concentrations are increasing, then further evaluation may be needed to determine if the barrier wall and collection system need adjustment, or if further investigations for corrective action are needed.	Groundwater results from monitoring wells will be evaluated to EPA Level 3 data validation requirements. Ten percent of this data will be validated according to the equivalent of EPA level 4 data validation requirements. All of the residential well data will be validated according to EPA level 4 data validation requirements. If QC criteria are not met, resampling may be required.	The number of monitoring and residential wells to be sampled will be provided in the upcoming Long-Term Groundwater Monitoring Plan. This monitoring plan will continue until cleanup at the ACS Site is complete to regulatory satisfaction. Its development will satisfy the DQOs and result in protection of human health and the environment.

TABLE 2-3
DATA QUALITY OBJECTIVES
AMERICAN CHEMICAL SERVICE, GRIFFITH, INDIANA

EFFLUENT & OFF-GAS SAMPLING FOR TREATMENT PLANT AND ISVE SYSTEM

Step 1 - State the Problem	Step 2 - Identify the Decisions	Step 3 - Identify inputs to the decisions	Step 4 - Define study Boundaries	Step 5 - Develop Decision Rules	Step 6 - Specifiy Limits on Decision Errors	Step 7 - Optimize Sampling Design
VOCs, SVOCs, and metals have been detected at high concentrations in the upper aquifer under the ACS facility. LNAPL and DNAPL are also present. This highly contaminated area is contained by the barrier wall. Groundwater is pumped from the upper aquifer within the barrier wall to the treatment plant where it is treated. NAPLs may also be pumped into the treatment system. All liquids will flow to the treatment plant.	Is the treatment plant efficiently removing the compounds of concern from the water stream? Do the effluent and offgas released by the treatment plant and ISVE system meet the established discharge requirements?	Validated defensible data from the effluent and off-gas samples.	Effluent and off-gas samples will be collected quarterly and analyzed per the performance monitoring program.	If compounds of concern are detected in the effluent or off-gas samples at concentrations higher than permitted, the treatment system will be evaluated for possible break through or capacity problems. If compounds of concern are not detected or detected at concentrations below permit requirements, then the treatment system and ISVE system are assumed to be performing adequately.	Effluent and off-gas analytical results will be evaluated according to EPA Level 3 requirements. If the data does not meet validation requirements, it may need to be resampled.	Effluent and off-gas samples will be collected quarterly. The frequency may increase or decrease if later deemed necessary.

TABLE 2-3
DATA QUALITY OBJECTIVES
AMERICAN CHEMICAL SERVICE, GRIFFITH, INDIANA

REMOVAL CONFIRMATION OF PCB-IMPACTED SOIL

Step 1 - State the Problem	Step 2 - Identify the Decisions	Step 3 - Identify inputs to the decisions	Step 4 - Define study Boundaries	Step 5 - Develop Decision Rules	Step 6 - Specifiy Limits on Decision Errors	Step 7 - Optimize Sampling Design
During the Wetlands Investigation conducted in 1996, PCBs were detected in the some regions of soil at concentrations which exceed target levels. All PCB-impacted soil containing concentrations which exceed target levels will be excavated and removed. Post-excavation samples are needed to determine if sufficient soil has been removed to meet the target cleanup level.	Have the PCB-impacted soils been adequately removed? Are the concentrations of PCBs which remain in the soil below the target cleanup level?	Validated defensible sampling results from the Wetland Investigation in 1996 will define impacted areas. Validated defensible post-excavation sampling results will determine if the target cleanup level has been met.	Soil samples will be taken from the topsoil in areas historically determined to have PCB concentrations which exceed target levels.	If the sampling results indicate PCB concentrations above target levels, the removal action will continue. If the sample results indicate PCB concentrations below target levels, no further removal will be required.	Once a validated confirmatory soil samples indicates PCB concentrations below 1 ppm, removal in that area will cease.	In accordance with U.S. EPA PCB spill guidance entitled Field Manual for Grid Sampling of PCB Spill Site to Verify Cleanup (dated May 1986), approximately nineteen (19) post-excavation samples will be taken and analyzed.

Table 2-4
Schedule of Work
American Chemical Service, Griffith, Indiana

Project Task	2001 Schedule	2002 Schedule	2003 Schedule	2004 Schedule
Groundwater Monitoring	Quarterly Sampling	Quarterly Sampling	Quarterly Sampling	Quarterly Sampling
Effluent and Off-gas Sampling for Treatment Plant and ISVE System	Quarterly Sampling*	Quarterly Sampling*	Quarterly Sampling*	Quarterly Sampling*
PCB-impacted Soils	Summer	No scheduled activity	No scheduled activity	No scheduled activity

Notes:
The groundwater monitoring schedule currently is for quarterly monitoring. As time and clean up progresses, the actual sampling periods may be modified as approved by U.S. EPA and IDEM.
* Some analytes may be monitored more frequently, based on guidelines in the PSVP (July, 1997).

Table 4-1
Chemical Data Quality Control Evaluation In Terms Of PARCC Parameters
American Chemical Service, Griffith, Indiana

PARCC PARAMETER	Quality Control Program	Evaluation Criteria
Precision	Field Replicate or Duplicate Sample Pairs	Relative Percent Difference
	Matrix Spike/Matrix Spike Duplicate Sample Pairs	Relative Percent Difference
Accuracy	Surrogate Spikes	Percent Recovery
	Matrix Spike	Percent Recovery
	Matrix Spike Duplicate	Percent Recovery
	Laboratory Control Sample	Percent Recovery
	Standard Reference Materials	Percent Recovery
Representativeness	Holding Time	Qualitative, Degree of Confidence
	Method Blanks	Qualitative, Degree of Confidence
	Trip Blanks	Qualitative, Degree of Confidence
	Equipment Blanks	Qualitative, Degree of Confidence
	Field Replicates/Duplicates	Quantitative/Qualitative, Degree of Confidence
Comparability	Standard Field Procedures	Qualitative, Degree of Confidence
	Standard Analytical Methods	Qualitative, Degree of Confidence
	Standard Units of Measure	Qualitative, Degree of Confidence
Completeness	Valid Data	Percent Acceptable Data

Notes:
PARCC Precision, Accuracy, Representativeness, Completeness, and Comparability

TABLE 4-2
QUALITY CONTROL ACCEPTANCE CRITERIA FOR VOLATILE ORGANIC COMPOUNDS BY SW846 8260B
AMERICAN CHEMICAL SERVICE, GRIFFITH, INDIANA

Analyte	Water		
	LCS (% Rec)	MS/MSD (% Rec)	MS/MSD (% RPD)
VOCs by SW-846 8260B			
1,1-Dichloroethene	60-140	60-140	≤14
Benzene	60-140	60-140	≤11
Chlorobenzene	60-140	60-140	≤13
Toluene	60-140	60-140	≤13
Trichloroethene	60-140	60-140	≤14
Surrogates:			
Dibromofluoromethane	80-120	80-120	N/A
Toluene-d8	80-120	80-120	N/A
4-Bromofluorobenzene	80-120	80-120	N/A
1,2-DCA-d4	80-120	80-120	N/A

Notes:
N/A Not Applicable
Rec Recovery
VOCs Volatile Organic Compounds
LCS Laboratory control sample
MS/MSD Matrix spike/matrix spike duplicate
RPD Relative percent difference
Limits from CompuChem

Table 4-3
Volatile Organic Compounds Gas Chromatography/Mass Spectrometry – Method SW846 8260B
Calibration Specification and Corrective Action Summary
American Chemical Service, Griffith, Indiana

Analytical Method[a]	Parameter	QC Element	Frequency	Acceptance Criteria	Corrective Action
SW-846, 8260B Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry	Volatile Organic Compounds	Tune instrument with a 4-bromofluorobenzene standard (BFB)	Every 12 hours	• Must meet key ions and ion abundance criteria established by method (Refer to Table 4-4)	• Retune instrument • Repeat standard analysis
		Initial multi-point calibration; 5 point minimum. Lowest point at or below PQL. Includes calibration check compounds (CCC) and system performance check compounds (SPCC), and Internal Standards Compounds (IS).	Prior to analysis, and as required	• RSD< 30 % for CCC; Average RF ≥ 0.1 for SPCC (≥0.3 for chlorobenzene, 1,1,2,2-Tetrachloroethane) • If mean % RSD for all compounds < 15%, average RF may be used; linear calibration required	• Evaluate system • Repeat calibration
		Continuing calibration verification (CCV): CCC, SPCC, and IS	Every 12 hours	• Percent difference (%D) <20% for CCC; RF ≥ 0.1 for SPCC (≥0.3 for chlorobenzene and 1,1,2,2-Tetrachloroethane). • Mean % D for all compounds < 20%. • Retention time for each internal standard must be within 30 seconds of most recent CCV and the EICP area for all internal standards must be within –50% to +100% of the most recent CCV.	• Evaluate system/standard • Reanalyze calibration check standard • Repeat initial calibration
		Method blank	1 per preparation batch (≤ samples)	• < Method Detection Limit	• Reanalyze method blank • Recalibrate
		Internal standards	Every sample, method blank, LCS, and MS/MSD	• Retention time for each internal standard must be within 30 seconds of most recent CCV and the EICP area for all internal standards must be within –50% to +100% of the most recent CCV	• Evaluate system/standard • Reanalyze samples • If still out, report both sets of data • Narrate all outliers

Table 4-3
Volatile Organic Compounds Gas Chromatography/Mass Spectrometry – Method SW846 8260B
Calibration Specification and Corrective Action Summary
American Chemical Service, Griffith, Indiana
(continued)

Analytical Method[a]	Parameter	QC Element	Frequency	Acceptance Criteria	Corrective Action
SW-846, 8260B Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (continued)	Volatile Organic Compounds	Surrogate spike	Every sample, method blank, LCS, MS/MSD	• Surrogate recoveries within QC acceptance criteria. (Refer to Table 4-2) • One surrogate may be out if > 10% recovery	• Reanalyze sample one • If still out, report both sets of data • Narrate all outliers
		Matrix spike (MS)	1 per preparation batch (≤20 samples)	• Percent recovery within QC acceptance criteria (Refer to Table 4-2)	• If LCS and surrogate recoveries are acceptable and MSD also outside criteria consistent with MS, problem may be attributed to matrix interference • Reprep/reanalyze both MS and MSD. • Narrate all outliers
		Matrix spike duplicate (MSD)	1 per preparation batch (≤20 samples)	• % Recovery and/or RPD within QC acceptance criteria (Refer to Table 4-2)	• Same as MS
		Laboratory control sample (LCS)	1 per preparation batch (≤20 samples)	• % Recovery within QC acceptance criteria (Refer to Table 4-2)	• Reanalyze LCS • Reprep/reanalyze LCS and all associated samples • Narrate all outliers

Notes:
EICP Extracted ion current profile
QC Quality control
RF Response factor
RPD Relative percent difference
RSD Relative Standard Deviation
(a) EPA Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW-846), (U.S. EPA Third Edition, Final Update III, December 1996).

Table 4-4
4-Bromofluorobenzene (BFB) Mass Intensity Criteria
American Chemical Service, Griffith, Indiana

Mass	Required Intensity (relative abundance)
50	15 to 40% of mass 95
75	30 to 60% of mass 95
95	Base peak, 100% relative abundance
96	5 to 9% of mass 95
173	Less than 2% of mass 174
174	Greater than 50% of mass 95
175	5 to 9% of mass 174
176	Greater than 95%, but less than 101% of mass 174
177	5 to 9% of mass 176

EPA Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW-846), (U.S. EPA Third Edition, Final Update III, December 1996).

TABLE 4-5
QUALITY CONTROL ACCEPTANCE CRITERIA FOR SEMI-VOLATILE ORGANIC COMPOUNDS BY SW846 8270C
AMERICAN CHEMICAL SERVICE, GRIFFITH, INDIANA

Analyte	Water		
	LCS (% Rec)	MS/MSD (% Rec)	MS/MSD (% RPD)
SVOCs by SW-846 8270C			
1,2,4-Trichlorobenzene	12-149	12-149	45
1,4-Dichlorobenzene	37-142	10-137	50
2,4-Dinitrotoluene	50-150	19-150	34
2-Chlorophenol	35-136	10-150	50
4-Chloro-3-methylphenol	35-150	10-150	50
4-Nitrophenol	10-150	10-150	50
Acenaphthene	45-141	11-149	40
N-Nitrosodi-n-propylamine	31-150	10-150	50
Pentachlorophenol	32-150	10-150	50
Phenol	10-100	10-116	50
Pyrene	37-150	18-150	35
Surrogates:			
2,4,6-Tribromophenol	25-120	25-120	N/A
2-Fluorobiphenyl	37-110	37-110	N/A
2-Fluorophenol	20-110	20-110	N/A
Nitrobenzene-d5	31-113	31-113	N/A
Phenol-d5	16-110	16-110	N/A
Terphenyl-d14	42-124	42-124	N/A

Notes:
N/A - Not Applicable
Rec - Recovery
SVOCs - Semi-volatile Organic Compounds
Limits from CompuChem
LCS - Laboratory Control Sample
MS/MSD - Matrix Spike/Matrix Spike Duplicate
RPD - Relative Percent Difference

Table 4-6
Semi-Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry-SW846 8270C
Calibration Specifications and Corrective Action Summary
American Chemical Service, Griffith, Indiana

Analytical Method[a]	Parameter	QC Element	Frequency	Acceptance Criteria	Corrective Action
SW-846 8270C Semi-Volatiles by GC/MS	Semi-Volatiles	Tune the instrument using a decafluorotriphenylphosine (DFTPP) standard	Every 12 hours	• Must meet the ion abundance criteria specified in the method (Refer to Table 4-7) • Degradation of DDT ≤ 20% • Benzidine and PCP present at normal response without excessive tailing	• Retune instrument • Repeat standard analysis • Perform injection port, column maintenance as necessary
		Initial calibration (5 point minimum); includes Calibration Check Compounds (CCC), System Performance Calibration Check (SPCC), and Internal Standard Compounds (IS)	Prior to analysis and as required	• % RSD for CCC ≤30%; average RF ≥0.05 for SPCC • If mean % RSD ≤15 % average RF may be used; linear calibration required	• Evaluate the system • Repeat calibration
		Continuing calibration verification (CCV); includes CCC, SPCC, and IS	Every 12 hours	• Percent difference (%D) <20% for CCC; RF ≥0.1 for SPCC (≥0.3 for chlorobenzene and 1,1,2,2-Tetrachloroethane). • Mean % D for all compounds < 20%. • Retention time for each internal standard must be within 30 seconds of most recent CCV and the EICP area for all internal standards must be within –50% to +100% of the most recent CCV.	• Evaluate system/standard • Reanalyze calibration check standard • Repeat the initial calibration as necessary
		Internal Standard	Every sample, method blank, LCS and MS/MSD	• Retention time for each internal standard must be within 30 seconds of most recent CCV and the EICP area for all internal standards must be within –50% to +100% of the most recent CCV	• Evaluate system/standard • Reanalyze the sample • If still out, report both sets of data

Table 4-6
Semi-Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry-SW-846 8270C
Calibration Specifications and Corrective Action Summary
American Chemical Service, Griffith, Indiana
(Continued)

Analytical Method[a]	Parameter	QC Element	Frequency	Acceptance Criteria	Corrective Action
SW-846 8270C Semi-Volatiles by GCMS (continued)	Semi-Volatiles	Method Blank	1 per preparation batch (≤20 samples)	• < Method Detection Limit	• Reanalyze blank • Reprep/reanalyze all associated samples
		Surrogate spike	Every sample, method blank, LCS and MS/MSD	• Recovery within acceptance criteria (Refer to Table 4-5) • One surrogate per fraction may be out if recovery > 10%	• Reanalyze sample once • If still out, report both sets of data • Narrate all outliers
		Matrix spike (MS)	1 per preparation batch (≤20 samples)	• % Recovery within QC acceptance criteria (Refer to Table 4-5)	• If LCS and surrogate recoveries are acceptable and MSD also outside criteria consistent with MS, problem may be attributed to matrix interference • Reprep/reanalyze both MS and MSD. • Narrate all outliers
		Matrix spike duplicate (MSD)	1 per preparation batch (≤20 samples)	• % Recovery and/or RPD within QC acceptance criteria (Refer to Table 4-5)	• Same as MS
		Laboratory control sample	1 per preparation batch (≤20 samples)	• % Recovery within project QC acceptance criteria for all spiked analytes (Refer to Table 4-5)	• Reanalyze LCS • Re-prep/reanalyze LCS and all associated samples • Narrate all outliers

Notes:
EICP Extracted ion current profile
QC Quality control
RF Response factor
RSD Relative standard deviation
(a) EPA Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW-846), (U.S. EPA Third Edition, Final Update III, December 1996)

Table 4-7
Decafluorotriphenyl Phosphine (DFTPP) Key Ions and Ion Abundance
American Chemical Service, Griffith, Indiana

Mass	Ion Abundance Criteria
51	30-60% of mass 198
68	<2% of mass 69
70	<2% of mass 69
127	40-60% of mass 198
197	<1% of mass 198
198	Base peak, 100% relative abundance
199	5-9% of mass 198
275	10-30% of mass 198
365	>1% of mass 198
441	Present, but less than mass 443
442	>40% of mass 198
443	17-23% of mass 442

EPA Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW-846), (U.S. EPA Third Edition, Final Update III, December 1996).

Table 4-8
Quality Control Acceptance Criteria for Organochlorinated Pesticides by SW846 8081A
American Chemical Service, Griffith, Indiana

Analyte	Water		
	LCS (% Rec)	MS/MSD (% Rec)	MS/MSD (% RPD)
Pesticides by SW-846 8081A			
gamma-BHC (Lindane)	35-140	56-123	15
Heptachlor	35-140	40-131	20
Aldrin	60-130	40-120	22
Dieldrin	55-170	52-126	18
Endrin	40-155	56-121	21
4,4'-DDT	56-121	38-127	27
Surrogates:			
Tetrachloro-m-xylene	30-150	30-150	N/A
Decachlorobiphenyl	30-150	30-150	N/A

Notes:
LCS Laboratory control sample
MS Matrix spike
MSD Matrix spike duplicate
RPD Relative percent difference
Limits from CompuChem

Table 4-9
Organochlorine Pesticides by Gas Chromatography-SW846 8081A
Calibrations Specifications and Corrective Action Summary
American Chemical Service, Griffith, Indiana

Analytical Method[a]	Parameter	QC Element	Frequency	Acceptance Criteria	Corrective Action
SW-846 8081A Organochlorine Pesticides by Gas Chromatography	Organochlorine Pesticides	Column Evaluation Mix	Prior to analysis, both initial and daily	• Degradation of DDT and Endrin < 15%	• Evaluate the system • Repeat standard
		Initial calibration (5 point minimum) Lowest at or below PQL Mid level multi-component standards for pattern recognition and retention times	Prior to analysis and as required	• RSD < 20%, average CF may be used; linear calibration required	• Average RSD <20% across all analytes may be used if any analyte fails • Evaluate the system • Repeat initial calibration
		Initial calibration verification (ICV) Mid level standard Expected multi-component compounds	Prior to each 12 hour shift	• % Difference =15% of expected concentration compared to response from ICAL	• Average % difference =15% across all analytes may be used if any analyte fails • Evaluate system/standard • Reanalyze ICV standard • Repeat initial calibration •
		Continuing calibration verification (CCV) Mid level standard Expected multi-component compounds	After every 20 samples and at the end of the analytical sequence	• % Difference =15% of expected concentration compared to response from ICAL for each bracketing standard	• Average % difference =15% across all analytes may be used if any analyte fails • Evaluate system/standard • Reanalyze CCV and affected samples • For CCV with response > initial calibration response and % difference >15%, samples need not be reanalyzed if no target compounds are detected

Table 4-9
Organochlorine Pesticides by Gas Chromatography-SW846 8081A
Calibrations Specifications and Corrective Action Summary
American Chemical Service, Griffith, Indiana
(Continued)

Analytical Method[a]	Parameter	QC Element	Frequency	Acceptance Criteria	Corrective Action
SW-846 8081A Organochlorine Pesticides by Gas Chromatography (con't)	Organochlorine Pesticides	Retention time windows	Established with each new column installation Updated with each daily initial calibration standard	• Retention times must be within retention time window established by the daily initial calibration standard • Every CCV and every sample	• Evaluate system/standard; pattern recognition may be sufficient for multi-component compounds only • Reanalyze CCV/affected samples
		Method Blank	1 per preparation batch (≤ 20 samples)	• < Method Detection Limit	• Reanalyze blank • Re-prep/reanalyze blank and associated samples
		Surrogate spike DCB and TCMX	Every sample, method blank, LCS and MS/MSD	• % Recovery within QC acceptance criteria (Refer to Table 4-8) • one surrogate must fall within established control limits	• Re-extract/reanalyze once • If still out, report both sets of data • Narrate all outliers
		Matrix spike (MS)	1 per preparation batch (≤20 samples)	• % Recovery within QC acceptance criteria (Refer to Table 4-8)	• If LCS and surrogate recoveries are acceptable and MSD also outside criteria consistent with MS, problem may be attributed to matrix interference • Reprep/reanalyze both MS and MSD. • Narrate all outliers
		Matrix spike duplicate(MSD) or Matrix Duplicate (MD)	1 per preparation batch (≤20 samples)	• % Recovery and/or RPD within QC acceptance criteria (Refer to Table 4-8) •	• Same as MS

Table 4-9
Organochlorine Pesticides by Gas Chromatography-SW846 8081A
Calibrations Specifications and Corrective Action Summary
American Chemical Service, Griffith, Indiana
(Continued)

Analytical Method[a]	Parameter	QC Element	Frequency	Acceptance Criteria	Corrective Action
SW-846 8081A Organochlorine Pesticides by Gas Chromatography (con't)	Organochlorine Pesticides	Laboratory control sample (LCS)	1 per preparation batch (≤ 20 samples)	• % Recovery within QC acceptance criteria (Refer to Table 4-8)	• Reanalyze LCS • Re-prep/reanalyze LCS and all associated samples • Narrate all outliers

Notes:
%RSD Relative standard deviation
CF Calibration factor
QC Quality control
RPD Relative percent difference
(a) EPA Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW-846), (U.S. EPA Third Edition, September 1986; Final Update I, July 1992; Final Update IIA, August 1993; Final Update II, September 1994; Final Update IIB, January 1995; Final Update III, December 1996).

Table 4-10
Quality Control Acceptance Criteria for Polychlorinated Byphenyls by SW846 8082
American Chemical Service, Griffith, Indiana

Analyte	Soil and Water		
	LCS (% Rec)	MS/MSD (% Rec)	MS/MSD (% RPD)
Polychlorinated Biphenyls by SW-846 8082			
Aroclor 1016	50-150	50-150	20
Aroclor 1260	50-150	50-150	20
Surrogates:			
Tetrachloro-m-xylene	30-150	30-150	N/A
Decachlorobiphenyl	30-150	30-150	N/A

Notes:
LCS Laboratory control sample
MS Matrix spike
MSD Matrix spike duplicate
RPD Relative percent difference
Limit from CompuChem

Table 4-11
Polychlorinated Biphenyls by Gas Chromatography-SW846 8082
Calibrations Specifications and Corrective Action Summary
American Chemical Service, Griffith, Indiana

Analytical Method[a]	Parameter	QC Element	Frequency	Acceptance Criteria	Corrective Action
SW-846 8082 Polychlorinated biphenyls (PCBs) by Gas Chromatography	PCBs	Initial calibration (5 point minimum) Lowest standard at or below PQL; • Expected Aroclors or Aroclor 1016/1260 five-point if unknown with single-point mid-level standards for other Aroclors for pattern recognition and retention times, or • Individual PCB congeners: five-point of all target congeners	Prior to analysis and as required	• RSD <20%, average calibration factor or response factor[a] may be used; linear calibration required	• Evaluate the system • Repeat initial calibration
		Initial calibration verification (ICV) Mid level standard Expected Aroclors or PCB congener or Aroclor 1016/1260 if unknown	Prior to each 12 hour shift	• % Difference ≤15% of expected concentration compared to response from ICAL	• Evaluate system/standard • Reanalyze ICV standard • Repeat initial calibration
		Continuing calibration verification (CCV) Mid level standard Expected Aroclors or PCB congener or Aroclor 1016/1260 if unknown	After every 20 samples and at the end of the analytical sequence	• % Difference ≤15% of expected concentration compared to response from ICAL for each bracketing standard	• Evaluate system/standard • Reanalyze CCV and samples back to last acceptable CCV

Table 4-11
Polychlorinated Biphenyls by Gas Chromatography-SW846 8082
Calibrations Specifications and Corrective Action Summary
American Chemical Service, Griffith, Indiana
(Continued)

Analytical Method[a]	Parameter	QC Element	Frequency	Acceptance Criteria	Corrective Action
SW-846 8082 Polychlorinated biphenyls (PCBs) by Gas Chromatography (con't)	PCBs	Retention time windows	Established with each new column installation Updated with each daily initial calibration standard	• Retention times must be within retention time window established by the daily initial calibration standard • Every CCV and every sample	• Evaluate system/standard; pattern recognition may be sufficient • Reanalyze CCV/affected samples
		Internal standards[h]	Highly recommended for PCB congeners	• Every CCV, blank, sample, MS/MSD, and LCS; area counts -50 to +100% of ICV	• Reanalyze CCV/affected samples
		Method Blank	1 per preparation batch (≤20 samples)	• < Method Detection Limit	• Reanalyze blank • Re-prep/reanalyze blank and associated samples
		Surrogate spike DCB (for Aroclors) TCMX (for PCB congeners)	Every sample, method blank, LCS and MS/MSD	• % Recovery within QC acceptance criteria (Refer to Table 4-10)	• Re-extract/reanalyze once • If still out, report both sets of data Narrate all outliers
		Matrix spike (MS)	1 per preparation batch (≤20 samples)	• % Recovery within QC acceptance criteria (Refer to Table 4-10)	• If LCS and surrogate recoveries are acceptable and MSD also outside criteria consistent with MS, problem may be attributed to matrix interference • Reprep/reanalyze both MS and MSD. • Narrate all outliers

Table 4-11
Polychlorinated Biphenyls by Gas Chromatography-SW846 8082
Calibrations Specifications and Corrective Action Summary
American Chemical Service, Griffith, Indiana
(Continued)

Analytical Method[a]	Parameter	QC Element	Frequency	Acceptance Criteria	Corrective Action
SW-846 8082 Polychlorinated biphenyls (PCBs) by Gas Chromatography (con't)	PCBs	Matrix spike duplicate (MSD) or Matrix duplicate (MD)	1 per preparation batch (≤20 samples)	• % Recovery and/or RPD within QC acceptance criteria (Refer to Table 4-10)	• Same as MS
		Laboratory control sample (LCS)	1 per preparation batch (≤20 samples)	• % Recovery within project QC acceptance criteria (Refer to Table 4-10)	• Reanalyze LCS • Re-prep/reanalyze LCS and all associated samples • Narrate all outliers

Notes:
%RSD Relative standard deviation
QC Quality control
(a) EPA Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW-846), (U.S. EPA Third Edition, September 1986; Final Update I, July 1992; Final Update IIA, August 1993; Final Update II, September 1994; Final Update IIB, January 1995; Final Update III, December 1996).
(b) If internal standards used, use response factor.

TABLE 4-12
Quality Control Acceptance Criteria for Metals by SW846 6010B/7470A
American Chemical Service, Griffith, Indiana

Analyte	LCS (% Rec)	MS/MSD (% Rec)	MS/MSD (% RPD)
Metals by SW6010B/7470A			
Aluminum	75-125	75-125	≤20
Antimony	75-125	75-125	≤20
Arsenic	75-125	75-125	≤20
Barium	75-125	75-125	≤20
Beryllium	75-125	75-125	≤20
Cadmium	75-125	75-125	≤20
Calcium	75-125	75-125	≤20
Chromium (Total)	75-125	75-125	≤20
Cobalt	75-125	75-125	≤20
Copper	75-125	75-125	≤20
Iron (Total)	75-125	75-125	≤20
Lead	75-125	75-125	≤20
Magnesium	75-125	75-125	≤20
Manganese	75-125	75-125	≤20
Mercury	75-125	75-125	≤20
Nickel	75-125	75-125	≤20
Potassium	75-125	75-125	≤20
Selenium	75-125	75-125	≤20
Silver	75-125	75-125	≤20
Sodium	75-125	75-125	≤20
Thallium	75-125	75-125	≤20
Vanadium	75-125	75-125	≤20
Zinc	75-125	75-125	≤20

Notes:
LCS Laboratory Control Standard
MS/MSD Matrix Spike/Matrix Spike Duplicate
Rec Recovery
Limits from CompuChem

Table 4-13
Inductively Coupled Plasma Cations and Trace Metals Analysis – Method SW846 6010B
Calibration Specification and Corrective Action Procedures
American Chemical Service, Griffith, Indiana

Analytical Method[a]	Parameter	QC Element	Frequency	Acceptance Criteria	Corrective Action
SW-846 6010B Inductively Coupled Plasma	Metals	Initial calibration (1 point + blank minimum)	Daily prior to analysis	• Correlation coefficient (r) ≥0.995	• Recalibrate
		Interference check standard (ICS)	Beginning and end of each analytical run	• Results +/- 20% of true value	• Terminate analysis • Recalibrate instrument • Reanalyze all samples back to last acceptable ICS
		Initial calibration verification (ICV)	After calibration, prior to sample analysis	• Results <10% from calibration standard	• Reanalyze ICV • Recalibrate, if ICV still out
		Continuing calibration verification (CCV)	Every 10 samples and end of analytical sequence	• Results < 10% from calibration standard	• Reanalyze affected samples back to the last acceptable CCV
		Calibration blank - Initial calibration blank (ICB), Continuing calibration blank (CCB)	After initial calibration verification, each subsequent calibration verification, and at the end of the run	• < Method Detection Limit (MDL)	• Reanalyze blank • Clean system • Reanalyze all samples back to last acceptable blank
		Method blank	1 per preparation batch (≤20 samples)	• < Method Detection Limit	• Reanalyze method blank. • If fails, analyze a calibration blank • Reprep/reanalyze analytical batch as appropriate
		Matrix spike (MS)	1 per preparation batch (≤20 samples)	• % Recovery +/-25% of actual value	• If LCS and surrogate recoveries are acceptable and MSD also outside criteria consistent with MS, problem may be attributed to matrix interference • Reprep/reanalyze both MS and MSD. • Narrate all outliers

Table 4-13
Inductively Coupled Plasma Cations and Trace Metals Analysis – Method SW846 6010B
Calibration Specification and Corrective Action Procedures
American Chemical Service, Griffith, Indiana
(Continued)

Analytical Method[a]	Parameter	QC Element	Frequency	Acceptance Criteria	Corrective Action
SW-846 6010B Inductively Coupled Plasma	Metals	Matrix spike duplicate (MSD) or Matrix duplicate (MD)	1 per preparation batch (≤20 samples)	• RPD <20%	• Same as MS
		Laboratory Control Sample (LCS)	1 per preparation batch (≤20 samples)	• % Recovery +/- 20% of actual value	• Reanalyze LCS • Reprep/reanalyze LCS and affected samples • Narrate all outliers

Notes:
RPD Relative percent difference
(a) EPA Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW-846), (U.S. EPA Third Edition, Final Update III, December 1996).

Table 4-14
Mercury by Cold Vapor Analysis - Method SW846 7470A/7471A
Calibration Specifications and Corrective Action Summary
American Chemical Service, Griffith, Indiana

Analytical Method[a]	Parameter	QC Element	Frequency	Acceptance Criteria	Corrective Action
SW-846 7470A/7471A Cold Vapor	Mercury	Initial multipoint calibration (3 point + blank minimum)	Daily, prior to analysis	• Correlation coefficient (r) • 0.995	• Recalibrate
		Initial calibration verification (ICV); mid-level standard	After calibration, prior to sample analysis	• ± 20% of true value	• Reanalyze ICV • Rerun initial calibration
		Continuing calibration verification (CCV); mid-level standard	Every 10 samples and at end of analytical sequence	• ± 20% of true value	• Reanalyze affected samples back to last acceptable CCV
		Initial and continuing calibration blank (ICB/CCB)	After calibration, and after each subsequent calibration verification	• < Method Detection Limit (MDL)	• Reanalyze blank • Clean system if still out • Reanalyze affected samples back to last acceptable CCB
		Method blank	1 per preparation batch (≤20 samples)	• < Method Detection Limit	• Reanalyze method blank. • If fails, analyze a calibration blank • Reprep/reanalyze analytical batch as appropriate
		Matrix spike (MS)	1 per preparation batch (≤20 samples)	• % Recovery within +/- 25% of true value	• If LCS and surrogate recoveries are acceptable and MSD also outside criteria consistent with MS, problem may be attributed to matrix interference • Reprep/reanalyze both MS and MSD. • Narrate all outliers

Table 4-14
Mercury by Cold Vapor Analysis - Method SW846 7470A/7471A
Calibration Specifications and Corrective Action Summary
American Chemical Service, Griffith, Indiana
(continued)

Analytical Method[a]	Parameter	QC Element	Frequency	Acceptance Criteria	Corrective Action
		Matrix spike duplicate (MSD) or Matrix Duplicate (MD)	1 per preparation batch (≤20 samples)	• RPD < 20%	• Same as MS
		Laboratory control samples (LCS)	1 per preparation batch (≤20 samples)	• % Recovery within +/- 20%	• Reanalyze LCS • Reprep/reanalyze LCS and affected samples • Narrate all outliers

Notes:
MDL Method detection limit
RPD Relative percent difference
(a) EPA Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW-846), (U.S. EPA Third Edition, Final Update III, December 1996).

Table 4-15
Quality Control Acceptance Criteria for Cyanide by SW846 9010B, Total Suspended Solids by EPA 160.2, and Biological Oxygen Demand by EPA BOD-5
American Chemical Sercice, Griffith, Indiana

Analytical Method	Analyte	LCS (% Rec)	MS/MSD (% Rec)	MS/MSD/MD (% RPD)
SW-846 9010B	Cyanide	80-120	75-125	20
E160.2	Total Suspended Solids	90-100	NA	20
BOD-5	Biological oxygen demand	NA	NA	25

Notes:
LCS Laboratory Control Standard
MS/MSD Matrix Spike/Matrix Spike Duplicate
Rec Recovery
MD Matrix Duplicate

Table 4-16
Gravimetric Determination of Total Suspended Solids EPA 160.2
Calibration Specifications and Corrective Action Summary
American Chemical Service, Griffith, Indiana

Analytical Method[a]	Parameter	QC Element	Frequency	Acceptance Criteria	Corrective Action
EPA 160.2 Gravimetric	Total Suspended Solids	4.7 cm diameter filter	Filter 100 ml of sample	• Weight of captured residue must be > 1.0 mg	• Increase sample volume
		Method blank	1 per preparation batch (≤ 20 samples)	• < Method Detection Limit	• Reanalyze blank • Reprep/reanalyze blank and all associated samples
		Matrix duplicate (MD)	1 per preparation batch (≤ 20 samples)	• RPD within ACS QC acceptance criteria (Refer to Table 4-15)	• Evaluate LCS
		Laboratory control sample (LCS)	1 per preparation batch (≤ 20 samples)	• % Recovery within ACS QC acceptance criteria (Refer to Table 4-15)	• Reanalyze LCS • Reprep/reanalyze all associated samples • Narrate all outliers

Notes:

g gram
RPD Relative percent difference
QC Quality control
(a) EPA 100-400 Series - Methods for Determination of Inorganic Substances in Environmental Samples (EPA/600R-93/100, August 1993).

Table 4-17
Quality Control Acceptance Criteria for Volatile Organic Compounds in Air by TO-14
American Chemical Service, Griffith, Indiana

Analyte	Air	
	LCS/LCD (% Rec)	LCS/LCD (% RPD)
VOCs by TO-14		
1,1,1-Trichloroethane	70-130	25
1,1,2,2-Tetrachloroethane	70-130	25
1,1,2-Trichloroethane	70-130	25
1,1-Dichloroethane	70-130	25
1,1-Dichloroethene	70-130	25
1,2-Dichloroethane	70-130	25
1,2-Dichloropropane	70-130	25
2-Butanone (MEK)	60-140	25
2-Hexanone	60-140	25
4-Methyl-2-pentanone (MIBK)	60-140	25
Acetone	60-140	25
Benzene	70-130	25
Bromodichloromethane	60-140	25
Bromoform	60-140	25
Bromomethane	70-130	25
Carbon Disulfide	60-140	25
Carbon Tetrachloride	70-130	25
Chlorobenzene	70-130	25
Chloroethane	70-130	25
Chloroform	70-130	25
Chloromethane	70-130	25
cis-1,2-Dichloroethene	70-130	25
cis-1,3-Dichloropropene	70-130	25
Dibromochloromethane	60-140	25
Ethylbenzene	70-130	25
Methylene chloride	70-130	25
Styrene	70-130	25
Tetrachloroethene	70-130	25
Toluene	70-130	25
trans-1,2-Dichloroethene	60-140	25
trans-1,3-Dichloropropene	70-130	25
Trichloroethene	70-130	25
Vinyl chloride	70-130	25
Xylenes (total)	70-130	25
Surrogates:		
Toluene-d8	70-130	N/A
4-Bromofluorobenzene	70-130	N/A
1,2-Dichloroethane-d4	70-130	N/A

Notes:
N/A Not Applicable
Rec Recovery
VOC Volatile Organic Compounds
LCS Laboratory control sample
LCD Laboratory consol sample duplicate
RPD Relative percent difference
Limits from Air Toxics Ltd

Table 4-18
Volatile Organics in Ambient Air Using Summa Canister Sampling by Gas Chromatography Or Gas Chromatography/Mass Spectrometry Analysis by Method - EPA TO-14
Calibration Specification and Corrective Action Summary
American Chemical Service, Griffith, Indiana

Analytical Method[a]	Parameter	QC Element	Frequency	Acceptance Criteria	Corrective Action
EPA TO-14 Volatile Organics in Ambient Air using Summa Canister Sampling by GC or GC/MS Analysis	VOCs	For GC/MS analysis, tune the instrument with a 4-bromofluorobenzene standard (BFB)	Daily, prior to analysis	• Must meet key ions and ion abundance criteria established by the method (Refer to Table 4-4)	• Retune instrument • Repeat standard analysis
		Initial multi-point calibration (3 levels plus zero humid air) Lowest point at or below PQL	Prior to analysis, and as required	• No acceptance criteria stated by the method	• None
		Routine calibration	Daily, prior to analysis	• No acceptance criteria stated by the method	• None
		Method blank	1 per analytical batch (≤20 samples)	• < Method Detection Limit	• Reanalyze method blank • Recalibrate
		Internal standards (for GC/MS analysis)	Every sample, method blank, LCS/LCD	• Retention time for each internal standard must be within 30 seconds of most recent CCV and the EICP area for all internal standards must be within -50% to +150% of the most recent CCV	• Evaluate system/standard • Reanalyze samples • If still out, report both sets of data
		Retention time windows	Established with each new column installation; updated with every daily routine calibration standard	• Retention times must be within daily retention time windows established by the daily routine calibration standard for every standard and sample	• Reanalyze standard and all affected samples

Table 4-18
Volatile Organics in Ambient Air Using Summa Canister Sampling by Gas Chromatography Or Gas Chromatography/Mass Spectrometry Analysis by Method - EPA TO-14
Calibration Specification and Corrective Action Summary
American Chemical Service, Griffith, Indiana
(Continued)

Analytical Method[a]	Parameter	QC Element	Frequency	Acceptance Criteria	Corrective Action
		Surrogate spike	Every sample, method blank, LCS, MS/MSD	• Surrogate recoveries within QC acceptance criteria. (Refer to Table 4-17) • One surrogate may be out if > 10% recovery	• Narrate all outliers
		Laboratory Control Sample (LCS)	1 per analytical batch of samples (≤20 samples)	• % Recovery within project QC acceptance criteria for all spiked analytes (Refer to Table 4-17)	• Narrate outlier
		Laboratory Control Sample Duplicate (LCD)	1 per analytical batch of samples (≤20 samples)	• %RPD within project QC acceptance criteria for all spiked analytes (Refer to Table 4-17)	• Same as LCS

Notes:

EICP	Extracted ion current profile
GC	Gas chromatography
GC/MS	Gas chromatography/mass spectroscopy
LCS	Laboratory Control Sample
LCD	Laboratory Control Sample Duplicate
ppbv	Parts per billion volume
RPD	Relative percent difference
(a)	Compendium of Methods for Determination of Toxic Organic Compounds in Ambient Air (EPA/600/4-89/017, June 1988).

Table 4-19
Quality Control Acceptance Criteria for Semi-Volatile Organic Compounds in Air by TO-13
American Chemical Service, Griffith, Indiana

Analyte	Air LCS (% Rec)
SVOCs by TO-13	
1,2,4-Trichlorobenzene	4-115
1,4-Dichlorobenzene	6-101
2,4-Dinitrotoluene	24-106
2-Chlorophenol	8-98
4-Chloro-3-methylphenol	10-104
4-Nitrophenol	11-125
Acenaphthene	7-106
N-Nitrosodi-n-propylamine	10-95
Pentachlorophenol	3-138
Phenol	7-96
Pyrene	48-108
Surrogates:	
2,4,6-Tribromophenol	9-98
2-Fluorobiphenyl	15-98
2-Fluorophenol	7-85
Nitrobenzene-d5	14-92
Phenol-d5	2-94
Terphenyl-d14	19-162

Notes:
N/A Not Applicable
Rec Recovery
SVOC Semi-volatile Organic Compounds
Limits from Air Toxics Ltd.

Table 4-20
Semi-Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry by Method TO-13
Calibration Specifications and Corrective Action Summary
American Chemical Service, Griffith, Indiana

Analytical Method[a]	Parameter	QC Element	Frequency	Acceptance Criteria	Corrective Action
TO-13 Semi-Volatiles by GC/MS	Semi-Volatiles	Tune the instrument using a decafluorotriphenylphosine (DFTPP) standard	Every 12 hours	• Must meet the ion abundance criteria specified in the method (Refer to Table 4-7) • Degradation of DDT = 20% • Benzidine and PCP present at normal response without excessive tailing	• Retune instrument • Repeat standard analysis • Perform injection port, column maintenance as necessary
		Initial calibration (5 point minimum); includes Calibration Check Compounds (CCC), System Performance Calibration Check (SPCC), and Internal Standard Compounds (IS)	Prior to analysis and as required	• % RSD for CCC =30%; average RF =0.05 for SPCC • If mean % RSD = 30 % average RF may be used; linear calibration required	• Evaluate the system • Repeat calibration
		Continuing calibration verification (CCV); includes CCC, SPCC, and IS	Every 12 hours	• Percent difference (%D) <30% for CCC; RF =0.05 for SPCC • Retention time for each internal standard must be within 30 seconds of most recent CCV and the EICP area for all internal standards must be within –50% to +100% of the most recent CCV.	• Evaluate system/standard • Reanalyze calibration check standard • Repeat the initial calibration as necessary
		Internal Standard	Every sample, method blank, LCS and MS/MSD	• Retention time for each internal standard must be within 30 seconds of most recent CCV and the EICP area for all internal standards must be within –50% to +100% of the most recent CCV	• Evaluate system/standard • Reanalyze the sample • If still out, report both sets of data

Table 4-20
Semi-Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry by Method TO-13
Calibration Specifications and Corrective Action Summary
American Chemical Service, Griffith, Indiana
(Continued)

Analytical Method[a]	Parameter	QC Element	Frequency	Acceptance Criteria	Corrective Action
TO-13 Semi-Volatiles by GC/MS (continued)	Semi-Volatiles	Method Blank	1 per preparation batch (≤20 samples)	• < Method Detection Limit	• Reanalyze blank • Narrate outliers
		Surrogate spike	Every sample, method blank, LCS and MS/MSD	• Recovery within acceptance criteria (Refer to Table 4-19) • One surrogate per fraction may be out if recovery > 10%	• Reanalyze sample once • If still out, report both sets of data • Narrate all outliers
		Laboratory control sample	1 per preparation batch (≤20 samples)	• % Recovery within project QC acceptance criteria for all spiked analytes (Refer to Table 4-19)	• Reanalyze LCS • Narrate all outliers

Notes:
EICP Extracted ion current profile
QC Quality control
RF Response factor
RSD Relative standard deviation
(a) EPA Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW-846), (U.S. EPA Third Edition, Final Update III, December 1996)

Table 4-21
Cyanide by SW846 9010B
Calibration Specifications and Corrective Action Summary
American Chemical Service, Griffith, Indiana

Analytical Method[a]	Parameter	QC Element	Frequency	Acceptance Criteria	Corrective Action
SW846 9010B	Total and Amenable Cyanide	Initial multipoint calibration (minimum of six concentrations plus blank)	Initial daily calibration prior to sample analysis and as needed	Correlation coefficient (r) ≤ 0.995	• Check calculations • Recalibrate
		Initial calibration standard (ICV)	1 per preparation batch (≤20 samples)	± 15% of true value	• Correct problem • Recalibrate
		Second-source calibration verification	Once per stock standard preparation	± 15% of expected value	• Correct problem • Recalibrate
		Continuing calibration verification (CCV) mid-range	Every 10 samples or every two hours and at end of run	± 15% of expected concentration	• Reanalyze affected samples back to last acceptable CCV
		Calibration blank- Initial calibration blank (ICB), Continuing calibration blank (CCB)	Daily after each ICV and CCV	< Method Detection Limit	• Reanalyze blank • Clean system • Reanalyze samples back to last clean blank
		Method blank	1 per preparation batch (≤20 samples)	< PQL	• Reanalyze blank • Reprep/reanalyze blank and all associated samples

Table 4-21
Cyanide by SW846 9010B
Calibration Specifications and Corrective Action Summary
American Chemical Service, Griffith, Indiana
(Continued)

Analytical Method[a]	Parameter	QC Element	Frequency	Acceptance Criteria	Corrective Action
SW846 9010B (Cont.)	Total and Amenable Cyanide	Matrix spike (MS)	1 per preparation batch (≤20 samples)	% Recovery within QC acceptance criteria (refer to Table 4-15)	• Assess data (4x rule) • If LCS recoveries are within acceptance criteria, matrix interference may be suspected • Reanalyze once if matrix is not a factor • Narrate all outliers
		Matrix spike duplicate (MSD) or Matrix duplicate (MD)	1 per preparation batch (≤20 samples)	% Recovery and/or RPD within QC acceptance criteria (refer to Table 4-15)	• Same as MS
		Laboratory control sample (LCS).	1 per preparation batch (≤20 samples)	± 20 % of true value	• Correct problem • Recalibrate • Reanalyze samples

Notes:
QC Quality control
RPD Relative percent difference
(a) EPA Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW-846), (U.S. EPA Third Edition, Final Update III December 1996).

TABLE 4-22

FIELD AND LABORATORY QUALITY CONTROL SAMPLE DESCRIPTIONS
AMERICAN CHEMICAL SERVICE, GRIFFITH INDIANA

Field/Laboratory QC Samples	QC Sample Type	Rationale	Frequency	Description	QC Sample Data Assessment
Field QC Samples	Trip Blank	Identify target analytes that may have been introduced into samples during sample handling, shipping, or storage at the laboratory.	One per each cooler containing samples for VOC analysis for groundwater samples only.	Two 40-milliliter (ml) amber glass vials with Teflon septum caps containing reagent-grade water and preserved to a pH of ≤2. Prepared by the laboratory.	All target analyte detections will be evaluated in accordance with the principles for data validation outlined in the *National Functional Guidelines for Organic and Inorganic Data Validation* (U.S. EPA, 1994).
	Field Duplicates or Replicates	Assess sampling and analytical precision. Applicable to all media.	Ten percent of the total number of samples for soil and groundwater for each analytical method (does not include treatment effluent or off-gas).	A field duplicate or replicate consists of a discrete sample split into two equal portions. One sample is labeled with the correct field identification, the other is submitted "blind" to the laboratory with a fictitious sample identification. Samples consisting of liquid are referred to as duplicates, solids samples are referred to as replicates.	The RPD will be calculated for each analyte (reported above the project practical quantitation limit) between the sample and its duplicate or replicate. Because these samples assess both sampling and analytical precision, replicate or duplicate sample data will not be used for data qualification. The data will be used qualitatively.
	Equipment Blank	Assess the completeness of the decontamination process for non-dedicated sampling equipment used for soil or water samples.	One per 10 groundwater samples for each analysis.	An equipment blank consists of rinseate from equipment decontamination that is carried through the same sample collection, handling, and analytical procedures as the investigative samples.	All target analyte detections will be evaluated in accordance with the principles for data validation outlined in the *National Functional Guidelines for Organic and Inorganic Data Validation* (U.S. EPA, 1994).
	Temperature Blank	Assess sample temperature criterion. Applicable to all samples that have specified temperature criteria.	Each sample cooler.	A 40-ml amber glass bottle filled with reagent-grade water. The temperature of this sample is measured at the time samples are received by laboratory.	Assess whether the temperature criterion of 4°C ± 2°C has been met, and if not to assess whether corrective actions are necessary.
Laboratory	Method Blank	Identify target analytes that may have been introduced into the sample during analysis. Applicable to all media.	Each sample- or extraction-batch (≤20 samples) for each analytical method.	Reagent-grade water that is carried through the same analytical process as native samples.	All target analyte detections will be evaluated in accordance with the principles for data validation outlined in the *National Functional Guidelines for Organic and Inorganic Data Validation* (U.S. EPA, 1994).
	Surrogate Spikes	Assess analytical accuracy. Applicable to all media.	Each sample for organic analysis including both investigative and QC samples for each method.	Each sample will be spiked in the laboratory with surrogate spikes in accordance with the laboratories SOPs for the respective methods.	Percent recovery is calculated for each spiked analyte and compared to the acceptance criteria for surrogate accuracy specified in this QAPP (Section 3.0).
	Matrix Spike/Matrix Spike Duplicate	Assess analytical accuracy and precision and identify media interference during analysis. Applicable to all media.	Each sample- or extraction-batch (≤20 samples) for each analytical method for each media type, except for treatment effluent and off-gas samples.	The samples for MS/MSD analysis are prepared in the laboratory by adding a standard of known concentration to the samples in accordance with the laboratory's SOPs for the respective methods.	Percent recovery and the relative percent difference (RPD) for each spiked analyte is calculated and compared to the acceptance criteria for accuracy and precision specified in this QAPP (Section 3.0).
	Laboratory Control Sample	Assess analytical accuracy. Applicable to all media.	Each sample- or extraction-batch (≤20 samples) for each analytical method.	The laboratory control sample is prepared by the laboratory and consists of reagent-grade water or sand spiked with a standard (either from a source other than, or the same source used for the initial calibration standard) in accordance with analytical method and the laboratories SOPs for each respective method.	Percent recovery for each spiked analyte is calculated and compared to the acceptance criteria for accuracy specified in this QAPP (Section 3.0).

EPA Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW846, (U.S. EPA Third edition, Final Update December 1996).
EPA 600 Series - Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater (U.S. EPA, CFR Title 40, Part 136, Appendix A, July 1996).
EPA 100-400 Series - Methods for the Determination of Inorganic Substances in Environmental Samples (EPA/600R-93/100, August 1993).
Compendium of Methods for Determination of Toxic Organic Compounds in Ambient Air (EPA/600/4-89/017, June 1988).

Table 5-1
Analytical Method, Sample Container, Preservative, Unit of Measure, And Holding Time Criteria
American Chemical Service, Griffith, Indiana

Analytical Method	Sample Container	Preservative	Unit of Measure	Holding Time
Water				
VOCs (SW-846 8260B, EPA 624)	Three 40-ml amber glass bottles with a Teflon™ septum cap; No head space	HCl; pH < 2 Chill to 4°C	µg/l	14 days from sample collection to analysis
SVOCs (SW-846 8270C)	Two 1-liter amber glass bottle with a Teflon™ lined cap	Chill to 4°C	µg/l	7 days from sample collection to extraction 40 days from sample extraction to analysis
Pesticides/PCBs (SW-846 8081A)	Two 1-liter amber glass bottle with a Teflon™ lined cap	Chill to 4°C	µg/l	7 days from sample collection to extraction 40 days from sample extraction to analysis
PCBs (SW-846 8082)	Two 1-liter amber glass bottle with a Teflon™ lined cap	Chill to 4°C	µg/l	7 days from sample collection to extraction 40 days from sample extraction to analysis
Metals (SW-846 6010B Trace, 7470A, 7000 Series)	One 1-liter polyethylene bottle with a Teflon™ lined cap	HNO_3; pH < 2 Chill to 4°C	µg/l	180 days from sample collection to analysis for all metals except mercury 28 days from sample collection to analysis for mercury
Cyanide (Method SW-846 9010B)	One 1-liter polyethylene bottle with a Teflon™ lined cap	NaOH; pH > 12 Chill to 4°C	µg/l	14 days from sample collection to analysis
Total Suspended Solids (EPA 160.2)	One 1-liter polyethylene bottle with a Teflon™ lined cap	Chill to 4°C	mg/l	7 days from sample collection to analysis
BOD (EPA 405.1)	One 1-liter polyethylene bottle	No preservation Chill to 4°C	mg/l	48 hours from sample collection to analysis

Table 5-1
Analytical Method, Sample Container, Preservative, Unit of Measure, And Holding Time Criteria
American Chemical Service, Griffith, Indiana

Analytical Method	Sample Container	Preservative	Unit of Measure	Holding Time
Soil				
PCBs (SW-846 8082)	4- or 8-oz glass wide-mouth with a Teflon™ lined cap	Chill to 4°C	µg/kg	14 days from sample collection to extraction 40 days from sample extraction to analysis
Air				
TO-13 SVOCs	PUF/XAD-2 Cartridge	Chill to 4°C	µg/sample	7 days from sample collection to analysis and 30 days from extraction to analysis
TO-14 VOCs	Summa Canister	None	ppbv	3 days from sample collection to analysis (Tedlar Bag) 14 days from sample collection to analysis (Summa Canister)

Notes:
EPA Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW846, (EPA Third edition, September 1986; Final Update III, December 1996).
EPA 100-400 Series Methods for the Determination of Inorganic Substances in Environmental Samples, (EPA/600R-93/100. August 1993).
EPA 600 Series - Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater (U.S. EPA, CFR Title 40, Part 136, Appendix A, July 1996).
Compendium of Methods for Determination of Toxic Organic Compounds in Ambient Air (EPA/600/4-89/017, June 1988)

µg/l	Microgram per liter	ppbv	Part per billion by volume	SVOCs	Semi-volatile organic compounds
µg/kg	Milligram per kilogram	mg/l	Milligram per liter	oz	Ounce
PCBs	Polychlorinated biphenyls	VOCs	Volatile organic compounds	µg/kg	Micrograms per kilogram
NaOH	Sodium hydroxide	HCl	Hydrochloric acid	HNO_3	Nitric acid
°C	degrees Celsius				

Table 8-1
Summary of Analytical Procedures
American Chemical Service, Griffith, Indiana

Method[a]	Analytical Procedure
SW-846 8260B, EPA 624 Volatile Organic Compounds by GC/MS	Volatile compounds are introduced onto a 30-meter capillary column in a gas chromatograph (GC), temperature programmed to separate the analytes, which are then detected with a mass spectrometer (MS) interfaced with the GC. A 25ml purge will be used for all water samples to meet the project reporting limits. Quantitation is accomplished by comparing response of a major (quantitation) ion relative to an internal standard using a 5-point calibration curve.
SW-846 8270C Semi-volatile Organic Compounds by GC/MS	Semi-volatile compounds are introduced onto a 30-meter capillary column in a gas chromatograph (GC), temperature programmed to separate the analytes, which are then detected with a mass spectrometer (MS) interfaced with the GC. Quantitation is accomplished by comparing response of a major (quantitation) ion relative to an internal standard using a 5-point calibration curve.
SW846 8081A, 8082 Pesticides/Polychlorinated Biphenyls by GC	Semi-volatile compounds are introduced onto a 30-meter capillary column in a gas chromatograph (GC), temperature programmed to separate the analytes, which are then detected by an electron capture detector (ECD) or a flame ionization detector (FID). Concentrations are calculated by comparing the response of a compound to a 5-point calibration curve.
TO-13 Semi-volatile Organic Compounds in Air	Sample is introduced into a gas chromatograph (GC) which is equipped with either a flame ionization detector (FID), mass spectrometer (MS), or high performance liquid chromatograph (HPLC). Sample concentrations are calculated using a 5-point calibration curve.
TO-14 Volatile Organic Compounds in Air	The volatile compounds are concentrated by collection on a cryogenically-cooled trap, then revolatilized and introduced onto a gas chromatograph (GC) coupled to one or more detectors. These detectors may include a flame ionization detector (FID), photoionization detector (PID), and mass spectrometer (MS), among others. Sample concentrations are calculated using a 5-point calibration curve.
SW-846 6010B ICP Metals	The inductively coupled plasma method measures element-emitted light by optical spectrometry. Samples are nebulized and the resulting aerosol is transported to the plasma torch. Element-specific atomic-line emission spectra are produced by a radio-frequency inductively coupled plasma. The spectra are dispersed by a grating spectrometer and the intensities of the emission lines are monitored by photo sensitive devices.
SW-846 7000 Series GFAA Metals	For the graphite furnace technique in conjunction with an atomic absorption spectrophotometer (GFAA), a sample aliquot is placed in the graphite tube in the furnace, evaporated to dryness, charred and atomized. The metal atoms to be measured are placed in the beam of radiation by increasing the temperature of the furnace, causing volatilization. The wavelength of the light beam is characteristic of only the metal being determined, and the light energy being absorbed is a measure of the concentration of that metal in the sample.

Table 8-1
Summary of Analytical Procedures
American Chemical Service, Griffith, Indiana
(Continued)

Method[a]	Analytical Procedure
SW-846 7470A/7471A, Cold Vapor AA	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 adsorption spectrophotometer. Absorbency (253.7 nm) is measured as a function of mercury concentration.
SW-846 9010 Total and Amenable Cyanide for Water	Cyanide in water samples is extracted by refluxing the sample with a strong acid and catalyst and distillation. Total cyanide in soils is determined after acidification of the soil and distillation. The cyanide ion in the absorbing solution is determined using spectrophotometry.
EPA 160.2 Total Suspended Solids	The filtrate is evaporated and dried to constant weight at 103-105° degrees centigrade.

Notes

(a) EPA Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW-846), (U.S. EPA Third Edition, September 1986; Final Update III, December 1996).
EPA 100-400 Series - Methods for the Determination of Inorganic Substances in Environmental Samples (EPA/600R-93/100, August 1993).
EPA 600 Series - Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater (U.S. EPA, CFR Title 40, Part 136, Appendix A, July 1996).
Compendium of Methods for Determination of Toxic Organic Compounds in Ambient Air (EPA/600/4-89/017, June 1988).

GFAA Graphite Furnace Atomic Adsorption

Table 10-1
Laboratory Data Qualifiers
American Chemical Service, Griffith, Indiana

Qualifier	Description
T	The analyte was positively identified, but the associated numerical value is below the practical quantitation limit and above the method detection limit; represents an estimated value
U	Analyte is not detected
B	The analyte was positively detected in a sample and in an associated blank
E	Reported concentration is estimated; outside the linear calibration range of the instrument
R	The data are unusable due to deficiencies in the ability to analyze the sample and meet QC criteria
D	Indicates that the concentration was calculated using a secondary dilution factor (i.e., the result is calculated from the analysis performed by diluting the sample)
G	Reporting limit elevated due to matrix interference

Table 10-2
Data Reporting Requirements
American Chemical Service, Griffith, Indiana

Data Type	*Analysis Type*	*Data Reporting Requirements*	*Report Format*
Groundwater general water quality data collected in the field using a portable meter.	pH	—Location, date, and time sample collected —Initial and continuing calibration data —pH data	—Project-specific field form or log book —Project-specific field form or log book —Project-specific field form or log book
	Specific conductivity (SC)	—Location, date, and time sample collected —Initial and continuing calibration data —SC data	—Project-specific field form or log book —Project-specific field form or log book —Project-specific field form or log book
	Temperature	—Location, date, and time sample collected —Initial and continuing calibration data —Temperature data	—Project-specific field form or log book —Project-specific field form or log book —Project-specific field form or log book
	Oxidation-reduction potential (ORP)	—Location, date, and time sample collected —Initial and continuing calibration data —ORP potential data as Eh	—Project-specific field form or log book —Project-specific field form or log book —Project-specific field form or log book
	Dissolved oxygen	—Location, date, and time sample collected —Initial and continuing calibration data —Dissolved oxygen data	—Project-specific field form or log book —Project-specific field form or log book —Project-specific field form or log book
	Turbidity	—Location, date, and time sample collected —Initial and continuing calibration data —Turbidity data in nephelometric units	—Project-specific field form or log book —Project-specific field form or log book —Project-specific field form or log book

Table 10-2
Data Reporting Requirements
American Chemical Service, Griffith, Indiana
(Continued)

Data Type	Analysis Type	Data Reporting Requirements	Report Format
Screening Data	Biological oxygen demand	—Location, date, and time sample collected —Initial and continuing calibration data —Method blank data —Target analyte data —Dilution factor (as applicable)	—Hard copy of data report —Hard copy of data report —Hard copy of data report —Hard copy of data report
Screening Data: Effluent	Total suspended solids	—Location, date, and time sample collected —Total suspended solids data	—Hard and electronic copy of data report —Hard and electronic copy of data report
Definitive organic or inorganic data generated by a laboratory.	Level IV data package for standard methods of analysis or modified standard methods of analysis for organic or inorganic compounds. Level III same as Level IV except that raw data are not provided.	—Case narrative (including samples not meeting QC criteria, out of control conditions, corrective actions, and matrix effects with justification) —Completed C-O-C and sample receipt and log in forms —Initial calibration summary form —Continuing calibration summary form —Internal standard area and RT summary (if applicable) —Injection logs —Target compound results for all samples, including field QC samples and dilution factors, reanalysis, batching information, and bracketing information —Method blank results —MS/MSD results (spike concentration, actual values, and percent recovery) —LCS results (spike concentration, actual values, and percent recovery)	—Hard copy of data report —Hard copy of data report —Hard copy of data report —Hard copy of data report —Hard copy of data report —Hard copy of data report —Hard and electronic copy of data report —Hard and electronic copy of data report —Hard and electronic copy of data report —Hard and electronic copy of data report

Table 10-2
Data Reporting Requirements
American Chemical Service, Griffith, Indiana
(Continued)

Data Type	Analysis Type	Data Reporting Requirements	Report Format
Definitive organic or inorganic data generated by a laboratory.	Level IV data package for standard methods of analysis or modified standard methods of analysis for organic or inorganic compounds. Level III same as Level IV except that raw data are not provided.	—Surrogate results, organic analysis (spike concentration, actual values, and percent recovery)	—Hard and electronic copy of data report
		—Raw data for all samples where matrix interference is invoked as the reason for MS/MSD, surrogate spike, or internal standard failure	—Hard copy of data report
		—ICP interference check sample data	—Hard copy of data report
		—Post digestions spike sample data	—Hard copy of data report
		—Method of standard addition data (if required)	—Hard copy of data report
		—Sample preparation logs	
		—Raw data as generated from the instrument	—Hard copy of data report
		—Holding time summary	—Hard copy of data report —Hard and electronic copy of data report

Notes:
EPA Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW-846), (U.S. EPA Third Edition, September 1986; Final Update III, December 1996).
EPA 100-400 Series - Methods for the Determination of Inorganic Substances in Environmental Samples (EPA/600R-93/100, August 1993).
EPA 600 Series - Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater (U.S. EPA, CFR Title 40, Part 136, Appendix A, July 1996).
Compendium of Methods for Determination of Toxic Organic Compounds in Ambient Air (EPA/600/4-89/017, June 1988).

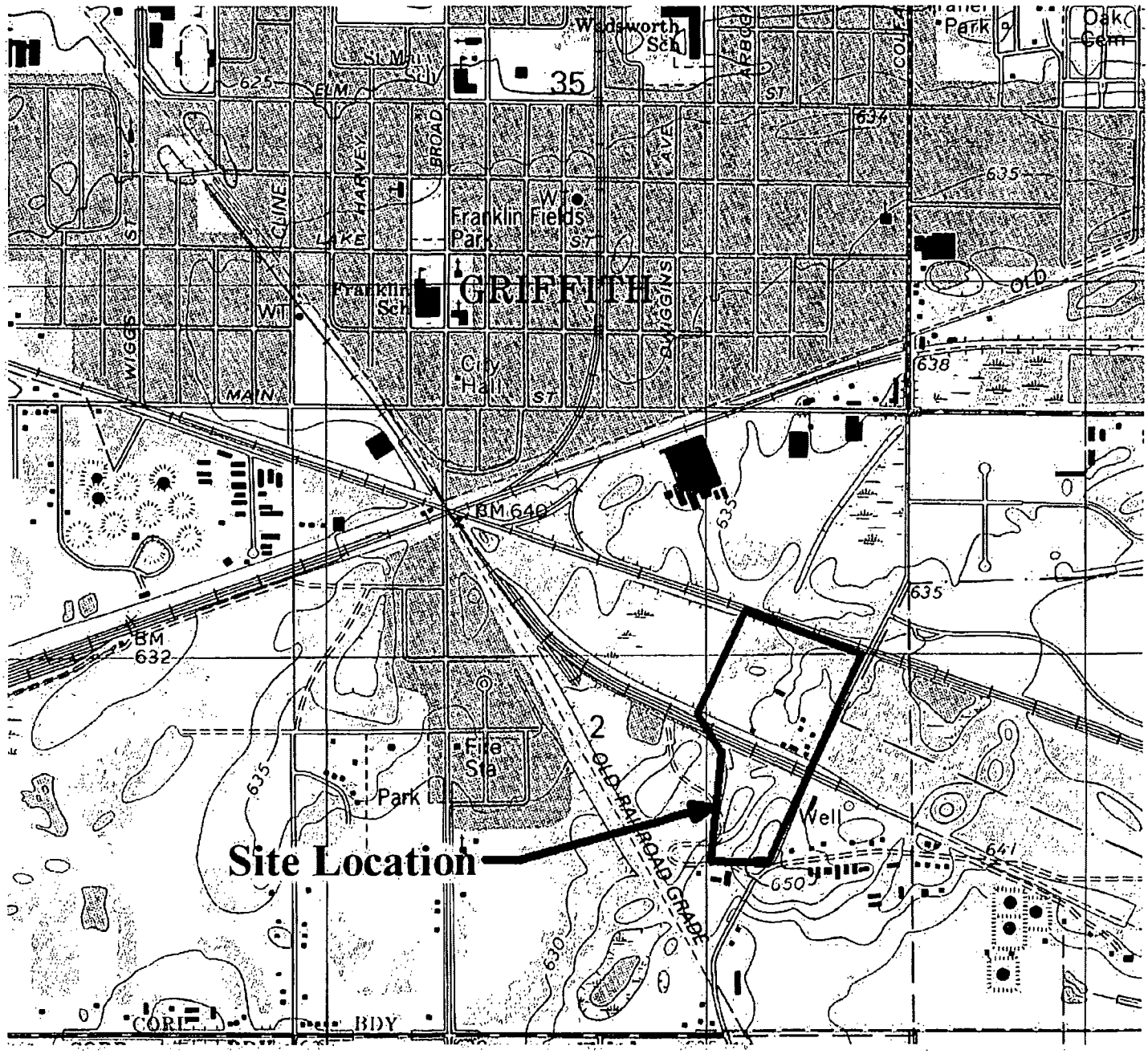
Table 10-3
Data Validation Data Qualifiers
American Chemical Service, Griffith, Indiana

Qualifier	Description
UB	Analyte is not detected at or above the indicated concentration due to blank contamination
B	The analyte was positively detected in a sample and in an associated blank
UK	Analyte is not detected at or above the indicated concentration based on the data validation (i.e. for analytes that are common laboratory contaminants but were not detected in an associated blank)
UJ	Possible false negative result due to related QC problems
J	Result is estimated based on MS/MSD or surrogate spike recoveries
R	Data are considered unusable based on the results of the data validation and/or field procedures evaluation

Table 12-1
Preventive Maintenance Schedule for Field Instruments
American Chemical Service, Griffith, Indiana

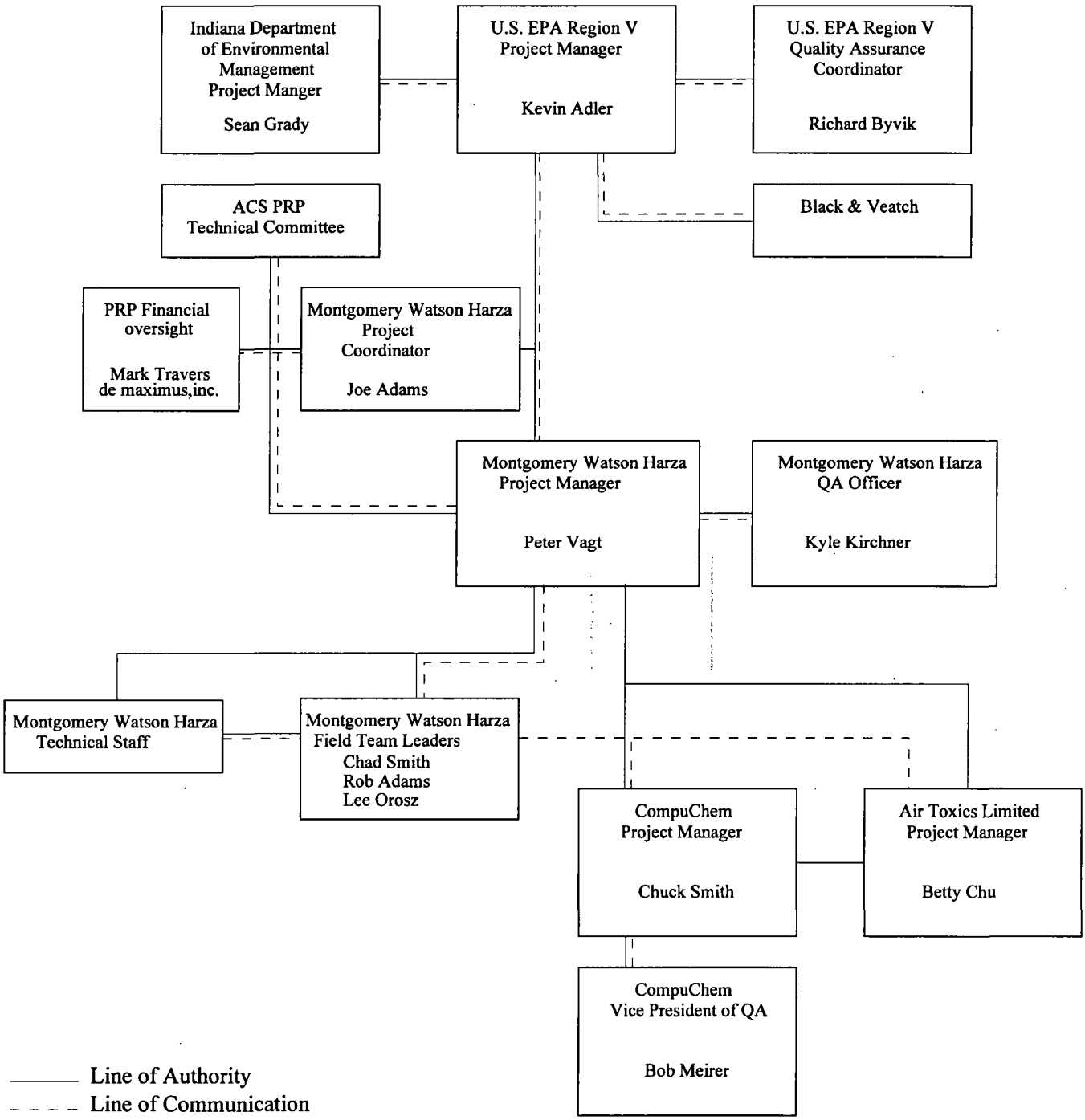
Instruments	Maintenance Procedures/Schedule	Spare Parts in Stock
Multi-parameter probe (oxidation-reduction potential, dissolved oxygen, specific conductivity, turbidity, pH, temperature)	1. Calibrate beginning of each day and as necessary during use. 2. Check battery charge or power source each day.	1. Batteries/battery charger 2. pH buffers and AutoCal solution

FIGURES



MWH MONTGOMERY WATSON HARZA	AMERICAN CHEMICAL SERVICE, INC. NPL SITE GRIFFITH, INDIANA	SITE LOCATION MAP	FIGURE 2-1

J:/209/0603 ACS/QAPP/2090603-SITE_MAP.dwg



MWH *MONTGOMERY WATSON HARZA*	AMERICAN CHEMICAL SERVICE, INC. NPL SITE GRIFFITH, INDIANA	PROJECT ORGANIZATION CHART	FIGURE 3-1

J:/209/0603 ACS/QAPP/2090603-org_chart.dgn

FIGURE 10-1A

ORGANIC DATA VALIDATION FORM

Analytical Method/Analytes: _____ Sample Collection Date(s): _____

Laboratory: _____ MW Job Number: _____

Batch Identification: _____ Matrix: _____

QC Identification[a]: _____ Page: 1 of _____

Validation Complete: (Signature and Date) _____

	Sample Identification	Lab Identification	Hits (Y/N)	Qualifications	Comments
1					
2					
3					
4					
5					
6					
7					
8					
9					
10					
11					
12					
13					
14					
15					
16					
17					
18					
19					
20					

FIGURE 10-1B

ORGANIC DATA VALIDATION FORM

Analytical Method/Analytes: _____ Page 2 of _____

Laboratory: _____

Batch Identification: _____

QC Identification[a]: _____

Data Validation Criteria	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
Holding Time																				
Analyte List																				
Reporting Limits																				
Tuning Standard (BFB)																				
Initial Calibration																				
Continuing Calibration																				
Injection Time																				
Internal Standard EICP Area (GC/MS)																				
Internal Standard Retention Time Window (GC/MS)																				
Retention Time Windows (GC)																				
Method Blank																				
Surrogate Spike Recovery																				
Laboratory Control Sample																				
Laboratory Control Sample Duplicate																				
Matrix Spike/Matrix Spike Duplicate																				
Trip Blanks																				
Field Duplicate/Replicate																				
Field Blank																				
Equipment Blank																				
Source Water																				

(a) List QC batch identification if different than Batch ID
A indicates validation criteria were met
X indicates validation criteria were not met
N indicates data review were not a project-specific requirement
N/A indicates criteria are not applicable for the specified analytical method

FIGURE 10-2A

INORGANIC DATA VALIDATION FORM

Analytical Method/Analytes: _____ Sample Collection Date(s): _____

Laboratory: _____ MW Job Number: _____

Batch Identification: _____ Matrix: _____

QC Identification[a]: _____ Page: 1 of _____

Validation Complete: (Signature and Date) _____

	Sample Identification	Lab Identification	Hits (Y/N)	Qualifications	Comments
1					
2					
3					
4					
5					
6					
7					
8					
9					
10					
11					
12					
13					
14					
15					
16					
17					
18					
19					
20					

FIGURE 10-2B

INORGANIC DATA VALIDATION FORM

Analytical Method/Analytes: _____ **Page 2 of** _____

Laboratory: _____

Batch Identification: _____

QC Identification[a]: _____

Data Validation Criteria	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**
Hardcopy vs. Chain of Custody																				
Holding Time																				
Analyte List																				
Reporting Limits																				
Initial Calibration																				
Initial Check Blank (ICP & AA only)																				
Continuing Calibration																				
Continuing Check Blank (ICP & AA only)																				
Analysis Time																				
Interference Check Standard (ICP only)																				
ICP Serial Dilution																				
Method of Standard Additions (ICP & AA only)																				
Method Blank																				
Laboratory Control Sample																				
Laboratory Control Sample Duplicate (lab specific)																				
Matrix Spike/Matrix Spike Duplicate																				
Matrix Duplicate (lab specific)																				
Field Duplicate/Replicate																				
Equipment Rinseate Blanks																				
Filter Blanks																				
Electronic Deliverable vs. Hardcopy																				
Electronic Deliverable vs. Chain of Custody																				

(a) List QC batch identification if different than Batch ID
A indicates validation criteria were met
X indicates validation criteria were not met
N indicates data review were not a project-specific requirement
N/A indicates criteria are not applicable for the specified analytical method

APPENDICES

A

APPENDIX A

LABORATORY STANDARD OPERATING PROCEDURES

COMPUCHEM
AIR TOXICS
SEVERN TRENT LABORATORIES

**(Gold sheets separate laboratory SOP groups,
Blue sheets separate individual SOPs)**

CompuChem
a division of Liberty Analytical Corporation

501 Madison Avenue
Cary, NC 27513

SOP DOCUMENTATION FORM

This form must accompany all new and revised Standard Operating Procedures (SOPs) when you turn them in to Quality Assurance for review. Please fill out the entire shaded area (except effective date).

This is a new procedure _____ revised procedure ✓ outdated procedure (archive) _____

- Procedure area, title, and SOP number: SAMPLE CONTROL SOP 4.1: RECEIVING SAMPLES — Effective date: (QA fills in) 10/27/99
- Procedure prepared by: Cathy Dorey — Date: 10/27/99
- Procedure approved by: (If the manager prepared the SOP, a qualified second party should sign) Linda Carter — Date: 10/27/99
- Reason for change: REVISION OF USEPA OLM04.2 DETERMINATION OF TEMPERATURE INDICATOR
- This procedure meets the requirements of the following approved method references: OLM04.0 (plus revisions), OLM03.0 (plus revisions), ILM04.0 (plus revisions) SW846, 40 CFR Part 136.

Procedure approved by Quality Assurance Representative: Bob Macaira — Date: 10/27/99

Effective 1-1-96, on an annual basis: Lab managers are required to review lab practices and revise the SOP if necessary. If no revision is necessary, indicate by your signature that the SOP has been reviewed.

Annual Review—Signature: _____ Date: _____

Annual Review—Signature: _____ Date: _____

Annual Review—Signature: _____ Date: _____

Sample Control SOP 4.1 Receiving Samples

1.0 Scope and Application

This Standard Operating Procedure (SOP) describes the process of receiving samples from the US EPA and commercial clients. It contains a full description of the log-in procedure.

Staff members performing the procedures described in this SOP are responsible for reading, understanding, and complying with the SOP requirements. Supervisors are responsible for directing the analyst to the controlled SOP, and providing adequate explanation of the material contained therein.

This procedure is restricted to use by or under the supervision of employees experienced or trained in the processes described below.

2.0 Summary

After all incoming samples have been received from the carrier **at the loading dock**, the Sample Control clerk logs them in. When they are received, the sample containers must be checked to ensure that they are intact. Any damage to the sample containers must be noted on the appropriate paperwork. Chains-of-custody (COCs) must be verified against the actual sample received. Sample information is entered into the Laboratory **Information** Management System (LIMS) for scheduling and tracking purposes. Finally, the samples are placed into cold storage until preparation and analysis.

3.0 Definitions

3.1 Sample Control Department - The name may be used interchangeably by the lab with "Receiving Department"

3.2 **LIMS – The Laboratory Information Management System used procedures to track samples and schedule procedures for preparation and analysis driven by CompuChem's mainframe computer.**

3.3 NJDEP - New Jersey Department of Environmental Protection

3.4 COC – a **chain-of-custody** form that arrives with the sample containers. It is located inside the cooler and it identifies the samples, the requested analyses, dates and signatures of people receiving and relinquishing custody of the samples, the number of sample containers, etc.

- organic water case/SDG
- **organic soil case/SDG**
- **inorganic water case/SDG**
- **inorganic soil case/SDG**

4.0 Safety

Glasses, gloves and lab coats are required to be worn when sample coolers are being unpacked and work is being performed with samples at the hood.

All samples should be treated and handled as if they are hazardous.

Laboratory staff is encouraged to review the Chemical Hygiene Plan for general safety policies, and Material Safety Data Sheets for reagents used in the laboratory.

5.0 Equipment and Supplies

5.1 NIST – traceable thermometer with a minimum measurable range of 0 - 50°C with a calibration tolerance of ± 1.0°C.

5.1.1 Other temperature measurement devices that can be calibrated to ± 1.0°C and have a range of 0 - 20°C, such as an IR gun.

5.1.2 Temp-Chex temperature measurement strips

5.2 narrow-range pH paper

5.3 lead acetate test strips

5.4 potassium iodide-starch test strips

6.0 Sample Collection, Preservation, & Storage

6.1 See Attachment 17 for table of sample preservation and holding times.

7.0 Quality Control/Corrective Action

7.1 Should any problems or questions arise which are not adequately addressed in the text of this SOP, consult your supervisor.

7.2 Discrepancies noted during receipt and log-in are documented in Quality Assurance (QA) notices, on the COC, or in communication

9.1.3 Remove all paperwork and each sample container and place them on the receiving table under the hood.

NOTE: For samples arriving from outside of the continental U.S, and designated quarantine states in the continental U.S. (N.C., S.C., GA., FL., TN., AR., OK., TX., LA., MS., AL.), place a piece of red striped tape on each sample container. This indicates that the raw sample must be heat treated before disposal.

9.1.4 Sign your full name and enter the current date and time on the COC under "received by laboratory." The "time" of delivery by courier. If the samples are hand-delivered, follow the step below for processing hand-delivered samples.

9.1.5 Check each sample container for signs of damage. Note any observed damage on the sample's COC.

If a sample container is completely broken, therefore unsalvageable, notify the Hazardous Waste technician for proper disposal.

If a sample container is broken or any type of spill occurs in the laboratory, whoever is handling the container should contact the Hazardous Waste technician. He or she will follow the guidelines described in the Chemical Hygiene and Contingency Plan.

If a soil sample container is broken or cracked and the raw sample has not come into contact with another sample, the sample may be salvageable. The decision of whether to salvage the sample is left to the client. The Customer Service staff or Project Manager will notify the client based on the notations of the log-in sheet and COC. If the client chooses to continue the analysis, note "Sample broken but salvageable" on the COC.

9.2 Processing hand-delivered samples

9.2.1 If samples are delivered by hand during normal business hours (Mon-Sat 8 a.m.-4 p.m.), write "HD" or "received by common carrier" next to the sample receipt time and date on the COC.

9.2.2 If samples are hand-delivered after normal business hours, the sample custodian or Sample Control clerk will record the receipt date on the COC (in column F on the inorganics traffic report).

9.3 Check and record the temperature of a Sample.

log in sheet.

9.3.3.2 The settings for the IR Gun should be:
Emissivity-86
Range-Hi

9.3.3 Back-up Procedure Using Temperature **Strips**

9.3.3.1 When the IR gun is not available for use, if one representative sample container inside the cooler has a calibrated temperature strip already attached, record the sample temperature on the log-in sheet in the "temp" column, and on the COC.

9.3.3.2 If a calibrated temperature strip is not present, place a strip on the outside of one sample taken from the middle of the cooler. If the temperature is above 4°C, put the sample container back middle of into the cooler for a three to five minutes period. Record the sample temperature on the log-in sheet and on the COC.

9.3.3.3 When sample coolers are received and the reading on the temperature strip is less than 4°C, place a NIST-traceable thermometer into an aliquot of an aqueous sample taken from the middle of the cooler or into the middle of the cooler, for soil samples, for a minimum of three but not more than five minutes and record that temperature.

9.3.3.4 If the temperature is out of range, complete the appropriate sections of the required QA Notice (Attachment 5). The Customer Service representative or Project Manager will notify the client of unacceptable temperature readings so the client can tell CompuChem how to process the samples.

For samples received out of the range specified by North Carolina (2-4.4°C), CompuChem is responsible to notify the state Laboratory of the excursion, if samples have been submitted to meet the regulatory requirements of NC.

9.3.4 Back-Up Procedure for EPA CLP **OLM03.2**

9.3.4.1 The temperature of the "Cooler Temperature Indicator"

Soil Samples
___A calibrated IR gun is used, as indicated for water samples.
___A temperature strip is affixed to the outside of a sample container and, after one minute, the temperature is read and recorded.

As required by the organic SOW, the alternative technique used to determine the cooler temperature must be documented in the SDG Narrative.

9.4 Verify that all information, including sample identifiers that appear on the sample container, matches the information on the COC, packing list, and traffic sheets, which are located inside the cooler. Note any discrepancies on the COC and log-in sheet. Contact the Customer Service person or Project Manager so that they can contact the client for resolution.

If EPA samples are being received, the Form DC-1 and the SDG Cover Sheet must be completed (Attachments 6 and 7). Note any discrepancies on the Traffic Report. The Sample Control clerk or supervisor will document the discrepancies and notify the Sample Management Office (SMO).

For EPA samples, if the Cooler Temperature Indicator exceeds 10 °C, the SMO must be contacted and informed of the temperature deviation. The SMO will obtain directions from the Region which must be documented and included in the SDG Narrative. The narrative information will list, by fraction, the EPA sample number of all samples received in a cooler with a temperature exceeding 10 °C. The actual temperature should also be included in the narrative.

The telephone conversation will be recorded on the Sample Management Telephone Log (Attachment 14) and processed with existing EPA paperwork.

Also, for EPA CLP dissolved metals samples, review the traffic report or C-O-C for digestion instructions. If there are none, the samples designated as dissolved metals will be digested.

If you are receiving New Jersey samples associated with the NJDEP, make sure the "Sample Analysis Request Form" (Form NJDEP095 and/or 096) is included with the samples. For a detailed explanation of handling NJ samples, see the corresponding Sample Control SOP.

Carolina, CompuChem is responsible for notifying the State Laboratory of the situation, **and if a replacement sample cannot be obtained, results of the original sample must be qualified.**

9.8 Perform a residual chlorine and sulfide check on all samples that are being analyzed for cyanides or phenols. **See Sample Control SOP "Handling and Verifying Proper Preservation of Samples Being Analyzed for Cyanide or Phenol".** Fill out the appropriate QA Notice (Attachments 9 **and 10**) if needed.

9.9 Check each volatile water sample for air bubbles and headspace (empty space inside the vials; vials must be filled completely with sample). Note any observance of air bubbles or headspace on the C-O-C and the log-in sheet. Air bubbles larger than the size of a pea should be brought to the attention of the Customer Service person or Project Manager so that their client can be contacted to obtain instructions to proceed.

Note: Pea size bubbles are those not exceeding ¼ inch or 6 mm in diameter. This is defined in SW-846 Chapter 4, Revision 3, 12/96.

For NJDEP aqueous VOA samples, no air bubbles/headspace is allowed.

9.9.1 In instances where aqueous samples have been submitted to meet the regulatory requirements of North Carolina, the State Laboratory must be notified if there is headspace or large air bubbles, and **if** no replacement sample **can be obtained, the results of the original sample must be qualified.**

9.10 Finish processing the commercial samples.

9.10.1 The sample receiving clerk completes all shaded area of the Receiving Log. He or she also completes the client name, received date, number of C-O-Cs, delivered by, freight number section at the top of the page. The paper work is then forwarded to Customer Service. The remaining information except for CCN is completed and the client contacted, if necessary, regarding discrepancies.

9.10.2 A member of the Receiving or Customer Service team performs the order entry procedure.

9.10.3 Once CCNs are assigned, Customer Service maintains a copy of the paperwork. These copies are bound by month for reference.

9.10.4 "Original" paperwork and C-O-Cs are maintained in client/project

- C-O-C--circle either y or n
- TAGS--for EPA only, circle y or n
- REMARKS--discrepancies observed during receipt
- SAMPLE ID--the sample ID is located on the sample container
- SD--sampling date (from the C-O-C and sample container)
- TEMP--sample temperature
- SUL--enter either a y or n based on the sulfide check
- CHL--enter a y or n based on the chloride check
- pH--based on the pH check
- SAMPLE'S Matrix:

  WA for water
  SO for soil
  SL for sludge
  SD for sand
  XX for other than above

- VOLUME--size and number of sample containers
- LOGGED-IN BY--write your initials here

9.11.2 Find the case/SDG number (located in the EPA log-in sheet) in the weekly EPA scheduling logbook, and note the order number on the log-in sheet in the "order number #" field. If the case number is not located in the logbook, see the Sample Control supervisor or Senior Sample Control clerk.

9.11.3 Log onto the HP3000.

- Access System H
- Choose option number 2 (Environmental Sample Tracking).
- Choose option number 2 (Receiving).
- Choose option number 4 (EOE Sample Receipt).
- Enter the order number (from the order sheet).
- **Place an "x" next to the first requisition number that reflects an analysis code that is shown on the C-O-C. See the Sample Control supervisor if you need help. Each unique requisition number.**
- Enter the following information from the EPA log-in sheet into the appropriate section on the screen:

  Sample ID - if your are entering information for an RAS only case, enter the following: "C#case number-lowest sample ID-DAS/SAS # DAS/SAS number # sas number" (see Attachment

- Repeat step 3.11.7 for all reaming samples.

9.11.4 Create volatile holding blanks at a rate of two holding blanks per SDG.

9.11.5 Label all sample containers with the labels generated in step 3.11.3.

Wrap each sample container with one of the HP3000-generated labels. Do not cover the sample ID that appears on the existing label, if possible.

If the samples are designated for long-term storage (as stated on the C-O-C or by the SMO, place an additional label with the disposal date noted, on each container.

9.11.6 Place all labeled samples on a cart.

9.11.7 Relinquish the samples to the Sample Custodian for storage in a secured, locked cooler.

9.11.8 Complete the following paperwork; these documents will comprise the gray envelope.

1. Organic and Inorganic Traffic Reports (OTR, ITR) (Attachments 12)

   Note: The following steps apply to both organic and inorganic reports; however, the document for the two analyses and matrices are never mixed.

   - Record the CompuChem numbers on the appropriate C-O-C. Whenever possible, record the CompuChem number in alignment with the associated sample ID.
   - Enter the contract number (from the EPA Scheduling Logbook) in the block entitled "Laboratory Contract Number."
   - Enter the unit price (from the EPA Scheduling Logbook) in the block entitled "Unit Price."
   - The number of copies is two each of the OTR and ITR.
   - Place the white sheet of the original OTR/ITR in the gray

OTR with 10 samples: SDG BG123
OTR with 20 samples: SDG BG123 and BG204

OTR with 10 samples: SDG BG204

If the first OTR has 10 samples for SDG BG123, the second OTR has 10 samples for BG123 and 10 samples for SDG BG204, and the third OTR has 10 samples for SDG BG204 then the yellow original of the second OTR is to be sent with the SMO cover letter for SDG BG123. A copy of the second OTR is to be sent with the SMO cover letter for BG204.

- There should be one copy in each SDG's gray envelope and one to be placed in the CDP.

- Send the original SMO cover letter and the yellow page of the OTR/ITR to the SMO at the following address:

SMO/U.S. Environmental Protection Agency
300 North Lee Street, Suite 200
Alexandria, VA 22314

4. Airbill(s)

Place the original airbill(s) in the associated gray envelope.

5. Tags (if applicable)

- Place the sample ID tags into a plastic bag. The tags should be representative of all the sample ID contained in the specific SDG.

- Write the following information on the outside of the plastic bag containing the sample ID tags:

Case Number

Receipt date--(one SDG's gray envelope could contain multiple bags containing sample ID tags. Therefore, the receipt date must reflect the day of receipt for the enclosed sample ID tags.)

Matrix

- **Organics - OLM04.0 (with revisions) and OLM03.0 (with revisions)**
- **Inorganics - ILM04.0 (with revisions, including ILM04.1).**

11.2 **Test Methods for Evaluating Solid Waste, Physical/Chemical Methods. SW-846, 3rd Edition, revised December. 1996.**

11.3 **Federal Register, 40 CFR 136**

11.4 **QCSOP: Proper Documentation Procedures**

11.5 **QCSOP: Numerical Data Reduction**

11.6 **"Less is Better: Laboratory Chemical Management for Waste Reduction," American Chemical Society Department of Government Relations and Science Policy, 1155 16th Street, N.W., Washington DC, 20036, (202) 872-4477.**

11.7 **Hazardous Waste Management & Safety SOPs: "Hazardous Waste Disposal" and "Spill Control & Cleanup."**

11.8 **NELAC Standards, July 1, 1999**

11.9 **QA-G6: Guidance for the Preparation of Standard Operating Procedures for Quality-Related Operations EPA/600/R-96/027, November 1995.**

12.0 Attachments as Tables, Diagrams, Flowcharts & Validation Data

Attachment 1 - Checklist of Receiving Procedures

Attachment 2 - Chain-of-Custody Record

Attachment 3 - EPA Receiving Log

Attachment 4 - Commercial Receiving Log

Attachment 5 - Quality Assurance Notices for Temperature Excursion

Attachment 6 - Sample Log-In Sheet (Form DC-1), Inorganics & Organics

Attachment 7 - SDG Traffic Report Cover Sheet

Attachment 8 - Quality Assurance Notice for pH

Attachment 1

Review of Receiving Procedures

- ☐ Check the Cooler and each sample for damage.
- ☐ Process hand-delivered
- ☐ Check and record the temperature of the cooler. For EPA samples follow correct temperature taking procedures if a USEPA Cooler Temperature Indicator is submitted in each cooler.
- ☐ Verify that all information, including the sample identifiers, which appear on the sample container, match the information presented on the C-O-C, packing list, and traffic sheets, which are located inside the cooler.
- ☐ On each complete log-in sheet and C-O-C/traffic report, stamp or write the statement "received in good condition," then place your initials and the date (mm/dd/yy) next to the stamp.
- ☐ If the samples do not meet the "good condition" criteria, ensure that the proper notations have been made on the C-O-C and log-in sheet, and initial and date the notations.
- ☐ Check and record the pH of every inorganic and wet chemistry sample.
- ☐ Perform a residual chlorine and sulfide check on all samples that are being analyzed for cyanides.
- ☐ Check each volatile water sample for air bubbles and headspace (empty space inside the vial). The vials must be filled completely with samples. Pea size bubbles are permitted.
- ☐ Complete processing commercial samples.
- ☐ Complete processing EPA samples.
- ☐ Notify the Customer Service Representative or Project Manager for any problems/deviations concerning the receipt of samples, so that any directions/resolutions can be obtained from the client.

Attachment 3

CompuChem EPA Receiving Log

Page ____ of ____

Received on : _____	Region : _____	Contract # _____	No. of COC's : _____
Delivered by : _____	Order # _____	Case # _____	Tags : Y / N
Freight # 's_____	SDG # _____	Account # _____	Case Folder Made : Y / N
		TAT : Verbal_____ Hardcopy _____	$ Amount : _____

	PARAMETER	REQ	SAMPLE ID	CCN	AMOUNT / CONTAINER	ANALYSIS CODE	SAMPLE DATE	MX	pH
1									
2									
3									
4									
5									
6									
7									
8									
9									
10									
11									
12									
13									
14									
15									
16									
17									
18									
19									
20									

Logged In By : _____ Order Entered By : _____

Cyanide samples checked for sulfide and chlorine Y / NA Temperature(s) _____ ° C

Holding Blank(s) : Counter / Page _____ / _____ CCN's _____ / _____

Attachment 5

CompuChem
a division of Liberty Analytical Corporation

QUALITY ASSURANCE NOTICE

CompuChem ID # _____
Client ID # _____
Case # _____
Type of Analysis _____
Receipt Date _____

For some organic and/or inorganic determinations temperature preservation at 4 degrees Celsius is required for environmental samples during shipment to the laboratory and prior to analysis. A temperature tolerance range is generally allowed. Temperature of a representative sample from the shipping container is taken and recorded by the receiving clerk at the time of sample receipt. This temperature is representative of all samples contained the cooler. The EPA CLP program requires the laboratory make notification when the temperature exceeds 10 degrees Celsius. The State of North Carolina allows a range of 2-4.4° Celsius. Notification to other clients is either client or project dependent.

The temperature of this sample at the time of receipt was determined to be _____.

A CompuChem customer service representative contacted the client. The client instructed the Receiving department to:

Analyze - qualify with notice _____

Dispose - client will resample _____

Supervisor Signature/ID _____/_____

Date _____

QAN-R-3
971022

Attachment 6 (continued)

SAMPLE LOG-IN SHEET

Lab Name					Page __ of __
Received By (Print Name)					Log-in Date
Received By (Signature)					
Case Number		Sample Delivery Group No.			SAS Number
Remarks:			Corresponding		
		EPA Sample #	Sample Tag #	Assigned Lab #	Remarks: Condition of Sample Shipment, etc.
1. Custody Seal(s)	Present/Absent* Intact/Broken				
2. Custody Seal Nos.	_____ _____				
3. Chain of Custody Records	Present/Absent*				
4. Traffic Reports or Packing Lists	Present/Absent*				
5. Airbill	Airbill/Sticker Present/Absent*				
6. Airbill No.	_____ _____				
7. Sample Tags	Present/Absent*				
Sample Tag Numbers	Listed/Not Listed on Chain-of-Custody				
8. Sample Condition	Intact/Broken*/ Leaking				
9. Cooler Temperature	_____				
10. Does information on custody records, traffic reports, and sample tags agree?	Yes/No*				
11 Date Received at Lab	_____				
12. Time Received	_____				
Sample Transfer					
Fraction	Fraction				
Area #	Area #				
By	By				
On	On				

* Contact SMO and attach record of resolution

Reviewed By	Logbook No.
Date	Logbook Page No.

FORM DC-1 OLM04.1

Attachment **8**

CompuChem
a division of Liberty Analytical Corporation

QUALITY ASSURANCE NOTICE

CompuChem ID # _____
Client ID # _____
Case # _____
Type of Analysis _____
Receipt Date _____

The pH reading for the sample above was _____: the required pH level is _____.

A CompuChem customer service representative contacted the client. The client instructed the Receiving department to:

Preserve in-house _____

Analyze - qualify with notice _____

Dispose - client will resample _____

Subcontract lab to preserve _____

Supervisor Signature/ID _____/_____

Date _____

QAN-R-2
971022

Attachment 10

CompuChem
a division of Liberty Analytical Corporation

Quality Assurance Notice

CompuChem ID#_____
Client ID#_____
Case #_____
SDG# _____
Receipt Date_____
Method_____

A chlorine check was performed on the above phenol sample and was determined to be present. A member of CompuChem's Customer Service Department contacted the client. The Receiving Department was instructed as follows:

Preserve in-house: _____
Analyze – Qualify with notice and address in narrative: _____
Dispose – Client will resample: _____

Supervisor Signature/ID _____/_____

Date _____

QAN-R-4
991105

Attachment 12

EPA CASE #s _____

EPA SAMPLE #s _____

C/C SAMPLE #s _____

DATE RECEIVED _____

AIRBILL INCLUDED: ( )

SAMPLES DELIVERED BY CUSTOMER: ( )

CHAIN OF CUSTODY: ( )

TAGS RECEIVED: ( )

COOLER RECEIVED SEALED: ( )

SAMPLES RECEIVED BELOW 4 C: ( )

Attachment 14

EPA United States Environmental Protection Agency Contract Laboratory Program

Inorganic Traffic Report & Chain of Custody Record
(For Inorganic CLP Analyis)

Case No.: MO4.1 PA-PES

1. Matrix (Enter in Column A): 1. Surface Water 2. Ground Water 3. Leachate 4. Field QC 5. Soil/Sediment 6. Oil (High only) 7. Waste (High only) 8. Other (specify in Column A)

2. Preservative (Enter in Column D): 1. HCl 2. HNO3 3. NaOH 4. H_2SO_4 5. $K_2CR_2O_7$ 6. Ice only 7. Other (specify in Column D) N. Not preserved

2. Region No.:
Sampling Co.:
Sampler (Name):
Sampler Signature:

3. Purpose*: Lead [ ] SF [ ] PRP [ ] ST [ ] FED; Early Action [ ] CLEM [ ] PA [ ] REM [ ] RI [ ] SI [ ] ESI; Long-Term Action [ ] FS [ ] RD [ ] RA [ ] O&M [ ] NPLD

4. Date Shipped: 11/16/99 Carrier: FEDEX
Airbill Number: 2669746877, 2669753195 ADG

5. Ship To: LIBERTY ANALYTICAL CORP. 501 MADISON AVENUE CARY, NC 27513
ATTN: LINDA CARTER

6. Date Received -- Received by: 11/17/99 Alice Evans
Laboratory Contract Number:
Unit Price:
7. Transfer to:
Date Received:
Received by:
Contract Number:
Price:

CLP Sample Numbers (from labels)	A Matrix (from Box 1) Other:	B Conc. Low Med High	C Sample Type: Comp./ Grab	D Preservative (from Box 2) Other:	E – RAS Analysis: Diss. Metals	Total Metals	Cyanide	Low only: NO_2/NO_3	Fluoride	High only: pH	Conductivity	F Regional Specific Tracking Number or Tag Numbers	G Station Location Identifier	H Mo/Day/ Year/Time Sample Collection	I Corresponding CLP Organic Sample No.	J Sampler Initials	K High Phases: Solids	Water-Miscible Liq.	Water-Immis. Liq.
	PE	4M				X						ILM41W1	968586						
						X						ILM41W1							
						X						ILM41W1							
					MERCURY							ILM41W2	968593						
							X					ILM41W3	968594						
					X							ILM41S1	968595						
							X					ILM41S2	968600						
ORIGINAL																			

Shipment for Case Complete? (Y/N): Page 1 of 1
Sample(s) to be Used for Laboratory QC:
Additional Sampler Signatures:
Chain of Custody Seal Number(s):

CHAIN OF CUSTODY RECORD

Relinquished by: (Signature)	Date / Time	Received by: (Signature)	Relinquished by: (Signature)	Date / Time	Received by: (Signature)
[signature]	11/16/99 4:00PM				
Relinquished by: (Signature)	Date / Time	Received by: (Signature)	Relinquished by: (Signature)	Date / Time	Received by: (Signature)
Relinquished by: (Signature)	Date / Time	Received for Laboratory by: (Signature) Alice Evans	Date / Time 11/17/99 9:36	Remarks: Is custody seal intact? (Y)/N/none 22° SDG ILM041, MO41S1	

DISTRIBUTION: Green - Region Copy; White - Lab Copy for Return to Region; Pink - CLASS Copy; Yellow - Lab Copy for Return to SMO

EPA Form 9110-1 (2/98)

SEE REVERSE FOR ADDITIONAL STANDARD INSTRUCTIONS
*SEE REVERSE FOR PURPOSE CODE DEFINITIONS

A2-012-14 REV.

Attachment 16

COMPUCHEM
a division of Liberty Analytical

SAMPLE MANAGEMENT TELEPHONE LOG

Sample Receipt Date _____ Case: _____ Region: _____

Question/Issues Discussed:

Contact Person(s): _____ Date: _____ Time: _____

Issue: _____

_____

_____

_____

_____

Resolution/Response:

Contact: _____ Date: _____ Time: _____

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_____

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_____

Signature/Title: _____ Date: _____ Time: _____

Attachment 17 (continued)

Table 4.1 (Cont.) **Requirements for Containers, Preservation, Holding Times, and Recommended Sample Volumes Published in the Clean Water Act, 40 CFR 136, 1990, *Federal Register***

Parameter	Preservation	Holding Time[a] (days)	Containers[b]	Volume (ml)
Solids (Total and Filterable)	Cool, 4°C	7	P or G	100
Solids (Non-filterable)	Cool, 4°C	7	P or G	200
Solids (Settleable)	Cool, 4°C	2	P or G	1000
Silica	Cool, 4°C	28	P	100
Specific Conductance	Cool, 4°C	28	P or G	250
Sulfate	Cool, 4°C	28	P or G	250
Sulfide	Cool, 4°C Add zinc acetate and NaOH to pH>9.	7	P or G	
Sulfite	NR[c]	0[d]	P or G	250
Surfactants	Cool, 4°C	2	P or G	250
Turbidity	Cool, 4°C	2	P or G	250
Purgeable Halocarbons	Cool, 4°C 0.008% $Na_2S_2O_3$[e]	14	G	80
Purgeable Aromatic Hydrocarbons	Cool, 4°C 0.008% $Na_2S_2O_3$[f] HCl to pH<2	14	G	80
Phenols	Cool, 4°C 0.008% $Na_2S_2O_3$[f]	7/40[g]	P or G	2000
Benzidines	Cool, 4°C 0.008% $Na_2S_2O_3$[f]	7/7[h]	P or G	2000
Phthalate Esters	Cool, 4°C	7/40[g]	G	2000
Nitrosamines	Cool, 4°C, dark 0.008% $Na_2S_2O_3$[f]	7/40[g]	P or G	2000
PCBs	Cool, 4°C	7/40[g]	P or G	2000
Nitroaromatics and isophorone	Cool, 4°C, dark 0.008% $Na_2S_2O_3$[f]	7/40[g]	P or G	2000
Polynuclear Aromatic Hydrocarbons	Cool, 4°C, dark 0.008% $Na_2S_2O_3$[f]	7/40[g]	G	2000
Haloethers	Cool, 4°C 0.008% $Na_2S_2O_3$[f]	7/40[g]	P or G	2000
Chlorinated Hydrocarbons	Cool, 4°C	7/40[g]	P or G	2000
TCDD	Cool, 4°C 0.008% $Na_2S_2O_3$[f]	7/40[g]	P or G	2000
Pesticides	Cool, 4°C; pH 5-9	7/40[g]	P or G	2000

[a] From time of sample collection

[b] Polyethylene (P) or glass (G)

[c] None required

[d] 0 days indicates that the sample must be analyzed immediately.

[e] $Na_2S_2O_3$ added if residual chlorine is present; approx. equal to 1 ml of 10% thiosulfate / liter of sample.

[g] To complete extraction (or initiate extraction if continuous liquid-liquid extraction is performed)/ to complete analysis following extraction

[h] Extracts may be stored up to 7 days before analysis if stored under an inert (oxidant-free) atmosphere.

Attachment 17 (continued)

Table 4.4 **Requirements for Containers, Preservation, Holding Times, and Recommended Sample Volumes for Residuals, Aqueous and Solid Matrices[a] Published in SW846 Test Methods for Evaluating Solid Waste, Third Edition, Update 3, December 1996.**

Parameter	Methods	References	Container	Preservation	Maximum Holding Times[b]
Volatile Organics in water	Purge and trap GC and GC/MS	8021B, 8015B, 8260B	Glass, 40-ml vial with zero headspace	4°C, 0.008% $Na_2S_2O_3$	14 days (A) (see below for soil)
Semivolatile Organics	GC, HPLC, and GC/MS	8081A, 8141A, 8151A, 8310, 8082, 8270C	Glass 8-oz wide mouth with PTFE-lined cap (50-g sample)	Cool to 4°C	7 days to extract (A); 14 days to extract (S); 40 days to analyze (A/S)
Total Metals – except Mercury and Chromium VI	Furnace AA and ICP	7000 series/ 6010B	Glass or plastic 8-oz wide mouth (200-g sample)	HNO_3 to pH<2 (A); filter dissolved on-site first; filter suspended-no acid	6 months (A/S)
Chromium VI	Colorimetric, automated	7196A	Glass or plastic 8-oz wide mouth (200-g sample)	Cool to, 4°C	24 hours (A); one mo. to extraction, 4 days after (S).
Mercury	Manual cold vapor AA	7470/7471A	Glass or plastic 8-oz wide mouth (200-g sample)	pH<2 HNO_3 (A); filter dissolved; Cool to 4°C (S)	28 days (A/S)
Chloride	Colorimetric, automated	9251	Glass or plastic	None required	28 days (A)
Cyanide	Colorimetric automated	9012A	Glass or plastic	Cool to 4°C; pH >12 NaOH (A)	14days (A)
Phenols	Colorimetric, automated	9066	Glass or plastic	Cool to 4°C; pH <4 H_2SO_4 (A)	28 days (A)
Specific conductance	conductivity	9050A	Glass or plastic	Cool to 4°C (A)	28 days (A)
Sulfate	turbidimetric	9038	Glass or plastic	Cool to 4°C (A)	28 days (A)
Sulfide	distillation, titration	9034	Glass or plastic	Cool to 4°C; Zinc acetate (A/S)	7 days (A/S)
Oil & grease	Gravimetric	9070/9071A	Glass	Cool to 4°C; 5 ml diluted HCl (A)	28 days (A/S)
TOC	Combustion analyzer	9060	Glass or plastic	Cool to 4°C; pH<2 HCl or H_2SO_4; Store in dark (A)	28 days
TOX	DX 208 analyzer	9020B	Glass, PTFE-lined cap	Cool to 4°C; pH<2 H_2SO_4	

[a] Table originally excerpted, in part, from Table II, 49 FR 28, October 26, 1984, and revised.

[b] Holding time begins at time of sample collection.

(A) aqueous

(S) solid

Attachment 17 (continued)

Table 4.6 **Requirements for Holding Times for Hazardous Characteristics Indicators Published in SW846 Test Methods for Evaluating Solid Waste, Third Edition, Update 3, December 1996.**

Parameter	Methods	References	Container	Preservation	Maximum Holding Times[c]
Reactivity-Total releasable cyanide	Reflux distillation, titrimetric	Chapter 7, 7.3.3, 9014	Glass, with zero headspace	4°C in dark, pH 12 NaOH	ASAP
Reactivity-Total releasable sulfide	Acid distillation, titration	Chapter 7, 7.3.4, 9034	Glass, with zero headspace	4°C in dark, pH 12 NaOH; zinc acetate	ASAP
Ignitability	Flash point	1010	Glass or plastic	NA	ASAP
Corrosivity	Electrometric	9040B	Glass or plastic	NA	ASAP
Paint filter liquids	filtration	9095A	Glass or plastic	NA	ASAP
EP Toxicity	Leachate generation	1310	Glass or plastic	NA	ASAP

Table 4.7 **Requirements for Containers, Preservation, Holding Times, and Recommended Sample Volumes for Toxicity Characteristics Leaching Procedure, TCLP, Method 1311, and Synthetic Precipitation Leaching Procedure, SPLP, Method 1312, Published in SW846 Test Methods for Evaluating Solid Waste, Third Edition, Update 3, December 1996.**

Sample Maximum Holding Times				
Parameter	**From: Field to collection** **To: TCLP extraction**	**From: TCLP extraction** **To: Preparative extraction**	**From: Preparative extraction** **To: Determinative Analysis**	**Total elapsed time in days**
Volatiles	14	NA	14	28
Semivolatiles	14	7	40	61
Mercury	28	NA	28	56
Metals, no Hg	180	NA	180	360

Exceeding the holding time is not acceptable in establishing that a waste does not exceed the regulatory level. Exceeding the holding time will not invalidate characterization if the waste exceeds the regulatory level.

CompuChem
a division of Liberty Analytical Corporation

501 Madison Avenue
Cary, NC 27513

SOP DOCUMENTATION FORM

This form must accompany all new and revised Standard Operating Procedures (SOPs) when you turn them in to Quality Assurance for review. Please fill out the entire shaded area (except effective date).

This is a new procedure ____ revised procedure ✓ outdated procedure (archive) ____

- Procedure area, title, and SOP number: Section #: 1.3.2.2 Effective date: (QA fills in)
  IP 480B: Analysis of Volatiles in Aqueous and Medium/High Concentration Soil Samples by SW846 and NYSASP 12/13/00
- Procedure prepared by: Lindi Carter Date: 10/18/00
- Procedure approved by: (If the manager prepared the SOP, a qualified second party should sign) BB McEllen Date: 10/18/00
- Reason for change: Annual review / NELAC format changes / additional requirements of the State of South Carolina
- This procedure meets the requirements of the following approved method references: Test Methods for Evaluating Solid Waste Physical / Chemical Methods, Update III, 3rd Edition, 12/96, Method 8260B; 5035/5030B; New York State Analytical Services Protocol, NYSASP, 10/95

Procedure approved by Quality Assurance Representative: Date:
(Not needed if signed above)

_____ _____

Effective 1-1-96, on an annual basis: Lab managers are required to review lab practices and revise the SOP if necessary. If no revision is necessary, indicate by your signature that the SOP has been reviewed.

Annual Review—Signature: _____ Date: _____

Annual Review—Signature: _____ Date: _____

Annual Review—Signature: _____ Date: _____

Instrument Procedure 480B: Analysis **of** Volatiles in Aqueous and Medium/High Concentration Soil Samples by SW846 **and** NYSASP

1.0 Scope and Application

This is a general purpose method for the identification and simultaneous measurement of purgeable volatile organic compounds in a variety of aqueous matrices **following Method 8260B**. It is also used to analyze medium to high level soil samples that have been extracted with methanol. The method is applicable to a wide range of organic compounds. It incorporates Method 5030B and Method 5035 (for medium/high concentration soil samples, extracted with methanol). **Target compounds for this method B are listed in Table 1, Attachment 1, along with their associated internal standards and quantitation ions. Note, however, that many of these compounds are not routinely analyzed.**

Method detection limits (MDL) and reporting limits are shown in Attachment 2.

Staff members performing the procedures described in this SOP are responsible for reading, understanding, and complying with the SOP requirements. Supervisors are responsible for directing the analyst to the controlled SOP, and providing adequate explanation of the material contained therein.

This procedure is restricted to use by or under the supervision of analysts experienced in the instrumentation or preparative methods and who have demonstrated the ability to generate acceptable results through QC samples and analyst capability studies.

2.0 Summary of Method

An inert gas (helium) is bubbled through a 5 mL or 25 mL aqueous sample spiked with internal standard and surrogate compounds. For medium/high level soil samples, an aliquot of the methanol extract (typically 100 µL) is added to 5 mL reagent water. That aliquot contains surrogates. The sample is purged in a specially designed glass frit bottom liquid sample purging vessel at ambient temperature, causing the purgeable volatile organic compounds to be transferred from the aqueous phase to the vapor phase. The vapor is swept onto a sorbent column where the purgeables are trapped. After purging is completed, the sorbent column is heated and backflushed with the inert gas to desorb the purgeables onto a gas chromatograph (GC) wide-bore capillary column. The GC is temperature-programmed to separate the purgeables which are then detected with a mass spectrometer (MS).

Note: For Method 8260B, a heated purge is also allowed.

3.0 Definitions

3.1 Method detection limit (MDL) – The minimum concentration of an analyte that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte (40 CFR, Part 136, Appendix B.)

3.2 Reporting Limit – The laboratory reporting limit is based on the lowest multipoint calibration standard concentration. For some inorganic methods, the reporting limit is based on the MDL, and is usually 4-8 times higher than the MDL. For organic methods, values detected below the reporting limit and above the MDL may be reported and qualified as an estimated concentration.

If the low level standard concentration is not at least three times higher than the MDL value, the standard concentration is adjusted upward in order to achieve this minimal ratio. It may be adjusted higher than three times depending on the concentration range of the calibration curve and the ability to meet method linearity requirements. An exception to this is for CLP methods where the MDL is only required to be lower than the reporting limit.

The reporting limit for CLP is the Contract Required Quantitation Limit (CRQL) for organics and the Contract Required Detection Limit (CRDL) for inorganics.

3.3 Reporting Units – ug/L for water and ug/kg for soil

3.4 An SDG is defined by the following, whichever is more frequent:

- **each 20 field samples received within a case, or**
- **each 14 calendar day period during which field samples in a case are received (7 calendar days for NYSASP, OLM04.0, plus revisions, and ILM04.0, plus revisions including ILM04.1) beginning with the receipt of the first sample.**

NOTE: The Army Corps of Engineers does not accept the SDG approach, unless the samples are prepared in a single batch. When a group of up to 20 field samples of a similar matrix are prepared as one batch, method-specified QC samples such as a method blank, laboratory control sample, matrix spike, matrix spike duplicate, and matrix duplicate must also be prepared together at a rate of 5%. If samples

are batched together from different sites, project-specific QC must be processed.

4.0 Interferences

4.1 Impurities in the purge gas or methanol, organic compounds out-gassing from the plumbing ahead of the trap, and solvent vapors in the laboratory account for the majority of contamination problems. Gas lines from the gas tanks to the instrument must be either stainless steel or copper tubing. Non-polytetrafluoroethylene (PTFE) thread sealants, or flow controllers with rubber components are not to be used. When potential interfering peaks are noted in laboratory method blanks, it may be necessary to reduce solvent contamination in the laboratory, purge the methanol used to prepare standard solutions, purge the **DI** water with helium or nitrogen, change the purge gas source, or regenerate the molecular sieve purge gas filter.

4.2 Samples can be contaminated by diffusion of purgeable organics (particularly methylene chloride, fluorocarbons, and other common laboratory solvents) through the septum seal into the sample during storage and handling. Therefore, these samples are stored in GC/MS VOA laboratory refrigerator #2; separate from laboratory standards, and they must be analyzed in a room in which the atmosphere is demonstrated to be free of all potential contaminants that will interfere with the analysis. Because methylene chloride will permeate PTFE tubing, all GC carrier gas lines and purge gas plumbing are to be constructed from stainless steel or copper tubing.

4.3 Contamination by carryover can occur whenever a sample is analyzed after a sample that contains high levels of organic compounds. Whenever an unusually concentrated sample is encountered, it must either be followed by analysis of an instrument blank or the next sample must be closely monitored to check for cross-contamination. For samples containing large amounts of water soluble materials, suspended solids, high boiling compounds, or high purgeable levels, it may be necessary to clean the purge and trap apparatus. **Do so** by purging a 10-20% methanol solution, followed by baking the purge and trap apparatus and the analysis of a **DI** water blank to confirm that the system is free from contamination. The trap and other parts of the system are also subject to contamination; therefore, frequent bakeout and purging of the entire system may be required.

4.4 Instrument Problems/Preventative Maintenance

4.4.1 If a low response is observed for the early eluting compounds such as the gases, replacement of the trap or septum may be necessary. In addition, adjustments to the purge flow may be necessary to achieve a desired

response for these compounds. If such adjustments do not help, it may be necessary to check the fittings on the purge and trap device and on the column for leaks. This is done with a helium leak detector and certain software utility programs.

4.4.2 Column maintenance or replacement may be necessary if peak tailing or broad chromatographic peaks are observed.

5.0 Safety

5.1 The toxicity and carcinogenicity of many chemicals used in this method have not been precisely determined. Each chemical should be treated as a potential health hazard. Exposure to these chemicals should be minimized. Preparation of calibration standards, blanks, and samples is performed in a fume hood to minimize risk.

5.2 The following method analytes have been tentatively classified as known or suspected human or mammalian carcinogens: benzene, carbon tetrachloride, 1,2-dichloroethane, 1,1,2,2-tetrachloroethane, 1,1,2- trichloroethane, chloroform, 1,2-dibromoethane, trichloroethene, and vinyl chloride.

5.3 Appropriate protective equipment and clothing must be used under the assumption that all samples are potentially hazardous. During sample preparation, safety glasses, gloves and lab coats are a minimum requirement. The persistent presence of noxious odors may be indicative of failure of the laboratory ventilation system and must be reported to a supervisor or manager.

5.4 Laboratory staff are encouraged to review the Chemical Hygiene Plan for general safety policies, and Material Safety Data Sheets (MSDS) for solvents and reagents used in the laboratory. The MSDS are located in the Quality Assurance department.

6.0 Equipment & Supplies

6.1 Syringes

6.1.1 5-ml Hamilton gastight syringe with Luerlock tip

6.1.2 10-ml Hamilton gastight syringe with Luerlock tip

6.1.3 25-ml Hamilton gastight syringe with Luerlock tip

6.1.4 10-µl Hamilton syringe

6.1.5 1-µl Hamilton syringe

6.2 Volumetric Flasks and Pipets

6.2.1 Assorted volumetric flasks ranging from 50-ml to 1000-ml

6.2.2 10-ml graduated pipet in 1/10-ml graduations

6.3 Analytical Column

6.3.1 J&W Scientific 30-or 75m DB624

6.3.2 Supelco SPB-624 75-m Megabore column

6.3.3 **Each with** 0.53-mm ID (internal diameter) with 3.0-µm film thickness or equivalent

6.4 Mass Spectrometer (MS)

6.4.1 The MS scans 35-300 amu at 0.7 sec**ond** scan time in the electron impact mode at 70 eV (nominal).

6.4.2 Finnigan INCOS 500 mass spectrometers

6.4.3 **Hewlett Packard 5890/5972**

6.5 Interface (GC to MS)

6.5.1 Type: Jet separator

6.5.2 Temperature: 250°C

6.5.3 Alternate: column direct to MS

6.6 Data System

6.6.1 A computer is interfaced to the mass spectrometer to allow the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program.

6.6.2 The data processing software searches any GC/MS data file for ions of a specified mass and plots abundance versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). The software integrates the abundance in any EICP between specified time or scan number limits. Also, for the non-target compounds, the software compares sample spectra against reference library spectra. The reference library used is the NIST Mass Spectral Library.

6.6.3 For data acquisition, The INCOS 500 systems use **Prolab** software **and Hewlett Packard uses ChemStation**.

6.6.4 For data processing, CompuChem uses the Hewlett Packard HP 9000 series 735 Unix Workstation employing HP Chemserver with Target3 and Envision software by Thru-Put Systems.

6.7 Gas Chromatograph

6.7.1 Varian 3400 (with INCOS 500 MS) with the conditions listed below:

- Carrier Gas — Helium
- GC mode — Capillary
- **Injection Port Temperature — 220° C**
- Interface Temperature — 220° C
- Initial Temperature — 0° C
- Final Temperature — 180° C
- Flow Rate — 25 ml/minute
  (10 ml/minute column flow +15 ml/minute makeup gas)

6.7.2 The listed column flow rate is approximate. Flow rate is adjusted to optimize linear velocity of an unretained compound (butane) through the column. Optimum linear velocity for the column is 30-45 cm/**second**.

6.7.3 GC program

Note: The following parameters may vary.

- **10° C for 3 minutes**

- **to 105 °C @ 10° C/minute**
- **to 185° C @ 26.7° C/minute**
- **Hold until all compounds elute.**

6.8 Data Storage

6.8.1 Magnetic tape storage device: The magnetic tape storage device is capable of recording data and is suitable for long-term, off-line storage.

6.9 Purge and Trap

6.9.1 Tekmar LSC

6.9.1.1 Tekmar LSC 2000 or LSC 3000 with glass frit bottom liquid sample purging vessel and Luerlock valve.

6.9.1.2 The Tekmar LSC 2000 may be equipped with a Tekmar ALS 2016 autosampler **for aqueous samples.**

6.9.1.3 For soil samples the Archon Model 5100, 4552 Purge and trap autosampler interfaces directly to a Tekmar 3000 Purge and Trap Concentrator.

6.9.1.4 The absorption trap must be at least 25 cm long and have an internal diameter of at least 0.105 inches (0.2667 cm).

6.9.2 Archon ALS

6.9.2 An autosampler designed for soil samples that utilizes 40 ml VOA vials with low bleed Teflon septa.

The Archon ALS has the capacity of up to 51 vials.

6.9.3 Trap Packing

6.9.3.1 Supelco "K" Trap

6.9.3.2 Carbopak B

6.9.3.3 Carboxen 1000 & 1001

7.0 Reagents and Standards

All standards are prepared by the Organic Standards chemist. Details for the preparation are contained in the standard operating procedures (SOP) for that area (Section 7.0 of the SOP collection.)

7.1 Reagent Water-All water used in this procedure must be equivalent to ASTM Type II water (as it relates to specific conductance and specific resistance) which is subsequently purged with an inert gas and demonstrated to meet the blank contamination acceptance criteria contained in this Standard Operating Procedure (SOP). **It is referred to throughout the remainder of this SOP as DI water.**

7.2 Methanol (B&J Scientific, purge and trap grade)

7.3 Tuning Standard

7.3.1 Bromofluorobenzene - Standard ID# 7008 at 25 µg/ml. Two µl are injected on the column every 12 hours.

7.4 Calibration Standards

7.4.1 Standard curve including a 10 ppb low level in a 5 ml purge analysis

7.4.1.1 For clients with projects requiring a 10 ug/L reporting limit, the five–point initial calibration curve includes a low level at 10 ppb. A sixth standard is added in the event that an alternate method of quantitation is needed. Quantitation methods are discussed below in Section 10.0.

7.4.1.2 Standards are prepared for a 5 mL purge analysis by spiking the appropriate volume of each standard solution, shown in Table 2A below, into a gastight syringe containing 5 mL sparged DI water.

Table 2A: Standard Preparation for 10 ppb 5 ml purge analysis. Units for column header values are µg/l.

Std. ID	10	20	50	(100)	150*	200
8260 I.S.	5.0	5.0	5.0	5.0	5.0	5.0
8260 S.S.	1.0	2.0	5.0	10.0	15.0	20.0
8260 Mix #1	0.5	1.0	2.5	5.0	7.5	10.0
8260 Gases	0.5	1.0	2.5	5.0	7.5	10.0
8260 Mix #2	0.5	1.0	2.5	5.0	7.5	10.0
8260 Mix #2B	0.5	1.0	2.5	5.0	7.5	10.0
8260 Mix #3A	0.5	1.0	2.5	5.0	7.5	10.0
8260 Mix #4A	0.25	0.5	1.25	2.5	3.75	5.0
8260 Mix #4C	0.5	1.0	2.5	5.0	7.5	10.0
8260 Mix #5	0.25	0.5	1.25	2.5	3.75	5.0
8260 Mix #6	0.25	0.5	1.25	2.5	3.75	5.0
8260 Mix #7	0.5	1.0	2.5	5.0	7.5	10.0

***This standard level only used with a 6-point initial calibration**

( ) Continuing calibration verification concentration.

7.4.1.3 The standard concentrations presented on table header are for the compounds in 8260 Mix #1, the gases, 8260 Mix #2, 8260 Mix #2B, and 8260 Mix #4C.

7.4.1.4 The standard concentrations for compounds in 8260 Mix #3A are 10, 20, 50, 100, 150, and 200 µg/l with THF at 40, 80, 200, 400, 600, and 800 µg/l.

7.4.1.5 The standard concentration for compounds in 8260 Mix #4A are 50, 100 , 250, 500, 750, and 1000 µg/l.

7.4.1.6 The standard concentration for compounds in 8260 Mix #5 are 250, 500, 1250, 2500, 3750, and 5000 µg/l.

7.4.1.7 The standard concentration for compounds in 8260 Mix #6 are 200, 400, 1000, 2000, 3000, and 4000 µg/l.

7.4.1.8 The standard concentration for compounds in Mix #7 are 100, 200, 500, 1000, 1500, 2000 µg/l.

7.4.2 Standard curve including a 5 ppb low level in a 5 ml purge analysis

7.4.2.1 For clients with projects requiring a 5 ug/L reporting limit, the five–point initial calibration curve includes a low level at 5 ppb.

A sixth standard is added when an alternate method of quantitation is needed. Quantitation methods are discussed below in Section 10.0.

Note: For samples submitted to meet the regulatory requirements of the State of South Carolina, this initial calibration curve must include a standard at 2 µg/L.

7.4.2.2 Standards are prepared for a 5 mL purge analysis by spiking the appropriate volume of each standard solution, shown in Table 2B below, into a gastight syringe containing 5 mL sparged DI water.

Table 2B1: Standard Preparations for 5 ppb 5 ml purge analysis. Units for column header values are ug/L.

Std. ID	2*	5	10	20**	50	(100)	200
8260 I.S.	5.0	5.0	5.0	5.0	5.0	5.0	5.0
8260 S.S.	0.2	0.5	1.0	2.0	5.0	10.0	20.0
TCL4-1	0.2	0.5	1.0	2.0	5.0	10.0	20.0
TCL4-Gases	0.2	0.5	1.0	2.0	5.0	10.0	20.0
TCL4-Ketones	0.1	0.25	0.5	1.0	2.5	5.0	10.0

*** This standard level only used with samples submitted to meet the regulatory requirements of the State of South Carolina**

****This standard level only used with a 6-point initial calibration**

( ) Continuing calibration verification concentration

Table 2B2: Standard Preparation for 5 ppb 5 ml purge analysis. These standards are used for specific projects requiring an expanded target analyte list. Units for column header values are ug/L.

Std. ID	2*	5	10	20**	50	(100)	200
8260 I.S.	5.0	5.0	5.0	5.0	5.0	5.0	5.0
8260 S.S.	0.25	0.5	1.0	2.0	5.0	10.0	20.0
TCL4-2	0.25	0.5	1.0	2.0	5.0	10.0	20.0
TCL4-Gases	0.25	0.5	1.0	2.0	5.0	10.0	20.0
TCL4-Ketones	0.125	0.25	0.5	1.0	2.5	5.0	10.0
TCL4-2B	0.25	0.5	1.0	2.0	5.0	10.0	20.0
TCL4-CEVE	0.25	0.5	1.0	2.0	5.0	10.0	20.0
1303-B	0.25	0.5	1.0	2.0	5.0	10.0	20.0
APPIX	0.25	0.5	1.0	2.0	5.0	10.0	20.0

*** This standard level only used with samples submitted to meet the regulatory requirements of the State of South Carolina**

****This standard level only used with a 6-point initial calibration**

( ) Continuing calibration verification concentration

7.4.2.3 The standard concentrations presented on table header are for the compounds in TCL4-1&2 TCL4-Gases, TCL4-2B, and TCL4-CEVE.

7.4.2.4 The standard concentrations for compounds in TCL4-Ketones are 10, 25, 50, 100, 250, 500, and 1000 ug/L.

7.4.2.5 The standard concentration for compounds in 1303-B are 20, 50, 100, 200, 500, 1000, and 2000 ug/L.

7.4.2.6 The concentration for compounds in the APPIX standard vary. All compounds have concentrations shown in the table 2B2, except the following.

- **methacrylonitrile**
- **methylmethacrylate**
- **ethylmethacrylate**
  at 20, 50, 100, 200, 500 ,1000, 2000

- **trans-1,4-dichloro-2-butene**
  at 80, 200, 400, 800, 2000, 4000, 8000

- **propionitrile**
- **isobutyl alcohol**

- **1,4-dioxane**
  at 100, 250, 500, 1000, 2500, 5000, 10000

7.4.3 Standard curve including a 0.5 ppb low level in a 25 ml purge analysis

7.4.3.1 For clients with projects requiring a 0.5 µg/L reporting limit, the five–point initial calibration curve includes a low level at 0.5 ppb. A sixth standard is added in the event that an alternate method of quantitation is needed. Quantitation methods are discussed below in Section 10.0.

7.4.3.2 Standards are prepared by spiking the volumes of each standard solution, shown in Table 2C below, into a 100 ml volumetric flask, diluting to the mark and aliquoting 25 ml of the solution. Alternatively, standards may be prepared by spiking the appropriate volume, i.e. the volumes shown in the table divided by 4, except I.S.) of each standard solution into a 25 ml gastight syringe containing 25 ml DI water.

Table 2C:Standard Preparation for 25 ml purge analysis. Units for column header values are ug/L.

Std. ID	0.5	1.0	5.0	(10)	15**	25
8260 I.S.*	2.5	2.5	2.5	2.5	2.5	2.5
8260 S.S.	1.0	2.0	10.0	20.0	30.0	50.0
8260 Mix #1	0.5	1.0	5.0	10.0	15.0	25.0
8260 Gases	0.5	1.0	5.0	10.0	15.0	25.0
8260 Mix #2	0.5	1.0	5.0	10.0	15.0	25.0
8260 Mix #2B	1.0	2.0	10.0	20.0	30.0	50.0
8260 Mix #3	0.5	1.0	5.0	10.0	15.0	25.0
8260 Mix #4A	0.5	1.0	5.0	10.0	15.0	25.0
8260 Mix #4B	0.5	1.0	5.0	10.0	15.0	25.0
8260 Mix #5	0.5	1.0	5.0	10.0	15.0	25.0
8260 Mix #6	0.5	1.0	5.0	10.0	15.0	25.0
8260 Mix #7	0.5	1.0	5.0	10.0	15.0	25.0

***Aliquot of I.S. added to aliquot of standard contained in a 25 mL gastight syringe.**

**** This standard level only used with a 6-point initial calibration.**

( ) Continuing calibration verification concentration

7.4.3.3 The standard concentrations presented on table header are for the compounds in 8260 Mix #1, the gases, and 8260 Mix #2.

7.4.3.4 The standard concentrations for the compounds in 8260 Mix #2B are 1.0, 2.0, 10, 20, 30, and 50 µg/l.

7.4.3.5 The standard concentrations for compounds in 8260 Mix #3 are 2.5, 5.0, 25, 50.0, 75, and 125 µg/l with THF at 2.0, 4.0, 20, 40, 60, and 100 µg/l.

7.4.3.6 The standard concentration for compounds in 8260 Mix #4A, 8260 Mix # 4B, and 8260 Mix #7 are 5.0, 10, 50, 100, 150, and 250 µg/l.

7.4.3.7 The standard concentration for compounds in 8260 Mix #5 are 25, 50, 250, 500, 750, and 1250 µg/l.

7.4.3.8 The standard concentration for compounds in 8260 Mix #6 are 20, 40, 200, 400, 600, and 1000 µg/l.

7.4.4 Composition of Standard Mixtures used in 10 ppb 5 ml purge and 25 ml purge

7.4.4.1 Compounds in 8260 Mix #1 at a concentration of 100 µg/ml

- **1,1-dichloroethene**
- **methylene chloride**
- **trans-1,2-dichloroethene**
- **1,1-dichloroethane**
- **2,2-dichloropropane**
- **cis-1,2-dichloroethene**
- **bromochloromethane**
- **chloroform**
- **1,1,1-trichloroethane**
- **carbon tetrachloride**
- **1,1-dichloropropene**
- **benzene**
- **1,2-dichloroethane**
- **trichloroethene**
- **1,2-dichloropropane**
- **dibromomethane**
- **bromodichloromethane**

- **cis-1,3-dichloropropene**
- **toluene**
- **trans-1,3-dichloropropene**
- **1,1,2-trichloroethane**
- **tetrachloroethene**
- **1,3-dichloropropane**
- **dibromochloromethane**
- **1,2-dibromoethane**
- **chlorobenzene**
- **1,1,1,2-tetrachloroethane**
- **ethylbenzene**
- **m,p-xylene**
- **o-xylene**
- **styrene**
- **bromoform**
- **isopropyl benzene**
- **bromobenzene**
- **1,1,2,2-tetrachloroethane**
- **1,2,3-trichloropropane**
- **n-propyl benzene**
- **2-chlorotoluene**
- **4-chlorotoluene**
- **1,2,4-trimethyl benzene**
- **1,3,5-trimethyl benzene**
- **sec-butyl benzene**
- **1,2-dichlorobenzene**
- **1,3-dichlorobenzene**
- **1,4-dichlorobenzene**
- **n-butylbenzene**
- **tert-butyl benzene**
- **p-isopropyl toluene**
- **1,2-dibromo-3-chloropropane**
- **1,2,4-trichlorobenzene**
- **hexachlorobutadiene**
- **naphthalene**
- **1,2,3-trichlorobenzene**

7.4.4.2 Compounds in 8260 Gases at a concentration of 100 µg/ml

- **dichlorodifluoromethane**
- **chloromethane**
- **vinyl chloride**

- **bromomethane**
- **chloroethane**
- **trichlorofluoromethane**

7.4.4.3 Compounds in 8260 Mix #2 at a concentration of 100 µg/ml

- **pentachloroethane**
- **pentafluorobenzene**
- **benzyl chloride**
- **carbon disulfide**
- **iodomethane**
- **1,1,1-trichloro-2,2,2-trifluoroethane**
- **1,1,2-trichloro-1,2,2-trifluoroethane**
- **acetonitrile**
- **1-chlorobutane**
- **1-chlorohexane**
- **3-chloropropene**
- **n-hexane**
- **1,2-diethylbenzene**
- **methyl-t-butyl ether**

7.4.4.4 Compound in 8260 Mix # 2B at a concentration of 100 µg/ml

- **vinyl acetate**

7.4.4.5 Compounds in 8260 Mix #3 at a concentration of 500 µg/ml, except THF at 400 µg/ml

- **acetone**
- **4-methyl-2-pentanone**
- **2-hexanone**
- **2-butanone**
- **tetrahydrofuran**

7.4.4.6 Compounds in 8260 Mix #3A at a concentration of 100 µg/ml, except THF at 400 µg/ml

- **acetone**
- **4-methyl-2-pentanone**
- **2-hexanone**
- **2-butanone**
- **tetrahydrofuran**

7.4.4.7 Compounds in 8260 Mix #4A at a concentration of 1000 µg/ml

- **methacrylonitrile**
- **diethylether**
- **methyl acrylate**
- **ethylmethacrylate**
- **methylmethacrylate**
- **crotonaldehyde**
- **tert-butyl alcohol**

7.4.4.8 Compound in 8260 Mix #4B at a concentration of 1000 µg/ml

- **2-chloroethyl vinyl ether**

7.4.4.9 Compound in 8260 Mix #4C (1301B) at a concentration of 100 µg/ml

- **2-chloroethyl vinyl ether**

7.4.4.10 Compounds in 8260 Mix #5 at a concentration of 5000 µg/ml

- **isobutyl alcohol**
- **1,4-dioxane**
- **ethyl cyanide**

7.4.4.11 Compounds in 8260 Mix #6 at a concentration of 4000 µg/ml

- **cis-1,4-dichloro-2-butene**
- **trans-1,4-dichloro-2-butene**

7.4.4.12 Compounds in 8260 Mix #7 (1303) at a concentration of 1000 µg/ml

- **acrolein**
- **acrylonitrile**

7.4.5 Composition of Standard Mixtures used in 5 ppb 5 ml purge

7.4.5.1 Compounds in TCL4-1 at a concentration of 50 µg/ml

- **1,1-dichloroethene**

- **1,1,2-trichloro-1,2,2-trifluoroethane**
- **carbon disulfide**
- **methyl acetate**
- **methylene chloride**
- **trans-1,2-dichloroethene**
- **methyl-tert-butyl ether**
- **1,1-dichloroethane**
- **cis-1,2-dichloroethene**
- **chloroform**
- **1,1,1-trichloroethane**
- **cyclohexane**
- **carbon tetrachloride**
- **1,2-dichloroethane**
- **benzene**
- **trichloroethene**
- **methylcyclohexane**
- **1,2-dichloropropane**
- **bromodichloromethane**
- **cis-1,2-dichloropropene**
- **toluene**
- **trans-1,3-dichloropropene**
- **1,1,2-trichloroethane**
- **tetrachloroethene**
- **dibromochloromethane**
- **1,2-dibromoethane**
- **chlorobenzene**
- **ethylbenzene**
- **m,p-xylene**
- **o-xylene**
- **styrene**
- **bromoform**
- **isopropyl benzene**
- **1,1,2,2-tetrachloroethane**
- **1,3-dichlorobenzene**
- **1,4-dichlorobenzene**
- **1,2-dichlorobenzene**
- **1,2-dibromo-3-chloropropane**
- **1,2,4-trichlorobenzene**

7.4.5.2 Compounds in TCL4-2 at a concentration of 50 µg/ml

- **All compounds included in TCL4 #1**

- **1,1,1-Trichloro-2,2,2-trifluoroethane**
- **isopropyl ether**
- **2,2-dichloropropane**
- **bromochloromethane**
- **1,1-dichloropropene**
- **dibromomethane**
- **1,3-dichloropropane**
- **1,1,1,2-tetrachloroethane**
- **1,2,3-trichloropropane**
- **bromobenzene**
- **n-propyl-benzene**
- **2-chlorotoluene**
- **4-chlorotoluene**
- **1,3,5-trimethylbenzene**
- **tert-butyl-benzene**
- **1,2,4-trimethylbenzene**
- **sec-butyl-benzene**
- **p-isopropyl toluene**
- **n-butyl-benzene**
- **hexachlorobutadiene**
- **naphthalene**
- **1,2,3-trichlorobenzene**

7.4.5.3 Compounds in TCL4 Gases at a concentration of 50 µg/ml

- **dichlorodifluoromethane**
- **chloroethane**
- **vinyl chloride**
- **bromomethane**
- **chloromethane**
- **trichlorofluoromethane**

7.4.5.4 Compounds in TCL4 CEVE at a concentration of 50 µg/ml

- **2-chloroethyl vinyl ether**

7.4.5.5 Compounds in TCL4 2B at a concentration of 50 µg/ml

- **vinyl acetate**

7.4.5.6 Compounds in TCL4 Ketones at a concentration of 250 µg/ml

- **acetone**
- **2-butanone**
- **4-methyl-2-pentanone**
- **2-hexanone**

7.4.5.7 Compounds in 1303B at a concentration of 500 µg/ml

- **acrolein**
- **acrylonitrile**

7.4.5.8 Compounds in APPIX

- **iodomethane**
- **3-chloropropene**
- **acetonitrile**
- **chloroprene**
- **propionitrile**
- **methacrylonitrile**
- **isobutyl alcohol**
- **1,4-dioxane**
- **methylmethacrylate**
- **ethylmethacrylate**
- **trans-1,4-dichloro-2-butene**

7.5 Initial Calibration Verification

7.5.1 The initial calibration curve must be verified using a standard from an independent source. The initial calibration verification (ICV) establishes the validity of the standards used to generate the curve. The laboratory purchases the ICV standard from a different vendor than the one used for the calibration standards.

7.5.2 The ICV contains the full list of target analytes at the same concentration as the continuing calibration verification (CCV) standard.

7.6 Compounds in 8260 I.S. (Internal standard) at a concentration of 50 µg/ml

- **fluorobenzene**
- **D5-chlorobenzene**
- **D4-1,4-dichlorobenzene**

7.7 **Compounds in 8260 S.S. (Surrogates) at a concentration of 50 µg/ml**

- **dibromofluorobenzene**
- **D4-1,2-dichloroethane**
- **D8-toluene**
- **4-bromofluorobenzene**

7.8 **Compounds in 8260 Spiking Mixture at a concentration of 25 µg/ml**

- **1,1-dichloroethene**
- **trichloroethene**
- **benzene**
- **toluene**
- **chlorobenzene**

Note: The spiking cocktail is project dependent. This spiking mixture can also be used as a Laboratory Control Sample (LCS) spike. Some projects may require full analyte spike, and in that case, the standard used for the full analyte spike LCS is the ICV. For some programs, the CCV may be used in place of the LCS.

7.9 Standard Storage

7.9.1 **Store the stock standards in Teflon- sealed screw-cap bottles with zero headspace at -10°C to -20°C. Protect the standards from light. Standards for gases usually need to be replaced after one week or as recommended by the manufacturer, unless the acceptability of the standard can be documented. Standards for the non-gases should be monitored and fresh standards prepared if a 20% drift is experienced. These standards need to be replaced after six months or as recommended by the manufacturer, unless the acceptability of the standard can be documented. CEVE and styrene may have to be prepared more frequently.**

7.9.2 **Store secondary dilution standards in Teflon-sealed screw-cap bottles with minimal headspace at -10°C to -20°C. Protect the standards from light. The secondary dilution standards must be checked frequently for signs of degradation or evaporation, especially just prior to their use in preparing the working calibration standards. Prepared from stock solution, they are stored with minimal headspace and replaced after one week. Secondary standards for gases should be replaced after one week unless the acceptability of the standard can be documented.**

7.9.3 Aqueous working standards must be prepared just prior to analysis unless they are to be purged by an autosampler. When an autosampler is used, the standards may be kept up to 12 hours in purge vessels connected via the autosampler to the purge and trap device. If premixed certified solutions are used store according to manufacturer's documented holding time and storage temperature recommendations.

7.9.4 Purgeable standards are stored in GC/MS VOA Freezer #1, separate from other standards and samples.

8.0 Sample Collection, Preservation, & Storage

8.1 Samples are collected, preserved, and stored according to the tables in Sample Control SOPs 4.1, "Receiving Samples" and 4.6, "Storing Samples." Sample holding times are also listed.

8.2 All samples must be analyzed within 14 days of collection.

8.3 Prior to analysis, all samples must be stored under refrigeration at 2-4.4° C in the reach-in storage unit in the laboratory. After analysis, samples are returned to Sample Control for long-term storage and disposal.

9.0 Quality Control

9.1 Surrogates

9.1.1 All samples, QC, and standards are spiked with the surrogate standard. Surrogates are used to assess the efficiency of the analytical system.

9.1.2 Surrogate compounds must meet recovery criteria as shown in Table 3.

Surrogate Compound	Aqueous % Recovery	Med./High Conc. Soil % Recovery
dibromofluorobenzene	80-120	61-130
D4-1,2-dichloroethane	80-120	56-134
D8-toluene	80-120	65-143
4-bromofluorobenzene	80-120	65-141

9.1.2.1 For NYSASP, the system monitoring compound (surrogate) recovery criteria are those in the current EPA CLP SOW for low concentration and multi-media, multi-concentration.

D4-1,2-dichloroethane:	**76-114%**
D8-toluene:	**88-110%**
4-bromofluorobenzene	**86-115%**

9.2 Internal Standards

9.2.1 The integrated areas of the quantitation ions of the internal standards **are monitored** in continuing calibration verification checks, **samples, and QC for a change in retention time and response or sensitivity**. These should remain reasonably constant over time.

9.2.1.1 Internal standard retention time and area responses must be assessed in each continuing calibration verification standard by comparison to the corresponding internal standard in the most recent initial calibration mid-point standard. Internal standard responses in samples and QC are compared to the most recent continuing calibration verification.

9.2.2 The area responses of the internal standards must be within 50 - 200% difference of the area responses compared to.

9.2.3 The retention time shift for the internal standards must be less than 30 seconds.

9.2.4 If any of these criteria cannot be met, the analytical system must be checked for malfunctions and corrections made. Re-analysis of any affected sample is required.

9.3 Method/Instrument Blanks

9.3.1 Before any samples are analyzed, it must be demonstrated through a laboratory reagent blank that the system is free of contamination that would prevent the determination of any analyte of concern. Sources of background contamination are glassware, purge gas, sorbents, and equipment. Background contamination must be reduced to an acceptable level before proceeding with the next analysis. In general, background from method analytes should be below the reporting limit.

9.3.2 All blanks must be analyzed on a GC/MS system meeting the BFB, initial calibration, and continuing calibration verification acceptance criteria.

9.3.3 A method blank is analyzed with each batch of up to 20 samples processed as a group within a 12-hour tune. If more than 20 samples are analyzed in a tune batch, a second method blank is required. Method blanks must be analyzed immediately following a valid continuing calibration verification analysis.

9.3.4 The concentration of the target compounds in the blank must be less than the reporting limit for each target compound except common lab solvents (methylene chloride, acetone) which must be less than twice the reporting limit.

For NYSASP, the contamination criteria are those presented in the current EPA CLP SOW for low concentration and multi-media, multi-concentration.

9.3.5 All samples processed within the same 12-hour tune with a method blank that does not meet the blank technical acceptance criteria must be reanalyzed.

Method interferences caused by contaminants in solvents, reagents, glassware, laboratory air, and other sample storage and processing hardware that lead to discrete artifacts and/or elevated baselines in gas chromatograms must be eliminated. The chromatographic system must be inspected for malfunctions, and corrections must be made as required before more samples are analyzed. An instrument blank is analyzed after a high concentration sample in order to eliminate carryover.

9.4 Laboratory Control Sample

9.4.1 A laboratory control sample (LCS, or blank spike, BS, or matrix spike blank for NYSASP) is prepared and analyzed with each tune batch of up to 20 samples.

9.4.2 Unless specified by a client or program, a subset of compounds is spiked into the LCS. The recovery criteria are shown below in Table 4.

LCS Spike Compound	5 ml % Recovery	25ml % Recovery
1,1-Dichloroethene	80-120	60-140
Trichloroethene	80-120	60-140
Benzene	80-120	60-140
Toluene	80-120	60-140
Chlorobenzene	80-120	60-140
Dibromofluorobenzene	80-120	80-120
D8-Toluene	80-120	80-120
Bromofluorobenzene	80-120	80-120
D4-1,2Dichloroethane	80-120	80-120

9.4.2.1 For the full analyte list LCS, compound recovery criteria for a *5 ml purge are 80-120% except for the gases and the "poor"* purging compounds listed below. The recovery criteria for the following compounds are 60-140%.

- **gases: bromomethane**
  chloromethane
  chloroethane
  vinyl chloride
  dichlorodifluoromethane
  trichlorofluoromethane
- **acetone**
- **2-butanone**
- **carbon disulfide**
- **crotonaldehyde**
- **1,2-dibromo-3-chloropropane**
- **1,4-dioxane**
- **isobutyl alcohol**
- **2-hexanone**
- **4-methyl-2-pentanone**
- **vinyl acetate**

9.4.2.2 For a 25 ml full analyte LCS spike, the compound recovery criteria are 60%-140%, except for the gases and the "poor" purging compounds, which have recovery criteria of 50-150%. Surrogates for the 25 ml purge have an 80-120% recovery criteria.

9.4.2.3 When the LCS fails to meet the criteria, the entire batch associated with it must be re-prepared and reanalyzed.

For NYSASP, the matrix spike blank recovery criteria are the same as the matrix spike criteria shown below. When the matrix spike blank fails criteria it must be re-prepared and re-analyzed along with the matrix spikes. Associated samples are not required to be re-processed.

9.5 Matrix Spikes

9.5.1 A matrix spike and matrix spike duplicate (MS/MSD) are prepared and analyzed with every SDG.

9.5.2 Matrix spikes have the following advisory recovery criteria as shown in Table 5A.

Spike Compound	Aqueous % Recovery	Med./High Conc. Soil % Recovery
1,1-dichloroethene	61-145	59-172
trichloroethene	71-120	62-137
benzene	76-127	66-142
toluene	76-125	59-139
chlorobenzene	75-130	60-133

9.5.3 Matrix spikes have the following advisory relative percent difference (RPD) criteria as shown in Table 5B.

Spike Compound	Aqueous % RPD	Med./High Conc. Soil % RPD
1,1-dichloroethene	14	22
trichloroethene	14	24
benzene	11	21
toluene	13	21
chlorobenzene	13	21

9.5.4 Most spike compounds should meet these criteria. If the criteria are not met in the MS/MSD but are met in the LCS, the results may be reported with the failures attributed to the matrix of the sample. If the LCS does not meet criteria, then all will have to be repeated as discussed above.

9.6 Duplicates

9.6.1 Duplicates, at a frequency of 10%, are required when processing samples submitted to meet the regulatory requirements of North Carolina **DENR. This can be satisfied with the MS/MSD.**

9.7 Initial Calibration Verification

9.7.1 A second source initial calibration verification (ICV) standard **is** run after the initial calibration standards have met criteria.

9.7.2 The ICV must be within 20% of its expected value for each target analyte and surrogate or within 40% for the poor purgers and the gases. Sporadic failure of up to three target compounds is allowed but they must not exceed 40% of their expected value. **Poor purgers are listed above.**

10.0 Calibration & Standardization

10.1 BFB Tuning

10.1.1 The analysis of the instrument performance check solution is performed by injecting 50 ng of BFB (2ul STD ID#7008) into the GC using a 10-µl Hamilton syringe. BFB may be analyzed simultaneously with a continuing calibration verification standard as long as all QC criteria are met.

10.1.2 The peak selection criteria for BFB analysis are as follows (in order of performance):

10.1.2.1 Average one scan prior to the apex of the BFB peak to one scan after the apex, subtracting a single background scan prior to the peak, but no more than 20 scans prior to the elution of BFB. Also, do not subtract part of the BFB peak.

Note: For work performed to comply with the requirements of the NYSASP, the U.S. Army Corps of Engineers (USACE), and the State of West Virginia, only this option is allowed.

10.1.2.2 Choose the apex of the BFB peak only and include background subtraction. *

*** Background subtraction is performed to eliminate interference and when performed, the subtracted scan must be no more than 20 scans prior to the elution of the BFB and no scans within the BFB peak may be subtracted.**

10.1.2.3 Choose a single scan or a range of scans within the BFB peak and include background subtraction.*

10.1.3 The analysis of the instrument performance check solution must meet the ion abundance criteria given in Table 6.

Table 6: BFB Key Ions and Ion Abundance Criteria

Mass	Ion Abundance Criteria
50	15-40% of m/z 95
75	30-60% of m/z 95
95	Base Peak; 100% relative abundance
96	5-9% of m/z 95
173	<2% of m/z 174
174	>50% of m/z 95
175	5-9% of m/z 174
176	>95% but less than 101% of m/z 174
177	5-9% of m/z 176

10.1.4 Alternatively, other documented tuning criteria may be used (e.g., CLP, Method 524.2) provided that method performance isn't adversely affected.

10.1.5 All criteria must be met according to requirements established by the U.S. EPA shown above. BFB technical acceptance criteria must be met before any standards, samples, or required blanks are analyzed.

GC/MS tuning and Mass Calibration forms must be printed and attached to the instrument runlog page for each tune. The relative abundance for each ion is calculated to two decimal places.

10.1.6 If BFB technical acceptance criteria are not met, retune the GC/MS system. It may also be necessary to clean the ion source, clean the quadrupole rods, or take other corrective action to achieve the technical acceptance criteria.

10.2 Initial Calibration

10.2.1 Prior to the analysis of samples and required blanks, and after the instrument performance check solution (BFB) criteria have been met, each GC/MS system must be calibrated at five concentrations to demonstrate instrument sensitivity and the linearity of responses for the purgeable target compounds.

10.2.2 Prepare standards according to the Initial Calibration Standard Preparation Table 2 in Section 7.4. All initial calibration standards must be analyzed at the concentration levels and frequency described in this SOP on a GC/MS system which meets the BFB technical acceptance criteria. The analysis of the five (or six) calibration standards determines the linearity of the five-point initial calibration curve.

10.2.3 The area response of the characteristic ions in the extracted ion current profile (EICP) is tabulated against the concentration for each compound and internal standard. Relative response factors (RRF) are calculated for each compound.

10.2.4 Initial calibration technical acceptance criteria must be met before any samples or required blanks are analyzed.

For the NYSASP, the initial calibration requirements, after meeting the instrument performance check (tune) requirements of this SOP, are those of the current EPA CLP SOW for low concentration water for 25 mL analyses and the current EPA CLP SOW for low/medium organics for 5 mL analyses.

10.2.5 Minimum relative response factors for the System Performance Check Compounds (SPCC) must be met and are listed below.

Table 7: Relative Response Factor Criteria for SPCCs

Volatile Compound	Minimum RRF
chloromethane	0.10
1,1-dichloroethane	0.10
chlorobenzene	0.30
bromoform	0.10
1,1,2,2-tetrachloroethane	0.30

10.2.6 The% RSD for each target analyte should be less than 15%, but the following compounds have maximum % RSD criteria of 30%. These Calibration Check Compounds (CCC) include:

- **1,1-dichloroethene**
- **chloroform**
- **1,2-dichloropropane**
- **toluene**
- ***ethylbenzene***
- **vinyl chloride**

10.2.6.1 While the remaining, non-CCC, target compounds do not have defined % RSD criteria, a warning limit of 50% RSD and an action limit of 90% RSD have been inserted as default values into the data reduction software program. This is based strictly on established U.S. EPA data validation guidelines where values greater than 90% RSD result in rejection of data.

10.2.6.2 If the % RSD is 15% or less, the average relative response factor may be used for quantitation. If the % RSD is greater than 15% then an alternate method for quantitation, such as least squares regression or a non-linear calibration method may be used. When one of these options is used, the correlation coefficient of the equation must be 0.99 or greater for a valid calibration. If a quadratic equation is used, six levels of standards must be used. If a third degree polynomial is used, seven levels are required. These alternate methods of quantitation are available in the ThruPut system.

For samples submitted to meet the regulatory requirements of the State of South Carolina, the option of using a quadratic fit to demonstrate linearity is not allowed. However, the use of a linear regression analysis for each target analyte is allowed.

10.2.6.3 Because of the large number of target analytes, some of them may exceed the 15% criteria. When this occurs, certain steps may be performed. These corrective actions also pertain to those instances where the 90% RSD action limits have been exceeded by the non-criteria compounds.

- **Check the instrument operating conditions and perform maintenance as necessary. It may be necessary to clean the ion source, perform column maintenance, change the column, service the purge and trap device, or take other corrective action to achieve the technical acceptance criteria.**

- **Compare responses for the analyte in each of the standard levels to verify that a single standard analysis is not producing the outliers. If so, reanalyze that standard and recalculate the %RSD.**

- **The calibration range may be narrowed to determine if linearity can be achieved. This may cause more dilution re-analyses or even change the reporting limit if the lower standard is eliminated. For this method, the method quantitation limit is defined by the lowest standard.**

10.2.7 The initial calibration may still be acceptable when some analytes exceed the 15% RSD criteria, if the following conditions are met:

- **The mean of <u>all</u> %RSD values for the analytes is less than or equal to 15%.**

- **<u>All</u> analytes the calibration standard must be included in the calculation.**

10.2.7.1 A summary of the initial calibration data and/or a list of the analytes not meeting the 15% RSD criteria with their actual %RSD must be included as a deliverable to our client. If the conditions in *10.2.7* are met, then the average relative response factor may be used to determine the concentration of analytes in samples.

10.2.7.2 For samples submitted to meet the regulatory requirements of the State of South Carolina, the option of demonstrating that the mean %RSD of all target analytes in the standard mixture is under 15% is not an allowed option. Because the State of South Carolina does not allow the grand mean, the following acceptance criteria for the initial calibration apply to samples received for compliance with the DHEC.

Of the remaining non-CCC analytes the %RSD should be less than 15%, but the following compounds have maximum %RSD criteria of 30%. These compounds are the gaseous analytes and those characterized with having poor purging efficiencies or poor responses.

- **dichlorodifluoromethane**
- **chloromethane**
- **vinyl chloride**
- **bromomethane**
- **chloroethane**
- **trichlorofluoromethane**
- **acrolein**
- **iodomethane**
- **carbon disulfide**
- **acetone**
- **acetonitrile**
- **acrylonitrile**
- **tert-butyl alcohol**
- **vinyl acetate**
- **2-butanone**
- **propionitrile**
- **methyl acrylate**
- **methacrylonitrile**
- **isobutyl alcohol**
- **crotonaldehyde**
- **1,4-dioxane**
- **methylmethacrylate**
- **2-chloroethyl vinyl ether**
- **4-methyl-2pentanone**
- **ethylmethacrylate**
- **2-hexanone**
- **benzyl chloride**
- **1,2-dibromo-3-chloropropane**

The exceptions to the 15% mean %RSD criteria discussed above in Section 10.2.6 are also allowed by the State of South Carolina.

10.2.8 The initial calibration verification must be analyzed after each initial calibration and must meet the acceptance criteria. If the ICV fails, then a new initial calibration curve must be generated.

10.3 Continuing Calibration Verification

10.3.1 Before the analysis of samples and blanks, but after BFB and initial calibration acceptance criteria have been met, each GC/MS system must be routinely checked by analyzing a continuing calibration verification standard. This standard must contain all purgeable target analytes and surrogate compounds. It is used to ensure that the instrument meets the sensitivity and linearity requirements of the method throughout the analytical sequence.

10.3.2 A check of the calibration curve must be performed once every 12 hours, beginning with the injection of BFB. A percent difference of the response for each compound compared to the mean relative response factor from the initial calibration is calculated when performing the average response factor model.

10.3.3 The calculated percent difference must be less than or equal to 20% (%D) for the CCCs listed above in Section 10.2.6. Minimum response factor criteria for the continuing calibration verification standard are also shown above in Table 7.

10.3.3.1 If a regression fit model was used for analytes in the initial calibration, the continuing calibration verification is performed using percent drift (difference) for the CCCs.

10.3.4 As indicated for the initial calibration acceptance criteria, for the continuing calibration verification, the remaining target analytes (non-CCC compounds) do not have defined % difference criteria. We have established a warning limit of 50%D and an action limit of 90%D. These values have been inserted as defaults into the data reduction software program. This is based strictly on established U.S. EPA data validation guidelines where values greater than 90% RSD result in rejection of data.

10.3.4.1 For samples submitted to meet the regulatory requirements of the State of South Carolina, the non-CCC target analytes should be less than 20%. Compounds listed in 10.2.7.2 have a warning limit of 40% D and an action limit of 50% D.

10.3.5 If continuing calibration verification acceptance criteria cannot be met after inspection and normal maintenance, a new initial calibration will have to be performed.

Note: Method 8260B indicates that if the CCCs are not required analytes, then all required analytes, must meet the 20% difference criterion. Our typical analysis includes all of the CCCs. Additionally, some programs may require all compounds to meet a % difference criterion. In these situations, if the average of the response for all analytes is within 20%, then the calibration has been verified. Requirements similar to those in 10.2.6 must be met.

10.3.6 For the NYSASP, the continuing calibration requirements, after meeting the instrument performance check (tune) requirements of this SOP, are those of the current EPA CLP SOW for low concentration water for 25 mL analyses and the current EPA CLP SOW for low/medium organics for 5 mL analyses.

11.0 Procedure

Documentation must follow the requirements in QC SOP: Proper Documentation Procedures. All injections must be recorded on the instrument runlog (Attachment 3) along with the date, time (use a 24 hour clock), the volume injected, operator ID, and any comments relevant to the injection.

All standards, blanks, samples and other required runs must be injected within exactly 12 hours from the time of the injection of BFB.

11.1 Instrument Software Conventions

11.1.1 Quantitation method: **Average of the whole**

11.1.2 File naming convention: **XX012345YZZ**

where:	**XX =**	**Analytical prefix**	
		where:	
		Calibration tune file =	**BF,BG,...**
		Instrument blank =	**CB,CC,...**
		Calibration standard =	**CS,CT,...**
		Initial sample analysis =	**CN**
		Sample reanalysis =	**CR0,C2R,C3R**
	Y =	**Shift indicator = A,B, or C**	
	ZZ =	**Instrument number**	
	12345 =	**Last five digits of lab ID**	

11.2 Analytical Sequence

11.2.1 Order of analysis for the instrument calibration

- **BFB (tune)**
- **initial calibration**
- **initial calibration verification**

11.2.2 Order of analysis for the twelve-hour tune

- **BFB**
- **continuing calibration verification**
- **instrument blank**
- **laboratory control samples-LCS**
- **samples**

11.2.3 In some cases, if tune time remains after the initial calibration standards have been run, samples may be analyzed as long as they are preceded by a valid instrument blank.

11.2.4 All samples must be analyzed on a GC/MS system meeting the BFB, initial calibration, continuing calibration verification, and instrument blank criteria.

11.3 Preparations

11.3.1 Standards

11.3.1.1 Load the standard solutions onto the purge and trap apparatus. Purge for 11 minutes at ambient temperature, or 40° C for heated purge, and desorb for 4 minutes, analyzing all target compounds.

11.3.2 Instrument Blank

11.3.2.1 An instrument blank is prepared by filling one 25 ml or 5 mL gastight syringe with DI water and spiking with internal standard solution and surrogate solution.

11.3.3 Laboratory Control Sample spikes

11.3.3.1 Laboratory control samples (LCS) are prepared at 5.0 µg/l with 5 µg/l of surrogates for 25 mL samples and at 50 µg/l with 50 µg/l of surrogates for 5 ml samples.

For certain projects and programs, a full list spike is required.

11.3.4 Samples

11.3.4.1 Liquid samples are **collected with zero headspace and** provided to the laboratory in 40-ml or 60-ml screw-cap vials with Teflon-lined silicon septa. To prepare liquid samples for analysis, pour the sample into a 5 mL or 25-ml Hamilton gastight syringe. **Re**place the plunger **and** adjust the volume to 5 mL or 25.0 ml. **Spike each 25 ml sample** with 2.5-**µl** of internal standard and 2.5-**µl** of surrogate solutions through the bore of the syringe. **Spike each 5 ml sample with** 5 µl **of** internal standard and 5 µl of surrogate solutions.

11.3.4.2 Methanol extracts of medium/high concentration soil samples are contained in an autosampler vial capped with a Teflon-faced septum. The vial contains 1 mL of the methanol extract **that** also contains surrogates. A 5 mL Hamilton gastight syringe is filled with **DI** water and adjusted to 4.9 mL. The plunger is pulled back to 5.0 mL to allow for the addition of the methanol extract and internal standard solution. Add 100 µL of the methanol extract and 5.0 µL of internal standard solution to the syringe. Based on prior or screening results, if less than 100 µL of the methanol extract is required in order to get target analytes within the initial calibration range, add an additional amount of methanol to total 100 µL.

11.3.4.3 For further details, see Sample Preparation Procedure –238, "Preparation of Soil/Sediment/Sludge Samples for the Analysis of Volatile Organic Compounds by Closed-System Purge and Trap."

11.3.5 Matrix Spikes

11.3.5.1 For sample spikes, in addition to spiking internal standard solution and surrogate solution, also add 5.0 **µl** of 8260**B** spike solution. For certain projects, a full **target** list **matrix spikes are** required. For medium/high concentration soil samples, the spiking solution is added at the time of the methanol extraction.

11.4 Analysis

11.4.1 Attach the Luerlock tip of the syringe to the valve on the purge and trap apparatus, open the valve, inject the sample, and close the valve.

11.4.2 Purge the sample for 11.0 (± 0.1) minutes.

11.4.3 After purging, the purge and trap apparatus will desorb onto the GC column by elevating the trap temperature to 260° C and back-flushing the trap with helium for 4 minutes at 20 to 60 ml/minute.

11.4.4 After desorbing, the trap is reconditioned by baking at 260° C for at least 7 minutes. When the trap has finished baking and is cool, it is ready for the next sample to be purged.

11.4.5 In each analytical run, all analytes must fall below the maximum calibration range established by the highest standard in the initial calibration. If an analyte is present at a concentration higher than the highest initial calibration standard, it must be reanalyzed at a lesser amount or dilution. A valid dilution is one in which the compound in question falls above the mid-point calibration standard concentration. The dilution is considered valid if the analyte concentration is above 50 µg/l.

11.5 Identification

11.5.1 Target compounds are identified in the samples by analyzing standards under the same condition. Resultant mass spectra are compared to established library spectra and GC retention times are compared to retention times from the most recent continuing calibration standard. The mass spectrum of the sample compound and a laboratory library-generated spectrum must match according to the following criteria.

11.5.1.1 All ions present in the library mass spectrum at a relative intensity >10% must be present in the sample spectrum.

11.5.1.2 The relative intensities of ions specified above must agree within ±20% between the library and sample spectra.

11.5.1.3 Ions >10% in the sample spectrum but not present in the library spectrum must be considered and accounted for.

11.5.2 If a compound analyzed by GC/MS techniques cannot be verified by all of the criteria listed above, but in the technical judgment of the mass spectral interpretation specialist the identification is correct, then the laboratory will report that identification.

11.5.3 Non-target compounds (tentatively identified compounds or TICs) are identified by comparing the mass spectra from the TICs to mass spectra contained in the National Institute of Standards and Technology (NIST) Mass Spectral Library.

11.6 Quantitation

11.6.1 A relative response factor is established for each target and surrogate compound during the initial and continuing calibration verification procedures. Quantitation of target analytes is based on the mean relative response factor from the initial five point calibration curve. For NYSASP, the RRF from the continuing calibration standard is used to calculate concentrations.

11.6.2 When a sample is analyzed that has saturated ions from a compound, this analysis must be followed by the analysis of a DI water blank (instrument blank) or the following sample must be monitored for contamination and interference from carryover. If the blank or sample is not free from interferences, the system must be decontaminated. Sample analysis may not resume until a blank or sample has been analyzed which is free from interferences. Being free from interferences means that whatever compound was present above the initial calibration range in a sample cannot be present in an instrument, or the sample analyzed immediately following, at a level above the reporting limit for that compound.

11.6.3 Secondary ion quantitation is allowed only when there are sample matrix interferences with the primary ion. If secondary ion quantitation is performed, document the reasons in the SDG narrative.

11.6.4 TICs are quantified by comparing the MS response from the reconstructed ion chromatogram (RIC) for the TIC peaks to the MS response for a peak produced by the nearest internal standard compound. A response factor of 1 is assumed.

12.0 <u>Data Analysis and Calculations</u>

Calculations must be consistent with the QC SOP: Numerical Data Reduction.

12.1 Calculation of the mean or average of a set of values:

$$\overline{X} = \frac{\sum_{i=1}^{n} X_i}{n}$$

where: n = total number of values
x_i = each individual value used to calculate the mean
x = the mean of n

12.2 Calculation of the standard deviation of a set of values:

$$\text{Standard deviation} = \sqrt{\frac{\sum_{i=1}^{n}\left(X_n - \overline{X}\right)^2}{n-1}}$$

12.3 Calculation of percent recovery:

12.3.1 LCS and surrogates:

$$\%R = \frac{Amount\ found}{Amount\ spiked}\ x\ 100$$

12.3.2 Matrix spikes:

$$\%\,R = \frac{Amount\ in\ spiked\ sample - Amount\ in\ unspiked\ (native)\ sample}{Amount\ spiked}\ x\ 100$$

12.4 Calculation of % RSD

$$\%RSD = \left(\frac{Standard\ deviation}{\overline{X}}\right) \times 100$$

12.5 Calculation of RPD

$$RPD = \frac{|Value\ 1\ -\ Value\ 2|}{(Value\ 1\ +\ Value\ 2)/2}\ x100$$

12.6 Calculation of %Difference (%D)

$$\%Diff = \frac{Value - \overline{Reference\ \ value}}{\overline{Reference\ \ value}} \times 100$$

12.7 Relative Response Factor

$$RRF = \frac{Ax \times C(is)}{A(is) \times Cx}$$

where: **Ax = Area of the characteristic ion (EICP) for the compound to be measured**

A(is) = Area of the characteristic ion (EICP) for the specific internal standard

C(is) = Concentration of the internal standard (in µg/l)

Cx = Concentration of the compound to be measured

12.8 Concentration

12.8.1 Concentration of aqueous samples by GC/MS analysis

$$ug/L = \frac{(Ax)(Is)(Df)}{(Ais)(\overline{RRF})(Vo)}$$

where: Ax = area of the characteristic ion from the EICP for the compound to be measured

Ais = area of the characteristic ion for the EICP for the internal standard

Is = amount of internal standard added (ng)

$\overline{RRF}$ = mean relative response factor from initial calibration standards

Vo = volume of water purged in milliliters

Df = dilution factor. If no dilution, Df = 1.0

The dilution factor for analysis of water samples for volatiles by this method is defined as the ratio of the number of milliliters of water purged (ie. Vo above) to the number of milliliters of the original water sample used for purging. For example, if 12.5 ml of sample is diluted to 25.0 ml with reagent water and purged, Df - 25.0 ml/12.5 ml = 2.0. If no dilution is performed, Df = 1.0.

12.8.2 Concentration of soil samples <u>(dry weight basis)</u> by GC/MS

$$\mu g / kg = \frac{(Ax)(Is)(Df)(Vt)(1000)}{(Ais)(\overline{RRF})(Ws)(Va)}$$

where: Ax, Ais, Is, $\overline{RRF}$ are the same as given for water

Df = Dilution factor which, for medium/high concentration soil extract is defined by the following formula:

$$\frac{\mu L \text{ concentrated extract used for dilution} + \mu L \text{ clean solvent}}{\mu L \text{ concentrated extract used for dilution}}$$

Vt = Total volume of methanol extract, in mL

Note: This is typically 10 mL or 5 mL even though only 1 mL is transferred to the autosampler vial.

Ws = Weight of soil/sediment sample extracted, in grams (g)

Va = Volume of the aliquot of methanol extract

Note: Typically this is 100 µL but can be the volume of sample extract (not including the methanol added to equal 100µL) in µL added to DI water.

Ws = weight of sample extracted, in grams

$$\text{D (dry weight)} = \frac{100 - \%\ \text{moisture}}{100}$$

12.8.3 Tentatively Identified Compound (TIC) Estimation

$$TIC\ Amount = \frac{(Area\ TIC)\ x\ Amount(Std)}{Area(IS)\ x\ 1(RF)}$$

where:
- **Area(TIC) = area response from RIC for non-target compound**
- **Amount(Std) = amount of internal standard added to the sample, in µg/L.**
- **Area(IS) = area response of the nearest internal standard in the reconstructed ion chromatogram**
- **1(RF) = assumed response factor of 1**

12.9 Calculating Dilutions

Attachment 1

Table 1: Volatile Target Compounds

Compounds	Internal Standard	Primary Quantitation Ion	Secondary Quantitation Ion(s)
dichlorodifluoromethane	1	85	87
chloromethane	1	50	52
vinyl chloride	1	62	64
bromomethane	1	94	96
chloroethane	1	64	66
trichlorofluoromethane	1	101	103
1,1-dichloroethene	1	96	61, 98
methylene chloride	1	84	49, 86
trans-1,2-dichloroethene	1	96	61, 98
1,1-dichloroethane	1	63	65, 83
2,2-dichloropropane	1	77	97
cis-1,2-dichloroethene	1	96	61, 98
bromochloromethane	1	128	49, 130
chloroform	1	83	85
1,1,1-trichloroethane	1	97	99, 61
carbon tetrachloride	1	117	119, 121
1,1-dichloropropene	1	75	110, 77
benzene	1	78	77, 51
1,2-dichloroethane	1	62	98
trichloroethene	1	130	95, 97
1,2-dichloropropane	1	63	112
dibromomethane	1	174	93, 95
bromodichloromethane	1	83	85, 127
2-chloroethyl vinyl ether	1	63	65, 106
cis-1,3-dichloropropene	1	75	77
acrolein	1	56	55, 58
iodomethane	1	142	127, 141
1,1,1-trichloro-2,2,2,-trifluoroethane	1	117	151, 153
1,1,2-trichloro-1,2,2,-trifluoroethane	1	85	101, 151
carbon disulfide	1	76	78
acetone	1	43	58
3-chloropropene	1	76	41, 78
acetonitrile	1	41	40, 39
acrylonitrile	1	53	52, 51
methyl-tert-butyl ether	1	73	41, 43

Attachment 1 (continued)

Table 1 (continued): Volatile Target Compounds

Compounds	Internal Standard	Primary Quantitation Ion	Secondary Quantitation Ion(s)
vinyl acetate	1	43	86
2-butanone	1	72	43, 57
propionitrile	1	54	55, 52
methacrylonitrile	1	41	39, 67
1-chlorobutane	1	56	49
1,4-dioxane	1	88	58
methylmethacrylate	1	69	100, 41
Surrogate #1: dibromofluoromethane	1	113	111, 192
Surrogate #2: d4-1,2-dichloroethane	1	65	102, 67
4-methyl-2-pentanone	2	43	85, 100
toluene	2	92	91
trans-1,3-dichloropropene	2	75	77
1,1,2-trichloroethane	2	97	83, 85
ethylmethacrylate	2	69	41, 99
tetrachloroethene	2	164	168, 129
1,3-dichloropropane	2	76	78
2-hexanone	2	43	58, 57
dibromochloromethane	2	129	127, 48
1,2-dibromoethane	2	107	109, 188
chlorobenzene	2	112	114, 77
1,1,1,2-tetrachloroethane	2	131	119, 133
ethylbenzene	2	106	91
m,p-xylene	2	106	91
o-xylene	2	106	91
styrene	2	104	91, 78
bromoform	2	173	175, 254
isopropyl benzene	2	105	120
bromobenzene	2	156	77,158
1,1,2,2-tetrachloroethane	2	83	85, 131
1,2,3-trichloropropane	2	110	75, 112
trans-1,4-dichloro-2-butene	2	53	88, 75
Surrogate #3: d8-toluene	2	98	70, 100

Attachment 1 (continued)

Table 1 (continued): Volatile Target Compounds

Compounds	Internal Standard	Primary Quantitation Ion	Secondary Quantitation Ion(s)
n-propyl benzene	3	91	120
2-chlorotoluene	3	126	91
4-chlorotoluene	3	91	126
1,2,4-trimethyl benzene	3	105	120
1,3,5-trimethyl benzene	3	105	120
pentachloroethane	3	167	130, 165
sec-butyl benzene	3	105	134
1,2-dichlorobenzene	3	146	111, 148
1,3-dichlorobenzene	3	146	111, 148
1,4-dichlorobenzene	3	146	111, 148
n-butyl benzene	3	91	92, 134
tert-butyl benzene	3	119	91, 134
p-isopropyl toluene	3	119	134, 91
1,2-dibromo-3-chloropropane	3	75	155, 157
1,2,4-trichlorobenzene	3	180	182, 145
hexachlorobutadiene	3	225	223, 227
naphthalene	3	128	64, 51
1,2,3-trichlorobenzene	3	180	182, 145
Surrogate #4: 4-bromofluorobenzene	3	95	174, 176

Internal Standard #1: fluorobenzene
Internal Standard #2: d5-chlorobenzene
Internal Standard #3: d4-1,4-dichlorobenzene

Attachment 2

Method Detection Limit Study

Study date: April 6, 2000
Instrument: F50051

GCMS Volatile SW846 8260B/5030B Aqueous, 25 ml Purge

Compound Name	Rep#1 ug/L	Rep#2 ug/L	Rep#3 ug/L	Rep#4 ug/L	Rep#5 ug/L	Rep#6 ug/L	Rep#7 ug/L	Rep#8 ug/L	Mean ug/L	Amt. ug/L	S.Dev. ug/L	MDL ug/L	Report Limit ug/L
Dichlorodifluoromethane	0.41	0.31	0.28	0.31	0.30	0.27	0.20	0.18	0.28	0.5	0.071	0.21	0.5
Chloromethane	0.53	0.43	0.40	0.45	0.42	0.39	0.35	0.31	0.41	0.5	0.066	0.20	0.5
Vinyl Chloride	0.49	0.36	0.32	0.37	0.35	0.33	0.22	0.19	0.33	0.5	0.093	0.28	0.5
Bromomethane	0.54	0.41	0.37	0.41	0.37	0.37	0.23	0.26	0.37	0.5	0.095	0.29	0.5
Chloroethane	0.52	0.39	0.34	0.39	0.34	0.33	0.25	0.24	0.35	0.5	0.088	0.27	0.5
Trichlorofluoromethane	0.54	0.42	0.37	0.42	0.39	0.36	0.26	0.25	0.38	0.5	0.093	0.28	0.5
Diethylether	4.91	4.29	4.18	5.94	5.60	6.09	4.27	4.69	5.00	5.0	0.779	2.33	5.0
Acrolein	3.52	3.34	2.98	4.26	4.29	4.97	3.80	3.82	3.87	5.0	0.626	1.88	5.0
1,1-Dichloroethene	0.57	0.44	0.40	0.53	0.48	0.45	0.32	0.29	0.44	0.5	0.096	0.29	0.5
1,1,1-Trichloro-2,2,2-trifluoroethane	0.50	0.40	0.35	0.48	0.43	0.39	0.32	0.36	0.40	0.5	0.063	0.19	0.5
Acetone	7.40	5.37	5.42	7.49	6.54	7.51	9.24	8.91	7.24	2.5	1.427	4.28	2.5
Iodomethane	0.60	0.46	0.43	0.53	0.46	0.44	0.30	0.32	0.44	0.5	0.099	0.30	0.5
1,1,2-trichloro-1,2,2-trifluoroethane	0.57	0.43	0.39	0.53	0.49	0.45	0.86	*	0.53	0.5	0.157	0.49	0.5
Carbon disulfide	0.56	0.44	0.41	0.51	0.47	0.44	0.36	0.31	0.44	0.5	0.080	0.24	0.5
3-Chloropropene	0.51	0.40	0.39	0.49	0.41	0.40	0.33	0.29	0.40	0.5	0.073	0.22	0.5
Acetonitrile	0.60	0.47	0.42	0.54	0.50	0.46	0.36	0.40	0.47	0.5	0.078	0.23	0.5
Methylene Chloride	1.02	0.78	0.82	0.93	0.92	1.04	1.86	2.81	1.27	0.5	0.709	2.12	0.5
Acrylonitrile	4.53	3.95	4.07	5.63	5.24	5.58	3.79	4.34	4.64	5.0	0.742	2.22	5.0
Tert-butyl-alcohol	3.51	3.96	3.74	5.45	5.48	7.14	3.13	3.91	4.54	5.0	1.357	4.07	5.0
trans-1,2-Dichloroethene	0.57	0.45	0.41	0.53	0.47	0.45	0.33	0.31	0.44	0.5	0.089	0.27	0.5
Methyl-tert-butyl-ether	0.50	0.45	0.43	0.56	0.52	0.59	0.41	0.45	0.49	0.5	0.064	0.19	0.5
n-Hexane	0.66	0.50	0.45	0.62	0.54	0.51	0.51	0.60	0.55	0.5	0.071	0.21	0.5
1,1-Dichloroethane	0.59	0.47	0.44	0.55	0.49	0.46	0.35	0.35	0.46	0.5	0.085	0.25	0.5
Chloroprene	0.59	0.47	0.42	0.54	0.49	0.46	0.35	0.31	0.45	0.5	0.093	0.28	0.5
Vinyl acetate	0.85	0.81	0.82	0.93	0.93	1.05	0.67	0.74	0.85	1.0	0.119	0.36	1.0
Isopropyl ether	0.58	0.50	0.49	0.61	0.56	0.58	0.44	0.46	0.53	0.5	0.063	0.19	0.5
cis-1,2-Dichloroethene	0.58	0.46	0.43	0.54	0.47	0.47	0.35	0.36	0.46	0.5	0.079	0.24	0.5
2,2-Dichloropropane	0.56	0.43	0.40	0.46	0.43	0.39	0.28	0.29	0.41	0.5	0.091	0.27	0.5
Propionitrile	32.56	29.32	29.91	35.77	35.17	37.44	28.32	32.28	32.60	25.0	3.306	9.91	25.0

Reporting Limit = Low Level Standard

Attachment 2 (continued)

Method Detection Limit Study

Study date: April 6, 2000 GCMS Volatile SW846 8260B/5030B Aqueous, 25 ml Purge
Instrument: F50051

Compound Name	Rep#1 ug/L	Rep#2 ug/L	Rep#3 ug/L	Rep#4 ug/L	Rep#5 ug/L	Rep#6 ug/L	Rep#7 ug/L	Rep#8 ug/L	Mean ug/L	Amt. ug/L	S.Dev. ug/L	MDL ug/L	Report Limit ug/L
Tetrachloroethene	0.62	0.48	0.41	0.53	0.45	0.49	0.62	0.35	0.49	0.5	0.095	0.28	0.5
2-Hexanone	3.44	3.23	2.91	3.69	3.26	3.79	2.82	3.13	3.28	2.5	0.344	1.03	2.5
Dibromochloromethane	0.51	0.46	0.45	0.52	0.48	0.52	0.41	0.40	0.47	0.5	0.047	0.14	0.5
1,2-Dibromoethane	0.57	0.51	0.50	0.60	0.56	0.57	0.43	0.46	0.53	0.5	0.060	0.18	0.5
Chlorobenzene	0.63	0.53	0.50	0.59	0.57	0.55	0.49	0.43	0.54	0.5	0.063	0.19	0.5
1-Chlorohexane	0.75	0.63	0.58	0.71	0.67	0.63	0.55	0.48	0.63	0.5	0.088	0.26	0.5
1,1,1,2-Tetrachloroethane	0.55	0.46	0.42	0.51	0.46	0.48	0.37	0.38	0.45	0.5	0.062	0.19	0.5
Ethylbenzene	0.65	0.52	0.49	0.59	0.56	0.54	0.46	0.37	0.52	0.5	0.085	0.26	0.5
m,p-Xylene	1.32	1.06	1.02	1.22	1.13	1.10	0.99	0.80	1.08	1.0	0.156	0.47	1.0
o-Xylene	0.64	0.51	0.50	0.60	0.56	0.54	0.49	0.40	0.53	0.5	0.073	0.22	0.5
Styrene	0.63	0.52	0.51	0.62	0.58	0.58	0.48	0.42	0.54	0.5	0.073	0.22	0.5
Bromoform	0.45	0.42	0.40	0.47	0.43	0.48	0.36	0.37	0.42	0.5	0.044	0.13	0.5
cis-1,4-dichloro-2-butene	17.83	16.59	17.38	17.40	17.74	16.27	*	16.01	17.03	20.0	0.732	2.30	20.0
Isopropyl benzene	0.64	0.51	0.49	0.60	0.56	0.53	0.49	0.37	0.52	0.5	0.082	0.25	0.5
1,1,2,2-Tetrachloroethane	0.60	0.56	0.60	0.66	0.66	0.63	0.27	0.50	0.56	0.5	0.129	0.39	0.5
1,2,3-Trichloropropane	0.48	0.45	0.46	0.54	0.50	0.61	0.40	0.43	0.48	0.5	0.067	0.20	0.5
Bromobenzene	0.59	0.51	0.48	0.56	0.52	0.54	0.48	0.43	0.51	0.5	0.051	0.15	0.5
trans-1,4-Dichloro-2-butene	18.63	17.86	18.54	19.26	19.49	17.80	*	17.69	18.47	20.0	0.722	2.27	20.0
n-Propyl benzene	0.67	0.55	0.55	0.61	0.59	0.53	0.50	0.39	0.55	0.5	0.083	0.25	0.5
2-Chlorotoluene	0.68	0.54	0.54	0.60	0.56	0.54	0.49	0.40	0.54	0.5	0.081	0.24	0.5
4-Chlorotoluene	0.69	0.56	0.56	0.63	0.62	0.56	0.49	0.43	0.57	0.5	0.082	0.25	0.5
1,3,5-Trimethyl benzene	0.69	0.55	0.56	0.63	0.60	0.55	0.51	0.40	0.56	0.5	0.086	0.26	0.5
Pentachloroethane	0.44	0.39	0.37	0.41	0.40	0.31	0.06	0.35	0.34	0.5	0.120	0.36	0.5
tert-butyl Benzene	0.59	0.49	0.48	0.55	0.54	0.47	0.41	0.35	0.49	0.5	0.078	0.23	0.5
1,2,4-Trimethyl benzene	0.67	0.55	0.56	0.64	0.61	0.56	0.53	0.42	0.57	0.5	0.077	0.23	0.5
sec-butyl Benzene	0.69	0.55	0.54	0.63	0.61	0.53	0.54	0.37	0.56	0.5	0.094	0.28	0.5
1,3-Dichlorobenzene	0.63	0.53	0.51	0.58	0.56	0.55	0.49	0.43	0.54	0.5	0.060	0.18	0.5
p-Isopropyl toluene	0.62	0.50	0.49	0.57	0.54	0.49	0.47	0.34	0.50	0.5	0.082	0.25	0.5
1,4-Dichlorobenzene	0.64	0.55	0.53	0.59	0.56	0.57	0.50	0.45	0.55	0.5	0.057	0.17	0.5

Reporting Limit = Low Level Standard

Attachment 2 (continued)

Method Detection Limit Study

Study date: April 6, 2000
Instrument: F50051

GCMS Volatile SW846 8260B/5030B Aqueous, 25 ml Purge

Compound Name	Rep#1 ug/L	Rep#2 ug/L	Rep#3 ug/L	Rep#4 ug/L	Rep#5 ug/L	Rep#6 ug/L	Rep#7 ug/L	Rep#8 ug/L	Mean ug/L	Amt. ug/L	S.Dev. ug/L	MDL ug/L	Report Limit ug/L
2-Butanone	2.13	2.20	2.17	2.57	2.61	3.06	2.19	1.90	2.35	2.5	0.369	1.11	2.5
Methyl acrylate	5.61	4.92	4.79	6.11	6.22	6.80	5.13	5.85	5.68	5.0	0.701	2.10	5.0
Methacrylonitrile	5.78	5.29	5.16	6.18	5.99	6.17	4.66	5.42	5.58	5.0	0.541	1.62	5.0
Bromochloromethane	0.53	0.47	0.43	0.52	0.45	0.52	0.38	0.42	0.47	0.5	0.055	0.16	0.5
Tetrahydrofuran	2.10	1.97	2.68	2.51	2.89	2.48	1.68	2.00	2.29	2.0	0.413	1.24	2.0
Chloroform	0.59	0.48	0.46	0.55	0.51	0.51	0.40	0.40	0.49	0.5	0.067	0.20	0.5
1,1,1-Trichloroethane	0.56	0.43	0.41	0.48	0.44	0.41	0.31	0.30	0.42	0.5	0.085	0.25	0.5
Pentafluorobenzene	0.61	0.48	0.42	0.54	0.47	0.46	0.48	0.37	0.48	0.5	0.072	0.22	0.5
1-Chlorobutane	0.64	0.50	0.46	0.57	0.52	0.49	0.41	0.38	0.50	0.5	0.084	0.25	0.5
1,1-Dichloropropene	0.59	0.47	0.42	0.53	0.47	0.45	0.37	0.32	0.45	0.5	0.085	0.26	0.5
Carbon tetrachloride	0.48	0.38	0.36	0.42	0.40	0.35	0.28	0.26	0.37	0.5	0.072	0.22	0.5
1,2-Dichloroethane	0.52	0.45	0.44	0.53	0.48	0.51	0.38	0.42	0.47	0.5	0.053	0.16	0.5
Isobutyl alcohol	41.17	36.37	45.69	43.08	*	45.66	32.10	40.03	40.59	25.0	4.974	15.63	25.0
Benzene	0.61	0.48	0.43	0.54	0.48	0.48	0.46	0.40	0.49	0.5	0.065	0.19	0.5
Crotonaldehyde	10.12	5.77	5.98	6.64	6.51	8.00	12.87	6.67	7.82	5.0	2.474	7.42	5.0
Trichloroethene	0.60	0.49	0.43	0.53	0.47	0.46	0.43	0.35	0.47	0.5	0.074	0.22	0.5
1,2-Dichloropropane	0.54	0.47	0.42	0.52	0.46	0.49	0.39	0.39	0.46	0.5	0.057	0.17	0.5
Dibromomethane	0.51	0.46	0.42	0.50	0.45	0.50	0.38	0.41	0.45	0.5	0.048	0.14	0.5
1,4-Dioxane	29.38	39.92	39.43	37.89	41.18	32.20	39.47	38.45	37.24	25.0	4.167	12.49	25.0
Methylmethacrylate	4.70	4.32	4.02	5.58	5.16	5.69	4.24	4.93	4.83	5.0	0.621	1.86	5.0
Bromodichloromethane	0.50	0.43	0.39	0.49	0.45	0.47	0.35	0.36	0.43	0.5	0.058	0.17	0.5
2-Chloroethyl vinyl ether	2.88	2.52	1.74	3.06	0.87	1.98	2.84	3.29	2.40	5.0	0.812	2.44	5.0
cis-1,3-Dichloropropene	0.47	0.41	0.38	0.45	0.41	0.44	0.33	0.35	0.41	0.5	0.049	0.15	0.5
4-Methyl-2-pentanone	3.15	2.91	2.68	3.64	3.17	3.77	2.66	3.00	3.12	2.5	0.407	1.22	2.5
Toluene	0.69	0.55	0.52	0.63	0.57	0.57	0.58	0.53	0.58	0.5	0.056	0.17	0.5
trans-1,3-Dichloropropene	0.44	0.41	0.39	0.48	0.42	0.45	0.32	0.34	0.41	0.5	0.054	0.16	0.5
1,1,2-Trichloroethane	0.56	0.54	0.53	0.62	0.55	0.59	0.46	0.46	0.54	0.5	0.056	0.17	0.5
Ethylmethacrylate	5.02	4.50	4.56	5.72	5.71	6.17	4.63	4.95	5.16	5.0	0.630	1.89	5.0
1,3-Dichloropropane	0.59	0.53	0.53	0.64	0.57	0.64	0.45	0.47	0.55	0.5	0.071	0.21	0.5

Reporting Limit = Low Level Standard

Attachment 2 (continued)

Method Detection Limit Study

Study date: April 6, 2000
Instrument: F50051

GCMS Volatile SW846 8260B/5030B Aqueous, 25 ml Purge

Compound Name	Rep#1 ug/L	Rep#2 ug/L	Rep#3 ug/L	Rep#4 ug/L	Rep#5 ug/L	Rep#6 ug/L	Rep#7 ug/L	Rep#8 ug/L	Mean ug/L	Amt. ug/L	S.Dev. ug/L	MDL ug/L	Report Limit ug/L
Benzyl chloride	0.51	0.50	0.49	0.50	0.51	0.43	0.29	0.41	0.46	0.5	0.077	0.23	0.5
1,2-Dichlorobenzene	0.62	0.54	0.53	0.60	0.57	0.58	0.50	0.47	0.55	0.5	0.051	0.15	0.5
n-Butyl benzene	0.67	0.54	0.53	0.60	0.57	0.51	0.53	0.38	0.54	0.5	0.083	0.25	0.5
1,2-Diethylbenzene	0.63	0.51	0.52	0.60	0.58	0.52	0.50	0.40	0.53	0.5	0.071	0.21	0.5
1,2-Dibromo-3-chloropropane	0.27	0.28	0.36	0.30	0.34	0.31	0.06	0.33	0.28	0.5	0.094	0.28	0.5
1,2,4-trichlorobenzene	0.47	0.42	0.40	0.50	0.47	0.48	0.41	0.38	0.44	0.5	0.044	0.13	0.5
Hexachlorobutadiene	0.48	0.40	0.35	0.44	0.39	0.39	0.39	0.28	0.39	0.5	0.059	0.18	0.5
Naphthalene	0.51	0.49	0.50	0.57	0.58	0.60	0.48	0.52	0.53	0.5	0.045	0.14	0.5
1,2,3-Trichlorobenzene	0.46	0.42	0.42	0.53	0.49	0.49	0.43	0.41	0.46	0.5	0.043	0.13	0.5

Reporting Limit = Low Level Standard

Attachment 2 (continued)

Method Detection Limit Study

Study date: March 4, 2000
Instrument: F50057

GCMS Volatile SW846 8260B/5030B Aqueous, 5 ml Purge

Compound Name	Rep#1	Rep#2	Rep#3	Rep#4	Rep#5	Rep#6	Rep#7	Rep#8	Rep#9	ep#10	Mean	Amt.	S.Dev.	MDL	Report Limit
	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L
Dichlorodifluoromethane	1.84	1.41	1.33	1.21	1.17	1.15	1.06	0.99	1.25	1.39	1.28	2.5	0.24	0.67	5.0
Chloromethane	1.89	1.46	1.51	1.36	1.36	1.41	1.29	1.27	1.46	1.67	1.47	2.5	0.19	0.53	5.0
Vinyl Chloride	2.02	1.60	1.52	1.42	1.34	1.32	1.19	1.16	1.37	1.57	1.45	2.5	0.25	0.70	5.0
Bromomethane	2.58	1.97	1.93	1.68	1.50	1.58	1.46	1.39	1.38	1.64	1.71	2.5	0.37	1.04	5.0
Chloroethane	2.31	1.75	1.69	1.62	1.52	1.55	1.49	1.38	1.63	1.78	1.67	2.5	0.26	0.72	5.0
Trichlorofluoromethane	2.35	1.84	1.73	1.63	1.50	1.50	1.40	1.33	1.59	1.78	1.67	2.5	0.29	0.82	5.0
1,1-Dichloroethene	2.24	1.71	1.65	1.51	1.38	1.41	1.30	1.25	1.44	1.64	1.55	2.5	0.29	0.81	5.0
Acetone	4.57	3.10	3.37	5.06	4.66	4.41	4.41	4.12	5.43	5.21	4.43	6.3	0.75	2.12	12.5
1,1,2-trichloro-1,2,2-trifluoroethane	2.14	1.63	1.51	1.39	1.25	1.28	1.20	1.13	1.53	1.72	1.48	2.5	0.30	0.85	5.0
Carbon disulfide	2.67	2.07	2.07	1.90	1.69	1.74	1.64	1.54	1.75	1.97	1.90	2.5	0.32	0.91	5.0
Methyl acetate	1.92	1.21	1.46	2.03	2.26	1.62	1.74	1.61	2.63	2.70	1.92	2.5	0.49	1.39	5.0
Methylene Chloride	3.08	2.40	2.48	2.37	2.23	2.43	2.32	2.39	2.50	2.82	2.50	2.5	0.26	0.72	5.0
trans-1,2-Dichloroethene	3.00	2.00	2.00	2.00	2.00	2.00	2.00	1.00	2.00	2.00	2.00	2.5	0.47	1.33	5.0
trans-1,2-Dichloroethene (in total)	2.57	1.89	1.91	1.76	1.62	1.65	1.56	1.49	1.66	1.88	1.80	2.5	0.31	0.87	5.0
Methyl-tert-butyl-ether	2.63	1.82	1.95	1.98	1.81	1.82	1.78	1.77	1.79	2.06	1.94	2.5	0.26	0.74	5.0
1,1-Dichloroethane	2.90	2.21	2.25	2.11	1.93	1.98	1.89	1.83	1.99	2.20	2.13	2.5	0.31	0.87	5.0
cis-1,2-Dichloroethene	3.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.10	2.5	0.32	0.89	5.0
cis-1,2-Dichloroethene (in total)	2.79	2.07	2.13	2.01	1.87	1.89	1.80	1.75	1.88	2.08	2.03	2.5	0.30	0.84	5.0
2-Butanone	3.53	1.72	2.24	3.39	2.82	3.05	2.95	3.07	2.33	3.11	2.82	6.3	0.56	1.58	12.5
Chloroform	3.19	2.65	2.31	2.23	2.45	2.45	2.26	2.17	2.48	2.62	2.48	2.5	0.30	0.84	5.0
1,1,1-Trichloroethane	2.89	2.15	2.07	1.91	1.88	1.84	1.75	1.68	1.93	2.13	2.02	2.5	0.34	0.96	5.0
Cyclohexane	2.11	1.65	1.49	1.38	1.31	1.30	1.22	1.10	1.40	1.56	1.45	2.5	0.28	0.79	5.0
Carbon tetrachloride	2.55	1.96	1.82	1.74	1.66	1.63	1.56	1.48	1.71	1.87	1.80	2.5	0.30	0.85	5.0
1,2-Dichloroethane	2.72	1.99	2.06	2.01	1.93	1.93	1.88	1.88	1.91	2.12	2.04	2.5	0.25	0.71	5.0
Benzene	2.65	2.11	2.07	1.99	1.90	1.93	1.83	1.77	1.93	2.15	2.03	2.5	0.25	0.70	5.0
Trichloroethene	2.32	1.75	1.44	1.62	1.54	1.60	1.48	1.43	1.60	1.78	1.66	2.5	0.26	0.74	5.0
Methylcyclohexane	1.89	1.41	1.01	1.18	1.11	1.09	1.00	0.93	1.12	1.33	1.21	2.5	0.28	0.79	5.0
1,2-Dichloropropane	2.59	1.99	1.62	1.91	1.82	1.88	1.79	1.72	1.84	2.05	1.92	2.5	0.27	0.75	5.0
Bromodichloromethane	2.77	2.12	1.76	2.06	1.95	1.99	1.89	1.84	1.92	2.14	2.04	2.5	0.28	0.80	5.0

Reporting Limit = Low Level Standard

Attachment 2 (continued)

Method Detection Limit Study

Study date: March 4, 2000
Instrument: F50057

GCMS Volatile SW846 8260B/5030B Aqueous, 5 ml Purge

Compound Name	Rep#1 ug/L	Rep#2 ug/L	Rep#3 ug/L	Rep#4 ug/L	Rep#5 ug/L	Rep#6 ug/L	Rep#7 ug/L	Rep#8 ug/L	Rep#9 ug/L	ep#10 ug/L	Mean ug/L	Amt. ug/L	S.Dev. ug/L	MDL ug/L	Report Limit ug/L
cis-1,3-Dichloropropene	2.56	1.93	1.50	1.86	1.79	1.78	1.66	1.64	1.71	1.90	1.83	2.5	0.29	0.81	5.0
4-Methyl-2-pentanone	5.88	3.37	3.01	4.47	3.93	4.27	4.09	4.29	3.59	4.40	4.13	6.3	0.78	2.20	12.5
Toluene	2.66	1.97	1.83	1.89	1.78	1.81	1.70	1.67	1.78	2.02	1.91	2.5	0.28	0.80	5.0
trans-1,3-Dichloropropene	2.44	1.72	1.66	1.83	1.73	1.72	1.66	1.64	1.65	1.85	1.79	2.5	0.24	0.68	5.0
1,1,2-Trichloroethane	2.52	1.80	1.78	2.04	1.95	1.95	1.93	1.91	1.87	2.15	1.99	2.5	0.22	0.61	5.0
Tetrachloroethene	2.39	1.78	1.64	1.70	1.58	1.61	1.48	1.45	1.60	1.99	1.72	2.5	0.28	0.79	5.0
2-Hexanone	4.04	2.63	2.67	4.18	3.50	3.98	3.74	3.96	3.07	3.94	3.57	6.3	0.58	1.64	12.5
Dibromochloromethane	2.57	1.87	1.78	1.99	1.90	1.90	1.85	1.82	1.82	2.03	1.95	2.5	0.23	0.65	5.0
1,2-Dibromoethane	2.38	1.73	1.74	2.00	1.89	1.90	1.88	1.86	1.84	2.09	1.93	2.5	0.19	0.54	5.0
Chlorobenzene	2.73	2.14	2.08	2.06	1.98	1.99	1.94	1.89	1.96	2.20	2.10	2.5	0.24	0.68	5.0
Ethylbenzene	2.30	1.75	1.67	1.70	1.61	1.67	1.54	1.52	1.64	1.85	1.73	2.5	0.22	0.63	5.0
m,p-Xylene	2.48	1.92	1.88	1.83	1.74	1.76	1.66	1.61	1.74	1.98	1.86	2.5	0.25	0.69	5.0
m,p-Xylene (in total)	2.48	1.92	1.88	1.83	1.74	1.76	1.66	1.61	1.74	1.98	1.86	2.5	0.25	0.69	5.0
o-Xylene	2.38	1.81	1.78	1.78	1.70	1.69	1.65	1.58	1.54	1.72	1.76	2.5	0.23	0.66	5.0
o-Xylene (in total)	2.38	1.81	1.78	1.77	1.70	1.69	1.65	1.58	1.54	1.72	1.76	2.5	0.23	0.66	5.0
Styrene	2.53	1.95	1.93	1.87	1.81	1.82	1.77	1.71	1.66	1.85	1.89	2.5	0.24	0.68	5.0
Bromoform	2.61	1.86	1.86	2.02	2.02	1.85	1.85	1.97	1.72	1.91	1.97	2.5	0.24	0.69	5.0
Isopropyl benzene	2.53	1.96	1.93	1.66	1.65	1.58	1.54	1.50	1.57	1.77	1.77	2.5	0.31	0.88	5.0
1,1,2,2-Tetrachloroethane	2.40	1.79	1.81	2.15	2.06	2.04	2.03	2.06	1.99	2.21	2.05	2.5	0.18	0.50	5.0
1,3-Dichlorobenzene	2.64	2.03	1.98	1.96	1.85	1.85	1.81	1.75	1.86	2.10	1.98	2.5	0.25	0.72	5.0
1,4-Dichlorobenzene	2.74	2.16	2.08	2.04	2.00	2.03	1.95	1.86	1.93	2.20	2.10	2.5	0.25	0.70	5.0
1,2-Dichlorobenzene	2.68	2.05	2.01	1.94	1.88	1.89	1.84	1.76	1.86	2.14	2.01	2.5	0.26	0.74	5.0
1,2-Dibromo-3-chloropropane	1.46	0.90	0.99	1.38	1.44	1.24	1.22	1.30	1.21	1.47	1.26	2.5	0.19	0.55	5.0
1,2,4-trichlorobenzene	2.61	1.90	1.92	1.79	1.70	1.51	1.72	1.53	1.51	2.01	1.82	2.5	0.33	0.93	5.0

Reporting Limit = Low Level Standard

COMPUCHEM, a division of Liberty Analytical Corp DATE ___/___/___ INITIAL TIME OF TUNE_____ SHIFT/S(A)_____(B)_____(C)_____

VOLATILE GC/MS RUN LOG TIME TUNE EXPIRES_____ LINKER /METHOD_____

COMPUCHEM LOGBOOK 11 Z 13 (F50055)

PREVENTIVE MAINTENANCE_____

	REJECTED	FILE NAME	REPORTED	DATE	TIME	CLIENT ID#	CASE/SDG#	AMOUNT INJECTED	CHEMIST	COMMENTS(ETC.)/DISPOSITION
1				/ /						
2				/ /						
3				/ /						
4				/ /						
5				/ /						
6				/ /						
7				/ /						
8				/ /						
9				/ /						
10				/ /						
11				/ /						
12				/ /						
13				/ /						
14				/ /						
15				/ /						
16				/ /						
17				/ /						
18				/ /						
19				/ /						
20				/ /						
21				/ /						
22				/ /						
23				/ /						
24				/ /						

STANDARDS

	Tune	Analytical	Int. Std.
Std. ID #			
Lot #			

SUPERVISOR APPROVAL_____

The presence of the Chemist's employee ID number, or signature, on this run log attests that strict compliance with the method's SOP has occurred. Any SOP deviations require documentation by the responsible chemist together with the chemist's initials and the initials of the lab supervisor and a QA department representative, signifying approval of the deviation.

7/18/00.mlj

Attachment 4

Analyst Capability Study

Laboratory Name/North Carolina Certificate Number: CompuChem/79
Analyst: Jeremy Smith
Study Date: April 18, 2000
Method: 5035/8260B, 5gm Soil
Instrument/Column/Detector: f50052

Compounds	TrueVal ug/kg	Rep #1 ug/kg	Rep #2 ug/kg	Rep #3 ug/kg	Rep #4 ug/kg	Mean ug/kg	Mean % R	EPA %R	SD(n-1) ug/kg	EPA %RSD	-3SD of (x)	+3SD of (x)	-3SD % R	+3SD %R	RSD %
Dibromofluoromethane	50	55.16	54.72	50.24	54.07	53.55	107	NA	2.25	NA	46.8	60.3	87	113	4.2
1,2-Dichloroethane-d4	50	55.39	56.72	52.84	54.28	54.81	110	NA	1.65	NA	49.9	59.8	91	109	3.0
Toluene-d8	50	48.85	49.86	45.84	48.42	48.24	96	NA	1.71	NA	43.1	53.4	89	111	3.5
Bromofluorobenzene	50	48.68	48.32	42.59	45.19	46.20	92	NA	2.87	NA	37.6	54.8	81	119	6.2
Chloromethane	50	48.03	46.52	41.81	45.74	45.53	91	NA	2.65	NA	37.6	53.5	83	117	5.8
Vinyl Chloride	50	46.69	44.65	38.97	44.32	43.66	87	34.2	3.30	13.0	33.8	53.5	77	123	7.5
Bromomethane	50	53.44	53.89	47.79	51.74	51.72	103	NA	2.78	NA	43.4	60.0	84	116	5.4
Chloroethane	50	60.40	59.08	53.29	58.47	57.81	116	NA	3.12	NA	48.5	67.2	84	116	5.4
1,1-Dichloroethene	50	53.53	55.28	48.78	52.65	52.56	105	79.2	2.75	5.7	44.3	60.8	84	116	5.2
Acetone	130	145.6	145.1	149.7	147.5	147.0	113	NA	2.08	NA	140.7	153.2	96	104	1.4
Carbon disulfide	50	53.52	55.46	49.62	53.18	52.95	106	NA	2.43	NA	45.6	60.2	86	114	4.6
Methylene Chloride	50	59.07	57.92	51.39	56.62	56.25	113	107	3.39	9.1	46.1	66.4	82	118	6.0
trans-1,2-Dichloroethene	50	54.97	55.73	49.14	53.05	53.22	106	104	2.95	0.7	44.4	62.1	83	117	5.5
Methyl tert butyl ether	50	58.46	59.68	54.58	56.71	57.36	115	NA	2.22	NA	50.7	64.0	88	112	3.9
1,1-Dichloroethane	50	51.63	54.30	47.29	50.78	51.00	102	84.4	2.89	6.4	42.3	59.7	83	117	5.7
cis-1,2-Dichloroethene	50	54.79	57.23	49.56	52.02	53.40	107	113	3.33	9	43.4	63.4	81	119	6.2
2-Butanone	130	128.5	124.5	126.4	132.0	127.9	98	NA	3.21	NA	118.3	137.5	92	108	2.5
Chloroform	50	55.08	58.27	51.15	54.26	54.69	109	116	2.93	12.2	45.9	63.5	84	116	5.4
1,1,1-Trichloroethane	50	51.59	53.51	47.34	51.33	50.94	102	117	2.59	21.2	43.2	58.7	85	115	5.1
Carbon tetrachloride	50	56.22	59.49	53.77	58.58	57.02	114	112	2.56	9.4	49.3	64.7	87	113	4.5
1,2-Dichloroethane	50	56.49	57.33	52.43	56.12	55.59	111	NA	2.17	NA	49.1	62.1	88	112	3.9
Benzene	50	49.77	52.32	44.86	48.70	48.91	98	103	3.10	11.2	39.6	58.2	81	119	6.3
Trichloroethene	50	53.47	55.09	48.43	50.17	51.79	104	94.6	3.03	12.7	42.7	60.9	82	118	5.9
1,2-Dichloropropane	50	51.36	52.93	46.55	48.84	49.92	100	117	2.81	10.5	41.5	58.3	83	117	5.6
Bromodichloromethane	50	56.84	59.52	52.46	55.27	56.02	112	117	2.95	13.1	47.2	64.9	84	116	5.3
cis-1,3-Dichloropropene	50	54.47	57.15	48.88	50.81	52.83	106	NA	3.70	NA	41.7	63.9	79	121	7.0

Attachment 4 (continued)

Analyst Capability Study

Laboratory Name/North Carolina Certificate Number: CompuChem/79
Analyst: Jeremy Smith
Study Date: April 18, 2000
Method: 5035/8260B, 5gm Soil
Instrument/Column/Detector: f50052

Compounds	TrueVal ug/kg	Rep #1 ug/kg	Rep #2 ug/kg	Rep #3 ug/kg	Rep #4 ug/kg	Mean ug/kg	Mean % R	EPA %R	SD(n-1) ug/kg	EPA %RSD	-3SD of (x)	+3SD of (x)	-3SD % R	+3SD %R	RSD %
4-Methyl-2-pentanone	130	122.1	116.4	120.0	127.6	121.5	93	NA	4.68	NA	107.5	135.6	88	112	3.9
Toluene	50	48.19	49.79	45.38	48.02	47.85	96	118	1.83	16.9	42.4	53.3	89	111	3.8
trans-1,3-Dichloropropene	50	53.69	54.96	51.11	52.83	53.15	106	NA	1.62	NA	48.3	58.0	91	109	3.0
1,1,2-Trichloroethane	50	50.80	51.03	48.82	54.06	51.18	102	111	2.16	12.1	44.7	57.7	87	113	4.2
Tetrachloroethene	50	51.16	52.03	48.45	51.95	50.90	102	NA	1.68	NA	45.9	55.9	90	110	3.3
2-Hexanone	130	120.6	119.6	119.7	122.5	120.6	93	NA	1.36	NA	116.5	124.7	97	103	1.1
Dibromochloromethane	50	56.73	57.40	52.38	56.46	55.74	111	118	2.28	12.5	48.9	62.6	88	112	4.1
Chlorobenzene	50	52.07	52.48	47.87	49.63	50.51	101	99.3	2.16	15	44.0	57.0	87	113	4.3
Ethylbenzene	50	50.75	52.58	46.32	47.34	49.25	98	112	2.92	17.5	40.5	58.0	82	118	5.9
m,p-Xylene	100	97.59	104.76	90.44	94.19	96.75	97	98.5	6.09	15.7	78.5	115.0	81	119	6.3
o-Xylene	50	50.15	52.09	45.95	46.33	48.63	97	103	2.99	17.3	39.7	57.6	82	118	6.1
Styrene	50	48.39	52.51	44.56	45.84	47.83	96	101	3.51	15.7	37.3	58.3	78	122	7.3
Bromoform	50	57.64	60.05	56.53	61.67	58.97	118	122	2.32	9.9	52.0	65.9	88	112	3.9
1,1,1,2-Tetrachloroethane	50	55.25	53.05	49.84	57.87	54.00	108	NA	3.40	NA	43.8	64.2	81	119	6.3
1,2-Dichloroethene (total)	100	109.8	112.6	98.6	105.3	106.6	107	NA	6.11	NA	88.2	124.9	83	117	5.7
Xylene (total)	150	161.7	171.8	149.3	154.0	159.2	106	NA	9.84	NA	129.7	188.7	81	119	6.2

CompuChem
a division of Liberty Analytical Corporation

501 Madison Avenue
Cary, NC 27513

SOP DOCUMENTATION FORM

This form must accompany all new and revised Standard Operating Procedures (SOPs) when you turn them in to Quality Assurance for review. Please fill out the entire shaded area (except effective date).

This is a new procedure _____ revised procedure ✓ outdated procedure (archive) _____

- Procedure area, title, and SOP number: Section #: 2.5.2.1 Effective date: (QA fills in)
  SPP-079: Preparation of Water Samples for the Analysis of Low Level Semivolatiles by SW846 and NYSASP — 12/5/00
- Procedure prepared by: Linda Carter — Date: 11/20/00
- Procedure approved by: (If the manager prepared the SOP, a qualified second party should sign): Bob [illegible] — Date: 11/21/00
- Reason for change: NELAC format changes
- This procedure meets the requirements of the following approved method references:
  Test Methods for Evaluating Solid Waste: Physical/Chemical Methods, 3rd Edition, Update III, 12/96, Method 3510C and 8270C, New York State Analytical Services Protocol (NYSASP), 10/95

Procedure approved by Quality Assurance Representative: Date:
(Not needed if signed above)

_____ _____

Effective 1-1-96, on an annual basis: Lab managers are required to review lab practices and revise the SOP if necessary. If no revision is necessary, indicate by your signature that the SOP has been reviewed.

Annual Review—Signature: _____ Date: _____

Annual Review—Signature: _____ Date: _____

Annual Review—Signature: _____ Date: _____

Sample Preparation Procedure -079: **Preparation of Water Samples for the Analysis of Low Level Semivolatiles by SW-846 and NYSASP**

1.0 Scope and Application

This procedure is **described the extraction of semivolatile organic compounds from water samples prior to GC/MS analysis.**

Method detection limits (MDL) and reporting limits are shown in Attachment 1.

Staff members performing the procedures described in this SOP are responsible for reading, understanding, and complying with the SOP requirements. Supervisors are responsible for directing the analyst to the controlled SOP, and providing adequate explanation of the material contained therein.

This procedure is restricted to use by or under the supervision of analysts experienced in the instrumentation or preparative methods and who have demonstrated the ability to generate acceptable results through QC samples and analyst capability studies.

2.0 Summary **of Method**

A 1-liter volume of sample is spiked with the semivolatile surrogate solution, and acid and base/neutral fractions are extracted **by separatory funnel** with methylene chloride. The acid and base/neutral methylene chloride extracts are dried, combined, concentrated, and submitted for GC/MS analysis. Alternatively, acid/neutral and base fractions may be generated **separately**.

3.0 Definitions

3.1 Method detection limit (MDL) – The minimum concentration of an analyte that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte (40 CFR, Part 136, Appendix B.)

3.2 Reporting Limit – The laboratory reporting limit is based on the lowest multipoint calibration standard concentration. For some inorganic methods, the reporting limit is based on the MDL, and is usually 4-8 times higher than the MDL. For organic methods, values detected below the reporting limit and above the MDL may be reported and qualified as an estimated concentration.

If the low level standard concentration is not at least three times higher than the MDL value, the standard concentration is adjusted upward in order to achieve this minimal ratio. It may be adjusted higher than three times depending on the concentration range of the calibration curve and the ability to

meet method linearity requirements. An exception to this is for CLP methods where the MDL is only required to be lower than the reporting limit.

The reporting limit for CLP is the Contract Required Quantitation Limit (CRQL) for organics and the Contract Required Detection Limit (CRDL) for inorganics.

3.3 Reporting Units – µg/L

3.4 An SDG is defined by the following, whichever is more frequent:

- **each 20 field samples received within a case, or**
- **each 14 calendar day period during which field samples in a case are received (7 calendar days for NYSASP, OLM04.0, plus revisions, and ILM04.0, plus revisions including ILM04.1) beginning with the receipt of the first sample.**

NOTE: The Army Corps of Engineers does not accept the SDG approach, unless the samples are prepared in a single batch. When a group of up to 20 field samples of a similar matrix are prepared as one batch, method-specified QC samples such as a method blank, laboratory control sample, matrix spike, matrix spike duplicate, and matrix duplicate must also be prepared together at a rate of 5%. If samples are batched together from different sites, project-specific QC must be processed.

4.0 Interferences

4.1 Method interferences may be caused by contaminants in reagents, solvents, glassware, and other sample-processing hardware that lead to discrete artifacts or elevated baselines in the total ion current profiles (TICPs). All of these materials must be routinely demonstrated to be free of interferences under the conditions of the analysis by preparing and analyzing laboratory reagent blanks.

4.2 Matrix interferences may be caused by contaminants that were inadvertently co-extracted from the sample. The extent of matrix interferences will vary considerably from sample to sample. Matrix spike/matrix spike duplicate (MS/MSD) analyses will be done to determine the possible matrix interferences.

4.2.1 For sample extracts demonstrating matrix interferences, gel permeation cleanup procedure, Method 3640A, is an option.

5.0 Safety

Appropriate protective equipment and clothing must be used under the assumption that all samples are potentially hazardous. During sample preparation, safety glasses, gloves and lab coats are a minimum requirement. The persistent presence of noxious

odors may be indicative of failure of the laboratory ventilation system and must be reported to a supervisor or manager.

Laboratory staff are encouraged to review the Chemical Hygiene Plan for general safety policies, and Material Safety Data Sheets (MSDS) for solvents and reagents used in the laboratory. The MSDS are located in the Quality Assurance department.

6.0 Equipment & Supplies

6.1 one 2-liter separatory funnel with ground-glass stopper and stopcock

6.2 one, 1-liter graduated cylinder

6.3 one Erlenmeyer Teflon flask

6.4 one drying column

6.5 one Kuderna-Danish apparatus (consists of a concentrator tube and a K-D flask)

6.6 one glass stirring rod (can be used for all samples)

6.7 boiling chips (silicon carbide, furnaced at 800°C for 30 minutes)

6.8 rubber bands

6.9 nitrogen evaporation device (Organomation, or equivalent)

6.10 pH paper (wide range)

6.11 glass wool (furnaced at 400°C for 4 hours)

6.12serological pipet (1.0 ml) with 1/100 ml graduations

6.13 one amber 2-ml vial with a Teflon-lined screw cap

7.0 Reagents & Standards

All standards are prepared by the Organic Standards chemist. Details for the preparation are contained in the standard operating procedures (SOP) for that area (Section 7.0 of the SOP collection.) Standards are stored separate from samples at 4 ± 2°C in the reach in unit in the laboratory when not in use.

7.1 Reagent water – All water used in this procedure must be equivalent to ASTM Type II water (as it relates to specific conductance and specific resistance) which is demonstrated to meet the blank contamination acceptance criteria

contained in this Standard Operating Procedure (SOP). It is referred to throughout the remainder of this SOP as DI water.

7.2 Sodium hydroxide solution 50%

7.3 Sulfuric acid - concentrated.

7.4 Acetone – **pesticide residue analysis grade, or equivalent**

7.5 Methanol - pesticide residue analysis grade, or equivalent

7.6 Methylene chloride - pesticide residue analysis grade or equivalent

7.7 Sodium sulfate (ACS) - powdered, anhydrous.

7.7.1 Purify by heating at 400°C for four hours in a shallow tray. Cool in a desiccator, and store in a glass bottle.

7.8 Surrogate Standard Spiking Solution

7.7.1 Base/neutral and acid surrogate #393 is used at a volume of 1.0 ml per 1000-ml sample.

7.9 Base/Neutral and Acid Matrix Standard Spiking Solution

7.9.1 The matrix standard spiking solution should consist of base/neutral and acid compounds (Table 1).

7.9.2 8270 validation spike is used at a volume of 1.0 ml per blank spike (1-liter sample volume).

Table 1. Base/Neutral and Acid Compounds in Matrix Spiking Solution

Bases/Neutrals	Acids
1,2,4-Trichlorobenzene	Pentachlorophenol
Acenaphthene	Phenol
2,4-Dinitrotoluene	2-Chlorophenol
Pyrene	4-Chloro-3-
Methyphenol	1,4-Dichlorobenzene
4-Nitrophenol	N-Nitroso-di-n-propylamine

8.0 Sample Collection, Preservation, & Storage

8.1 Samples are collected, preserved, and stored according to the tables in Sample Control SOPs 4.1, "Receiving Samples" and 4.6, "Storing Samples." Sample holding times are also listed.

8.2 All extracts must be analyzed within 40 days of extraction.

8.3 Prior to analysis, all extracts must be stored under refrigeration at 2-4.4° C in the reach-in storage unit in the laboratory. After analysis, extracts are returned to Sample Control for long-term storage and disposal.

9.0 Quality Control

9.1 Method Blank

9.1.1 A method blank is prepared with each extraction batch of up to 20 samples.

9.2 Laboratory Control Sample

9.2.1 A laboratory control sample (LCS, or blank spike, BS, or matrix spike blank for NYSASP) must be prepared with each extraction batch of up to 20 samples.

9.3 A matrix spike and matrix spike duplicate (MS/MSD) are prepared for each sample delivery group (SDG).

9.4 Duplicates, at a frequency of 10%, are required when processing samples submitted to meet the regulatory requirements of North Carolina. The MS/MSD satisfy the duplicate requirement for the NC DENR.

10.0 Calibration & Standardization

NA

11.0 Procedure

Documentation must follow the requirements in QC SOP: Proper Documentation Procedures. All standards are prepared by the Organic Standards chemist. Details for the preparation are contained in the standard operating procedures (SOP) for that area (Section 7.0 of the SOP collection.) Standards are stored separately from samples in the reach-in refrigeration unit in the Sample Preparation laboratory at 2-4.4° C when not in use.

11.1 Preparation of Equipment

11.1.1 Cover all work areas with plastic-backed, absorbent table covering, with the plastic side down.

11.1.2 Assemble the following glassware for each sample to be processed:

11.1.2.1 one 2-liter separatory funnel with ground-glass stopper and stopcock

11.1.2.2 one, 1-liter graduated cylinder

11.1.2.3 one Erlenmeyer Teflon flask

11.1.2.4 one drying column

11.1.2.5 one Kuderna-Danish apparatus (consists of a concentrator tube and a K-D flask)

11.1.2.6 one glass stirring rod (can be used for all samples)

11.1.3 Rinse each of the items listed above with methylene chloride. Empty the methylene chloride into a solvent waste container.

NOTE: By rinsing and emptying each item, all glassware and spatula surfaces have been extracted with methylene chloride before the sample extraction has begun. This practice is intended to keep sample contamination to a controlled minimum. Please adhere to this practice. If the glassware selected for use is wet, it must be rinsed with acetone prior to the methylene chloride rinses. Several additional methylene chloride rinses should be performed to remove all possible contaminants contained in the acetone.

11.1.4 Add a small plug of furnaced glass wool to each drying column, then add 1-2 inches of prepared sodium sulfate to each drying column. Rinse the sodium sulfate with approximately 20 ml of methylene chloride. Allow the methylene chloride to drain through the column into a waste container.

11.1.5 Place the 2-liter separatory funnels in the rings located on one side of the rack. Place the Erlenmeyer flasks on the counter-top under each funnel. *Place the drying columns and K-D apparatus in the clamp on the other side of* the rack, so that the tip of each prepared drying column is inside the neck of a K-D flask.

11.1.6 Label each piece of glassware with the sample number.

11.2 Sample Preparation and Extraction

11.2.1 Using a 1 liter graduated cylinder measure 1 liter (nominal) of sample. If samples arrive in a 1 liter bottle, pour up and measure the entire sample volume. Rinse the sample container with the first 60 ml aliquot of methylene chloride. Record the initial volume on the worksheet. (Attachment **2**)

11.2.2 Pour the sample into its associated separatory funnel.

11.2.3 Add 1.0 ml of surrogate standard #393 to each production sample by using the serological pipet. It is important to add exactly 1.0 ml, since surrogate recoveries are used to judge the efficiency of the extraction. Record the surrogate standard ID number, the lot number, and volume added, on the extraction worksheet.

11.2.4 **A method blank is prepared using 1000 ml DI water and spiking with 1.0 ml of surrogate standard #393.**

11.2.5 Use 1000-ml sample volume for **the matrix** spikes and 1000 mL of **DI** water for the blank spike (BS). **Add 1.0 ml of surrogate standard #393 and 1.0 ml of the 8270 validation spike standard to the LCS and MS/MSD. Record the standard ID numbers, the lot numbers, and volume added on the extraction worksheet.**

11.2.6 Measure the initial pH, using wide range pH paper.

11.2.7 Add a few **milliliters** of 50% sodium hydroxide. Stopper the separatory funnel and shake for 20-30 seconds, venting the stopcock several times. Check the pH. If the value is 11 or greater, note the pH on the Extraction Worksheet. If the pH is not 11 or greater, continue to add 1 ml at a time of the base, and shake until the pH has reached a value of 11 or greater. The sample is now ready for the base-neutral extraction.

11.2.8 Add 60 ml of methylene chloride to each raw sample bottle or sample-measuring container. Rotate the containers to rinse all surfaces with the solvent, and pour the methylene chloride into the appropriate 2-liter separatory funnel. Stopper each funnel and shake vigorously for 2 minutes. Be careful to vent the stopcock frequently, until the pressure equalizes.

11.2.9 Allow each separatory funnel to hang undisturbed for approximately 10 minutes, to allow the layers to separate. If an emulsion larger than two thirds the size of the bottom layer (methylene chloride) forms, steps must be taken to break it up. Emulsions may be broken by stirring, passing through the stopcock very slowly, or centrifugation. The method used is determined by the severity of the emulsion.

11.2.10 When two distinct layers are obtained, drain the lower layer (methylene chloride) into the Erlenmeyer flask. Close the stopcock when the water layer reaches the stopcock. The object is to collect all of the methylene chloride and none of the water.

11.2.11 Repeat steps **11.2.8 - 11.2.10** two more times.

11.2.12 Upon completion of the third extraction, collect all of the organic layer in the Erlenmeyer flask. Pour the total extract through the drying column into the K-D apparatus. Rinse the Erlenmeyer flask with a small amount of methylene chloride and add the rinse to the drying column. Rinse the

drying column with approximately 20 ml of methylene chloride and collect the rinse in the K-D apparatus.

11.2.13 Slowly add concentrated sulfuric acid to each separatory funnel. Stopper the separatory funnel and shake for 20-30 seconds, venting the stopcock several times. Check the pH. If the pH is now 2 or less, note the pH on the **extraction worksheet**. If the pH is not 2 or less, continue to add 10-ml volumes of acid. Shake and measure the pH until a value of 2 or less is reached.

Note: The pH adjustment may be reversed if necessary, i.e. acids first, then base/neutral. Some projects such as those from the Army Corps of Engineers require an acid first extraction.

11.2.14 Once a pH of 2 or less has been reached and the pH recorded, the sample is ready for the acid extraction. Perform steps **11.2.8 – 11.2.10** which will result in a combined base/neutral and acid extract.

11.3 Extract Concentration

11.3.1 Add 2-3 boiling chips to each K-D flask and attach a Snyder column. If the Snyder column is dry after the rinsing process, add 1-2 ml of methylene chloride to the top of the Snyder column.

11.3.2 Place the combined base/neutral and acid extract on a water bath set at 85-95°C.

11.3.3 Remove each K-D flask from the bath as soon as an apparent volume of 4 ml is reached and allow it to drain.

11.3.4 Remove the Snyder column and K-D flask from the concentrator tube and remember to label the concentrator tubes with the proper label. Place the concentrator tube in the rack and continue the concentration on the Organomation.

11.3.5 Final concentration volume should be 1.0 ml for production samples and blanks. For sample spikes and blank spikes the volume should also be 1.0 ml.

11.3.6 Transfer the entire extract volume with a transfer pipet to an amber, 2-ml autosampler vial. Label the vial appropriately to indicate fraction type (orange to indicate S-V fraction), Prep Code, CompuChem number, and completion date. At the time of transfer, note the final volume on the **Extraction worksheet**.

11.3.7 Complete the paperwork, mark the volume on the vials, and forward both to the person responsible for reviewing the paperwork.

11.3.8 Place the paperwork and the extracts in the turn-in box. **The extract is now ready for GC/MS analysis described in Instrument Procedure**

477, "GC/MS Analysis of Extractable Semivolatiles in Aqueous and Solid Samples by SW-846 and NYSASP."

11.4 **Work Area** Cleanup

11.4.1 Remove all water from each separatory funnel and place it in a labeled water-waste container.

11.4.2 Rinse all glassware with methylene chloride and return it to the glassware preparation area for cleaning.

11.4.3 Pour all waste solvent into an appropriate container next to the low level, solid preparation area.

11.4.4 Roll up all absorbent counter covers and place them in the trash.

12.0 Data Analysis & Calculations

Calculations must be consistent with the QC SOP: Numerical Data Reduction.

13.0 Method Performance

This method was validated through in-house laboratory studies of method detection limits (Attachment 1) and precision and accuracy for single analyst (Attachment 3). The data are retained by the QA department.

14.0 Pollution Prevention

The solvents used in this procedure pose little threat to the environment when recycled and managed properly. Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best thing.

15.0 Waste Management

It is the laboratory's responsibility to comply with all federal, state, and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions, and to protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench

operations. Compliance with all sewage discharge permits and regulations is also required.

Samples preserved with HCl, HNO_3, or H_2SO_4 to pH <2 are hazardous and must be neutralized before being disposed, or must be handled as hazardous waste.

Refer to the Hazardous Waste Management and Safety SOPs located in the lab.

16.0 References

16.1 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846,3rd Edition, **12/96,** Methods 3510C **and 8270C**

16.2 New York State Analytical Services Protocol (NYSASP), **10/95**

16.3 Standard Methods for the Examination of Water and Wastewater, 18th Edition (1992) and 19th Edition (1995), upon promulgation, Method 1080

16.4 Code of Federal Register, 40 CFR, Part 136, "Guidelines for Establishing Test Procedures for Priority Pollutants"

16.5 QCSOP: Proper Documentation Procedures

16.6 QCSOP: Numerical Data Reduction

16.7 "Less is Better: Laboratory Chemical Management for Waste Reduction," American Chemical Society Department of Government Relations and Science Policy, 1155 16th Street, N.W., Washington DC, 20036, (202) 872-4477.

16.8 Hazardous Waste Management & Safety SOPs: "Hazardous Waste Disposal" and "Spill Control & Cleanup."

16.9 NELAC Standards, July 1, 1999, plus revisions

16.10 QA-G6: Guidance for the Preparation of Standard Operating Procedures for Quality-Related Operations EPA/600/R-96/027, November 1995.

16.11 New York State Environmental Laboratory Approval Program, Certification Manual, October 15, 1999, plus revisions.

16.12 CompuChem Quality Manual, Revision 0, 2/1/00, plus revisions

16.13 Sample Control SOP 4.1, "Receiving Samples"

16.14 Sample Control SOP 4.6, "Storing Samples"

16.15 Instrument Procedure 477, "GC/MS Analysis of Extractable Semivolatiles in Aqueous and Solid Samples by SW-846 and NYSASP."

17.0 **Attachments as Tables, Diagrams, Flowcharts & Validation Data**

17.1 Attachment 1 – Method Detection Limits

17.2 Attachment 2 - Extraction Worksheet **(-079)**

17.3 Attachment 3 – Single Analyst Capability Study

Attachment 1

Method Detection Limit Study

Study Date: February 9, 2000			GCMS Method 3510C/8270C Aqueous											
Instrument: 5972HP68														
Compound Name	Rep#1	Rep#2	Rep#3	Rep#4	Rep#5	Rep#6	Rep#7	Rep#8	Rep#9	Mean	Amt.	S.Dev.	MDL	Report Limit
	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L
n-Nitrosodimethylamine	2.35	2.53	2.76	3.43	2.52	1.87	2.18	2.63	2.97	2.58	5.0	0.45	1.31	10
Pyridine	4.73	6.47	5.60	6.57	4.98	4.06	7.21	4.98	4.79	5.49	5.0	1.04	3.03	10
Benzaldehyde	3.83	5.73	5.79	6.26	6.32	4.57	6.26	5.44	6.13	5.59	5.0	0.86	2.50	10
Phenol	1.97	2.45	2.40	3.01	2.65	1.96	2.81	2.47	2.51	2.47	5.0	0.35	1.00	10
Bis(2-chloroethyl)ether	3.62	4.34	3.99	4.95	4.31	3.40	4.71	4.02	4.41	4.19	5.0	0.49	1.43	10
2-Chlorophenol	3.47	4.50	3.94	4.94	4.26	3.68	4.49	4.00	4.01	4.14	5.0	0.45	1.31	10
1,3-Dichlorobenzene	3.37	3.94	3.86	4.29	3.60	2.90	4.23	3.94	3.83	3.77	5.0	0.43	1.25	10
1,4-Dichlorobenzene	3.21	3.55	3.80	4.25	3.54	2.81	4.39	3.45	3.71	3.63	5.0	0.49	1.41	10
Benzyl alcohol	2.36	3.12	3.73	3.81	3.20	2.72	3.07	3.27	3.63	3.21	5.0	0.47	1.37	10
1,2-Dichlorobenzene	3.11	3.86	3.63	4.35	3.85	2.97	4.40	3.66	3.86	3.74	5.0	0.48	1.40	10
2-Methylphenol	2.98	3.41	3.58	3.98	3.26	2.65	3.55	3.38	3.54	3.37	5.0	0.38	1.10	10
2,2'-oxybis(1-Chloropropane)	4.07	4.95	4.65	5.63	5.11	4.08	5.58	4.74	4.96	4.86	5.0	0.56	1.61	10
Acetophenone	3.85	4.73	4.95	5.02	4.53	4.00	5.31	4.94	5.03	4.71	5.0	0.49	1.43	10
3-Methylphenol	5.21	6.39	5.97	6.64	6.86	5.26	6.55	6.30	6.15	6.15	5.0	0.58	1.68	5
4-Methylphenol	5.21	6.39	5.97	6.64	6.86	5.26	6.55	6.30	6.15	6.15	5.0	0.58	1.68	5
n-Nitroso-di-n-propylamine	2.57	3.44	3.38	3.73	3.56	3.02	3.64	3.07	3.31	3.30	5.0	0.36	1.05	10
Hexachloroethane	3.16	3.77	3.87	4.29	3.51	2.61	4.24	3.28	3.74	3.61	5.0	0.54	1.55	10
Nitrobenzene	4.67	5.53	5.65	6.16	6.01	4.84	6.71	5.97	6.43	5.77	5.0	0.68	1.97	10
Isophorone	3.71	4.51	4.37	4.94	4.15	3.52	4.76	4.45	4.56	4.33	5.0	0.47	1.35	10
2-Nitrophenol	3.00	3.84	3.54	4.14	3.41	2.84	3.98	3.29	3.49	3.50	5.0	0.43	1.25	10
2,4-Dimethylphenol	1.51	1.95	2.08	2.11	2.07	1.30	2.13	2.08	2.08	1.92	5.0	0.30	0.88	10
Bis(2-chloroethoxy)methane	3.96	4.69	4.26	5.12	4.51	3.66	5.21	4.58	4.55	4.50	5.0	0.50	1.44	10
2,4-Dichlorophenol	3.03	3.38	3.28	3.56	3.16	3.08	3.78	3.38	3.25	3.32	5.0	0.24	0.69	10
1,2,4-Trichlorobenzene	3.02	3.53	3.48	3.73	3.78	2.86	4.27	3.58	3.74	3.55	5.0	0.42	1.21	10
Naphthalene	2.71	3.29	3.27	3.58	3.59	2.78	4.05	3.27	3.46	3.33	5.0	0.41	1.19	10
4-Chloroaniline	2.98	3.88	4.10	3.90	3.80	3.31	4.04	3.71	3.92	3.74	5.0	0.36	1.06	10
Hexachlorobutadiene	2.78	3.44	3.46	4.19	3.60	2.62	4.19	3.38	3.42	3.45	5.0	0.53	1.54	10
Caprolactam	2.42	4.26	4.03	3.49	3.90	3.43	1.70	3.31	2.90	3.27	20.0	0.82	2.37	10
4-Chloro-3-methylphenol	3.20	3.90	3.78	3.85	3.78	3.14	4.36	3.41	3.68	3.68	5.0	0.38	1.10	10

Reporting Limit = Low Level Standard

Attachment 1 (continued)

Method Detection Limit Study

Study Date: February 9, 2000 GCMS Method 3510C/8270C Aqueous
Instrument: 5972HP68

Compound Name	Rep#1 ug/L	Rep#2 ug/L	Rep#3 ug/L	Rep#4 ug/L	Rep#5 ug/L	Rep#6 ug/L	Rep#7 ug/L	Rep#8 ug/L	Rep#9 ug/L	Mean ug/L	Amt. ug/L	S.Dev. ug/L	MDL ug/L	Report Limit ug/L
2-Methylnaphthalene	4.05	4.86	4.62	4.85	4.83	3.78	5.36	4.52	4.59	4.61	5.0	0.47	1.35	10
1-Methylnaphthalene	3.38	3.84	4.18	4.21	3.99	3.37	4.44	4.00	4.23	3.96	5.0	0.37	1.08	10
Hexachlorocyclopentadiene	1.89	2.92	2.58	2.90	2.19	1.84	3.13	2.10	2.27	2.42	10.0	0.48	1.38	10
2,4,6-Trichlorophenol	6.44	7.97	7.71	8.75	8.08	6.62	7.82	6.50	7.67	7.51	10.0	0.81	2.33	10
2,4,5-Trichlorophenol	6.10	8.37	7.87	8.66	7.97	6.75	8.05	7.46	7.61	7.65	10.0	0.80	2.31	10
1,1'-Biphenyl	4.00	5.00	4.74	5.62	4.67	3.87	5.55	4.63	5.00	4.79	5.0	0.60	1.73	10
2-Chloronaphthalene	3.42	4.23	4.23	4.61	4.24	3.18	4.52	4.05	4.07	4.06	5.0	0.47	1.37	10
2-Nitroaniline	2.29	4.19	3.76	4.10	3.57	2.44	4.23	3.39	4.61	3.62	5.0	0.80	2.32	20
Dimethylphthalate	2.18	2.48	2.41	1.95	1.79	1.33	4.14	1.38	1.03	2.08	5.0	0.92	2.67	10
2,6-Dinitrotoluene	2.62	3.58	3.03	3.65	3.40	2.47	3.65	3.17	3.11	3.19	5.0	0.43	1.25	10
Acenaphthylene	2.73	3.65	3.37	3.73	3.47	2.71	3.78	3.16	3.23	3.31	5.0	0.40	1.15	10
3-Nitroaniline	4.95	7.72	7.63	8.91	7.50	6.59	8.56	6.92	7.50	7.36	10.0	1.16	3.35	20
Acenaphthene	2.81	3.52	3.33	3.80	3.39	2.95	3.74	3.15	3.28	3.33	5.0	0.33	0.96	10
2,4-Dinitrophenol	22.26	36.70	30.57	29.82	24.52	21.33	10.18	9.15	25.95	23.39	50.0	9.09	26.32	50
4-Nitrophenol	4.20	7.17	7.08	7.44	6.63	5.32	5.29	4.84	6.17	6.02	20.0	1.15	3.33	20
2,4-Dinitrotoluene	2.81	4.28	3.79	4.59	3.56	3.34	3.98	3.36	3.70	3.71	5.0	0.53	1.54	10
Dibenzofuran	3.84	4.81	4.23	5.13	4.44	3.72	4.94	4.25	4.46	4.42	5.0	0.48	1.38	10
Diethylphthalate	3.34	4.26	3.53	3.78	3.32	2.78	4.78	2.93	2.64	3.48	5.0	0.70	2.03	10
4-Chlorophenyl-phenylether	3.80	5.14	4.15	5.03	4.47	3.67	5.08	4.10	4.28	4.41	5.0	0.56	1.61	10
Fluorene	2.89	3.48	3.00	3.84	3.37	2.69	3.70	3.16	3.26	3.27	5.0	0.38	1.09	10
4-Nitroaniline	6.45	10.21	9.28	11.14	9.05	8.13	9.78	9.03	9.09	9.13	10.0	1.32	3.81	20
4,6-Dinitro-2-methylphenol	4.22	5.44	5.51	5.00	5.10	4.16	3.21	3.63	4.89	4.57	10.0	0.81	2.34	20
n-Nitrosodiphenylamine	3.57	4.08	4.31	4.58	4.24	3.56	4.54	4.03	3.83	4.08	5.0	0.38	1.09	10
1,2-Diphenylhydrazine	4.91	6.41	5.94	6.81	6.02	4.97	6.84	5.76	6.33	6.00	5.0	0.70	2.03	10
4-Bromophenyl phenylether	2.94	3.94	3.68	4.51	3.88	3.14	4.22	3.61	3.67	3.73	5.0	0.49	1.41	10
Hexachlorobenzene	3.56	4.30	3.77	4.33	3.91	3.01	3.91	4.22	3.87	3.88	5.0	0.41	1.20	10
Atrazine	2.86	4.09	3.64	3.53	3.81	3.06	3.89	3.15	3.14	3.46	5.0	0.43	1.24	10
Pentachlorophenol	5.13	6.23	6.05	6.17	6.37	4.93	5.52	3.82	5.63	5.54	10.0	0.82	2.36	20
Phenanthrene	3.18	3.51	3.51	3.81	3.48	2.87	3.56	3.38	3.34	3.40	5.0	0.26	0.76	10

Reporting Limit = Low Level Standard

Attachment 1 (continued)

Method Detection Limit Study

Study Date: February 9, 2000 GCMS Method 3510C/8270C Aqueous
Instrument: 5972HP68

Compound Name	Rep#1	Rep#2	Rep#3	Rep#4	Rep#5	Rep#6	Rep#7	Rep#8	Rep#9	Mean	Amt.	S.Dev.	MDL	Report Limit
	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L
Anthracene	2.94	3.52	3.74	3.82	3.55	2.96	3.85	3.67	3.50	3.51	5.0	0.34	0.98	10
Carbazole	3.78	4.96	4.85	4.67	4.88	4.16	5.11	4.65	5.09	4.68	5.0	0.44	1.29	10
Di-n-butylphthalate	3.18	3.60	3.85	3.43	3.50	2.98	4.45	3.45	3.27	3.52	5.0	0.43	1.24	10
Fluoranthene	3.09	3.39	3.65	3.98	3.51	3.00	4.05	3.56	3.29	3.50	5.0	0.36	1.04	10
Benzidine	0.64	1.19	1.05	1.34	0.99	0.66	0.86	0.43	0.69	0.87	100.0	0.29	0.85	20
Pyrene	2.73	3.38	3.15	3.31	3.06	2.34	3.14	2.82	2.83	2.97	5.0	0.33	0.94	10
Butylbenzylphthalate	2.33	2.53	2.38	2.13	2.02	1.40	3.31	1.61	1.12	2.09	5.0	0.66	1.91	10
3,3'-Dichlorobenzidine	6.67	9.75	8.53	10.00	8.59	7.48	8.81	8.40	8.04	8.47	5.0	1.03	2.99	10
bis(2-ethylhexyl)phthalate	2.88	3.47	3.26	3.44	3.33	2.47	3.47	2.75	2.81	3.10	5.0	0.37	1.08	10
Benzo(a)anthracene	2.66	3.45	3.29	3.47	3.36	2.51	3.40	3.05	3.04	3.14	5.0	0.35	1.02	10
Chrysene	2.85	3.75	3.51	3.59	3.49	2.98	3.75	3.41	3.35	3.41	5.0	0.31	0.91	10
Di-n-octylphthalate	2.25	2.80	2.68	2.78	2.72	2.05	2.99	2.32	2.32	2.55	5.0	0.32	0.92	10
Benzo(b)fluoranthene	2.52	2.86	2.69	3.62	2.86	2.20	3.62	2.51	2.68	2.84	5.0	0.49	1.41	10
Benzo(k)fluoranthene	2.71	3.79	3.70	3.22	3.47	3.28	3.33	3.56	3.67	3.41	5.0	0.33	0.96	10
Benzo(a)pyrene	2.36	3.13	3.01	3.14	2.88	2.25	3.15	2.70	2.96	2.84	5.0	0.34	0.98	10
Indeno(1,2,3-c,d)pyrene	3.58	4.04	3.83	4.06	4.00	3.19	4.23	3.54	3.61	3.79	5.0	0.33	0.96	10
Dibenzo(a,h)anthracene	2.97	3.63	3.42	3.78	3.50	2.76	3.91	3.15	3.54	3.41	5.0	0.38	1.10	10
Benzo(g,h,i)perylene	2.98	3.36	3.41	3.76	3.37	2.95	3.90	3.16	3.21	3.34	5.0	0.32	0.93	10

Reporting Limit = Low Level Standard

Attachment 2

CompuChem
EXTRACTION WORKSHEET
SEMI-VOLATILE WATER, Method 3510C for 8270C

ASSIGNED TO: _____ DATE EXTRACTED/POSTED: _____

EMP ID NUMBER: _____ 079

	SAMPLE NUMBER	QC SAMPLE TYPE	SAMPLE VOLUME (ml)	FINAL VOLUME (ml)	Adjusted pH: B/N	Adjusted pH: ACID	COMMENTS
1							
2							
3							
4							
5							
6							
7							
8							
9							
10							
11							
12							
13							
14							
15							
16							
17							
18							
19							
20							
21							
22							
23		BLK					
24		LCS					*Add 1.0 mL validation spike to LCS and SSs unless otherwise noted

		S-VOL	Acid	B/N	8270
SURROGATE	NO.	393			
	AMT.	1.0 ml			
	LOT				
SPIKE	NO.		3012	2021	VALID.
	AMT.		1.0 ml	1.0ml	1.0 ml
	LOT				

FINAL VOLUME VERIFIED: _____

SUPERVISOR REVIEWED: _____

SURROGATE & SPIKE ADDED BY: _____ / _____
Initials Date

Analyst initials. Extracted _____ KD _____ N2 _____ Bottle up _____

Witness _____ / _____
Initials Date

Manufacturer and lot number of reagents/solvents used _____

Rev. 2/28/00 mlj

Attachment 3

Analyst Capability Study

Laboratory Name/North Carolina Certificate Number: CompuChem/79
Analyst: Girgis Mikhael
Study Date: April 13, 2000
Method: 3510C/8270C Aqueous
Instrument/Column: 5972hp68

Compounds	True Val	Rep #1	Rep #2	Rep #3	Rep #4	Mean	Mean	SD(n-1)	-3SD	+3SD	- 3SD	+3SD	RSD
	ug/l	ug/l	ug/l	ug/l	ug/l	ug/l	% Rec.	ug/l	ug/l	ug/l	%R	%R	%
Phenol-d5	100	73.29	82.76	64.04	74.59	73.67	73.67	7.67	51	97	69	131	10
Nitrobenzene-d5	100	79.08	85.12	67.56	81.21	78.24	78.24	7.55	56	101	71	129	10
2-Fluorobiphenyl	100	79.18	84.64	74.36	76.61	78.70	78.70	4.42	65	92	83	117	6
2,4,6-Tribromophenol	100	162.51	167.46	140.5	153.51	156.00	156.0	11.83	120	191	77	123	8
Terphenyl-d14	100	82.94	84.66	73.25	75.98	79.21	79.21	5.46	63	96	79	121	7
n-Nitrosodimethylamine	100	49.52	62	53.98	58.21	55.93	55.93	5.38	40	72	71	129	10
Pyridine	100	43.83	47.25	46.88	57.17	48.78	48.78	5.80	31	66	64	136	12
Benzaldehyde	100	16.38	19.78	15.89	16.86	17.23	17.23	1.75	12	22	70	130	10
Phenol	100	40.86	49.91	39.44	45.86	44.02	44.02	4.80	30	58	67	133	11
Bis(2-chloroethyl)ether	100	77.4	89.83	73.78	85.24	81.56	81.56	7.30	60	103	73	127	9
2-Chlorophenol	100	77.49	91.97	75.41	83.32	82.05	82.05	7.41	60	104	73	127	9
1,3-Dichlorobenzene	100	95.38	112.88	90.18	101.23	99.92	99.92	9.75	71	129	71	129	10
1,4-Dichlorobenzene	100	99.48	115.63	92	98.33	101.36	101.4	10.07	71	132	70	130	10
Benzyl alcohol	100	73.26	85.64	72.25	80.75	77.98	77.98	6.36	59	97	76	124	8
1,2-Dichlorobenzene	100	99.24	119.2	92.63	102.17	103.31	103.3	11.32	69	137	67	133	11
2-Methylphenol	100	78.16	89.44	75.11	79.5	80.55	80.55	6.20	62	99	77	123	8
2,2'-oxybis(1-Chloropropane)	100	73.59	87.04	72.72	78.23	77.90	77.90	6.56	58	98	75	125	8
Acetophenone	100	81.23	95.87	78.2	89.39	86.17	86.17	8.01	62	110	72	128	9
3-Methylphenol	100	133.6	159.05	129.38	144.32	141.59	141.6	13.23	102	181	72	128	9
4-Methylphenol	100	133.6	159.05	129.38	144.32	141.59	141.6	13.23	102	181	72	128	9
n-Nitroso-di-n-propylamine	100	73.75	96.04	77.36	86.65	83.45	83.45	10.00	53	113	64	136	12
Hexachloroethane	100	104.47	119.22	96.6	104.98	106.32	106.3	9.42	78	135	73	127	9
Nitrobenzene	100	106.35	120.07	97.45	104.84	107.18	107.2	9.43	79	135	74	126	9
Isophorone	100	106.76	118.33	97.12	110.84	108.26	108.3	8.84	82	135	76	124	8
2-Nitrophenol	100	85.26	94.41	79.77	89.07	87.13	87.13	6.18	69	106	79	121	7
2,4-Dimethylphenol	100	61.09	62.78	51.32	57.33	58.13	58.13	5.08	43	73	74	126	9

Attachment 3 (continued)

Analyst Capability Study

Laboratory Name/North Carolina Certificate Number: CompuChem/79
Analyst: Girgis Mikhael
Study Date: April 13, 2000
Method: 3510C/8270C Aqueous
Instrument/Column: 5972hp68

Compounds	True Val	Rep #1	Rep #2	Rep #3	Rep #4	Mean	Mean	SD(n-1)	-3SD	+3SD	- 3SD	+3SD	RSD
	ug/l	ug/l	ug/l	ug/l	ug/l	ug/l	% Rec.	ug/l	ug/l	ug/l	%R	%R	%
Benzoic acid	100	5.99	3.66	1.08	5.28	4.00	4.00	2.18	-3	11	-63	263	54
Bis(2-chloroethoxy)methane	100	80.03	92.7	76.59	84.36	83.42	83.42	6.96	63	104	75	125	8
2,4-Dichlorophenol	100	88.33	97.21	83	89.01	89.39	89.39	5.87	72	107	80	120	7
1,2,4-Trichlorobenzene	100	108.01	117.31	99.17	103.02	106.88	106.9	7.84	83	130	78	122	7
Naphthalene	100	60.42	68.74	56.51	60.29	61.49	61.49	5.16	46	77	75	125	8
4-Chloroaniline	100	76.67	91.46	77.5	82.93	82.14	82.14	6.81	62	103	75	125	8
Hexachlorobutadiene	100	106.54	115.89	97.54	105.98	106.49	106.5	7.50	84	129	79	121	7
Caprolactam	100	30.28	39.19	30.49	36.72	34.17	34.17	4.49	21	48	61	139	13
4-Chloro-3-methylphenol	100	89.31	103.2	86.39	94.26	93.29	93.29	7.36	71	115	76	124	8
2-Methylnaphthalene	100	84.36	90.16	76.71	80.23	82.87	82.87	5.78	66	100	79	121	7
1-Methylnaphthalene	100	86.83	95.85	79.8	86.55	87.26	87.26	6.59	67	107	77	123	8
Hexachlorocyclopentadiene	100	118.71	131.9	116.38	127.62	123.65	123.7	7.33	102	146	82	118	6
2,4,6-Trichlorophenol	100	86.27	87.81	80.02	86.97	85.27	85.27	3.55	75	96	87	113	4
2,4,5-Trichlorophenol	100	83.62	98.76	84.96	88.89	89.06	89.06	6.84	69	110	77	123	8
1,1'-Biphenyl	100	75.62	83.07	74.75	80.32	78.44	78.44	3.94	67	90	85	115	5
2-Chloronaphthalene	100	104.81	110.32	100.09	105.72	105.24	105.2	4.19	93	118	88	112	4
2-Nitroaniline	100	72.28	84.62	75.19	86.02	79.53	79.53	6.82	59	100	74	126	9
Dimethylphthalate	100	74.9	84.02	69.14	66.9	73.74	73.74	7.64	51	97	69	131	10
2,6-Dinitrotoluene	100	105.27	119.53	106.2	115.19	111.55	111.5	6.95	91	132	81	119	6
Acenaphthylene	100	64.83	72.05	63.94	69.59	67.60	67.60	3.87	56	79	83	117	6
3-Nitroaniline	100	76.27	83.18	75.7	80.09	78.81	78.81	3.51	68	89	87	113	4
Acenaphthene	100	61.68	67.16	59.57	64.45	63.22	63.22	3.30	53	73	84	116	5
2,4-Dinitrophenol	100	88.79	74.98	49.63	81.98	73.85	73.85	17.10	23	125	31	169	23
4-Nitrophenol	100	106.75	118.15	100.65	117.15	110.68	110.7	8.44	85	136	77	123	8
2,4-Dinitrotoluene	100	104.99	118.46	105.77	115.85	111.27	111.3	6.89	91	132	81	119	6
Dibenzofuran	100	80.7	90.34	78.75	86.61	84.10	84.10	5.34	68	100	81	119	6

Attachment 3 (continued)

Analyst Capability Study

Laboratory Name/North Carolina Certificate Number: CompuChem/79
Analyst: Girgis Mikhael
Study Date: April 13, 2000
Method: 3510C/8270C Aqueous
Instrument/Column: 5972hp68

Compounds	True Val	Rep #1	Rep #2	Rep #3	Rep #4	Mean	Mean	SD(n-1)	-3SD	+3SD	- 3SD	+3SD	RSD
	ug/l	ug/l	ug/l	ug/l	ug/l	ug/l	% Rec.	ug/l	ug/l	ug/l	%R	%R	%
Diethylphthalate	100	80.52	88.48	78.46	80.95	82.10	82.10	4.39	69	95	84	116	5
4-Chlorophenyl-phenylether	100	83.67	89.92	83.8	84.78	85.54	85.54	2.96	77	94	90	110	3
Fluorene	100	62.46	69.25	60.93	67.04	64.92	64.92	3.88	53	77	82	118	6
4-Nitroaniline	100	66.97	78.85	71.8	75.52	73.29	73.29	5.10	58	89	79	121	7
4,6-Dinitro-2-methylphenol	100	83.78	86.31	71.4	89.22	82.68	82.68	7.84	59	106	72	128	9
n-Nitrosodiphenylamine	100	78.99	88.45	74.84	79.25	80.38	80.38	5.75	63	98	79	121	7
1,2-Diphenylhydrazine	100	85.1	102.62	86.49	96.44	92.66	92.66	8.34	68	118	73	127	9
4-Bromophenyl phenylether	100	85.52	92.42	76	82.86	84.20	84.20	6.79	64	105	76	124	8
Hexachlorobenzene	100	112.44	125.49	112.42	120.32	117.67	117.7	6.41	98	137	84	116	5
Atrazine	100	111.81	129.62	106.71	123.54	117.92	117.9	10.51	86	149	73	127	9
Pentachlorophenol	100	81.31	83.88	70.05	80.46	78.93	78.93	6.09	61	97	77	123	8
Phenanthrene	100	60.14	68.95	60.43	63.9	63.36	63.36	4.10	51	76	81	119	6
Anthracene	100	61.47	68.04	60.28	61.68	62.87	62.87	3.50	52	73	83	117	6
Carbazole	100	94.36	114.39	93.04	102.65	101.11	101.1	9.82	72	131	71	129	10
Di-n-butylphthalate	100	81.14	87	80.21	87.56	83.98	83.98	3.84	72	95	86	114	5
Fluoranthene	100	64.17	72.52	61.09	64.45	65.56	65.56	4.88	51	80	78	122	7
Benzidine	100	6.01	7.55	8.2	8.26	7.51	7.51	1.05	4	11	58	142	14
Pyrene	100	65.42	70.41	62.31	64.45	65.65	65.65	3.43	55	76	84	116	5
Butylbenzylphthalate	100	78.75	91.58	75.54	85.54	82.85	82.85	7.16	61	104	74	126	9
3,3'-Dichlorobenzidine	100	57.19	73.68	59.39	66.69	64.24	64.24	7.49	42	87	65	135	12
bis(2-ethylhexyl)phthalate	100	79.29	86.89	80.51	84.08	82.69	82.69	3.46	72	93	87	113	4
Benzo(a)anthracene	100	63.48	71.29	61.94	66.47	65.80	65.80	4.12	53	78	81	119	6
Chrysene	100	63.78	73.25	63.3	65.42	66.44	66.44	4.63	53	80	79	121	7
Di-n-octylphthalate	100	79.97	77.07	73.67	83.48	78.55	78.55	4.18	66	91	84	116	5
Benzo(b)fluoranthene	100	59.6	66.41	70.27	66.06	65.59	65.59	4.42	52	79	80	120	7
Benzo(k)fluoranthene	100	69.18	59.99	50.63	62.43	60.56	60.56	7.68	38	84	62	138	13

Attachment 3 (continued)

Analyst Capability Study

Laboratory Name/North Carolina Certificate Number: CompuChem/79
Analyst: Girgis Mikhael
Study Date: April 13, 2000
Method: 3510C/8270C Aqueous
Instrument/Column: 5972hp68

Compounds	True Val	Rep #1	Rep #2	Rep #3	Rep #4	Mean	Mean	SD(n-1)	-3SD	+3SD	- 3SD	+3SD	RSD
	ug/l	ug/l	ug/l	ug/l	ug/l	ug/l	% Rec.	ug/l	ug/l	ug/l	%R	%R	%
Benzo(a)pyrene	100	65.08	69.75	61.67	67.46	65.99	65.99	3.45	56	76	84	116	5
Indeno(1,2,3-c,d)pyrene	100	69.2	86.8	72.48	77.99	76.62	76.62	7.70	54	100	70	130	10
Dibenzo(a,h)anthracene	100	60.93	72.06	62.39	68.35	65.93	65.93	5.20	50	82	76	124	8
Benzo(g,h,i)perylene	100	62.35	71.91	60.87	68.55	65.92	65.92	5.20	50	82	76	124	8

CompuChem
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SOP DOCUMENTATION FORM

This form must accompany all new and revised Standard Operating Procedures (SOPs) when you turn them in to Quality Assurance for review. Please fill out the entire shaded area (except effective date).

This is a new procedure _____ revised procedure ✓ outdated procedure (archive) _____

- Procedure area, title, and SOP number: Section #: 2.5.27 Effective date: (QA fills in)

IP477: GC/MS Analysis of Extractable Semivolatiles in Aqueous & Solid Samples by SW846 and NYSASP 12/7/00

- Procedure prepared by: Linda Carter Date: 10/31/00
- Procedure approved by: (If the manager prepared the SOP, a qualified second party should sign) B. Mercer Date: 11/1/00
- Reason for change: NELAC format change, State of South Carolina requirements
- This procedure meets the requirements of the following approved method references: Test Methods for Evaluating Solid Waste: Physical/Chemical Methods, 3rd Edition, Update III, 12/96 Method 8270C; New York State Analytical Services Protocol, NYSASP, 10/95

Procedure approved by Quality Assurance Representative: Date:
(Not needed if signed above)

_____ _____

Effective 1-1-96, on an annual basis: Lab managers are required to review lab practices and revise the SOP if necessary. If no revision is necessary, indicate by your signature that the SOP has been reviewed.

Annual Review—Signature: _____ Date: _____

Annual Review—Signature: _____ Date: _____

Annual Review—Signature: _____ Date: _____

Instrument Procedure 477: **GC/MS Analysis of Extractable** Semivolatiles in Aqueous and Solid Samples **by** SW846 **and** NYSASP

1.0 Scope and Application

This method covers the determination of a variety of semivolatile compounds in aqueous and solid samples. These compounds are partitioned into an organic solvent and are amenable to analysis by gas chromatograph/mass spectrometer (GC/MS) instrumentation. The method involves solvent extraction of the matrix, and GC/MS analysis to determine the semivolatile compounds present in the sample. Target compounds for this method are listed in Table 1, **Attachment 1,** along with associated internal standards, **surrogates** and quantitation ions.

Method detection limits (MDL) and reporting limits are shown in Attachment 2.

Staff members performing the procedures described in this SOP are responsible for reading, understanding, and complying with the SOP requirements. Supervisors are responsible for directing the analyst to the controlled SOP, and providing adequate explanation of the material contained therein.

This procedure is restricted to use by or under the supervision of analysts experienced in the instrumentation or preparative methods and who have demonstrated the ability to generate acceptable results through QC samples and analyst capability studies.

2.0 Summary of Method

Water samples are **extracted prior to** analysis **following Sample Preparation Procedure – 079, "Preparation of Water Samples for the Analysis of Low Level Semivolatile Organic Compounds by SW846 and NYSASP." Soil samples are extracted using Sample Preparation Procedure –176, "Preparation of Soil/Sediment/Sludge Samples for the Analysis of Low-Level Semivolatile Organic Compounds SW846 and NYSASP" or Sample Preparation Procedure –236, "Soxhlet Extraction of S/S/S Samples by Method 3540C in SW846 & NYSASP."**

Sample concentrates are injected into a GC/MS system equipped with a narrow bore, fused silica capillary column. The GC is temperature programmed in order to separate the analytes for detection by the MS. Target compounds are identified in the samples by analyzing standards under the same conditions used for samples, comparing mass spectra to established library spectra, and comparing GC retention times to retention times from the latest continuing calibration verification standard.

Internal standards and surrogate compounds are added to all samples, **QC** and standards. A relative response factor is established for each target and surrogate compound during the initial

and continuing calibration verification procedures **and is used to calculate the analyte concentration.**

3.0 Definitions

3.1 Method detection limit (MDL) – The minimum concentration of an analyte that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte (40 CFR, Part 136, Appendix B.)

3.2 Reporting Limit – The laboratory reporting limit is based on the lowest multipoint calibration standard concentration. For some inorganic methods, the reporting limit is based on the MDL, and is usually 4-8 times higher than the MDL. For organic methods, values detected below the reporting limit and above the MDL may be reported and qualified as an estimated concentration.

If the low level standard concentration is not at least three times higher than the MDL value, the standard concentration is adjusted upward in order to achieve this minimal ratio. It may be adjusted higher than three times depending on the concentration range of the calibration curve and the ability to meet method linearity requirements. An exception to this is for CLP methods where the MDL is only required to be lower than the reporting limit.

The reporting limit for CLP is the Contract Required Quantitation Limit (CRQL) for organics and the Contract Required Detection Limit (CRDL) for inorganics.

3.3 Reporting Units – µg/L for water and µg/Kg for soil

3.4 An SDG is defined by the following, whichever is more frequent:

- **each 20 field samples received within a case, or**
- **each 14 calendar day period during which field samples in a case are received (7 calendar days for NYSASP, OLM04.0, plus revisions, and ILM04.0, plus revisions including ILM04.1) beginning with the receipt of the first sample.**

NOTE: **The Army Corps of Engineers does not accept the SDG approach, unless the samples are prepared in a single batch. When a group of up to 20 field samples of a similar matrix are prepared as one batch, method-specified QC samples such as a method blank, laboratory control sample, matrix spike, matrix spike duplicate, and matrix duplicate must also be prepared together at a rate of 5%. If samples**

are batched together from different sites, project-specific QC must be processed.

4.0 Interferences

4.1 Contamination by carryover can occur whenever high concentration and low concentration samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed with solvent between sample injections. Whenever an unusually concentrated sample is encountered, the following sample must be evaluated for carryover.

4.2 If any contamination is present in blanks, samples or QC, the source must be identified and re-extraction of part or the entire analytical batch may be required.

5.0 Safety

5.1 Appropriate protective equipment and clothing must be used under the assumption that all samples are potentially hazardous. During sample preparation, i.e. extraction, safety glasses, gloves and lab coats are a minimum requirement. Sample extracts should be prepared under a hood. The persistent presence of noxious odors may be indicative of failure of the laboratory ventilation system and must be reported to a supervisor or manager.

5.2 Laboratory staff are encouraged to review the Chemical Hygiene Plan for general safety policies, and Material Safety Data Sheets (MSDS) for solvents and reagents used in the laboratory. The MSDS are located in the Quality Assurance department.

6.0 Equipment & Supplies

6.1 Analytical Columns

6.1.1 J & W DB 5.625 0.32 mm i.d., 1µm film thickness

6.1.2 Hewlett Packard HP-5MS, 0.25 mm i.d., 0.25 mm film thickness

6.1.3 RTX-5 MS, 0.25 mm i.d., 0.25 mm film thickness

6.2 GC

6.2.1 Hewlett Packard 5890 Series with Electronic Pressure Control (EPC)

6.2.2 Thermoquest Trace GC

6.3 Mass Spectrometer **(MS)**

6.3.1 Hewlett Packard 5972A MSD

6.3.2 Thermoquest Trace MS

6.4 AutoSampler

6.4.1 Hewlett Packard 7673 Automated Liquid Sampler

6.4.2 CTC A200S Autosampler

6.5 Data System

6.5.1 A computer is interfaced to the mass spectrometer to allow the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program.

6.5.2 The data processing computer has software that searches any GC/MS data file for ions of a specified mass and plots ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). The software integrates the abundance of any EICP between specified time or scan number limits. Also, for the non-target compounds, the software compares sample spectra against reference library spectra. The reference library used is the NIST Mass Spectral library which was provided with the computer system.

6.5.3 For data processing, CompuChem uses the Hewlett Packard HP 9000 series 735 Unix Workstation employing HP Chemserver with Target3 software by Thru-Put Systems.

6.6 Syringes

6.6.1 10 µl Hamilton syringe

7.0 <u>**Reagents &**</u> <u>Standards</u>

All standards are prepared by the Organic Standards chemist. Details for the preparation are contained in the standard operating procedures (SOP) for that area (Section 7.0 of the SOP collection.)

7.1 **Reagent water – All water used in this procedure must be equivalent to ASTM Type II water (as it relates to specific conductance and specific resistance) which is demonstrated to meet the blank contamination acceptance criteria contained in this Standard Operating Procedure (SOP). It is referred to throughout the remainder of this SOP as DI water.**

7.2 Stock standards (1 mg/mL)

7.2.1 The standards can be prepared from pure standard materials or purchased as certified solutions.

7.2.2 Stock standards are stored at -10°C or less **in the Organic Standards Preparation laboratory** or as recommended by the manufacturer.

7.2.3 The standards must be replaced after 1 year or sooner if problems occur.

7.3 Internal standards

7.3.1 The internal standards are present at 40 ng per 2 µl injection.

7.3.2 These solutions are stored at -10°C (or less) **in the Organic Standards Preparation laboratory** when not in use according to the manufacturer's documented holding time and storage temperature recommendations.

7.4 Calibration standards

7.4.1 All standards should be stored at -10°C or less and should be freshly prepared once per year, or sooner if check standards indicate a problem. Calibration standards are stored at -10°C in the **Organic** Standards **Preparation** laboratory freezer except for one set which is stored at **2-4.4°** C in the instrumentation lab.

7.4.2 The calibration verification standard should be prepared weekly and stored at **2-4.4°** C. When using premixed certified solutions, store according to the manufacturer's documented holding time and storage temperature recommendations. The standard is replaced when acceptance criteria cannot be met.

7.5 Initial Calibration Verification (ICV) and Laboratory Control Sample (LCS) Spike Solutions.

7.5.1 An ICV **prepared** from a second source **is required to verify the validity of the calibration curve**. This **is** prepared at **50 ng/2µl.**

7.6 Matrix Spike Standard

7.6.1 A full list of target analytes is spiked into the MS/MSD prior to extraction at a concentration of 100 µg/L. A subset of analytes may be reported from this list depending on project or client requirements.

7.7 LCS Spike Standard

7.7.1 A full list of target analytes is spiked into the LCS prior to extraction at a concentration of 100 µg/L.

8.0 Sample Collection, Preservation, & Storage

8.1 Samples are collected, preserved, and stored according to the tables in Sample Control SOPs 4.1, "Receiving Samples" and 4.6, "Storing Samples." Sample holding times are also listed.

8.2 All extracts must be analyzed within 40 days of extraction.

8.3 Prior to analysis, all extracts must be stored under refrigeration at 2-4.4° C in the reach-in storage unit in the laboratory. After analysis, extracts are returned to Sample Control for long-term storage and disposal.

9.0 Quality Control and Corrective Action

9.1 Surrogates

9.1.1 Surrogates are added to all samples, standards, and QC and are used to measure the efficiency and accuracy of the analytical system.

Table 2. Surrogate Recovery Limits

Compound	Aqueous (% Recovery)	Soil (% Recovery)
Nitrobenzene-d_5	31-113	25-136
2-fluorobiphenyl	37-110	29-131
Terphenyl-d_{14}	42-124	34-149
Phenol-d_5	16-110	25-131
2-fluorophenol	20-110	23-131
2,4,6-tribromophenol	25-120	22-143

9.2 Internal Standards

9.2.1 Internal standard is added to an aliquot of the extract just prior to analysis in the instrumentation laboratory and is used in the quantitation of target analytes and surrogates.

9.2.2 Retention times for any internal standard cannot change by more than 30 seconds when compared to the corresponding internal standard in the continuing calibration. The internal standards in the continuing calibration are compared to the internal standards in the same level standard (80 ng/2 µl) from the initial calibration. Additionally, the EICP area for any internal standard cannot change by more than a factor of two (-50% to +100%).

9.3 Method Blanks

9.3.1 A method blank is prepared with every analytical batch of up to 20 samples. It is used to indicate extraction efficiency and contamination control within the analytical system. The method blank must be analyzed on each GC/MS system used to analyze the associated samples.

9.3.2 Any target analyte detected in the method blank must be less than the reporting limit, except for phthalates, which are allowed to be present at up to two time the reporting limit. (For some client projects, this exception may not be allowed.) Surrogate and internal standard responses must be within acceptance windows.

9.3.3 If the method blank fails acceptance criteria for surrogate recovery or contamination, the analytical system is considered to be out of control. The source of the contamination must be investigated and appropriate corrective measures taken and documented before more samples are analyzed. All samples processed with a method blank that is out of control must be re-extracted and reanalyzed, unless the method blank meets acceptance criteria upon reinjection.

9.4 Laboratory Control Sample

9.4.1 A laboratory control sample (LCS, or blank spike, BS, or for NYSASP, matrix spike blank) for aqueous matrix is DI water and for solid matrix is furnaced Ottawa sand, or an additional portion of furnaced sodium sulfate, which has been fortified with target compounds and surrogate standards. The LCS is prepared with each extraction batch of up to 20 samples. The LCS should be analyzed after any method blank associated with the group of samples. The LCS data are used to ensure that any

failing spiked target compound in the matrix spike and matrix spike duplicate is due to interference and not representative of an analytical system that is out of control.

9.4.2 LCS acceptance criteria are listed in Table 3.

9.4.2.1 The acceptance criteria for the NYSASP matrix spike blank are the same as the matrix spike.

Table 3: LCS Recovery Limits *

SV Compound	Aqueous (% Recovery)	Solid (% Recovery)
n-nitrosodiphenylamine	20-112	28-145
pyridine	16-100	23-100
phenol	10-100	34-150
bis(2-chloroethyl)ether	38-137	34-134
2-chlorophenol	35-136	32-147
1,3-dichlorobenzene	39-135	34-145
1,4-dichlorobenzene	37-142	29-150
1,2-dichlorobenzene	39-140	34-150
2-methylphenol	13-100	13-100
bis(2-chloroisopropyl)ether	10-150	26-142
3-methylphenol	13-100	14-100
4-methylphenol	13-100	14-100
n-nitroso-di-n-propylamine	31-150	29-150
hexachloroethane	37-136	31-139
nitrobenzene	38-150	36-150
isophorone	43-150	42-150
2-nitrophenol	35-150	35-150
2,4-dimethylphenol	28-150	30-150
benzoic acid	10-120	10-103
bis(2-chloroethoxy)methane	33-150	34-148
2,4-dichlorophenol	34-150	32-150
1,2,4-trichlorobenzene	43-150	36-150
naphthalene	39-144	36-149
4-chloroaniline	40-150	19-143
hexachlorobutadiene	22-150	31-150
4-chloro-3-methylphenol	35-150	35-150
2-methylnaphthalene	36-150	31-150
1-methylnaphthalene	35-134	33-134
hexachlorocyclopentadiene	37-151	29-150
2,4,6-trichlorophenol	33-150	30-150
2,4,5-trichlorophenol	22-100	14-100
2-chloronaphthalene	46-150	36-159

Table 3: LCS Recovery Limits * (continued)

SV Compound	Aqueous (% Recovery)	Solid (% Recovery)
2-nitroaniline	31-150	31-148
dimethylphthalate	29-145	34-150
acenaphthylene	43-144	35-148
2,6-dinitrotoluene	47-150	33-150
3-nitroaniline	41-150	20-143
acenaphthene	45-141	34-147
2,4-dinitrophenol	10-100	10-105
4-nitrophenol	10-150	10-150
2,4-dinitrotoluene	50-150	31-150
dibenzofuran	44-150	32-150
diethylphthalate	41-150	33-150
4-chlorophenyl-phenylether	45-150	32-150
fluorene	45-149	34-150
4-nitroaniline	40-150	30-150
4,6-dinitro-2-methylamine	23-100	15-100
n-nitrosodiphenylamine	22-100	19-100
1,2-diphenylhydrazine	35-150	28-142
4-bromophenyl-phenylether	46-150	33-150
hexachlorobenzene	49-150	33-150
pentachlorophenol	32-150	23-150
phenanthrene	44-150	37-144
anthracene	45-147	38-146
carbazole	31-150	16-150
di-n-butylphthalate	45-150	31-150
fluoranthene	45-145	33-150
benzidine	10-142	10-100
pyrene	37-150	35-144
butylbenzylphthalate	41-150	35-142
3,3'-dichlorobenzidine	24-150	12-150
bis(2-ethylhexyl)phthalate	42-150	34-142
benzo(a)anthracene	44-149	36-145
chrysene	47-145	40-140
di-n-octylphthalate	41-150	33-150
benzo(b)fluoranthene	44-146	32-149
benzo(k)fluoranthene	36-150	30-150
benzo(a)pyrene	43-147	35-143
indeno(1,2,3-cd)pyrene	30-118	25-112
dibenz(a,h)anthracene	39-150	34-146
benzo(g,h,i)perylene	39-146	34-139

* **The LCS recovery limits are based on in-house performance statistics. A subset of analytes may be reported, depending on the specific project requirements.**

9.4.3 **If the LCS fails acceptance criteria on the low side, the entire extraction batch must be reprocessed. Failures on the high side will be evaluated on a case-by-case basis.**

9.4.3.1 **For NYSASP, if the matrix spike blank criteria are not met, the matrix spike blank and the MS and MSD are required to be re-extracted/re-analyzed.**

9.5 Matrix Spike and Matrix Spike Duplicate

9.5.1 **A matrix spike (MS) and matrix spike duplicate (MSD) must be prepared for each SDG.**

9.5.2 The majority of the acid spiked compound recoveries **and relative percent differences (RPDs)** and the majority of the base/neutral spiked compound recoveries **and RPDs** must be within the control limits **in** Table **4**. **A subset of analytes may be reported depending on specific project requirements.**

Table **4:** Matrix Spike Recovery and Relative Percent Difference (RPD) Limits

SV Compound	Aqueous % Recovery	Aqueous (RPD)	Solid % Recovery	Solid (RPD)
n-nitrosodiphenylamine	**10-150**	**50**	**13-150**	**40**
pyridine	**10-100**	**50**	**10-105**	**50**
phenol	**10-116**	**50**	**16-150**	**38**
bis(2-chloroethyl)ether	**10-147**	**50**	**22-137**	**47**
2-chlorophenol	**10-150**	**50**	**14-150**	**44**
1,3-dichlorobenzene	**12-137**	**50**	**19-140**	**42**
1,4-dichlorobenzene	**10-137**	**50**	**17-139**	**43**
1,2-dichlorobenzene	**14-136**	**50**	**20-142**	**39**
2-methylphenol	**10-100**	**50**	**10-100**	**35**
bis(2-chloroisopropyl)ether	**10-150**	**48**	**16-143**	**39**
3-methylphenol	**10-100**	**50**	**10-100**	**44**
4-methylphenol	**10-100**	**50**	**10-100**	**44**
n-nitroso-di-n-propylamine	**10-150**	**35**	**19-160**	**39**
hexachloroethane	**10-139**	**50**	**10-147**	**43**
nitrobenzene	**11-150**	**43**	**20-150**	**34**
isophorone	**10-150**	**37**	**29-150**	**32**
2-nitrophenol	**16-147**	**50**	**11-150**	**50**
2,4-dimethylphenol	**10-150**	**50**	**11-150**	**34**
benzoic acid	**10-100**	**50**	**10-100**	**50**
bis(2-chloroethoxy)methane	**10-150**	**45**	**26-141**	**30**

Table 4: Matrix Spike Recovery and Relative Percent Difference (RPD) Limits (continued)

SV Compound	Aqueous % Recovery	Aqueous (RPD)	Solid % Recovery	Solid (RPD)
2,4-dichlorophenol	10-150	50	16-150	50
1,2,4-trichlorobenzene	12-149	45	20-150	34
naphthalene	11-149	41	28-139	33
4-chloroaniline	10-150	43	10-129	42
hexachlorobutadiene	10-148	50	20-150	33
4-chloro-3-methylphenol	10-150	50	16-150	43
2-methylnaphthalene	10-150	38	23-148	31
1-methylnaphthalene	18-127	37	22-128	36
hexachlorocyclopentadiene	10-150	50	10-150	50
2,4,6-trichlorophenol	10-150	50	14-150	50
2,4,5-trichlorophenol	10-116	50	10-100	50
2-chloronaphthalene	10-150	42	22-150	39
2-nitroaniline	11-150	30	25-146	36
dimethylphthalate	10-150	40	27-138	33
acenaphthylene	15-147	36	29-132	33
2,6-dinitrotoluene	13-150	33	15-150	34
3-nitroaniline	10-150	36	19-128	41
acenaphthene	11-149	40	25-141	33
2,4-dinitrophenol	10-126	50	10-100	50
4-nitrophenol	10-150	50	10-137	50
2,4-dinitrotoluene	19-150	34	16-150	31
dibenzofuran	16-150	33	27-147	34
diethylphthalate	10-150	37	25-143	36
4-chlorophenyl-phenylether	10-150	36	28-141	35
fluorene	19-146	34	27-147	31
4-nitroaniline	11-191	36	17-148	34
4,6-dinitro-2-methylamine	10-118	50	10-100	50
n-nitrosodiphenylamine	10-100	39	13-100	34
1,2-diphenylhydrazine	10-150	42	10-147	35
4-bromophenyl-phenylether	11-150	40	27-142	29
hexachlorobenzene	10-150	43	18-150	32
pentachlorophenol	10-150	50	10-150	50
phenanthrene	16-147	42	16-150	43
anthracene	15-149	43	28-140	31
carbazole	10-150	37	10-150	32
di-n-butylphthalate	10-150	41	29-144	34
fluoranthene	18-150	41	27-145	34
benzidine	10-131	50	10-100	49
pyrene	18-150	35	27-147	34
butylbenzylphthalate	16-150	32	27-146	37
3,3'-dichlorobenzidine	10-150	50	10-147	38

Table 4: Matrix Spike Recovery and Relative Percent Difference (RPD) Limits (continued)

SV Compound	Aqueous % Recovery	Aqueous (RPD)	Solid % Recovery	Solid (RPD)
bis(2-ethylhexyl)phthalate	20-150	50	10-150	39
benzo(a)anthracene	18-150	36	26-146	35
chrysene	16-150	30	30-142	34
di-n-octylphthalate	22-150	35	26-150	35
benzo(b)fluoranthene	10-150	38	15-150	47
benzo(k)fluoranthene	17-150	31	30-138	40
benzo(a)pyrene	15-150	30	29-136	33
indeno(1,2,3-cd)pyrene	14-122	27	15-110	35
dibenz(a,h)anthracene	10-150	30	20-143	37
benzo(g,h,i)perylene	10-150	27	16-140	37

9.5.3 If the sample and associated MS/MSD show the same recovery trend, then re-extraction is not required. If the original associated with the MS/MSD does not meet QC criteria, it should be reanalyzed, or re-extracted then reanalyzed, if the MS/MSD surrogate recoveries are within limits.

9.5.4 If the recovery of any of the spike compounds is less than 10%, the following steps are required:

- **Check for errors in calculations.**
- **Do not reanalyze dilutions if surrogate recoveries are outside the limits.**
- **Do not reanalyze the MS or MSD even if surrogates are outside the limits.**

9.6 Initial Calibration Verification

9.6.1 An Initial Calibration Verification (ICV) is performed immediately after the initial calibration has been completed.

9.6.2 Target analytes should be in the range of ± **30% of the expected value.** An allowance of 10% of the analytes **can** be within 4% of the expected value, to account for compounds **that** exhibit poor chromatography.

9.7 Duplicates

9.7.1 Duplicates, at a frequency of 10%, are required when processing samples submitted to meet the regulatory requirements of North Carolina **DENR. This may be satisfied with the MS/MSD.**

9.8 Chromatography Controls

9.**8.1** The % breakdown of DDT and the tailing factors for benzidine and pentachlorophenol are determined following the formulas presented in **Section 12.0**.

9.8.2 The following criteria apply.

9.8.2.1 The % breakdown for DDT should not exceed 20%.

9.8.2.2 The tailing factor for benzidine should not exceed 3.0.

9.8.2.3 The tailing factor for pentachlorophenol should not exceed 5.0.

9.8.3 When the breakdown or tailing factor criteria are not met it is indicative that instrument maintenance is necessary for the column and/or the injector port.

10.0 Calibration **& Standardization**

10.1 Tuning the GC/MS

10.1.1 Prior to analysis of any samples, blanks, or calibration standards, the laboratory must establish that the GC/MS system meets the mass spectral ion abundance criteria for a tuning standard performance check solution containing Decafluorotriphenylphosphine (DFTPP).

10.1.1.1 At the time of tuning the instrument, the laboratory clock and instrument system clock must be verified to be in agreement for both time and date. "LCD=SCD" must be recorded in the comments section of the runlog to document that they are.

10.1.2 The instrument is standardized (tuned) by analyzing the DFTPP tuning compound every 12 hours. Two µl of the 25 ng/µl DFTPP solution (50 ng) is injected into the GC/MS. The acceptance criteria for the ion abundances found in the DFTPP spectrum are as follows. This is the criteria found in Method 8270C and is required for NYASP work.

Table 5: Ion Abundance Criteria

Mass	Ion Abundance Criteria
51	30-60% of mass 198
68	< 2% of mass 69
70	< 2% of mass 69
127	40-60% of mass 198
197	<1% of mass 198
198	Base peak, 100% relative abundance(see note)
199	5-9% of mass 198
275	10-30% of mass 198
365	Greater than 1% of mass 198
441	Present but < mass 443
442	>40% of mass 198
443	17-23% of mass 442

Note: All ion abundances are normalized to m/z 198, the normal base peak.

10.1.2.1 An allowable option in Method 8270C, although not allowed by the NYSASP, is the tuning criteria taken from the CLP. Alternate tuning criteria may be used provided that method performance is not adversely affected. This is the criteria routinely used by the lab in performing Method 8270C.

Table 5A: Alternate Ion Abundance Criteria

Mass	Ion Abundance Criteria
51	30.0-80.0% of mass 198
68	< 2.0% of mass 69
69	present
70	< 2.0% of mass 69
127	25.0-75.0% of mass 198
197	<1.0% of mass 198
198	Base peak, 100% relative abundance(see note)
199	5.0-9.0% of mass 198
275	10.0-30.0% of mass 198
365	Greater than 0.75% of mass 198
441	Present but < mass 443
442	40.0-110.0% of mass 198
443	15.0-24.0% of mass 442

Note: All ion abundances are normalized to m/z 198, the normal base peak.

10.1.3 The peak selection criteria for DFTPP analysis are as follows.

10.1.3.1 Average one scan prior to the apex of the DFTPP peak to one scan after the apex, subtracting a single background scan prior to the peak, but no more than 20 scans prior to the elution of DFTPP. Also, do not subtract part of the DFTPP peak.

10.1.4 The DFTPP solution also contains the following compounds:

- **d10-phenenthrene**
- **benzidine**
- **pentachlorophenol**
- **4,4'-DDT**
- **endrin.**

10.1.4.1 Benzidine, pentachlorophenol, and 4,4′-DDT are added as evaluation aids to indicate injector port and GC column efficiencies.

10.1.4.2 Endrin and 4,4′-DDT are used to assess the instrument condition prior to GC/MS confirmations of pesticide and PCB analytes.

10.1.4.3 Excessive 4,4′-DDT/endrin breakdown and poor peak shape and response for benzidine and pentachlorophenol indicate maintenance is required for the injector port or GC column.

10.1.5 The DFTPP portion of the data package should include a hardcopy of the DFTPP spectrum, a mass list that corresponds to the spectrum, the GC/MS Tuning and Calibration (DFTPP) Form, and a reconstructed ion chromatograph (RIC).

10.1.6 All valid injections must be made within the 12-hour calibration period that begins with the time of the injection of the DFTPP. Each injection thereafter must be recorded on the instrument run log (Attachment 3).

10.2 Initial Calibration

10.2.1 An initial **six**-point calibration ("multipoint") must be performed if a valid multipoint for the **method** has not already been analyzed on the instrument or if

the calibration check standard (12-hour continuing calibration standard) does not meet all acceptance criteria.

10.2.2 The initial calibration standards are at **six** concentration levels (10, 20, 50, **80,** 120, and 160 total ng per 2 µl). Each calibration standard contains each compound of interest and each surrogate.

10.2.3 Generation of the Multipoint Files

10.2.3.1 All quantitations for Method 8270C are performed based on the response list created from the multipoint data. Therefore, it is critical that the multipoint data be correct.

10.2.3.2 Process the data files for each standard in Target 3 on Thru-Put. **Pr**oduce the Initial Calibration Report containing the response list. The Initial Calibration Report contains the relative response factor for each standard level, the average relative response factor, and the percent relative standard deviation (%RSD) for each compound.

10.2.3.3 If the percent relative standard deviation is greater than 15% for a target analyte, then an alternate method for quantitation, such as least squares regression or a non-linear calibration may be used. When one of these methods is used, the correlation coefficient of the equation must be 0.99 or greater for a valid calibration. If a quadratic equation is used, six levels of standards are required. If a third degree polynomial is used, seven levels are required. These alternate methods of quantitation are available in the ThruPut system.

For samples submitted to meet the regulatory requirements of the State of South Carolina, the option of using a quadratic fit to demonstrate linearity is not allowed. The use of a linear regression analysis for each target analyte is permitted.

10.2.4 Definition of a Valid Multipoint

- One valid injection of each standard level
- All standards acquired under a valid tune
- All compounds present in each standard
- All isomer pairs must be resolved with the exception of 3-/4-methylphenol and 1,2,4,5- and 1,2,3,5-tetrachlorobenzene.

- All System Performance Check Compound (SPCC) and Calibration Check Compound (CCC) criteria must be met (these criteria are already setup in the method file).

10.2.5 Contents of the Multipoint Package

10.2.5.1 A complete tune package, the quantitation report for each standard level, a labeled RIC starting immediately before the first eluting compound for each standard, and the Initial Calibration Report.

10.2.6 System Performance Check Compounds (SPCCs)

The following compounds must have an average response factor greater than or equal to 0.050 in each multipoint:

- n-nitroso-di-n-propylamine
- hexachlorocyclopentadiene
- 2,4-dinitrophenol
- 4-nitrophenol

10.2.7 Calibration Check Compounds (CCCs)

The **% RSD for the** following compounds **in the multipoint should be** less than **15%, but have a maximum % RSD of 30%. The CCC's include:**

- phenol
- 1,4-dichlorobenzene
- 2-nitrophenol
- hexachlorobutadiene
- 4-chloro-3-methylphenol
- 2,4-dichlorophenol
- acenaphthene
- pentachlorophenol
- diphenylamine
- 2,4,6-trichlorophenol
- fluoranthene
- di-n-octylphthalate
- benzo(a)pyrene

10.2.7.1 While the remaining target compounds do not have defined % RSD criteria, a warning limit of 50% RSD and an action limit of 90% RSD have been **inserted into the data reduction software program. This is based strictly on established U.S. EPA data validation guidelines where values greater than 90% RSD result in rejection of data.**

10.2.7.2 Because of the large number of target analytes, some of them may exceed the 15% criteria. When this occurs, certain steps may be performed.

- Check the instrument operating conditions and perform maintenance as necessary. **It may be necessary to clean the ion source, perform column maintenance, change the column, or take other corrective action to achieve the technical acceptance criteria.**

- **Compare responses for the analyte in each of the standard levels to verify that a single standard analysis is not producing the outliers. If so, reanalyze that standard and recalibrate the %RSD.**

- **The calibration range may be narrowed to determine if linearity can be achieved. This may cause more dilution re-analyses or even change the reporting limit if the lower standard is eliminated.**

10.2.8 The initial calibration may still be acceptable when some analytes exceed the 15% RSD criteria, if the following conditions **(grand mean)** are met:

10.2.8.1 The mean of <u>all</u> of the %RSD values for the analytes is less than or equal to 15%.

10.2.8.2 If the target analyte is part of the calibration standard, it must be included in the calculation.

10.2.8.3 A summary of the initial calibration data and/or a list of the analytes not meeting the 15% RSD criteria and the actual %RSD for each of these analytes must be included as a deliverable to our client. If the conditions in **10.2.7** are met, then the average relative response factor may be used to determine the concentration of analytes in samples.

10.2.8.4 For samples submitted to meet the regulatory requirements of the State of South Carolina, the option of demonstrating that the mean %RSD of all target analytes in the standard mixture is under 15% is not an allowed option. Because the State of South Carolina does not allow the grand mean, the following acceptance criteria for the initial calibration apply to samples received for compliance with the DHEC.

Of the remaining non-CCC analytes the %RSD should be less than 15%, but the following compounds have maximum %RSD criteria of 30%. These compounds are characterized with having erratic chromatographic behavior and limits.

- **hexachlorocyclopentadiene**
- **2,4-dinitrophenol**
- **4-nitrophenol**
- **atrazine**
- **benzidine**
- **3,3'-dichlorobenzidine**
- **1,3,5-trinitrobenzene**
- **phorate**
- **Sulfotepp**
- **benzoic acid**
- **famphur**
- **p-phenylenediamine**

10.2.9 For NYSASP, the initial calibration acceptance criteria after meeting the instrument performance check (tune) requirements of this SOP are the same as those from the current EPA CLP SOW for Multi-Media, Multi-Concentration Organics.

10.3 Initial Calibration Verification

10.3.1 The initial calibration is verified once after acquisition using a second source standard and must meet the acceptance criteria. If the ICV fails, a second injection may be attempted. If it still fails, then a new initial calibration curve must be generated.

10.4 Continuing Calibration Verification

10.4.1 For continuing calibration verification, **exactly** two µl of the **40** ng/µl standard are injected using the cold needle technique.

10.4.2 The standard should be processed in Target 3 on the Thru-Put system. If major column maintenance has been performed, the retention times may have shifted. If retention times are not consistent, the cause must be determined before proceeding.

Shifting retention times can usually be traced to one of a few sources. The two primary sources of instability are plugged columns and leaky septa. To prevent leaking septa, the septum should be changed at the beginning of each 12-hour

calibration period. Column plugging is generally caused by dirty samples clogging the column head, or small amounts of septum material becoming lodged in the column. T**o correct,** remove a small segment from the front end of the column. This must be done before the 12-hour calibration period **begins**.

10.4.3 **The** continuing calibration verification **portion of the data package** includes the **DFTPP** tune **information (see 10.1.5)**, the quantitation report from the standard, **the instrument run log,** an RIC starting immediately before the first eluting compound of the standard, the sample.x.map, any required extracted ion current profiles (EICPs), and the continuing calibration verification report.

10.4.4 The assessment of the continuing calibration verification standard involves evaluating the percent drift or difference. This compares the response of each CCC in the calibration verification standard with the response from the initial calibration. For the initial calibration to be valid, the percent difference (drift) for each CCC should be less than or equal to 20%. If a regression fit model was used for analytes in the initial calibration, the continuing calibration verification is performed by using percent drift for the CCCs.

Note: Method 8270C instructs that if the CCCs are not analytes of interest, then all required analytes must meet the 20% drift criterion.

The SPCCs must also meet a minimum response factor of 0.050 in the continuing calibration standard.

10.4.5 Internal standard retention time and area responses are to be assessed in each continuing calibration verification standard. Each internal standard is checked against the **corresponding** mid-point standard in the most recent initial calibration.

If any of the criteria listed in Section 7.0 above cannot be met, the analytical system must be checked for malfunctions and corrections made. Reanalyses of any affected samples are required.

10.4.6 Some programs may require that <u>all</u> compounds meet a % difference/drift criteria. In these situations, if the average of the response for all analytes is within 20%, then the calibration has been verified. Requirements similar to those **above** must be met.

10.4.7 For NYSASP, the continuing calibration acceptance criteria (after meeting the instrument performance check (tune) requirements of the SOP) are the same as those from the current EPA CLP SOW for Multi-Media, Multi-Concentration Organics.

10.4.8 If continuing calibration acceptance criteria cannot be met after inspection and normal maintenance, a new initial calibration will have to be performed. As indicated for the initial calibration acceptance criteria, for the continuing calibration the remaining target analytes do not have defined % difference/drift criteria. We have established a warning limit of 50% and an action limit of 90% D. **These values have been inserted as defaults into the data reduction software program. This based strictly on established U.S. EPA data validation guidelines where values greater than 90% result in rejection of data.**

10.4.8.1 For samples submitted to meet the regulatory requirements of the State of South Carolina, the non-CCC target analytes should be less than 20%. Compounds listed in 10.2.8.4 have a warning limit of 40% D and an action limit of 50%D.

11.0 Procedure

Documentation must follow the requirements in QC SOP: Proper Documentation Procedures. The run log (Attachment 3) must contain the date and time of the injection, the volume of the extract injected, standard identification numbers, sample identification numbers, case/SDG numbers, and any comment relevant to the injection.

11.1 Instrument Conditions

11.1.1 Inlet: GC

- **Tune File:** **ATUNE**
- **Acquisition Mode:** **Scan**
- **Mode:** **Splitless capillary**

11.1.2 MS Information

Note: The following conditions may vary.

- **Solvent Delay:** **3.00**
- **EMV offset:** **-105.9 from tune file**
- **Scan Parameters:**
  - **Low Mass:** **35 amu**
  - **High Mass:** **500 amu**
  - **Threshold:** **150 amu**
  - **Sampling #:** **2**
  - **A/D Samples:** **4**

11.1.3 GC Inlet Information

Note: The following conditions may vary.

- **Direct Injection**
- **Carrier Gas:** **Helium**
- **Inlet Temperature:** **315 degrees Celcius**
- **Inlet Pressure:** **20 psi**
- **Initial Time:** **1.34**
- **Rate:** **99.0 psi to 4.0 psi**
- **Column Flow:** **2.0 ml/minute @ 4.0 psi with constant flow for entire acquisition**
- **Split Vent Flow:** **100 ml/minute**
- **Septum Purge Flow:** **2-3 ml/minute (equivalent to Sweep Flow)**

11.1.4 GC Oven Temperature Information

Note: The following conditions may vary.

- **Initial Temp:** **40 degrees C**
- **Initial Time:** **2.00 minute**
- **Rate:** **15 degrees/minute**
- **Final Temp:** **310 degrees C**
- **Final Time:** **3 minute**

11.1.5 Purge Information

Note: The following conditions may vary.

- **Purge B:** **On time @ 1.00 after injection; off @ 0.00**

11.1.6 Tuning and Calibration

- **Tuning Compound: PFTBA**
- **Tuning Sensitivity: 1 x 10^6 counts on total ion RIC**
- **Instrument Performance Check Compound: DFTPP. Std. ID# 7053**
- **Calibration Frequency: Every 12 hours**

11.1.7 File Naming Conventions: XX123456X78

where: XX = Analysis type

123456 = Date/Lab ID with first digit dropped

Y = shift

78 = instrument #

11.1.8 Analysis type prefixes

11.1.8.1 Standard: HG, HH, HI, HJ, HK, HL

11.1.8.2 Initial Sample Injection:

- **SDG-Sample Number-Shift-Instrument, e.g. Q1636-1A60**

11.1.8.3 Sample reinjection:

- **SDG-Sample Number-J-Shift-Instrument, e.g. Q1636-1JA60**

11.1.8.4 Sample reextraction:

- **SDG-Sample Number-R-Shift-Instrument, e.g. Q1636-1RA60**

11.1.8.5 Sample dilution:

- **SDG-Sample Number-D-Shift-Instrument, e.g Q1636-1DA60**

11.1.8.6 Additional repeats:

- **SDG-Sample Number-(J2, R2, D2)-Shift-Instrument, e.g. Q1636-1J2A60**

11.2 Sample Analysis

All valid injections must be made within the 12-hour calibration period that begins at the moment of injection of the DFTPP. Each injection thereafter must be recorded on the instrument run log (Attachment 3).

11.2.1 Injection

Aliquot 50 µl of **methylene chloride** into an autosampler vial. Add 50 µl of **the sample extract (at room temperature)** and 2.5 µl of internal standard solution (800 ng/µl). All injections must be made using the cold needle injection technique. The injection volume is 2.0 µl and this will yield 40 ng per 2 µl **on column** of each of the internal standards.

11.2.2 **Target Processing**

11.2.2.1 Process each sample in Target 3 on the Thru-Put system. If any of the internal **standards**, surrogates, or spike **compounds** are missing or failing, the chemist can manually check the peak in "Target Review". Changes can be made in Target Review and EICPs can be generated. **Any compound for which a manual peak integration has occurred will have an "M" flag displayed on the quantitaion report. These entries** need to be initialed, dated, and an explanation **code assigned**.

11.2.2.2 The GC/MS Operator has the initial review responsibility. The operator must be sure the internal **standards** have acceptable areas and are within ±30 seconds of the continuing calibration verification standard, the surrogates **and spikes** pass recovery criteria, and all target analyte **concentrations** are within **the** analytical range.

11.2.2.3 If internal standards do not meet acceptance criteria, the sample must be re-injected to confirm a matrix effect or discount a mis-injection.

11.2.2.4 If surrogates do not meet acceptance criteria and there are no problems with the surrogate or internal standard solutions, the sample must be scheduled for re-extraction and reanalysis.

11.2.2.5 If the on-column amount of any target analyte exceeds the initial calibration range, the extract must be diluted, internal standard added, and the sample re-injected.

11.2.3 Generation of Compound List

11.2.3.1 The HP Target 3 program automatically generates the compound list. The program asks for information that is found on the extractions

worksheet and on the GC/MS worksheet. The required information consists of:

- amount extracted
- volume of surrogates added
- dry weight factor for soil samples
- final extract volume

11.2.4 Generation of Dual Mass Spectra

11.2.4.1 The dual mass spectra and library comparisons are generated under the HP Target 3 software.

11.2.5 Identification

11.2.5.1 The mass spectrum of the sample compound and a laboratory library-generated spectrum must match according to the following criteria.

- **All ions present in the library mass spectrum at a relative intensity >10% must be present in the sample spectrum.**
- **The relative intensities of ions specified above must agree within ±20% between the library and sample spectra.**
- **Ions >10% in the sample spectrum but not present in the library spectrum must be considered and accounted for.**

11.2.5.2 If a compound analyzed by GC/MS techniques cannot be verified by all of the criteria listed above, but in the technical judgment of the mass spectral interpretation specialist the identification is correct, then the laboratory will report that identification.

11.2.5.3 Identification of TICs

Non-target compounds are identified by comparing the mass spectra from the non-target compounds to mass spectra contained in the National Institute of Standards and Technology (NIST) Mass Spectral Library. Non-target compounds are quantified by comparing the MS response of the peak from the reconstructed ion chromatogram (RIC) to the MS response for a peak produced by the nearest internal standard compound. A response factor of 1 is assumed.

12.0 <u>Data Analysis & Calculations</u>

Calculations must be consistent with the QC SOP: Numerical Data Reduction.

12.1 Calculation of the mean or average of a set of values:

$$\overline{X} = \frac{\sum_{i=1}^{n} X_i}{n}$$

where: n = total number of values
x_i = each individual value used to calculate the mean
x = the mean of n

12.2 Calculation of the standard deviation of a set of values:

$$\text{Standard deviation} = \sqrt{\frac{\sum_{i=1}^{n}\left(X_n - \overline{X}\right)^2}{n-1}}$$

12.3 Calculation of percent recovery:

12.3.1 LCS and surrogates:

$$\%R = \frac{Amount\ found}{Amount\ spiked} x\ 100$$

12.3.2 Matrix spikes:

$$\%\,\mathrm{R} = \frac{Amount\ in\ spiked\ sample - Amount\ in\ unspiked\ (native)\ sample}{Amount\ spiked} x\ 100$$

12.4 Calculation of % RSD

$$\%\mathrm{RSD} = \left(\frac{Standard\ deviation}{\overline{\mathrm{X}}}\right) \times 100$$

12.5 Calculation of RPD

$$RPD = \frac{|Value\ 1\ -\ Value\ 2|}{(Value\ 1\ +\ Value\ 2)/2} x100$$

12.6 Calculation of %Difference (%D)

$$\%Diff = \frac{Value - \overline{Reference \quad value}}{\overline{Reference \quad value}} \times 100$$

12.7 Relative Response Factor

$$RRF = \frac{Ax \times C(is)}{A(is) \times Cx}$$

where: **Ax = Area of the characteristic ion (EICP) for the compound to be measured**

A(is) = Area of the characteristic ion (EICP) for the specific internal standard

C(is) = Concentration of the internal standard (in µg/l)

Cx = Concentration of the compound to be measured

12.8 Concentration

12.8.1 Concentration of aqueous samples by GC/MS analysis

$$ug/L = \frac{(Ax)(Is)(Vt)(Df)}{(Ais)(\overline{RRF})(Vo)(Vi)}$$

where: Ax = area of the characteristic ion from the EICP for the compound to be measured
Ais = area of the characteristic ion for the EICP for the internal standard
Is = amount of internal standard injected (ng)
$\overline{RRF}$ = mean relative response factor from initial calibration standards
Vo = volume of water extracted (ml)
Vi = volume of extract injected (µl)
Vt = volume of the concentrated extract (µl)
Df = dilution factor. If no dilution, Df = 1.0

12.8.2 Concentration of soil samples <u>(dry weight basis)</u> by GC/MS

$$ug/kg = \frac{(Ax)(Is)(Vt)(Df)(2.0)}{(Ais)(\overline{RRF})(Vi)(Ws)(D)}$$

where: Ax, Ais, ~~Is,~~ Vt, Vi, RRF, and Df are the same as given for water
2.0 = GPC factor (if used)
Ws = weight of sample extracted, in grams

$$\textbf{D (dry weight)} = \frac{\textbf{100 - \% moisture}}{\textbf{100}}$$

12.8.3 Concentration of TICs

$$TIC\ amount = \frac{A(TIC) * Amt(Std)}{A(IS) * 1(RF)}$$

where: A(TIC): area response from RIC for non-target compound

Amt(Std): amount of internal standard added to the sample

A(I.S.): area response of the nearest internal standard from the reconstructed ion chromatogram

1(RF): assumed response factor of 1

12.9 Calculating Dilutions

If a sample concentration exceeds the high level standard a dilution must be performed. Determine a level of dilution that will result in a value within the upper half of the calibration range. This is an acceptable dilution. A 10x dilution is performed using 1 mL sample plus 9 mL diluent for a total volume of 10 mL. It should be recorded on the run log as "10x (1 mL in 10 mL)."

12.10 Percent Breakdown of DDT in DFTPP Solution

$$\%\ DDT = \frac{DDD + DDE\ (Summation\ of\ degradation\ peak\ areas)}{DDT + DDD + DDE\ (Summation\ of\ all\ peak\ areas)}\ x\ 100$$

12.11 Tailing Factor for Benzidine and Pentachlorophenol

See the diagram, Attachment 4.

13.0 Method Performance

This method was validated through in-house laboratory studies of method detection limits (Attachment 2) and precision and accuracy for single analyst (Attachment 5). The data are retained by the QA department.

14.0 Pollution Prevention

The solvents used in this procedure pose little threat to the environment when recycled and managed properly. Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best thing.

15.0 Waste Management

It is the laboratory's responsibility to comply with all federal, state, and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions, and to protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Compliance with all sewage discharge permits and regulations is also required.

Samples preserved with HCl, HNO_3, or H_2SO_4 to pH <2 are hazardous and must be neutralized before being disposed, or must be handled as hazardous waste.

Refer to the Hazardous Waste Management and Safety SOPs located in the lab.

16.0 References

16.1 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods. SW-846, 3rd edition, Method 8270C, Update 3, and December, 1996

16.2 Standard Methods for the Examination of Water and Wastewater, 18th Edition (1992) and 19th Edition (1995), upon promulgation, Method 1080

16.3 Code of Federal Register, 40 CFR, Part 136, "Guidelines for Establishing Test Procedures for Priority Pollutants"

16.4 New York State Analytical Services Protocol **(NYSASP), 10/95**

16.5 QCSOP: Proper Documentation Procedures

16.6 QCSOP: Numerical Data Reduction

16.7 "Less is Better: Laboratory Chemical Management for Waste Reduction," American Chemical Society Department of Government Relations and Science Policy, 1155 16th Street, N.W., Washington DC, 20036, (202) 872-4477.

16.8 Hazardous Waste Management & Safety SOPs: "Hazardous Waste Disposal" and "Spill Control & Cleanup."

16.9 NELAC Standards, July 1, 1999, plus revisions

16.10 QA-G6: Guidance for the Preparation of Standard Operating Procedures for Quality-Related Operations EPA/600/R-96/027, November 1995.

16.11 New York State Environmental Laboratory Approval Program, Certification Manual, October 15, 1999, plus revisions.

16.12 CompuChem Quality Manual, Revision 0, 2/1/00, plus revisions

16.13 Sample Control SOP 4.1, "Receiving Samples"

16.14 Sample Control SOP 4.6, "Storing Samples"

16.15 Sample Preparation Procedure –079, "Preparation of Water Samples for the Analysis of Low Level Semivolatile Organic Compounds by SW-846 and NYSASP."

16.16 Sample Preparation Procedure –176, "Preparation of Soil/Sediment/Sludge Samples for the Analysis of Low-Level Semivolatile Organic Compounds SW-846 and NYSASP."

16.17 Sample Preparation Procedure –236, "Soxhlet Extraction of S/S/S Samples by Method 3540C in SW846 & NYSASP."

17.0 **Attachments as Tables, Diagrams, Flowcharts & Validation Data**

17.1 Attachment 1 – **Target Analyte List**

17.2 Attachment 2 - Method Detection Limits

17.3 Attachment 3 - Semivolatile Instrument Run Log

17.4 Attachment 4 – Peak Tailing Factor Demonstration

17.5 Attachment 5 – Single Analyst Capability Study

Attachment 1

Table 1:Target Compounds, Corresponding Internal Standards, and Quantitation Ions

Compounds	Internal Standard	Primary Quantitation	Secondary Quantitation
d4-1,4-dichlorobenzene	1	152	150, 115
n-nitrosodimethylamine	1	42	74, 43
pyridine	1	79	52, 78
paraldehyde	1	89	117, 145
2-picoline	1	93	66, 92
nitrosomethylethylamine	1	88	56, 71
methyl methanesulfonate	1	80	79, 65
n-nitrosodiethylamine	1	102	56, 57
ethyl methanesulfonate	1	109	79, 97
phenol	1	94	66, 65
aniline	1	93	66, 92
pentachloroethane	1	167	165, 117
bis(2-chloroethyl)ether	1	93	95, 63
2-chlorophenol	1	128	130, 92
1,3-dichlorobenzene	1	146	148, 111
1,4-dichlorobenzene	1	146	148, 111
benzyl alcohol	1	108	107, 79
1,2-dichlorobenzene	1	146	148, 111
2-methylphenol	1	108	90, 107
bis(2-chloroisopropyl)ether	1	45	121, 123
3-methylphenol	1	108	107, 79
4-methylphenol	1	108	107, 79
n-nitrosopyrrolidine	1	100	42, 68
n-nitrosomorpholine	1	116	86, 56
acetophenone	2	105	120, 77
n-nitroso-di-n-propylamine	1	70	130, 113
o-toluidine hydrochloride	1	106	107, 89
hexachloroethane	1	117	119, 166
d8-naphthalene	2	136	68, 137
nitrobenzene	2	77	123, 93
n-nitrosopiperidine	2	114	55, 42
isophorone	2	82	138, 95
2,4-dimethylphenol	2	107	91, 77

Attachment 1 (continued)

Table 1:Target Compounds, Corresponding Internal Standards, and Quantitation Ions

Compounds	Internal Standard	Primary Quantitation Ion	Secondary Quantitation Ion(s)
2-nitrophenol	2	139	92, 65
benzal chloride	2	125	127, 160
o,o,o-triethylphosphorothioate	2	198	170, 115
benzoic acid	2	122	105, 77
bis(2-chloroethoxy)methane	2	93	95, 123
2,4-dichlorophenol	2	162	164, 178
1,2,4-trichlorobenzene	2	180	182, 145
naphthalene	2	128	129, 92
4-chloroanaline	2	127	129, 92
2,6-dichlorophenol	2	162	164, 126
4-chloro-3-methylphenol	2	107	144, 77
n-nitroso-di-n-butylamine	2	84	99, 116
hexachlorobutadiene	2	225	227, 260
hexachloropropene	2	213	215
p-phenylenediamine	3	108	162
safrole	2	162	104, 131
2-methylnaphthalene	2	142	141, 115
1-methylnaphthalene	2	142	141, 115
d10-acenaphthene	3	164	162, 181
1,2,4,5-tetrachlorobenzene	3	216	218, 181
hexachlorocyclopentadiene	3	237	239, 235
2,4,6-trichlorophenol	3	196	200, 97
2,4,5-trichlorophenol	3	196	200, 97
isosafrole	3	162	104, 131
2-chloronaphthalene	3	162	164, 127
2-nitroaniline	3	65	138, 92
1,4-napthoquinone	3	158	102, 130
1,3-dinitrobenzene	3	168	122, 75
dimethyl phthalate	3	163	194, 164
1,2-dinitrobenzene	3	168	63
2,6-dinitrotoluene	3	165	148, 121
acenaphthylene	3	152	151, 153
3-nitroaniline	3	138	92, 65

Attachment 1 (continued)

Table 1:Target Compounds, Corresponding Internal Standards, and Quantitation Ions

Compounds	Internal Standard	Primary Quantitation Ion	Secondary Quantitation Ion(s)
acenaphthene	3	154	153, 152
2,4-dinitrophenol	3	184	107, 91
4-nitrophenol	3	109	93, 65
2,4-dinitrotoluene	3	165	89, 119
dibenzofuran	3	168	139, 169
pentachlorobenzene	3	250	252, 215
2-naphthylamine	3	143	115, 89
1-naphthylamine	3	143	115, 89
2,3,4,6-tetrachlorophenol	3	232	234, 166
diethyl phthalate	3	149	177, 105
zinophos	3	97	143, 107
4-chlorophenyl phenyl ether	3	204	206, 141
fluorene	3	166	165, 139
4-nitroaniline	3	138	108, 65
5-nitro-o-toluidine	3	152	106, 77
1,2-diphenylhydrazine	3	77	182, 105
d10-phenanthrene	4	188	94, 80
4,6-dinitro-2-methylphenol	4	198	168, 121
n-nitrosodiphenylamine*	4	169	168, 167
diphenylamine*	4	169	168, 167
sulfotep	3	322	202
1,3,5-trinitrobenzene	4	213	120, 74
phenacetin	4	108	109, 179
diallate (cis isomer)	4	234	236, 86
4-bromophenyl phenyl ether	4	248	250, 141
diallate (trans isomer)	4	234	236, 188
phorate	4	75	121, 97
dimethoate	4	125	87
hexachlorobenzene	4	284	286, 142
4-aminobiphenyl	4	169	168, 141
pronamide	4	173	175, 145

***These compounds cannot be differentiated since N-Nitrosodipheylamine breaks down to Diphenylamine in the injector port of the GC.**

Attachment 1 (continued)

Table 1:Target Compounds, Corresponding Internal Standards, and Quantitation Ions

Compounds	Internal Standard	Primary Quantitation Ion	Secondary Quantitation Ion(s)
pentachlorophenol	4	266	268, 230
pentachloronitrobenzene	4	237	295, 142
phenanthrene	4	178	176, 89
disulfoton	4	88	60, 129
anthracene	4	178	176, 89
methly parathion	4	109	125, 263
di-n-butyl phthalate	4	149	150, 278
parathion	4	97	109, 291
4-nitroquinoline-1-oxide	4	190	128, 75
methapyrilene	4	97	191, 72
isodrin	4	193	195, 263
fluoranthene	4	202	101, 200
d12-chrysene	5	240	120, 236
benzidine	5	184	185, 156
pyrene	5	202	101, 200
p-dimethylaminoazobenzene	5	225	120, 148
chlorobenzilate	5	139	251, 111
famfur	5	218	77, 125
3,3'-dimethylbenzidine	5	212	213, 180
butylbenzyl phthalate	5	149	206, 91
2-acetylamino fluorene	5	181	180, 223
3,3'-dichlorobenzidine	5	252	254, 154
bis(2-ethylhexyl) phthalate	5	149	167, 150
benzo(a)anthracene	5	228	226, 114
chrysene	5	228	226, 114
d12-perylene	6	264	260, 265
di-n-octyl phthalate	6	149	150, 279
benzo(b)fluoranthene	6	252	126, 250
7,12-Dimethylbenzanthracene	6	256	239, 241
benzo(k)fluoranthene	6	252	126, 250
benzo(a)pyrene	6	252	126, 250
3-methylchloranthrene	6	268	252, 126

Attachment 1 (continued)

Table 1:Target Compounds, Corresponding Internal Standards, and Quantitation Ions

Compounds	Internal Standard	Primary Quantitation Ion	Secondary Quantitation Ion(s)
dibenzo(a,j)acridine	6	279	139, 277
indeno(1,2,3-c,d)pyrene	6	276	138, 274
dibenzo(a,h)anthracene	6	278	139, 276
benzo(g,h,i)perylene	6	276	138, 274
Surrogate #1 – 2-fluorophenol	1	112	64, 92
Surrogate #2 – phenol-d5	1	99	71, 42
Surrogate #3 – nitrobenzene-d5	2	82	128, 54
Surrogate #4 – 2-fluorobiphenyl	3	172	171, 174
Surrogate #5 – 2,4,6-tribromo-phenol	3	330	332, 141
Surrogate #6 – terphenyl-d14	5	244	122, 212

Internal Standard #1:	d4-1,4-dichlorobenzene
Internal Standard #2	d8-naphthalene
Internal Standard #3	d10-acenaphthene
Internal Standard #4	d10-phenanthrene
Internal Standard #5	d12-chrysene
Internal Standard #6	d12-perylene

Attachment 2

Method Detection Limit Study

Study Date: February 9, 2000
Instrument: 5972HP68

GCMS Method 3510C/8270C Aqueous

Compound Name	Rep#1 ug/L	Rep#2 ug/L	Rep#3 ug/L	Rep#4 ug/L	Rep#5 ug/L	Rep#6 ug/L	Rep#7 ug/L	Rep#8 ug/L	Rep#9 ug/L	Mean ug/L	Amt. ug/L	S.Dev. ug/L	MDL ug/L	Report Limit ug/L
n-Nitrosodimethylamine	2.35	2.53	2.76	3.43	2.52	1.87	2.18	2.63	2.97	2.58	5.0	0.45	1.31	10
Pyridine	4.73	6.47	5.60	6.57	4.98	4.06	7.21	4.98	4.79	5.49	5.0	1.04	3.03	10
Benzaldehyde	3.83	5.73	5.79	6.26	6.32	4.57	6.26	5.44	6.13	5.59	5.0	0.86	2.50	10
Phenol	1.97	2.45	2.40	3.01	2.65	1.96	2.81	2.47	2.51	2.47	5.0	0.35	1.00	10
Bis(2-chloroethyl)ether	3.62	4.34	3.99	4.95	4.31	3.40	4.71	4.02	4.41	4.19	5.0	0.49	1.43	10
2-Chlorophenol	3.47	4.50	3.94	4.94	4.26	3.68	4.49	4.00	4.01	4.14	5.0	0.45	1.31	10
1,3-Dichlorobenzene	3.37	3.94	3.86	4.29	3.60	2.90	4.23	3.94	3.83	3.77	5.0	0.43	1.25	10
1,4-Dichlorobenzene	3.21	3.55	3.80	4.25	3.54	2.81	4.39	3.45	3.71	3.63	5.0	0.49	1.41	10
Benzyl alcohol	2.36	3.12	3.73	3.81	3.20	2.72	3.07	3.27	3.63	3.21	5.0	0.47	1.37	10
1,2-Dichlorobenzene	3.11	3.86	3.63	4.35	3.85	2.97	4.40	3.66	3.86	3.74	5.0	0.48	1.40	10
2-Methylphenol	2.98	3.41	3.58	3.98	3.26	2.65	3.55	3.38	3.54	3.37	5.0	0.38	1.10	10
2,2'-oxybis(1-Chloropropane)	4.07	4.95	4.65	5.63	5.11	4.08	5.58	4.74	4.96	4.86	5.0	0.56	1.61	10
Acetophenone	3.85	4.73	4.95	5.02	4.53	4.00	5.31	4.94	5.03	4.71	5.0	0.49	1.43	10
3-Methylphenol	5.21	6.39	5.97	6.64	6.86	5.26	6.55	6.30	6.15	6.15	5.0	0.58	1.68	5
4-Methylphenol	5.21	6.39	5.97	6.64	6.86	5.26	6.55	6.30	6.15	6.15	5.0	0.58	1.68	5
n-Nitroso-di-n-propylamine	2.57	3.44	3.38	3.73	3.56	3.02	3.64	3.07	3.31	3.30	5.0	0.36	1.05	10
Hexachloroethane	3.16	3.77	3.87	4.29	3.51	2.61	4.24	3.28	3.74	3.61	5.0	0.54	1.55	10
Nitrobenzene	4.67	5.53	5.65	6.16	6.01	4.84	6.71	5.97	6.43	5.77	5.0	0.68	1.97	10
Isophorone	3.71	4.51	4.37	4.94	4.15	3.52	4.76	4.45	4.56	4.33	5.0	0.47	1.35	10
2-Nitrophenol	3.00	3.84	3.54	4.14	3.41	2.84	3.98	3.29	3.49	3.50	5.0	0.43	1.25	10
2,4-Dimethylphenol	1.51	1.95	2.08	2.11	2.07	1.30	2.13	2.08	2.08	1.92	5.0	0.30	0.88	10
Bis(2-chloroethoxy)methane	3.96	4.69	4.26	5.12	4.51	3.66	5.21	4.58	4.55	4.50	5.0	0.50	1.44	10
2,4-Dichlorophenol	3.03	3.38	3.28	3.56	3.16	3.08	3.78	3.38	3.25	3.32	5.0	0.24	0.69	10
1,2,4-Trichlorobenzene	3.02	3.53	3.48	3.73	3.78	2.86	4.27	3.58	3.74	3.55	5.0	0.42	1.21	10
Naphthalene	2.71	3.29	3.27	3.58	3.59	2.78	4.05	3.27	3.46	3.33	5.0	0.41	1.19	10
4-Chloroaniline	2.98	3.88	4.10	3.90	3.80	3.31	4.04	3.71	3.92	3.74	5.0	0.36	1.06	10
Hexachlorobutadiene	2.78	3.44	3.46	4.19	3.60	2.62	4.19	3.38	3.42	3.45	5.0	0.53	1.54	10
Caprolactam	2.42	4.26	4.03	3.49	3.90	3.43	1.70	3.31	2.90	3.27	20.0	0.82	2.37	10
4-Chloro-3-methylphenol	3.20	3.90	3.78	3.85	3.78	3.14	4.36	3.41	3.68	3.68	5.0	0.38	1.10	10

Reporting Limit = Low Level Standard

Attachment 2 (continued)

Method Detection Limit Study

Study Date: February 9, 2000 GCMS Method 3510C/8270C Aqueous
Instrument: 5972HP68

Compound Name	Rep#1 ug/L	Rep#2 ug/L	Rep#3 ug/L	Rep#4 ug/L	Rep#5 ug/L	Rep#6 ug/L	Rep#7 ug/L	Rep#8 ug/L	Rep#9 ug/L	Mean ug/L	Amt. ug/L	S.Dev. ug/L	MDL ug/L	Report Limit ug/L
2-Methylnaphthalene	4.05	4.86	4.62	4.85	4.83	3.78	5.36	4.52	4.59	4.61	5.0	0.47	1.35	10
1-Methylnaphthalene	3.38	3.84	4.18	4.21	3.99	3.37	4.44	4.00	4.23	3.96	5.0	0.37	1.08	10
Hexachlorocyclopentadiene	1.89	2.92	2.58	2.90	2.19	1.84	3.13	2.10	2.27	2.42	10.0	0.48	1.38	10
2,4,6-Trichlorophenol	6.44	7.97	7.71	8.75	8.08	6.62	7.82	6.50	7.67	7.51	10.0	0.81	2.33	10
2,4,5-Trichlorophenol	6.10	8.37	7.87	8.66	7.97	6.75	8.05	7.46	7.61	7.65	10.0	0.80	2.31	10
1,1'-Biphenyl	4.00	5.00	4.74	5.62	4.67	3.87	5.55	4.63	5.00	4.79	5.0	0.60	1.73	10
2-Chloronaphthalene	3.42	4.23	4.23	4.61	4.24	3.18	4.52	4.05	4.07	4.06	5.0	0.47	1.37	10
2-Nitroaniline	2.29	4.19	3.76	4.10	3.57	2.44	4.23	3.39	4.61	3.62	5.0	0.80	2.32	20
Dimethylphthalate	2.18	2.48	2.41	1.95	1.79	1.33	4.14	1.38	1.03	2.08	5.0	0.92	2.67	10
2,6-Dinitrotoluene	2.62	3.58	3.03	3.65	3.40	2.47	3.65	3.17	3.11	3.19	5.0	0.43	1.25	10
Acenaphthylene	2.73	3.65	3.37	3.73	3.47	2.71	3.78	3.16	3.23	3.31	5.0	0.40	1.15	10
3-Nitroaniline	4.95	7.72	7.63	8.91	7.50	6.59	8.56	6.92	7.50	7.36	10.0	1.16	3.35	20
Acenaphthene	2.81	3.52	3.33	3.80	3.39	2.95	3.74	3.15	3.28	3.33	5.0	0.33	0.96	10
2,4-Dinitrophenol	22.26	36.70	30.57	29.82	24.52	21.33	10.18	9.15	25.95	23.39	50.0	9.09	26.32	50
4-Nitrophenol	4.20	7.17	7.08	7.44	6.63	5.32	5.29	4.84	6.17	6.02	20.0	1.15	3.33	20
2,4-Dinitrotoluene	2.81	4.28	3.79	4.59	3.56	3.34	3.98	3.36	3.70	3.71	5.0	0.53	1.54	10
Dibenzofuran	3.84	4.81	4.23	5.13	4.44	3.72	4.94	4.25	4.46	4.42	5.0	0.48	1.38	10
Diethylphthalate	3.34	4.26	3.53	3.78	3.32	2.78	4.78	2.93	2.64	3.48	5.0	0.70	2.03	10
4-Chlorophenyl-phenylether	3.80	5.14	4.15	5.03	4.47	3.67	5.08	4.10	4.28	4.41	5.0	0.56	1.61	10
Fluorene	2.89	3.48	3.00	3.84	3.37	2.69	3.70	3.16	3.26	3.27	5.0	0.38	1.09	10
4-Nitroaniline	6.45	10.21	9.28	11.14	9.05	8.13	9.78	9.03	9.09	9.13	10.0	1.32	3.81	20
4,6-Dinitro-2-methylphenol	4.22	5.44	5.51	5.00	5.10	4.16	3.21	3.63	4.89	4.57	10.0	0.81	2.34	20
n-Nitrosodiphenylamine	3.57	4.08	4.31	4.58	4.24	3.56	4.54	4.03	3.83	4.08	5.0	0.38	1.09	10
1,2-Diphenylhydrazine	4.91	6.41	5.94	6.81	6.02	4.97	6.84	5.76	6.33	6.00	5.0	0.70	2.03	10
4-Bromophenyl phenylether	2.94	3.94	3.68	4.51	3.88	3.14	4.22	3.61	3.67	3.73	5.0	0.49	1.41	10
Hexachlorobenzene	3.56	4.30	3.77	4.33	3.91	3.01	3.91	4.22	3.87	3.88	5.0	0.41	1.20	10
Atrazine	2.86	4.09	3.64	3.53	3.81	3.06	3.89	3.15	3.14	3.46	5.0	0.43	1.24	10
Pentachlorophenol	5.13	6.23	6.05	6.17	6.37	4.93	5.52	3.82	5.63	5.54	10.0	0.82	2.36	20
Phenanthrene	3.18	3.51	3.51	3.81	3.48	2.87	3.56	3.38	3.34	3.40	5.0	0.26	0.76	10

Reporting Limit = Low Level Standard

Attachment 2 (continued)

Method Detection Limit Study

Study Date: February 9, 2000			GCMS Method 3510C/8270C Aqueous											
Instrument: 5972HP68														
Compound Name	Rep#1	Rep#2	Rep#3	Rep#4	Rep#5	Rep#6	Rep#7	Rep#8	Rep#9	Mean	Amt.	S.Dev.	MDL	Report Limit
	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L
Anthracene	2.94	3.52	3.74	3.82	3.55	2.96	3.85	3.67	3.50	3.51	5.0	0.34	0.98	10
Carbazole	3.78	4.96	4.85	4.67	4.88	4.16	5.11	4.65	5.09	4.68	5.0	0.44	1.29	10
Di-n-butylphthalate	3.18	3.60	3.85	3.43	3.50	2.98	4.45	3.45	3.27	3.52	5.0	0.43	1.24	10
Fluoranthene	3.09	3.39	3.65	3.98	3.51	3.00	4.05	3.56	3.29	3.50	5.0	0.36	1.04	10
Benzidine	0.64	1.19	1.05	1.34	0.99	0.66	0.86	0.43	0.69	0.87	100.0	0.29	0.85	20
Pyrene	2.73	3.38	3.15	3.31	3.06	2.34	3.14	2.82	2.83	2.97	5.0	0.33	0.94	10
Butylbenzylphthalate	2.33	2.53	2.38	2.13	2.02	1.40	3.31	1.61	1.12	2.09	5.0	0.66	1.91	10
3,3'-Dichlorobenzidine	6.67	9.75	8.53	10.00	8.59	7.48	8.81	8.40	8.04	8.47	5.0	1.03	2.99	10
bis(2-ethylhexyl)phthalate	2.88	3.47	3.26	3.44	3.33	2.47	3.47	2.75	2.81	3.10	5.0	0.37	1.08	10
Benzo(a)anthracene	2.66	3.45	3.29	3.47	3.36	2.51	3.40	3.05	3.04	3.14	5.0	0.35	1.02	10
Chrysene	2.85	3.75	3.51	3.59	3.49	2.98	3.75	3.41	3.35	3.41	5.0	0.31	0.91	10
Di-n-octylphthalate	2.25	2.80	2.68	2.78	2.72	2.05	2.99	2.32	2.32	2.55	5.0	0.32	0.92	10
Benzo(b)fluoranthene	2.52	2.86	2.69	3.62	2.86	2.20	3.62	2.51	2.68	2.84	5.0	0.49	1.41	10
Benzo(k)fluoranthene	2.71	3.79	3.70	3.22	3.47	3.28	3.33	3.56	3.67	3.41	5.0	0.33	0.96	10
Benzo(a)pyrene	2.36	3.13	3.01	3.14	2.88	2.25	3.15	2.70	2.96	2.84	5.0	0.34	0.98	10
Indeno(1,2,3-c,d)pyrene	3.58	4.04	3.83	4.06	4.00	3.19	4.23	3.54	3.61	3.79	5.0	0.33	0.96	10
Dibenzo(a,h)anthracene	2.97	3.63	3.42	3.78	3.50	2.76	3.91	3.15	3.54	3.41	5.0	0.38	1.10	10
Benzo(g,h,i)perylene	2.98	3.36	3.41	3.76	3.37	2.95	3.90	3.16	3.21	3.34	5.0	0.32	0.93	10

Reporting Limit = Low Level Standard

Attachment 2 (continued)

Method Detection Limit

Study Date: February 8, 2000			GCMS Method 3550B/8270C Solid Matrix, TCL and PPL Compounds												
Instrument: 5972HP68															
Compound Name	Rep#1	Rep#2	Rep#3	Rep#4	Rep#5	Rep#6	Rep#7	Rep#8	Rep#9	Rep#10	Mean	Amt.	S.Dev.	MDL	Report Limit
	ug/Kg	ug/Kg	ug/Kg	ug/Kg	ug/Kg	ug/Kg	ug/Kg	ug/Kg	ug/Kg	ug/Kg	ug/Kg	ug/Kg	ug/Kg	ug/Kg	ug/Kg
n-Nitrosodimethylamine	58.24	88.11	91.73	99.15	78.19	78.26	92.72	101.93	71.14	103.10	86.3	167	14.6	41.1	330
Pyridine	117.04	115.48	118.23	110.52	120.15	98.58	90.67	89.15	88.51	94.82	104.3	167	13.2	37.1	330
Benzaldehyde	172.48	145.66	156.71	107.54	148.78	155.32	114.12	126.48	145.26	142.85	141.5	167	20.0	56.4	330
Phenol	107.07	114.76	95.13	101.17	98.57	102.62	90.08	95.10	106.66	106.27	101.7	167	7.3	20.5	330
Bis(2-chloroethyl)ether	90.32	102.99	89.01	82.34	90.09	91.76	78.34	86.48	87.27	85.33	88.4	167	6.5	18.4	330
2-Chlorophenol	96.95	105.86	87.25	88.64	89.33	98.10	78.86	84.47	89.22	96.40	91.5	167	7.8	22.0	330
1,3-Dichlorobenzene	89.35	97.19	79.84	86.36	91.27	82.73	75.85	78.32	84.62	86.28	85.2	167	6.4	18.1	330
1,4-Dichlorobenzene	84.64	94.42	80.57	88.37	82.24	82.32	73.88	77.30	76.23	87.06	82.7	167	6.2	17.5	330
Benzyl alcohol	70.73	81.92	70.46	63.54	74.72	73.45	64.91	65.66	71.49	66.99	70.4	167	5.5	15.5	330
1,2-Dichlorobenzene	81.38	99.59	87.64	88.99	88.71	87.50	77.86	85.00	80.49	92.53	87.0	167	6.3	17.8	330
2-Methylphenol	83.92	94.72	72.71	80.40	72.30	78.38	73.46	66.81	75.21	73.12	77.1	167	7.8	22.1	330
2,2'-oxybis(1-Chloropropane)	85.56	93.49	83.17	79.65	85.85	83.06	75.32	78.94	84.63	94.12	84.4	167	6.0	16.8	330
Acetophenone	90.85	98.91	95.58	81.13	92.95	94.03	83.52	88.03	77.55	87.34	89.0	167	6.8	19.1	330
3-/4-Methylphenol	147.95	179.71	155.41	142.69	171.17	176.69	140.26	136.55	157.88	144.50	155.3	330	15.7	44.3	330
n-Nitroso-di-n-propylamine	73.89	92.44	80.61	73.21	79.22	78.79	64.31	74.77	72.29	78.90	76.8	167	7.3	20.5	330
Hexachloroethane	81.05	84.92	75.93	83.29	84.67	77.99	71.84	77.91	71.68	80.49	79.0	167	4.8	13.6	330
Nitrobenzene	119.80	116.79	98.19	101.27	106.20	110.36	84.87	86.32	98.65	107.89	103.0	167	11.6	32.7	330
Isophorone	96.36	102.68	86.21	82.25	85.41	89.51	68.39	77.04	76.03	85.39	84.9	167	9.9	28.1	330
2-Nitrophenol	74.32	95.20	76.11	71.23	75.66	75.13	62.82	67.27	67.42	72.19	73.7	167	8.7	24.6	330
2,4-Dimethylphenol	25.14	58.05	27.55	51.65	31.50	40.57	36.42	13.24	20.83	17.87	32.3	167	14.5	41.0	330
Benzoic acid	33.35	57.67	40.39	26.45	32.37	34.85	28.71	27.68	28.74	38.63	34.9	167	9.3	26.1	330
Bis(2-chloroethoxy)methane	102.22	101.47	91.32	82.97	86.90	87.17	78.79	85.91	85.10	90.03	89.2	167	7.5	21.2	330
2,4-Dichlorophenol	81.56	98.91	81.01	73.18	78.91	88.65	74.41	72.94	84.54	84.60	81.9	167	8.0	22.5	330
1,2,4-Trichlorobenzene	99.97	106.05	82.95	91.83	84.12	94.82	73.58	76.31	91.64	93.79	89.5	167	10.2	28.8	330
Naphthalene	80.48	80.93	71.67	68.91	71.12	72.61	66.09	67.75	71.35	74.40	72.5	167	4.9	13.9	330
4-Chloroaniline	21.26	45.01	17.12	26.67	16.28	36.45	30.59	22.77	32.18	19.28	26.8	167	9.3	26.2	330
Hexachlorobutadiene	94.50	92.67	87.91	81.25	81.75	83.93	83.69	88.84	80.77	92.64	86.8	167	5.2	14.7	330
Caprolactam	52.93	61.92	60.20	46.99	49.40	61.61	34.65	45.98	48.23	51.74	51.4	167	8.4	23.8	330
4-Chloro-3-methylphenol	77.26	90.98	80.95	66.63	71.39	78.15	69.27	70.92	68.96	78.48	75.3	167	7.3	20.7	330

Reporting Limit = Low Level Standard

Attachment 2 (continued)

Method Detection Limit

Study Date: February 8, 2000
Instrument: 5972HP68
GCMS Method 3550B/8270C Solid Matrix, TCL and PPL Compounds

Compound Name	Rep#1 ug/Kg	Rep#2 ug/Kg	Rep#3 ug/Kg	Rep#4 ug/Kg	Rep#5 ug/Kg	Rep#6 ug/Kg	Rep#7 ug/Kg	Rep#8 ug/Kg	Rep#9 ug/Kg	Rep#10 ug/Kg	Mean ug/Kg	Amt. ug/Kg	S.Dev. ug/Kg	MDL ug/Kg	Report Limit ug/Kg
2-Methylnaphthalene	101.78	115.17	101.48	95.34	95.34	105.15	91.81	88.89	93.05	95.30	98.3	167	7.7	21.8	330
1-Methylnaphthalene	97.17	103.59	83.69	81.51	83.86	92.30	81.37	79.19	88.33	91.58	88.3	167	7.9	22.2	330
Hexachlorocyclopentadiene	60.14	67.92	59.08	63.70	54.54	65.52	50.39	52.51	65.81	58.89	59.9	333	6.0	16.8	330
2,4,6-Trichlorophenol	170.97	181.90	169.23	151.14	164.73	168.65	137.88	154.25	150.54	156.93	160.6	333	12.8	36.2	330
2,4,5-Trichlorophenol	166.54	171.62	173.19	135.63	159.37	176.32	148.26	143.96	166.30	149.65	159.1	333	13.9	39.3	330
1,1'-Biphenyl	109.96	112.58	103.95	98.61	101.72	109.78	93.68	101.13	106.04	96.23	103.4	167	6.3	17.6	330
2-Chloronaphthalene	92.67	98.44	90.89	82.32	86.48	93.23	82.26	81.42	90.31	89.05	88.7	167	5.6	15.7	330
2-Nitroaniline	36.68	38.09	48.15	31.53	40.38	38.73	44.01	36.42	45.85	35.87	39.6	167	5.1	14.4	670
Dimethylphthalate	100.57	102.26	93.75	87.16	86.31	95.10	83.99	86.85	92.37	93.58	92.2	167	6.1	17.3	330
2,6-Dinitrotoluene	73.66	80.32	67.58	56.69	53.36	67.66	62.37	61.54	65.11	65.42	65.4	167	7.8	22.0	330
Acenaphthylene	72.92	73.50	69.80	60.46	61.81	64.16	60.25	62.56	65.90	65.06	65.6	167	4.9	13.8	330
3-Nitroaniline	63.52	91.45	61.45	53.40	52.00	86.75	66.80	65.15	62.09	57.62	66.0	333	13.1	37.0	670
Acenaphthene	76.56	83.06	72.44	66.17	68.70	75.70	66.07	63.41	65.76	65.73	70.4	167	6.3	17.9	330
2,4-Dinitrophenol	385.32	488.37	419.98	325.30	352.87	539.62	370.95	406.28	398.42	425.90	411.3	1670	63.2	178.4	670
4-Nitrophenol	130.16	166.15	150.93	113.70	121.16	181.16	128.54	145.53	142.81	148.71	142.9	667	20.6	58.0	670
2,4-Dinitrotoluene	62.35	68.05	63.39	53.08	55.11	70.68	49.20	55.55	63.84	59.88	60.1	167	6.8	19.2	330
Dibenzofuran	92.08	94.37	84.63	76.25	77.06	86.96	77.85	79.18	84.73	84.66	83.8	167	6.3	17.6	330
Diethylphthalate	93.98	100.62	97.10	79.98	82.81	91.99	77.88	81.68	86.23	90.80	88.3	167	7.7	21.8	330
4-Chlorophenyl-phenylether	90.37	93.82	83.39	79.41	77.50	88.75	69.31	83.51	89.19	82.40	83.8	167	7.2	20.3	330
Fluorene	66.59	67.65	63.22	58.61	59.14	64.59	52.52	59.70	63.59	61.32	61.7	167	4.4	12.5	330
4-Nitroaniline	41.49	53.31	54.46	41.39	37.14	69.70	54.16	59.73	55.60	62.67	53.0	333	10.3	28.9	670
4,6-Dinitro-2-methylphenol	99.31	102.57	97.42	70.13	76.34	97.27	74.40	74.14	89.04	87.92	86.9	333	12.2	34.4	670
n-Nitrosodiphenylamine	103.50	102.97	104.41	91.45	82.40	90.22	80.01	78.35	97.60	86.70	91.8	167	10.0	28.1	330
1,2-Diphenylhydrazine	73.91	79.35	74.18	61.45	65.19	79.29	64.28	68.35	70.80	69.26	70.6	167	6.1	17.2	330
4-Bromophenyl phenylether	88.33	99.88	103.19	78.87	96.87	88.39	76.95	81.26	91.51	84.47	89.0	167	8.9	25.2	330
Hexachlorobenzene	109.59	113.57	114.30	89.89	102.80	103.73	94.21	96.36	94.67	101.46	102.1	167	8.4	23.8	330
Atrazine	85.18	79.41	84.96	66.14	69.41	77.82	75.53	65.09	80.37	73.51	75.7	167	7.2	20.3	330
Pentachlorophenol	101.00	116.42	116.73	83.44	97.84	94.92	93.99	80.63	82.70	98.01	96.6	670	12.7	35.8	670
Phenanthrene	71.37	78.65	77.71	64.26	74.12	72.68	65.97	67.75	71.91	66.94	71.1	167	4.9	13.8	330

Reporting Limit = Low Level Standard

Attachment 2 (continued)

Method Detection Limit

Study Date: February 8, 2000				GCMS Method 3550B/8270C Solid Matrix, TCL and PPL Compounds											
Instrument: 5972HP68															
Compound Name	Rep#1	Rep#2	Rep#3	Rep#4	Rep#5	Rep#6	Rep#7	Rep#8	Rep#9	Rep#10	Mean	Amt.	S.Dev.	MDL	Report Limit
	ug/Kg	ug/Kg	ug/Kg	ug/Kg	ug/Kg	ug/Kg	ug/Kg	ug/Kg	ug/Kg	ug/Kg	ug/Kg	ug/Kg	ug/Kg	ug/Kg	ug/Kg
Anthracene	66.37	73.37	66.28	59.14	62.12	69.35	62.94	64.00	69.27	63.59	65.6	167	4.2	11.8	330
Carbazole	39.62	49.81	43.11	34.69	39.64	49.20	42.11	46.00	44.37	45.66	43.4	167	4.6	13.1	330
Di-n-butylphthalate	95.99	109.82	105.72	72.82	86.04	89.23	77.47	81.63	84.60	79.53	88.3	167	12.1	34.2	330
Fluoranthene	55.05	59.93	53.57	49.47	54.95	58.27	51.13	53.99	54.04	51.56	54.2	167	3.2	8.9	330
Benzidine	1066.5	545.76	1111.1	769.41	480.14	862.11	*	1430.9	1724.1	*	999	1670	426.9	1280	6670
Pyrene	85.37	86.85	87.46	75.13	89.90	85.13	79.72	77.45	92.45	86.11	84.6	167	5.5	15.5	330
Butylbenzylphthalate	79.89	101.91	98.63	65.86	89.17	78.88	68.49	63.10	86.14	68.66	80.1	167	13.7	38.7	330
3,3'-Dichlorobenzidine	14.04	36.98	18.29	12.85	8.53	33.42	14.44	21.89	18.26	10.31	18.9	167	9.5	26.7	330
bis(2-ethylhexyl)phthalate	92.15	95.60	103.92	61.31	79.14	78.52	58.79	66.69	84.16	77.34	79.8	167	14.8	41.7	330
Benzo(a)anthracene	64.03	74.19	63.69	60.03	60.11	67.82	53.25	62.82	59.44	63.08	62.8	167	5.5	15.6	330
Chrysene	69.99	74.47	74.02	61.18	71.85	75.56	60.49	68.84	70.58	64.30	69.1	167	5.4	15.3	330
Di-n-octylphthalate	79.79	81.39	84.19	47.62	60.26	65.93	53.95	48.39	63.87	49.75	63.5	167	14.1	39.8	330
Benzo(b)fluoranthene	64.14	67.54	84.04	44.75	60.95	79.74	62.72	58.76	75.63	53.52	65.2	167	12.0	33.9	330
Benzo(k)fluoranthene	64.26	62.72	62.68	62.54	61.27	61.41	56.49	58.20	62.87	72.45	62.5	167	4.2	11.9	330
Benzo(a)pyrene	63.76	64.60	51.23	45.44	45.94	48.93	39.49	56.11	43.35	41.03	50.0	167	8.9	25.1	330
Indeno(1,2,3-c,d)pyrene	69.21	78.36	65.71	57.44	64.50	77.62	41.15	62.04	62.10	64.68	64.3	167	10.5	29.7	330
Dibenzo(a,h)anthracene	52.01	57.70	48.84	50.31	43.79	64.61	39.96	51.19	46.16	56.07	51.1	167	7.1	20.2	330
Benzo(g,h,i)perylene	58.13	69.39	63.31	45.04	56.43	64.11	53.29	56.00	54.40	57.44	57.8	167	6.7	18.9	330

Reporting Limit = Low Level Standard

Attachment 3

COMPUCHEM a division of Liberty Analytical Corp DATE ___/___/___ INITIAL TIME OF TUNE_____ SHIFT/S(A)_____(B)_____(C)_____

GC/MS SEMIVOLATILE RUN LOG TIME TUNE EXPIRES_____ LINKER /METHOD_____

COMPUCHEM .LOGBOOK 4 YYY 1 (5972hp64)

PREVENTIVE MAINTENANCE_____

#	REJECTED	FILE NAME	REPORTED	DATE	TIME	CLIENT ID#	CASE/SDG#	AMOUNT INJECTED	CHEMIST	COMMENTS(ETC.)/DISPOSITION
1				/ /						
2				/ /						
3				/ /						
4				/ /						
5				/ /						
6				/ /						
7				/ /						
8				/ /						
9				/ /						
10				/ /						
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16				/ /						
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21				/ /						
22				/ /						
23				/ /						
24				/ /						

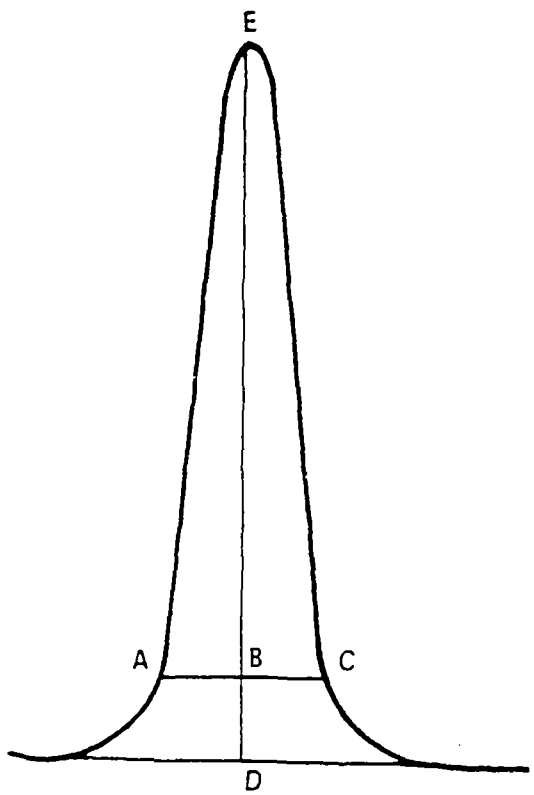
	Tune	STANDARDS Analytical	Int. Std.	Column Type
Std. ID #				
Lot #				

SUPERVISOR APPROVAL_____

DATE _____

The presence of the Chemist's employee ID number, or signature, on this run log attests that strict compliance with the method's SOP has occurred. Any SOP deviations require documentation by the responsible chemist together with the chemist's initials and the initials of the lab supervisor and a QA department representative, signifying approval of the deviation. 8/11/00:mlj

Attachment 4



TAILING FACTOR= $\frac{BC}{AB}$

Example calculation: Peak Height = DE = 100 mm
10% Peak Height = BD = 10 mm
Peak Width at 10% Peak Height = AC = 23 mm
AB = 11 mm
BC = 12 mm

Therefore: Tailing Factor = $\frac{12}{11}$ = 1.1

Figure 13. Tailing factor calculation.

Attachment 5

Analyst Capability Study

Laboratory Name/North Carolina Certificate Number: CompuChem/79
Analyst: Valgena Respass
Study Date: June 13, 2000
Method: 8270C Aqueous
Instrument/Column: 5972hp68

Compounds	True Val ug/l	Rep #1 ug/l	Rep #2 ug/l	Rep #3 ug/l	Rep #4 ug/l	Mean ug/l	Mean % Rec.	SD(n-1) ug/l	-3SD ug/l	+3SD ug/l	- 3SD %R	+3SD %R	RSD %
n-Nitrosodimethylamine	100	48.46	50.52	37.96	47.95	46.22	46.2	5.62	29.4	63.1	63.5	136.5	12.2
Pyridine	100	43.09	40.72	43.38	46.2	43.35	43.3	2.24	36.6	50.1	84.5	115.5	5.2
Benzaldehyde	100	32.59	36.38	27.35	37.69	33.50	33.5	4.64	19.6	47.4	58.5	141.5	13.8
Phenol	100	38.14	44.3	35.02	41.71	39.79	39.8	4.06	27.6	52.0	69.4	130.6	10.2
Bis(2-chloroethyl)ether	100	73.94	79.89	63.41	78.81	74.01	74.0	7.53	51.4	96.6	69.5	130.5	10.2
2-Chlorophenol	100	82.77	92.86	75.02	90.23	85.22	85.2	8.03	61.1	109.3	71.7	128.3	9.4
1,3-Dichlorobenzene	100	51.89	53.89	39.1	48.01	48.22	48.2	6.55	28.6	67.9	59.2	140.8	13.6
1,4-Dichlorobenzene	100	52.04	53.87	41.09	48.3	48.83	48.8	5.65	31.9	65.8	65.3	134.7	11.6
Benzyl alcohol	100	85.8	87.66	72.97	89.72	84.04	84.0	7.55	61.4	106.7	73.0	127.0	9.0
1,2-Dichlorobenzene	100	56.55	58.35	43.73	52.48	52.78	52.8	6.51	33.2	72.3	63.0	137.0	12.3
2-Methylphenol	100	78.17	87	71.17	84.71	80.26	80.3	7.12	58.9	101.6	73.4	126.6	8.9
2,2'-oxybis(1-Chloropropane)	100	72.42	78.96	64.24	77.1	73.18	73.2	6.56	53.5	92.9	73.1	126.9	9.0
Acetophenone	100	75.3	81.68	67.76	80.15	76.22	76.2	6.26	57.4	95.0	75.3	124.7	8.2
3-Methylphenol	200	133.34	148.57	122.66	141.69	136.57	68.3	11.17	34.8	101.8	50.9	149.1	8.2
4-Methylphenol	200	133.34	148.57	122.66	141.69	136.57	68.3	11.17	34.8	101.8	50.9	149.1	8.2
n-Nitroso-di-n-propylamine	100	72.41	78.69	66.48	81.8	74.85	74.8	6.81	54.4	95.3	72.7	127.3	9.1
Hexachloroethane	100	47.82	47.25	34.35	41.99	42.85	42.9	6.25	24.1	61.6	56.3	143.7	14.6
Nitrobenzene	100	60.24	67.65	51	63.36	60.56	60.6	7.06	39.4	81.7	65.0	135.0	11.7
Isophorone	100	59.74	69.31	55.8	67.07	62.98	63.0	6.29	44.1	81.9	70.0	130.0	10.0
2-Nitrophenol	100	94.55	103.7	83.59	108.68	97.63	97.6	11.04	64.5	130.7	66.1	133.9	11.3
2,4-Dimethylphenol	100	94.89	104.79	82.99	96.17	94.71	94.7	8.97	67.8	121.6	71.6	128.4	9.5
Benzoic acid	100	1.96	2.41	1.61	8.61	3.65	3.6	3.32	-6.3	13.6	-173.4	373.4	91.1
Bis(2-chloroethoxy)methane	100	76.83	87.73	71	84.81	80.09	80.1	7.61	57.3	102.9	71.5	128.5	9.5
2,4-Dichlorophenol	100	88.93	105.12	80.96	103.29	94.58	94.6	11.61	59.7	129.4	63.2	136.8	12.3
1,2,4-Trichlorobenzene	100	58.59	64.81	47.45	57.49	57.09	57.1	7.19	35.5	78.6	62.2	137.8	12.6
Naphthalene	100	78.82	86.47	65.47	78.74	77.38	77.4	8.73	51.2	103.6	66.2	133.8	11.3

Attachment 5 (continued)

Analyst Capability Study

Laboratory Name/North Carolina Certificate Number: CompuChem/79
Analyst: Valgena Respass
Study Date: June 13, 2000
Method: 8270C Aqueous
Instrument/Column: 5972hp68

Compounds	True Val ug/l	Rep #1 ug/l	Rep #2 ug/l	Rep #3 ug/l	Rep #4 ug/l	Mean ug/l	Mean % Rec.	SD(n-1) ug/l	-3SD ug/l	+3SD ug/l	- 3SD %R	+3SD %R	RSD %
4-Chloroaniline	100	82.15	93.19	72.26	89.2	84.20	84.2	9.18	56.7	111.7	67.3	132.7	10.9
Hexachlorobutadiene	100	47	48.28	34.15	41.29	42.68	42.7	6.45	23.3	62.0	54.7	145.3	15.1
Caprolactam	100	27.75	29.9	25.25	28.95	27.96	28.0	2.01	21.9	34.0	78.4	121.6	7.2
4-Chloro-3-methylphenol	100	90.45	104.93	85.76	103.21	96.09	96.1	9.44	67.8	124.4	70.5	129.5	9.8
2-Methylnaphthalene	100	79.9	89.94	72.57	84.28	81.67	81.7	7.33	59.7	103.7	73.1	126.9	9.0
1-Methylnaphthalene	100	94.37	105.88	83.52	99.03	95.70	95.7	9.40	67.5	123.9	70.5	129.5	9.8
Hexachlorocyclopentadiene	100	45.63	48.54	37.69	43.51	43.84	43.8	4.59	30.1	57.6	68.6	131.4	10.5
2,4,6-Trichlorophenol	100	91.9	100.72	82.44	103.44	94.63	94.6	9.50	66.1	123.1	69.9	130.1	10.0
2,4,5-Trichlorophenol	100	92.77	102.37	78.09	100.18	93.35	93.4	10.97	60.4	126.3	64.7	135.3	11.8
1,1'-Biphenyl	100	82.34	92.11	76.51	83.26	83.56	83.6	6.44	64.2	102.9	76.9	123.1	7.7
2-Chloronaphthalene	100	64.78	70.75	58.68	63.78	64.50	64.5	4.95	49.6	79.3	77.0	123.0	7.7
2-Nitroaniline	100	74.74	86.51	71.39	82.97	78.90	78.9	7.03	57.8	100.0	73.3	126.7	8.9
Dimethylphthalate	100	5.33	21.58	9.31	8.92	11.29	11.3	7.09	-10.0	32.6	-88.6	288.6	62.9
2,6-Dinitrotoluene	100	69.25	82.55	66.14	78.35	74.07	74.1	7.67	51.1	97.1	68.9	131.1	10.4
Acenaphthylene	100	83.2	93.49	77.09	87.47	85.31	85.3	6.92	64.6	106.1	75.7	124.3	8.1
3-Nitroaniline	100	83.09	95.29	79.63	92.77	87.70	87.7	7.52	65.1	110.3	74.3	125.7	8.6
Acenaphthene	100	82.29	94.42	76.13	88.56	85.35	85.4	7.89	61.7	109.0	72.3	127.7	9.2
2,4-Dinitrophenol	100	43.94	81.31	44.89	95.84	66.50	66.5	26.18	-12.0	145.0	-18.1	218.1	39.4
4-Nitrophenol	100	124.88	150.74	121.19	143.65	135.12	135.1	14.33	92.1	178.1	68.2	131.8	10.6
2,4-Dinitrotoluene	100	72.75	80.94	69.02	77.86	75.14	75.1	5.30	59.2	91.0	78.8	121.2	7.1
Dibenzofuran	100	83.77	96.81	79.91	91.77	88.07	88.1	7.64	65.1	111.0	74.0	126.0	8.7
Diethylphthalate	100	38.13	63.63	44.73	46.61	48.28	48.3	10.86	15.7	80.9	32.5	167.5	22.5
4-Chlorophenyl-phenylether	100	85.62	96.33	84.57	92.64	89.79	89.8	5.64	72.9	106.7	81.1	118.9	6.3
Fluorene	100	86.94	99.29	86.48	95.44	92.04	92.0	6.35	73.0	111.1	79.3	120.7	6.9
4-Nitroaniline	100	86.85	96.63	80.94	93.02	89.36	89.4	6.91	68.6	110.1	76.8	123.2	7.7
4,6-Dinitro-2-methylphenol	100	76.94	97.63	72.05	118.58	91.30	91.3	21.30	27.4	155.2	30.0	170.0	23.3

Attachment 5 (continued)

Analyst Capability Study

Laboratory Name/North Carolina Certificate Number: CompuChem/79
Analyst: Valgena Respass
Study Date: June 13, 2000
Method: 8270C Aqueous
Instrument/Column: 5972hp68

Compounds	True Val	Rep #1	Rep #2	Rep #3	Rep #4	Mean	Mean	SD(n-1)	-3SD	+3SD	- 3SD	+3SD	RSD
	ug/l	ug/l	ug/l	ug/l	ug/l	ug/l	% Rec.	ug/l	ug/l	ug/l	%R	%R	%
n-Nitrosodiphenylamine	200	87.5	97.92	85.67	96.34	91.86	45.9	6.17	27.4	64.4	59.7	140.3	6.7
1,2-Diphenylhydrazine	100	84.77	95.67	82.98	90.53	88.49	88.5	5.77	71.2	105.8	80.4	119.6	6.5
4-Bromophenyl phenylether	100	86.27	96.98	84.86	94.64	90.69	90.7	6.02	72.6	108.7	80.1	119.9	6.6
Hexachlorobenzene	100	70.2	80.97	69.98	78.35	74.88	74.9	5.63	58.0	91.8	77.4	122.6	7.5
Atrazine	100	171.93	198.66	168.23	192.63	182.86	182.9	15.04	137.7	228.0	75.3	124.7	8.2
Pentachlorophenol	100	87.25	97.08	69.76	113.79	91.97	92.0	18.42	36.7	147.2	39.9	160.1	20.0
Phenanthrene	100	86.29	95.7	83.93	96.72	90.66	90.7	6.49	71.2	110.1	78.5	121.5	7.2
Anthracene	100	84.08	94.42	83.73	94.49	89.18	89.2	6.09	70.9	107.5	79.5	120.5	6.8
Carbazole	100	103.43	114.82	102.19	114.2	108.66	108.7	6.78	88.3	129.0	81.3	118.7	6.2
Di-n-butylphthalate	100	68.38	87.05	74.42	79.35	77.30	77.3	7.90	53.6	101.0	69.3	130.7	10.2
Fluoranthene	100	89.68	99.31	86.27	100.55	93.95	94.0	7.06	72.8	115.1	77.5	122.5	7.5
Benzidine	100	13.01	14.99	9.01	13.78	12.70	12.7	2.59	4.9	20.5	38.8	161.2	20.4
Pyrene	100	85.89	99.38	81.28	95.65	90.55	90.6	8.40	65.4	115.7	72.2	127.8	9.3
Butylbenzylphthalate	100	46.89	70.14	61.14	60.16	59.58	59.6	9.58	30.8	88.3	51.8	148.2	16.1
3,3'-Dichlorobenzidine	100	67.72	74.99	63.22	72.07	69.50	69.5	5.14	54.1	84.9	77.8	122.2	7.4
bis(2-ethylhexyl)phthalate	100	85.36	99.95	85.9	99.66	92.72	92.7	8.19	68.2	117.3	73.5	126.5	8.8
Benzo(a)anthracene	100	84.91	96.51	82.77	94.14	89.58	89.6	6.76	69.3	109.9	77.4	122.6	7.5
Chrysene	100	84.42	100.24	82.81	94.34	90.45	90.5	8.28	65.6	115.3	72.5	127.5	9.2
Di-n-octylphthalate	100	84.92	96.92	82.88	97.42	90.54	90.5	7.71	67.4	113.7	74.5	125.5	8.5
Benzo(b)fluoranthene	100	85.39	93.25	90.66	95.75	91.26	91.3	4.43	78.0	104.6	85.4	114.6	4.9
Benzo(k)fluoranthene	100	82.23	98.6	72.92	95.11	87.22	87.2	11.85	51.7	122.8	59.2	140.8	13.6
Benzo(a)pyrene	100	85.08	97.78	81.17	95.01	89.76	89.8	7.91	66.0	113.5	73.6	126.4	8.8
Indeno(1,2,3-c,d)pyrene	100	133.76	152.27	127.13	147.15	140.08	140.1	11.64	105.2	175.0	75.1	124.9	8.3
Dibenzo(a,h)anthracene	100	86.23	98.46	81.69	95.72	90.53	90.5	7.88	66.9	114.2	73.9	126.1	8.7
Benzo(g,h,i)perylene	100	87.32	98.7	83.26	96.36	91.41	91.4	7.32	69.4	113.4	76.0	124.0	8.0

SOP Documentation Form

This form must accompany all new and revised Standard Operating Procedures (SOPs) when you turn them in to Quality Assurance for review. Please fill out the entire shaded area.

This is a new procedure _____ revised procedure X outdated procedure (archive) _____

- Procedure area, title, and SOP number: Effective Date:

Instrument Procedure 976: GC/MS Semivolatiles in Low Concentration Water Samples (EPA CLP Low Concentration SOW + NYASP) 6/25/98

- Procedure ~~prepared~~ revised by: Date:

Paul S. Brandon 6/25/98

- Procedure approved by: (If the lab manager prepared the SOP, a qualified second party should sign.) Date:

Bob Mueia 6/26/98

- Reason for change: Annual Review

- This procedure meets the requirements set forth in the following References for Approved Methods:

OLC02 + Revisions

- Procedure approved by Quality Assurance Representative: Date:

Linda Carter 6/26/98

Effective 1-1-96, on an annual basis: Lab managers are required to review lab practices and revise the SOP if necessary. If no revision is necessary, indicate by your signature that the SOP has been reviewed.

nual Review--Signature and Date: _____

Annual Review--Signature and Date: _____

Annual Review--Signature and Date: _____

Instrument Procedure 476: GC/MS Semivolatiles in Low Concentration Water Samples (EPA CLP Low Concentration SOW + NYSASP)

1.0 Scope and Application

This method is for the analysis of extractable, low concentration water samples for semivolatile compounds. The majority of these samples are for well or drinking water samples from and around Superfund sites.

The full list of CLP target compounds is presented in Table 1 below.

Table 1.
Semivolatile
Target Compound List (TCL) and Contract Required Quantitation Limits (CRQLs)

Target Compounds	CRQL (µg/L)
phenol	5
bis(2-chloroethyl)ether	5
2-chlorophenol	5
2-methylphenol	5
2,2'-oxybis(1-chloropropane)	5
4-methylphenol	5
N-nitroso-di-n-propylamine	5
hexachloroethane	5
nitrobenzene	5
isophorone	5
2-nitrophenol	5
2,4-dimethylphenol	5
bis(2-chloroethoxy)methane	5
2,4-dichlorophenol	5
naphthalene	5
4-chloroaniline	5
hexachlorobutadiene	5
4-chloro-3-methylphenol	5
2-methylnaphthalene	5
hexachlorocyclopentadiene	5
2,4,6-trichlorophenol	5
2,4,5-trichlorophenol	20
2-chloronaphthalene	5
2-nitroaniline	20
dimethyl phthalate	5
acenaphthylene	5
3-nitroaniline	20
acenaphthene	5
2,4-dinitrophenol	20
4-nitrophenol	20
dibenzofuran	5
2,4-dinitrotoluene	5

Target Compounds	CRQL (µg/L)
2,6-dinitrotoluene	5
Diethylphthalate	5
4-chlorophenyl-phenylether	5
Fluorene	5
4-nitroaniline	20
4,6-dinitro-2-methylphenol	20
n-nitrosodiphenylamine	5
4-bromophenyl-phenylether	5
Hexachlorobenzene	5
Pentachlorophenol	20
Phenanthrene	5
Anthracene	5
di-n-butylphthalate	5
Fluoranthene	5
pyrene	5
butylbenzylphthalate	5
3,3'-dichlorobenzidine	5
benzo(a)anthracene	5
bis(2-ethylhexyl)phthalate	5
chrysene	5
di-n-octyl phthlate	5
benzo(b)fluoranthene	5
benzo(k)fluoranthene	5
benzo(a)pyrene	5
indeno(1,2,3-cd)pyrene	5
dibenz(a,h)anathracene	5
benzo(g,h,i)perylene	5

Surrogates

phenol-d_5
2-fluorophenol
2,4,6-tribromophenol
nitrobenzene-d_5
2-fluorobiphenyl
terphenyl-d_{14}

2.0 Summary of Method

A one-liter aliquot of sample is acidified to pH 2.0 and extracted with methylene chloride using a continuous liquid-liquid extractor. The sample is then concentrated down to a volume of 1.0 ml. An aliquot of the 1.0-ml extract is injected onto a gas chromatograph capillary column. The gas chromatograph is temperature programmed to separate the semivolatile compounds, which are in turn detected with a mass spectrometer.

Target and surrogate compounds are identified in the samples by analyzing standards under the same conditions used for samples and comparing resultant mass spectra and GC retention times. Internal standards are added to all samples and standards. A response factor is established for each target and surrogate compound during the initial and continuing calibrations by comparing the MS response for the primary ion produced by the compound extracted ion current profile (EICP) to the MS response for the primary ion produced by an internal standard. Each identified target and surrogate compound in a sample is quantified by comparing the response for the target compound and the internal standard, while taking into account the response factor from the most recent calibration, the sample volume, and any sample dilutions.

Nontarget compounds are identified by comparing the resultant mass spectra from the nontarget compounds to mass spectra contained in the National Institute of Standards and Technology Mass Spectral Library. Nontarget compounds are quantified by comparing the MS response from the reconstructed ion chromatogram (RIC) for the nontarget compound peaks to the MS response produced by the nearest internal standard. A response factor of 1 is assumed. Nontarget compounds are referred to as Tentatively Identified Compounds (TICs).

The standards, samples, and other required runs must be injected within the 12-hour calibration period which begins at the time of injection of the Decafluorotriphenylphosphine (DFTPP) instrument performance check, or tuning compound. All injections must be recorded on the instrument run log. The run log should contain the date and time of injection, the volume of extract injected, standard ID numbers, sample ID numbers, case/SDG numbers, and comments relevant to the injection.

3.0 Apparatus and Materials

3.1 Gas Chromatograph/Mass Spectrometer

3.1.1 Gas Chromatograph - The gas chromatograph (GC) system must be capable of temperature programming and have a flow controller that maintains a constant column flow rate throughout the temperature program. The system must be suitable for splitless injection and have all required accessories including syringes, analytical columns, and gases. All GC carrier gas lines must be constructed from stainless steel or copper tubing. Non-polytetrafluoroethylene (PTFE) thread sealants,

or flow controllers with rubber components are not to be used.

Gas Chromatography Column - A 30 m x 0.25 mm ID (or 0.32 mm) bonded-phase silicone coated fused silica capillary column (J&W Scientific DB-5 or equivalent). A film thickness of 0.25 to 1.0 µm may be used. Alternative columns are presented in the EPA CLP SOW and others may be used of equivalency can be demonstrated. Specifications for equivalency are presented in the SOW.

3.1.2 Mass Spectrometer - The mass spectrometer must be capable of scanning from 35 to 500 amu every 1 second or less, utilizing 70 volts (nominal) electron energy in the electron impact ionization mode and producing a mass spectrum that meets all the tuning acceptance criteria when 50 ng of decafluorotriphenylphosphine (DFTPP) is injected through the gas chromatograph inlet. To ensure sufficient precision of mass spectral data, the MS scan rate must allow acquisition of at least five spectra while a sample compound elutes from the GC. The GC/MS system must be in a room whose atmosphere is demonstrated to be free of all potential contaminants that could interfere with the analysis. The instrument must be vented outside the facility or to a trapping system which prevents the release of contaminants into the instrument room.

3.1.3 Data System

A computer system must be interfaced to the mass spectrometer to allow the continuous acquisition and storage on machine readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that searches any GC/MS data file for ions of a specified mass and plots ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available to integrate the abundance in any EICP between specified time or scan number limits. Also, for the nontarget compounds, software must be available to compare sample spectra against reference library spectra. The most recent release of

the National Institute of Standards and Technology Mass Spectral library will be used as the reference library.

The standards and samples are processed using the Hewlett Packard HP 9000 735 Unix Workstation, employing HP Chemserver with Target 3 and Envision software from Thru-Put Systems.

3.2 Magnetic Tape Storage Device - The magnetic tape storage device must be capable of recording data and suitable for long-term, off-line storage.

3.3 Glassware - Sample preparation vials: amber, 1.5 ml with 1 ml inserts with crimp tops 5.1/PTFE Septum. Hamilton microliter syringes: 10 µl with low heat transfer from hand to sample.

4.0 Reagents

Reagents - Methylene chloride, optima grade

5.0 Standards

5.1 Instrument Performance Check (Tuning) Solution - Decafluorotriphenylphosphine (DFTPP)

Prepare a 50 ng/µl solution of DFTPP in methylene chloride. The DFTPP solution must be prepared fresh once every twelve months, or sooner, if the solution has degraded or concentrated.

5.2 Initial and Continuing Calibration Solutions

5.2.1 Five initial calibration standard solutions are required for all target and surrogate compounds. Standard concentrations listed below are required for five of the surrogates and all but eight of the target compounds.

Standard concentration (ng/µl)	ID#
5	
10	
20	
50	
80	

Nine compounds require calibration at 20, 50, 80, 100, and 120 ng/µl:

- 2,4-dinitrophenol
- 2,4,5-trichlorophenol
- 2-nitroaniline
- 3-nitroaniline
- 4-nitroaniline
- 4-nitrophenol
- 4,6-dinitro-2-methylphenol
- pentachlorophenol
- 2,4,6-tribromophenol (surrogate)

5.2.2 To prepare a calibration standard solution, add an appropriate volume of secondary dilution standard to methylene chloride in a volumetric flask. Dilute to volume with methylene chloride.

5.2.3 Add internal standard to each calibration standard for a concentration of 20 ng/µl for each internal standard.

5.2.4 The 20 ng/µl initial calibration solution (80 ng/µl for the nine compounds listed in 5.2.1) is the continuing calibration solution.

5.2.5 The five initial calibration solutions must be prepared fresh before use. The continuing calibration standard solution must be prepared or aliquoted from the Standards Laboratory weekly, or sooner, if the solution has degraded or concentrated.

5.3 Surrogate Standard Spiking Solution

5.3.1 Prepare a surrogate standard spiking solution in methanol that contains 2,4,6-tribromophenol (an acid surrogate compound) at a concentration of 120 µg/ml. The other acid surrogate compounds: phenol-d_5 and 2-fluorophenol, and the base/neutral compounds: nitrobenzene-d_5, terphenyl-d_{14}, and 2-fluorobiphenyl are at a concentration of 40 µg/ml.

5.3.2 The surrogate standard spiking solution must be prepared every twelve months, or sooner, if the solution has degraded or concentrated.

5.4 Internal Standard Spiking Solution

5.4.1 Prepare an internal standard spiking solution in methylene chloride that contains

- 1,4-dichlorobenzene-d_4
- naphthalene-d_8
- acenaphthene-d_{10}
- phenanthrene-d_{10}
- chrysene-d_{12}
- perylene-d_{12}

at 800 ng/µl. It may be necessary to use 5-10% benzene or toluene in this solution and a few minutes of ultrasonic mixing to dissolve all the constituents. Note: While the SOW indicates that a concentration of 2000 ng/ml should be prepared, it also provides for preparing the internal standard solution at a different concentration.

5.4.2 The internal standard spiking solution must be prepared every six months, or sooner, if the solution has degraded or concentrated.

5.5 Laboratory Control Sample (LCS) Spiking Solution

Prepare a laboratory control sample spiking solution that contains each of the compounds at the concentrations listed below in methanol.

Compounds	Concentration (µg/ml)
phenol	40.0
2-chlorophenol	40.0
4-chloroaniline	40.0
2,4,6-trichlorophenol	40.0
bis(2-chloroethyl)ether	20.0
N-nitroso-di-n-propylamine	20.0
hexachloroethane	20.0
isophorone	20.0
naphthalene	20.0
2,4-dinitrotoluene	20.0
diethylphthalate	20.0
N-nitrosodiphenylamine	20.0
hexachlorobenzene	20.0
benzo(a)pyrene	20.0

5.6 The current edition of the NYSASP requires that a matrix spike, matrix spike duplicate, and a matrix spike blank be performed instead of the single LCS. The compounds for these tests are the same as those for water analyses following the current EPA CLP SOW for multi-media, multi-concentration samples. The acceptance criteria are those for water samples.

6.0 Interferences

Contaminants in solvents, reagents, glassware, and other sample processing hardware may cause method interferences such as discrete artifacts and/or elevated baselines in the reconstructed ion current (RIC) profiles. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory method blanks. Matrix interference may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from source to source.

7.0 Instrument Standardization Procedure

7.1 GC/MS Instrument Performance Check

The instrument's mass calibration and resolution are verified by analyzing the DFTPP tuning compound every 12 hours. One µl of the 50 ng/µl DFTPP solution is injected into the GC using the cold needle technique. The acceptance criteria for the ion abundances found in the DFTPP spectrum are

Mass	Ion Abundance Criteria	
51	30-80% of mass 198	(30-60%)
68	< 2% of mass 69	(<2%)
69	Present	
70	< 2% of mass 69	(<2%)
127	25-75% of mass 198	(40-60%)
197	< 1% of mass 198	(<1%)
198	Base peak, 100% relative abundance (see note)	
199	5-9% of mass 198	(5-9%)
275	10-30% of mass 198	(10-30%)
365	Greater than 0.75% of mass 198	(>1.00%)
441	Present but < mass 443	
442	40-110% of mas 198	(40-110%)
443	15-24% of mass 442	(17-23%)

Note: All ion abundances MUST be normalized to m/z 198, the nominal base peak, even though the ion abundances of m/z 442 may be up to 110% that of m/z 198. Note: The values in parentheses are those required by the NYSASP.

These abundance criteria must be met for a 50-ng injection of DFTPP. The mass spectrum of DFTPP must be acquired in the following manner. Three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged.

Background subtraction is required, and must be accomplished using a single scan prior to the beginning of the elution of DFTPP.

The DFTPP solution contains DFTPP, D10-phenanthrene, benzidine, pentachlorophenol, p,p'-DDT and endrin. While there is no criterion for the pentachlorophenol response factor, a very low response factor (<0.50) indicates that the column and/or the injector is degraded or dirty and needs to be cleaned. If this is the case, the operator should clean the injection port and perform column maintenance prior to continuing with the chromatography check standard or shift standard. The other compounds also assist in diagnosing the condition of the instrument. Endrin is only assessed when the indtrument is used for GC/MS pesticide/PCB confirmations because of the lower injector temperture.

The DFTPP package should include a hardcopy of the DFTPP spectrum, a mass listing that corresponds to the spectrum, the GC/MS Tuning and Calibration (DFTPP) Form, and an EICP containing the ions 184 (benzidine), 266 (pentachlorophenol), 198 (DFTPP), and 188 (D10-phenanthrene) and reconstructed ion chromatograph (RIC).

7.2 Generating the Multipoint Files

Each of the five initial calibrations are injected individually using 1 µl to create the multipoint. All quantitations for this method are performed with the response list created from the multipoint data. Therefore, it is critical that the multipoint data be correct.

8.0 Initial Calibration Procedure

An initial five-point calibration ("multipoint") must be performed if a valid multipoint for the analysis has not already been analyzed on the instrument or if the calibration check standard (12-hour continuing calibration standard) does not meet all acceptance criteria. The calibration standards are at five concentration levels (20, 50, 80, 120, and 160 total ng per 2 µl). Each calibration standard contains each compound of interest and each surrogate. Eight compounds (2,4-dinitrophenol, 2,4,5-trichlorophenol, 2-nitroaniline, 3-nitroaniline, 4-nitroaniline, 4-nitrophenol, 4,6-dinitro-2-methylphenol, and pentachlorophenol) may require only a four-point initial calibration at 50, 80, 120 and 160 total ng since detection at less than 50 ng per injection is difficult.

NOTE: An initial five-point calibration is also required whenever a column is changed or an ion source cleaned.

8.1 Generating the multipoint Files

Each of the five initial calibrations are injected individually using 1 µl to create the multipoint. All quantitations for this method are performed with the response list created from the multipoint data. Therefore, it is critical that the multipoint data be correct

The system program prompts the operator for the file names of the 5 initial calibration standards. The program produces a report detailing the response factors for each level, the average response factor and the percent relative standard deviation (%RSD) for each compound. Note: Each compound must have a response factor for all five levels. If the response factor is missing for one or more compounds, the standards used to create the multipoint will be incorrect.

8.2 Definition of a Valid Multipoint

- One valid injection of each of the five standard concentrations
- All standards acquired under a valid DFTPP tune
- All compounds present in all five standard levels
- All isomer pairs must be resolved
- Napthalene and 4-chloroaniline must be resolved.
- **2 methylnaphthalene and 4-chloro-3-methyphenol must be resolved**

8.3 Response Factor Criteria

8.3.1 Response factor criteria have been established for the semivolatile target compounds and semivolatile surrogate compounds.

8.3.1.1 The compounds listed in Table 2 must meet the minimum RRF and maximum %RSD criteria for the initial calibration, with allowance made for up to four semivolatile target and surrogate compounds. However, the RRFs for those four compounds must be greater than 0.010, and the %RSD of those four compounds must be less than or equal to 40.0% for the initial calibration to be acceptable.

Table 2
Acceptance Criteria For Initial and Continuing
Calibration For Semivolatile Organic Compounds

Semivolatile Compounds	Minimum RRF	Maximum %RSD	Maximum %Diff
phenol	0.800	20.5	±25.0
bis(2-chloroethyl)ether	0.700	20.5	±25.0
2-chlorophenol	0.800	20.5	±25.0
2-methylphenol	0.700	20.5	±25.0
4-methylphenol	0.600	20.5	±25.0
N-nitroso-di-n-propylamine	0.500	20.5	±25.0
hexachloroethane	0.300	20.5	±25.0
nitrobenzene	0.200	20.5	±25.0
isophorone	0.400	20.5	±25.0
2-nitrophenol	0.100	30.0	±30.0
2,4-dimethylphenol	0.200	30.0	±30.0
bis(2-chloroethoxy)methane	0.300	20.5	±25.0
2,4-dichlorophenol	0.200	20.5	±25.0
naphthalene	0.700	20.5	±25.0
4-chloro-3-methylphenol	0.200	20.5	±25.0
2-methylnaphthalene	0.400	20.5	±25.0
2,4,6-trichlorophenol	0.200	20.5	±25.0
2,4,5-trichlorophenol	0.200	20.5	±25.0
2-chloronaphthalene	0.800	20.5	±25.0
acenaphthylene	0.900	20.5	±25.0
acenaphthene	0.900	20.5	±25.0
dibenzofuran	0.800	20.5	±25.0
2,4-dinitrotoluene	0.200	30.0	±30.0
2,6-dinitrotoluene	0.200	20.5	±25.0
4-chlorophenyl-phenylether	0.400	20.5	±25.0
fluorene	0.900	20.5	±25.0
4-bromophenyl-phenylether	0.100	20.5	±25.0
hexachlorobenzene	0.100	20.5	±25.0
pentachlorophenol	0.050	20.5	±25.0
phenanthrene	0.700	20.5	±25.0
anthracene	0.700	20.5	±25.0
fluoranthene	0.600	20.5	±25.0
pyrene	0.600	20.5	±25.0
benzo(a)anthracene	0.800	20.5	±25.0
chrysene	0.700	20.5	±25.0
benzo(b)fluoranthene	0.700	20.5	±25.0
benzo(k)fluoranthene	0.700	20.5	±25.0
benzo(a)pyrene	0.700	20.5	±25.0
indeno(1,2,3-cd)pyrene	0.500	20.5	±25.0
dibenzo(a,h)anthracene	0.400	20.5	±25.0
benzo(g,h,i)perylene	0.500	20.5	±25.0
phenol-d_5	0.800	20.5	±25.0
2-fluorophenol	0.600	20.5	±25.0
terphenyl-d_{14}	0.500	20.5	±25.0
2-fluorobiphenyl	0.700	20.5	±25.0

The following compounds have no maximum %RSD criteria but must meet a minimum RRF criterion of 0.010:

- 2,2'-oxybis(1-chloropropane)
- 4-chloroaniline
- hexachlorobutadiene
- hexachlorocyclopentadiene
- 2-nitroaniline
- dimethylphthalate
- 3-nitroaniline
- 2,4-dinitrophenol
- 4-nitrophenol
- diethylphthalate
- 4-nitroaniline
- 4,6-dinitro-2-methylphenol
- N-nitrosodiphenylamine
- di-n-butylphthalate
- butylbenzylphthalate
- 3,3'-dichlorobenzidine
- bis(2-ethylhexyl)phthalate
- di-n-octylphthalate
- 2,4,6-tribromophenol
- nitrobenzene-d_5

9.0 Continuing Calibration

One µl of the 20-ng/µl standard is injected using the cold needle technique. It is important to use exactly 1.0 µl so that the internal standards for the subsequent analyses will fall within the required acceptance range (-50% to +100% of the continuing calibration standard response).

9.1 A check of the calibration curve must be performed once every 12 hours. Check the relative response factors of those compounds for which RRF values have been established. If these criteria are met, the relative response factors for all compounds are calculated and reported. A percent difference of the daily relative response factor (12 hour) compared to the average relative response factor from the initial curve is calculated. Calculate the percent difference for each compound and compare with the maximum percent difference criteria listed in Table 2.

As with the initial calibration, up to four semivolatile target compounds in Table 2 may fail to meet the minimum RRF or maximum percent difference criteria, but the RRFs of those four compounds must be greater than or equal to 0.010, and the percent

differences must be less than or equal to 40.0% for the continuing calibration to be acceptable. A complete calibration package contains the DFTPP tune data specified above, the quantitation report form for each standard, a labeled RIC for each standard, any needed EICPs and the multipoint form generated by the EPAMP program.

9.2 The standard should be quantitated using the appropriate Target 3 procedure. If major column maintenance has been performed, the retention times may have shifted inward. If the retention times are not consistent, the cause should be determined before proceeding. Shifting retention times can usually be traced to one of a few sources. The two primary sources of instability are plugged columns and leaky septa. To prevent leaking septa, the septum should be changed at the beginning of each 12-hour calibration period. Column plugging is generally caused by dirty samples clogging the column head. It may also be caused by small amounts of septum material breaking off and lodging inside the column. The cure in both cases is to remove a small segment of the front end of the column. This must be done before running a valid shift standard because the retention times, as well as the internal standard areas, are critical to the validity of the data.

The CLP standard validity is checked using the appropriate Target 3 program. The program sets the library amounts correctly, and prints the continuing calibration form. This form lists the percent difference in the response factor in the shift standard and the average response factor in the multipoint. All isomeric pairs must be resolved.

10.0 Sample Analysis

10.1 Injection

All injections must be made using the cold needle injection technique. The injection volume is 1.0 µl. (Internal standard addition of extract to aliquot will be expanded in this section.)

Sample Preparation: Each sample is prepared by adding **2.5** µl of the internal standard solution to **100** µl of sample extract.

10.2 Quantitation

Quantitate each sample using the appropriate HP target 3 procedure. The procedure is biased in favor of false positives; however, the operator should exercise good analytical judgment in assessing the quantitation report for false negatives. All internal standards should be found. If any internal standards are not found but are in the 20-second window, they can be added to the quantitation list only if all compounds that reference them are checked manually. The quantitation report should also be inspected for missing surrogates. If a surrogate is missed, the validity of the data for the compounds in the same general retention time area is in question.

The surrogates may be updated manually; however, if this is done, great care must be taken to manually look for missed compounds in the same retention time range.

10.3 Generation of Compound List

The HP Target 3 program, automatically generates the QAQC list. The program asks for information that is found on the extractions worksheet and on the GC/MS worksheet and includes the following:

- Sublist name
- amount extracted
- volume of surrogates added
- final extracted volume

10.4 Generation of Dual Spectra

The dual spectra and library comparisons are generated automatically.

10.5 Library Searches

The spectra for tentatively identified compounds (TICs) are generated under the Target 3 software. It will search the RIC for any unknown compound and produce an enhanced forward library search of up to 30 identifiable GC peaks that are greater than 50% of the nearest internal standard.

10.6 Initial Data Review

Initial data review of samples analyzed under the OLC02.0 plus revisions SOW involves the following steps:

- verifying header information
- checking internal standard area monitor and surrogate recovery located in the Target 3 report.
- verifying that all hits greater than .500 ppb have library comparison
- checking for concentration levels of TCL analytes greater than 80 ng on column (greater than 120 ng for those compounds listed in Section 5.2.1.)
- checking reconstructed ion chromatograph for any extraneous peak that could have been missed or not picked up during the forward library search
- filling out any chain of custody and signing all paper work
- checking quantitation report for any target compounds the software may have missed or that are coeluting or eluting at the incorrect retention time

11.0 Quality Control

11.1 Method Blank

The method blank for an extraction must meet the following criteria:

- No TCL compound present at a concentration greater than the CRQL. This **includes** phthalates.
- All surrogate recoveries must fall within acceptance ranges shown in the table below.

Table 3
CONTRACT REQUIRED SURROGATE SPIKE RECOVERY LIMITS

Compound	(% Recovery)
nitrobenzene-d_5	23-120
2-fluorobiphenyl	30-115
terphenyl-d_{14}	18-140
phenol-d_5	15-115
2-fluorophenol	15-121
2,4,6-tribromophenol	15-130

- No non-TCL/nonsolvent may exceed 10 µg/L.
  The internal standard area response must be within the inclusive range of -50 to 100 percent of the

respective response in the most recent continuing calibration standard.

The retention time shift for each of the internal standards must be within ± 20 seconds of the respective internal standard in the most recent continuing calibration standard.

The surrogates relative retention times must be within ± 0.06 RRT units compared to the most recent continuing calibration standard.

11.2 Laboratory Control Samples (LCS)

- Must meet surrogate recovery criteria as shown in Table 3.

- No TCL compound present above CRQL, except spike compounds, as detailed below.

  Must be prepared and analyzed with an acceptable method blank.

  Must meet analyte recovery criteria as presented in Table 4. One compound may be outside the % recovery criteria but the recovery must be greater than or equal to 10% and less than or equal to 200.0%.

  The internal standard area response must be within -50 to 100% of the response in the most recent continuing calibration standard.

  The internal standard retention time shift must be within ± 20 seconds compared to the most recent continuing calibration standard.

  The relative retention time of each surrogate must be writhin ± 0.06 RRT units compared to the most recent continuing calibration standard.

Prepare a laboratory control sample spiking solution that contains each of the compounds listed in Table 4. One LCS is required per SDG. The percent recoveries for each of the surrogates in the LCS must be within the acceptance windows listed in Table 4.

Table 4
Laboratory Control Sample Percent Recovery Limits

Compound	% Recovery
phenol	40-120
2-chlorophenol	50-110
4-chloroaniline	10-120
2,4,6-trichlorophenol	40-120
bis(2-chloroethyl)ether	50-110
N-nitroso-di-n-propylamine	30-110
hexachloroethane	20-110
isophorone	50-110
naphthalene	30-110
2,4-dinitrotoluene	30-120
diethylphalate	50-120
N-nitrosodiphenylamine	30-110
hexachlorobenzene	40-120
benzo(a)pyrene	50-120

Note: The recovery limits for any of the compounds in the LCS may be expanded at any time during the period of performance if SMO determines that the limits are too restrictive.

12.0 Instrument Conditions and Maintenance

12.1 Mass Spectrometer Conditions

Manifold Temp:	80°C	First Mass:	35
Filament/Multiplier Actuation:	120 sec	Final Mass:	500
	Scan Speed:		0.96

12.2 Tuning and Calibration

Tuning Compound:	PFTBA
Tuning Sensitivity:	<300,000 area counts d10-phenathrene
Calibration Compound:	DFTPP
Standard Identification:	#7053
Calibration Criteria:	See Form V OLM02.0 + revisions SOW
Calibration Frequency:	Every 12 hours

12.3 Chromatographic Maintenance

Benzidine response factor of 0.05 or greater
PCB response factor of 0.05 or greater

12.4 Analytical Column

①DB-**5.625** (30 m X 0.32 mm **ID x** 1 um **film thickness)**
②**HP-5MS (30m x 0.25 mm ID x 025 um film thickness)**

12.5 Gas Chromatographic Conditions

Carrier Gas:	Helium	GC Mode:	Splitless Capillary
Inj. Port Temp:	315 CC	Flow Rate:	30-40 cm/sec
Initial Temp:	40°C	Interface Temp:	295°C
Initial Time:	2 min	Final Temp:	310°C
Split Flow:	100 ml/min Split/Sweep	Final Hold:	3 min*
Sweep Flow:	6 ml/min	Actuation Time:	60 sec
Ramp Rate:	15 degrees/minute		

12.6 Interface

Type: Direct Insertion
Interface Temp: 295°C
Solvent Diverter Time: N/A

12.7 Miscellaneous

Quantification Method: Library Entry
Quantification Method Name: RW11
Compound List: 652
Library Names: RW
File Naming Conventions: XX123456X78

Where:

1) XX - Analysis Type
2) 123456 = Date/Sample ID #
3) X = Shift
4) 78 = instrument #

Analysis Type Prefixes

Calibration File: DF
Standard: HG
Initial Sample Injection: GH
Sample Reinjection: GJ
Sample Reextraction: GR
Sample Dilution: GD
Additional Repeats: G2D, GJD, G2J, etc.

13.0 Temperature Records for Storage of Standards

The temperature of all storage refrigerators used for standards and standard extracts shall be recorded daily. Corrective action SOP's shall be posted on the refrigerators.

14.0 Calculations

Attachment 1-- Calculations Used in Data reduction

15.0 Documentation Description

Attachment 2 is a copy of the semivilatile GC/MS runlog.

16.0 References

This procedure complies with the "USEPA CLP SOW or Organics Analysis Low Concentration Water," Document No. OLM2.0 plus revisions and the New York State Analytical Services Protocol (NYSASP).

Attachment 1

1. Relative Response Factor (RRFs)

$$RRF = \frac{Ax \times Cis}{Ais \times Cx}$$

Where:

Ax = area of the characteristic ion from the extracted ion current profile (EICP) for the compound to be measured.

Ais = area of the characteristic ion from the EICP for the specific internal standard.

Cis = concentration of the internal standard

Cx = concentration of the compound to be measure in the standard

2. Percent Relative Standard Deviation (%RSD)

$$\%RSD = \frac{SD}{\overline{x}} \times 100$$

Where:

SD = Standard deviation of initial five response factors (per compound)

$\overline{x}$ = mean of initial five response factors (per compound)

and:

$$SD \sqrt{\sum_{i=1}^{n} \frac{(Xi-\overline{X})^2}{n-1}}$$

3. Percent Recovery (%R) - for surrogate/spike compounds

$$\%R = \frac{\text{concentration found (determined by analysis)}}{\text{concentration spiked (added to sample/blank)}} \times 100$$

4. Concentration (C), in µg/L, of Semivolatile Aqueous Samples

$$C = \frac{(Ax)(Is)(Vt)(Df)}{(Ais)(RRF)(Vo)(Vi)}$$

Where:

Ax = area of the characteristic ion from the EICP for the compound to be measured

Ais = area of the characteristic ion for the EICP for the internal standard

Is = amount of internal standard injected (ng)

RRF = relative response factor from continuing calibration standard

Vo = volume of water extracted (ml)

Vi = volume of extract injected (µl)

Vt = volume of the concentrated extract (µl)

Df = dilution factor. Dilution factor for semivolatile water samples is defined as the µl of the most concentrated extract plus the µl of solvent added divided by the µl of the most concentrated extract. If no dilution, Df = 1.0

COMPUCHEM a division of Liberty Analytical Corp DATE ___/___/___ INITIAL TIME OF TUNE_____ SHIFT/S(A)_____(B)_____(C)_____

SEMIVOLATILE GC/MS RUN LOG TIME TUNE EXPIRES_____ LINKER /METHOD_____

COMPUCHEM .LOGBOOK 11 CC 4 (5972hp68)

PREVENTIVE MAINTENANCE_____

Attachment 2

		TIME		DATE	TIME	CLIENT ID#	CASE/SDG#	AMOUNT INJECTED	CHEMIST	COMMENTS(ETC.)/DISPOSITION
1				/ /						
2				/ /						
3				/ /						
4				/ /						
5				/ /						
6				/ /						
7				/ /						
8				/ /						
9				/ /						
10				/ /						
11				/ /						
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24				/ /						

Section No. 2.4.2.2
Revision No. 1
Date: June 25, 1998
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STANDARDS

Tune Analytical Int. Std.

SUPERVISOR APPROVAL_____

Std. ID # _____ _____ _____

SOP Documentation Form

This form must accompany all new and revised Standard Operating Procedures (SOPs) when you turn them in to Quality Assurance for review. Please fill out the entire shaded area.

This is a new procedure _____ revised procedure ✓ outdated procedure (archive) _____

- Procedure area, title, and SOP number: IP 192 — Effective Date:
  Organochlorine Pesticides by GC/ECD - Capillary Column Technique - Method 8081A (SW-846 and NYSASP) — 1/20/99
- Procedure prepared by: [signature] — Date: 8/28/98
- Procedure approved by: (If the lab manager prepared the SOP, a qualified second party should sign.) — Date:
  Bob Meeker — 8/28/98
- Reason for change: _____
- This procedure meets the requirements set forth in the following References for Approved Methods:
  "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods" (SW-846), Method 8081A, Revision 1, Dec. 1996, Method 8000B, Revision 2, 12/96, NYSASP and the NCDENR

- Procedure approved by Quality Assurance Representative: — Date:
  Linda Carter — 8/28/98

Effective 1-1-96, on an annual basis: Lab managers are required to review lab practices and revise the SOP if necessary. If no revision is necessary, indicate by your signature that the SOP has been reviewed.

Annual Review--Signature and Date: _____

Annual Review--Signature and Date: _____

Annual Review--Signature and Date: _____

Instrument Procedure 192: Organochlorine Pesticides by GC/ECD-Capillary Column Technique-Method 8081A (SW-846 and NYSASP)

1.0 Scope and Application

1.1 Method 8081 is used to determine the concentration of various organochlorine pesticides in extracts from solid and liquid matrices. Open-tubular, capillary columns are employed with electron capture detectors (ECD). The following are amenable to analysis using this method:

Compound Name	CAS Registry No.
Aldrin	309-00-2
alpha-BHC	319-84-6
beta-BHC	319-85-7
delta-BHC	319-86-8
gamma-BHC (Lindane)	58-89-9
alpha-Chlordane	5103-71-9
gamma-Chlordane	5103-74-2
4,4'-DDD	72-54-8
4,4'-DDE	72-55-9
4,4'-DDT	50-29-3
Dieldrin	60-57-1
Endosulfan I	959-98-8
Endosulfan II	33213-65-9
Endosulfan sulfate	1031-07-8
Endrin	72-20-8
Endrin aldehyde	7421-93-4
Endrin ketone	53494-70-5
Heptachlor	76-44-8
Heptachlor epoxide	1024-57-3
Isodrin	465-73-6
Kepone[1]	143-50-0
Methoxychlor	72-43-5
Toxaphene	8001-35-2

[1] While Kepone is analyzableby this method, it may exhibit atypical chromatographic behavior. Kepone is not a routine target analyte.

1.2 Although the above analytes have been analyzed by this method, limitations exist due to co-elution of some analytes.

1.3 Toxaphene is a multicomponent analyte. When samples contain more than one multi-component analyte, a more experienced analyst may be required to process/assess the data. Similar conditions exist when multicomponent analytes have been subjected to environmental degradation.

1.4 Compound identification is based on dual column confirmation, with the second column being of a dissimilar nature.

1.5 CompuChem employs the dual column option described in Method 8081A, where the hardware is configured to allow two analytical columns joined to a single injection port. In this way, a single injection can be used for dual column analysis.

1.6 This method must be restricted to use by or under the supervision of analysts experienced in the use of GC and in the interpretation of gas chromatograms.

1.7 CompuChem **determines** a Practical Quantitation Limit (PQL) from in-house method detection limit (MDL) studies. PQLs are, generally, 4-8X the MDL. **The reporting limit is at the low-level standard concentration. The PQL will generally be at or below the reporting limit for most analytes.**

2.0 Summary of Method

2.1 A measured volume of sample (1 L for liquids, 2 to 30 grams for solids) is extracted using a separatory funnel for water and either a Soxhlet or Ultrasonic Extraction method, for soils. A variety of cleanup steps may be used, including Gel Permeation Chromatography (GPC). After cleanup, the extract is analyzed by injecting 4 µL (2 µL per column) into a GC with dual wide-bore, fused silica, capillary columns with dual electron capture detectors (GC/ECD).

3.0 Interferences

3.1 Interferences in this method can be grouped into three broad categories: contaminated solvents, reagents, or glassware; contaminated GC carrier gas, parts, column surfaces, detector surfaces; and the presence of co-eluting compounds in the sample matrix that also are detected by the ECD. Specific cleanups may be necessary for samples, depending on the compounds of interest.

3.2 Interferences by phthalate esters introduced during the sample preparation procedures can be a major problem. Common flexible plastics found in certain gloves and other objects contain varying amounts of phthalates which may be introduced during lab operations. Cross-contamination of clean glassware routinely occurs when plastics are handled during extraction steps, especially when solvent wetted surfaces are handled.

These interferences can be minimized by cleanup of solvents, reagents, and glassware.

3.3 Glassware must be scrupulously cleaned as soon as possible after use by rinsing with the last solvent used. This should be followed by detergent washing with hot water, and rinses with tap water and organic-free reagent water. Drain the glassware and dry in an oven at 130 degrees C for several hours or rinse with methanol and drain.

3.4 The presence of elemental sulfur will result in broad peaks that interfere with early eluting pesticides, and can be removed by cleaning the extract with shiny copper, or TBA clean up, or by the use of GPC cleanup.

3.5 Waxes, lipids, and other high molecular weight compounds are also removed using GPC.

3.6 Co-elution of certain single component pesticides also exists. alpha-Chlordane/Endosulfan I and DDD/Endosulfan II on the DB-608 column are partially resolved.

4.0 Apparatus and Materials

4.1 Gas chromatograph: Varian 3400 and HP5890 Series II gas chromatographs suitable for on-column and splitless injection with all required accessories, including syringes, analytical columns, gases, ECDs, and or data system.

4.2 The following wide-bore columns **or equivalent** are used in the analysis:

Column 1: 30 m x 0.53 mm ID fused silica capillary column bonded with 35% phenyl methylpolysiloxane (DB-608), 0.83 um film thickness.

Column 2: 30 m x 0.53 mm ID fused silica capillary column chemically bonded with 50% phenyl methylpolysiloxane (RTX-1701), 1.0 um film thickness.

Column 1: 30 m x 0.53 mm ID fused silica capillary column the bonded phase is proprietary information not made available by the vendor.

Column 2: 30 m x 0.53 mm ID fused silica capillary column the bonded phase is proprietary information not made available by the vendor.

4.2.1 Wide-bore columns are installed in a 1/4 inch injectors, with deactivated liners designed specifically for use with mega-bore columns.

4.3 Restek Y-shaped fused silica connector.

5.0 Reagents

5.1 Reagent or pesticide grade chemicals must be used for all tests.

5.2 All standard solutions should be stored at 4 degrees C in Teflon-sealed containers in the dark. All stock standard solutions must be replaced after one year or sooner if routine QC indicates a problem. All other standard solutions must be replaced after six months or sooner if QC indicates a problem.

5.3 Stock standard solutions (1 mg/mL) are purchased from Restek Corp. or other vendors, as certified solutions, or they may be prepared from neat material.

5.4 Calibration standards are prepared at five concentrations by diluting the stock standards solutions with hexane.

5.5 Because some of the single component analytes co-elute, two separate solutions are prepared for the single component analytes. This allows the minimization of potential resolution problems.

5.6 Separate calibration standards are used for toxaphene and technical chlordane (if required). Alpha and gamma chlordane are included in the single component standard solutions.

5.7 Surrogate standards are added to all samples, method blanks, matrix spikes, laboratory control samples (blank spikes), and calibration standards.

5.7.1 Decachlorobiphenyl (DCB) and tetrachloro-m-xylene (TCX) are the surrogates used. Corrective action is taken when both surrogates are recovered outside of acceptance criteria on both columns.

6.0 Procedure

6.1 Extractions (see sample preparation SOPs)

6.2 GC Conditions

6.2.1 Dual Column Analysis:

6.2.1.1 The dual column/dual detector approach involves the use of two 30 m x 0.53 mm ID fused silica open-tubular columns of different polarities (DB-608 and RTX-1701 or CLPesticides I and CLPesticides II), thus having different selectivities towards the target compounds. The columns are connected to a "Y-splitter" and ECD detectors.

6.2.1.2 GC operating conditions are as follows:

Column 1: Type: DB-608
Dimensions: 30 m x 0.53 mm ID
Film Thickness: 0.83 um

Column 2: Type: RTX-1701
Dimensions: 30 m x 0.53 mm ID
Film Thickness: 1.0 um

Column 1: Type: CLPesticides I
Dimensions: 30 m x 0.53 mm ID
Film Thickness: 0.5 um

Column 2: Type: CLPesticides II
Dimensions: 30 m x 0.53 mm ID
Film Thickness: 0.42 um

Carrier gas flow rate (mL/min): 6 (Helium)

Makeup gas flow rate (mL/min): 20 (Argon/methane))

Temperature program: 150°C (0.5 min hold) to 275°C (10 min hold) at 7 degrees/min

Injector temp: 200°C

Detector temp: 300°C

Injection volume: 4 uL (2 uL per column)

Solvent: Hexane

Detector Dual ECD's

Range: 10

6.3 Calibration:

6.3.1 Calibration standards for the single component pesticides are prepared at five concentration levels. Due to co-elution possibilities, particularly on older columns, two separate calibration solutions are used, with the following analytes in each solution:

Individual Mix A (MIXA): Gamma-BHC
Heptachlor
Aldrin
Isodrin
gamma-chlordane
Endosulfan I
Dieldrin
Endosulfan II
4,4'-DDT
Methoxychlor
Tetrachloro-m-xylene
Decachlorobiphenyl

Individual Mix B (MIXB): alpha-BHC
beta-BHC
delta-BHC
Heptachlor epoxide
alpha-chlordane
4,4'-DDE
Endrin
4,4'-DDD
Endrin aldehyde
Endosulfan sulfate
Endrin ketone
Tetrachloro-m-xylene
Decachlorobiphenyl

Calibration Concentrations are as follows:
MIXA

CONCENTRATION (µg/mL)

Analyte	L	M1	M2	M3	H
Gamma-BHC	.0025	.005	.01	.02	.04
Heptachlor	.0025	.005	.01	.02	.04
Aldrin	.0025	.005	.01	.02	.04
Isodrin	.0025	.005	.01	.02	.04
Gamma-chlordane	.0025	.005	.01	.02	.04
Endosulfan I	.005	.01	.02	.04	.08
Dieldrin	.005	.01	.02	.04	.08
Endosulfan II	.01	.02	.04	.08	.16
4,4'-DDT	.015	.03	.06	.12	.24
Methoxychlor	.025	.05	.10	.20	.40
Tetrachloro-m-xylene	.02	.04	.08	.16	.32
Decachlorobiphenyl	.02	.04	.08	.16	.32

MIXB

CONCENTRATION (µg/mL)

Analyte	L	M1	M2	M3	H
alpha-BHC	.0025	.005	.01	.02	.04
beta-BHC	.005	.01	.02	.04	.08
delta-BHC	.0025	.005	.01	.02	.04
Heptachlor epoxide	.0025	.005	.01	.02	.04
alpha-Chlordane	.005	.01	.02	.04	.08
4,4'-DDE	.005	.01	.02	.04	.08
Endrin	.01	.02	.04	.08	.16
4,4'-DDD	.01	.02	.04	.08	.16
endrin aldehyde	.01	.02	.04	.08	.16
Endosulfan sulfate	.01	.02	.04	.08	.16
endrin ketone	.025	.05	.10	.20	.40
Tetrachloro-m-tylene	.02	.04	.08	.16	.32
Decachlorobiphenyl	.02	.04	.08	.16	.32

Analyte	Multi-comp. stds.	L	M1	M2	M3	H
Toxaphene	4411-4415	.25	.50	1.0	2.0	4.0
Tech. Chlordane	4416-4420	.05	.10	.20	.40	.80
Tetrachloro-m-xylene		.02	.04	.08	.16	.32
Decachlorobiphenyl		.02	.04	.08	.16	.32

Note: Each multicomponent standard has the two surrogates at the indicated levels.

6.3.2 Unless specified for a particular project/program, a single calibration standard of toxaphene is analyzed to provide pattern recognition information. The mid-point standard is used. The alpha- and-gamma Chlordane isomers are part of the single component standards. If both isomers are confirmed to be present in a sample, arrangements may be made, depending on client requirements, to include a technical chlordane mid-concentration standard for pattern recognition and quantitation or, alternatively, a 5-point calibration can be generated. Additionally, a 5-point calibration can be performed for toxaphene detected in samples. When Method 8082 for PCBs is being used in conjunction with Method 8081A a five-point calibration has to be performed for Aroclor-1660 followed by individual mid-level stds for the remaining Aroclors. (See Method 8082 SOP for stds and concentrations.) An example of an initial calibration follows:

Injection No.			
	1	PEM 8081A	1
	2	MIXA-3	
	3	MIXB-3	
	4	MIXA-5	
	5	MIXB-5	
	6	MIXA-1	
	7	MIXB-1	
	8	MIXA-4	
	9	MIXB-4	
	10	MIXA-2	
	11	MIXB-2	
	12	TECH-3	2
	13	TECH-5	
	14	TECH-1	
	15	TECH-4	
	16	TECH-2	
	17	TOXAPH-3	3
	18	TOXAPH-5	
	19	TOXAPH-1	
	20	TOXAPH-4	
	21	TOXAPH-2	
	22	AR1660-3	
	23	AR1660-5	
	24	AR1660-1	
	25	AR1660-4	
	26	AR1660-2	
	27	AR1254-3	
	28	AR1221-3	
	29	AR1232-3	
	30	AR1242-3	
	31	AR1248-3	

1 = PEM 8081 is a Performance Evaluation Mixture for the method and is used only to assess the breakdown of endrin and 4-4'-DDT.

2 = TECH represents technical chlordane

3 = TOXA represents Toxaphene.

Note: This is an example initial calibration sequence when five levels of technical chlordane and toxaphene are required by a specific project/project. A normal initial calibration sequence only contains a mid-concentration level of toxaphene so the initial calibration sequence would conclude after bottle 12 which would contain a mid concentration level of toxaphene.

4 = For certain programs an initial calibration verification standard from a second source is required.

6.3.3 For calibration verification (performed during each 12 hour shift), all target

analytes must be injected with the exception of toxaphene. If toxaphene and/or technical chlordane are detected in any samples, the mid-concentration level of those standards must be injected. Samples may be required to be reinjected against those mid-concentration standards. When Method 8082 is employed for PCBs a verification std of AR1660 must be performed during each 12 hour shift for every 10 samples. The Aroclor can be injected after 8081A mix. Sequencing should look like the following example:

12 Hr. Sequence Injection No.[1]	Whole Sequence Bottle No.[1]	Description
1	13	Instrument Blank (IB)
2	14	PEM 8081A
3	15	MIXA-3D[2]
4	16	MIXB-3D[2]
5-14	17-26	10 Samples
15	27	PIBLK
16	28	MIXA-3
17	**29**	**MIXB**
18-27	**30-39**	10 Samples
28	**40**	PIBLK
29	**41**	PEM8081A
30	**42**	**MIXA**
31	**43**	MIXB-3
32-41	**44-53**	10 samples
42	**54**	PIBLK
43	**55**	MIXA-3
44	**56**	**MIXB**
45-54	**57-66**	10 samples
55	**67**	PIBLK
56	**68**	PEM8081A
57	**69**	MIXA-3D[2]
58	**70**	MIXB-3D[2]

[1] The number in the first column represents the injection sequence at the start of a twelve-hour time period. The number in the second column represents the actual bottle number in the injection sequence which would have begun at the start of the initial calibration.

[2] The "D" indicates this standard to be the "daily" or first continuing calibration verification standard run during a 24-hour period. The MIXA-3D and MIXB-3D are mid-level, single component standards and the absolute retention times for each component of these standards

establishes the midpoint of the retention time window. See Section 6.5.

[3] The requirements of Method 8081 include a calibration standard after each 20 samples although one is recommended after each 10 samples. The method also indicates that the continuing calibration verification standards be run each 12 hour shift. If toxaphene or technical chlordane are seen in samples, it is required that the mid-concentration level standard of those be injected. The method does not specify the requirement or the frequency for instrument blanks which we feel are important tools for assessing instrument performance. The method also specifies that endrin and DDT breakdown be assessed before samples are analyzed and at the beginning of each 12-hour shift. This breakdown is best evaluated by the injection of a QC standard containing only endrin and DDT. Therefore, assuming approximately 30 minutes per analytical run, the 12-hour shift begins with the injection of the MIXA-3D (Injection No. 3, bottle 15). The first two injections, the instrument blank and the degradation standard are QC measures and not characterized as calibration verification standards. The 12-hour sequence period would end after Injection No. 26, bottle 38 in the total sequence. During the sequence from Injection No. 3 through Injection No. 26, sample chromatograms would be assessed to determine if multicomponent analytes were detected in the samples. If detected, they would be incorporated into the next 12- hour sequence. Also during that 12-hour sequence a MIXA-3 continuing calibration verification standard would be injected (at bottle 16) after the injection of the first set of 10 samples. Injection Nos. 27 and 28 are considered QC samples "closing out" the first 12-hour shift and also beginning the next period such that Injection No. 29 would be the injection of the calibration verification for the next 12-hour shift. Injection No. 29 therefore is a MIXB-3 standard (It is not labeled with a D since it is not the "daily" standard used to set retention time windows). The injection sequence beyond Injection No. 53 (bottle 65) would constitute the beginning of a new 24-hour period and therefore mimic the sequence beginning with Injection No. 3 (bottle 13), the only difference being the possible insertion of appropriate multicomponent standards. We feel this sequencing meets the

intent and the letter of the Method 8081 requirements.

6.3.4 Because of the relatively low concentration of pesticide standards injected on the GC/ECD, column adsorption may be a problem if the GC has been unused for several days. Deactivation (priming) can be achieved by injecting a standard at least 20 times more concentrated than the mid-level standard before beginning the initial calibration or continuing calibration verification.

6.4 Gas chromatographic analysis:

6.4.1 The GC is set up according to section 6.2.1.2. An initial oven temperature at or below 150 degrees C is required to resolve the BHC's. A final temperature of 240-275 degrees C is necessary to elute decachlorobiphenyl.

6.4.2 The initial calibration is performed according to section 6.3.2.

6.4.3 The calibration is verified during each 12 hour shift according to section 6.3.3. Calibration verification standards are also injected after every 10 samples (although it is required after every 20 samples) and at the end of the analytical sequence. Since an analytical sequence may continue as long as instrumental QC criteria are met, the end of one 12-hour sequence is considered to be the beginning of the next 12-hour sequence. The calibration factor for each analyte must not exceed ±15 percent difference when compared to the initial calibration curve. When this criteria is exceeded, perform corrective action (see corrective action section) and re-inject the continuing calibration verification standard (s) or analyze a new initial calibration before more samples analyzed.

6.4.4 Each sample analysis must be bracketed with an acceptable initial calibration, continuing calibration verification standards (each 12 hr shift), or calibration standards interspersed with the samples. If a "closing" standard, which is injected after a group of samples contains analyte responses that are >15% different, when compared to the

mean calibration factor from the initial calibration, and the analyte was not detected in that group of samples, the samples do not require reinjection. However, if the standard is more than 15% below the mean calibration factor from the initial calibration, then re-injection is required.

6.5 Retention time windows are established for each analyte. The width of the retention time windows should be based upon actual retention times of standards, assessed over 72 hours. The windows are defined as ± three times the standard deviation of the absolute retention times of each standard. Analyst experience, however, is critical in the interpretations of chromatograms. Absolute retention time windows are established for each analyte, including five component peaks for multicomponent analytes. For each analyte, the absolute retention time from each standard injected at the beginning of a 24-hour period is used as the midpoint of the window ± three times the standard deviation as determined from above.

6.5.1 Tentative identification of an analyte occurs when a peak from a sample extract falls within the retention time window.

6.5.2 The continuing calibration verification standards are used to evaluate retention time stability. If any of the standards fall outside their retention time windows, the system is out of control and corrective action must be taken to correct the problem. If, after re-injection of the standard following corrective action, the retention times are still outside the windows, a new initial calibration must be analyzed.

6.6 Use the external calibration procedure (which establishes mean response factors for each analyte from the initial calibration by dividing peak area by mass injected). Peak areas from peaks within an analyte's retention time window on analytical columns are used to calculate the quantity of each target analyte while retention times are used to identify each component. The concentration reported is the higher of the two values obtained from the dual column analysis. If one result is >40% different, verify that there are not overlapping peaks causing this to occur. Also examine the baseline to verify that the baseline parameters are set properly. The concentration of a specific analyte is calculated as follows:

Aqueous Samples

$$\text{Concentration } (\mu g/L) = \frac{(Ax)(Vt)(Df)}{(CF)(Vi)(Vs)}$$

Where:

Ax = Area response for the analyte.
Vt = Volume of total extract, in µL
Df = Dilution factor. If no dilution, Df=1
CF = Mean calibration factor from the initial calibration. (See 8.1)
Vi = Volume of extract injected, in µL.
Vs = Volume of sample extracted, in mL.

Non-Aqueous Samples

$$\text{Concentration } (\mu g/kg) = \frac{(Ax)(Vt)(Df)}{(CF)(Vi)(W)(D)}$$

Where:

W= Weight of sample extracted, in g.

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

Ax, Vt, Df, CF, Vi have the same definitions.

6.7 If the response of an analyte exceeds the on column amount of the high level standard, dilute and re-analyze. This can be done by comparing a component peak area to the corresponding analyte in the high level standard. Within the H-P Target data system the "A" flag is used on the quantitation report to indicate that an analyte is outside the upper initial calibration range.

6.8 Identification of multi-component analytes is based on the characteristic pattern and retention times of the indicator peaks; and quantitation is based on the area under the characteristic peaks as compared to the area under the corresponding calibration peaks at the same retention times using the external calibration method.

6.9 Quantitation of multi-component analytes:

6.9.1 Toxaphene and technical chlordane are quantitated using response factors of five major peaks (minimum of three) of the sample pattern compared to the response factors of five peaks in the standard.

6.9.2 Chlordane is a technical mixture of at least 11 major components and 30 or more minor components. The two major components are the trans and cis (alpha and gamma) isomers. The exact percentage of each, however, is uncertain. Chlordane is also influenced by environmental factors such as water and sunlight and can also, therefore, contain degradation products. Because of this, Chlordane should be quantitated using only the main two components (alpha and gamma-Chlordane) whenever the sample does not resemble the total chlordane standard, and these isomers should be reported separately along with heptachlor, heptachlor epoxide, etc. If the sample does resemble the technical chlordane standards, then it should be quantitated as a multicomponent analyte using total areas of the sample and the standard and reported as technical chlordane.

6.9.3 **To quantitate PCBs refer to the instrument procedure SOP for Method 8082.**

7.0 Corrective Actions

7.1 Since the dual capillary columns used in this method are connected by press-fit Y-shaped glass splitters, the splitter should be replaced along with the insert (uniliner) when DDT and/or endrin degradation is a problem or when calibration verifications fail. Along with this, remove the first few inches of the injector port side of the column and pre-column. If this fails to correct the degradation problems, it may be necessary to deactivate the injector port or replace the columns.

7.2 Other corrective actions include removal of 0.5 meters of the detector end of the columns when linearity is difficult to achieve.

7.3 To silanize the injector when DDT and endrin degradation is a problem, the following steps should be taken. Remove the analytical columns after cooling the GC oven. Remove the glass insert (uniliner). Lower the injector port temperature to room temperature. Remove any foreign materials observed while inspecting the injector port. Prepare a solution of deactivating agent (Sylon-CT) following the manufacturer's instructions. Place a beaker under the injector port inside the oven, and rinse the inside of the

injector port with acetone and then toluene, catching the rinsate in the beaker. Coat the inside of the injector port with the solution thoroughly and allow to dry. Finally, rinse the injector with toluene, methanol, acetone, and then hexane, in that order. Reassemble the injector and replace the columns.

7.4 When retention times shift, change the injector port septum. Note the ambient air temperature as well. If the septum change does not correct the problem, a new initial calibration must be analyzed. Do not attempt to correct retention time shifts for all the analytes in this method.

8.0 Quality Control Acceptance Criteria

8.1 The percent Relative Standard Deviation (%RSD) of the calibration factors for the initial calibration must be less than or equal to 20% for all analytes. Calibration factors are calculated by dividing total peak area by mass injected (in nanograms):

$$\text{Calibration Factor (CF)} = \frac{\text{Total peak area}}{\text{Mass injected}}$$

The %RSD is calculated using the following formula:

$$\%RSD = \frac{SD}{CF} \times 100$$

where:

SD = Standard deviation of the initial five calibration factors (per compound)

CF = mean of initial calibration factors (per compound)

and:

$$SD \sqrt{\sum_{i=1}^{n} \frac{(CFi-CF)^2}{n-1}}$$

where:

Cfi = individual CF for each of the five standards (per compound)

n = total number of values (5)

When the %RSD is ≤ 20%, the instrument response is considered to be linear and the mean calibration factor can be used for quantitation. If the %RSD is greater than 20%, the initial calibration may still be acceptable if the following conditions are met:

8.1.1 The mean of all of the %RSD values for the analytes is less than or equal to 20%.

8.1.2 If an analyte is part of the calibration standard, it must be included in the calculation.

8.1.3 A summary of the initial calibration data and/or a list of the analytes not meeting the 20% RSD criteria and the actual %RSD for each of these analytes must be included as a deliverable to our client. If the conditions in 8.1.1 are met, then the average relative response factor may be used to determine the concentration of analytes in samples. If the above mean RSD cannot be achieved the analyst must use a calibration model available in the ThruPut system.

8.2 All continuing calibration verification standards analyte response factors must be within ± 15% difference (%D) when compared to the response factors of the initial calibration on both analytical columns. %D is calculated by the following equation:

$$\text{Percent Difference} = (\%D) \frac{CF_v - CF}{CF} X100$$

where:

CF = Mean Calibration Factor from initial calibration

CF_v = Calibration Factor from continuing calibration verification standard

If the ± 15% criterion is exceeded for any analyte, calculate the average percent difference across all analytes. If this average is within ±

15%, the calibration has been verified. When this occurs the following conditions must be met:

- the average must include all analytes,
- clients must be provided with the calibration verification data or a list of those analytes exceeding the ± 15% limit, together with their actual Calibration Factors.

If the %D exceeds ± 15%, then corrective action must be taken and the continuing calibration verification re-injected. If the calibration still exceeds the criteria, a new initial calibration must be analyzed.

8.3 Surrogate recoveries must be within 30-150% for all samples, blanks, blank spikes, matrix spikes, and matrix spike duplicates. If both surrogates (tetrachloro-m-xylene and decachlorobiphenyl) are outside the control range on both columns, the sample must be re-extracted and re-analyzed unless interfering peaks are the reason for the recovery to be out of control. Carefully examine all chromatograms to make certain the out of control surrogate recoveries are not caused by interferences or a partial injection before re-extracting the sample. Partial injections should be re-injected and can be diagnosed by comparing the solvent peak of the sample to the solvent peak of the standard. They should be similar in size.

8.4 Degradation of endrin and DDT is indicated by the presence of 4,4'-DDE, 4,4'-DDD, endrin aldehyde, or endrin ketone and is caused by the injector port becoming contaminated from high boiling residue from sample injection. Degradation of either endrin or 4,4'-DDT must not exceed 15%. Calculate percent breakdown as follows:

$$\text{\% breakdown for 4,4'-DDT} = \frac{\text{Total DDT degradation peak area (DDE + DDD)}}{\text{peak areas (DDT + DDE + DDD)}} \times 100$$

$$\text{\% breakdown for endrin} = \frac{\text{Total endrin degradation area*}}{\text{peak areas (endrin + aldehyde + ketone)}} \times 100$$

* = endrin aldehyde + endrin ketone

8.5 Method blanks are prepared and analyzed once for the following, whichever is most frequent:

- Each case/SDG of field samples received,

- Each 14 calendar day period (7 calendar day period for NYSASP) during which samples in a case, are received, or,
- Each 20 samples in a case, including the matrix spikes, that are of a similar matrix or similar concentration, or
- Whenever samples are extracted by the same procedure.

The acceptance criteria for method blanks includes the following:

- Surrogates are within recovery criteria,
- No target analytes are present above the PQL.

The percent recovery (%R) of a surrogate or target analyte is calculated in the following manner:

$$\%R = \frac{\text{Concentration found (determined by analysis)}}{\text{Concentration spiked (added to sample/blank)}} \times 100$$

If the method blank exceeds acceptance criteria, the source of the problem (s) must be investigated and appropriate corrective action taken. All samples processed with a method blank that does not meet acceptance criteria must be re-extracted and reanalyzed.

8.6 A matrix spike and matrix spike duplicate must be performed for each group of samples of a similar matrix, for whichever is germane:

- Each case/SDG of field samples received, or
- Each 20 field samples in a case, or
- Each 14 calandar day period (7 calendar day period for NYSASP) during which field samples in a case are received.

The percent recovery of matrix spikes (MS %R) is determined from the following equation:

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

where:

SSR = sample spike result
SR = sample result
SA = spike added

NYSASP, the blank spike is called the matrix spike blank.

If the LCS does not meet acceptance criteria, all samples in the associated batch must be re-extracted and reanalyzed.

Blank Spike Recovery Limits *

Analyte	Aqueous % Recovery	Solid % Recovery
Heptachlor	35-140	30-130
Aldrin	35-140	65-100
Dieldrin	60-130	35-135
4,4'-DDT	55-170	30-170
Gamma-BHC	40-155	35-140
Endrin	56-121	42-139

* The blank spike recovery limits are based on in-house data. For NYSASP, the matrix spike blank acceptance criteria are the same as the MS/MSD criteria.

8.8 Duplicates, at a frequency of 10%, are required when processing samples submitted to meet the regulatory requirements of North Carolina.

9.0 References

This procedure complies with Test Methods for Evaluating Solid Waste Physical/Chemical Methods, SW-846, Third Edition, Method 8081A, December, 1996, and the New York State Analytical Services Protocol (NYSASP) and the NCDEHNR.

The relative percent difference (RPD) for the MS/MSD tests, is calculated by the following:

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

where:

MSR = matrix spike recovery
MSDR = matrix spike duplicate recovery.

The percent recoveries criteria of the matrix spikes and the RPD criteria are:

Analyte	Aqueous %	Aqueous RPD	Solid % Recovery	Solid RPD
gamma-BHC (Lindane)	56-123	15	46-127	50
Heptachlor	40-131	20	35-130	31
Aldrin	40-120	22	34-132	43
Dieldrin	52-126	18	31-134	38
Endrin	56-121	21	42-139	45
4,4'-DDT	38-127	27	23-134	50

The objective for the MS/MSD tests is for the majority of the spiked compounds to be recovered within criteria and the majority of the RPD values to be within criteria. However, the recoverability of spiked analytes in environmental samples is very much influenced by the particular matrix and , therefore, these objectives may not be able to be met. When recoveries do not meet the acceptance criteria or interferences preclude proper assessment of the data, results of a Laboratory Control Sample (LCS) or Blank Spike (BS) are evaluated to verify that the analytical systems (sample preparation and analysis) are under control. If the original sample, used for the MS/MSD tests does not meet surrogate acceptance criteria, it should be reanalyzed or re-extracted/reanalyzed, if the MS/MSD surrogate recoveries are within limits. If the original sample and the MS/MSD tests yield the same unacceptable surrogate recoveries, then the sample does not require re-extraction/ reanalysis since matrix interferences would be confirmed.

8.7 A BS (LCS) is reagent water (or furnaced Ottawa sand for solid matrices) fortified with the target analyte spiking compounds and surrogates. The BS is prepared with the MS/MSD tests and is also included in every extraction batch with a method blank. For

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Cary, NC 27513

SOP DOCUMENTATION FORM

This form must accompany all new and revised Standard Operating Procedures (SOPs) when you turn them in to Quality Assurance for review. Please fill out the entire shaded area (except effective date).

This is a new procedure ____ revised procedure ✓ outdated procedure (archive) ____

- Procedure area, title, and SOP number: Section #: 2.2.5.1 Effective date: (QA fills in)

  SOP-1049 PCBs in Water Preparation Procedure (SW846 & NYSASP) 1/24/01

- Procedure prepared by: [signature] Date: 1/12/01

- Procedure approved by: (If the manager prepared the SOP, a qualified second party should sign) Linda Carter Date: 1/22/01

- Reason for change: Change in PCB spiking solution. Comments added to cleanup section

- This procedure meets the requirements of the following approved method references:

  SW846, 3rd Ed, Methods 3510C/3520C, NYSASP, NC DENR

Procedure approved by Quality Assurance Representative: Date:
(Not needed if signed above)

Effective 1-1-96, on an annual basis: Lab managers are required to review lab practices and revise the SOP if necessary. If no revision is necessary, indicate by your signature that the SOP has been reviewed.

Annual Review—Signature: _____ Date: _____

Annual Review—Signature: _____ Date: _____

Annual Review—Signature: _____ Date: _____

Sample Preparation Procedure -1049: PCBs in Water Preparation Procedure: (SW-846, NYSASP)

1.0 Scope and Application

The following sample preparation procedure is designed to prepare water samples for Aroclor analysis by GC/ECD. The water samples may be extracted by separatory funnel or continuous liquid/liquid extraction.

The method detection limits (MDL) **and reporting limits** are shown in Attachment 1.

Staff members performing the procedures described in this SOP are responsible for reading, understanding, and complying with the SOP requirements. Supervisors are responsible for directing the analyst to the controlled SOP, and providing adequate explanation of the material contained therein.

This procedure is restricted to use by or under the supervision of analysts experienced in the instrumentation or preparative methods and who have demonstrated the ability to generate acceptable results through QC samples and analyst capability studies.

2.0 Summary of Sample Preparation Methods

A 1-liter (l) volume of sample is spiked with the surrogate solution and is extracted with methylene chloride by using a separatory funnel or a continuous extractor. The methylene chloride extract is dried and concentrated. For SW-846 requirements, clean-up techniques are optional and include florisil cleanup, Method 3620B, and sulfuric acid cleanup, Method 3665A.

3.0 Definitions

3.1 Method detection limit (MDL) – The minimum concentration of an analyte that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined form analysis of a sample in a given matrix containing the analyte (40 CFR, Part 136, Appendix B.)

3.2 Reporting Limit – The laboratory reporting limit is based on the lowest multipoint calibration standard concentration. For some inorganic methods, the reporting limit is based on the MDL, and is usually 4-8 times higher than the MDL. For organic methods, values detected below the reporting limit and above the MDL may be reported and qualified as an estimated concentration.

3.3 Reporting Units – µg/L

3.4 An SDG is defined by the following, whichever is more frequent:

- Each 20 field samples received within a case, or

- Each 14 calendar day period (7 calendar day period for the NYSASP) during which field samples in a case are received (period beginning with the receipt of the first sample in the SDG)

4.0 Interferences

4.1 Method interferences might be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware. These contaminants lead to discrete artifacts or to elevated baselines in gas chromatograms. Routinely, all of these materials must be demonstrated to be free from interferences under the conditions of the analysis by running reagent blanks. Interferences caused by phthalate esters can pose a major problem in pesticide analysis. Common flexible plastics contain varying amounts of phthalates, which are easily extracted during laboratory operations, so cross-contamination of glassware frequently occurs when plastics are handled. Interferences from phthalates can best be minimized by avoiding the use of such plastics in the laboratory.

4.2 Matrix interferences might be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending on the nature of the site being sampled. Cleanup procedures must be used to remove such interferences in order to achieve contract required quantitation limits (CRQL) or practical quantitation limits (PQLs).

5.0 Safety

5.1 Wear the proper personal safety equipment (lab coat, gloves, safety glasses) when performing this procedure.

Laboratory staff is encouraged to review the Chemical Hygiene Plan for general safety policies, and Material Safety Data Sheets for reagents used in the laboratory.

6.0 Equipment and Supplies

6.1 Continuous liquid-liquid extractors with Teflon or glass connecting lines for use with methylene chloride (Corning One-Step Continuous Extractor Apparatus or equivalent, Corning Glass Co., P/N 3928-M with jacketed Kuderna Danish (K-D) Concentrator Tube)

6.2 Separatory funnel--2000-ml with Teflon stopcock

6.3 K-D apparatus

6.3.1 Concentrator tube--10-ml, graduated (Kontes K-570050-1025, or equivalent)

6.3.2 Evaporative flask--500-ml (Kontes K-470001-0500, or equivalent)

6.3.3 Snyder column--three-ball macro (Kontes K-503000-0121, or equivalent)

6.4 Funnels and Filter Paper

6.4.1 Powder funnels--10-cm diameter (optional), for filtration/drying

6.4.2 Buchner funnels--9-cm diameter, for filtration (optional)

6.4.3 Filter paper--No. 41 Whatman (or equivalent), 9-cm circles (optional)

6.5 Silicon carbide boiling chips--Approximately 10 to 40 mesh. Heat the chips to 400°C for 30 min or solvent rinse before use.

6.6 Water bath--heated, with concentric ring cover, capable of ± 5°C temperature control

NOTE: Always use the water bath in a hood.

6.7 Nitrogen evaporation device, equipped with a heated bath that can be maintained at 35-40°C--N-Evap by Organomation Associates, Inc., South Berlin, MA (or equivalent)

6.8 Vials and caps--2-ml for GC autosampler

6.9 Pyrex glass wool--heated in a 400°C oven for 4 hr, then stored in a glass container. Prepped with methylene chloride prior to use

6.10 Drying column--chromatographic column approximately 400 mm long x 19 mm ID, with coarse frit. (Substitution of a small pad of disposable Pyrex glass wool for the frit will help prevent cross-contamination of sample extracts.)

6.11 Glass vials--minimum of 20-ml, with screw-cap and Teflon or aluminum foil liner

6.12 Spatula--stainless steel or Teflon

6.13 pH paper--wide range, (Hydrion Papers, Microessential Laboratory, Brooklyn, NY, or equivalent)

6.14 Pipet--volumetric 1.0-ml or 2.0-ml (optional)

6.15 Syringe--1.0-ml or 2.0-ml (optional)

6.16 Vials--10-ml, with screw-cap and Teflon liner (optional)

6.17 Tube--centrifuge, 12- to 15-ml with 19-mm ground glass joint (optional)

6.18 Snyder Column--macro, two- or three-ball with a 24/40 ground glass joint

6.19 Centrifuge--table top (optional)

6.20 Vortex mixer--Genie, Model 550-6, Scientific Industrial, Inc., Bohemia, NY, or equivalent

6.21 pH meter with a combination glass electrode

6.22 Magnetic stirrer motor--Model PC353, Corning Co., Corning, NY, or equivalent

6.23 Magnetic stir bar--Teflon-coated, at least 4 cm long

6.24 Graduated cylinder--1-l capacity

6.25 Glas-Col 2-l shaker for shaking of separatory funnels

6.26 Disposable glass culture tubes--16- x 100-mm

7.0 Reagents and Standards

All standards are prepared by the Organic Standards chemist. Details for the preparation are contained in that area.

7.1 Reagent water – All water used in this procedure must be equivalent to ASTM Type II water (as it relates to specific conductance and specific resistance) which is demonstrated to meet the blank contamination acceptance criteria contained in this Standard Operating Procedure (SOP).

7.2 Sodium sulfate--granular, anhydrous reagent grade, heated at 400°C for 4 hr, or at 120°C for 16 hr, cooled in a desiccator, and stored in a glass bottle

7.3 Methylene chloride, hexane, acetone, and methanol (optional)--pesticide quality or equivalent. It is recommended that each lot of solvent used be analyzed by GC/ECD to demonstrate that it is free of interference before use. Methylene chloride must be certified as acid free or must be tested to demonstrate that it is free of hydrochloric acid. Acidic methylene chloride must be passed through basic alumina and then demonstrated to be free of hydrochloric acid.

7.4 Sodium hydroxide solution (10 N)--Carefully dissolve 40 g of sodium hydroxide in reagent water and dilute the solution to 100 ml.

7.5 Concentrated sulfuric acid--18 N

7.6 Surrogate solution #426--the surrogates, tetrachloro-m-xylene and decachlorobiphenyl, are added to all standards, samples, MS, MSD< BS, and

blanks. Prepare a surrogate spiking solution of 0.2 µg/ml of each of the two compounds in acetone.

CAUTION: Analysts must allow all spiking solutions to equilibrate to room temperature before use.

7.7 Pesticide matrix spiking solution **#4615**--Prepare a spiking solution in acetone or methanol that contains the following arochlor at the concentration specified:

Aroclor	µg/ml
1660	5.0

8.0 Sample Collection, Preservation, & Storage

8.1 Samples are collected, preserved, and stored according to the tables in Sample Control SOP 4.1, "Receiving Samples" and 4.6, "Storing Samples." Sample holding times are also listed.

8.2 Samples are obtained from the Custodian out of cold storage at 2.0 – 4.4°C. They should be allowed to come to room temperature prior to sample preparation. After preparation, they are returned to the Custodian and placed in the cooler.

8.3 Samples are collected and preserved in the field according to the tables in Sample Control SOP 4.1.

8.4 Extraction of water samples by separatory funnel must be completed within 7 days of collection in order to meet method holding time. Extraction of water samples by continuous liquid – liquid extraction must be started within 7 days of collection.

9.0 Quality Control

9.1 Prepare a matrix spike (MS) and, matrix spike duplicate (MSD), for every sample delivery group (SDG).

9.2 Prepare a method blank and a **laboratory control sample (LCS;** blank spike, BS) with each extraction batch **of up to 20 samples**. For NYSASP, the **LCS** is called a matrix spike blank.

9.3 If problems or questions arise which are not addressed in the text, consult the laboratory supervisor or manager.

10.0 Calibration & Standardization

10.1 Sample Preparation Procedure –940, **"GPC Cleanup of Soil or Water Extracts before GC/ECD Analysis for Pesticides/PCBs."** contains details for the calibration of the GPC units.

11.0 Procedure

Water samples may be extracted by either a separatory funnel procedure or a continuous liquid-liquid extraction procedure. If an emulsion prevents acceptable solvent recovery with the separatory funnel procedure, continuous liquid-liquid extraction must be employed.

The Extraction Worksheet (Attachment 2) is completed by the technician performing the sample extraction. The worksheet accompanies the samples to the GC laboratory. Include on the worksheet, the manufacturer and lot number of the reagent/solvent used.

11.1 Separatory Funnel Extraction

11.1.1 Rinse all glassware to be used for extraction with methylene chloride before use. Thoroughly mix sample before aliquotting. Measure out each 1-l sample aliquot in a separate graduated cylinder. If a sample arrives in a 1 L bottle pour up and measure the entire contents. Measure and record the pH of the sample with wide range pH paper and adjust the pH to between 5 and 9 with 10 N sodium hydroxide or concentrated sulfuric acid, if required. Samples requiring pH adjustment must be noted in the comment section of the Extraction Worksheet (Attachment **2**). Place the sample into a 2-l separatory funnel. For sample received in 1-liter bottles, the first aliquot of methylene chloride, used for extractions should be used to rinse out the sample bottle. That methylene chloride should be added to the separatory funnel.

11.1.2 For each sample selected for MS and MSD analyses, measure out two additional 1000-ml portions and transfer those portions into separate funnels. Adjust the pH of each, if required, and fortify each with 1.0 ml of **#4615** PCB spike solution. Also add 1.0 ml of #426 surrogate solution to sample spikes (SS). For BSs, use 1000 ml reagent water and add 1.0 ml #426 surrogate and 1.0 ml of **#4615** PCB spike solution. The final volume for SSs and BSs is 10.0 ml.

11.1.3 Using a syringe or a volumetric pipet, add 1.0 ml of #426 surrogate solution to all water samples and blanks.

11.1.4 Prepare a method blank and a BS with each group of water samples extracted. For PCB analyses, a method blank for water samples consists of a 1-l volume of reagent water (see section 6.6), spiked with the surrogates and carried through the entire analytical procedure.

11.1.5 Add 60 ml of methylene chloride to the separatory funnel and extract the sample by shaking the funnel for two minutes on the Glas-Col shaker.

Before placing them on the shaker, shake and vent the separatory funnels until all pressure has been released from them. Then, invert the funnels and place them on the shaker. After securing the funnels on the shaker, slightly open the stopcock to prevent excess pressure from building during the extraction. Allow the organic layer to separate from the water phase for at least 10 minutes. If the emulsion interface between the layers is more than one-third the volume 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 means. Drain the methylene chloride into a 250-ml Erlenmeyer flask.

11.1.6 Add a second 60-ml volume of methylene chloride to the sample bottle and repeat the extraction procedure a second time, combining the extracts in the Erlenmeyer flask. Perform a third extraction in the same manner.

11.2 Continuous Liquid-Liquid Extraction (if needed for samples that cannot be extracted using separatory funnels)

11.2.1 Add 600 ml of methylene chloride to the bottom of the Corning One-Step extractor body.

11.2.2 Measure out each 1-l sample aliquot in a separate graduated cylinder or entire sample if it arrives in a 1 L bottle. Measure and record the pH of the sample with wide range pH paper and adjust the pH to between 5 and 9 with 10 N sodium hydroxide or concentrated sulfuric acid, if required. Samples requiring pH adjustment must be noted in the comment section of the Extraction Worksheet (Attachment 2). Pour the sample into the continuous extractor.

11.2.3 With some samples it may be necessary to place a layer of glass wool between the methylene chloride and the water layers in the extractor to prevent precipitation of suspended solids into the methylene chloride during extraction.

11.2.4 For each sample selected for MS and MSD analyses, measure out two additional 1000-ml portions and transfer those portions into separate continuous extractors. Adjust the pH of each, if required, and fortify each with 1.0 ml of PCB spike solution **#4615** before continuing the extraction. For all BSs use 1000 ml of reagent water. Add 1.0 ml of spike solution **#4615** to all BSs. See Section 7.1.1 as it pertains to rinsing out 1-liter sample bottles with methylene chloride.

11.2.5 Using a syringe or a volumetric pipet, add 1.0 ml of the surrogate solution #426 to all water samples and blanks. Add 1.0 ml of surrogate solution to all SSs and 1.0 ml surrogate solution to all BSs.

11.2.6 Adjust the level of methylene chloride in the extractor so that the crossover-arm is half filled with solvent.

11.2.7 After solvent and samples have been added to all extractor bodies, slowly open the stopcocks and allow the solvent to equilibrate in the continuous extractor/K-D flasks apparatus. Proceed with the extraction. Extract for 18 hours.

11.2.8 Prepare a method blank and BS with each group of water samples extracted. For Aroclor analysis, a method blank for water samples consists of a 1-l volume of reagent water (see section 6.6), spiked with the surrogates and carried through the entire analytical procedure.

11.3 Extract Drying and Concentration

11.3.1 Assemble a K-D concentrator by attaching a 10-ml concentrator tube to a 500-ml evaporative flask.

11.3.2 Pour the extract through a drying column containing about 10 cm of anhydrous granular sodium sulfate, or a powder funnel containing a plug of glasswool and approximately 10-20 g of sodium sulfate. Collect the extract in the K-D concentrator. Rinse the Erlenmeyer flask and the column with at least two additional 10- to 20-ml portions of methylene chloride to complete the quantitative transfer.

11.3.3 Add one or two clean boiling chips to the evaporative flask and attach a three-ball Snyder column. Pre-wet the Snyder column by adding about 1 ml of methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (80-90°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. **Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15-30 minutes.** At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 3-5 ml, remove the K-D apparatus. Allow it to drain and cool for at least 10 min. DO NOT ALLOW THE K-D EVAPORATOR TO GO DRY.

11.4 Solvent Exchange into Hexane

11.4.1 Momentarily remove the Snyder column, add 60 ml of hexane and a new boiling chip, and reattach the Snyder column. Pre-wet the column by adding about 1 ml of hexane to the top. Concentrate the solvent extract as before. When the apparent volume of liquid reaches 3-5 ml, remove the K-D apparatus and allow it to drain and cool for at least 10 minutes. DO NOT ALLOW THE K-D EVAPORATOR TO GO DRY. Alternatively, hexane may be added to the top of the Snyder column without allowing the K-D apparatus to cool.

11.4.2 Remove the Snyder column; using 1-2 ml of hexane, rinse the flask and its lower joint into the concentrator tube.

11.4.3 Concentrate the volume of the hexane extract to 5.0 ml. Refer to **Sample Preparation** Procedure –938A, **"Manual Florisil Cartridge Cleanup for Pesticide/PCB Analysis by CLP, SW846, and NYSASP"** for details on the required Florisil cartridge cleanup or **Sample Preparation Procedure –945, "Sulfuric Acid Wash of PCB-only Hexane Extracts"** for sulfuric acid cleanup, **if needed.**

12.0 Data Analysis & Calculations

12.1 Calculations must be consistent with the QC SOP: Numerical Data Reduction.

13.0 Method Performance

13.1 This method was validated through in-house laboratory studies of method detection limits (Attachment 1) and precision and accuracy for single analyst (Attachment **3**). The data are retained by the QA department.

14.0 Pollution Prevention

14.1 The solvents used in this procedure pose little threat to the environment when recycled and managed properly. Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best thing.

15.0 Waste Management

It is the laboratory's responsibility to comply with all federal, state, and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions, and to protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Compliance with all sewage discharge permits and regulations is also required.

Samples preserved with HCl or H_2SO_4 to pH <2 are hazardous and must be neutralized before being disposed, or must be handled as hazardous waste.

Refer to the Hazardous Waste Management and Safety SOPs located in the lab.

16.0 References

16.1 **Test Methods for Evaluating Solid Waste: Physical/Chemical Methods,** SW-846, 3rd **Edition, Udate III, 12/96, Methods 3510C and 3520C**

16.2 **Standard Methods for the Examination of Water and Wastewater, 18th Edition (1992) and 19th Edition (1995), upon promulgation, Method 1080**

16.3 New York State Analytical Services Protocol (NYSASP), **6/2000, plus revisions.**

16.4 QCSOP: Proper Documentation Procedures

16.5 QCSOP: Numerical Data Reduction

16.6 "Less is Better: Laboratory Chemical Management for Waste Reduction," American Chemical Society Department of Government Relations and Science Policy, 1155 16th Street, N.W., Washington DC, 20036, (202) 872-4477.

16.7 Hazardous Waste Management & Safety SOPs: "Hazardous Waste Disposal" and "Spill Control & Cleanup."

16.8 NELAC Standards, July 1, 1999, plus revisions

16.9 QA-G6: Guidance for the Preparation of Standard Operating Procedures for Quality-Related Operations EPA/600/R-96/027, November 1995.

16.10 New York State Environmental Laboratory Approval Program, Certification Manual, October 15, 1999, plus revisions.

16.11 CompuChem Quality Manual, Revision 0, 2/1/00

16.12 Sample Preparation Procedure –940, "GPC Cleanup of Soil or Water Extracts before GC/ECD Analysis for Pesticide Compounds."

16.13 Instrument Procedure 194, "Polychlorinated Biphenyls (PCBs) as Aroclors by GC/ECD – Capillary Column Techniques – Method 8082 (SW846 and NYSASP)."

16.14 **Sample Preparation Procedure –938A, "Manual Florisil Cartridge Cleanup for Pesticide/PCB Analysis by CLP, SW846, and NYSASP"**

16.15 Sample Preparation Procedure –945, "Sulfuric Acid Wash of PCB-only Hexane Extracts"

16.16 Sample Control SOP 4.1, "Receiving Samples" and 4.6, "Storing Samples"

17.0 Attachments as Tables, Diagrams, Flowcharts & Validation Data

17.1 Attachment 1 - MDL Study

17.2 Attachment 2 - Extraction Worksheet

17.3 Attachment 3 - Single Analyst Capability Study

Attachment 1

Method Detection Limit Study

Study Date & Instrument: Various				GC PCB Method 608/3510C/8082 Aqueous										
				Using higher of two column MDLs										
Aroclor	Rep#1	Rep#2	Rep#3	Rep#4	Rep#5	Rep#6	Rep#7	Rep#8	Rep#9	Mean	Amt.	S.Dev.	MDL	ReportLim
(Study date)(Varian)	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L
1016(2/22/00) (72)	1.20	0.75	1.00	1.10	1.10	1.10	1.40	0.98	1.10	1.08	1.0	0.17	0.51	2.0
1260 (2/22/00) (72)	1.10	0.76	0.90	1.00	1.10	0.94	1.40	0.92	1.10	1.02	1.0	0.18	0.52	2.0
1242(4/18/00)(70)	0.78	0.60	1.10	0.88	0.97	0.89	1.00	0.92	0.80	0.88	1.0	0.14	0.42	2.0
1232 (1/20/00) (37)	1.20	1.10	1.20	1.00	1.10	1.10	0.98	1.00	0.94	1.07	1.0	0.09	0.27	2.0
1221 (1/16/00) (37)	3.30	3.70	3.00	3.40	3.00	3.10	3.90	3.00	3.30	3.30	2.0	0.32	0.94	3.0
1248 (2/5/00) (42)	1.20	1.40	1.20	1.10	1.50	1.40	1.40	1.40	1.40	1.33	1.0	0.13	0.38	2.0
1254 (1/21/00) (37)	0.930	0.84	0.98	0.88	0.84	0.91	0.81	0.94	NA	0.89	1.0	0.06	0.18	2.0

Reporting Limit = Low Level Standard

Calculations based on 10 mL final extract volume and 1L sample volume, w/o GPC

Attachment 2

EXTRACTION WORKSHEET
PCB Only 3510C and 3520C for 8082
CompuChem
-1049

ASSIGNED TO: _____

EMP ID NUMBER: _____

DATE EXTRACTED/POSTED: _____

	SAMPLE NUMBER	QC SAMPLE TYPE	SAMPLE VOLUME (ml)	INITIAL pH	Adjusted pH (Y/N)	Final Volume (ml)	COMMENTS
1							Florisil (3620B) performed Y / N
2							Acid Wash (3665A) performed Y / N
3							
4							
5							
6							
7							
8							
9							
10							
11							
12							
13							
14							
15							
16							
17							
18							
19							
20							
21							
22							
23		BLK					
24		LCS					

		Pest/PCB	SURROGATE & SPIKE ADDED BY:
SURROGATE	NO.	426	
	AMT.	1.0 ml	_____ / _____
	LOT		INITIALS DATE
PCB SPIKE SOLUTION	NO.	4615	
	AMT.	1.0 ml	Witness _____ / _____
	LOT		Initials Date

FINAL VOLUME VERIFIED: _____

SUPERVISOR REVIEWED: _____

Analyst initials. Extracted _____ KD _____ N2 _____ Bottle up _____

Manufacturer and lot number of reagents/solvents used_____

Rev 4/11/00 mlj

Attachment 3

Analyst Capability Study

Laboratory Name/North Carolina Certificate Number: CompuChem/79
Analyst: Jennifer Priest
Study Date: January 20, 2000
Method: PCBs in Water, Method 608/8082
Instrument/Column: Varian 32/33

Compounds	True Va	Rep #1	Rep #2	Rep #3	Rep #4	Mean	Mean	SD(n-1)	-3SD	+3SD	- 3SD	+3SD	RSD
	ug/l	ug/l	ug/l	ug/l	ug/l	ug/l	% Rec.	ug/l	ug/l	ug/l	%R	%R	%
Aroclor 1254	1.0	0.74	0.82	0.77	0.79	0.78	78.1	0.03	0.7	0.9	87	113	4.4
Aroclor 1254	1.0	0.76	0.81	0.81	0.82	0.80	80.1	0.03	0.7	0.9	90	110	3.4

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Cary, NC 27513

SOP DOCUMENTATION FORM

This form must accompany all new and revised Standard Operating Procedures (SOPs) when you turn them in to Quality Assurance for review. Please fill out the entire shaded area (except effective date).

This is a new procedure ____ revised procedure ✓ outdated procedure (archive) ____

◆ Procedure area, title, and SOP number: SOP-735 Low Level Preparation for Analysis of PCBs only in Soil/Sediment/Sludge (SW-846 and NYSASP)

Effective date: (QA fills in) 2/23/00

◆ Procedure prepared by: Bob Wilson

Date: 11/4/99

◆ Procedure approved by: (If the manager prepared the SOP, a qualified second party should sign)

Date: 11/4/99

◆ Reason for change: Change concentration of PCB spiking solution

◆ This procedure meets the requirements of the following approved method references: SW-846, 3rd Edition, Method 3550B; NYSASP; NCDENR

Procedure approved by Quality Assurance Representative: Linda Carter

Date: 11/4/99

Effective 1-1-96, on an annual basis: Lab managers are required to review lab practices and revise the SOP if necessary. If no revision is necessary, indicate by your signature that the SOP has been reviewed.

Annual Review—Signature: _____ Date: _____

Annual Review—Signature: _____ Date: _____

Annual Review—Signature: _____ Date: _____

Sample Preparation Procedure -735 (-233-->945) Low Level Preparation for Analysis of PCBs Only in Soil/Sediment/Sludge (SW-846 and NYSASP)

1.0 Scope and Application

The following sample preparation procedure is designed to prepare soil/sediment/sludge samples for Aroclor only analysis by GC/ECD. The soil samples are extracted by sonication and the extracts subjected to an acid wash to remove interferences. The procedure is based on SW-846, Method 3550B and Method 3665A (for sulfuric acid wash).

The current MDLs acquired on are shown in Attachment 1. Reporting limits are also shown.

Staff members performing the procedures described in this SOP are responsible for reading, understanding, and complying with the SOP requirements. Supervisors are responsible for directing the analyst to the controlled SOP, and providing adequate explanation of the material contained therein.

This procedure is restricted to use by or under the supervision of analysts experienced in the instrumentation or preparative methods and who have demonstrated the ability to generate acceptable results through QC samples and analyst capability studies.

2.0 Summary

A 30-g aliquot of sample is spiked with the surrogate solution and then mixed with sodium sulfate, and extracted with a 1:1 methylene chloride/distilled acetone solvent mixture by sonication. The extract is then filtered, dried, and concentrated by Kuderna Danish (K-D) evaporation flask. Mandatory sulfuric acid wash of the extract is then performed.

3.0 Definitions

3.1 Method detection limit(MDL) – The minimum concentration of an analyte that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined form analysis of a sample in a given matrix containing the analyte (40 CFR, Part 136, Appendix B.)

3.2 Reporting Limit – The laboratory reporting limit is based on the lowest multipoint calibration standard concentration. For some inorganic methods, the reporting limit is based on the MDL, and is usually 4-8 times higher than the MDL. For organic methods, values detected below the reporting limit and above the MDL may be reported and qualified as an estimated concentration.

3.3 Reporting Units – µg/Kg

3.4 An SDG is defined by the following, whichever is more frequent:

- **Each 20 field samples received within a case, or**
- **Each 14 calendar day period (7 calendar day period for NYSASP) during which field samples in a case are received (period beginning with the receipt of the first sample in the SDG)**

4.0 Interferences

4.1 Method interferences might be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware. These contaminants lead to discrete artifacts or to elevated baselines in gas chromatograms (GC). Routinely, all of these materials must be demonstrated to be free from interferences under the conditions of the analysis by running reagent blanks. Interferences caused by phthalate esters can pose a major problem in pesticide analysis. Common flexible plastics contain varying amounts of phthalates which are easily extracted during laboratory operations, so cross-contamination of glassware frequently occurs when plastics are handled. Interferences from phthalates can best be minimized by avoiding the use of such plastics in the laboratory.

4.2 Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending on the nature of the site being sampled. The cleanup procedures must be used to remove such interferences in order to achieve the Contract Required Quantitation Limits (CRQL) or Practical Quantitation Limits (PQL). Extract cleanup procedures include a mandatory sulfuric acid wash (Method 3665A) and the optimal gel permeatim cleanup (Method 3640A).

5.0 Safety

5.1 Wear the proper personal safety equipment (gloves, lab coat, safety glasses) while performing this procedure.

Laboratory staff is encouraged to review the Chemical Hygiene Plan for general safety policies, and Material Safety Data Sheets for reagents used in the laboratory.

6.0 Equipment and Supplies

6.1 Sonic cell disruptor--Heat Systems, Ultrasonics, Inc., Model W-990 (475-watt with pulsing capability, No. 207 3/4-inch tapped disrupter horn), or equivalent device with a minimum 375-watt output capability.

NOTE: In order to ensure that sufficient energy is transferred to the sample during extraction, the horn must be replaced if the tip begins to erode. Erosion of the tip is indicated by a rough surface.

6.2 Sonabox (or equivalent)--for use with disrupter to decrease noise level

6.3 250-ml centrifuge bottles--Corning 1250 bottle, Corning glass

6.4 K-D apparatus

6.4.1 Concentrator tube--10-ml, graduated (Kontes K-570040-1029, or equivalent)

6.4.2 Evaporative flask--500-ml (Kontes K-470001-0500, or equivalent)

6.4.3 Snyder column--three-ball macro (Kontes K-503000-0121, or equivalent)

6.5 Funnels and Filter Paper

6.5.1 Powder funnels--10-cm diameter (optional), for filtration/drying

6.5.2 Filter paper--No. 41 pre-prepped Whatman (or equivalent), 9-cm circles (optional)

6.6 Silicon carbide boiling chips--approximately 10 to 40 mesh. Heat the chips to 400°C for 30 min or solvent rinse before use.

6.7 Water bath--heated, with concentric ring cover, capable of temperature control (±5°C).

NOTE: Always use the water bath in a hood.

6.8 Top-loading balance--capable of weighing accurately to ± 0.01 g

6.9 Nitrogen evaporation device--equipped with a heated bath that can be maintained at 35°C to 40°C, N-Evap by Organomation Associates, Inc., South Berlin, MA (or equivalent)

6.10 Vials and caps--2-ml for GC autosampler

6.11 Bottle or test tube--20-ml with Teflon-lined screw-cap for sulfur removal, if needed.

6.12 Glass vials--minimum of 20-ml, with screw-cap and Teflon or aluminum foil liner

6.13 Spatula--stainless steel

6.14 Pipet--Volumetric 1.0-ml or 2.0-ml (optional)

6.15 Syringe--1.0-ml or 2.0-ml (optional)

6.16 Vials--10-ml, with aluminum crimp-top and Teflon-faced silicone rubber seal

6.17 Tube--centrifuge, 20- to 15-ml with 19-mm ground glass joint

6.18 Centrifuge--table top (IEC model Centra-8)

6.19 Vortex mixer--Genie, Model 550-6, Scientific Industrial, Inc., Bohemia, NY, or equivalent.

6.20 Disposable Pasture glass pipets, 1-ml.

7.0 Reagents **and Standards**

7.1 Reagent water – Ali water used in this procedure must be equivalent to ASTM Type II water (as it relates to specific conductance and specific resistance) which is demonstrated to meet the blank contamination acceptance criteria contained in this Standard Operating Procedure (SOP).

7.2 Sodium sulfate--granular, anhydrous reagent grade, heated at 400°C for 4 hr, cooled, and stored in a glass bottle. Mallinckrodt anhydrous granular, or equivalent.

CAUTION: An open container of sodium sulfate may become contaminated during storage in the laboratory.

7.3 Methylene chloride, hexane, acetone--pesticide quality or equivalent. Each lot of solvent is tested to demonstrate that it is free of interferences before use. Methylene chloride must be certified as acid free or must be tested to demonstrate that it is free of hydrochloric acid.

7.4 Surrogate solution #426--the surrogates, tetrachloro-m-xylene and decachlorobiphenyl are added to all, samples, MSs, BSs and blanks. The surrogate solution is **provided** by the Organic Standards Chemist **and stored at 2-4.4°C when not in use**.

7.5 PCB matrix spiking solution #4551-- Prepare a spiking solution in acetone or methanol that contains the following Arochlor at the concentration specified:

PCB	µg/ml
1254	5.0

NOTE: Both of these solutions must be prepared every six months or sooner if comparison with quality control check samples indicates degradation or concentration of solution compounds.

The matrix spiking solution is **provided** by the Organic Standards Chemist **and stored at 4 ±2°C**.

8.0 **Sample Collection, Preservation, & Storage**

8.1 Samples are collected in 8 oz. wide mouth jars with PTFE – lined caps. They are obtained from the custodian out of cold storage.

8.2 Samples are stored at 2-4.4°C in the laboratory. Samples should be allowed to come to room temperature prior to sample preparation. After preparation, they are returned to the custodian and placed in the cooler.

8.3 Samples are extracted within 14 days of collection and analyzed within 40 days of extraction.

9.0 Quality Control

9.1 A matrix spike (MS) and matrix spike duplicate (MSD) are prepared for every sample delivery group (SDG).

9.2 Prepare a method blank and a blank spike (BS) with each separate extraction batch. For NYSASP, the BS is called a matrix spike blank.

9.3 Duplicates, at a frequency of 10%, are required when processing samples submitted to meet the regulatory requirements of North Carolina.

9.4 Ensure the balance has been calibrated for the day before use.

10.0 Calibration & Standardization

10.1 Ensure the balance has been calibrated for the day before use. Refer to Organic Sample Preparation laboratory SOP 8.6 "Top Loading Balance Calibration and Maintenance."

11.0 Procedure

11.1 Mix samples thoroughly, especially composited samples. Discard any foreign objects such as sticks, leaves, and rocks. Also, decant and discard any standing aqueous phase. Samples must be at room temperature.

11.2 The Extraction Worksheet (Attachment 1) is completed by the technician performing the sample extration The worksheet accompanies the samples for acid washing (SPP -945) and then to the GC laboratory. Also, a witness observes the addition of the surrogate and spike solutions and signs off on the Extraction Worksheet, verifying that the additions were done correctly. Include on the worksheet, the manufacturers and lot numbers of the reagents/solvents used.

11.3 Documentation must follow the requirements in QC SOP: Proper Documentation Procedures.

11.4 Extraction with Sonication

11.4.1 Weigh approximately 30 g of sample into a 250-ml centrifuge bottle (record weight to the nearest 0.1 g on the Extraction Worksheet, Attachment 1) and add 60 g of anhydrous sodium sulfate (granular). Mix the sample thoroughly.

11.4.2 For a sample to be used for MS and MSD analysis, weigh out two additional 30-g portions of sample, (record weight to nearest 0.1 g), add 60 g of sodium sulfate, and add 1.0 ml of the pesticide matrix spike solution #4551 to the MS and MSD aliquot. To prepare a BS, weigh an additional 30.0 g of sodium sulfate (furnaced), and add 60.0 g sodium sulfate. Add 1.0 ml of pesticide matrix spike solution #4551 to the BS.

11.4.3 Prepare a method blank with each group of soil/sediment samples extracted. A method blank for soil/sediment samples consists of 90 g of sodium sulfate spiked with the 2.0 ml of the surrogate solution #426 and is carried through the entire analytical procedure.

11.4.4 Add 2.0 ml of surrogate solution #426 to all soil samples, the MS, MSD, BS, and blanks by using a volumetric pipet or a syringe. Mix the solution well. The sample and the added sodium sulfate should be an homogeneous, granular mixture at this point.

11.4.5 Immediately add 80-100 ml of 1:1 methylene chloride acetone to the sample.

11.4.6 Place the bottom surface of the sonicator probe about 1/2 inch below the surface of the solvent but above the sediment layer.

11.4.7 Sonicate for 3 min using a 3/4-inch horn at 100% power output with PULSE set on 1 sec ON and PERCENT DUTY CYCLE knob set at 50%. Do NOT use a microtip.

11.4.8 Centrifuge each sample for 2 min at 2000 rpm, then decant and filter the extracts through pre-prepped Whatman No. 41 filter paper and a powder funnel into the K-D apparatus. An alternative to this would be Buchner funnel filtration with Whatman 41 filter paper.

11.4.9 Repeat the extraction two more times with additional 80-100 ml portions of the 1:1 methylene chloride/distilled acetone. Before each extraction, thoroughly mix the solid residue, and make certain that the sodium sulfate is free flowing and not a consolidated mass. As needed, break up large lumps with a clean spatula. Decant and filter the extraction solvent after each sonication by using the same funnel described in paragraph 7.2.8. After the final sonication, pour the entire sample into the funnel and rinse the beaker and funnel with 20-30 mL of methylene chloride.

If particulate matter is observed, filter the entire extracted sample again by placing a new prepped filter in the original funnel and pouring the extracted sample through the funnel. Rinse with methylene chloride.

11.5 Soil Extract Concentration

11.5.1 Add one or two clean boiling chips to the evaporative flask and attach a three-ball macro-Snyder column, while adding about 1 ml of methylene chloride to the top of the Snyder. Place the K-D apparatus on a hot water bath (80-85°C) so that the concentrator tube is partially immersed

in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15-30 min. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood with condensed solvent. Reduce the volume of liquid to 3-5 ml. Remove the K-D apparatus and allow it to drain and cool for at least 10 min. DO NOT ALLOW THE K-D EVAPORATOR TO GO DRY.

11.6 Solvent Exchange into Hexane

11.6.1 Momentarily remove the Snyder column, add 60 ml of hexane and a new boiling chip, and reattach the Snyder column. Pre-wet the column by adding about 1 ml of hexane to the top. Concentrate the solvent extract as before. When the apparent volume of liquid reaches 3-5 ml, remove the K-D apparatus and allow it to drain and cool for at least 10 min. DO NOT ALLOW THE K-D EVAPORATOR TO GO DRY. **Alternatively, hexane may be added to the top of the Snyder column without allowing the K-D apparatus to cool.**

11.6.2 Remove the Snyder column using 1-2 ml of hexane, rinse the flask and its lower joint into the concentrator tube.

11.6.3 Using the nitrogen evaporation (N-EVAP) technique, concentrate the extract to a final volume of **5**.0 mL.

11.6.4 Bottle up the extract which is now ready for sulfuric acid clean-up by SPP-945.

12.0 Data Analysis & Calculations

12.1 Calculations must be consistent with the QC SOP: Numerical Data Reduction.

13.0 Method Performance

13.1 This method was validated through in-house laboratory studies of method detection limits (Attachment 1) and precision and accuracy for single analyst (Attachment 2). The data are retained by the QA department.

14.0 Pollution Prevention

14.1 The solvents used in this procedure pose little threat to the environment when recycled and managed properly. Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address

their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best thing.

15.0 Waste Management

15.1 It is the laboratory's responsibility to comply with all federal, state, and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions, and to protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Compliance with all sewage discharge permits and regulations is also required.

Samples preserved with HCl or H_2SO_4 to pH <2 are hazardous and must be neutralized before being disposed, or must be handled as hazardous waste.

Refer to the Hazardous Waste Management and Safety SOPs located in the lab.

16.0 References

16.1 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846. 3rd Edition, revised 12/96. (Method 3550B)

16.2 NYSASP

16.3 NCDEHNR requirements

16.4 **QCSOP: Proper Documentation Procedures**

16.5 **QCSOP: Numerical Data Reduction**

16.6 **"Less is Better: Laboratory Chemical Management for Waste Reduction," American Chemical Society Department of Government Relations and Science Policy, 1155 16th Street, N.W., Washington DC, 20036, (202) 872-4477.**

16.7 **Hazardous Waste Management & Safety SOPs: "Hazardous Waste Disposal" and "Spill Control & Cleanup."**

16.8 **NELAC Standards, July 1, 1999, plus revisions**

16.9 QA-G6: Guidance for the Preparation of Standard Operating Procedures for Quality-Related Operations EPA/600/R-96/027, November 1995.

16.10 New York State Environmental Laboratory Approval Program, Certification Manual, October 15, 1999, plus revisions.

16.11 CompuChem Quality Manual, Revision 0, 2/1/00

16.12 Organic Sample Preparation Laboratory SOP 6.8, "Top Loading Balance Calibration and Maintenance."

16.13 Instrument Procedure 194 (SOP Section 2.2.5.3) "Polychlorinated Biphenyls (PCBs) as Aroclors by GC/ECD – Capillary Column Technique – Method 8082 (SW 846 and NYSASP)."

17.0 Attachments as Tables, Diagrams, Flowcharts & Validation Data

17.1 Attachment 1 – MDL Study

17.2 Attachment 2 – Extraction Worksheet

17.3 Attachment 3 - Single Analyst Capability Study

Attachment 1

CompuChem
Method Detection Limit Study

Study Date & Instrument: Various

GC Pesticide/PCB Method 8082 Soil
Using higher of two column MDLs
Based on 10 ml final extract volume

Aroclor Name (Study date)(Instrument)	ID#	Rep#1 ug/kg	Rep#2 ug/kg	Rep#3 ug/kg	Rep#4 ug/kg	Rep#5 ug/kg	Rep#6 ug/kg	Rep#7 ug/kg	Rep#8 ug/kg	Rep#9 ug/kg	Rep#10 ug/kg	Mean ug/kg	Amt. ug/kg	S.Dev. ug/kg	MDL ug/kg	Report Limit ug/kg
1260(8/25/99)(Varian 72)	723	39.6	36.2	35.7	32.1	34.7	36.3	35.2	37.8	NA	NA	35.9	50.0	2.22	6.64	63
1016(8/25/99)(Varian 72)	724	41.0	35.6	37.8	32.4	31.3	34.0	33.6	39.3	NA	NA	35.6	50.0	3.42	10.2	42
1242(8/25/99)(Varian 72)	718	19.5	16.4	21.6	19.8	20.8	18.2	19.3	14.0	18.8	NA	18.7	33.0	2.30	6.87	42
1232(3/12/99)(Varian 72)	721	73.2	76.2	70.5	72.2	89.4	60.2	93.7	83.9	99.0	NA	79.8	31.2	12.5	36.2	63
1221(8/25/99)(Varian 72)	720	42.5	41.3	43.6	98.3	41.8	85.8	43.6	86.4	42.7	NA	58.4	67.0	24.1	69.7	83
1248(3/12/99)(Varian 72)	722	46.2	45.7	30.9	32.8	43.0	43.8	44.0	41.2	39.5	41.53	40.8	20.8	5.18	14.6	42
1254(8/24/99)(Varian 70)	719	34.8	37.1	36.6	32.9	31.7	29.0	28.5	29.8	41.1	NA	33.5	33.0	4.24	12.3	42

Reporting Limit = Low Level Standard

CompuChem
a division of Liberty Analytical Corporation
501 Madison Avenue
Cary, NC 27513

SOP DOCUMENTATION FORM

This form must accompany all new and revised Standard Operating Procedures (SOPs) when you turn them in to Quality Assurance for review. Please fill out the entire shaded area (except effective date).

This is a new procedure ____ revised procedure ✓ outdated procedure (archive) ____

- Procedure area, title, and SOP number: Section # 2.2.5.3 Effective date: (QA fills in)

IP194 Analysis of Polychlorinated Biphenyls (PCBs) as Aroclors by GC/ECD Capillary Column Technique by SW846 1/26/01

- Procedure prepared by: Date:

Linda Carter for Katrina Travis 9/8/00

- Procedure approved by: (If the manager prepared the SOP, a qualified second party should sign) Date:

Linda Carter 9/8/00

- Reason for change: Annual review, NELAC format changes, additional column types

- This procedure meets the requirements of the following approved method references:

Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW846, 3rd Edition, Update III, Method 8082, New York State Analytical Services Protocol, NYSASP, 10/95

Procedure approved by Quality Assurance Representative: Date:
(Not needed if signed above)

_____ _____

Effective 1-1-96, on an annual basis: Lab managers are required to review lab practices and revise the SOP if necessary. If no revision is necessary, indicate by your signature that the SOP has been reviewed.

Annual Review—Signature: _____ Date: _____

Annual Review—Signature: _____ Date: _____

Annual Review—Signature: _____ Date: _____

Instrument Procedure 194: **Analysis of** Polychlorinated Biphenyls (PCBs) as Aroclors by GC/ECD-Capillary Column Technique **by SW846**

1.0 Scope and Application

Method 8082 is used to determine the concentration of various polychlorinated biphenyls (PCBs) as Aroclors in extracts from solid and liquid matrices. Open-tubular, capillary columns are employed with electron capture detectors (ECD). While Method 8082 also provides for the analysis of individual PCB congeners, this procedure only deals with the determination of PCBs as Aroclors. The following are amenable to analysis using this method:

Compound Name	CAS Registry No.
Aroclor-1016	12674-11-2
Aroclor-1221	11104-28-2
Aroclor-1232	11141-16-5
Aroclor-1242	53469-21-9
Aroclor-1248	12672-29-6
Aroclor-1254	11097-69-1
Aroclor-1260	11096-82-5

Staff members performing the procedures described in this SOP are responsible for reading, understanding, and complying with the SOP requirements. Supervisors are responsible for directing the analyst to the controlled SOP, and providing adequate explanation of the material contained therein.

This procedure is restricted to use by or under the supervision of analysts experienced in the instrumentation or preparative methods and who have demonstrated the ability to generate acceptable results through QC samples and analyst capability studies.

2.0 Summary of Method

Prior to analysis the sample must be extracted following Sample Preparation Procedure – 1049, "PCBs in Water Preparation Procedure" or Sample Preparation Procedure –735 (-233→945), "Low Level Preparation for Analysis of PCBs only in Soil/Sediment/Sludge". A variety of optional cleanup steps may be used, including Florisil, Gel Permeation Chromatography (GPC) or acid wash.

The analysis is performed using the dual column option described in Method 8082 where a Y-splitter joins a single injection port with two dissimilar analytical columns. In this manner, confirmation may be performed simultaneously with the primary analysis.
After cleanup, the extract is analyzed by injecting 4 µL (2 µL per column) into a GC with dual wide-bore, fused silica, capillary columns with dual electron capture detectors (GC/ECD).

3.0 Definitions

3.1 Method detection limit (MDL) – The minimum concentration of an analyte that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte (40 CFR, Part 136, Appendix B.)

3.2 Reporting Limit – The laboratory reporting limit is based on the lowest multipoint calibration standard concentration. For some inorganic methods, the reporting limit is based on the MDL, and is usually 4-8 times higher than the MDL. For organic methods, values detected below the reporting limit and above the MDL may be reported and qualified as an estimated concentration.

If the low level standard concentration is not at least three times higher than the MDL value, the standard concentration is adjusted upward in order to achieve this minimal ratio. It may be adjusted higher than three times depending on the concentration range of the calibration curve and the ability to meet method linearity requirements. An exception to this is for CLP methods where the MDL is only required to be lower than the reporting limit.

For CLP the reporting limit is the Contract Required Quantitation Limit (CRQL) for organics and the Contract Required Detection Limit (CRDL) for inorganics.

3.3 Reporting Units – ug/L for water and ug/Kg for soil

3.4 An SDG is defined by the following, whichever is more frequent:

- each 20 field samples received within a case, or
- each 14 calendar day period during which field samples in a case are received (7 calendar days for NYSASP, OLM04.0, plus revisions, and ILM04.0, plus revisions including ILM04.1) beginning with the receipt of the first sample.

NOTE: The Army Corps of Engineers does not accept the SDG approach, unless the samples are prepared in a single batch. When a group of up to 20 field samples of a similar matrix are prepared as one batch, method-

specified QC samples such as a method blank, laboratory control sample, matrix spike, matrix spike duplicate, and matrix duplicate must also be prepared together at a rate of 5%. If samples are batched together from different sites, project-specific QC must be processed.

3.5 Aroclor 1660 – Term to denote a mixture of Aroclor 1016 and 1260

4.0 Interferences

4.1 Interferences in this method can be grouped into three broad categories: contaminated solvents, reagents, or glassware; contaminated GC carrier gas, parts, column surfaces, detector surfaces; and the presence of co-eluting compounds in the sample matrix that also are detected by the ECD. Specific cleanups may be necessary for samples, depending on the compounds of interest.

4.2 Interferences by phthalate esters introduced during the sample preparation procedures can be a major problem. Common flexible plastics found in certain gloves and other objects contain varying amounts of phthalates which may be introduced during lab operations. Cross-contamination of clean glassware routinely occurs when plastics are handled during extraction steps, especially when solvent wetted surfaces are handled. These interferences can be minimized by cleanup of solvents, reagents, and glassware.

4.3 Glassware must be scrupulously cleaned as soon as possible after use by rinsing with the last solvent used. This should be followed by detergent washing with hot water, and rinses with tap water and organic-free reagent water. Drain the glassware and dry in an oven at 130 degrees C for several hours or rinse with methanol and drain.

4.4 The presence of elemental sulfur will result in broad peaks that interfere with early eluting pesticides, and can be removed by cleaning the extract with shiny copper or by the use of GPC cleanup, or with tetrabutylammonium (TBA) sulfite reagent

4.5 Waxes, lipids, and other high molecular weight compounds are also removed using GPC.

5.0 Safety

Appropriate protective equipment and clothing must be used under the assumption that all samples are potentially hazardous. During sample preparation glasses, gloves and lab coats are a minimum requirement. The persistent presence of noxious odors may be indicative of failure of the laboratory ventilation system and must be reported to a supervisor or manager.

Laboratory staff are encouraged to review the Chemical Hygiene Plan for general safety policies, and Material Safety Data Sheets for reagents used in the laboratory.

6.0 Equipment & Supplies

6.1 Gas chromatograph: Varian 3400 and **Trace 2000** suitable for splitless injection with all required accessories, including syringes, analytical columns, gases, ECDs, and integrator or data system.

6.2 The following wide-bore columns are used in the analysis:

6.2.1 Column 1-30 m x 0.53 mm Id fused silica capillary column bonded with 35% phenyl methylpolysiloxane (**CLPesticides**), **0.50** µm film thickness

6.2.2 Column 2 - 30 m x 0.53 mm ID fused silica capillary column chemically bonded with 50% phenyl methylpolysiloxane (**CLPesticides2**), **0.42** µm film thickness

6.2.3 Wide-bore columns are installed in a 1/4 inch injectors, with deactivated liners designed specifically for use with mega-bore columns

6.2.4 Restek Y-shaped fused silica connector

7.0 Reagents & Standards

All standards are prepared by the Organic Standards chemist. Details for the preparation are contained in the standard operating procedures (SOP) for that area (Section 7.0 of the SOP collection.)

7.1 Reagent water – All water used in this procedure must be equivalent to ASTM Type II water (as it relates to specific conductance and specific resistance) which is demonstrated to meet the blank contamination acceptance criteria contained in this Standard Operating Procedure (SOP). It is referred to throughout the remainder of this SOP as DI water.

7.2 Reagent or pesticide grade chemicals must be used for all tests.

7.3 All standard solutions should be stored at 4 degrees C in Teflon-sealed containers in the dark. All stock standard solutions must be replaced after one year or sooner if routine QC indicates a problem. All other standard solutions must be replaced after six months or sooner if QC indicates a problem.

7.4 Stock standard solutions (1 mg/mL) are purchased from Restek Corporation, for example, as certified solutions, or they may be prepared from neat material.

7.5 Calibration standards are prepared at five concentrations by diluting the stock standards solutions with hexane.

7.6 Separate calibration standards are used for each multi-component analyte, with the exception of Aroclors 1016 and 1260 which can be run as a mixture. The mixture is referred to as Aroclor 1660.

7.7 Surrogate standards are added to all samples, method blanks, matrix spikes, laboratory control samples (blank spikes), and calibration standards.

7.7.1 Decachlorobiphenyl (DCB) and tetrachloro-m-xylene (TCX) are the surrogates used. Corrective action is taken when the recoveries of both surrogates fall outside acceptance limits on both columns.

8.0 Sample Collection, Preservation, & Storage

8.1 Samples are collected, preserved, and stored according to the tables in Sample Control SOP 4.1, "Receiving Samples" and 4.6, "Storing Samples." Sample holding times are also listed.

8.2 All extracts must be analyzed within 40 days of extraction.

8.3 Prior to analysis, all extracts must be stored under refrigeration at 2-4.4° C in the reach-in storage unit in the laboratory. After analysis, extracts are returned to Sample Control for long-term storage and disposal.

9.0 Quality Control

9.1 Instrument Failure for GC analysis

9.1.1 When linearity is difficult to achieve, verify that the appropriate length of column is inserted in the detector. Examine all column ends and determine if the ends of the columns need to be trimmed. The removal of 0.5 meters of the detector end of the column may be indicated when linearity is difficult to achieve.

9.1.2 When the instrument blanks fail, examine the chromatography to determine if there is contamination in the column that is causing the failure. If so, bake the column for 1 hour or less to see if this can be

corrected. If the contamination is such that baking for 1 hour does not improve the baseline, it may be necessary to change the liner.

9.1.3 When calibration verifications fail recovery low, verify that the correct peaks are being named. Also verify that the syringe is not plugged and change the septa. If the calibration verification fails again, examine the chromatography to determine if there is a problem with the baseline that is causing the failure. If so, bake the column for 1 hour or less to see if this can be corrected. Also, if the calibration verification is failing on only one column, the y-splitter may be plugged. If the calibration verification continues to fail, the instrument will need a new calibration curve.

9.1.4 When calibration verifications fail recovery high, verify that the correct peaks are being named. Examine the chromatography to determine if there is contamination on the column that is causing the failure. If so, bake the column for 1 hour or less to see if this can be corrected. If the calibration verification fails again, the instrument will need a new calibration curve.

9.1.5 When the calibration verification fails due to drift, change the septa and verify that all the column fittings are secure. Also, determine if there is contamination on the column that is causing the failure. If so, bake the column for 1 hour or less to see if this can be corrected. If the calibration verification still fails, it is permissible to update retention times once per 24 hours period. Record in the instrument run log when the retention times are updated.

9.1.6 All preventive and routine maintenance as mentioned above is recorded in the instrument run log. Major maintenance is recorded in the maintenance log (Attachment 2).

9.2 Initial Calibration

9.2.1 The percent Relative Standard Deviation (%RSD) of the calibration factors for each selected Aroclor component in the initial calibration must be less than or equal to 20%. **The % RSD for Aroclors is calculated by determining the mean of the average of the five selected peaks in each standard level. Acceptance criteria must be met by the average of the five peaks, as opposed to each individual peak.**

9.2.2 When the %RSD is ≤ 20%, the instrument response is considered to be linear and the mean calibration factor can be used for quantitation. If the %RSD is greater than 20%, the analyst must use a calibration model, **such**

as a least squares regression or a non-linear calibration method may be used. These are available in the ThruPut system.

Note: For samples submitted to meet the regulatory requirements of the State of South Carolina, the use of a quadratic fit to demonstrate the linearity of the initial calibration is not allowed. The use of a linear regression is permitted.

9.2.2.1 When one of these options is used, the correlation coefficient of the equation must be 0.99 or greater for a valid calibration.

9.2.2.2 If a quadratic equation is used, six levels of standards must be used.

9.2.2.3 If a third degree polynomial is used, seven levels are required.

9.2.2.4 The calibration range may be narrowed to determine if linearity can be achieved. This may cause more dilution re-analyses or even change the reporting limit if the lower standard is eliminated. For this method, the method quantitation limit is defined by the lowest standard.

10.2 Initial Calibration Verification

10.2.1 Analyze a second source initial calibration verification (ICV) standard to verify the standard curve before proceeding with analyses.

9.3 Continuing Calibration

9.3.1 The calibration factors in all continuing calibration verification standards must be within ± 15% difference (%D) when compared to the mean calibration factors from the initial calibration on both analytical columns. **The % D is calculated by determining the average %D of the five selected peaks for each Aroclor. Acceptance criteria must be met by the average of the five peaks, as opposed to each individual peak.**

9.3.2 If the %D exceeds ± 15%, then corrective action must be taken and the continuing calibration verification re-injected. If the calibration still exceeds the criteria, a new initial calibration must be analyzed.

9.3.3 If any of the continuing calibration Aroclor components fall outside their retention time windows, the system is out of control and corrective action must be taken to correct the problem. If, after re-injection of the standard following corrective action, the retention times are still outside the windows, a new initial calibration must be analyzed.

9.4 Surrogates

9.4.1 Surrogate recoveries must be within 30-150% for all samples, blanks, blank spikes, matrix spikes, and matrix spike duplicates. If both surrogates (tetrachloro-m-xylene and decachlorobiphenyl) are outside the control range on both columns, the sample must be re-extracted and re-analyzed.

9.4.2 An exception to the above criteria is allowed for field samples and matrix spikes if the recovery is out of range due to interfering peaks. Chromatograms must be examined to determine if the out of control condition may be attributed to sample interferences, or to a partial injection, before re-extracting the sample.

9.4.2.1 Partial injections should be re-injected and can be diagnosed by comparing the solvent peak of the sample to the solvent peak of the standard. They should be similar in size.

9.5 Method blanks

9.5.1 Method blanks are extracted with each preparation batch of samples.

9.5.2 The acceptance criteria for method blanks includes the following:

9.5.2.1 Surrogates recoveries must be within recovery criteria.

9.5.2.2 No target analytes may be present above the reporting limit.

9.5.3 If the method blank exceeds acceptance criteria, the source of the problem (s) must be investigated and appropriate corrective action taken. All samples processed with a method blank that does not meet acceptance criteria must be re-extracted and reanalyzed.

9.6 Matrix Spikes

9.6.1 A matrix spike and matrix spike duplicate (MS/MSD) must be performed for each sample delivery group of up to 20 field samples.

9.6.2 The percent recovery and relative percent difference (RPD) criteria for the MS/MSD are shown in the following table.

Analyte	Aqueous % Recovery	Aqueous RPD	Solid % Recovery	Solid RPD
Aroclor 1660	50-150	20	50-150	20

9.6.3 The recoverability of spiked analytes in environmental samples is highly influenced by the particular matrix. When recoveries do not meet the acceptance criteria or interferences preclude proper assessment of the data, results of a Laboratory Control Sample (LCS) or Blank Spike (BS) are evaluated to verify that the analytical systems (sample preparation and analysis) are in control.

If the original unspiked sample does not meet surrogate acceptance criteria and the MS/MSD do meet criteria, the sample should be reanalyzed or re-extracted then reanalyzed. If the original sample and the MS/MSD yield the same unacceptable surrogate recoveries, then further action is not required since matrix interference would be confirmed.

9.7 Laboratory Control Sample (LCS)

9.7.1 A LCS, or blanks spike (BS) (method spike blank for NYSASP), is DI water, or furnaced Ottawa sand or sodium sulfate for solid matrices, spiked with a target Aroclor and surrogates. The BS is prepared with each preparation batch of samples.

9.7.2 LCS recovery limits are as follows.

Analyte	Aqueous % Recovery	Solid % Recovery
Aroclor 1660	50-150	50-150

9.7.3 If the LCS fails to meet acceptance criteria, all samples in the associated batch must be re-extracted and reanalyzed.

9.8 Duplicates

9.8.1 Sample duplicates are required at a frequency of 10% when processing samples submitted to meet the regulatory requirements of North Carolina DENR. This requirement can be met with the MS/MSD.

10.0 Calibration & Standardization

10.1 Initial Calibration

10.1.1 For the initial calibration five concentration levels are prepared for Aroclors 1016/1260. Single standards for the remaining Aroclors are prepared at the mid-concentration. The M3 level for Aroclors 1221, 1232, 1242, 1248, and 1254 are used for pattern recognition and to generate calibration factors for them.

On a project-specific basis, three or five concentration levels may be required for the remaining Aroclors. The following table presents the concentrations in µg/mL of Aroclor standards if five levels are required. Additionally, 5-point calibrations are performed for those Aroclors that are detected in samples but normally have only a single mid-level concentration standard analyzed. Each multicomponent standard contains the two surrogates at the indicated levels.

Analyte	Standard Ids	L	M1	M2	M3	H
AR1660	4566-4570	0.1875	.375	.75	1.5	3.0
AR1221	4571-4575	0.25	.50	1.0	2.0	4.0
AR1232	4576-4585	0.1875	.375	.75	1.5	3.0
AR1242	4581-4585	0.125	.25	.50	1.0	2.0
AR1248	4605-4609	0.125	.25	.50	1.0	2.0
AR1254	4610-4614	0.125	.25	.50	1.0	2.0
TCX		0.02	.04	.08	.16	.32
DCB		0.02	.04	.08	.16	.32

10.1.2 A minimum of five sets of calibration factors is generated for the Aroclor 1016/1260 standards. Each set consists of the calibration factor for each of the five or more peaks chosen. The single standard of the remaining Aroclors will each produce a minimum of three calibration factors, one for each selected peak.

10.1.3 The initial calibration standard sequence is as follows.

12 hour Sequence Injection Number	Initial Calibration Standard Sequence
1	AR1660-**1**
2	AR1660-**2**
3	AR1660-**3**
4	AR1660-**4**
5	AR1660-**5**

10.2 Initial Calibration Verification (ICV)

10.2.1 The initial calibration is verified using a standard prepared from a separate source than that used for the calibration curve. An acceptable recovery must be achieved before proceeding with analysis.

10.3 Continuing Calibration

10.3.1 The continuing calibration verification standards are used to evaluate retention time stability.

10.3.2 For continuing calibration verification, the mid level Aroclor 1660 from the initial calibration is injected. Sequencing should be as follows.

12 Hour Sequence Injection No.[1]	Whole Sequence Bottle No.[1]	Description
1	6	Instrument Blank (PIBLK)
2	7	AR1660-**M3**
3-12	8-17	10 Samples
13	18	PIBLK
14	19	AR1660-**M3**
15-24	20-29	10 Samples
25	30	PIBLK
26	31	AR1660-**M3**
27	32	3

[1] The number in the first column represents the injection sequence at the start of a twelve-hour time period. The number in the second column represents the actual bottle number in the injection sequence that would have begun at the start of the initial calibration.

[2] The "D" indicates this standard to be the "daily" or first calibration verification standard run during a 24 hour period. The AR1660-3D is the

mid-level, Aroclor standard and the absolute retention time for each chosen characteristic Aroclor component peak establishes the midpoint of the retention time window.

[3] The requirements of Method 8082 include a calibration standard after each 20 samples although one is recommended after each 10 samples. The method also indicates that the calibration verification standards be run each 12 hour shift. The method does not specify the requirement or the frequency for instrument blanks. These are important tools for assessing instrument performance. Assuming approximately 30 minutes per analytical run, the 12-hour shift begins with the injection of the AR1660-3D standard (Injection No. 2, bottle 7). The first injection, the instrument blank, is a QC measure and not characterized as a calibration verification standard. The 12-hour sequence period would end after Injection No. 25, bottle 30 in the total sequence. At the end of the next 12-hour sequence, the closing AR1660-3 standard would also represent the start of the next 24-hour period so that standard would be used to establish the midpoint of the retention time windows for that period. If other Aroclors are detected during the analytical sequence they may be injected to replace an AR1660 calibration verification standard.

11.0 Procedure

Documentation must follow the requirements in QC SOP: Proper Documentation Procedures.

11.1 Dual Column Analysis and Confirmation

11.1.1 The dual column/dual detector approach involves the use of two 30 m x 0.53 mm ID fused silica open-tubular columns of different polarities (**CLPesticides and CLPesticides2**). Each has different selectivities towards the target compounds. The columns are connected to a "Y-splitter" and dual ECD detectors.

11.2 GC operating conditions are as follows:

11.2.1 Column 1

- Type: **CLPesticides**
- Dimensions: 30 m x 0.53 mm ID
- Film Thickness: 0.**50** µm

11.2.2 Column 2

- Type: **CLPesticides2**
- Dimensions: 30 m x 0.53 mm ID
- Film Thickness: **0.42** µm

11.2.3 Carrier gas

- Helium
- Flow rate: 6 mL/minute

11.2.4 Makeup gas

- Argon/methane
- Flow rate 20 mL/minute

11.2.5 Temperature program

- Hold at 150°C for **1.0** minute
- Ramp to 275°C at **5** degrees/minute
- Hold for **2.0** minutes

11.2.6 Injector temperature: 250°C

11.2.7 Detector temperature: 300°C

11.2.8 Injection volume: 4 µL (2 µL per column)

11.2.9 Solvent

- Hexane

11.2.10 Detector: Dual ECD's

11.2.11 Range: 10

11.3 Analytical Sequence

11.3.1 The analytical sequence is discussed in Section 10 above. All information is recorded on the run log for the instrument (Attachment 3)

11.4 Gas chromatographic analysis:

11.4.1 The GC is set up according to the operating conditions detailed above. A final temperature of 240-275° C is necessary to elute decachlorobiphenyl.

11.4.2 The initial calibration is performed according to the discussion in Section 10.0. The initial calibration is verified once using a second source standard (ICV).

11.4.3 A continuing calibration standard is run during each 12 hour shift using a mid-point calibration standard. Calibration standards are also injected after every 10 samples (although it is required after every 20 samples) and at the end of the analytical sequence. Since an analytical sequence may continue as long as instrumental QC criteria are met, the end of one 12-hour sequence is considered to be the beginning of the next 12-hour sequence. The calibration factor must meet acceptance criteria when compared to the initial calibration curve. When this criteria is exceeded, corrective action is required as described in Section 7.0 and may include re-injection of the calibration verification standard or analysis of a new initial calibration before more samples are analyzed.

11.4.4 Each sample analysis must be bracketed with an acceptable initial calibration, continuing calibration verification standards (each 12 hr shift), or calibration standards interspersed with the samples. If a "closing" standard, which is injected after a group of samples fails to meet criteria and the Aroclor was not detected in that group of samples, then the samples do not require reinjection. However, if the standard is more than 15% below the mean calibration factor from the initial calibration, then re-injection is required.

11.5 Retention Time Windows

11.5.1 Retention time windows are established for each chosen characteristic Aroclor component (peak). The width of the retention time windows is based on actual retention times of selected peaks in the standards that are assessed over a 72 hour period. A standard deviation calculated for each component.

11.5.2 For each Aroclor component chosen (3-5 peaks) the absolute retention time from each "daily" standard is used as the midpoint of the window. A ± three times standard deviation value is applied to the absolute retention time. Windows are defined as ± three times the standard deviation of the absolute retention times of each chosen Aroclor component. Analyst experience is critical in the interpretations of the chromatograms.

11.6 Identification and Quantitation

11.6.1 Compound identification is based on a second column confirmation, with the second column being of a dissimilar nature. Target analyte peaks must fall within the retention time windows on both columns.

11.6.2 Tentative identification of an analyte occurs when three or more of the chosen Aroclor component peaks from a sample extract fall within the retention time windows and the pattern matches that of the Aroclor standard.

11.6.3 Identification of Aroclors is based on the characteristic pattern and retention times of the indicator peaks.

11.6.4 Quantitation is based on the area under the characteristic peaks as compared to the area under the corresponding peaks in the calibration standard at the same retention times. The external calibration method is used for quantitation.

11.6.5 When samples contain more than one multi-component analyte, a more experienced analyst may be required to process or assess the data. Similar conditions exist when multicomponent analytes have been subjected to environmental degradation, resulting in weathered Aroclors that may have significant differences in peak patterns than the standards.

11.6.6 Use the external calibration procedure to establish mean response factors for each chosen Aroclor component by dividing peak area in the standard by the mass injected. Peak areas from peaks within the chosen Aroclor component's retention time window are used to calculate the quantity of each target Aroclor while retention times are used to identify each component.

The concentration reported on the reporting form is the higher of the two values obtained from the dual column analysis. If the result is >40% different, the data reviewer should verify that there are not overlapping

peaks causing this to occur. Also, the data reviewer will examine the baseline to verify that the baseline parameters are set properly.

11.6.7 The Aroclors are quantitated using responses of five major peaks (minimum of three) of the sample pattern compared to the calibration factors of the same peaks in standard. Those concentrations are averaged to arrive at the reported concentration.

12.0 Data Analysis & Calculations

Calculations must be consistent with the QC SOP: Numerical Data Reduction.

12.1 Calculation of the mean or average of a set of values:

$$\overline{X} = \frac{\sum_{i=1}^{n} X_i}{n}$$

where: n = total number of values
x_i = each individual value used to calculate the mean
x = the mean of n

12.2 Calculation of the standard deviation of a set of values:

$$\text{Standard deviation} = \sqrt{\frac{\sum_{i=1}^{n}\left(X_n - \overline{X}\right)^2}{n-1}}$$

12.3 Calculation of percent recovery:

12.3.1 LCS and surrogates:

$$\%R = \frac{Amount\ found}{Amount\ spiked} x\ 100$$

12.3.2 Matrix spikes:

$$\%\,R = \frac{Amount\ in\ spiked\ sample - Amount\ in\ unspiked\ (native)\ sample}{Amount\ spiked} x\ 100$$

12.4 Calculation of % RSD

$$\%RSD = \left(\frac{Standard\ deviation}{\overline{X}}\right) \times 100$$

12.5 Calculation of RPD

$$RPD = \frac{|Value\ 1 - Value\ 2|}{(Value\ 1 + Value\ 2)/2} x100$$

12.6 Calculation of %Difference (%D)

$$\%Diff = \frac{Value - \overline{Reference\ value}}{\overline{Reference\ value}} x\ 100$$

12.7 Calibration factors are calculated by dividing the total peak area for each chosen Aroclor component in the standard by the total mass injected (in nanograms).

$$Calibration\ Factor\ (CF) = \frac{Peak\ area}{Total\ mass\ injected}$$

12.8 Concentration

12.8.1 Concentration of aqueous samples

$$ug/L = \frac{(Ax)(Vt)(Df)}{(\overline{CF})(Vi)(Vs)}$$

where: Ax = area response for the analyte
Vt = volume of the concentrated extract (µl)
Df = dilution factor. If no dilution, Df = 1.0
$\overline{CF}$ = mean calibration factor from the initial calibration
Vo = volume of water sample extracted (ml)
Vi = volume of extract injected (µl)

12.8.2 Concentration of soil samples <u>(dry weight basis)</u>

$$ug/kg = \frac{(Ax)(Vt)(Df)}{(\overline{CF})(Vi)(Ws)(D)}$$

where: Ws = weight of sample extracted, in grams

$$D \text{ (dry weight)} = \frac{100 - \%\text{ moisture}}{100}$$

Ax, Vt, Df, $\overline{CF}$, Vi have the same definitions as for water.

12.9 Calculating Dilutions

12.9.1 If the response of the majority of the chosen Aroclor components exceeds the on-column amount of the high level Aroclor 1660 standard, it must be diluted and re-analyzed. Comparing the on-column nanogram amount of the chosen Aroclor components with the nanogram amounts of the same chosen Aroclor components from the high level standard used in the initial calibration will allow you to determine an appropriate dilution.

12.9.2 If a sample concentration exceeds the high level standard a dilution must be performed. Determine a level of dilution that will result in a value within the upper half of the calibration range. This is an acceptable dilution. A 10x dilution is performed using 1 mL sample plus 9 mL diluent for a total volume of 10 mL. It should be recorded on the run log as "10x (1 mL in 10 mL)."

13.0 Method Performance

This method was validated through in-house laboratory studies of method detection limits (Attachment 1) and precision and accuracy for single analyst (Attachment 4). The data are retained by the QA department.

14.0 Pollution Prevention

The solvents used in this procedure pose little threat to the environment when recycled and managed properly. Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best thing.

15.0 Waste Management

It is the laboratory's responsibility to comply with all federal, state, and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions, and to protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Compliance with all sewage discharge permits and regulations is also required.

Samples preserved with HCl, HNO_3, or H_2SO_4 to pH <2 are hazardous and must be neutralized before being disposed, or must be handled as hazardous waste.

Refer to the Hazardous Waste Management and Safety SOPs located in the lab.

16.0 References

16.1 "Test Methods for Evaluating Solid Wastes: Physical/Chemical Methods", SW846, 3rd Edition, Update III, 12/96, Method 8082

16.2 Standard Methods for the Examination of Water and Wastewater, 18th Edition (1992) and 19th Edition (1995), upon promulgation, Method 1080

16.3 New York State Analytical Services Protocol (NYSASP), **6/2000, plus revisions.**

16.4 QCSOP: Proper Documentation Procedures

16.5 QCSOP: Numerical Data Reduction

16.6 "Less is Better: Laboratory Chemical Management for Waste Reduction," American Chemical Society Department of Government Relations and Science Policy, 1155 16th Street, N.W., Washington DC, 20036, (202) 872-4477.

16.7 Hazardous Waste Management & Safety SOPs: "Hazardous Waste Disposal" and "Spill Control & Cleanup."

16.8 NELAC Standards, July 1, 1999, plus revisions

16.9 QA-G6: Guidance for the Preparation of Standard Operating Procedures for Quality-Related Operations EPA/600/R-96/027, November 1995.

16.10 New York State Environmental Laboratory Approval Program, Certification Manual, October 15, 1999, plus revisions.

16.11 CompuChem Quality Manual, Revision 0, 2/1/00

16.12 Sample Control SOP 4.1, "Receiving Samples"

16.13 Sample Control SOP 4.6, "Storing Samples"

17.0 Attachments as Tables, Diagrams, Flowcharts & Validation Data

17.1 Attachment 1 – Method detection limits (MDL)

17.2 Attachment 2 – Instrument Maintenance Log

17.3 Attachment 3 – Instrument Run Log

17.4 Attachment 4 – Analyst Capability Study

Attachment 1

Method Detection Limit Study

Study Date & Instrument: Various				GC PCB Method 608/3510C/8082 Aqueous Using higher of two column MDLs										
Aroclor	Rep#1	Rep#2	Rep#3	Rep#4	Rep#5	Rep#6	Rep#7	Rep#8	Rep#9	Mean	Amt.	S.Dev.	MDL	ReportLim
(Study date)(Varian)	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L
1016(2/22/00) (72)	1.20	0.75	1.00	1.10	1.10	1.10	1.40	0.98	1.10	1.08	1.0	0.17	0.51	2.0
1260 (2/22/00) (72)	1.10	0.76	0.90	1.00	1.10	0.94	1.40	0.92	1.10	1.02	1.0	0.18	0.52	2.0
1242(4/18/00)(70)	0.78	0.60	1.10	0.88	0.97	0.89	1.00	0.92	0.80	0.88	1.0	0.14	0.42	2.0
1232 (1/20/00) (37)	1.20	1.10	1.20	1.00	1.10	1.10	0.98	1.00	0.94	1.07	1.0	0.09	0.27	2.0
1221 (1/16/00) (37)	3.30	3.70	3.00	3.40	3.00	3.10	3.90	3.00	3.30	3.30	2.0	0.32	0.94	3.0
1248 (2/5/00) (42)	1.20	1.40	1.20	1.10	1.50	1.40	1.40	1.40	1.40	1.33	1.0	0.13	0.38	2.0
1254 (1/21/00) (37)	0.930	0.84	0.98	0.88	0.84	0.91	0.81	0.94	NA	0.89	1.0	0.06	0.18	2.0

Reporting Limit = Low Level Standard

Calculations based on 10 mL final extract volume and 1L sample volume, w/o GPC

Attachment 1 (continued)

CompuChem Method Detection Limit Study

Study Date & Instrument: Various

GC PCB Method 3550B/8082 Soil
Using higher of two column MDLs

Based on 30 g sample weight, 10 mL extract volume, without GPC

Aroclor (Study date)(Varian)	Rep#1 ug/Kg	Rep#2 ug/Kg	Rep#3 ug/Kg	Rep#4 ug/Kg	Rep#5 ug/Kg	Rep#6 ug/Kg	Rep#7 ug/Kg	Rep#8 ug/Kg	Rep#9 ug/Kg	Mean ug/Kg	Amt. ug/Kg	S.Dev. ug/Kg	MDL ug/Kg	ReportLim ug/Kg
1016(2/3/00)(70)	32.0	42.0	36.0	41.0	32.0	38.0	30.0	30.0	40.0	35.7	33	4.80	14	63
1260(2/3/00)(70)	32.0	29.0	30.0	34.0	28.0	28.0	29.0	26.0	30.0	29.6	33	2.35	6.8	63
1242(2/15/00)(70)	25.0	25.0	17.0	17.0	27.0	19.0	20.0	31.0	NA	22.6	33	5.13	15	42
1232(3/17/00)(70)	64.0	56.0	64.0	61.0	63.0	65.0	65.0	72.0	NA	63.8	66.7	4.46	13	63
1221 (2/10/00) (67)	65.0	62.0	62.0	50.0	59.0	60.0	68.0	51.0	NA	59.6	67	6.30	19	83
1248 (2/4/00) (72)	38.0	38.0	36.0	48.0	37.0	33.0	42.0	36.0	31.0	37.7	33	4.97	14	42
1254 (1/22/00) (42)	28.0	29.0	27.0	26.0	31.0	35.0	28.0	26.0	27.0	28.6	33	2.88	8.3	42

Attachment 2

CompuChem a division of Liberty Analytical Corp. Logbook 4 H(4) 1

GC Extractables Instrument Maintenance Log: 66/67

Date: _____ Time: _____

System: _____

Problem: _____

_____

_____

_____

_____

Action Taken: _____

_____

_____

_____

_____

_____

Parts used:

Part Number	Description	Quantity

File Name Indicating Instrument In Control: _____

Performed By: _____ Date: _____

Reviewed By: _____ Date: _____

2/11/00:mlj

Attachment 3

COMPUCHEM a division of Liberty Analytical Corp Instrument ID 66 / 67 DATE ___/___/___
GC EXTRACTABLES RUN LOG Sequence ID: _____ SHIFT/S(A)_____(B)_____(C)___
COMPUCHEM .LOGBOOK 4 WWW 1 Amt. Inj. 2 µl

Method : 8081A 8082 8151A CLP Other_____

	REJECTED	FILE NAME	REPORTED	DATE	CompuChem #	CASE/SDG#	CHEMIST	COMMENTS(ETC.)/DISPOSITION
1				/ /				
2				/ /				
3				/ /				
4				/ /				
5				/ /				
6				/ /				
7				/ /				
8				/ /				
9				/ /				
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12				/ /				
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21				/ /				
22				/ /				
23				/ /				
24				/ /				

SUPERVISOR APPROVAL_____

The presence of the Chemist's employee ID number, or signature, on this run log attests th strict compliance with the method's SOP has occurred. Any SOP deviations require documentation by the responsible chemist together with the chemist's initials and the initials of the lab supervisor and a QA department representative, signifying approval of the deviation.

12/30/99 mlj

Attachment 4

Analyst Capability Study

Laboratory Name/North Carolina Certificate Number: CompuChem/79													
Analyst: Jennifer Priest													
Study Date: January 20, 2000													
Method: PCBs in Water, Method 8082													
Instrument/Column: Varian 32/33													
Compounds	rue Va	Rep #1	Rep #2	Rep #3	Rep #4	Mean	Mean	D(n-1)	-3SD	+3SD	- 3SD	+3SD	RSD
	ug/l	ug/l	ug/l	ug/l	ug/l	ug/l	% Rec.	ug/l	ug/l	ug/l	%R	%R	%
Aroclor 1254	1.0	0.74	0.82	0.77	0.79	0.78	78.1	0.03	0.7	0.9	87	113	4.4
Aroclor 1254	1.0	0.76	0.81	0.81	0.82	0.80	80.1	0.03	0.7	0.9	90	110	3.4
Laboratory Name/North Carolina Certificate Number: CompuChem/79													
Analyst: Jennifer Priest													
Study Date: April 21, 2000													
Method: 8082 Soil													
Instrument/Column: Varian 70/clpest and 71/clpest2													
	rue Va	Rep #1	Rep #2	Rep #3	Rep #4	Mean	Mean	D(n-1)	-3SD	+3SD	- 3SD	+3SD	RSD
	mg/Kg	mg/Kg	mg/Kg	mg/Kg	mg/Kg	mg/Kg	% Rec.	mg/Kg	mg/Kg	mg/Kg	%R	%R	%
Aroclor 1016	166.7	143.56	129.59	134.20	143.62	137.74	82.6	7.01	116.7	158.8	85	115	5.1
Aroclor 1016	166.7	150.81	140.18	137.16	149.91	144.51	86.7	6.87	123.9	165.1	86	114	4.8
Aroclor 1260	166.7	144.3	128.1	132.5	144.9	137.43	82.5	8.48	112.0	162.9	81	119	6.2
Aroclor 1260	166.7	151.2	133.6	139.2	154.1	144.54	86.7	9.73	115.4	173.7	80	120	6.7

CompuChem
a division of Liberty Analytical Corporation

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SOP DOCUMENTATION FORM

This form must accompany all new and revised Standard Operating Procedures (SOPs) when you turn them in to Quality Assurance for review. Please fill out the entire shaded area (except effective date).

This is a new procedure ____ revised procedure ✓ outdated procedure (archive) ____

◆ Procedure area, title, and SOP number: Section # 2.12.2 Effective date: (QA fills in)

IP197 GC/ECD Analysis of Pesticides/PCBs in Low Concentration Water Samples by CLP and NYSASP — ~~7/14/00~~ 8/4/00 mg 8/9/00

◆ Procedure prepared by: Date:

Linda Carter 7/14/00

◆ Procedure approved by: (If the manager prepared the SOP, a qualified second party should sign) Date:

John Jones 7/14/00

◆ Reason for change: NELAC format changes / yearly review and update

◆ This procedure meets the requirements of the following approved method references:

U.S. EPA CLP SOW for Organics Analysis, Low Concentration Water, OLM02.1, 2/96, plus revisions

Procedure approved by Quality Assurance Representative: Date:
(Not needed if signed above)

_____ _____

Effective 1-1-96, on an annual basis: Lab managers are required to review lab practices and revise the SOP if necessary. If no revision is necessary, indicate by your signature that the SOP has been reviewed.

Annual Review—Signature: _____ Date: _____

Annual Review—Signature: _____ Date: _____

Annual Review—Signature: _____ Date: _____

Instrument Procedure 197: GC/ECD Analysis of Pesticides/PCBs in Low Concentration Water Samples **by CLP &** NYSASP

1.0 Scope and Application

This method covers the determination of organochlorinated pesticides for liquid samples following preparation by Sample Preparation Procedure –737 (-1072→-938), "Water Preparation for Low Concentration Pesticides/PCBs".

Contract Required Quantitation Limits (CRQLs) and a list of target analytes are shown in Attachment 1.

Staff members performing the procedures described in this SOP are responsible for reading, understanding, and complying with the SOP requirements. Supervisors are responsible for directing the analyst to the controlled SOP, and providing adequate explanation of the material contained therein.

This procedure is restricted to use by or under the supervision of analysts experienced in the instrumentation or preparative methods and who have demonstrated the ability to generate acceptable results through QC samples and analyst capability studies.

2.0 Summary of Method

Aqueous samples are extracted using continuous liquid-liquid or separatory funnel extraction procedures followed by Florisil adsorption column cleanup. The extracts are analyzed by a two-column gas chromatography/electron capture detector (GC/ECD) technique.

3.0 Definitions

3.1 Method detection limit (MDL) – The minimum concentration of an analyte that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte (40 CFR, Part 136, Appendix B.)

3.2 Reporting Limit – The laboratory reporting limit is based on the lowest multipoint calibration standard concentration. For some inorganic methods, the reporting limit is based on the MDL, and is usually 4-8 times higher than the MDL. For organic methods, values detected below the reporting limit and above the MDL may be reported and qualified as an estimated concentration.

If the low level standard concentration is not at least three times higher than the MDL value, the standard concentration is adjusted upward in order to achieve this minimal ratio. It may be adjusted higher than three times depending on the concentration range of the calibration curve and the ability to meet method linearity requirements. An exception to this is for CLP methods where the MDL is only required to be lower than the reporting limit.

For CLP the reporting limit is the Contract Required Quantitation Limit (CRQL) for organics and the Contract Required Detection Limit (CRDL) for inorganics.

3.3 Reporting Units – ug/L

3.4 An SDG is defined by the following, whichever is more frequent:

- each 20 field samples received within a case, or
- each 14 calendar day period during which field samples in a case are received (7 calendar days for NYSASP, OLM04.0, plus revisions, and ILM04.0, plus revisions including ILM04.1) beginning with the receipt of the first sample.

NOTE: The Army Corps of Engineers does not accept the SDG approach, unless the samples are prepared in a single batch. When a group of up to 20 field samples of a similar matrix are prepared as one batch, method-specified QC samples such as a method blank, laboratory control sample, matrix spike, matrix spike duplicate, and matrix duplicate must also be prepared together at a rate of 5%. If samples are batched together from different sites, project-specific QC must be processed.

3.5 SOW - Statement of Work

3.6 CLP – Contract Laboratory Program

3.7 RT – Retention time

3.8 CRQL – Contract-Required Quantitation Limit

4.0 Interferences

4.1 Method interference may be caused by contaminants in solvents, reagents, glassware, and sample processing hardware. These contaminants lead to discrete artifacts or to elevated baselines in gas chromatograms. These materials must be routinely demonstrated to be

free from interference under the sample preparation and analysis conditions by analyzing instrument blanks and method blanks.

4.2 Interference caused by phthalate esters can pose a major problem in pesticide analysis. Because common flexible plastics contain varying amounts of phthalates that are easily extracted during laboratory operations, cross-contamination of glassware frequently occurs when plastics are handled. Avoiding the use of plastics in the laboratory can best minimize interference from phthalates.

4.3 Matrix interference may be caused by contaminants that are co-extracted from the sample. The extent of matrix interference will vary considerable from source to source, depending upon the nature of the site being sampled. Cleanup procedures are effective in removing such interference.

5.0 Safety

Appropriate protective equipment and clothing must be used under the assumption that all samples are potentially hazardous. During sample preparation glasses, gloves and lab coats are a minimum requirement. The persistent presence of noxious odors may be indicative of failure of the laboratory ventilation system and must be reported to a supervisor or manager.

Laboratory staff are encouraged to review the Chemical Hygiene Plan for general safety policies, and Material Safety Data Sheets for reagents used in the laboratory.

6.0 Equipment & Supplies

6.1 Gas Chromatograph - Varian 3400 GCs equipped with autosamplers and dual Electron Capture Detectors (ECD) are used.

6.2 Columns

6.2.1 Two wide-bore (0.53 mm ID) fused silica GC columns are required. CompuChem uses a Restek **CLPesticides** capillary column, **30 m x 0.53 mm ID x 0.5 µm, with a Restek CLPesticides2,** 30 m x 0.53 mm ID **x 0.42 µm. These are equivalent to Restek DB-608 and RTX-1701 phase respectively.**

Resolution difficulties are associated with the following pairs of compounds:

- On the DB-608 or equivalent column, DDE and Dieldrin; Methoxychlor and Endrin ketone; and Endosulfan I and gamma-Chlordane

- On the RTX-1701 or equivalent column, Endosulfan I and gamma-Chlordane; and Methoxychlor and Endosulfan sulfate

6.2.2 Descriptions of acceptable capillary columns are presented in the SOW. Additionally, alternative columns may be used if demonstrated to be equivalent. Equivalency requirements are presented in the SOW. The equivalency documentation must be maintained and made available during an on-site audit.

6.3 Glass or other tee adapters **are** used in 0.25 inch injector ports with glass adapters, allowing simultaneous injections onto both columns.

6.4 Carrier gas is helium, make-up is P-5 (argon/methane)

6.5 Data system

6.5.1 Hewlett-Packard Target 3 data acquisition

6.5.2 ThruPut's Quick Form generation software

7.0 Reagents & Standards

All standards are prepared by the Organic Standards chemist. Details for the preparation are contained in the standard operating procedures (SOP) for that area (Section 7.0 of the SOP collection.)

7.1 Reagent water – All water used in this procedure must be equivalent to ASTM Type II water (as it relates to specific conductance and specific resistance) which is demonstrated to meet the blank contamination acceptance criteria contained in this Standard Operating Procedure (SOP). It is referred to throughout the remainder of this SOP as DI water.

7.2 Surrogate solution

Analyte	Concentration in µg/ml
Tetrachloro-m-xylene	0.2
Decachlorobiphenyl	0.2

7.3 LCS Spiking solution

Analyte	Concentration in µg/ml
gamma-BHC (Lindane)	0.10
Heptachlor epoxide	0.10
Dieldrin	0.20
4,4′-DDE	0.20
Endrin	0.20
Endosulfan sulfate	0.20
Gamma-chlordane	0.10

7.4 Florisil cartridge check solution containing 2,4,5-trichlorophenol at 0.1 µg/ml and 0.5 ml of mid-level INDA.

7.5 Calibration Standards

7.5.1 Resolution Check Mixture

7.5.1.1 Prepared in hexane every six months

Analyte	Concentration (ng/ml)
gamma-chlordane	10.0
Endosulfan I	10.0
DDE	20.0
Dieldrin	20.0
Endosulfan sulfate	20.0
Endrin ketone	20.0
Methoxychlor	100.0
Tetrachloro-m-xylene	20.0
Decachlorobiphenyl	20.0

7.5.2 Performance Evaluation Mixture (PEM)

7.5.2.1 Prepared in hexane weekly

Analyte	Concentration (ng/ml)
alpha-BHC	10.0
4,4'-DDT	100.0
beta-BHC	100.0
Endrin	50.0
Methoxychlor	250.0
Tetrachloro-m-xylene	20.0
Decachlorobiphenyl	20.0

7.5.3 Individual Standard Mixtures A and B

INDA (ng/ml)

Analyte	Low	Mid	High
alpha-BHC	5.0	20	80
Heptachlor	5.0	20	80
gamma-BHC	5.0	20	80
Endosulfan I	5.0	20	80
Dieldrin	10.0	40	160
Endrin	10.0	40	160
4,4'-DDD	10.0	40	160
4,4'-DDT	10.0	40	160
Methoxychlor	50.0	200	800
TCX	5.0	20	80
DCB	10.0	40	160

INDB (ng/ml)

Analyte	Low	Mid	High
beta-BHC	5.0	20	80
delta-BHC	5.0	20	80
Aldrin	5.0	20	80
Heptachlor epoxide*	5.0	20	80
alpha-chlordane	5.0	20	80
gamma-chlordane	5.0	20	80
4,4'-DDE	10.0	40	160
Endosulfan sulfate	10.0	40	160
Endrin aldehyde	10.0	40	160
Endrin ketone	10.0	40	160
Endosulfan II	10.0	40	160
TCX	5.0	20	80
DCB	10.0	40	160

*(exo-epoxy isomer)

NOTE: Only the exo-epoxy isomer (isomer B) of Heptachlor Epoxide is used as an analytical standard.

7.5.4 Multicomponent Standards

7.5.4.1 Prepared individually, except for Aroclor 1016 and 1260, which may be combined. Each solution contains both TCX and DCB at 20.0 ng/ml.

Analyte	Concentration (ng/ml)
Aroclor 1016	100
Aroclor 1221	200
Aroclor 1232	100
Aroclor 1242	100
Aroclor 1248	100
Aroclor 1254	100
Aroclor 1260	100
Toxaphene	500

8.0 Sample Collection, Preservation, & Storage

8.1 Samples are collected, preserved, and stored according to the tables in Sample Control SOP 4.1, "Receiving Samples" and 4.6, "Storing Samples." Sample holding times are also listed.

8.2 All extracts must be analyzed within 40 days of extraction.

8.3 Prior to analysis, all extracts must be stored under refrigeration at 2-4.4° C in the reach-in storage unit in the laboratory. After analysis, extracts are returned to Sample Control for long-term storage and disposal.

9.0 Quality Control

9.1 Instrument Failure for GC analysis

9.1.1 When linearity is difficult to achieve, verify that the appropriate length of column is inserted in the detector. Examine all column ends and determine if the ends of the columns need to be trimmed.

9.1.2 When the instrument blanks fail, examine the chromatography to determine if there is contamination in the column that is causing the failure. If so, bake the column for 1 hour or less to see if this can be corrected. If the contamination is such that baking for 1 hour does not improve the baseline, it may be necessary to change the liner.

9.1.3 When calibration verifications fail recovery low, verify that the correct peaks are being named. Also verify that the syringe is not plugged and change the septa. If the calibration verification fails again, examine the chromatography to determine if there is a problem with the baseline that is causing the failure. If so, bake the column for 1 hour or less to see if this can be corrected. Also, if the calibration verification is failing on only one column, the y-splitter may be plugged. If the calibration verification continues to fail, the instrument will need a new calibration curve.

9.1.4 When calibration verifications fail recovery high, verify that the correct peaks are being named. Examine the chromatography to determine if there is contamination on the column that is causing the failure. If so, bake the column for 1 hour or less to see if this can be corrected. If the calibration verification fails again, the instrument will need a new calibration curve.

9.1.5 When the calibration verification fails due to drift, change the septa and verify that all the column fittings are secure. Also, determine if there is contamination on the column that is causing the failure. If so, bake the column for 1 hour or less to see if this can be corrected. If the calibration verification still fails, **a new initial calibration must be performed.**

9.1.6 All preventive and routine maintenance as mentioned above is recorded in the instrument run log. Major maintenance is recorded in the maintenance log.

9.2 Initial Calibration

9.2.1 Acceptance Criteria

9.2.1.1 The resolution between two adjacent peaks in the Resolution Check Mixture must be ≥ 60.0%.

9.2.1.2 Resolution of any two adjacent peaks in the midpoint concentrations of INDA and INDB must be ≥ 90.0%.

9.2.1.3 All single component pesticides and surrogates in both runs of the PEM must be ≥ 90.0% resolved on both columns.

9.2.1.4 The absolute retention times of each of the single component pesticides and surrogates in both runs of the PEM must be within the retention time window determined from the initial calibration.

9.2.1.5 The percent difference of the amount found and amount added for each of the single components and surrogates in both of the PEM runs must be ≥ 25.0% or ≤ 25.0%.

9.2.1.6 The percent breakdown for endrin and DDT must be ≤ 20.0% on both columns individually and ≤ 30.0% combined.

9.2.1.7 The % RSD of the calibration factors for each single component analyte must be ≤ 20.0 % except for alpha-BHC and delta-BHC, both of which must be ≤ 25.0%.

- The % RSD of the calibration factors for the two surrogates must be ≤ 30.0%.

- Other than surrogates, the calibration factors of up to two single-component target analytes per column are allowed to exceed 20.0% RSD, but must be ≤ 30.0%.

If the linearity requirements listed above are met, the calibration factor from the mid-point concentration standard is used for quantitation of each single-component pesticide.

9.2.1.8 All instrument blanks must meet technical acceptance criteria.

9.2.2 Corrective Action

9.2.2.1 Initial calibration technical acceptance criteria must be met before any samples are analyzed.

9.2.2.2 Instrument maintenance described in Section 9.1 may be required.

9.2.2.3 After corrective action is taken, the initial calibration sequence must be repeated.

9.3 Continuing Calibration Verification

Three types of analyses are used to verify the calibration and evaluate instrument performance. Instrument Blanks, PEM's, and the mid point concentration of INDA and INDB constitute the continuing calibration.

9.3.1 Frequency and Sequence of the Calibration Verification Standards

9.3.1.1 Each 12 hour tune period must be bracketed by an Instrument Blank (IB) and the PEM and a second IB and the mid-point concentration of INDA and INDB.

9.3.1.2 For the first 12-hour period immediately following the initial calibration sequence, the IB and the PEM in the last two steps of the initial calibration sequence are considered to bracket the front end of that 12-hour period.

9.3.1.3 The injection of the IB starts the beginning of that 12-hour period. Samples may be injected for 12 hours from the injection of the IB. The three injections at the end of that 12-hour period must be an IB, INDA, and INDB. The IB must be analyzed first, then the INDA and INDB may be analyzed in either order.

9.3.1.4 The analyses of the IB and INDA and INDB immediately following one 12-hour period may be used to begin the subsequent 12-hour period, provided they meet acceptance criteria described below. In that case, the subsequent 12-hour period must be bracketed by the acceptable analyses of an IB followed by a PEM (only in that order). Those two analyses may in turn be used to bracket the front end of the next another 12-hour period.

This progression may continue every 12 hours until such time as any of the IBs, PEMs, or INDA or INDB fails to meet acceptance criteria.

9.3.1.5 If more than 12 hours have elapsed since the injection of an IB that bracketed a previous 12-hour period, an acceptable IB and PEM must be analyzed in order to start a new sequence and use the current initial calibration for quantitation. This applies even if no analyses were performed since that standard was injected.

9.3.1.6 If the entire 12-hour period is not required for the analyses of all samples then the sequence must be ended early with either the IB/PEM combination or the IB/INDA and INDB combination, whichever was due to be performed at the end of the 12-hour period.

9.3.2 Acceptance Criteria for the Calibration Verification

9.3.2.1 All single component pesticide or surrogate peaks in the PEM used to demonstrate continuing calibration must be ≥ 90.0% resolved.

The resolution between any two adjacent peaks in the m

9.3.2.2 The absolute retention time for single-component pesticides and surrogates in the PEM and midpoint INDA and INDB must be within the windows as described in section 4.5.

9.3.2.3 The % difference of the calculated amount (amount found) and the nominal amount (amount added) for each of the single component pesticides and surrogates in the PEM and midpoint concentration of the Individual Standard Mixtures used to demonstrate continuing calibration must be ≥ -25.0%, and ≤ 25.0%.

9.3.2.4 The percent breakdown for endrin and DDT must be ≤ 20.0% on both columns individually and ≤ 30.0% combined.

9.3.2.5 All instrument blanks must not have any target analytes detected at greater than one half the CRQL, and surrogates must be within the RT windows.

9.3.3 Corrective Action

9.3.3.1 When a continuing calibration standard fails any acceptance criteria sample analysis is stopped. If two consecutive unacceptable standards are run, corrective action is taken and may include the instrument maintenance described in Section 9.1.

9.3.3.2 The initial calibration must be repeated and meet acceptance criteria.

9.3.3.3 Any samples analyzed after the last acceptable standard verification in the sequence must be reanalyzed.

9.4 Surrogates

9.4.1 The two surrogates, 2,4,5,6-Tetrachloro-m-xylene (TCX) and Decachlorobiphenyl (DCB), and must be added to all samples, blanks, and the LCS prior to extraction.

9.4.2 The RT of both surrogates must fall within the RT windows for an analysis to be acceptable.

9.4.3 The acceptance criteria of 30-150% recovery must be met and are not advisory.

9.4.4 If surrogate criteria are not met, re-extraction is performed.

9.5 Blanks

9.5.1 Method Blanks

9.5.1.1 A method blank is extracted with each preparation batch.

9.5.1.2 One liter of reagent water is spiked with the surrogate solution, extracted, florisiled, and analyzed by the same procedure as the samples. The requirements below apply independently to each column.

- Method blanks must be analyzed on each GC/ECD system used to analyze samples.

- Method blanks cannot contain any **confirmed** target analytes above the CRQL.
- Surrogate acceptance criteria MUST be met.
- Surrogate RTs must be within the RT windows from the initial calibration as described below.
- All samples associated with an unacceptable method blank must be re-extracted and reanalyzed.

9.5.2 Sulfur Cleanup Blank.

9.5.2.1 Hexane is spiked with surrogates and undergoes sulfur cleanup. The requirements below apply independently to each column.

- The sulfur cleanup blank is prepared when only part of a set of samples extracted together requires sulfur cleanup. It is associated only with the part of the set that requires sulfur cleanup.
- If all samples in a given Sample Delivery Group (SDG) require sulfur cleanup, then the method blank must be subjected to sulfur cleanup, and no sulfur cleanup blank is required.
- The sulfur cleanup blank cannot contain any confirmed target analytes above the CRQLs.
- RTs of both surrogates must be within the RT window calculated during the initial calibration.
- Surrogate recoveries must fall within the acceptance window of 30-150%.

9.5.2.2 **For** samples associated with an unacceptable sulfur cleanup blank **another aliquot of the back-up extract for the blank and samples must be reprocessed through sulfur clean-up. If the blank still fails, then the associated samples must be re-extracted.**

9.5.3 Instrument Blank.

9.5.3.1 An instrument blank is hexane containing 20.0 ng/ml of tetrachloro-m-xylene and decachlorobiphenyl. The following acceptance criteria apply independently to each column.

- All acceptable sample analyses are to be bracketed by acceptable instrument blanks.
- The instrument blank must not contain target analytes at concentrations greater than one half the CRQLs.
- Surrogates must be within the RT criteria established in section 11.0.

9.5.3.2 If analytes are detected at greater than one half the CRQL or the surrogate RTs are outside the RT windows, all data collection must be stopped and an acceptable instrument blank run before samples can be analyzed.

All samples run between the last acceptable instrument blank and one that fails must be re-analyzed.

9.6 Laboratory Control Sample (LCS)

9.6.1 A LCS must be prepared, extracted, and analyzed at least once every SDG according to the SOW. It must be extracted concurrently with the samples in the SDG and analyzed using the same instrumentation.

For non-EPA clients, a LCS is prepared with each preparation batch.

9.6.2 The surrogate RTs must be within the RT windows and the surrogate recovery criteria of 30-150% must be met.

9.6.3 The percent recovery for each of the compounds in the LCS must be within the following limits:

Compound	% Recovery
gamma-BHC	50-120
Heptachlor epoxide	50-150
Dieldrin	30-130
4,4'-DDF	50-150
Endrin	50-120
Endosulfan sulfate	50-120
Gamma-Chlordane	30-130

9.6.4 The technical acceptance criteria for the LCS apply independently to each column.

10.0 Calibration & Standardization

Calibration and analysis sequence specifications of the GC/ECD method apply independently to both GC columns.

10.1 Initial Calibration

10.1.1 A three-point calibration curve for single component analytes and surrogates must be generated during the initial calibration. A linear response range must be demonstrated from the Contract Required Quantitation Limits (CRQL) to a high point at least 16 times greater than the CRQL.

Single-point calibrations for multicomponent analytes are sufficient for quantitation by this method.

10.1.2 GC/ECD analysis begins with an initial demonstration of instrument performance and the calibration of all pesticides and Aroclors. Initial calibration must be repeated whenever calibration verification fails, or when major instrument maintenance is performed (new columns, detectors, etc.).

10.1.3 Standards for all tentatively identified multicomponent analytes must be run within 72 hours of the sample analysis in which they were observed. These standards are used for qualitative identification only. Quantitation is based on the standard analyzed during initial calibration.

10.2 Calibration Verification

10.2.1 An instrument blank followed by a Performance Evaluation Mixture (PEM) or an instrument blank followed by the midpoint concentration of Individual Standard Mixtures A and B are analyzed no less than once in every 12-hour analytical sequence in order to monitor retention times, calibration factors, and column performance. Data can be collected only as long as the results for these standards and instrument blanks fall within the acceptable limits.

10.3 Resolution Check Mixture

10.3.1 The resolution between two adjacent peaks in the Resolution Check Mixture is used to verify column performance. The resolution criteria MUST be met before proceeding with the initial calibration. If it is not met, perform column maintenance or replace the column.

Problem compounds are DDE and Dieldrin on the **CLPesticides** column and Endosulfan I and gamma-Chlordane on the **CLPesticides2**. It is VITAL that the operating guidelines are followed in order to meet the criteria.

10.4 Calibration Factors for Single Component Pesticides

10.4.1 The linearity of the instrument is determined by calculating a percent relative standard deviation (%RSD) of the calibration factors from a three-point calibration curve for each single component pesticide and surrogate. Either peak area or peak height may be used to calculate calibration factors used in the %RSD equation. However, it is not acceptable to use both peak area and peak height for the same compound across the three- point calibration. The calibration factors for surrogates are calculated from the three analyses of Individual Standard Mix A only.

10.4.2 Toxaphene and Aroclors require only a single-point calibration. A calibration factor is calculated for each peak in a selected set of three to five major peaks for each multicomponent analyte.

10.5 Acceptance Criteria for Chromatograms of Calibration Standards (Initial Calibrations and Calibration Verification):

10.5.1 Chromatograms for the Resolution Check Mixture, the Performance Evaluation Mixture, and Individual Standard Mixtures A and B during the initial calibration sequence must display the single component analytes at greater than 10% of full scale but less than 100% of full scale.

10.5.2 The chromatograms for at least one of the three analyses each of Individual Standard Mixtures A and B from the initial calibration sequence must display the single component analytes at greater than 50% and less than 100% of full scale.

10.5.3 Chromatograms of the standards for the multicomponent analytes analyzed during the initial calibration must display the peaks chosen for identification of each analyte at greater than 25% and less than 100% of full scale.

10.5.4 For any standard containing alpha-BHC, the baseline of the chromatogram must return to below 50% of full scale before the elution time of alpha-BHC, and return to below 25% of full scale after the elution time of alpha-BHC and before the elution time of decachlorobiphenyl.

10.5.5 If a chromatogram is re-plotted electronically to meet requirements, the scaling factor used must be displayed on the chromatogram.

Note: While the Target software does not provide a scaling factor, it does indicate intensity values.

If a chromatogram is re-plotted electronically to meet these requirements, both the initial chromatogram and the re-plotted chromatogram must be submitted in the data package.

11.0 Procedure

Documentation must follow the requirements in QC SOP: Proper Documentation Procedures.

11.1 Determination of Absolute Retention Times (RTs)

11.1.1 Absolute RTs are used for the ID of pesticides/Aroclors. The absolute RT window is calculated during initial calibration from the mean RT of the standard, as described in Section 11.0

11.1.2 During the initial calibration sequence, absolute RTs are determined for all single response pesticides, the surrogates, and at least three major peaks of each multicomponent analyte.

11.1.3 For single component pesticides, an RT is measured in each of three calibration standards, and the mean RTs calculated as the average of the three values. For

surrogates, an RT is measured from each of the three analyses of Individual Mixture A, and the mean RT is calculated as the average of the three values.

11.1.4 An RT window is calculated for each single component analyte and surrogate by using the following list. Windows are centered around the mean absolute retention time for the analyte established during the initial calibrations. Retention time windows are set as follows:

Compound	RT window(min)
alpha-BHC	±0.05
beta-BHC	±0.05
gamma-BHC	±0.05
delta-BHC	±0.05
Heptachlor	±0.05
Aldrin	±0.05
alpha-Chlordane	±0.07
gamma-Chlordane	±0.07
Heptachlor epoxide	±0.07
Dieldrin	±0.07
Endrin	±0.07
Endrin Aldehyde	±0.07
Endrin Ketone	±0.07
DDD	±0.07
DDE	±0.07
DDT	±0.07
Endosulfan I	±0.07
Endosulfan II	±0.07
Endosulfan sulfate	±0.07
Methoxychlor	±0.07
Aroclors	±0.07
Toxaphene	±0.07
TCX	±0.05
DCB	±0.10

11.1.5 For each multicomponent analyte, the RTs for three to five peaks are calculated from the initial calibration standard. A RT window of ±0.07 minutes is used for all multicomponent analyte peaks.

11.1.6 A single component pesticide is identified and confirmed as present when a peak is detected within the corresponding retention time window on each of two columns.

Toxaphene and Aroclors are identified primarily by pattern recognition, but RTs of 3 to 5 major peaks must also be taken into consideration.

11.2 GC Operating Conditions

- Carrier gas is helium for column flow of 10 ml/minute.
- Make-up gas is argon/methane (P - 5).
- Injector temperature is 225°C.
- Detector (ECD) temperature is 330°C.
- Injection volume is 1 µl per column.
- Initial oven temp is 150°C.
- Initial hold time is 1.0 to 3.0 minutes.
- Temperature ramp is 5.5° C to 8° C/minute.
- Final temperature is 275°C.
- Final hold time is 1.0 minutes.

11.3 Analytical Sequences for Standards and Samples

11.3.1 Initial Calibration (Bottles 1-17) performed as follows:

1. Resolution Check
2. Performance Evaluation Mixture
3. Aroclor 1016/1260
4. Aroclor 1221
5. Aroclor 1232
6. Aroclor 1242
7. Aroclor 1248
8. Aroclor 1254

9. Toxaphene
10. Low Point Standard A
11. Low Point Standard B
12. Midpoint Standard A
13. Midpoint Standard B
14. High Point Standard A
15. High Point Standard B
16. Instrument Blank
17. Performance Evaluation Mixture

11.3.2 After initial calibration, the analytical sequence may continue as long as acceptable instrument blanks, Performance Evaluation Mixtures, and Individual Standard Mixtures A and B are analyzed at the required frequency and meet acceptance criteria. A full sequence will looks as follows:

Time	**Bottle**	**Standards/Samples**
	1-15	Initial Calibration
0 hour	16	Instrument Blank
	17	PEM
	18	First Sample
		Subsequent Samples
12th hour		Last Sample
	1st injection past 12 hours	Instrument Blank
	2nd & 3rd injections past 12 hours	Mid INDA and INDB
		Samples
24th hour		Last Sample
	1st injection past 2nd 12 hours	Instrument Blank
	2nd injection past 24 hours	Performance Evaluation Mix
		Subsequent Samples
36th hour		Last Sample
	1st injection past 3rd 12 hours	Instrument blank
	2nd & 3rd injections past 3rd 12 hours	INDA and INDB
		Samples

Note: The sequence may continue alternating between PEMs and INDA and INDB as long as acceptance criteria are met, and represents a MINIMUM of required blanks and standards.

11.3.3 The first 12 hours are counted from injection # 16 (the instrument blank at the end of the initial calibration, and NOT from injection #1). Samples may be **injected** until 12 hours have elapsed.

11.3.4 An analytical sequence must also include all required blanks, blank spikes, matrix spikes, and matrix spike duplicates.

11.3.5 A standard for any identified multicomponent analyte in a sample must be analyzed on the same instrument within 72 hours of the sample analysis.

11.3.6 The initial calibration may continue to be used as long as the analytical system remains under control. The proof of this is provided by the PEMs. However, major corrective action, such as replacing a GC column or baking out the detector, will require a new initial calibration.

11.4 GC/ECD Analysis of Pesticides and Aroclors

11.4.1 Analysis of a sample on both GC columns is required for all samples, blanks, the LCS and any Laboratory Evaluation Sample, regardless of the presence of target analytes on the primary column. The sample must be analyzed at the most concentrated level.

11.4.2 Sample acceptance criteria apply to both GC columns. Quantitation must be performed on both columns and reported.

11.4.3 Target analytes are identified based on RTs and calibration factors established during the initial calibration, as long as acceptable calibration verification is performed every 12 hours. Pattern recognition is combined with RTs for multicomponent analytes. Sample must be bracketed by acceptable verification standards.

11.4.4 Sample Dilutions

11.4.4.1 The sample must be analyzed at the most concentrated level consistent with achieving satisfactory chromatography. If a dilution is done solely to bring a peak within the calibration range or to get a multicomponent pattern on scale, the results for both the more and the less concentrated extract must be reported.

11.4.4.2 The resulting changes in quantitation limits and surrogate recovery must be reported also for the diluted samples.

11.4.4.3 If the response **(peak area) or ng on column amount** of any single component analyte is greater than its response in the high level initial calibration standard, a dilution must be performed that produces a response for the analyte that is between the low and high level initial calibration standard.

11.4.4.4 If the largest peak for a multicomponent analyte in a sample yields **an area** response that is greater than the most intense single component analyte from the high level initial calibration standard, the sample must be diluted. The sample dilution must yield a response for the most intense multicomponent peak that falls between the mid and high level standards for that single component standard.

11.4.4.5 If an acceptable chromatogram is achieved with the diluted extract, an additional analysis 10 times the concentration of the dilute sample must be performed and reported with the sample data.

11.4.4.6 No target analyte concentrations may exceed the upper limit of the initial calibration.

11.4.5 Chromatograms

11.4.5.1 If no analytes are identified in a sample, the chromatogram of the sample must use the same scaling factor as the low point standard of the initial calibration. Since ThruPut does not have scaling factors, the intensity of the chromatograms should be similar.

11.4.5.2 Chromatograms must display single component pesticides detected in the sample at less than full scale. If an extract is diluted, chromatograms must display single component pesticides between 10 and 100 percent of full scale, or for multicomponent analytes, the largest peak between 25 and 100 percent of full scale.

11.4.5.3 For any sample, the baseline of the chromatogram must return to below 50% of full scale before the elution time of alpha-BHC, and return to below 25% of full scale after the elution time of alpha-BHC and before decachlorobiphenyl.

11.4.6 <u>Sample Flow through the GC Laboratory</u>

11.4.6.1 Samples are received in the GC Lab by GC chemists from the extractions lab with the associated extraction sheet. EPA extracts are stored at 4°C ± 2°C in GC refrigerators #2 **and #8**, and commercial extracts are stored in GC refrigerator #**4**. The extraction sheet has information pertaining to the extraction procedure (i.e., sample identification number, final volume, sample weight/volume used, lab identification number, dates, whether or not GPC was performed, etc.).

11.4.6.2 Once samples are received in the GC Lab, the chemists assume custody and become responsible for them. Water samples are loaded immediately on a GC (all GCs are equipped with an autosampler) following appropriate sequence setup. Analytical sequences are described in detail above. The samples are then analyzed.

11.4.6.3 **As they are acquired** the chemist checks each **standard**. **After sample data acquisition,** paperwork **is** generated **and** forwarded to the Data Review staff.

12.0 Data Analysis & Calculations

Calculations must be consistent with the QC SOP: Numerical Data Reduction.

12.1 Quantitation

12.1.1 Quantitation must be performed and reported on both columns.

12.1.2 Quantitative analysis of pesticides/Aroclors is accomplished by the external standard method.

12.1.3 The ECD response for all analytes must be within the three-point calibration range. If target analytes are detected at a level greater than the high calibration point, the sample must be diluted either to a maximum of 1:100,000 or until the response is within the upper half of the calibration, or linear, range.

12.1.4 If analytes are detected below the CRQL, they are reported and flagged with a "J" to indicate an estimated value.

12.1.5 Calibration factors:

$$CF = \frac{peak\ area\ (or\ height)}{mass\ injected\ (ng)}$$

12.1.6 Concentration of single component pesticides and surrogates

$$ug/L = \frac{(Ax)(Vt)(Df)}{(CF_{mp})(Vi)(Vx)}$$

where: Ax = Area of the peak in sample
CF_{mp} = Calibration factor of mid-point from the initial calibration
Vx = Volume of water extracted (ml)
Vi = Volume of extract injected in (µl)
Vt = Volume of the concentrated extract in (µl)
Df = Dilution Factor. If no dilution, DF = 1.0

12.1.7 Quantitation of toxaphene or Aroclors is done by comparing areas of each of three to five major peaks of the sample with the calibration factor for the same peaks established in the initial calibration. The concentration of each peak is determined in this way, and then an average concentration for three to five major peaks is determined and reported.

12.1.8 If more than one multicomponent analyte is observed in a sample, separate peaks must be chosen for each analyte. A peak common to both analytes must not be used to quantitate either compound. Additionally, one peak cannot be used for both a single and multicomponent analyte.

12.2 Calculation of the mean or average of a set of values:

$$\overline{X} = \frac{\sum_{i=1}^{n} X_i}{n}$$

where: n = total number of values
x_i = each individual value used to calculate the mean
x = the mean of n

12.3 Calculation of the standard deviation of a set of values:

$$Standard\ deviation = \sqrt{\frac{\sum_{i=1}^{n}(X_n - \overline{X})^2}{n-1}}$$

12.4 Calculation of percent recovery:

12.4.1 LCS and surrogates:

$$\%R = \frac{Amount\ found}{Amount\ spiked} x\ 100$$

12.5 Calculation of % RSD

$$\%RSD = \left(\frac{Standard\ deviation}{\overline{X}}\right) \times 100$$

12.6 Calculation of %Difference (%D)

$$\%Diff = \frac{Value - Reference\ value}{Reference\ value} x\ 100$$

where, value = calculated concentration
reference value = nominal value

12.7 The following equations are used to calculate breakdown:

$$\%\ Breakdown\ DDT = \frac{Amount\,(ng)\,DDD + DDE\ found}{Amount\,(ng)\,DDT\ found} x100$$

$$\%\ Breakdown\ Endrin = \frac{Amount\,(ng)\,Endrin\ Aldehyde + Endrin\ Ketone\ found}{Amount\,(ng)\,Endrin\ injected} x100$$

Combined % Breakdown = % Breakdown DDT + % Breakdown Endrin

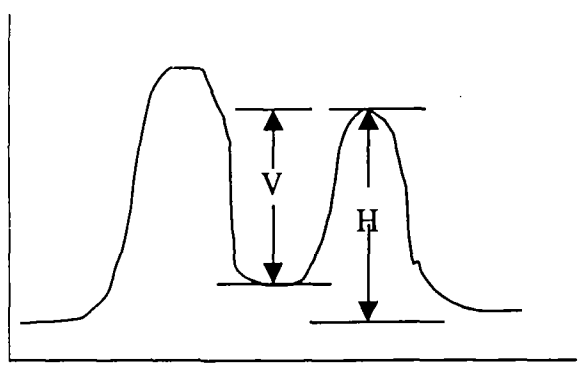
12.8 Mean Absolute Retention Time

$$\overline{RT} = \sum_{i=1}^{n} \frac{RT_i}{n}$$

where: $\overline{RT}$ = Mean absolute retention time of analyte
RT_i = Absolute retention time of analyte
n = number of measurements

12.9 Resolution Check Criteria

Calculate the resolution between the analytes in the Resolution Check Mixture, the Performance Evaluation Mixture, and the midpoint concentration of the Individual Standard Mixures A and B using the following equation.



where: x axis = time
y axis = peak area or height
V = depth of the valley between two adjacent peaks
H = height of the shorter of the two adjacent peaks

$$\text{Percent resolution} = \frac{V}{H} x \ldots 100$$

12.10 Calculating Dilutions

If a sample concentration exceeds the high level standard a dilution must be performed. Determine a level of dilution that will result in a value within the upper half of the calibration range. This is an acceptable dilution. A 10x dilution is performed using 1 µL sample plus 9 µL diluent for a total volume of 10 µL. It should be recorded on the run log as "10x (1 µL in 10 µL)."

13.0 Method Performance

This method was validated through in-house laboratory studies of method detection limits and precision and accuracy for single analyst. The data are retained by the QA department.

14.0 Pollution Prevention

The solvents used in this procedure pose little threat to the environment when recycled and managed properly. Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best thing.

15.0 Waste Management

It is the laboratory's responsibility to comply with all federal, state, and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions, and to protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Compliance with all sewage discharge permits and regulations is also required.

Samples preserved with HCl, HNO_3, or H_2SO_4 to pH <2 are hazardous and must be neutralized before being disposed, or must be handled as hazardous waste.

Refer to the Hazardous Waste Management and Safety SOPs located in the lab.

16.0 References

16.1 USEPA SOW for Organics Analysis, Low Concentration Water, **2/96** (Document No. OLC02.1 plus revisions)

16.2 Standard Methods for the Examination of Water and Wastewater, 18th Edition (1992) and 19th Edition (1995), upon promulgation, Method 1080

16.3 New York State Analytical Services Protocol (NYSASP), 10/95

16.4 QCSOP: Proper Documentation Procedures

16.5 QCSOP: Numerical Data Reduction

16.6 "Less is Better: Laboratory Chemical Management for Waste Reduction," American Chemical Society Department of Government Relations and Science Policy, 1155 16th Street, N.W., Washington DC, 20036, (202) 872-4477.

16.7 Hazardous Waste Management & Safety SOPs: "Hazardous Waste Disposal" and "Spill Control & Cleanup."

16.8 NELAC Standards, July 1, 1999, plus revisions

16.9 QA-G6: Guidance for the Preparation of Standard Operating Procedures for Quality-Related Operations EPA/600/R-96/027, November 1995.

16.10 New York State Environmental Laboratory Approval Program, Certification Manual, October 15, 1999, plus revisions.

16.11 CompuChem Quality Manual, Revision 0, 2/1/00

16.12 Sample Control SOP 4.1, "Receiving Samples"

16.13 Sample Control SOP 4.6, "Storing Samples"

16.14 Sample Preparation Procedure –737 (-1072→-938), "Water Preparation for Low Concentration Pesticides/PCBs

17.0 Attachments as Tables, Diagrams, Flowcharts & Validation Data

17.2 Attachment 1 - List of target compounds and CRQLs

Attachment 1

Exhibit C -- Section 3
Pesticides/Aroclors (PEST/ARO)

TARGET COMPOUND LIST (TCL) AND
CONTRACT REQUIRED QUANTITATION LIMITS
(CONT'D.)

	Pesticides/PCBs	CAS Number	Quantitation Limits Water ug/L
1.	alpha-BHC	319-84-6	0.01
2.	beta-BHC	319-85-7	0.01
3.	delta-BHC	319-86-8	0.01
4.	gamma-BHC (Lindane)	58-89-9	0.01
5.	Heptachlor	76-44-8	0.01
6.	Aldrin	309-00-2	0.01
7.	Heptachlor epoxide[1]	1024-57-3	0.01
8.	Endosulfan I	959-98-8	0.01
9.	Dieldrin	60-57-1	0.02
10.	4,4'-DDE	72-55-9	0.02
11.	Endrin	72-20-8	0.02
12.	Endosulfan II	33213-65-9	0.02
13.	4,4'-DDD	72-54-8	0.02
14.	Endosulfan sulfate	1031-07-8	0.02
15.	4,4'-DDT	50-29-3	0.02
16.	Methoxychlor	72-43-5	0.10
17.	Endrin ketone	53494-70-5	0.02
18.	Endrin aldehyde	7421-93-4	0.02
19.	alpha-Chlordane	5103-71-9	0.01
20.	gamma-Chlordane	5103-74-2	0.01
21.	Toxaphene	8001-35-2	1.0
22.	Aroclor-1016	12674-11-2	0.20
23.	Aroclor-1221	11104-28-2	0.40
24.	Aroclor-1232	11141-16-5	0.20
25.	Aroclor-1242	53469-21-9	0.20
26.	Aroclor-1248	12672-29-6	0.20
27.	Aroclor-1254	11097-69-1	0.20
28.	Aroclor-1260	11096-82-5	0.20

[1]Only the exo-epoxy isomer (Isomer B) of heptachlor epoxide is reported on data reporting forms (Exhibit B).

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SOP DOCUMENTATION FORM

This form must accompany all new and revised Standard Operating Procedures (SOPs) when you turn them in to Quality Assurance for review. Please fill out the entire shaded area (except effective date).

This is a new procedure ____ revised procedure ✓ outdated procedure (archive) ____

- Procedure area, title, and SOP number: Section # 2.3.2.1.6 Effective date: (QA fills in)

Instrument Procedure 309 11/7/00

Inductively Coupled Plasma Atomic Emission Spectroscopy by SW846

- Procedure prepared by: Date:

Linda Costa 11/3/00

- Procedure approved by: (If the manager prepared the SOP a qualified second party should sign) Date:

Bob Nieves 11/4/00

- Reason for change: Correct grade of acid used

- This procedure meets the requirements of the following approved method references:

Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, Update III, 3rd Edition, 12/96, Method 6010B; New York State Analytical Services Protocol, NYSASP, 10/95

Procedure approved by Quality Assurance Representative: Date:
(Not needed if signed above)

_____ _____

Effective 1-1-96, on an annual basis: Lab managers are required to review lab practices and revise the SOP if necessary. If no revision is necessary, indicate by your signature that the SOP has been reviewed.

Annual Review—Signature: _____ Date: _____

Annual Review—Signature: _____ Date: _____

Annual Review—Signature: _____ Date: _____

Instrument Procedure 309: Inductively Coupled Plasma Atomic Emission Spectroscopy by SW-846

1.0 Scope and Application

1.1 Inductively coupled plasma/atomic emission spectroscopy (ICP/AES) is used in the determination of elements, including metals, in solution. The method is applicable to a large number of metals and wastes. All matrices, including groundwater, aqueous samples, EP extracts, industrial wastes, soils, sludges, sediments, and other solid wastes, require digestion prior to analysis.

1.2 Method 6010B is applicable to the elements listed in Attachment 1 for Trace ICP P3 and Attachment 2 for Trace ICP P4. Detection limits, sensitivity, and optimum ranges of the metals will vary with the matrices and model of spectrometer. The data shown in Table 1 provide concentration ranges for clean aqueous samples.

1.3 Current method detection limit (MDL) studies and reporting limits are shown in Attachment 3.

1.4 Staff members performing the procedures described in this SOP are responsible for reading, understanding, and complying with the SOP requirements. Supervisors are responsible for directing the analyst to the controlled SOP, and providing adequate explanation of the material contained therein.

1.5 This procedure is restricted to use by or under the supervision of analysts experienced in the instrumentation or preparative methods and who have demonstrated the ability to generate acceptable results through QC samples and analyst capability studies. Use of this method is restricted to spectroscopists who are knowledgeable in the correction of spectral, chemical, and physical interferences.

2.0 Summary of Method

2.1 Prior to analysis, samples must be solubilized or digested using appropriate sample preparation methods (e.g., Methods 3005A or 3010A for water or 3050B for soil).

2.2 Method 6010B is executed by the laboratory using the simultaneous, multielemental determination of elements by ICP. The method measures element-emitted light by optical spectrometry. Samples are nebulized and the resulting aerosol is transported to the plasma torch. Element-specific atomic-line emission spectra are produced by a radio-frequency inductively coupled plasma. The spectra are dispersed by a grating spectrometer, and the intensities of the lines are monitored by photomultiplier tubes. Background correction is required for trace element determination. Background must be measured adjacent to analyte lines on samples during analysis. The position selected for the background-intensity measurement, on either or both sides of the

analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used must be free of spectral interference and reflect the same change in background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result. The possibility of additional interferences named in Section 3.0 should also be recognized and appropriate corrections made.

*The wavelength listed are recommended because of their sensitivity and overall acceptance. Other wavelengths may be substituted if they can provide the needed sensitivity and are treated with the same corrective techniques for spectral interference (see Paragraph 3.1). In time, other elements may be added as more information becomes available and as required.

**The instrumental detection limits shown are taken from the Quarterly IDL study performed for the 2nd quarter 1999. They are given as a guide for an instrumental limit. The actual method detection limits are sample dependent and may vary as the sample matrix varies. Quarterly detection limit studies are performed by CompuChem.

3.0 Definitions

3.1 Method detection limit (MDL) – The minimum concentration of an analyte that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte (40 CFR, Part 136, Appendix B.)

3.2 Reporting Limit – The laboratory reporting limit is based on the lowest multipoint calibration standard concentration. For some inorganic methods, the reporting limit is based on the MDL, and is usually 4-8 times higher than the MDL. For organic methods, values detected below the reporting limit and above the MDL may be reported and qualified as an estimated concentration.

If the low level standard concentration is not at least three times higher than the MDL value, the standard concentration is adjusted upward in order to achieve this minimal ratio. It may be adjusted higher than three times depending on the concentration range of the calibration curve and the ability to meet method linearity requirements. An exception to this is for CLP methods where the MDL is only required to be lower than the reporting limit.

For CLP the reporting limit is the Contract Required Quantitation Limit (CRQL) for organics and the Contract Required Detection Limit (CRDL) for inorganics.

3.3 Reporting Units – µg/L for water and mg/Kg for soil

3.4 An SDG is defined by the following, whichever is more frequent:

- each 20 field samples received within a case, or
- each 14 calendar day period during which field samples in a case are received (7 calendar days for NYSASP, OLM04.0, plus revisions, and ILM04.0, plus revisions including ILM04.1) beginning with the receipt of the first sample.

NOTE: The Army Corps of Engineers does not accept the SDG approach, unless the samples are prepared in a single batch. When a group of up to 20 field samples of a similar matrix are prepared as one batch, method-specified QC samples such as a method blank, laboratory control sample, matrix spike, matrix spike duplicate, and matrix duplicate must also be prepared together at a rate of 5%. If samples are batched together from different sites, project-specific QC must be processed.

4.0 Interferences

4.1 Spectral Interferences are caused by: (1) overlap of a spectral line from another element; (2) unresolved overlap of molecular band spectra; (3) background contribution from continuous or recombination phenomena; and (4) stray light from the line emission of high-concentration elements. Spectral overlap can be compensated for by computerized correction of the raw data after monitoring and measuring the interfering element. Unresolved overlap requires selection of an alternate wavelength. Background contribution and stray light can usually be compensated for by a background correction adjacent to the analyte line.

Users of simultaneous multi-element instruments must verify the absence of spectral interference from an element in a sample for which there is no instrument detection channel. Potential spectral interferences for the recommended wavelengths are given in Table 4. The data in Table 4 are intended as rudimentary guides for indicating potential interferences; for this purpose, linear relations between concentration and intensity for the analytes and the interferents can be assumed.

4.1.1 The interference is expressed as analyte concentration equivalents (i.e., false analyte concentrations) arising from 100 mg/l of determined As (at 193,696 nm) in a sample containing approximately 10 mg/l of Al. According to Table 3, 100 mg/l of Al would yield a false signal for As equivalent to approximately 1.3 mg/l. Therefore, the presence of 10 mg/l of Al would result in a false signal for As equivalent to approximately 0.13 mg/l. The user is cautioned that other instruments may exhibit somewhat different effects and must be evaluated individually since the intensities will vary with operating conditions, power, viewing height, argon flow rate, etc.

4.1.2 The dashes in Table 3 indicate that no measurable interferences were observed even at higher interferent concentrations. Generally, interferences were discernible if they produced peaks, or background shifts, corresponding to 2 to 5% of the peaks generated by the analyte concentrations.

4.1.3 At present, information on the listed silver and potassium wavelengths is not available, but it has been reported that second-order energy from the magnesium 393.231 nm wavelength interferes with the listed potassium line at 766.491 nm.

4.2 Physical Interferences are effects associated with the sample nebulization and transport processes. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples containing high dissolved solids or high acid concentrations. If physical interferences are present, they must be reduced by diluting the sample, by using a peristaltic pump or by using the standard additions method. Another problem that can occur with high dissolved solids is salt buildup at the tip of the nebulizer, which affects aerosol flow rate and causes instrumental drift. The problem can be controlled by wetting the argon using a tip washer prior to nebulization or by diluting the sample. Also, it has been reported that better control of the argon flow rate improves instrument performance; this is accomplished with the use of mass flow controllers.

4.3 Chemical Interferences include molecular compound formation, ionization effects, and solute vaporization effects. Normally, these effects are not significant with the ICP technique. If observed, they can be minimized by careful selection of operating conditions (incident power, observation position, and so forth), by buffering of the sample, by matrix matching, and by standard addition procedures. Chemical interferences are highly dependent on matrix type and the specific analyte element.

4.4 The Thermo Jarrell Ash ICAP 61E Trace Analyzer uses yttrium as an internal standard and takes into account any interference by ratioing the elements detected against the yttrium detected. All standards, blanks, and samples are spiked with yttrium.

5.0 Safety

Appropriate protective equipment and clothing must be used under the assumption that all samples are potentially hazardous. Safety glasses, gloves and lab coats are a minimum requirement. The persistent presence of noxious odors may be indicative of failure of the laboratory ventilation system and must be reported to a supervisor or manager.

Laboratory staff are encouraged to review the Chemical Hygiene Plan for general safety policies, and Material Safety Data Sheets for reagents used in the laboratory.

6.0 Equipment & Supplies

6.1 Inductively coupled argon plasma emission spectrometer

6.1.1 Computer-controlled emission spectrometer with background correction

6.1.2 Radio frequency generator

6.1.3 Argon gas supply: Welding grade or better

6.2 Operating conditions

6.2.1 The analyst should follow the instructions provided by the instrument manufacturer.

6.2.2 For operation with organic solvents, use of the auxiliary argon inlet, solvent-resistant tubing, increased plasma (coolant) argon flow, decreased nebulizer flow, and increased RF power (to obtain stable operation and precise dynamic range) are recommended. Interference effects must be established for each individual analyte line on that particular instrument.

6.2.3 All measurements must be within instrument linear range where coordination factors are valid. The analyst must

- verify that the instrument configuration and operating conditions satisfy the analytical requirements
- maintain quality control data confirming instrument performance and analytical results

7.0 Reagents & Standards

Refer to the Standards/QC Preparation for Trace ICP logbook (Attachment 5) for details of all standard preparations. Label each standard bottle with the lot number as described in the logbook.

7.1 Reagent Water-All water used during preparation should be reagent-grade Type I with regard to resistivity of > 10 megohm-cm (18th and 19th Editions of Standard Methods, Method 1080), and referred throughout this SOP as DI water.

7.2 Use only high-purity grade acids such as J.T. Baker Instra-Analyzed **or EM High Purity** in the preparation. **The same grade/purity of acids is to be used for all sample preparation, calibration standards, blanks, and QC samples.**

7.2.1 Concentrated hydrochloric acid (HCl).

7.2.2 Concentrated nitric acid (HNO_3)

7.3 Stock standard solutions

Use commercially available (e.g., "Spex") Metals Standards as stock solutions (e.g., XCL-11, XCL-2, XCL-3A, and PLSB2-2X).

Note: Prepare calibration standards weekly. Calibration standards must be verified using an EPA Quality Control sample immediately after instrument calibration (ICV).

7.4 Instrument Check Standards

7.4.1 Prepare calibration blanks using the same acid volumes as used for calibration standards, i.e. 5% HCl and 6% HNO_3.

7.4.2 Prepare and analyze interference check samples (ICSA/ICSAB) to check for spectral interferences.

7.4.3 Analyze a Low Range Standard (LRS), which is at the level of the reporting limit, after the CCB 1.

7.5 Internal Standard

7.5.1 For the TJA 61E Trace analyzer, yttrium is introduced into the sample injection system as an internal standard. See the Standards/QC Preparation for Trace ICP logbook for instructions on making the yttrium internal standard.

8.0 Sample Collection, Preservation, & Storage

8.1 Samples are collected, preserved, and stored according to the tables in Sample Control SOP 4.1, "Receiving Samples" and 4.6, "Storing Samples." Sample holding times are also listed.

8.2 All samples must be preserved to a pH <2 with HNO_3 and digested and analyzed within 180 days of collection.

8.3 Soil samples must be stored under refrigeration at 2-4.4° C.

8.4 After preparation, the raw sample is returned to the sample custodian for long-term storage and disposal. After analysis residual digestate is disposed of the in the acid waste stream.

9.0 Quality Control

9.1 Initial Calibration Verification (ICV)

9.1.1 Use the following solutions are used to verify the calibration.

- ICV1 (Al, Ba, Be, Cd, Ca, Cr, Co, Cu, Fe, Mg, Mn, Ni, K, Na, V, and Zn)
- ICV3 Sb (As, Se, Pb, Ag, and Tl)
- SPEXASSE (Non-CLP analytes)= Sn, Bi, Ti, Mo, additional elements if requested per client
- Initial Calibration Blank= (ICB)

9.1.2 The results of the initial calibration verification must agree within 10% of the "true" value for each component. If not, the run must be terminated and the instrument re-calibrated. If the re-calibration does not produce acceptable ICV results, shut down the instrument and request instrument service.

9.1.3 Follow the ICV with the ICB. The laboratory will deviate from the method for calibration blank acceptance criteria by substituting the following: The absolute value of the blank must be less than the statistically-determined laboratory reporting limit (PQL). If not, repeat the blank analysis, and if still above the limit terminate the analysis and recalibrate. If re-calibration does not produce acceptable ICB results, shut down the instrument and request instrument service.

9.2 Continuing Calibration Verification Analysis

9.2.1 Verify the calibration every 10 samples and at the end of analytical run.

9.2.2 The results of the check standard must agree within ±10% of the true value. If not, terminate the analysis, correct the problem, and recalibrate the instrument.

9.3 Continuing Calibration Blank Analysis

9.3.1 A calibration blank must be analyzed at each wavelength used for analysis immediately after every initial and continuing calibration verification at a frequency of 10% or every 2 hours during the run, whichever is more frequent.

9.3.2 The laboratory will deviate from the method for calibration blank acceptance criteria by substituting the following: The absolute value of the blank must be less than the statistically-determined laboratory reporting limit (PQL). If not, repeat the blank analysis and if still above the limit, terminate the analysis, correct the problem, and recalibrate the instrument.

9.4 Interference Check Sample

9.4.1 Analyze the standard reference solutions obtained from EPA or NIST. Determine that the measured values agree with the certified values. If so, proceed with the analysis of the Interference Check Sample (ICSA/ICSAB). If not, prepare fresh standards and recalibrate.

9.4.2 Analyze the Interference Check Samples at the beginning and the end of each 8-hour shift.

9.4.3 The ICS must agree within +/-20% of the accepted values. If not terminate the analysis and recalibrate the instrument. If re-calibration does not fix the problem, shut down the instrument and request instrument service.

9.5 Low Range Standard (LRS)

9.5.1 Analyze a standard at the reporting limit. This reporting limit standard is used to verify linearity and the ability to detect low levels reliably. The criteria for this standard is +/- 50%.

9.6 Method Blank Analysis

9.6.1 For each digestion batch of up to 20 samples, a method reagent blank is prepared. This blank is used to ascertain whether sample concentrations reflect contamination.

9.6.2 The blank must contain absolute values of analyte concentrations below the reporting limit (PQL). If the blank exceeds the reporting limit, the entire sample batch must be re-prepared along with a new method blank.

If the concentration of any analyte detected in the blank falls between the PQL and IDL, flag the corresponding blank element, if present in any associated samples, with a "B" and report the data with a discussion in the SDG narrative.

9.7 Spiked Sample Analysis

9.7.1 One matrix spike/matrix spike duplicate (MS/MSD) pair must be prepared with each sample delivery group of up to 20 samples.

9.7.2 If the sample spikes do not meet the acceptance criteria of 75-125% recovery, the corresponding element is flagged with an "N" on the Form 1 to indicate that the element did not recover in the matrix spike acceptably. (See Table 3 for spiking levels.) A post-digestion spike is performed for those elements that fall outside the limit.

9.7.3 Post Digestion Spike (PDS)

9.7.3.1 Prepare and analyze a PDS, if necessary. The spike addition should result in a value that is 2x the PQL or 2x the indigenous level, whichever is greater. The PDS levels should be noted on run log.

9.7.3.2 The PDS results should be within 75% to 125%. If not, the data are reported and discussed in the SDG narrative.

No further action is taken at the bench since the internal standard, yttrium, is employed. The instrument uses the element intensity as an internal standard to ratio the analyte intensity signals for both calibration and quantitation. This technique is very useful in overcoming matrix interference, especially in high solids matrices.

9.8 Duplicate Sample Analysis

9.8.1 One duplicate sample should be performed for each sample delivery group of up to 20 samples. NC DENR requires a duplicate to be performed at the rate of 10%, and this is satisfied with the use of the MS/MSD and sample duplicate.

9.8.2 If the sample and duplicate do not agree within 20% RPD when the concentration is greater than 10x the IDL, then the affected element is flagged with an "*" to indicate poor duplication of results.

9.9 Laboratory Control Sample (LCS)

9.9.1 A matrix-specific Laboratory Control Sample is prepared with every digestion batch of up to 20 samples.

9.9.2 The vendor supplies the certified acceptance limits for the solid LCS. If the LCS falls outside these control limits, the analysis must be terminated, the problem corrected, and the samples associated with that LCS re-digested and reanalyzed.

9.10 Serial Dilution

9.10.1 One serial dilution must be performed for each sample delivery group of up to 20 samples.

9.10.2 Perform a 5x serial dilution on the sample to determine if a chemical or physical interference exists. If the analyte concentration is 50 times or more above the instrument detection limit in the original sample, the serial dilution

must then agree within 10%. If not then flag the appropriate elements with an "E" to indicate that an interference exists.

9.11 Field and/or Equipment Blanks

9.11.1 Samples identified as field and/or equipment blanks should not be used for sample spike, duplicate, or serial dilution analysis. They are supplied to the laboratory at the discretion of the client.

10.0 Calibration & Standardization

10.1 The instrument calibration standards are analyzed at the beginning of the analytical sequence, in the order shown in the Trace ICP Runlog (Attachment 6), and must meet acceptance criteria before samples can be analyzed. Calibration is further discussed in the Procedure section that follows.

10.2 The ICV must meet criteria to verify the curve before proceeding with sample analysis.

11.0 Procedure

Documentation must follow the requirements in QC SOP: Proper Documentation Procedures.

11.1 TJA 61E Trace Analyzer Set Up and Operating Procedure

11.1.1 Cooling Water

11.1.1.1 Turn on the recirculation pump. Thirty (30) psig is required at a flow rate of 700 ml/min.

11.1.2 Argon Supply

11.1.2.1 Open the argon supply to the instrument.

11.1.2.2 A volume rate of 30 SCFH and delivery pressure of 60 psig is required.

11.1.3 Venting System

11.1.3.1 A permanent vent has been installed to provide a proper draft in the torch compartment. A torch fan is permanently installed to force a 22 mph-draft across the end of the plasma torch.

11.1.4 Water in Drain Barrel

11.1.4.1 A hose is connected to the drain outlet from the spray chamber to allow the flow of unused sample waste from the chamber. This drain line acts as a positive seal to the spray chamber; therefore, liquid must always be present in the drain line.

11.2 Power Up (TJA 61E Trace Analyzer)

11.2.1 To start the ICP 61E Trace Analyzer, turn on the video display, the printer, the computer**, and the autosampler**.

11.2.2 At the "C" **prompt**, Type "P" and press "ENTER." This will start the Thermospec™ software and bring up the main menu.

11.2.3 To start the RF generator and the plasma torch, select "SETUP." Then select "PLASMA CONTROL PANEL" and press "ENTER." Select "F1."

11.2.4 The default startup time, during which argon purges the spray chamber and the plasma torch, is 90 seconds. The purge time can be reduced to as little as 20 seconds by pressing "PURGE TIME" if the plasma has been off for less than 15 minutes.

11.2.5 After the purge time and power have been set, the automated plasma startup sequence is initiated by pressing "CONTINUE."

11.2.6 If the pump and gas have not been started, select "F2" and start the pump rate at **99** RPM and switch the nebul**izer** gas to "ON."

11.2.7 The total flush time and rinse time between samples is set at 60 seconds.

11.2.8 Press "LEVELS" if you want to change any of the plasma operating conditions.

11.2.9 The plasma torch should be allowed to run for at least 30 minutes after ignition to reach optimum stability.

11.2 Analysis

11.2.1 Profile

11.2.1.1 Profiling the instrument assures that the optical pathway is clean and in alignment. Emission intensities are essential to accurate data.

11.2.1.2 At the THERMOSPEC main menu, select setup and highlight profile then enter.

11.2.1.3 Begin aspirating 1ppm As standard for analysis.

11.2.1.4 Press F3 to Automatic Profile. When the sample is sufficiently saturating the spray chamber and torch (60 seconds), press "F1", "RUN".

At the end of the integration, a peak graph will be displayed. Note the intensity reading. This will indicate a need to clean the optical path or adjust the alignment.

Also note the peak position on the graph. This value should be between 0.1 and –0.1. If it is not, the spectrum shifter must be adjusted, and the profile rerun. Continue this process until the peak position is acceptable.

11.2.1.5 Discontinue the arsenic when profiling is complete. Exit profile to the main menu.

11.3 Autosampler Table Setup

11.3.1 Obtain all data necessary from each case that will be set up on the run, i.e. preparation logs, log-in chain of custody reports from the LIMS (Attachment 7). The information contained on these sheets will be used to create the autosampler table.

11.3.2 From the main menu of Thermospec, select "OPERATION," and then "Autosampler Setup," then press enter. The software will prompt for an autosampler table name. An existing table can be edited from this point, or a new autosampler table name can be typed in at this point. Press enter. Press F3 "Add Set." Enter the appropriate run parameters to be used. Parameters that should always be entered here are Method Name, Rinse Time (60 seconds), # of Unknowns in this set, Default Limit Check Table Name (Sample). Press the F1 "EdSamples" key. This will allow for sample IDs to be entered.

11.3.3 Under the column titled "Sample Name," enter the CompuChem sample ID. Be certain the proper check table is selected for each analysis that is assigned. The "F" key allow for various modifications to the autosampler table. Use these keys as necessary. It is **very important** that the proper QC samples be inserted into the table at the necessary frequencies. See section 9.0 for a description of necessary QC and frequencies.

11.3.4 Also, if the "Alt" key on the keyboard is pressed, additional options will appear. One of these options is "EdSampInfo." This option is selected by

pressing the "Alt" key and the "F2" key simultaneously. From this screen, additional comments can be added that will appear on the raw data printout. Under the column titled "Comment," the SDG, client sample ID and dilution of the sample should be entered.

11.3.5 When all entries are finished, press the "F9," Done/Keep key to save the table. It is important to remember the name of the table created, as this will be used to start the analysis.

11.3.6 Create a configuration file to store all analytical data. From the main menu of THERMOSPEC select "SETUP" and highlight "CONFIGURATION." Press "Enter" twice then "F9" four times. This will provide the screen to enter the configuration file name. Configuration file names should identify the analyst and the date of the analysis, as well as the instrument being used (P3 or P4). Use the following scheme (iimmdd) to construct the file name. The letter "i" for initials, the "m" for the month, and the letter "d" for the day. If there are more runs in a day, letters of the alphabet are used as a suffix. In this example: P3JCQ922B, identifies a third run on September 22 by analyst JC on instrument P3. JUNK files should be used between analyses to prevent files from being corrupted with other data.

11.3.7 Proceed to analysis. From the main menu of THERMOSPEC select "OPERATION." Highlight "ANALYSIS" then "Enter." Confirm that the correct method is being used and select the autosampler table to be used. Continue to follow on-screen instructions to initiate the run.

IMPORTANT: If the run should fail at any time, remember to change the configuration file name before restarting the analytical run.

11.4 Standardization and Analysis

11.4.1 Start autosampler table and follow the instructions.

11.4.1.1 Select "Operation" and highlight "Analysis."

11.4.1.2 Enter the correct method of analysis and select the autosampler table for samples to be analyzed.

11.4.2 Solid samples and liquid samples have different matrices due to sample preparation procedures. Calibration standards and quality control standards should be prepared to match the matrix of the samples being analyzed. While constructing autosampler tables, give consideration to the matrix of the samples.

11.4.3 Fill all standards cups and QC cups with the appropriate solutions following the sequence hardcoded on the Trace ICP Run Log (Attachment 6.) The autosampler table provides the information for cup positions. Standards cups positioning may change depending on the number of samples.

Caution: Accuracy of the sequence setup is extremely important. Improper cup positioning will seriously affect analysis to the point that there may not be any salvageable data.

11.4.4 Press "F1" to begin the analytical run.

Caution: Sample racks should be loaded accurately following the rows and positions provided by the autosampler table. Samples in the wrong position can produce erroneous data that may not be detectable.

11.4.5 Although, software drives the instrument operation, the instrument should not be left completely unattended. In the course of the run, matrix spike analyses must be evaluated to determine percent recoveries. Some samples will have concentrations of analytes that are beyond the established linear ranges and will need to be diluted and reanalyzed within those ranges. Serial dilution analyses should be evaluated for proper dilution. Responding to the need for dilutions or a PDS analysis quickly within the same analytical run saves time by not requiring an additional run and improves productivity.

11.4.6 Attention should be given to the QC analyses. Analytes may be found to be outside of their established control limits. The loss of one or more analytes does not necessarily mean the run has ended. Early detection of failed analytes by the analyst will prevent lost time and productivity.

11.4.7 Standards cups have limited capacity and should be filled frequently and monitored at all times.

11.4.8 The sequence includes an ICSA and ICSAB analyses performed every 20 analytical sample. The structure of the autosampler table must incorporate this requirement. LRS, ICSA and ICSAB are numbered with the analytical samples. If this maximum is exceeded, the run has ended and all data that does not comply is lost. The ICSA and ICSAB must immediately be followed by a CCV/CCB.

Based on client-specific project requirements, additional QC may be run. An example is the CRI standard that is required by the CLP.

11.4.9 The analytical run is not complete until all final paperwork is complete. The runlog must be completed by the analyst and the QC/Standards Preparation

log completed for the day, as well as completing the internal chain of custody form.

11.5 Transferring Data

11.5.1 At the completion of the analytical run, exit analysis and return to the THERMOSPEC main menu. Change the configuration file name.

11.5.2 Exit THERMOSPEC **and return to Desktop. Double-click on the Explorer icon. While in Explorer, open the STATION directory in the left column, and then open the BIN directory. In the right column, find the name of the file from the analytical run that was just finished. Next, find the MARRS directory in the left column and open that directory. Click on the file name in the right column and copy it to the appropriate directory in MARRS (P3 ICP Trace Files or P4 ICP Trace Files.) Explorer can then be closed.**

11.5.3 Transfer the file to the computer used to run the SQUEEZE program. The squeeze function combines two pages of data onto one page. Type "SQZ61E" and follow the instructions to squeeze the data file, and then print the .SQZ file.

11.6 Instrument Shutdown

11.6.1 TJA 61E Trace Analyzer (P3)

11.6.1.1 Aspirate **DI** water for approximately one minute.

11.6.1.2 From the MAIN MENU go to SETUP and PLASMA CONTROL PANEL and press enter.

11.6.1.3 Press F7 for PLASMA SHUT off.

11.6.1.4 Remove pump tubing from peristaltic pumps.

12.0 Data Analysis & Calculations

Calculations must be consistent with the QC SOP: Numerical Data Reduction.

12.1 Calculation of the mean or average of a set of values:

$$\overline{X} = \frac{\sum_{i=1}^{n} X_i}{n}$$

where: n = total number of values
x_i = each individual value used to calculate the mean
x = the mean of n

12.2 Calculation of the standard deviation of a set of values:

$$Standard\ deviation = \sqrt{\frac{\sum_{i=1}^{n}\left(X_n - \overline{X}\right)^2}{n-1}}$$

12.3 Calculation of percent recovery:

12.3.1 LCS and surrogates:

$$\%R = \frac{Amount\ found}{Amount\ spiked} x\ 100$$

12.3.2 Matrix spikes:

$$\%\,R = \frac{Amount\ in\ spiked\ sample - Amount\ in\ unspiked\ (native)\ sample}{Amount\ spiked} x\ 100$$

12.4 Calculation of % RSD

$$\%RSD = \left(\frac{Standard\ deviation}{\overline{X}}\right) \times 100$$

12.5 Calculation of RPD

$$RPD = \frac{|Value\ 1\ -\ Value\ 2|}{(Value\ 1\ +\ Value\ 2)/2} x100$$

12.6 Calculation of %Difference (%D)

$$\%Diff = \frac{Value\ -\ \overline{Reference\ \ value}}{\overline{Reference\ \ value}} x\ 100$$

12.7 Calculating Dilutions

If a sample concentration exceeds the high level standard a dilution must be performed. Determine a level of dilution that will result in a value within the upper half of the calibration range. This is an acceptable dilution. A 10x dilution is performed using 1 mL sample plus 9 mL diluent for a total volume of 10 mL. It should be recorded on the run log as "10x (1 mL in 10 mL)."

12.8 Concentration

12.8.1 All results for aqueous samples are reported in ug/l as follows.

$$\text{Concentration } (\mu g/L) = \frac{C \times V \times D}{W}$$

Where: C = Concentration (µg/L) from curve
V = Final volume of digestate (L)
W = Volume of sample (L)
D = Dilution factor

12.8.2 All results for solid samples are reported in mg/kg as follows.

12.8.2.1 A separate determination of percent solids must be performed.

12.8.2.2 The concentration determined in the digestate are to be reported on the basis of the dry weight of the sample.

Concentration (mg/kg) = C * V / W * S

Where: C = Concentration (ug/L)
V = Final volume of digestate (L)
W = Weight of wet sample (gm)
S = % Solid / 100
D = Dilution factor

13.0 Method Performance

This method was validated through in-house laboratory studies of method detection limits (Attachment 3) and precision and accuracy for single analyst (Attachment 8). The data are retained by the QA department.

14.0 Pollution Prevention

The solvents used in this procedure pose little threat to the environment when recycled and managed properly. Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best thing.

15.0 Waste Management

It is the laboratory's responsibility to comply with all federal, state, and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions, and to protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Compliance with all sewage discharge permits and regulations is also required.

Samples preserved with HCl, HNO_3, or H_2SO_4 to pH <2 are hazardous and must be neutralized before being disposed, or must be handled as hazardous waste.

Refer to the Hazardous Waste Management and Safety SOPs located in the lab.

16.0 References

16.1 "Test Methods for Evaluating Solid Wastes: Physical/Chemical Methods", SW846, 3rd Edition, Update III, 12/96, Method 6010B

16.2 Standard Methods for the Examination of Water and Wastewater, 18th Edition (1992) and 19th Edition (1995), upon promulgation, Method 1080

16.3 Code of Federal Register, 40 CFR, Part 136, "Guidelines for Establishing Test Procedures for Priority Pollutants"

16.4 New York State Analytical Services Protocol (NYSASP), 10/95

16.5 QCSOP: Proper Documentation Procedures

16.6 QCSOP: Numerical Data Reduction

16.7 "Less is Better: Laboratory Chemical Management for Waste Reduction," American Chemical Society Department of Government Relations and Science Policy, 1155 16th Street, N.W., Washington DC, 20036, (202) 872-4477.

16.8 Hazardous Waste Management & Safety SOPs: "Hazardous Waste Disposal" and "Spill Control & Cleanup."

16.9 NELAC Standards, July 1, 1999, plus revisions

16.10 QA-G6: Guidance for the Preparation of Standard Operating Procedures for Quality-Related Operations EPA/600/R-96/027, November 1995.

16.11 New York State Environmental Laboratory Approval Program, Certification Manual, October 15, 1999, plus revisions.

16.12 CompuChem Quality Manual, Revision 0, 2/1/00

16.13 Sample Control SOP 4.1, "Receiving Samples"

16.14 Sample Control SOP 4.6, "Storing Samples"

16.15 Code of Federal Register, 40 CFR, Part 136, "Guidelines for Establishing Test Procedures for Priority Pollutants"

16.16 TJA 61E Trace Analyzer and TJA Analyzer 61E Set-up and Operating Manual

17.0 Attachments as Tables, Diagrams, Flowcharts & Validation Data

17.1 Attachment 1 – **Wavelength and Estimated Instrumental Detection Limits on Instrument Numbers P3, Trace ICP, 2nd Quarter, 2000**

17.2 Attachment 2 – **Wavelength and Estimated Instrumental Detection Limits on Instrument Numbers P4, Trace ICP, 2nd Quarter, 2000**

17.3 Attachment 3 – Method Detection Limit (MDL) Study

17.4 Attachment 4 - Analyte Concentration Equivalents Arising from Interference at the 100-mg/l Level

17.5 Attachment 5 - Standards/QC Preparation for Trace ICP logbook

17.6 Attachment 6 – Trace ICP Run Log (P3) (An identical logbook exists for P4, Log book ID 1 O (7)

17.7 Attachment 7 – Internal Chain of Custody

17.8 Attachment 8 – Single Analyst Capability Study

Attachment 1: Wavelength and Estimated Instrumental Detection Limits on Instrument Numbers P3, Trace ICP, 2nd Quarter, 2000

Elements	Wavelength* (nm)	Instrument Detection Limits** (ug/L)	Instrument Detection Limits (ug/L) NYSASP
Aluminum	308.215	37.0	33.0
Antimony	206.831/206.832	2.1	2.6
Arsenic	189.042	2.3	2.5
Barium	493.409	0.1	0.1
Beryllium	313.042	0.2	0.2
Bismuth	223.061	3.6	5.2
Cadmium	226.502	0.2	0.2
Calcium	317.933	10.9	22.5
Chromium	267.716	0.4	0.4
Cobalt	228.616	0.5	0.5
Copper	324.753	0.6	2.1
Iron	271.441	14.3	17.7
Lead	220.351/220.352	1.3	1.5
Magnesium	279.078	6.3	7.6
Manganese	257.610	0.2	0.2
Molybdenum	202.030	1.1	1.4
Nickel	213.604	0.7	1.2
Potassium	766.491	26.5	66.5
Selenium	196.021/196.022	2.2	2.1
Silver	328.068	0.6	0.9
Sodium	330.232	299.5	259.3
Thallium	190.864	3.2	5.5
Tin	189.989	3.5	3.0
Titanium	334.941	8.8	10.7
Vanadium	292.402	0.4	0.6
Zinc	213.856	0.8	3.6

Attachment 3

Method Detection Limit Study

Study Date: February 1, 2000 SW846 Aqueous Digested Metals Method 3010A/6010B
Instrument: P3 (Trace)

Parameter	Rep#1 ug/L	Rep#2 ug/L	Rep#3 ug/L	Rep#4 ug/L	Rep#5 ug/L	Rep#6 ug/L	Rep#7 ug/L	Rep#8 ug/L	Rep#9 ug/L	Rep#10 ug/L	Mean ug/L	Amt. ug/L	S.Dev. ug/L	MDL ug/L	Report Limit ug/L
Aluminum	112.7	92.12	105.7	91.06	99.4	101.9	93.76	105.3	93.5	97.9	99.34	100	7.06	19.92	100
Antimony	10.49	16.51	16.03	12.12	10.91	10.23	11.16	11.50	10.43	10.13	11.95	9.0	2.36	6.66	10
Arsenic	4.552	3.473	3.150	4.032	3.993	4.040	5.36	4.872	4.11	4.79	4.24	5.0	0.67	1.88	10
Barium	1.880	1.948	1.893	2.009	1.972	1.051	1.130	1.024	1.088	1.041	1.50	0.75	0.46	1.31	10
Beryllium	1.150	1.043	1.123	1.053	1.047	1.080	1.044	1.086	1.061	1.045	1.07	1.0	0.04	0.10	5
Bismuth	11.61	14.54	13.28	12.70	12.68	14.26	11.55	13.16	14.05	14.55	13.24	12	1.12	3.15	50
Cadmium	1.191	1.045	0.965	1.037	0.990	1.037	0.952	1.185	1.037	0.968	1.04	1.0	0.08	0.24	5
Calcium	58.03	49.07	52.83	52.68	47.03	45.08	50.34	45.78	46.44	44.03	49.13	100	4.37	12.34	1000
Chromium	3.415	3.736	3.504	3.228	3.300	3.547	3.332	3.350	3.614	3.142	3.42	3.0	0.18	0.52	5
Cobalt	1.411	1.545	1.636	1.353	1.708	1.515	1.488	1.567	1.303	1.389	1.49	3.0	0.13	0.36	5
Copper	3.481	3.503	3.879	3.615	4.013	3.650	3.607	3.637	3.589	3.516	3.65	4.0	0.17	0.48	5
Iron	130.7	135.0	*	131.8	131.9	131.3	132.8	142.8	136.9	128.6	133.53	120	4.23	12.24	100
Lead	7.643	7.135	7.097	8.191	7.072	7.758	8.087	7.104	7.261	6.551	7.39	14.0	0.51	1.45	3
Magnesium	113.5	114.7	116.0	115.9	114.8	116.0	115.1	113.0	113.3	112.1	114.44	110	1.39	3.92	1000
Manganese	3.467	3.594	4.165	3.514	3.848	3.453	3.516	3.448	1.785	3.377	3.42	3.0	0.62	1.75	10
Molybdenum	5.260	5.177	5.407	5.441	5.084	5.120	5.190	5.592	5.629	5.122	5.30	5.0	0.20	0.57	5
Nickel	4.769	4.745	4.831	5.025	4.562	4.742	4.764	4.423	4.528	4.472	4.69	4.5	0.19	0.52	5
Potassium	137.8	134.3	119.6	126.7	114.9	135.7	115.1	118.0	134.7	116.1	125.29	140	9.54	26.90	1000
Selenium	11.12	12.52	11.92	10.76	10.63	9.915	11.33	9.536	10.97	11.31	11.00	10	0.88	2.47	5
Silver	2.079	2.447	1.840	1.914	2.024	2.141	2.189	2.041	2.048	1.988	2.07	2.0	0.17	0.47	5
Sodium	1466	1583	1505	1479	1558	1495	1565	1480	1634	1542	1531	1200	54.59	154.0	2000
Thallium	21.05	22.58	21.87	21.73	22.17	21.25	21.36	19.98	22.91	21.61	21.65	20	0.83	2.34	10
Tin	20.88	19.78	22.62	20.60	22.31	20.13	20.76	19.62	21.99	18.64	20.73	20	1.27	3.59	20
Titanium	59.15	59.23	53.74	53.47	51.71	58.63	52.04	54.95	56.58	52.32	55.18	50	3.00	8.47	40
Vanadium	2.888	3.116	2.910	2.865	2.894	2.862	3.022	2.870	3.008	3.158	2.96	3.0	0.11	0.31	20
Zinc	20.56	19.51	20.52	19.37	19.19	19.12	19.35	18.24	19.41	18.21	19.35	40	0.78	2.20	20

Reporting Limit = Practical Quantitation Limit (PQL)

Attachment 2: Wavelength and Estimated Instrumental Detection Limits on Instrument Numbers P4, Trace ICP, 2nd Quarter, 2000

Elements	Wavelength* (nm)	Instrument Detection Limits** (ug/L)	Instrument Detection Limits (ug/L) NYSASP
Aluminum	308.215	26.7	68.8
Antimony	206.838	1.5	2.0
Arsenic	189.042	2.1	4.2
Barium	493.409	0.2	0.2
Beryllium	313.042	0.1	0.3
Bismuth	223.061	2.5	2.4
Cadmium	226.502	0.3	0.3
Calcium	317.933	25.0	54.9
Chromium	267.716	2.1	1.9
Cobalt	228.616	0.7	0.6
Copper	324.753	1.3	4.0
Iron	271.441	14.1	11.8
Lead	220.351/220.352	1.1	1.5
Magnesium	279.078	6.8	64.1
Manganese	257.610	0.4	0.5
Molybdenum	202.030	0.8	1.0
Nickel	231.604	3.2	3.9
Potassium	766.491	36.9	42.1
Selenium	196.021/196.022	1.7	1.7
Silver	328.068	0.5	1.5
Sodium	330.232	158.6	159.2
Thallium	190.864	2.2	2.2
Tin	189.989	2.8	3.5
Titanium	334.942	5.4	8.2
Vanadium	292.402	0.4	0.4
Zinc	206.200	3.6	3.5

Attachment 3 (continued)

Method Detection Limit Study

Study date: February 1, 2000 SW846 Solid Digested Metals Method 3050A/6010B
Instrument: P3 (Trace)

Parameter	Rep#1	Rep#2	Rep#3	Rep#4	Rep#5	Rep#6	Rep#7	Rep#8	Rep#9	Rep#10	Mean	Amt.	S.Dev.	MDL	Report Limit
	mg/Kg	mg/Kg	mg/Kg	mg/Kg	mg/Kg	mg/Kg	mg/Kg	mg/Kg	mg/Kg	mg/Kg	mg/Kg	mg/Kg	mg/Kg	mg/Kg	mg/Kg
Aluminum	7.952	6.133	8.985	6.786	7.537	6.704	6.427	7.623	5.624	8.537	7.231	10	1.08	3.04	10
Antimony	1.319	1.254	1.039	1.091	1.062	0.972	1.004	0.913	0.977	0.991	1.062	0.9	0.13	0.36	1
Arsenic	0.633	0.597	0.680	0.637	0.614	0.709	0.649	0.660	0.661	0.585	0.643	1.0	0.04	0.11	1
Barium	0.230	0.208	0.233	0.226	0.219	0.212	0.199	0.321	0.215	0.241	0.230	0.15	0.03	0.10	1
Beryllium	0.097	0.086	0.101	0.095	0.093	0.092	0.085	0.099	0.086	0.099	0.093	0.10	0.01	0.02	0.5
Bismuth	1.295	1.206	1.093	1.386	1.127	1.414	1.366	1.533	1.321	1.780	1.352	1.2	0.20	0.57	5
Cadmium	0.048	0.047	0.032	0.045	0.048	0.048	0.052	0.044	0.049	0.051	0.046	0.10	0.01	0.02	0.5
Calcium	8.616	9.904	13.47	10.15	10.11	10.06	8.836	10.18	8.939	11.29	10.16	10	1.41	3.98	100
Chromium	0.386	0.337	0.456	0.364	0.324	0.352	0.324	0.427	0.343	0.407	0.372	0.30	0.05	0.13	0.5
Cobalt	0.278	0.281	0.291	0.292	0.299	0.293	0.279	0.311	0.304	0.311	0.294	0.30	0.01	0.03	0.5
Copper	1.028	0.889	0.979	0.905	0.910	0.865	0.885	0.894	0.899	*	0.917	0.80	0.05	0.15	0.5
Iron	7.90	8.28	16.19	7.29	8.09	8.47	7.64	15.49	8.40	9.52	9.73	6.0	3.28	9.25	10
Lead	1.587	1.680	1.721	1.818	1.804	1.711	1.677	1.761	1.857	*	1.735	1.40	0.08	0.24	0.3
Magnesium	11.56	11.37	11.80	11.69	12.08	12.11	11.58	11.86	11.58	12.08	11.77	11.0	0.26	0.73	100
Manganese	0.454	0.436	0.535	0.576	0.468	0.411	0.391	0.517	0.436	0.563	0.479	0.30	0.07	0.18	1
Molybdenum	0.563	0.492	0.517	0.485	0.492	0.497	0.469	0.510	0.517	0.508	0.505	0.50	0.03	0.07	0.5
Nickel	0.861	0.804	0.859	0.887	0.843	0.854	0.837	0.892	0.836	1.009	0.868	0.90	0.06	0.16	0.5
Potassium	13.26	9.22	11.08	13.12	11.49	11.67	10.39	14.14	10.66	13.58	11.86	14	1.60	4.52	100
Selenium	0.965	0.936	0.832	1.024	0.927	0.932	0.913	0.987	0.730	0.950	0.919	1.00	0.08	0.24	0.5
Silver	0.189	0.207	0.195	0.202	0.190	0.226	0.184	0.212	0.175	0.199	0.198	0.2	0.01	0.04	0.5
Sodium	222.2	234.7	238.2	266.6	229.9	228.2	222.9	247.5	242.1	231.1	236.3	120	13.31	37.56	200
Thallium	1.458	1.777	1.577	1.522	1.466	1.651	1.524	1.840	1.621	1.583	1.602	2.0	0.13	0.36	1
Tin	4.100	4.058	4.397	4.105	4.217	3.992	4.024	4.065	4.044	3.995	4.100	2.0	0.12	0.35	2
Titanium	5.498	3.616	4.290	4.890	3.971	4.938	4.282	5.615	4.272	5.317	4.669	5.0	0.68	1.92	4
Vanadium	0.283	0.306	0.290	0.280	0.304	0.300	0.295	0.307	0.321	0.313	0.300	0.3	0.01	0.04	2
Zinc	3.908	3.811	4.013	3.761	3.708	3.661	3.545	3.882	3.747	*	3.782	4.0	0.14	0.41	2

Reporting Limit = Practical Quantitation Limit (PQL)

Attachment 4

Table 4: Analyte Concentration Equivalents Arising from Interference at the 100-mg/l Level

Analyte	Wavelength (nm)	Al	Ca	Cr	Cu	Fe	Mg	Mn	Ni	Tl	V
Aluminum	308.215	--	--	--	--	--	0.21	--	--	--	1.4
Antimony	206.833	0.47	--	2.9	--	0.08	--	--	--	0.25	0.45
Arsenic	193.696	1.3	--	0.44	--	--	--	--	--	--	1.1
Barium	455.403	--	--	--	--	--	--	--	--	--	--
Beryllium	313.042	--	--	--	--	--	--	--	--	0.04	0.05
Boron	249.773	0.04	--	--	--	0.32	--	--	--	--	--
Cadmium	226.502	--	--	--	--	0.03	--	--	0.02	--	--
Calcium	317.933	--	--	0.08	--	0.01	0.01	0.04	--	0.03	0.03
Chromium	267.716	--	--	--	--	0.003	--	0.004	--	--	0.04
Cobalt	228.616	--	--	0.03	--	0.005	--	--	0.03	0.15	--
Copper	324.754	--	--	--	--	0.003	--	--	--	0.05	0.02
Iron	259.940	--	--	--	--	--	0.12	--	--	--	--
Lead	220.353	0.17	--	--	--	--	--	--	--	--	--
Magnesium	231.604	--	0.02	0.11	--	0.13	--	0.25	--	0.07	0.12
Manganese	196.026	0.005	--	0.01	--	0.002	0.002	--	--	--	--
Molybedenum	202.030	0.05	--	--	--	0.03	--	--	--	--	--
Nickel	279.079	--	--	--	--		--	--	--	--	--
Selenium	257.610	0.23	--	--	--	0.09	--	--	--	--	--
Silicon	288.158	--	--	0.07	--	--	--	--	--	--	0.01
Sodium	588.995	--	--		--	--	--	--	--	0.08	--
Thallium	190.864	0.30	--		--	--	--	--	--	--	--
Vanadium	292.402	--	--	0.05	--	0.005	--	--	--	0.02	--
Zinc	213.856	--	--	--	0.14	--	--	--	0.29	--	--

[a]Dashes indicate that no interference was observed even when interferents were introduced at the following levels:
Al, Ca, Mg - 1000 mg/l,Ca, Fe - 1000 mg/l,Cr, Cu, Mn, Tl, V - 200 mg/l,
[b]The figures recorded as analyte concentrations are not the actual observed concentrations; to obtain those figures, add the listed concentration to the interferent figure.

Attachment 5

Standards/QC Preparation for Trace ICP (P3) 1 of 4 CompuChem a division of Liberty Analytical Corp. LOGBOOK 1 QQQQ 38

STANDARDS and REAGENTS TRACEABILITY Date: _____

HNO3 [Baker Instra-analyzed Trace-Metals grade,	Ref#*: _____
HCl [Baker Instra-analyzed Trace-Metals grade,	Ref#: _____
XCL-11 multi-element standard mix	Ref#: _____
XCL-2 multi-element standard mix	Ref#: _____
XCL-3A multi-element standard mix	Ref#: _____
ICV1 multi-element standard mix	Ref#: _____
ICV2 multi-element standard mix	Ref#: _____
ICV3 multi-element standard mix	Ref#: _____
ICV4 multi-element standard mix	Ref#: _____
ICSA multi-element standard mix	Ref#: _____
ICSAB multi-element standard mix	Ref#: _____
LRS-1 multi-element standard mix	Ref#: _____
LRS-2 multi-element standard mix	Ref#: _____
Spex multi-element standard mix	Ref#: _____
COM Lab mix 5	Ref#: _____
CRDL-1 multi-element standard mix	Ref#: _____
ANTIMONY (Sb) 1,000 PPM single-element standard	Ref#: _____
BISMUTH (Bi) 1,000 PPM single-element standard	Ref#: _____
TITANIUM (Ti) 1,000 PPM single-element standard	Ref#: _____
TIN (Sn) 1,000 PPM single-element standard	Ref#: _____
IRON (Fe) 10,000 PPM single-element standard	Ref#: _____
ALUMINUM (Al) 1,000 PPM single-element standard	Ref#: _____
CALCIUM (Ca) 10,000 PPM single-element standard	Ref#: _____
MAGNESIUM (Mg) 10,000 PPM single-element standard	Ref#: _____
MOLYBDENUM (Mo) 1,000 PPM single-element standard	Ref#: _____
ARSENIC (As) 1, 000 PPM single-element standard	Ref#: _____

The following standard solutions are applicable only when dissolved samples are analyzed.

XCL-LCS multi-element standard mix Ref#: N/A Reviewed By: _____
XCL-20 multi-element standard mix Ref#: N/A Date: _____

The following spaces are provided for non-CLP metals standards not previously identified.

N/A ml of N/A 1,000 PPM standard Ref#: N/A
N/A ml of N/A 1,000 PPM standard Ref# N/A

*Ref# = Logbook ID, Page number and Item number. from Materials Receipt Log

10/31/00:mlj

Attachment 5 (continued)

Standards/QC Preparation for Trace ICP

Standard Lot Number*	Preparation instructions
SO/ICB/CCB-__ __ __ __ __ __-__ __	Place in a 500-ml volumetric flask: 100 ml of deionized water ____ml concentrated HNO_3, and ____ml concentrated HCl. Bring up to volume with deionized water. Prepare weekly.
XCL-11-__ __ __ __ __ __-__ __	Place in a 100-ml volumetric flask: 50 ml of deionized water ____ml concentrated HNO_3, and _____ml concentrated HCl. Pipet 0.2 ml XCL-11 into flask. Bring up to volume with deionized water. Prepare weekly.
XCL-2-__ __ __ __ __ __-__ __	Place in a 100-ml volumetric flask: 50 ml of deionized water ____ml concentrated HNO_3, and _____ml concentrated HCl. Pipet 0.2 ml of XCL-2 into flask. Bring up to volume with deionized water. Prepare weekly.
XCL-3A-__ __ __ __ __ __-__ __	Place in a 100-ml volumetric flask: 50 ml of deionized water ____ml concentrated HNO_3, and _____ml concentrated HCl. Pipet 1.0 ml of XCL-3A into flask. Bring up to volume with deionized water. Prepare weekly.
PLSB2-2X-__ __ __ __ __ __-__ __	Place in a 100-ml volumetric flask: 50 ml of deionized water ____ml of concentrated HNO_3, and _____ml concentrated HCl. Pipet 0.2 ml of Sn, Bi, Ti, Sb, N/A, N/A, into flask. Bring up to volume with deionized water. Prepare weekly.
STD3-__ __ __ __ __ __-__ __	Place in a 100-ml volumetric flask: 50 ml of deionized water _____ml concentrated HNO_3 _____ml concentrated HCl 1.0 ml of 1,000-ppm Al, 0.5 ml of 10,000-ppm Fe, 1.0 ml of 10,000-ppm Mg 1.0 ml of 10,000-ppm Ca, Bring up to volume with deionized water. Prepare weekly.
CVS1-__ __ __ __ __ __-__ __	Place in a 500-ml volumetric flask: 400 ml of deionized water ____ml concentrated HNO_3 ___ml of concentrated HCl 0.5ml of Sb, 0.5 ml of Sn, 0.5 ml of Bi, 0.5 ml of Ti, 2.5 mL Ca, Mg. 0.5 ml of Al, 0.5 ml of Fe 0.500 ml of XCL-2, 0.500 ml of XCL-11, 2.5 ml of XCL-3A Bring to volume with deionized water. Prepare weekly.

*Standard Lot Number consists of standard ID, date prepared, and initials of preparer.

Reviewed By: _____ Date: _____

10/31/00:mlj

Attachment 5 (continued)

Standards/QC Preparation for Trace ICP

Standard Lot Number*	Preparation Instructions*
ICV1-_____-____	Place in a 200-ml volumetric flask: 100 ml of deionized water ____ml of concentrated HNO_3 ____ml concentrated HCl, Pipet 20.0 ml of ICV1 into flask. Bring up to volume with deionized water. Prepare as needed.
ICV3-_____-____	Place in a 200-ml volumetric flask: 100 ml of deionized water ____ml concentrated. HNO_3 ____ml concentrated HCl Pipet:20.0 ml of ICV3, 20.0 ml of ICV2, and 20.0 ml of ICV4 into flask. Bring to volume with deionized water. Prepare as needed.
SPEXAS-_____-____	Place in a 200-ml volumetric flask: 100 ml of deionized water ____ml concentrated HNO_3 ____ml concentrated HCl Pipet 0.2 ml of CompuChem SPEX into flask. Bring up to volume with deionized water. Prepare as needed.
ICSA-_____-____	Place in a 200-ml volumetric flask: 100 ml of deionized water ____ml concentrated HNO_3 ____ml concentrated HCl Pipet 20.0 ml ICSA into flask. Bring up to volume with deionized water. Prepare as needed.
ICSAB-_____-____	Place in a 200-ml volumetric flask: 50 ml of deionized water ____ml concentrated HNO_3 ____ml concentrated HCl Pipet 20.0 ml ICSA and 2.0 ml ICSB into flask. Pipet: ____ ml Bi standard ____ ml Sn standard ____ ml Ti standard ____ ml Mo standard into flask. Bring up to volume with deionized water. Prepare as needed.
LRS-_____-____	Place in a 100-ml volumetric flask: 50 ml of deionized water ____ml concentrated HNO_3 and ____ml concentrated HCl Pipet 0.10 ml LRS-1 and 0.10 ml LRS-2 into flask. Prepare as needed.

*Standard Lot Number consists of standard ID, date prepared, and initials of preparer.

Reviewed By: _____ Date: _____

10/31/00:mlj

Attachment 5 (continued)

Standards/QC Preparation for Trace ICP

Standard Lot Number*	Preparation instructions*
CRI -_____-____	Place in a 200-ml volumetric flask: 100 ml of deionized water ____ml concentrated HNO_3 ____ml concentrated HCl Pipet: 0.20 CRDL-1 into flask. 0.008 ml Bi into flask. 0.008 ml Sn into flask. 0.004 ml Mo into flask. 0.012 ml Ti into flask. N/A ml N/A 1000 standard into flask. N/A ml N/A 1000 standard into flask. N/A ml N/A 1000 standard into flask. Bring up to volume with deionized water. Prepare as needed.
Internal Standard-_____-____	Place in a 2000-ml volumetric flask: 1000 ml of deionized water 20 ml of concentrated HNO_3 Pipet: 10 ml. of COM LAB MIX #5 internal standard. Bring up to volume with DI water. Prepare as needed. Yttrium, introduced into the sample stream yielding a final concentration in the plasma of 1 ppm, is used as an internal standard. Cesium, introduced into the sample stream yielding a final concentration in the plasma of 50ppm, is used as a reducing agent.
As-_____-____	Place 100 ml volumetric flask 50 ml DI water 1 ml concentrated HNO_3 0.1 ml 1000 ppm As Bring to volume. Prepare as needed.

	Prepared By	Date Prepared	Preparation Instructions
Dissolved Metals only: LCS			Add 1.0 ml of XCL-LCS solution to 9.0 ml of acidified water ____ml HNO_3 + ____ml HCl .
Prep Blank			Use acidified water (1% HNO_3 + 5% HCl ____ml HNO_3 + ____ml HCl
Sample Spike			Add 0.1 ml of XCL-20 to 10.0 ml of sample.

*Standard Lot Number consists of standard ID, date prepared, and initials of preparer.

Reviewed by: _____ Date: _____ _____

10/31/00 mlj

Attachment 6

COMPUCHEM a division of Liberty Analytical Corp. LOGBOOK 1 OOOO 34

Trace ICP Run Log (P3) **Part (A) of a two part form** Page ____ of _____

Method (Circle one.): **Case:** _____ Date: _____

CLP ILM04.0 _____ Operator: _____

SW-846 6010B _____ File name: _____

MCAWW 200.7 _____ WSL.NAME _____

Instrument ID: P3 _____

No.	Sample ID	Comments	Action needed	No.	Sample ID	Comments	Action Needed
	S0	Blank			CCV		
	S	XCL-11			CCB		
	S	STD3		1			
	S	XCL-2		2			
	S	XCL-3A		3			
	S	PLSBR		4			
	ICV1			5			
	SPEXASSE			6			
	ICV3			7			
	ICB			8			
	LRS			9			
	CRI			10			
	ICSA				CCV		
	ICSAB				CCB		
	CCV			1			
	CCB			2			
1				3			
2				4			
3				5			
4				6			
5				7			
6				8			
7				9			
8				10			
9					CCV		
10					CCB		

COMMENTS

Reviewed By: _____

Date: _____

The presence of the Chemist's employee ID number, or signature, on this run log attests that strict compliance with the method's SOP has occurred. Any SOP deviations require documentation by the responsible chemist together with the chemist's initials and the initials of the lab supervisor and a QA department representative, signifying approval of the deviation.

10/18/00:mlj

Attachment 6 (continued)

COMPUCHEM a division of Liberty Analytical Corp. LOGBOOK 1 OOOO 34

Trace ICP Runlog (P3) **Part (B) of a two part form** Page ____ of ____

Method (Circle one.): **Case:** _____ Date: _____

CLP ILM04.0 _____ Operator: _____

SW-846 6010B _____ File name: _____

MCAWW 200.7 _____ WSL.NAME _____

Instrument ID: P3 _____

No.	Sample ID	Comments	Action needed	No.	Sample ID	Comments	Action Needed
1				1			
2				2			
3				3			
4				4			
5				5			
6				6			
7				7			
8				8			
9				9			
10				10			
	CCV				CCV		
	CCB				CCB		
1				1			
2				2			
3				3			
4				4			
5				5			
6				6			
7				7			
8				8			
9				9			
10				10			
	CCV				CCV		
	CCB				CCB		

COMMENTS

Reviewed By: _____

Date: _____

The presence of the Chemist's employee ID number, or signature, on this run log attests that strict compliance with the method's SOP has occurred. Any SOP deviations require documentation by the responsible chemist together with the chemist's initials and the initials of the lab supervisor and a QA department representative, signifying approval of the deviation.

10/18/00:mlj

Attachment 7

Internal Chain of Custody

ICP ANALYSIS

Project:_____

Case:_____ SDG:_____

Matrix:_____

COC for: raw sample extract digestates leachates aliquots other(explain):_____

CompuChem Numbers for Associated Samples

Released by	Received by	Date	Reason

This form generated on: 5/21/00

Attachment 8

Analyst Capability Study

Laboratory Name/North Carolina Certificate Number: CompuChem/79
Analyst: Adam Rothacker, Jean Tan
Study Date: February 4, 2000
Instrument: P3 (Trace)
Method: Aqueous ICP Metals by 3010A, 6010B

Parameter	TruVal ug/l	Rep #1 ug/l	Rep #2 ug/l	Rep #3 ug/l	Rep #4 ug/l	Mean (x)ug/l	Mean % R	EPA %R	SD(n-1) ug/l	RSD %	EPA SD	-3SD of (x)	+3SD of (x)	-3SD % R	+3SD %R
Aluminum	20000	19380	19350	19460	19730	19480	97	80-120	173	0.9	NS	18961	19999	97	103
Antimony	6000	6102	6142	6118	6271	6158	103	80-120	77	1.2	NS	5927	6389	96	104
Arsenic	1000	1025	1031	1029	1050	1034	103	80-120	11	1.1	NS	1000	1067	97	103
Barium	20000	21370	21530	21570	22270	21685	108	80-120	399	1.8	NS	20487	22883	94	106
Beryllium	500	496.9	501.5	499.8	513.1	503	101	80-120	7	1.4	NS	481	524	96	104
Cadmium	500	498.1	500.8	500.2	511.3	503	101	80-120	6	1.2	NS	485	520	96	104
Calcium	50000	50120	50530	50310	51640	50650	101	80-120	681	1.3	NS	48607	52693	96	104
Chromium	1000	1004	1010	1007	1034	1014	101	80-120	14	1.4	NS	973	1055	96	104
Cobalt	5000	5036	5068	5044	5173	5080	102	80-120	63	1.2	NS	4890	5270	96	104
Copper	2500	2568	2572	2588	2631	2590	104	80-120	29	1.1	NS	2503	2676	97	103
Iron	10000	10120	10170	10150	10390	10208	102	80-120	123	1.2	NS	9837	10578	96	104
Lead	300	300.9	303.1	301.0	307.4	303	101	80-120	3	1.0	NS	294	312	97	103
Magnesium	50000	50470	50740	50530	51840	50895	102	80-120	641	1.3	NS	48973	52817	96	104
Manganese	1500	1503	1513	1506	1548	1518	101	80-120	21	1.4	NS	1455	1580	96	104
Nickel	4000	3969	3984	3981	4069	4001	100	80-120	46	1.1	NS	3863	4139	97	103
Potassium	50000	52070	51810	51590	53180	52163	104	80-120	706	1.4	NS	50044	54281	96	104
Selenium	500	504.4	507.8	506.2	516.9	509	102	80-120	6	1.1	NS	492	526	97	103
Silver	1000	1024	1022	1026	1039	1028	103	80-120	8	0.7	NS	1005	1051	98	102
Sodium	50000	52000	52500	52010	53820	52583	105	80-120	857	1.6	NS	50010	55155	95	105
Thallium	1000	1034	1037	1036	1060	1042	104	80-120	12	1.2	NS	1005	1078	96	104
Vanadium	5000	5177	5219	5218	5372	5247	105	80-120	86	1.6	NS	4989	5504	95	105
Zinc	2000	2055	2069	2058	2115	2074	104	80-120	28	1.3	NS	1991	2158	96	104

Attachment 8 (continued)

Analyst Capability Study

Laboratory Name/North Carolina Certificate Number: CompuChem/79
Analyst: Adam Rothacker, Jean Tan
Study Date: February 4, 2000
Instrument: P3 (Trace)
Method: Soil ICP Metals, Method 3050B, 6010B

Parameter	TruVal mg/Kg	Rep #1 mg/Kg	Rep #2 mg/Kg	Rep #3 mg/Kg	Rep #4 mg/Kg	Mean mg/Kg	Mean % R	EPA %R	SD(n-1) mg/Kg	RSD %	EPA SD	-3SD of (x)	+3SD of (x)	-3SD % R	+3SD %R
Aluminum	4130	7226	6996	7148	7274	7161	173	NS	122	1.7	NS	6796	7526	95	105
Antimony	72.1	56.3	56.66	55.02	54.98	55.74	77	NS	0.9	1.6	NS	53	58	95	105
Arsenic	58.6	106.36	107.04	103.28	110.82	106.88	182	NS	3.1	2.9	NS	98	116	91	109
Barium	73.6	145	145.56	140.78	153.7	146.26	199	NS	5.4	3.7	NS	130	162	89	111
Beryllium	108	195.9	204	190.88	215.2	201.50	187	NS	10.6	5.3	NS	170	233	84	116
Cadmium	185	347.2	348	339.4	367.2	350.5	189	NS	12	3.4	NS	315	386	90	110
Calcium	1600	2802	2884	2740	3030	2864.0	179	NS	125	4.4	NS	2488	3240	87	113
Chromium	50.7	87.28	89.12	84.84	93.56	88.70	175	NS	3.7	4.2	NS	78	100	88	112
Cobalt	151	275.2	285.4	267	301.4	282.3	187	NS	14.8	5.3	NS	238	327	84	116
Copper	63.6	125.68	127.52	123.04	134.9	127.79	201	NS	5.1	4.0	NS	113	143	88	112
Iron	8610	12430	12388	12286	12244	12337	143	NS	87	0.7	NS	12077	12597	98	102
Lead	56.6	102.7	104.3	100.58	110.02	104.4	184	NS	4.0	3.9	NS	92	117	88	112
Magnesium	1310	2296	2272	2284	2360	2303.0	176	NS	39	1.7	NS	2185	2421	95	105
Manganese	295	528.8	544.6	517.2	566.2	539.2	183	NS	21	3.9	NS	476	603	88	112
Nickel	75.4	137	141.9	133.7	149.22	140.46	186	NS	6.7	4.8	NS	120	161	86	114
Potassium	1520	111.58	111.4	109.06	113.48	111.38	7.3	NS	1.8	1.6	NS	106	117	95	105
Selenium	61.4	111.58	111.4	109.06	113.48	111.38	181	NS	1.8	1.6	NS	106	117	95	105
Silver	149	282.6	284	274.4	284.2	281.30	189	NS	4.7	1.7	NS	267	295	95	105
Sodium	243	220.6	211.6	215	224.2	217.85	90	NS	5.6	2.6	NS	201	235	92	108
Thallium	114	220.6	211.6	215	224.2	217.85	191	NS	5.6	2.6	NS	201	235	92	108
Vanadium	101	183.84	189.24	178.96	195.84	186.97	185	NS	7.3	3.9	NS	165	209	88	112
Zinc	69.6	117.62	121.46	118.4	122.28	119.94	172	NS	2.3	1.9	NS	113	127	94	106

Sample Preparation Procedure -093: Aqueous Sample Cyanide Midi Distillation by SW846 and NYSASP

1.0 Scope and Application

This method is applicable to the determination of total cyanide in aqueous matrices including wastes or leachates and complies with requirements in SW846 and the New York Analytical Services Protocol (NYSASP).

The current method detection limits (MDL) and reporting limits are shown in Attachment 1.

Staff members performing the procedures described in this SOP are responsible for reading, understanding, and complying with the SOP requirements. Supervisors are responsible for directing the analyst to the controlled SOP, and providing adequate explanation of the material contained therein.

This procedure is restricted to use by or under the supervision of analysts experienced in the instrumentation or preparative methods and who have demonstrated the ability to generate acceptable results through QC samples and analyst capability studies.

2.0 Summary of Method

The basis for the method includes a reflux-distillation of a known amount of sample releasing cyanide from its complexes in the form of hydrogen cyanide gas. The released gas is drawn by vacuum and absorbed in a sodium hydroxide solution. The cyanide is released from the sodium hydroxide solution by means of UV digestion and distillation and converted into cyanogen chloride by reaction with chloramine -T. In this form it reacts with pyridine and barbituric acid to give a red-colored complex. The intensity is measured colorimetrically at 578 nm.

3.0 Definitions

3.1 Cyanide – cyanide ion and complex cyanides converted to hydrocyanic acid by reaction in a reflux system with mineral acid in the presence of magnesium ion.

3.2 Method detection limit (MDL) – The minimum concentration of an analyte that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined form analysis of a sample in a given matrix containing the analyte (40 CFR, Part 136, Appendix B.)

3.3 Reporting Limit – The laboratory reporting limit is based on the lowest multipoint calibration standard concentration. For some inorganic methods, the reporting limit is based on the MDL, and is usually 4-8 times

higher than the MDL. For organic methods, values detected below the reporting limit and above the MDL may be reported and qualified as an estimated concentration.

3.4 Reporting Units – µg/L

4.0 Interferences

Interferences are eliminated or reduced by distilling the samples.

4.1 Sulfide Check for SW-846

Sulfide interference can be removed by adding an excess of bismuth nitrate to the waste (to precipitate the sulfide) before distillation. Samples that contain hydrogen sulfide, metal sulfides, or other compounds that may produce hydrogen sulfide during the distillation should be treated by the addition of bismuth nitrate.

4.1.1 Sulfide Check Materials for SW-846

Bismuth nitrate (0.062M), $Bi(NO)_3 \bullet 5H_2O$. Dissolve $Bi(NO)_3 \bullet 5H_2O$ in 100 mL of water. While stirring, add 250 mL of glacial acetic, CH_3COOH. Stir until dissolve and dilute to 1 liter with water.

4.1.2 Sulfamic acid (0.4N), H_2NSO_3H. Dissolve 40 g H_2NSO_3H in 1 liter of water.

4.2 Nitrate/Nitrite Checks for SW846

High results may be obtained for samples that contain nitrate and/or nitrite. During the distillation, nitrate and nitrite will form nitrous acid, which will react with some organic compounds to form oximes. These compounds once formed will decompose under test conditions to generate HCN. The possibility of interference of nitrate and nitrite is eliminated by pretreatment with sulfamic acid just before distillation. Nitrate and nitrite are interferences when present at levels higher than 10 mg/L and in conjunction with certain organic compounds.

4.2.1 Nitrite check materials for SW846

Microquant 1.14774.0001 nitrite kit - Use syringe to fill both glass bottles with 6 mL of aqueous sample. Add 1 flat microspoon of NO_2-AN to right hand bottle, dissolve and set aside for 3 minutes. Compare color with wheel. Treat with sulfamic acid if above 10 mg/L.

4.2.2 Nitrate check materials for SW846

Spectroquant 1.14773.0001 nitrate kit – Add 1 mircospoon of NO_3-IA to tube. Add 5 mL of NO_3-2A to dissolve NO_3-1A. Add 1.5

mL of sample and mix immediately. Let stand 10 minutes. Measure at 515nm on Spect 20.

4.2.3 Sulfamic acid (0.4N), H_2NSO_3H. Dissolve 40 g H_2NSO_3H in 1 liter of water.

4.3 pH Check

Samples received must be preserved with sodium hydroxide at the time of collection. Review the sample receiving report and check to see that the sample pH is equal to or greater than 12. If the pH of the sample is not within that range, contact Customer Service/Project Management. They will notify the client. The client will then say whether of not to proceed (must be in writing). If approval is granted, then add 2.0 ml of 10N sodium hydroxide per liter of sample to adjust the pH appropriately.

pH check materials: pH paper colorpHast strips

5.0 Safety

5.1 As with all laboratory procedures, you must wear the proper protective equipment (gloves, safety glasses, lab coat) when performing this procedure.

5.2 Laboratory staff is encouraged to review the Chemical Hygiene Plan for general safety policies, and Material Safety Data Sheets for reagents used in the laboratory.

6.0 Equipment and Supplies

6.1 Midi reflux distillation apparatus

6.2 Heating block capable of maintaining 125 ±5°C

6.3 Assorted volumetric glassware, pipets, or micropipets

7.0 Reagents and Standards

7.1 Reagent Water-All water used during preparation should be reagent-grade Type I with regard to resistivity of > 10 megohm-cm (18th and 19th Editions of Standard Methods, Method 1080), and referred throughout this SOP as DI water.

7.2 Sodium hydroxide solution, 0.25 N: Dissolve 10g of NaOH in DI H_2O, then dilute to 1 liter.

7.3 Magnesium Chloride Solution: Weigh 510 grams of $MgCl_2/.6H_2O$ into a 1 L flask and dissolve it in DI water. Dilute to 1 liter with DI water. Shake the flask well to thoroughly mix.

7.4 Sulfuric Acid: 50% (v/v): Carefully add 100 mL of conc. Sulfuric acid to 100 mL DI H_2O. Adjust volumes as needed.

7.5 Stock cyanide solution, 1000 ppm: Dissolve 2.51 g of KCN and 2 g of KOH in a one liter volumetric flask. Standardize to determine the appropriate final volume. This solution should be refrigerated in a labeled polypropylene bottle at 4°C.

7.6 Stock intermediate cyanide solution, 10 ppm: Prepare daily. To a 250-ml volumetric flask, add about 125 ml of 0.25 N sodium hydroxide. Pipet calculated volume of standardized stock cyanide solution from equation on standards prep log into a class "A" 250 mL volumetric flask. Dilute to volume with 0.25 N NaOH. Mix well and transfer to a labeled polypropylene bottle and refrigerate at 4°C ± 2°C.

Note: Use this solution for sample spike LRS, HRS, and calibration standards.

7.7 Complete the documentation contained in Attachment 2.

8.0 Sample Collection, Preservation, and Storage

8.1 The sample should be collected in a 500 mL plastic bottle. All such bottles must be thoroughly cleaned and dried before collection.

8.2 Samples are preserved with 2 mL of 10N sodium hydroxide per liter of sample (pH >12) at the time of collection.

8.3 Samples must be stored in a refrigerator maintained at a temperature of 2-4.4°C.

8.4 Samples should be analyzed as rapidly as possible to meet holding time. Any redistillation due to problems during sample analysis must be taken into consideration to meet these holding times.

Note: Samples must be distilled and analyzed within 12 days from time of receipt in order to meet holding times for CLP and (14) days from date of sampling for SW846.

8.5 The sample preparation technician should visually inspect all glassware before use. Any glassware with residues, dust, or discoloration of any kind should be rejected and recleaned.

8.6 Soap and hot water wash all glassware immediately after use. Rinse well with DI water.

9.0 Quality Control

9.1 Preparation Blank

For every 20 samples or for each prep batch, whichever is more frequent, prepare a preparation blank. A preparation blank is prepared by aliquoting 50 ml of DI water and distilling according to sample preparation instructions. This blank is used to ascertain whether sample concentrations reflect contamination.

9.2 Sample Spike

For every 20 samples or for each SDG, whichever is more frequent, at least one spike sample preparation must be prepared. For sample spikes, pipet 0.5 ml of 10 ppm stock intermediate cyanide solution before distillation into the flask containing the sample to be spiked. True value of spike is 100 ppb.

9.3 Duplicate

For every 20 samples or for each SDG, whichever is more frequent, at least one duplicate sample must be prepared. Samples identified as field blanks should not be used for sample spike or duplicate analysis.

9.4 Initial Calibration Verification, ICV

One ICV must be distilled with each day of distillation.

To prepare, pipet 0.5 ml of ICV-6 cyanide solution into a distillation flask containing 50 ml of DI water. Distill according to the sample preparation instructions.

Note: This solution is supplied by EPA and must be ordered. Maintain a supply of this solution and store it in a refrigerator kept at 4°C ± 2°C. It takes about 2 weeks to obtain.

9.5 High-range standard (HRS) (for SW-846)

At least one calibration standard (high-range) must be distilled with each analytical run to ensure that the distillation technique is reliable. The concentration of the HRS is 300 ppb. To prepare, pipet 1.5 ml of the 10 ppm stock intermediate cyanide solution into the distillation flask, which contains 50 ml of DI water. Distill according to sample preparation instructions.

9.6 Low-range standards (LRS) (for SW-846)

At least one calibration standard (low-range) must be distilled with each analytical run to ensure that the distillation technique is reliable. The concentration of the HRS is 40 ppb. To prepare, pipet 0.200 ml of the 10 ppm stock intermediate cyanide solution into the distillation flask, which

contains 50 ml of DI water. Distill according to sample preparation instructions.

9.7 LCS

One liquid LCS must be prepared for every 20 samples or prep batch, whichever is more frequent. This liquid LCS is 0.5 mL of ICV 6 solution into 50 mL DI H_2O and must be ordered. Maintain a supply of this material and store in refrigerator at 4°C ±2°C. It takes about 2 weeks to obtain.

10.0 Calibration and Standardization

10.1 The stock cyanide solution should be standardized weekly with 0.0192 N silver nitrate and Rhodanine indicator. Perform the standardization according to instructions on the attached Weekly Cyanide Stock Standardization Log page (Attachment 3). Refer to the log page for the standardization calculation.

11.0 Procedure

Documentation must follow the requirements in QC SOP: Proper Documentation Procedures.

11.1 Manual distillation: set up the apparatus as shown in Attachment 3.

Note: If samples are known or suspected to contain sulfide, add 5.0 mL of 0.062M bismuth nitrate solution through the air inlet tube. Mix for three minutes. Use lead acetate paper to check the sample for the presence of sulfide. A positive test is indicated by a black color on the paper.

If samples are known or suspected to contain nitrate or nitrite, or if bismuth nitrate was added to the sample, add 5.0 mL of 0.4N sulfamic acid solution through the air inlet tube. Mix for three minutes.

11.2 Thoroughly mix sample before aliquotting. Transfer 50 mL of aqueous sample into the distillation flask along with 2 or 3 boiling chips.

11.2.1 Add 50 ml of 0.25 N NaOH solution to the absorber tube.

11.2.2 Connect the apparatus as shown in Attachment 4.

11.2.3 Adjust suction so that about 3 air bubbles/sec enters through the distillation flask. This air will carry HCN gas from the flask to the absorber tube for collection.

11.2.4 After 5 minutes of vacuum flow, add 5 ml of 1:1 H_2SO_4 through the inlet tube. This volume should be sufficient to bring the pH of the solution to below 2.

Warning: Violent reaction may occur with the acid addition. Add slowly and observe the sample's response.

11.2.5 Allow air to mix the contents of the distillation flask for 5 minutes.

11.2.6 Add 2 ml $MgCl_2$ reagent through the inlet tube. Excessive foaming from sample containing surfactants may be quelled by the addition of another 2 mL $MgCl_2$.

11.2.7 Turn on the heating block and set for 123-125°C. Heat the flask to rapid boiling. Do not allow the solution to back up and overflow into the air inlet tube.

11.2.8 Distill for an hour and a half and then discontinue heating, but continue air flow.

11.2.9 Cool and aerate for 15 minutes. Disconnect absorber tube and close off the vacuum source.

11.2.10 Carefully transfer the solution from the scrubber to a 50 mL plastic centrifuge tube which is properly labelled with CompuChem number and "CN-" identification to ensure that the cyanide sample is not confused with a sample that was prepared for metals. Replace cap.

11.2.11 Record prep information in the cyanide prep log. (Attachment 5) All information must be properly entered, the sheet reviewed, signed and copied.

12.0 Data Analysis & Calculations

Calculations must be consistent with the QC SOP: Numerical Data Reduction.

13.0 Method Performance

This method was validated through in-house laboratory studies of method detection limits (Attachment 5) and precision and accuracy for single analyst (Attachment 6). The data are retained by the QA department.

14.0 Pollution Prevention

The solvents used in this procedure pose little threat to the environment when recycled and managed properly. Pollution prevention encompasses any technique

that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best thing.

15.0 Waste Management

It is the laboratory's responsibility to comply with all federal, state, and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions, and to protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Compliance with all sewage discharge permits and regulations is also required.

Samples preserved with HCl or H_2SO_4 to pH <2 are hazardous and must be neutralized before being disposed, or must be handled as hazardous waste.

Refer to the Hazardous Waste Management and Safety SOPs located in the lab.

16.0 References

16.1 SW846, 3rd Edition, Update III, 12/96, Methods 9012A (with the exception of midi distillation) and 9010B (with the exception of midi distillation and cyanide content determination by 9012A).

16.2 The New York Analytical Services Protocol (9/89 with revisions through 10/95).

16.3 Methods for Chemical Analysis of Water and Wastes, 3/93, Methods 335.2 (off-line distillation) and 335.3 (colorimetric determination)

16.4 QCSOP: Proper Documentation Procedures

16.5 QCSOP: Numerical Data Reduction

16.6 "Less is Better: Laboratory Chemical Management for Waste Reduction," American Chemical Society Department of Government Relations and Science Policy, 1155 16th Street, N.W., Washington DC, 20036, (202) 872-4477.

16.7 Hazardous Waste Management & Safety SOPs: "Hazardous Waste Disposal" and "Spill Control & Cleanup."

16.8 NELAC Standards, July 1, 1999, plus revisions

16.9 QA-G6: Guidance for the Preparation of Standard Operating Procedures for Quality-Related Operations EPA/600/R-96/027, November 1995.

16.10 New York State Environmental Laboratory Approval Program, Certification Manual, October 15, 1999, plus revisions.

17.0 Attachments

17.1 Attachment 1 - Method Detection Limit Study

17.2 Attachment 2 - QC Standards Log

17.3 Attachment 3 - Weekly Cyanide Stock Standardization Log

17.4 Attachment 4 - Cyanide Distillation Apparatus Diagram

17.5 Attachment 5 - Preparation Log

17.6 Attachment 6 – Single Analyst Capability Study

Attachment 1

Method Detection Limit Study

Study Date: January 14, 2000 | Aqueous Distilled Cyanide Methods 9010B, 9012A
Instrument: Lachat

Parameter	ID #	Rep#1 ug/L	Rep#2 ug/L	Rep#3 ug/L	Rep#4 ug/L	Rep#5 ug/L	Rep#6 ug/L	Rep#7 ug/L	Rep#8 ug/L	Mean ug/L	Amt. ug/L	S.Dev. ug/L	MDL ug/L	Report Limit ug/L
Cyanide	1001	11.7	10.1	10.8	10.8	10.7	11.2	10.8	11.5	10.95	10.0	0.50	1.51	10.0

Reporting Limit = Low Level Standard

Attachment 2

Standards/QC Preparation for Cyanide by Lachat

COMPUCHEM a division of Liberty Analytical. Corp.. LOGBOOK 1 00000 8

STANDARDS AND REAGENTS TRACEABILITY	
Potassium Cyanide	Ref#
Potassium Hydroxide	Ref#
Sodium hydroxide Pellets	Ref#
Chloramine-T	Ref#
Hydrochloric Acid	Ref#
Barbituric Acid	Ref#
Pyridine	Ref#
Sodium Phosphate	Ref#
Silver Nitrate	Ref#
ICV-6	Ref#
STANDARD LOT NUMBER	**PREPARATION INSTRUCTIONS**
CN1000 mg/L-__ __ __ __ __ __ -__ __	Place in a 1000 ml volumetric flask: • Standardized value is _____ mg/L • 2.510 g of dried KCN • 2.0 g of KOH Dilute to mark with DI water and mix well
CN10 mg/L-__ __ __ __ __ __ -__ __	Place in a 250 ml volumetric flask: Volume (mL) of stock = 2.5 x 1000 / Value of stock CN in (mg/L) Pipet _____ mL of stock cyanide standard into the flask Dilute to the mark with 0.25 NaOH solution and mix well
CN400-__ __ __ __ __ __ -__ __	Place in a 100 ml volumetric flask: 400 µg/L standard Pipet 4.0 ml of 10 mg/L cyanide solution into the flask. Dilute to 100 ml with 0.25 N NaOH and mix well

*Standard Lot Number consists of standard ID, date prepared, and initials of preparer.

Reviewed By: _____ Date: _____

Rev 10/11/99.mlj

Attachment 2 (continued)

Standards/QC Preparation for Cyanide by Lachat

COMPUCHEM a division of Liberty Analytical. Corp.. LOGBOOK 1 OOOOO 8

STANDARD LOT NUMBER	PREPARATION INSTRUCTIONS
CN100-__ __ __ __ __ __ -__ __	Place in a 100 ml volumetric flask: 100 µg/L standard Pipet 1.0 ml of 10 mg/L cyanide solution into the flask. Dilute to 100 ml with 0.25 N NaOH solution
CN200-__ __ __ __ __ __ -__ __	Place in a 100 ml volumetric flask: 200 µg/L standard Pipet 2.0 ml of 10 mg/L cyanide solution into the flask. Dilute to 100 ml with 0.25 N NaOH solution
CN300-__ __ __ __ __ __ -__ __	Place in a 100 ml volumetric flask: 300 µg/L standard Pipet 3.0 ml of 10 mg/L cyanide solution into the flask. Dilute to 100 ml with 0.25 N NaOH solution
CN50-__ __ __ __ __ __ -__ __	Place in a 100 ml volumetric flask: 50 µg/L standard Pipet 0.5 ml of 10 mg/L cyanide solution into the flask. Dilute to 100 ml with 0.25 N NaOH solution.
CN40-__ __ __ __ __ __ -__ __	Place in a 1000 ml volumetric flask: 40 µg/L standard Pipet 0.4 ml of 10 mg/L cyanide solution into the flask. Dilute to 100 ml with 0.25 N NaOH solution.
CN20-__ __ __ __ __ __ -__ __	Place in a 100 ml volumetric flask: 20 µg/L standard Pipet 0.2 ml of 10 mg/L cyanide solution into the flask. Dilute to 100 ml with 0.25 N NaOH solution
CN10-__ __ __ __ __ __ -__ __	Place in a 1000 ml volumetric flask: 10 µg/L standard Pipet 0.1 ml of 10 mg/L cyanide solution into flask. Dilute to 100 ml with 0.25 N NaOH solution

*Standard Lot Number consists of standard ID, date prepared, and initials of preparer.

Reviewed By: _____ Date: _____

Rev. 10/11/99 mlj

Attachment 2 (continued)

Standards/QC Preparation for Cyanide by Lachat

COMPUCHEM a division of Liberty Analytical. Corp.. LOGBOOK 1 OOOOO 8

STANDARD LOT NUMBER	PREPARATION INSTRUCTIONS
Blank-__ __ __ __ __ __ __ -__ __	0.25 N NaOH solution Dissolve a 10 g of NaOH into a 1000-ml volumetric flask: with DI water
Chloramine-T-__ __ __ __ __ __ __ -__ __	Dissolve (by swirling) in a 500-ml volumetric flask containing 400 ml of deionized water: • 2.0 g of Chloramine-T Bring to volume with DI water, and mix until homogeneous.
Pyridine barbituric acid -__ __ __ __ __ __ __ -__ __	Into a 1000 ml volumetric flask add: • 15.0 g of barbituric acid and just enough DI water to wash the sides of the flask and wet the barbituric acid. • Add 75 mL of pyridine and mix. • Add 15 mL of concentrated HCl, mix and cool. • Dilute to 1000 mL with DI water and mix. • Store in a cool, 4°C dark place
Phosphate Buffer-__ __ __ __ __ __ __ -__ __	Place in a 1000 ml volumetric flask containing 800 ml of deionized water: • 138 g of $Na_2HPO_4 \bullet H_2O$ Mix vigorously until the salts have dissolved. Bring to volume and continue to mix until homogeneous.
Adjusted DI H_2O-__ __ __ __ __ __ __ -__ __	Place in a 1000 ml volumetric flask containing 800 ml of deionized water • 10 g of NAOH pellets swirl to dissolve. Bring to volume with DI water.
LRS-__ __ __ __ __ __ __ -__ __	Place in a 50 ml glass sample tube • Pipet 0.2 ml of 10 mg/L cyanide solution into tube • Dilute to 50 ml with DI water • True Value = 40 µg/L
MRS-__ __ __ __ __ __ __ -__ __	Place in a 50 ml glass sample tube • Pipet 0.5 ml of 10 mg/L cyanide solution into tube • Dilute to 50 ml with DI water • True Value = 100 µg/L

*Standard Lot Number consists of standard ID, date prepared, and initials of preparer.

Reviewed By: _____ Date: _____

Rev. 10/11/99 mlj

Attachment 2 (continued)

Standards/QC Preparation for Cyanide by Lachat

COMPUCHEM a division of Liberty Analytical. Corp.. LOGBOOK 1 00000 8

Page 4 of 4

STANDARD LOT NUMBER			PREPARATION INSTRUCTIONS
HRS-__ __ __ __ __ __ __ - __ __			Place in a 50 ml glass sample tube • Pipet 1.5 ml of 10 mg/L cyanide solution into tube • Dilute to 50 ml with DI water • True Value = 300 µg/L
ICV-__ __ __ __ __ __ __ - __ __			Place in a 50 ml glass sample tube • Pipet 0.5 ml of ICV 6 solution into tube • Dilute to 50 ml with DI water
Standardized By		Date Standardized	PREPARATION INSTRUCTIONS
Standardize cyanide stock solution A (1000 mg/L) against standard silver nitrate ($AgNO_3$) titrant as described in the SOP weekly.			Place in a 125 ml Erlenmeyer flask. • Cyanide stock solution A (1000 mg/L) Place in a 10 mL microburet 0.1920 N $AgNO_3$

*Standard Lot Number consists of standard ID, date prepared, and initials of preparer.

Reviewed By: _____ Date: _____

Attachment 3

Weekly Cyanide Stock Standardization Log

CompuChem a division of Liberty Analytical Corp. Logbook 1 UUUUU 1

Date	Lot # KCN Stock Standard *	Lot # Certified $AgNO_3$	Volume $AgNO_3$ Titrated for Standard (mL)	Volume $AgNO_3$ Titrated for Blanks (mL)	Concentration CN^- (g/l) **	Final Volume of New Stock Standard

* Prepared by dissolving 2.51g of KCN and 2.00g KOH in 900 mL DI water. This is standardized with certified 0.0192N silver nitrate ($AgNO_3$) and diluted to appropriate concentration to achieve 1 mL = 1mg CN^-.

Formula Conc. CN^- (mg/mL) = $\frac{\text{ml AgNO3 (std) - ml AgNO3(blk)}}{\text{25 ml KCN Stock}} \times \frac{\text{1 eq. AgNO3}}{\text{L}} \times \frac{\text{2 moles CN-}}{\text{1 eq. AgNO3}} \times \frac{\text{26.02g CN}^-}{\text{1 mole CN}^-}$

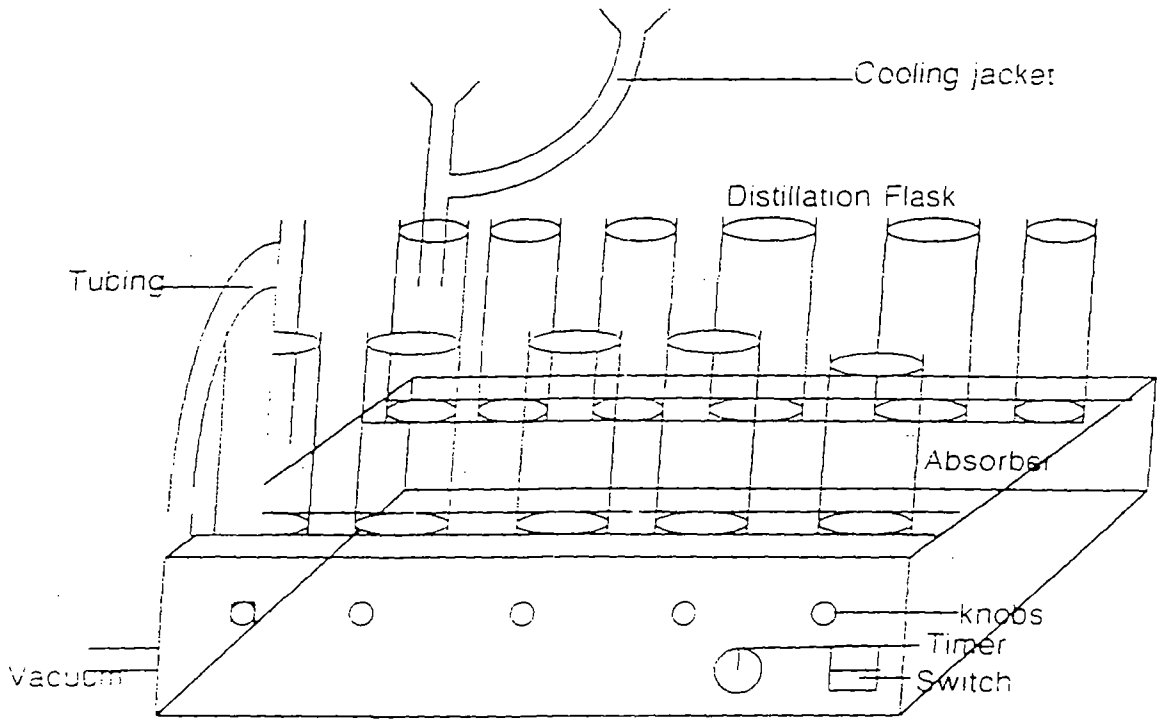
Final vol. requirement (mL) for new KCN Stock = Conc. mg/mL CN^- (calculated from titration) x 875 ml

** Reprepare KCN Stock Standard if < 0.9500mg/ml or > 1.050 mg/ml

Reviewed By: _____ Date: _____

Attachment 4

Cyanide Distillation Apparatus



Note the distillation flask and absorber are connected by a tube

Attachment 5

Cyanide Preparation Log

Method (circle one): CLP 335.3 SW-846: 9012A (Modified)

CompuChem a division of Liberty Analytical Corp.

Prep Log Generated on: 2/8/2001

Case/SDG: Prepared by: Date:

#	CCN (Lab ID)	Client ID	Date Rec'd	Initial mL g	Final (mL)	Description Before	Description After	S-*	Cl2*	pH	Amen Prep
1											
2											
3											
4											
5											
6											
7											
8											
9											
10											
11											
12											
13											
14											
15											
16											
17											
18											
19											
20											
21	Sample Spike:					Ref CCN # : ( )					
22	Sample Spike Dup:					Ref CCN # : ( )					
23	Duplicate Sample:					Ref CCN # : ( )					
24	Lab Control Sample:					Reviewed by:					
25	Prep Blank:					Date:					

QC (SS) :

REF #:

QC (LCS) :

REF #:

NaOH:
Lot #:
Ref #:
MgCl2:
Lot #:
Ref #:
H2SO4:
Lot #:
Ref #:
CN Stock Std. Ref #:
CN Intermediate Ref #:
Calcium Hypochlorite:
Lot #:
Ref #:
Ascorbic Acid:
Lot #:
Ref #:

Check if prepared
LRS 40 ppb=0.2ml 10ppm
MRS 100 ppb=0.5ml 10ppm
HRS 300 ppb=1.5ml 10ppm

Chlorination Time
Start:
Stop:
Distillation Time
Start:
Stop:
Cool Down Time
Start:
Stop:

LRS=Low-range standard MRS=Mid-range standard HRS=High-range standard *D = Detected *ND = Not Detected

Attachment 6

Analyst Capability Study

Laboratory Name/North Carolina Certificate Number: CompuChem/79				
Analyst: Lori Cooke				
Method: Cyanide in Water, 9012A				
Date	Sample ID	Std.Lot #	True Value	mg/L
			mg/L	
8/24/99	965655	7M1-7-6	90	98.3
10/5/99	968409	7M1-7-6	90	101.7
11/4/99	960046	7M1-7-6	90	98.0
12/8/99	952212	7M1-7-6	90	86.9
			Mean	96.2
			Std.deviation	6.4
			% RSD	6.7

Instrument Procedure 930: Cyanide **Analysis of** Water and Soil/Sediment Distillates by CLP, MCAWW, SW846, NYSASP, and Lachat

1.0 Scope and Application

This procedure is applicable to the determination of total cyanide in water wastes, including soils/sediments, at concentrations of 10 ppb-200 ppb for CLP and MCAWW and 10ppb-400 ppb for SW846. The method detects inorganic cyanides that are present as either soluble salts or complexes. **The procedure for calculating cyanide amenable to chlorination is also included.**

The current method detection limits (MDL) and reporting limits are shown in Attachment 1.

Staff members performing the procedures described in this SOP are responsible for reading, understanding, and complying with the SOP requirements. Supervisors are responsible for directing the analyst to the controlled SOP, and providing adequate explanation of the material contained therein.

This procedure is restricted to use by or under the supervision of analysts experienced in the instrumentation or preparative methods and who have demonstrated the ability to generate acceptable results through QC samples and analyst capability studies.

2.0 Summary

Total cyanide from alkaline distillates of water and soil/sediment is converted to cyanogen chloride, CNCl, by reaction with choramine-T at pH lower than 8. The CNCl then forms a red-blue dye reacting with pyridine-barbituric acid reagent. The color is read at 570 nm. The concentration of NaOH must be the same in the standards, the scrubber solutions, and any dilution of the original scrubber solutions to obtain colors of comparable intensity.

Prior to analysis samples are distilled according the Sample Preparation Procedure –072, "Aqueous Sample Midi-Distillation by CLP and NYSASP," Sample Preparation Procedure –093, "Aqueous Sample Cyanide Midi-Distillation for Cyanide by SW846 and NYSASP," Sample Preparation Procedure –139, "Solid Sample for Total Cyanide Midi-Distillation by CLP and NYSASP," or Sample Preparation Procedure –191, "Solid Sample for Total Cyanide Midi-Distillation by SW846 and NYSASP."

Amendable cyanide is calculated by subtracting the amount of cyanide determined in the pre-treated sample (using Sample Preparation Procedure –094, "Midi Distillation of Aqueous Samples for Amenable Cyanide by CLP and NYSASP" or following Sample Preparation Procedure –245: Cyanide

Extraction Procedure for Solids and Oils by SW846") from the amount of total cyanide determined from the untreated sample distillate.

3.0 Definitions

3.1 Method detection limit (MDL) – The minimum concentration of an analyte that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined form analysis of a sample in a given matrix containing the analyte (40 CFR, Part 136, Appendix B.)

3.2 Reporting Limit – The laboratory reporting limit is based on the lowest multipoint calibration standard concentration. For some inorganic methods, the reporting limit is based on the MDL, and is usually 4-8 times higher than the MDL. For organic methods, values detected below the reporting limit and above the MDL may be reported and qualified as an estimated concentration.

3.3 Reporting Units – (will vary with the method)

3.4 An SDG is defined by the following, whichever is more frequent:

- each 20 field samples received within a case, or
- each 14 calendar day period during which field samples in a case are received (7 calendar days for NYSASP, OLM04.0, plus revisions, and ILM04.0, plus revisions including ILM04.1) beginning with the receipt of the first sample.

For total cyanide, most interferences are eliminated or minimized by the distillation procedure. Sulfides, fatty acids, aldehydes and thiocyanates may distill over.

4.0 Interferences

4.1 For total cyanide, most interferences are eliminated or minimized by the distillation procedure. Sulfides, fatty acids, aldehydes and thiocyanates may distill over.

5.0 Safety

5.1 Always wear the proper safety equipment (labcoat, safety glasses, and gloves) when performing this procedure.

5.2 Laboratory staff are encouraged to review the Chemical Hygiene Plan for general safety policies, and Material Safety Data Sheets for reagents used in the laboratory.

6.0 Equipment & Supplies

6.1 Cyanide manifold 10.204.00.1.A

6.2 Heating unit

6.3 Vacuum pump

7.0 Reagents & Standards

Note: Standard preparations and reagent lot numbers are documented on the Standards/QC Preparation for Cyanide Analysis on Lachat log (Attachment 2).

Note: To prevent bubble formation, degas all solutions except the standards using a vacuum pump.

7.1 Reagent Water-All water used during preparation should be reagent-grade Type I with regard to resistivity of > 10 megohm-cm (18th and 19th Editions of Standard Methods, Method 1080), and referred throughout this SOP as DI water.

7.2 Reagent 1 - Carrier, 0.25M NaOH

7.2.1 In a 1-L volumetric flask, dissolve 10.0 g of NaOH in 800 mL of water. Dilute to the mark and invert three times.

7.3 Reagent 2 - Phosphate Buffer

7.3.1 In a 1-L volumetric flask, dissolve 138 g of sodium dihydrogen phosphate (NaH_2PO_4 H_{20}) in 800 mL of water. Dilute to the mark and invert three times.

7.4 Reagent 3 - Chloramine-T

7.4.1 To a 500-mL volumetric flask, add 250 mL of water followed by 2 g of chloramine-T. Dilute to the mark and invert three times. Prepare fresh daily.

7.5 Reagent 4 - Pyridine-Barbituric Acid

CAUTION - Always use a fume hood when preparing this reagent. Always wear a face shield when dispensing concentrated acids.

7.5.1 In the fume hood, place 15.0 g of barbituric acid in a 1-L beaker and add 100 mL of water, rinsing down the sides of the beaker to wet the barbituric acid. Stir in 75 mL of pyridine (C_5H_5N) and mix until the barbituric acid dissolves. Add 15 mL of concentrated hydrochloric acid (12M HC1) and mix. Transfer to a 1-L volumetric flask, dilute to the mark, and invert three times.

7.6 Stock Standard at 1000.0 mg CN-/L

CAUTION - KCN IS HIGHLY TOXIC. AVOID INHALATION OF DUST. AVOID CONTACT WITH THE SOLID OR SOLUTIONS.

7.6.1 In a 1-L volumetric flask, dissolve 2.0 g of potassium hydroxide (KOH) in 500 mL of water. Add 2.5026 g of potassium cyanide (KCN). Dilute to the mark and invert three times. Prepare weekly.

7.7 Intermediate Standard at 10.0 mg CN-/L

7.7.1 Pipet 1.0 ml of the Stock Standard into a 100-ml volumetric flask. Dilute to the mark with Reagent 1. Invert three times. Prepare with each day of sample analysis.

7.8 Calibration Curve

7.8.1 Five working standards are prepared daily when samples are analyzed at 200, 100, 50, 20, 10 µg CN-/L for CLP.

7.8.1.1 To five 100-ml volumetric flasks add, respectively, 2.0, 1.0, 0.5, 0.2, and 0.1 ml of the 10 mg/L intermediate standard. Dilute to the mark with Reagent 1 and invert at least three times. A zero standard is used which contains only Reagent 1.

7.8.2 Six working standards are prepared daily when samples are analyzed at 400, 300, 200, 100, 40, 20, 10 ug/L for SW846.

7.8.2.1 To six 100-ml volumetric flasks add, respectively, 4.0, 3.0, 2.0, 1.0, 0.4, 0.2, and 0.1 ml of the 10 mg/L intermediate standard. Dilute to the mark with Reagent 1

and invert at least three times. A zero standard is used which contains only Reagent 1.

7.9 A duplicate must be analyzed from each group of samples of a similar matrix (up to 20 samples) or for each SDG.

A control limit of 20% for RPD shall be used for values greater than or equal to 5x CRDL/reporting limit or ± CRDL/reporting limit if either value is less than 5x CRDL/reporting limit.

8.0 Sample Collection, Preservation, & Storage

8.1 Oxidizing agents destroy cyanide during storage and handling. Add ascorbic acid to prevent this.

8.2 Because of the reactivity of cyanide, analyze samples immediately after collection.

8.3 If samples must be held, add NaOH to bring the pH to 12. The color reaction is pH sensitive. Therefore, distillates or preserved water samples and standards should be carefully matched with respect to NaOH concentration.

8.4 Samples are collected, preserved, and stored according to Sample Control SOPs 4.1 "Receiving Samples" and 4.6 "Storing Samples."

9.0 Quality Control

9.1 After instrument calibration, the correlation coefficient must be determined to be 0.995 or better before sample analysis can begin. An initial calibration verification (ICV) and initial calibration blank (ICB) must be analyzed. The ICV must be distilled with each batch of samples analyzed and the samples distilled with an ICV must be analyzed with that particular ICV. For aqueous cyanide samples, the ICV for cyanide also serves as the Laboratory Control Sample (LCS). The ICV must fall within 85-115% of the true value. The absolute ICB value must not be greater than the Contract Required Detection Limit (CRDL) or reporting limit. If these control limits cannot be met, determine and correct the problem, recalibrate and reanalyze until all control limits can be met. If instrument problems are suspect, notify your supervisor, document the problem in the maintenance log, and notify the instrumentation repair personnel.

9.2 A continuing calibration verification (CCV) and a continuing calibration blank (CCB) must be analyzed at a 10% frequency or every 2 hours

throughout the analytical run. The control limits for these are the same as for the ICV and ICB above. In the event of a CCV/CCB failure, determine and correct the problem, recalibrate the instrument, and reanalyze all affected samples.

9.3 A method blank should be analyzed for every 20 samples of a similar matrix or for each case, whichever is more frequent. The method blank value must not be greater than the reporting limit. If the blank exceeds the Contract Required Detection Limit (CRDL) or reporting limit, analysis is stopped, the problem is determined and corrected, and any affected samples are reanalyzed, or reprepped and reanalyzed. If the problem is with the instrumentation, the instrument should be fixed, recalibrated, and the affected samples rerun. Document the problem in the instrument maintenance log.

9.4 A laboratory control sample (LCS) must be analyzed with every 20 samples or with each case, whichever is more frequent. The LCS must agree within ± 20% of the true value. If the LCS falls outside these control limits, the analysis must be evaluated and it must be determined if an instrument problem exists. If so, the problem must be corrected and the affected samples reanalyzed. If not, the affected case must be reprepared and reanalyzed. As indicated, for aqueous cyanide samples, the ICV also serves as the LCS and it must be distilled. A separate LCS is required for soil cyanide samples.

9.5 For every 20 samples of a similar matrix or for each Case/SDG, whichever is more frequent, a matrix spike analysis must be performed. If the spike recovery is not within 75-125% recovery limits, and the sample result does not exceed 4x the spike added, a matrix interference is suspected. Spike the unspiked aliquot of the sample at 2x the indigenous level or 2x the CRDL/reporting limit, whichever is greater.

9.6 The distilled standards, i.e. a mid range standard for CLP and MCAWW and low and high range standards for SW846, are evaluated. The recoveries should be within +/-15% of the true value for CLP and MCAWW and +/-10% for SW846. If this criteria are not met, the analyst should find the cause of the apparent error before proceeding.

10.0 Calibration & Standardization

10.1 The stock cyanide solution is standardized weekly with 0.0192 N silver nitrate and Rhodanine indicator. Perform the standardization according to instructions on the attached Weekly Cyanide Stock Standardization Log

page (Attachment 3). Refer to the log page for the standardization calculation.

10.2 The instrument calibration curve is analyzed according to the sequence in section 11.0 (Procedure) below. The correlation coefficient must be 0.995 or greater for the calibration curve to be approved.

11.0 Procedure

Documentation must follow the requirements in QC SOP: Proper Documentation Procedures.

11.1 Timing

11.1.1 Sample throughput: 80 samples/h; 40s/samples

11.1.2 Pump speed: 35

11.1.3 Cycle period: 45s

11.1.4 Inject to start of peak period: 28s

11.1.5 Inject to end of peak period: 61s

11.2 System Notes

11.2.1 Allow 15 min for heating unit to warm up to 60°C.

11.2.2 Analyze distillates from water and soil/sediment preparation.

11.3 Operating System

11.3.1 Inspect the manifold for proper connections

11.3.2 Turn on the power to the instrument.

11.3.3 Secure the pump cassettes and place transmission lines in the corresponding solutions.

11.3.4 Select and download the method for cyanide (CN for SW846 or CLPCN for CLP.)

11.3.5 Allow the system to pump until the baseline is steady.

11.3.6 Place the standards in the rack in descending order of concentration.

11.3.7 "Submit and Calibrate Now" in software to begin calibration.

11.3.8 Under "Edit and Identification" enter the sample laboratory numbers and client ID numbers.

11.3.9 Once calibration is approved and sample tray is poured up, the tray can be submitted. Under "Submit", you can now submit the current tray.

11.3.10 When the tray is complete, rinse the lines and place in DI water.

11.3.11 When the manifold has been flushed with DI water, remove the lines and allow the system to continue pumping until all lines are dry.

11.3.12 Turn off pump and remove all cassettes.

11.3.13 Turn off power to the instrument.

12.0 Data Analysis & Calculations

Calculations must be consistent with the QC SOP: Numerical Data Reduction.

12.1 Calculation of the mean or average of a set of values:

$$\overline{X} = \frac{\sum_{i=1}^{n} X_i}{n}$$

where: n = total number of values
x_i = each individual value used to calculate the mean
x = the mean of n

12.2 Calculation of the standard deviation of a set of values:

$$\text{Standard deviation} = \sqrt{\frac{\sum_{i=1}^{n}\left(X_n - \overline{X}\right)^2}{n-1}}$$

12.3 Calculation of percent recovery:

12.3.1 LCS and surrogates:

$$\%R = \frac{Amount\ found}{Amount\ spiked} x\ 100$$

12.3.2 Matrix spikes:

$$\%\,R = \frac{Amount\ in\ spiked\ sample - Amount\ in\ unspiked\ (native)\ sample}{Amount\ spiked} x\ 100$$

12.4 Calculation of % RSD

$$\%RSD = \left(\frac{Standard\ deviation}{\overline{X}}\right) \times 100$$

12.5 Calculation of RPD

$$RPD = \frac{|Value\ 1\ -\ Value\ 2|}{(Value\ 1\ +\ Value\ 2)/2} x100$$

12.6 Calculation of %Difference (%D)

$$\%Diff = \frac{Value\ -\ \overline{Reference\ \ value}}{\overline{Reference\ \ value}} x\ 100$$

12.7 Concentration

12.7.1 Calculate the **total** cyanide in aqueous samples in µg/L as follows:

$$CN, ug/L = \frac{(A)(D)(F)}{(B)}$$

Where, A = µg/L CN of sample from regression analysis
B = Liter of original sample for distillation (0.050L, typically)
D = Any dilution factor
F = Sample receiving solution volume (0.050L, typical)

12.7.2 Calculate the **total** cyanide in soil/sediment samples in mg/kg as follows:

$$CN, ug/kg = \frac{(A)(D)(F)}{(B)(E)}$$

Where, A = µg/L CN of sample from regression analysis
B = Wet weight of original sample
D = Any dilution factor
E = % solids
F = Sample receiving solution volume

12.7.3 Calculate amenable cyanide as follows:

$$Amenable\ CN, ug/L = total\ CN - chlorinated\ CN$$

12.6 Example dilution calculation

Any sample with a value for total cyanide that exceeds the upper calibration range, must be analyzed at a dilution. For example, if a 5x dilution is determined to be needed, 1ml sample is added to 4ml 0.25 NaOH.

13.0 Method Performance

This method was validated through in-house laboratory studies of method detection limits (Attachment 1) and precision and accuracy for single analyst (Attachment 3). The data are retained by the QA department.

14.0 Pollution Prevention

The solvents used in this procedure pose little threat to the environment when recycled and managed properly. Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best thing.

15.0 Waste Management

It is the laboratory's responsibility to comply with all federal, state, and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions, and to protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Compliance with all sewage discharge permits and regulations is also required.

Samples preserved with HCl, HNO_3, NaOH, Zn Acetate, or H_2SO_4 to pH <2 are hazardous and must be neutralized before being disposed, or must be handled as hazardous waste.

Refer to the Hazardous Waste Management and Safety SOPs located in the lab.

16.0 References

16.1 U.S. EPA CLP SOW ILM04.0, with revisions including ILM04.1, EPA 335.2 CCP-M

16.2 The New York State Analytical Services Protocol (NYSASP), 6/2000, plus revisions

16.3 Test Methods for Evaluating Solid Wastes, Physical/Chemical Methods, 3rd Edition, Update III, 12/96, Method 9010B and 9012A

16.4 Methods for Chemical Analysis of Water and Wastes, March 1983, Methods 335.2 and 335.3

16.5 Lachat QuickChem AE, Method 10-204-001-1-A, November 1992

16.6 QCSOP: Proper Documentation Procedures

16.7 QCSOP: Numerical Data Reduction

16.8 "Less is Better: Laboratory Chemical Management for Waste Reduction," American Chemical Society Department of Government Relations and Science Policy, 1155 16th Street, N.W., Washington DC, 20036, (202) 872-4477.

16.9 Hazardous Waste Management & Safety SOPs: "Hazardous Waste Disposal" and "Spill Control & Cleanup."

16.10 NELAC Standards, July 1, 1999, plus revisions

16.11 QA-G6: Guidance for the Preparation of Standard Operating Procedures for Quality-Related Operations EPA/600/R-96/027, November 1995.

16.12 New York State Environmental Laboratory Approval Program, Certification Manual, October 15, 1999, plus revisions.

16.13 CompuChem Quality Manual, Revision 0, 2/1/00

16.14 Sample Preparation Procedure –072, "Aqueous Sample Midi-Distillation by CLP and NYSASP"

16.15 Sample Preparation Procedure –093, "Aqueous Sample Cyanide Midi-Distillation for Cyanide by SW846 and NYSASP"

16.16 Sample Preparation Procedure –139, "Solid Sample for Total Cyanide Midi-Distillation by CLP and NYSASP"

16.17 Sample Preparation Procedure –191, "Solid Sample for Total Cyanide Midi-Distillation by SW846 and NYSASP"

16.18 Sample Preparation Procedure –094, "Midi Distillation of Aqueous Samples for Amenable Cyanide by CLP and NYSASP"

16.19 Sample Preparation Procedure –245: Cyanide Extraction Procedure for Solids and Oils by SW846" with Sample Preparation Procedure

17.0 Attachments as Tables, Diagrams, Flowcharts & Validation Data

17.1 Attachment 1 – MDL Study

17.2 Attachment 2 – Standards/QC Preparation for Cyanide by Lachat Log

17.3 Attachment 3 – Weekly Cyanide Stock Standardization Log

17.4 Attachment 4 – Cyanide Analysis Log

17.5 Attachment 5 – Single Analyst Capability Study

Attachment 1

CompuChem Method Detection Limit Study

Study Date: January 14, 2000					Aqueous Distilled Cyanide Methods 9010B, 9012A								
Instrument: Lachat													
Parameter	Rep#1	Rep#2	Rep#3	Rep#4	Rep#5	Rep#6	Rep#7	Rep#8	Mean	Amt.	S.Dev.	MDL	Report Limit
	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L
Cyanide	11.7	10.1	10.8	10.8	10.7	11.2	10.8	11.5	10.95	10.0	0.50	1.51	10.0
Study Date: January 14, 2000					Solid Distilled Cyanide Methods 9010B, 9012A								
Instrument: Lachat													
Parameter	Rep#1	Rep#2	Rep#3	Rep#4	Rep#5	Rep#6	Rep#7	Rep#8	Mean	Amt.	S.Dev.	MDL	Report Limit
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
Cyanide	0.535	0.515	0.525	0.540	0.530	0.515	0.530	0.535	0.53	0.50	0.01	0.03	0.50

Attachment 1 (continued)

CompuChem Method Detection Limit Study

Study Date: January 14, 2000					Aqueous Distilled Cyanide Method ILM04.0								
Instrument: Lachat													
Parameter	Rep#1	Rep#2	Rep#3	Rep#4	Rep#5	Rep#6	Rep#7	Rep#8	Mean	Amt.	S.Dev.	MDL	Report Limit
	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L
Cyanide	10.8	10.1	10.5	10.2	10.4	10.9	10.6	11.2	10.59	10.0	0.37	1.10	10.0
Study Date: January 14, 2000					Solid Distilled Cyanide Method ILM04.0								
Instrument: Lachat													
Parameter	Rep#1	Rep#2	Rep#3	Rep#4	Rep#5	Rep#6	Rep#7	Rep#8	Mean	Amt.	S.Dev.	MDL	Report Limit
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
Cyanide	0.53	0.53	0.54	0.54	0.52	0.52	0.52	0.52	0.53	0.50	0.01	0.02	0.50

Attachment 2

Standards/QC Preparation for Cyanide by Lachat

COMPUCHEM a division of Liberty Analytical. Corp.. LOGBOOK 1 O(5) 11 Page 1 of 4

STANDARDS AND REAGENTS TRACEABILITY	
Potassium Cyanide	Ref# 1M2-
Potassium Hydroxide	Ref# 7M1-
Sodium hydroxide Pellets	Ref# 1M2-
Chloramine-T	Ref# 1M2-
Hydrochloric Acid	Ref# 1M2-
Barbituric Acid	Ref# 1M2-
Pyridine	Ref# 1M2-
Sodium Phosphate	Ref# 1M2-
Silver Nitrate	Ref# 1M2-
ICV-6	Ref# 7M1-
STANDARD LOT NUMBER	**PREPARATION INSTRUCTIONS**
CN1000 mg/L-__ __ __ __ __ __ __ - __ __	Place in a 1000 ml volumetric flask: • Standardized value is _____ mg/L • 2.510 g of dried KCN • 2.0 g of KOH Dilute to mark with DI water and mix well
CN10 mg/L-__ __ __ __ __ __ __ - __ __	Place in a 50 ml volumetric flask: Volume (mL) of stock = $\frac{05 \times 1000}{\text{Value of stock CN in (mg/L)}}$ Pipet 0.5 mL of stock cyanide standard into the flask Dilute to the mark with 0.25 NaOH solution and mix well
CN400-__ __ __ __ __ __ __ - __ __	Place in a 100 ml volumetric flask: 400 µg/L standard Pipet 4.0 ml of 10 mg/L cyanide solution into the flask. Dilute to 100 ml with 0.25 N NaOH and mix well

*Standard Lot Number consists of standard ID, date prepared, and initials of preparer.

Reviewed By: _____ Date: _____

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Attachment 2 (continued)

Standards/QC Preparation for Cyanide by Lachat

COMPUCHEM a division of Liberty Analytical. Corp.. LOGBOOK 1 O(5) 11 Page 2 of 4

STANDARD LOT NUMBER	PREPARATION INSTRUCTIONS
CN100-__ __ __ __ __ __ -__ __	Place in a 100 ml volumetric flask: 100 µg/L standard Pipet 1.0 ml of 10 mg/L cyanide solution into the flask. Dilute to 100 ml with 0.25 N NaOH solution
CN200-__ __ __ __ __ __ -__ __	Place in a 100 ml volumetric flask: 200 µg/L standard Pipet 2.0 ml of 10 mg/L cyanide solution into the flask. Dilute to 100 ml with 0.25 N NaOH solution
CN300-__ __ __ __ __ __ -__ __	Place in a 100 ml volumetric flask: 300 µg/L standard Pipet 3.0 ml of 10 mg/L cyanide solution into the flask. Dilute to 100 ml with 0.25 N NaOH solution
CN50-__ __ __ __ __ __ -__ __	Place in a 100 ml volumetric flask: 50 µg/L standard Pipet 0.5 ml of 10 mg/L cyanide solution into the flask. Dilute to 100 ml with 0.25 N NaOH solution.
CN40-__ __ __ __ __ __ -__ __	Place in a 1000 ml volumetric flask: 40 µg/L standard Pipet 0.4 ml of 10 mg/L cyanide solution into the flask. Dilute to 100 ml with 0.25 N NaOH solution.
CN20-__ __ __ __ __ __ -__ __	Place in a 100 ml volumetric flask: 20 µg/L standard Pipet 0.2 ml of 10 mg/L cyanide solution into the flask. Dilute to 100 ml with 0.25 N NaOH solution
CN10-__ __ __ __ __ __ -__ __	Place in a 1000 ml volumetric flask: 10 µg/L standard Pipet 0.1 ml of 10 mg/L cyanide solution into flask. Dilute to 100 ml with 0.25 N NaOH solution

*Standard Lot Number consists of standard ID, date prepared, and initials of preparer.

Reviewed By: _____ Date:_____

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Attachment 2 (continued)

Standards/QC Preparation for Cyanide by Lachat

COMPUCHEM a division of Liberty Analytical. Corp.. LOGBOOK 1 O(5) 11 Page 3 of 4

STANDARD LOT NUMBER	PREPARATION INSTRUCTIONS
Blank-__ __ __ __ __ __ -__ __	0.25 N NaOH solution Dissolve a 10 g of NaOH into a 1000-ml volumetric flask: with DI water
Chloramine-T-__ __ __ __ __ __ -__ __	Dissolve (by swirling) in a 500-ml volumetric flask containing 400 ml of deionized water: • 2.0 g of Chloramine-T Bring to volume with DI water, and mix until homogeneous.
Pyridine barbituric acid -__ __ __ __ __ __ -__ __	Into a 1000 ml volumetric flask add: • 15.0 g of barbituric acid and just enough DI water to wash the sides of the flask and wet the barbituric acid. • Add 75 mL of pyridine and mix. • Add 15 mL of concentrated HCl, mix and cool. • Dilute to 1000 mL with DI water and mix. • Store in a cool, 4°C dark place
Phosphate Buffer-__ __ __ __ __ __ -__ __	Place in a 1000 ml volumetric flask containing 800 ml of deionized water: • 138 g of $Na_2HPO_4 \bullet H_2O$ Mix vigorously until the salts have dissolved. Bring to volume and continue to mix until homogeneous.
Adjusted DI H_2O-__ __ __ __ __ __ -__ __	Place in a 1000 ml volumetric flask containing 800 ml of deionized water • 10 g of NAOH pellets swirl to dissolve. Bring to volume with DI water.
LRS-__ __ __ __ __ __ -__ __	Place in a 50 ml glass sample tube • Pipet 0.2 ml of 10 mg/L cyanide solution into tube • Dilute to 50 ml with DI water • True Value = 40 µg/L
MRS-__ __ __ __ __ __ -__ __	Place in a 50 ml glass sample tube • Pipet 0.5 ml of 10 mg/L cyanide solution into tube • Dilute to 50 ml with DI water • True Value = 100 µg/L

*Standard Lot Number consists of standard ID, date prepared, and initials of preparer.

Reviewed By: _____ Date:_____

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Attachment 2 (continued)

Standards/QC Preparation for Cyanide by Lachat

COMPUCHEM a division of Liberty Analytical. Corp.. LOGBOOK 1 O(5) 11 Page 4 of 4

STANDARD LOT NUMBER			PREPARATION INSTRUCTIONS
HRS-__ __ __ __ __ __ -__ __			Place in a 50 ml glass sample tube • Pipet 1.5 ml of 10 mg/L cyanide solution into tube • Dilute to 50 ml with DI water • True Value = 300 µg/L
ICV-__ __ __ __ __ __ -__ __			Place in a 50 ml glass sample tube • Pipet 0.5 ml of ICV 6 solution into tube • Dilute to 50 ml with DI water
Standardized By		Date Standardized	PREPARATION INSTRUCTIONS
Standardize cyanide stock solution A (1000 mg/L) against standard silver nitrate ($AgNO_3$) titrant as described in the SOP weekly.			Place in a 125 ml Erlenmeyer flask. • Cyanide stock solution A (1000 mg/L) Place in a 10 mL microburet 0.1920 N $AgNO_3$

*Standard Lot Number consists of standard ID, date prepared, and initials of preparer.

Reviewed By: _____ Date:_____

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Attachment 3

Weekly Cyanide Stock Standardization Log

CompuChem a division of Liberty Analytical Corp. Logbook 1 U(5) 2

Date	Lot # KCN Stock Standard	Lot # Certified $AgNO_3$	Volume $AgNO_3$ Titrated for Standard (mL)	Volume $AgNO_3$ Titrated for Blanks (mL)	Concentration* CN^- (mg/L)	Pass/Fail**	Comments

** Re-prepare KCN Stock Standard if < 950 mg/L or > 1050 mg/L (95% of expected)

$$*Conc.CN^-(mg/L) = \frac{ml\ AgNO_3(std) - ml\ AgNO_3(blk)}{25ml\ KCN\ stock(titrant)} x\ N\ AgNO_3\ x\ \frac{1eq.AgNO_3}{L}\ x\ \frac{2moles\ CN^-}{1eq.AgNO_3}\ x\ \frac{26.02CN^-}{1mole\ CN^-}\ x\ \frac{1000mg}{1g}$$

Reviewed By. _____ Date: _____

11/20/00:mlj

Attachment 4

Cyanide Analysis Log
(Lachat 10-204-001-1-A)
CompuChem a division of Liberty Analytical Corp. Logbook 1 I 23

Page ____ of ____

Method (**Circle One**) CLP – ILM04.0/ILM04.1
SW-846 – 9010B/9012A
MCAWW – 335.2/335.3

Case Name: _____
_____
_____

Operator: _____

Date: _____

File Name: _____

#	Sample ID	Comments	#	Sample ID	Comments
	S400 S300		3		
	S200 S100		4		
	S50 S40		5		
	S20 S10		6		
	S0		7		
	ICV		8		
	ICB		9		
	CCV		10		
	CCB			CCV	
1				CCB	
2			1		
3			2		
4			3		
5			4		
6			5		
7			6		
8			7		
9			8		
10			9		
	CCV		10		
	CCB			CCV	
1				CCB	
2			1		

Reviewed by: _____ **Date:** _____

Rev 1/16/01:mlj

Attachment 4 (continued)

Cyanide Analysis Log
(Lachat 10-204-001-1-A)
CompuChem a division of Liberty Analytical Corp. Logbook 1 I 23

Page ____ of ____

Method (Circle One) CLP – ILM04.0/ILM04.1
SW-846 – 9010B/9012A
MCAWW – 335.2/335.3

Case Name: _____

Operator: _____

Date: _____

File Name: _____

#	Sample ID	Comments	#	Sample ID	Comments
2			1		
3			2		
4			3		
5			4		
6			5		
7			6		
8			7		
9			8		
10			9		
	CCV		10		
	CCB			CCV	
1				CCB	
2			1		
3			2		
4			3		
5			4		
6			5		
7			6		
8			7		
9			8		
10			9		
	CCV		10		
	CCB			CCV	
				CCB	

Reviewed by: _____ **Date:** _____

Rev. 1/16/01:mlj

Attachment 5

Analyst Capability Study

Laboratory Name/North Carolina Certificate Number: CompuChem/79

Analyst: Lori Cooke

Method: Cyanide in Water, ILM04.0

Date	Sample#	Std.Lot #	rue Value mg/L	mg/L
8/24/99	965655	7M1-7-6	90	98.3
10/5/99	968409	7M1-7-6	90	101.7
11/4/99	960046	7M1-7-6	90	98.0
12/8/99	952212	7M1-7-6	90	86.9
			Mean	96.2
			Std.dev.	6.4
			% RSD	6.7

Method: Cyanide in Soil, ILM04.0

Date	Sample#	Std.Lot #	rue Value	mg/Kg	% Rec
10/21/99	962562	7M3-3-13	5.6	5.80	103.6
10/27/99	963630	7M3-3-13	5.6	5.52	98.6
11/23/99	968805	7M1-9-1	5.6	5.42	96.7
1/31/00	WG1282-2	7M1-9-1	5.6	5.71	102.0
				Mean	100.2
				Std.dev.	3.1
				% RSD	3.1

Method: Cyanide in Water, 9012A

Date	Sample#	Std.Lot #	TrueVal mg/L	mg/L
8/24/99	965655	7M1-7-6	90	98.3
10/5/99	968409	7M1-7-6	90	101.7
11/4/99	960046	7M1-7-6	90	98.0
12/8/99	952212	7M1-7-6	90	86.9
			Mean	96.2
			Std.dev.	6.4
			% RSD	6.7

Method: Cyanide in Soil, 9012A

Date	Sample#	Std.Lot #	rue Value mg/Kg	mg/Kg	% Rec
10/21/99	962562	7M3-3-13	5.6	5.80	103.6
10/27/99	963630	7M3-3-13	5.6	5.52	98.6
11/23/99	968805	7M1-9-1	5.6	5.42	96.7
1/31/00	WG1282-2	7M1-9-1	5.6	5.71	102.0
				Mean	100.2
				Std.dev.	3.1
				% RSD	3.1

CompuChem
a division of Liberty Analytical Corporation
501 Madison Avenue
Cary, NC 27513

SOP DOCUMENTATION FORM

This form must accompany all new and revised Standard Operating Procedures (SOPs) when you turn them in to Quality Assurance for review. Please fill out the entire shaded area (except effective date).

This is a new procedure ____ revised procedure ✓ outdated procedure (archive) ____

- Procedure area, title, and SOP number: Section #: 3.5.19.1 — Effective date: (QA fills in) 11/3/00
  IP 610: Non Filterable Residue: Total Suspended Solids by MCAWW
- Procedure prepared by: Linda Carter — Date: 10/12/00
- Procedure approved by: (If the manager prepared the SOP, a qualified second party should sign) Bob Mauer — Date: 10/12/00
- Reason for change: NELAC format changes, annual review
- This procedure meets the requirements of the following approved method references:
  Methods for Chemical Analysis of Water & Wastes, 3/83, Method 160.2; New York State Analytical Services Protocol, 10/95, NYSASP

Procedure approved by Quality Assurance Representative: Date:
(Not needed if signed above)

_____ _____

Effective 1-1-96, on an annual basis: Lab managers are required to review lab practices and revise the SOP if necessary. If no revision is necessary, indicate by your signature that the SOP has been reviewed.

Annual Review—Signature: _____ Date: _____

Annual Review—Signature: _____ Date: _____

Annual Review—Signature: _____ Date: _____

Instrument Procedure 610: Nonfilterable Residue; Total Suspended Solids, by MCAWW

1.0 Scope and Application

This method is used to determine total suspended solids in drinking, surface, and saline waters, **domestic and industrial wastes**.

A method detection limit is not applicable to this determination. The reporting limit is 1.0 mg/L and is adjusted based on the volume of sample used. This is discussed in detail below.

Staff members performing the procedures described in this SOP are responsible for reading, understanding, and complying with the SOP requirements. Supervisors are responsible for directing the analyst to the controlled SOP, and providing adequate explanation of the material contained therein.

This procedure is restricted to use by or under the supervision of analysts experienced in the instrumentation or preparative methods and who have demonstrated the ability to generate acceptable results through QC samples and analyst capability studies.

2.0 Summary of Method

A well-mixed sample is filtered through a glass fiber filter disc (2.1 cm) and the non-filterable residue on the filter is dried to a constant weight at 103-105°C.

3.0 Definitions

3.1 Non-filterable residue - the solid mass retained by a glass fiber filter disc and dried to a constant weight at 103-105°C.

3.2 **Method detection limit (MDL) – The minimum concentration of an analyte that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte (40 CFR, Part 136, Appendix B.)**

3.3 **Reporting Limit – The laboratory reporting limit is based on the lowest multipoint calibration standard concentration. For some inorganic methods, the reporting limit is based on the MDL, and is usually 4-8 times higher than the MDL. For organic methods, values detected below the reporting limit**

taken in selecting the filtering apparatus so that washing the filter and any dissolved solids in the filter minimizes this potential interference.

5.0 Safety

Appropriate protective equipment and clothing must be used under the assumption that all samples are potentially hazardous. During sample preparation safety glasses, gloves and lab coats are a minimum requirement. The persistent presence of noxious odors may be indicative of failure of the laboratory ventilation system and must be reported to a supervisor or manager.

Laboratory staff are encouraged to review the Chemical Hygiene Plan for general safety policies, and Material Safety Data Sheets (MSDS) for reagents used in the laboratory. The MSDS are located in the Quality Assurance department.

6.0 Equipment & Supplies

6.1 **"ProWeight Filters" pre-weighed 4.7 mm glass fiber filters catalog number F93447mm from Environmental Express, or equivalent**

6.2 Suction flasks

6.3 Drying oven--103-105°C

6.4 Dessicator

6.5 Analytical balance, capable of weighing to 0.1 mg

7.0 Reagents & Standards

7.1 Reagent water - All water used during preparation should be reagent-grade Type I with regard to resistivity of >10 megohm-**cm (18th and** 19th Editions of Standard Methods, Method 1080), and referred throughout this SOP as DI water.

8.0 Sample Collection, Preservation, & Storage

8.1 **Samples are collected, preserved, and stored according to the tables in Sample Control SOP 4.1, "Receiving Samples" and 4.6, "Storing Samples." Sample holding times are also listed.**

8.2 **Preservation of the sample is not practical; analysis should begin as soon as possible. Refrigeration at 4°C, to minimize microbiological decomposition of solids, is recommended. The holding time is seven days.**

11.1.2 An initial weight is located on the tin. Remove the tin and weigh the filter. Record the weight on the Residue Determination Log.

Note: The filter weight does not include the tin.

11.2 Selection of sample volume

11.2.1 For a 4.7 mm diameter filter, filter 100 ml of sample. If the weight of captured residue is less than 1.0 mg, the sample must be increased to provide at least 1.0 mg of residue. Minimum field sample volume is 300 ml up to 1000 ml. Additional aliquots of sample may be added to the filter when increasing the sample amount to collect more residue.

Note: If other filter diameters are used, start with a volume of sample equal to 7ml/cm2 of filter area and collect at least 1.0 mg.

11.2.2 If greater than 200 mg are contained on the filter, a lesser sample volume must be used that results in a filter charged with 1-200 mg sample residue.

11.2.3 The reporting limit is adjusted based on the sample volume used. If there is not enough sample provided to filter 1000 ml, the reporting limit should be adjusted accordingly, and the value obtained is a qualified estimated value. The reporting limit for each sample is based on the volume of sample filtered. For example, a reporting limit of <4.0 mg/L would be reported if only 250 ml of sample was available for filtering. If one liter is filtered and the residue collected is <1.0 mg, the reporting limit is <1.0 mg/L.

11.2.4 The true value may vary with each lot of LCS solution purchased from the vendor. The volume of LCS solution filtered depends on the true value and must always yield >1.0 mg of residue charged to the filter.

11.2 TSS determination

11.2.1 Using forceps, remove filter from tin and assemble the filtering apparatus and begin suction. Wet the filter with a small volume of DI water to seat it against the fritted support.

11.2.2 Shake the sample vigorously and quantitatively transfer a 100 ml sample aliquot to the filter using a graduated cylinder.

- **Plot the observed time versus volume filtered. Select the proper filtration volume as that just short of the time a significant change in filtration rate occurred.**

12.0 Data Analysis & Calculations

Calculations must be consistent with the QC SOP: Numerical Data Reduction.

12.1 Calculation of the mean or average of a set of values:

$$\overline{X} = \frac{\sum_{i=1}^{n} X_i}{n}$$

where: n = total number of values
x_i = each individual value used to calculate the mean
x = the mean of n

12.2 Calculation of the standard deviation of a set of values:

$$\text{Standard deviation} = \sqrt{\frac{\sum_{i=1}^{n}\left(X_n - \overline{X}\right)^2}{n-1}}$$

12.3 Calculation of percent recovery:

12.3.1 LCS and surrogates:

$$\%R = \frac{Amount\ found}{Amount\ spiked}\ x\ 100$$

12.3.2 Matrix spikes:

$$\%\,R = \frac{Amount\ in\ spiked\ sample\ -\ Amount\ in\ unspiked\ (native)\ sample}{Amount\ spiked}\ x\ 100$$

12.4 Calculation of % RSD

15.0 Waste Management

It is the laboratory's responsibility to comply with all federal, state, and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions, and to protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Compliance with all sewage discharge permits and regulations is also required.

Samples preserved with HCl, HNO_3, or H_2SO_4 to pH <2 are hazardous and must be neutralized before being disposed, or must be handled as hazardous waste.

Refer to the Hazardous Waste Management and Safety SOPs located in the lab.

16.0 References

16.1 Methods for Chemical Analysis of Water and Wastes, EPA 600/4-79-020, Method 160.2.

16.2 **Standard Methods for the Examination of Water and Wastewater, 18th Edition (1992) and 19th Edition (1995), upon promulgation, Method 1080**

16.3 **New York State Analytical Services Protocol (NYSASP), 10/95**

16.4 **QCSOP: Proper Documentation Procedures**

16.5 **QCSOP: Numerical Data Reduction**

16.6 **"Less is Better: Laboratory Chemical Management for Waste Reduction," American Chemical Society Department of Government Relations and Science Policy, 1155 16th Street, N.W., Washington DC, 20036, (202) 872-4477.**

16.7 **Hazardous Waste Management & Safety SOPs: "Hazardous Waste Disposal" and "Spill Control & Cleanup."**

16.8 **NELAC Standards, July 1, 1999, plus revisions**

16.9 **QA-G6: Guidance for the Preparation of Standard Operating Procedures for Quality-Related Operations EPA/600/R-96/027, November 1995.**

16.10 **New York State Environmental Laboratory Approval Program, Certification Manual, October 15, 1999, plus revisions.**

Attachment 1

CompuChem a division of Liberty Analytical Corp.. LOGBOOK 1 S(5) 4 Page ____ of ____

Residue Determination Log

Filterable Residue (TDS) EPA 160.1
Non-Filterable Residue (TSS) EPA 160.2
_____
Total Residue EPA 160.3

Case/SDG: _____

Oven Temp: In: **/Out:**
TDS:
TSS:
TS:

Analyst: **Date:** / /

Dish #	CompuChem ID	Client ID	Dish Tare (g)	Gross Weight Dish + Residue (g) init:final wt.	Net Residue (g)	Sample Volume (ml)	Concentrat. to Report (mg/L)	Comment
	LCSW	QC:						
	PBW	Blank						

Calculation: mg/L total dissolved solids = $\frac{\text{gross weight - tare weight (mg)}}{\text{sample volume (L)}}$
mg/L total suspended solids = $\frac{\text{gross weight – tare weight (mg)}}{\text{sample volume (L)}}$

LCS Acceptance Range= ± 10%

Comments:

Reviewed By: _____ Date: _____

Control Copy #: 1-QA

@ Air Toxics Limited
STANDARD OPERATING PROCEDURE

RECEIVING, LOGIN, AND TRACKING OF SAMPLES

SOP #50

Revision Date:	01/31/00
Revision #:	2
Reason for Revision:	To meet NELAP requirements and add login section.

	Signature	Print	Title	Date
Updated By:	Camelia Nyegre	Camelia Nyegre	QA Officer	1-31-00
Technical Review:	[illegible]	SAM CADWELL	Review	1/31/00
QA Review:	Ravi Sandhu	RAVI SANDHU	QA MANAGER	1/31/00
Laboratory Director:	Linda L. Freeman			1-31-00

1.0 SCOPE AND APPLICATON

The purpose of this Standard Operating Procedure is to outline the procedures for receiving air samples, login of samples in the database and in the proper storage area, and tracking these samples through the laboratory.

2.0 RECEIPT OF SAMPLES

2.1 The sample receiving team assumes the custodial responsibilities associated with receiving, inspecting, and logging samples into ATL's File Maker Pro (FMPro), an internal sample tracking database, to maintain a current inventory of in-house samples.

2.1.1 Upon arrival at the laboratory, samples are received and inspected following a written Sample Acceptance Policy (see Section 2.2). The Technical Director ensures that all samples are accepted in accordance with this Policy.

2.1.2 The policy establishes specific guidelines for sample acceptance, which are generally accepted practices under EPA, AFCEE, Army Corps of Engineers, Navy, and NELAC protocols.

2.1.3 When samples do not meet the established guidelines, discrepancies are documented and the client is notified. Samples are flagged in the individual work order and discrepancies noted in the Laboratory Narrative portion of the sample report.

2.1.4 The Sample Acceptance Policy is posted in the sample receiving area and a copy is provided to field staff with every shipment of containers or media.

The following terms are used in defining the receipt condition of the samples:

Good:	No obvious damage, proper temperature/pressure
Questionable:	Evidence of possible shipping damage, custody seals not intact, received with improper temperature/pressure, COC form not received or incomplete
Poor:	Definite shipping damage, integrity of samples obviously compromised, broken sample media.

2.2 <u>Sample Acceptance Policy</u>

2.2.1 Samples received by Air Toxics Ltd. are relinquished following standard EPA approved guidelines. These include full and complete Chain-of-Custody documentation indicating: unique sample name, location, date and time of collection, collector's

name, preservation type (if applicable), matrix, and any special remarks.

2.2.2 The chain-of-custody form is filled out in ink and indicates proper preservation and use of sample container specified by the method.

2.2.3 Each sample is labeled with unique, durable, and indelible identification and must be of adequate volume for the tests requested.

2.2.4 Never affix a label directly on a Summa™ canister. A tag is attached to each canister for this purpose.

2.2.5 Proper, full, and complete inspection and documentation is performed upon laboratory receipt in the following areas:

- evidence of container's physical damage
- status of the container's custody seal
- presence or absence of a chain-of-custody form
- incomplete or incorrect chain-of-custody form
- number of samples
- name of each sample
- sample collection date/time
- sample location
- name of the collector
- preservation type (if applicable)
- sample type (canister, XAD, DNPH etc.)
- sample tag information complete
- temperature (when applicable)
- pressure (canisters)
- presence of unlabelled samples
- presence of mislabeled samples
- presence of unused media
- method required trip blanks, field blanks, equipment blanks, field duplicates, or field spikes

2.2.7 Any sample discrepancies against the above criteria are documented on the Sample Discrepancy Form (Appendix A) and communicated to the client via Login Fax within 1 day of sample receipt.

2.2.8 The client is contacted by the project manager for discrepancies of a more serious nature, e.g.,

- Custody seal on the outside of the container was broken.
- Chain-of-Custody Record was not received with sample(s).
- Analysis method(s) is(are) not specified.
- Sample(s) received out of holding time.
- Flow controller used - canister samples received at <2.5"Hg.
- Sample container (Tube/VOA vial) was received broken.

- Container for VOA analysis received with headspace.
- Tedlar Bag received leaking.
- Tedlar Bag received flat.
- Canister received with a leaky valve.
- Tedlar bag/canister received emitting a strong odor (sample cannot be analyzed).
- Initial laboratory Vacuum/Pressure does not match final field pressure

2.2.9 Documentation of client notification is included on the sample discrepancy form along with any instructions from the client on how to proceed.

2.2.10 Project managers complete this section and return the form to the receiving group to complete the login process. The form is archived in the Work Order (WO) folder.

2.2.11 Whenever there is any uncertainty of how the laboratory is to proceed or when the desired method is unclear, the receiving staff places the Login process ON HOLD and delivers the WO file to a Project Manager for follow-up.

2.2.12 The project manager contacts the client to clarify the situation. Phone calls between the project manager and the client are documented in the Client Services database.

2.2.13 The phone contact and client instructions to resolve the issue are logged into the database and a hardcopy report is placed in the WO folder.

2.2.14 The folder is then returned to the Receiving team to complete the Login process. Air bills, packing lists, chain-of-custody records, and any other documentation that may accompany the samples are placed in the WO folder.

2.2.15 Laboratory malfunctions that may occur during or after sample receipt are documented via the laboratory Corrective Action system.

2.2.16 Examples of receiving problems which would necessitate a Corrective Action Request include:

- Sample was broken during handling.
- Hold time expired due to laboratory error.
- Canister sample pressurized with wrong type of gas.
- Sample placed "on hold" was released in error.
- Sample logged in for incorrect analysis method.
- DANGER tag was not affixed to an odiferous canister sample before sending to the lab.
- Canister was released and cleaned before second analysis method was run. Receiving did not affix the multiple analysis tag.

- Canister valve was left open following pressurization. Sample vented to ambient.

2.3 If a sample is received that may be hazardous to handle, the following procedures are used:

2.3.1 SUMMA™ Canisters and Tedlar Bags:

- Any canister or Tedlar bag that is received emitting a strong odor, is immediately placed in a fume hood by the sample receiver.
- The Hazardous Materials Coordinator is contacted to assess the level of hazard associated with the sample(s) and to ensure proper handling.
- Any leaking Tedlar bag sample, which contains high levels of Hydrogen Sulfide, will not be analyzed. The client is notified immediately so that re-sampling may be scheduled if necessary.

2.3.2 Liquid and Sorbent Media Samples:

- The sample recipient always wears protective gloves while unpacking these types of samples.
- If a liquid sample is received in a leaking or broken container the Hazardous Materials Coordinator is notified for proper cleanup and handling of the sample.
- The Hazardous Materials Coordinator is also notified if a sample on sorbent media is received broken, to ensure proper handling.

2.4 After above inspections, receiving personnel fill out the COC form(s) accurately. After signing the COC in the "Received for lab" location (or any "Received by" location if it is not indicated) the Sample Recipient must follow the signature with "ATL". The correct time and date as well as the following information, given the circumstance, is filled in:

- If it is ATL's COC, the bottom portion of the COC, designated for the person responsible for opening the sample package (includes shipping and custody seal information), is filled in.
- If it is not ATL's COC, the "Condition when received" and "Custody Seals intact" ink stamps on the bottom portion of the COC are used and the appropriate information is filled out.

Any discrepancies found by the sample receiving team member must be documented on a Sample Receipt Discrepancy Form (see Appendix A).

2.5 After the samples have been properly received (the samples noted on the COC), the number of samples, media and analysis type, and significant dates (promised and expiration) are listed in the FMPro database.

The following information describes both the sample holding times and how to set up the promised due date in the FMPro database: (*It is important to note that both due dates are referenced to working days unless otherwise specified.)*

HOLDING TIMES
Sulfur -->1 day (Tedlar bag) & **3 days** (Silco can) from date of collection.
Tedlar Bags --> 3 days from date of collection.
Formaldehyde extraction --> 7 calendar days from the date of collection.
TO-8 extraction--> 48 hours from time of collection
TO-13 extraction, liquids, PUF's--> 7 days from the date of collection.
Canisters, Tubes, and Natural Gas bombs --> 14 days from date of collection.

- If the analysis is to be performed with a quick turn around time, the sample receiving personnel put all documents (COC, air-bill, bid/ship, etc.) into a red folder.
- If the analysis is to be performed on a standard turn around time, the documents are placed in a yellow folder.
- The turnaround time is written on the outside of the red folders so that one is able to distinguish rush work orders quickly.
- The receiving duty is prioritized based on the following questions when considering which samples to give a work order number first (in order of highest to lowest priority).

1. Are the samples previously expired or expiring the same day of receipt?
2. Do the samples have a short hold time?
3. Do the samples need to stay cold?
4. Is the analysis requested a rush turn?
5. If the samples can be run the day of receipt, does the lab need them quickly?
6. Is the analysis a standard turn? Do the samples have a long hold time?

3.0 LOGIN PROCEDURE

After the samples (noted on the COC) have been received appropriately by entering all the required information (e.g., number of samples, media and analysis type, expiration and promised dates) in the FMPro, the samples are logged-in. The steps involved in the login process are as follows:

3.1 Previous WOs are searched for the particular client by using ATLAS Project ID number.

3.2 The located WO is opened in 'EXCEL' and from the old WO a new WO is created.

3.3 New WO information is filled out, or if appropriate, information from previous WO can be used.

3.4 Analysis information is entered from ATLAS Project Profile, e.g., Report To, Bill To, Sample ID, Analysis, etc.

3.5 All the information in project profile in "Notes to Receiving" section is verified.

3.6 Following the information verification all the billing information for analysis, rush, turn-around-time, miscellaneous media, shipping, etc.

3.7 A Reporting List pertaining to a particular method is printed from ATLAS 2000 and is matched with project profile.

3.8 Laboratory Narrative is created for each WO and non-conformities are documented, if any. Following steps are used to create Laboratory Narrative:

3.8.1 NARR TEMP folder in the "O" drive is selected.

3.8.2 From the analysis specific template options, required file is opened.

3.8.3 Company name and WO number are inserted in the laboratory narrative.

3.8.4 After confirming the applicable method name, sample number, media type, date the samples were received by the lab, etc. are noted. Any nonconformity is noted in the laboratory narrative.

3.8.5 After all the required information has been put in, this file is saved as the WO number and is available for the analyst/scientist use in the laboratory.

3.9 Financial status of the client is confirmed and fax copies are prepared that include login information, reporting list, COC, and coversheet (any non-conformities, for client's information, are noted on the coversheet.

3.10 The person carrying out login process updates FMPro by putting in his/her initials, date, and estimated invoice amount.

3.11 <u>The Login Fax</u>

3.11.1 When Login is completed, a fax is sent to the client to confirm receipt of samples. The Login fax has three parts:

Page 1 Cover page with discrepancies noted
Page 2 Log-in summary (sample names etc.)
Page 3 Reporting template showing referenced method, target compound list, and reporting limits

3.11.2 Discrepancies are noted on the cover page using a template of pre-approved statements. QA is responsible for maintaining the approved template. Receiving staff electronically copy relevant statements from the template and onto the FAX cover page.

4.0 CREATING THE WORK ORDER

4.1 Upon receipt, each WO is assigned a project profile. The shipping forms (media provided by the ATL) are assigned a project profile number. When the laboratory receives the media, the project profile is matched for both shipping form and work order through bar code number or manually by matching company and project information.

4.2 The samples, in which the media did not originate at ATL are matched with a project profile by the client service's representative who has been in contact with the client.

4.3 The Sample Receiver must include the following items in each WO when it is created:

1. Chain-of-Custody (COC)
2. Air-bill
3. Bid/ship*, Contacts*, Quotes* – *if applicable
4. Project Profile
5. Other documents (i.e. CLP check sheet, special receiving form)*

4.4 It is critical for the sample receiver to search out information on any unknown situation when receiving samples using Project Profiles, ATLAS (i.e. Contacts, Bid/ships, Quotes) Faxes, E-mail, or any other significant source.

4.5 Second, the sample receiver attaches a print out of the Project Profile to the inside front cover of the WO folder. The Project Profiles contains the specific information laboratory personnel will need in order to process the samples. This information includes general client information as well as any specific project requirements that differ from ATL's SOPs.

4.6 Next, a unique number is assigned to a WO using FileMakerPro Sample Tracking log. For example, the first batch of samples received in the year 2000, month of January would be distinguished by the number **0001001**. Here, **00** refers to the year, **01** designates the month, and **001** determines the batch number. The Sample Receiver then enters the WO information into the Sample Tracking Log of FileMakerPro, making sure that all information is correct regarding the samples just received.

The following are guidelines to assigning WO numbers when multiple analyses are requested and/or multiple COCs are received for samples:

a. When multiple analyses are requested on given samples on the same COC(s), the work order is divided by adding a letter to the end of the WO number. For example, if three analyses are requested from samples to be assigned work order **9901001**, each given WO would be defined as **9901001A, 9901001B, and 9901001C**.

b. If multiple COCs are received for samples analyzed for the same analysis, client, and project, all COCs may be placed in one WO.
c. When multiple COCs are received and the samples on each COC are from different projects, there must be as many WOs assigned as the number of COCs.

4.7 Fraction numbers and specific QA/QC samples (laboratory duplicates, etc.) are assigned to the samples in a WO based on the information in the Project Profiles, and the following instructions.

- **When samples of different media type are received on the same COC and each media has a different analysis -** fraction numbers are assigned by sequentially numbering the samples in order starting from fraction (01A) for that specific media type.
- **If samples are received of the same media type, on the same COC, and for multiple analysis only on <u>some</u> of the samples -** fractions are assigned by numbering <u>all</u> the samples sequentially, and writing only the fractions that apply to each WO on the COC.
- VOST tubes are given the fraction "**A**" for the Tenax (front) tube and "**B**" for the Tenax/charcoal (back) tube. If there is an anasorb tube present, the anasorb is always combined with a Tenax tube to be analyzed properly. Sorbent tubes and charcoal tubes are labeled "**A**" as front tube and "**B**" as a back tube as well.
- For work orders involving an extraction, <u>only</u> TO-4 and TO-13 samples are assigned fractions. For other cases, samples are labeled the work order number only.
- Samples in VOST tubes and Carbotraps cannot be duplicated.
- Condensates can be duplicated, and are only assigned a duplicate if QA/QC calls for it.
- Composite samples or samples that are to be combined into one are given fractions starting with the first sample labeled fraction "A", and subsequent samples labeled the next letter. For example, if three Tedlar bags were composited, the fractions would be 01A, 01B, and 01C.

4.8 Any equipment returned on a Bid/ship must be checked in using the Canister Asset Tracking System (CATS).

ANY SPECIAL CIRCUMSTANCE REGARDING LABELING AND ANALYSIS OF SAMPLES IS ALWAYS DOCUMENTED IN THE PROJECT PROFILE.

5.0 SAMPLE STORAGE, TRACKING AND DISPOSAL

5.1 **Samples received, which do not require an extraction, <u>must</u> be stored in the sample cage in the main laboratory.** The Sample Receiver has to

be sure that all samples received are placed in the sample cage by the end of the day.

5.2 **Those samples, which require an extraction,** are placed in the formaldehyde refrigerator, extractions refrigerator, or VOST refrigerator (depending on analysis).

The following list identifies sample media type and their proper storage location in the lab.

Location in Sample Cage	Contents
Section A1	Tedlar Bags
Sections A2 – D4	Pressurized canisters, tanks, and vacutainers

Location	Freezers	Contents
Cage	4	Charcoal tubes for NIOSH

Location	Refrigerators	Contents
Extractions Lab	1	Semivolatile samples and preparation media
Cage	4	VOST samples only
	5	Water samples for headspace analysis
Warehouse	6	Semivolatile extracts, PCB and PEST extracts, and any other samples which do not belong in the other refrigerators
	7	Aldehyde and Ketone samples and preparation media
	8	Extracted samples for BIF0011

5.3 The Sample Receiver logs in the samples in either the Internal Sample Tracking logbook or logbooks in the extraction's lab labeled "Samples" or "Extracts." The Sample Receiver logs in samples receiving an extraction in the "Samples" logbook, and those samples which normally get an extraction but the extraction has previously been done go in the "Extracts" logbook. When entering the samples, the Sample Receiver has to include the WO number and specific fractions, location of samples, name and date. Samples on "hold" are designated this way with an asterisk (*) in the logbook.

5.4 As the samples are removed for analysis, the responsible analyst/scientist documents each step in the Internal Sample Tracking logbook. The following procedures are used:

- When removing a set of samples for the day's analysis, the analyst records their initials, the time and date of removal from the secure area and acceptance of sample custody.

- As each sample is analyzed, it is logged into the instrument logbook indicating date of analysis and unique computer file number.
- Samples removed from the secure area but not currently being analyzed are still considered to be in the possession of the analyst/scientist. The samples always remain in his/her working view.
- Following analysis, the analyst/scientist returns the samples to the secure area and relinquishes possession.
- Samples remain in the secure area until time of disposal. Permission to dispose of samples is given only by the Laboratory Manager, Sample Receiving Team member or Laboratory Director or a qualified designee. Disposal is indicated in the Internal Sample Tracking logbook.

List of Appendices

Appendix A Sample Receipt Discrepancy Report

Appendix A

Sample Receipt Discrepancy Report

Sample Receipt Discrepancy Report

Initiated By: _____ Date: _____ Given To: _____

Sections I - III must be filled out by the person initiating this sample discrepancy report.

I. Work order affected: _____

Sample(s) affected: _____

II. Discrepancies:

To be noted in Log-in FAX

- ❑ Chain of Custody Record (COC) improperly relinquished.
- ❑ COC was not filled out in ink.
- ❑ Number of samples on the COC do not match the number of samples that were received.
- ❑ Sampling date is not documented.
- ❑ Sample tags do not match the COC.
- ❑ Samples received at wrong temperature.
- ❑ Canister sample received at >15"Hg.
- ❑ Sample container (Tube/VOA vial) was received broken, however, sample was intact.
- ❑ Other

To be noted by Client Services Call

- ❑ Custody seal on the outside of the container was broken.
- ❑ Chain of Custody Record (COC) was not received with sample(s).
- ❑ Analysis method(s) is not specified on the COC.
- ❑ Sample(s) received out of holding time.
- ❑ Flow controller used - canister samples received at <2.5"Hg.
- ❑ Sample container (Tube/VOA vial) was received broken.
- ❑ Container for VOA analysis received with headspace.
- ❑ Tedlar Bag received leaking.
- ❑ Tedlar Bag received flat.
- ❑ Canister received with a leaky valve.
- ❑ Tedlar bag / canister received emitting a strong odor (sample cannot be analyzed).
- ❑ Initial laboratory Vac./Press. does not match final field pressure.
- ❑ Other

III. Describe the discrepancy.

_____

_____

_____

(continued)

Variance to Calibration Procedure
AIR TOXICS, LTD
SOP #6
Analysis of volatile organic compounds in Summa polished canisters
EPA Methods TO-14/TO-14A/TO-15

- Table 1 (page 2) - The internal standard retention time criteria for the daily CCV will be ± 0.33 minutes, instead of ± 0.5 minutes as stated in the SOP.
- Section 7.1 (page 4) - The tuning check will be done every 12 hours.
- Section 7.4 (page 5) - The CCV will be run every 12 hours.
- Section 7.8 (page 6) - A humidified blank will be analyzed after the CCV at the beginning of every 12 hours of instrument operation.
- Section 9.2 (page 8) – The 24-hour periods will be changed to 12-hour periods for both cases.

Control Copy #: NA

@ AIR TOXICS LIMITED
STANDARD OPERATING PROCEDURE

ANALYSIS OF VOLATILE ORGANIC COMPOUNDS IN Summa™ POLISHED CANISTERS

EPA METHODS TO-14/TO-14A/TO-15

SOP #6

Revision Date: 6/02/00
Revision #: 15
Reason for Revision: External Use

Updated By:

Signature	Print	Title	Date

Technical Review:

Signature	Print	Title	Date

QA Review:

Signature	Print	Title	Date
James Parker	James Parker	Quality Assurance Manager	2/13/0

Laboratory Director:

Linda L. Freeman	Date

1.0 SCOPE AND APPLICATION

The procedures in this SOP describe the use of EPA Methods TO-14/TO-14A/TO-15 to determine the concentration of volatile organic compounds in ambient air using an evacuated stainless steel Summa canister. This SOP details the GC/MS procedures and the required QC for volatile analysis. A list of target compounds can be found in *Appendix A*.

2.0 METHOD SUMMARY

2.1 Description

EPA Methods TO-14/TO-14A/TO-15 describe techniques for the analysis of airborne VOCs collected as whole air samples in stainless steel canisters. Up to 0.5 liters of air is withdrawn from the canister through a mass flow controller and is either cryofocused via liquid Argon or concentrated using a multisorbent bed. The focused air sample is then flash heated through a hydrophobic drying system which removes water from the sample stream prior to analysis by full scan GC/MS. For low level analysis, a cryogenic valve is employed to cold trap the gases onto the GC column. Cooling is achieved through the use of Liquid Nitrogen.

A summary of the method QC can be found in the *Appendix A*.

2.2 Deviations

Modifications to EPA Methods TO-14/TO-14A/TO-15 used to carry out the analyses of air samples can be found in Table 1.

3.0 HEALTH AND SAFETY

Normal laboratory safety precautions must be used when preparing standards from neat materials for this method and when analyzing samples. These precautions include working in a fume hood, wearing eye protection, and wearing a laboratory coat when handling neat materials. Also, precautions must be taken to avoid skin contact with neat materials. Refer to the compound specific MSDS for additional information. Care must also be taken when handling syringes to ensure that a needle stick does not occur.

4.0 SAMPLE PRESERVATION, CONTAINERS, HANDLING, AND STORAGE

An air sample is collected in an evacuated stainless steel Summa canister or Tedlar bag. Upon receipt, the canisters will be between ca. 10" Hg vacuum and ambient pressure. Canister receipt vacuum/pressure is reported on the first page of the data report. If abnormal conditions exist the project contact is notified by the sample custodian or a client service representative before analysis can begin. Data from such samples will be qualified. Prior to analysis, the canister is pressurized to 5 psig for 6 L canisters and 15 psig for 1 L canisters. Samples are

1. Summary of Method Modifications

Requirement	TO-14	TO-14A	TO-15	ATL Modifications
Sampling/concentrator system	Nafion Drier	Nafion Drier	Multisorbent concentrator	Multisorbent concentrator
Canister cleaning - clean air supply	Cryogenic Trap	Cryogenic Trap	Cryogenic Trap	Use of Humidified UHP Air
Canister certification	Pressurize w/humidified zero air.	Pressurize w/humidified zero air.	Pressurize w/humidified zero air.	Pressurize w/dry UHP nitrogen
Sample load volume	400 mL	400 mL	Not mandated	Up to 0.5 liter
Blank	Humid air blank	Humid air blank	Humid air blank	Humid air blank for standard analysis. Dry air blank for low level analysis.
Blank acceptance criteria	< 0.2 ppbv	< 0.2 ppbv	< DL	< DL
BFB absolute abundance criteria	Within 10% of that from previous day.	Within 10% of that from previous day.	Not addressed	CCV surrogate recoveries demonstrate stability from one day to the next
BFB acceptance criteria	SW-846 Protocol	SW-846 Protocol	CLP protocol	SW-846 protocol
Concentration of IS spike	Not specified	Not specified	10 ppbv	25 ppbv for TO-14; 10 ppbv for low level
Dilutions for initial calibration	Dynamic dilutions or static using canisters.	Dynamic dilutions or static using canisters.	Dynamic dilutions or static using canisters.	Syringe dilutions
Flow rates/operating parameters				Optimized. See procedures section.
ICAL RRF %RSD acceptance criteria	Not specified	Not specified	30% or less, 40% or less for up to two compounds	30% or less for standard compounds, 40% or less for non-standard and polar compounds
IS recoveries	Not specified	Not specified	Within 40% of mean over ICAL for blanks, and w/in 40% of daily CCV for samples.	Within 40% of CCV recoveries for blank and samples.
IS RTs	Not specified	Not specified	Within .33 min from most recent calibration (either ICAL or daily)	Within 0.5 min of RT in daily CCV
Daily CCV	Not specified	Not specified	70 - 130%	Standard compounds: 70 - 130% for at least 90%; Non-standard and polar compounds: 60 - 140% for at least 80%
RF for quantitation	From ICAL	From ICAL	From daily CCV	From ICAL
Canister leak check	24 hour, positive pressure	24 hour, positive pressure	24 hour, positive pressure	20 min, vacuum check
MSD scan range	18 - 250 amu	18 – 250 amu	35 - 300 amu	35 - 350 amu

stored in the sample cage in the main laboratory. Analysis must occur within 3 days for Tedlar bags and 30 days for canisters.

5.0 INTERFERENCES AND POTENTIAL PROBLEMS

Interferences to this method generally include high levels of carbon dioxide, water and/or heavy hydrocarbons. High levels of CO_2 in the samples can cause freezing of the trap and thus a flow drop on the sample interface. When this occurs a smaller amount of sample is collected resulting in higher dilution factors. Very high levels of moisture in the samples cause erratic internal standard and surrogate responses and therefore likely erratic target compound responses. When a sample has high levels of heavy hydrocarbons, the analyst may have to dilute the sample more than the target compound level requires, ensuring the system is not contaminated.

6.0 EQUIPMENT/APPARATUS

6.1 List of Equipment

- Column: RTX-624 105 m x 0.53mm Megabore ™column (Restek)
- Gas Chromatograph: Hewlett-Packard 6890 equipped with Electronic Pressure Control & a split/splitless injection port, & for low level analysis, a cryo valve
- Mass Spectrometer: Hewlett-Packard 5973
- HP Chemstation Software for Data Acquisition
- Thru-Put Target Software (UNIX Operating System) for Data Analysis
- NIST/NBS54.1K Library Search Software
- Certified NIST Traceable VOC blends - Scott Specialty Gases
- Aldrich Chemical High Purity Neat Standards
- Tedlar Bags (1L, 3L, and 10L) SKC
- Ultra High Purity Helium (Local Supplier)
- Liquid Nitrogen (Local Supplier)
- Laboratory designed focusing interface
- Laboratory designed drying system
- Tylan Mass Flow Control Module (1 to 100 mL/min air)
- Edwards Vacuum Pump
- Laboratory Designed Heated Dynamic Gas Dilution Manifold - based on Porter flow controllers and Sierra digital flow sensors for calibration and diluent gases
- Laboratory Designed Canister Receiving Station equipped with high-resolution vacuum/pressure gauge and diluent gas inlet.
- Laboratory-designed automated sampler

Analysis is carried out on a GC/MS system equipped with a packed column injection port, a Megabore™ inlet adapter, a J & W DB-624

column and a Hewlett-Packard Mass Selective Detector. Cryofocusing is used in low level TO-14 analysis for better compound separation and sharper peak shape.

7.0 CALIBRATION AND QUALITY CONTROL PROCEDURES

7.1 Tuning Criteria

A daily (at the start of every 24 hours, or every 12 hours if project requires) tune check with 4-bromofluorobenzene is achieved by directly injecting 2 µL of the BFB check standard into the GC in accordance with SW-846 tuning criteria. Analysis cannot proceed unless all criteria of the tune check are met.

7.2 Calibration Procedures

Calibration of the GC/MS is achieved via the internal standard technique. The concentrations used for standard analysis typically range from 0.5 to 200 ppbv for standard TO-14 compounds, and 5.0 to 200 ppbv for non-standard and polar compounds. The concentrations used for low level analysis typically range from 0.1 to 40 ppbv for standard TO-14 compounds, and 0.5 to 40 ppbv for non-standard and polar compounds.

The percent relative standard deviations (%RSD) for all standard TO-14 compounds must be ≤ 30%, and for all non-standard and polar compounds, must be ≤ 40%. Otherwise a new initial calibration curve is performed.

In those instances where the RSD for one or more analytes exceeds 30%, the average of the RSD values is determined by summing the RSD value for each analyte and dividing by the total number of analytes. Calibration curve is considered acceptable if the mean RSD for all analytes in the calibration is ≤ 30%.

7.3 Independent Source Calibration Verification

An independently-prepared (i.e., same vendor, different lot number*) standard containing all target compounds is analyzed after each initial

curve, to verify that the standards are correct and the calibration is accurate.

* *Currently only one company reliably prepares VOC gas standards. Therefore, for the standard TO-14 compounds, there are no options to obtain a second source standard (i.e., a standard from a different vendor). In addition, for the non-standard and polar compounds, the independently prepared standard is prepared by a second ATL analyst, using the same neat standards as the primary standard.*

7.4 Continuing Calibration Verification (CCV)

A continuing calibration verification (CCV) is performed at the start of each day and, if required by a specific project, every 12 hours. This is an analysis of the primary source mid-level calibration standard that has been loaded through the mass flow controller. If the CCV fails to meet the performance criteria then system maintenance should be performed and the test repeated. If the system still fails the calibration check, a new 5 point calibration curve is performed.

Certain projects have different CCV acceptance criteria (e.g., $\leq$ 25% for 100% of compounds). A specific list of target analytes is requested when the CCV acceptance criteria required differ than the ATL standard criteria noted above.

Software Verification: A manual verification of the computer-generated results is performed on one randomly chosen target compound for each CCV.

7.5 Laboratory Control Spike (LCS)

When required for specific projects, a mid-level spike using a subset of the independent source standard is analyzed daily prior to sample analysis. If the stated criteria are not met, the system is checked and the standard re-analyzed. In the event that the criteria cannot be met, the instrument is re-calibrated.

7.6 Internal Standards

1.0 mL of the IS blend is injected into the canister interface as each standard, blank, and sample is being loaded. The final concentration is 25 ppbv for each of the following:

Bromochloromethane
Chlorobenzene-d_5
1,4-Difluorobenzene

If the ISs in a sample do not pass the acceptance criteria, the sample must be reanalyzed unless obvious matrix interference is documented. If the ISs are within limits in the re-analysis, the second analysis will be reported. If the ISs are out-of-limits a second time, then the data is reported from the first analysis and the matrix effect narrated in the laboratory narrative included with the data report. Upon request, the data from the matrix effect confirmation analysis is provided to the client.

7.7 Surrogates

One mL of the surrogate blend is injected into the canister interface as each standard, blank, and sample is being loaded. The acceptance limits for surrogate recoveries are 70 to 130%. The final concentration is 25 ppbv for each of the following:

1,2-Dichloroethane-d_4
Toluene-d_8
4-Bromofluorobenzene.

If the surrogate recoveries for a sample are outside of these limits, the sample is reanalyzed unless an obvious matrix interference is documented. If the surrogate recoveries are within limits in the re-analysis, the second analysis will be reported. If the surrogate recoveries are out-of-limits a second time, the data from the first analysis will be reported with a narrative indicating the acceptance criteria for surrogate recoveries were exceeded. Upon request, the data from the matrix effect confirmation analysis is provided to the client.

7.8 Laboratory Blank

A humidified blank (> 20 RH at 25°C) is analyzed after the CCV at the beginning of each day and at least once in every 24 hour shift. A blank is also analyzed in the event saturation-level concentrations* are incurred to demonstrate that contamination does not exist in the chromatographic system. The acceptance criterion for laboratory blanks is a result less than the laboratory detection limit *(Appendix A)*.

The laboratory blank submitted for low level analysis is a dry air blank, which is more representative of the conditions of ambient air samples.

7.9 Laboratory Duplicates

A duplicate sample analysis is performed on 10% of the samples. The relative percent difference (RPD) between the two analyses must be ≤ 25% for all compounds detected at greater than 5 times the detection limit.

8.0 CALCULATIONS

8.1 Response Factor

$$\text{Relative Response Factor (RRF)} = \frac{\text{Area of Compound}}{\text{Area of Int. Standard}} \times \frac{\text{Conc. Int. Standard (ppbv)}}{\text{Conc. of Compound (ppbv)}}$$

8.2 Sample Results

$$\underset{\text{(ppbv on-column)}}{\text{Results Calculation}} = \frac{\text{Area of Compound in Sample}}{\text{Area of Int. Standard in Sample}} \times \frac{\text{Conc. Int. Standard (ppbv)}}{\text{ICAL RRF*}}$$

* *The average RRF from the initial calibration curve is used to quantitate results.*

ppbv in sample = ppbv on-column X Dilution factor

Note: The dilution factor includes canister pressurization dilution and any subsequent dilution required to ensure all results are within the instrument calibration range.

8.3 Total Petroleum Hydrocarbon (TPH) and Non-Methane Organic Compound (NMOC) calculations by GC/MS:

An area percent report is generated and evaluated based on the total area for an individual sample. This total value is used to calculate both TPH and NMOC. Before the final values are processed certain peaks must be subtracted out of the total area. These peaks include CO_2 and system peaks, and in the case of TPH any chlorinated compounds.

NMOC is typically referenced to either hexane (MW=86) or heptane (MW=100). The response factors for these compounds are generated from a one-point calibration that is analyzed once per month per instrument. The mathematical formula for deriving the response factor is as follows:

$$\underset{\text{(hexane/heptane)}}{\text{Response Factor}} = \frac{\text{Total ion area of the compound}}{\text{Concentration of the compound}}$$

$$\text{Sample Result} = \frac{\text{Total ion chromatographic area}}{\text{RF}} \times \text{Dilution factor of the sample}$$

The total ion chromatographic area is qualified in two ways. First, as discussed above, any system peaks are subtracted from the area. Second,

the internal standard and surrogate areas are summed from the lab blank. This value is subtracted from the total area before the final calculation is processed.

TPH is calculated in much the same manner with the exception that a response factor of gasoline (MW=100) is used to calculate a final referenced value. Again, a one-point calibration is run once per month per instrument, and this response factor is used to calculate a final concentration. As stated above, any chlorinated peaks are subtracted from the final area before the calculation is processed. The mathematical formula to calculate TPH is as follows:

$$\text{Sample Result} = \frac{\text{Total ion chromatographic area}}{\text{RF of gasoline}} \times \text{Dilution factor of the sample}$$

9.0 SAMPLE ANALYSIS

9.1 Analytical Batch

The analytical batch is defined as the number of samples analyzed in one analytical day. The number of samples analyzed in one analytical day varies depending on the number of samples received for a particular project, the age of the samples upon receipt, the sample holding times (three days for Tedlar bag samples and 30* days for Summa canister samples), and the project-specific QC requirements.

* *Some projects require a 14-day holding time for canister samples.*

Samples are logged into a work order as noted on the chain-of-custody. As many samples on one work order as physically possible are analyzed within one analytical batch. If samples extend to more than one analytical batch, appropriate QC will be reported.

9.2 Analytical Sequence

Initial 24 hour period:
BFB Tune Check
Detection Limit Verification
Initial Calibration
Independent Calibration Check
Laboratory Blank
Samples

Subsequent 24 hour period:
BFB Tune Check
CCV
LCS - if required by project
Laboratory Blank
Samples

The "Subsequent 24 hour" sequence is followed every 24 hour period (every 12 hours when specified by the project) that samples are analyzed, until the system is found to be out of calibration.

10.0 REFERENCES

EPA Method TO-14
Methods for Determination of Toxic Organic Compounds in Air, EPA Methods, Revision 1 June, 1988.

EPA Method TO-14A
Compendium of Methods for Determination of Toxic Organic Compounds in Air, EPA Methods, Second Edition, January 1997. *EPA/625/R-96/010b*

EPA Method TO-15
Compendium of Methods for Determination of Toxic Organic Compounds in Air, EPA Methods, Second Edition, January 1997. *EPA/625/R-96/010b*

SW-846 Method 8000B
Test Methods for Evaluating Solid Waste, SW-846, Third Edition, Final Update III, Revision 1, December, 1996.

Volatile Organic Analysis of Ambient Air in Canisters - *Draft Method*
USEPA Contract Laboratory Program, Revision VCAA01.0, December 1991

List of Appendices

Appendix A. Detection and QC Limits

Table A-1. Method TO-14/TO-15 Standard Compounds and Non-Standard and Polar Compounds
Table A-2. Internal Standards
Table A-3. Surrogates
Table A-4. Summary of Calibration and QC Procedures for Methods TO-14/TO-15 for Volatile Organic Compounds

Appendix B. BFB Tune Criteria
Appendix C. Standard Reporting Format

Appendix A

Detection and QC Limits

Table A-1. Method TO-14/TO-15
(Standard Compounds)

Analyte	DL (ppbv) Low Level/ Standard	Low Point of Curve (ppbv) Low Level/ Standard	QA Acceptance Criteria	
			Accuracy Limits (%R)	Precision Limits (Max. RPD)
1,1,2,2-Tetrachloroethane	0.1 / 0.5	0.1 / 0.5	70 - 130	± 25
1,1,2-Trichloroethane	0.1 / 0.5	0.1 / 0.5	70 - 130	± 25
1,1-Dichloroethane	0.1 / 0.5	0.1 / 0.5	70 - 130	± 25
1,1-Dichloroethene	0.1 / 0.5	0.1 / 0.5	70 - 130	± 25
1,2,4-Trichlorobenzene	0.1 / 0.5	0.1 / 0.5	70 - 130	± 25
1,2,4-Trimethylbenzene	0.1 / 0.5	0.1 / 0.5	70 - 130	± 25
1,2-Dibromoethane (EDB)	0.1 / 0.5	0.1 / 0.5	70 - 130	± 25
1,2-Dichlorobenzene	0.1 / 0.5	0.1 / 0.5	70 - 130	± 25
1,2-Dichloroethane	0.1 / 0.5	0.1 / 0.5	70 - 130	± 25
1,2-Dichloropropane	0.1 / 0.5	0.1 / 0.5	70 - 130	± 25
1,3,5-Trimethylbenzene	0.1 / 0.5	0.1 / 0.5	70 - 130	± 25
1,3-Dichlorobenzene	0.1 / 0.5	0.1 / 0.5	70 - 130	± 25
1,4-Dichlorobenzene	0.1 / 0.5	0.1 / 0.5	70 - 130	± 25
Benzene	0.1 / 0.5	0.1 / 0.5	70 - 130	± 25
Bromomethane	0.1 / 0.5	0.1 / 0.5	70 - 130	± 25
Carbon Tetrachloride	0.1 / 0.5	0.1 / 0.5	70 - 130	± 25
Chlorobenzene	0.1 / 0.5	0.1 / 0.5	70 - 130	± 25
Chloroethane	0.1 / 0.5	0.1 / 0.5	70 - 130	± 25
Chloroform	0.1 / 0.5	0.1 / 0.5	70 - 130	± 25
Chloromethane	0.1 / 0.5	0.1 / 0.5	70 - 130	± 25
Chlorotoluene (Benzyl Chloride)	0.1 / 0.5	0.1 / 0.5	70 - 130	± 25
cis-1,2-Dichloroethene	0.1 / 0.5	0.1 / 0.5	70 - 130	± 25
cis-1,3-Dichloropropene	0.1 / 0.5	0.1 / 0.5	70 - 130	± 25
Dichloromethane (Methylene Chloride)	0.1 / 0.5	0.1 / 0.5	70 - 130	± 25
Ethylbenzene	0.1 / 0.5	0.1 / 0.5	70 - 130	± 25
Freon 11 (Trichlorofluoromethane)	0.1 / 0.5	0.1 / 0.5	70 - 130	± 25
Freon 113 (Trichlorotrifluoroethane)	0.1 / 0.5	0.1 / 0.5	70 - 130	± 25
Freon 114	0.1 / 0.5	0.1 / 0.5	70 - 130	± 25
Freon 12 (Dichlorodifluoromethane)	0.1 / 0.5	0.1 / 0.5	70 - 130	± 25
Hexachlorobutadiene	0.1 / 0.5	0.1 / 0.5	70 - 130	± 25
m,p-Xylene	0.1 / 0.5	0.1 / 0.5	70 - 130	± 25
Methyl Chloroform (1,1,1-Trichloroethane)	0.1 / 0.5	0.1 / 0.5	70 - 130	± 25
o-Xylene	0.1 / 0.5	0.1 / 0.5	70 - 130	± 25
Styrene	0.1 / 0.5	0.1 / 0.5	70 - 130	± 25
Tetrachloroethene	0.1 / 0.5	0.1 / 0.5	70 - 130	± 25
Toluene	0.1 / 0.5	0.1 / 0.5	70 - 130	± 25
trans-1,3-Dichloropropene	0.1 / 0.5	0.1 / 0.5	70 - 130	± 25
Trichloroethene	0.1 / 0.5	0.1 / 0.5	70 - 130	± 25
Vinyl Chloride	0.1 / 0.5	0 1 / 0.5	70 - 130	± 25

Continued

Table A-1 Method TO-14/TO-15 (continued)
(Non-Standard and Polar Compounds)

Analyte	DL (ppbv) Low Level/ Standard	Low Point of Curve (ppbv) Low Level/ Standard	QA Acceptance Criteria	
			Accuracy Limits (%R)	Precision Limits (Max. RPD)
1,3-Butadiene	0.5 / 2.0	0.5 / 2.0	60 – 140	± 25
1,4-Dioxane	0.5 / 2.0	0.5 / 2.0	60 – 140	± 25
2-Butanone (Methyl Ethyl Ketone)	0.5 / 2.0	0.5 / 2.0	60 – 140	± 25
2-Hexanone	0.5 / 2.0	0.5 / 2.0	60 – 140	± 25
4-Ethyltoluene	0.5 / 2.0	0.5 / 2.0	60 – 140	± 25
4-Methyl-2-Pentanone (MIBK)	0.5 / 2.0	0.5 / 2.0	60 – 140	± 25
Acetone	0.5 / 2.0	0.5 / 2.0	60 – 140	± 25
Bromodichloromethane	0.5 / 2.0	0.5 / 2.0	60 – 140	± 25
Bromoform	0.5 / 2.0	0.5 / 2.0	60 – 140	± 25
Carbon Disulfide	0.5 / 2.0	0.5 / 2.0	60 – 140	± 25
Cyclohexane	0.5 / 2.0	0.5 / 2.0	60 – 140	± 25
Dibromochloromethane	0.5 / 2.0	0.5 / 2.0	60 – 140	± 25
Ethanol	0.5 / 2.0	0.5 / 2.0	60 – 140	± 25
Heptane	0.5 / 2.0	0.5 / 2.0	60 – 140	± 25
Hexane	0.5 / 2.0	0.5 / 2.0	60 – 140	± 25
Isopropanol	0.5 / 2.0	0.5 / 2.0	60 – 140	± 25
Methyl t-Butyl Ether (MTBE)	0.5 / 2.0	0.5 / 2.0	60 – 140	± 25
Propylene	0.5 / 2.0	0.5 / 2.0	60 – 140	± 25
Tetrahydrofuran	0.5 / 2.0	0.5 / 2.0	60 – 140	± 25
trans-1,2-Dichloroethene	0.5 / 2.0	0.5 / 2.0	60 – 140	± 25
Vinyl Acetate	0.5 / 2.0	0.5 / 2.0	60 – 140	± 25

Table A-2. Internal Standards (I.S.)

Analyte	Accuracy Limits (%R)
Bromochloromethane	60 – 140
1,4-Difluorobenzene	60 – 140
Chlorobenzene-d_5	60 – 140

Table A-3. Surrogates

Analyte	Accuracy Limits (%R)
1,2-Dichloroethane-d_4	70 – 130
Toluene-d_8	70 – 130
4-Bromofluorobenzene	70 – 130

Table A-4. Summary of Calibration and QC Procedures for Methods TO-14/TO-15 (Volatile Organic Compounds)

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action
Tuning Criteria	Every 24 hours, or every 12 hours if project Requires	SW - 846 tune criteria	Correct problem then repeat tune
5 Point Calibration	Prior to sample Analysis	%RSD ≤ 30% for all "Standard" compounds and %RSD ≤ 40% for all "Non-standard" compounds	Correct problem then repeat initial calibration curve
Independent Source Calibration Verification	After each initial Calibration curve	Recoveries for 90% of "Standard" compounds must be ± 30%; for 80% of "Non-standard" compounds recoveries must be ± 40%.	Investigate the problem and if warranted, analyze a new analytical curve for the out-of-limits compounds
Continuing Calibration Verification (CCV)	At the start of each day and, if required by a Specific project, every 12 hours	%D ≤ 30% for 90% of "Standard" compounds; %D ≤ 40% for 80% of the "Non-standard" compounds	Perform maintenance and repeat test. If the system still fails the CCV, perform a new 5 point calibration curve
LCS (Subset of Target Compounds	Daily prior to sample Analysis, when required for specific projects	%D ≤ 30% for 90% of "Standard" compounds; %D ≤ 40% for 80% of the "Non-standard" compounds	Check the system and reanalyze the standard. Re-prepare the standard if necessary. Recalibrate the instrument if the criteria cannot be met.
Laboratory Blank	After the CCV	Results less than the laboratory detection limit (Tables A-1 & 2).	Inspect the system and reanalyze the blank.
Internal Standard (IS)	As each standard, Blank, and sample is Being loaded	Retention time (RT) for the blanks and samples must be within ± 0.5 min of the R.T. in the CCV The IS area must be within ± 40% of the CCV's IS area for the blanks and samples	**For blanks:** inspect the system and reanalyze the blank **For samples:** reanalyze the sample unless obvious matrix interference is documented. If the IS are within limits in the re-analysis, report the second analysis. If IS are out-of-limits a second time, report data from first analysis and narrate
Surrogates	As each standard, blank, and sample is being loaded	70 - 130%	**For blanks:** inspect the system and reanalyze the blank **For samples:** reanalyze sample unless obvious matrix interference is documented. If the %R are within limits in the re-analysis, report the second analysis. If %R are out-of-limits a second time report data from first analysis and narrate.
Laboratory Duplicates	10% of the samples	RPD ≤ 25% for detections > 5 X's the DL.	Reanalyze the sample a third time. If the limit is exceeded again, investigate the cause and bring the system back to working order. If no problem is found on the system, flag the data

Appendix B

BFB Tune Criteria

4-BROMOFLUOROBENZENE KEY IONS AND ION ABUNDANCE CRITERIA

Mass	Ion Abundance Criteria
50	15 to 40% of mass 95
75	30 to 60% of mass 95
95	Base Peak, 100% Relative Abundance
96	5 to 9% of mass 95
173	< 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

Appendix C

Standard Reporting Format

Variance to Calibration Procedure
AIR TOXICS, LTD
SOP #10
Analysis of semi-volatile organic compounds collected on PUF cartridges by GS/MS full scan & selective ion monitoring (SIM)
Modified EPA Methods TO-13

- Table 1 (page 1) – Initial calibration: The 20 percent criteria for %RSD for initial and continuing calibration will be used for all PAH analytes listed in method TO-13. The 30 percent criteria will be used for all other semi-volatile organic analytes.

- Table 1 (page 1) – Daily check standard: The 20 percent criteria for %D for initial and continuing calibration will be used for all PAH analytes listed in method TO-13. The 30 percent criteria will be used for all other semi-volatile organic analytes.

- Table 1 (page 2) – Surrogate recovery limits: The surrogate recovery acceptance criteria of 80 to 120 percent will be used.

Control Copy #: NA

@ Air Toxics Limited
STANDARD OPERATING PROCEDURE

ANALYSIS OF SEMI-VOLATILE ORGANIC COMPOUNDS COLLECTED ON PUF CARTRIDGES BY GC/MS FULL SCAN & SELECTIVE ION MONITORING (SIM)

Modified EPA Method TO-13

SOP #10

Revision Date: 10/20/99
Revision #: 5
Reason for Revision: External Use

	Signature	Print	Title	Date
Updated By:	Lisa M. Bettencourt	Lisa M. Bettencourt	Task Leader	1/16/01
Technical Review:	[illegible]	HEIDI HAYES	LAB MANAGER	1/16/01
QA Review:	James Parker	James Parker	Quality Assurance Manager	1/16/01
Laboratory Director:	Linda L. Freeman	Linda L. Freeman		1/16/01

1.0 SCOPE AND APPLICATION

The procedures in this SOP describe the use of EPA Method TO-13 protocols to determine the concentration of semivolatile organic compounds on PUF (polyurethane foam)/XAD2 cartridges. This SOP details the GC/MS procedures and the required QC for semivolatile analysis.

2.0 METHOD SUMMARY

2.1 Description

Samples are collected on PUF (polyurethane foam)/XAD2 cartridges, extracted using a modification of SW-846 EPA Method 3542 (see Air Toxics Ltd's SOP #15), and analyzed for polynuclear aromatic hydrocarbons using a quadrupole GC/MS in the full scan or Selected Ion Monitoring (SIM) mode by TO-13 protocol. In addition, the target compound list can be extended to include full scan analysis of Method 8270 semi-volatile compounds.

The full scan target compound list and detection limits can be found in *Appendix A*. Detection limits range between 1 to 30 µg/sample for the ATL standard list of compounds. SIM target compounds and detection limits are based on the MDL study and typically range between 0.05 to 0.20 µg/sample.

2.2 Deviations

Modifications to EPA Method TO-13 used to carry out the analyses of air samples are as follows:

Table 1. Summary of Method Modifications

Requirements	EPA Method TO-13	ATL Modifications
MS Scan Mode	SIM	SIM - PAH List Full Scan – 8270 full list
IS concentration	40 ng/µL	SIM – 2.0 ng/µL Full Scan – 80 ng/µL
Detection limit	Not specified	SIM – see Table A-1 Full Scan – see Table A-2
Initial calibration	SIM PAH %RSD ≤ 20	SIM PAH % RSD ≤ 30 Full Scan CCC %RSD ≤ 30; SPCC ≥ 0.05
Daily check standard	SIM PAH %D ≤ 20	SIM PAH %D ≤ 30 Full Scan CCC %D ≤ 30; SPCC ≥ 0.05

Table 1. Summary of Method Modifications (continued)

Requirements	EPA Method TO-13	ATL Modifications
Surrogate recovery limit	80 – 120%	In house generated control limits
Duplicate analysis	Not specified	10%

3.0 HEALTH AND SAFETY

Normal laboratory safety precautions must be used when preparing standards from neat materials for this method and when analyzing samples. These precautions include working in a fume hood, wearing eye protection and wearing a laboratory coat when handling neat materials. Also, precautions must be taken to avoid skin contact with neat materials. Refer to the compound specific MSDS for additional information. Care must also be taken when handling syringes to ensure that a needle stick does not occur.

4.0 SAMPLE PRESERVATION, CONTAINERS, HANDLING, AND STORAGE

Sample extracts are stored at 4 $\pm$2°C prior to analysis, as is required by SW846 Method 3542, the extraction method. Extraction must be performed within seven days of sample collection. Analysis of the extracts must occur within 40 days of extraction.

5.0 INTERFERENCES AND POTENTIAL PROBLEMS

Method Blanks are analyzed with each analytical batch to monitor possible interferences in the preparation of the samples. Interferences to this method generally include contamination from phthlate esters found in plastic products. The use of plastic products is kept to a minimum to help eliminate this problem.

Carryover from a high level sample may also cause interference. Therefore if a target analyte is detected above the highest level of the calibration curve, the next sample in the autosampler sequence is re-analyzed if it contains that target analyte.

6.0 EQUIPMENT/APPARATUS

- Column: J&W 30 m X 0.25 mm DB-5.625 with 0.5 µm film thickness
- Gas Chromatograph: Hewlett-Packard 6890 Series II equipped with Electronic Pressure Control and a split/splitless injection port.
- Mass Spectrometer: Hewlett-Packard 5973
- Autosampler: Hewlett-Packard 6890 Series Injector
- HP Chemstation Software for Data Acquisition

- Thru-put Target Software for Data Analysis
- Ultra High Purity Helium (Local Supplier)
- Methylene Chloride (reagent grade)
- Purchased certified stock standards (e.g. Supelco, Ultra, Restek)

7.0 STANDARDS PREPARATION

7.1. Stock Standards

Commercially prepared, EPA certified stock standards at a concentration of 2000 µg/mL are purchased from Restek, or equivalent. These standards are stored tightly sealed at -18 ± 5°C and expire one year after opening the ampule, or the manufacturer's expiration date, whichever comes first. Prepared stock solutions are stored tightly sealed at –18 ± 5°C and expire one year after the preparation date. Working solutions generated from the stock have a maximum expiration date no later than that of the stock solution.

The low point of the calibration curve is at or below the detection limit. Because the detection limits vary by analyte, the levels used for calibration vary by analyte as well. However, for any given analyte, the curve includes a minimum of 5 concentration levels.

7.2 DFTPP

A commercially prepared 1000 µg/mL solution of DFTPP is purchased from Ultra Scientific, or equivalent. 1 mL of this standard is diluted with Methylene chloride to a final volume of 20 mL, giving a concentration of 50 µg/mL. These standards are stored tightly sealed at -18 ±5°C and expire one year after the preparation date, or the manufacturer's expiration date, whichever comes first.

7.3 Internal Standard Solution

A commercially prepared 2000 µg/mL internal standard spiking solution is purchased from Supelco. This standard is stored at -18 ±5°C and expires six months after opening the ampule.

7.4 Surrogate Solutions

Commercially prepared standards are purchased from Restek, or equivalent at the following concentrations.

7.4.1 Surrogates Added to Calibration and Independent Source Standards

A dilution of stock surrogate mix (concentration of 4000 µg/mL) containing acid and base/neutral (B/N) compounds is added to the standards. This standards is stored tightly sealed at -18 ±5°C and expires one year after opening, or the manufacturer's expiration date, whichever comes first.

7.5 LCS Solutions

Full Scan: The acid mix is at a concentration of 2000 µg/mL and the B/N mix is at a concentration of 1000 µg/mL. 1 mL of the acid mix and 2 mL of the B/N mix are diluted with methylene chloride to a final volume of 10 mL, giving a concentration of 200 µg/mL.

SIM: A target mix of PAHs is made at a final concentration of 10 µg/mL using the above procedure.

These standards are stored tightly sealed at -18 ±5°C and expire one year after the preparation date, or the manufacturer's expiration date, whichever comes first.

7.6 Independent Source for Calibration Verification

Commercially prepared, EPA certified stock standards at a concentration of 2000 µg/mL are purchased from a different source than the primary calibration standards. These standards are stored tightly sealed at –18 ±5°C and expire one year after opening the ampule, or the manufacturer's expiration date, whichever comes first.

8.0 CALIBRATION AND QUALITY CONTROL PROCEDURES

8.1 Tuning Criteria

The GC/MS system is hardware tuned to meet the criteria for a 50 ng injection of DFTPP (*Appendix B*). Analysis will not begin until all of these criteria are met. The GC/MS hardware tune check is performed prior to calibration and at the start of every 12-hour shift.

8.2 Internal Standards

Full Scan: Four µL of the 2000 µg/mL internal standard spiking solution is added to a 100 µL aliquot of every standard, blank and sample extract prior to analysis. The final concentration is 80 µg/mL of each of the following:

Acenaphthene-d_{10}	Naphthalene-d_8
Chrysene-d_{12}	Perylene-d_{12}
1,4-Dichlorobenzene-d_4	Phenanthrene-d_{10}

SIM: The 2000 µg/mL internal standard is diluted to a concentration of 50 µg/mL. Four µL of the 50 µg/mL internal standard spiking solution is

added to a 100 µL aliquot of every standard, blank and sample extract prior to analysis. The final concentration is 2 µg/mL of each of the internal standard compounds.

The internal standards are selected to permit most of the target species to elute within 0.80 to 1.20 relative retention time units to the nearest internal standard. The base ion from the specific internal standard is used for quantitation. If interferences are noted, then a secondary ion may be selected. The EICP area counts for any of the internal standards in the continuing calibration verification (CCV) must be within -50 to +100% and the retention times must be within ±30 seconds of the mid-level standard from the most recent initial calibration.

For method blanks and samples and all non-CCV QC Checks, the internal standards' retention times must be within ±30 seconds of the retention times in the continuing calibration check, and the area counts within -50 to +100% of the IS area counts in the CCV.

8.3 Calibration Procedures

Calibration of the GC/MS is achieved via the internal standard technique. Relative response factors (RRFs) are generated based on the ratio of the standard quantitation ion area over the standard concentration and the ratio of the internal standard concentration over the internal standard quantitation ion area. See Section 9.0 for the calculation of RRF. The initial calibration curve includes a minimum of five concentration levels for each analyte.

*8.3.1 System Performance Check Compounds (**Full Scan**)*

The system performance check compounds (SPCC) must yield a minimum average relative response factor of 0.050. Samples cannot be analyzed until this criterion is met. The SPCCs include:

N-Nitroso-di-n-propylamine	Hexachlorocyclopentadiene
2,4-Dinitrophenol	4-Nitrophenol

Poor response of any of the SPCC compounds is indicative of active sites in the chromatographic system. Corrective action such as injection port liner replacement or removal of the first meter of the capillary column must be undertaken until the system is capable of meeting the minimum average relative response factor.

*8.3.2 Calibration Check Compounds (**Full Scan**)*

The relative standard deviation (RSD) for each the calibration check compounds' (CCCs') response factors must be ≤ 30%. The CCCs are noted below. The analytical system is corrected and a new initial calibration curve is performed if this criterion cannot be met.

CCC's

Acenaphthene	4-Chloro-3-methylphenol
1,4-Dichlorobenzene	2,4-Dichlorophenol
Hexachlorobutadiene	2-Nitrophenol
N-Nitrosodiphenylamine	Phenol
Fluoranthene	Pentachlorophenol
Benzo (a) pyrene	2,4,6-Trichlorophenol
Di-n-octyl phthalate	

Criteria for all non-CCC is a RSD of ≤ 30%. In those instances where the RSD for one or more non-CCC analytes exceeds 30%, the average of the RSD values is determined by summing the RSD value for each analyte and dividing by the total number of analytes. Calibration curve is considered acceptable if the mean RSD for all analytes in the calibration is ≤ 30%.

For projects in which the target analyte list consists of PAHs only, the RSD for all PAHs are evaluated instead of the CCCs. The RSD criteria for PAHs in this scenario is ≤ 30%. In order to use the average relative response factor for quantitation, this criteria must be met. Otherwise a new initial calibration is performed.

8.3.3 Calibration (SIM)

Calibration of the GC/MS is achieved via the internal standard technique. The relative standard deviation (RSD) for each of the target compound's response factors must be ≤ 30%. Otherwise, a new initial calibration curve is performed for the compounds that failed to meet the criterion. The average RRF from the initial calibration curve will be used for quantitation of all compounds.

8.4 Independent Source Calibration Verification

Full Scan: Following initial calibration, a mid-level concentration standard (typically 40 - 80 µg/sample) prepared from a separate source of calibration standards is analyzed to verify accuracy of the primary source standards used for the initial calibration. Concentrations of compounds for the 80 µg/sample standard should fall between 40 and 120 µg/sample (50 - 150% recoveries).

SIM: An independent source standard made at a mid-level concentration (typically 2.5 to 5.0 µg/sample) is analyzed and recoveries should also meet ±50% criteria.

If more than 10% of the target compound recoveries fail to meet this criterion, corrective action is taken to determine the source of the discrepancy between the primary and secondary source standards. If the integrity of the primary source standards cannot be verified by some independent means, a new set of standards is obtained and the instrument is recalibrated.

8.5 Continuing Calibration Verification (CCV)

Full Scan: A mid-level concentration (typically 40 to 80 µg/mL) standard is analyzed at the start of every shift immediately after the DFTPP tune check. Acceptance criteria for the CCV are as follows.

8.5.1 SPCCs

Each SPCC in the calibration verification standard must meet a minimum response factor of 0.050. If the minimum response factors are not met, corrective action, up to and including recalibration must be performed. This criterion must be met before sample analysis begins.

8.5.2 CCCs

The %D criterion for each CCC ≤ 30%. If this criterion is not met, corrective action, up to and including recalibration must be performed prior to the analysis of samples. If the target compound list includes PAHs only, the %D criteria for the PAH recoveries is ≤ 30%.

SIM: A mid-level concentration (typically 2.5 to 5.0 µg/sample) standard is analyzed at the start of every shift immediately after the DFTPP tune check. The %D acceptance criteria for the target compound recoveries is ≤ 30%.

8.6 Laboratory Control Spike (LCS)

Full Scan: An independent source standard containing 100 µg of the subset of compounds noted in Table A-5 of *Appendix A*, is spiked and extracted with each set of up to 20 extracted samples. The laboratory-generated acceptance limits are noted in *Appendix A*.

SIM: A 5 µg LCS is spiked and extracted with each set of samples extracted. The LCS contains the subset of the PAH compounds noted Table A-5 of *Appendix A*. The laboratory-generated acceptance limits are noted in *Appendix A*.

For both full scan and SIM analyses, if a LCS exceeds these limits, the analyst will re-aliquot and re-analyze the extract. It is not possible to re-extract air samples. If the LCS recoveries are within limits in the re-analysis, the second analysis will be reported. If the LCS recoveries are out of limits a second time, the samples will be reported with a narrative indicating the acceptance limits were exceeded for the associated LCS.

8.7 Surrogates

Full Scan: A surrogate standard containing 100 µg of the following compounds is spiked into all samples, standards and blanks prior to extraction. The laboratory-generated acceptance limits are noted in *Appendix A*.

Nitrobenzene-d_5	2-Fluorobiphenyl
p-Terphenyl-d_{14}	Phenol-d_5
2-Fluorophenol	2,4,6-Tribromophenol

SIM: The surrogate is spiked into all samples and blanks prior to extraction at a level of 10 µg/sample. The laboratory-generated acceptance limits are noted in *Appendix A*.

If surrogate recoveries exceed these limits, the analyst will re-aliquot and re-analyze the extract. It is not possible to re-extract PUF samples. If the surrogate recoveries are within limits in the re-analysis, the second analysis will be reported. If the surrogate recoveries are out of limits a second time, the sample will be reported with a narrative indicating the acceptance criteria for surrogate recoveries were exceeded.

8.8 Method and Solvent Blanks

A method blank is extracted with each set of up to 20 extracted samples and is analyzed immediately after the calibration standard to ensure both the instrument and extraction process are free from contamination. When samples that are extracted together are analyzed on different analytical shifts, a solvent blank is analyzed to demonstrate that the instrument is free from contamination.

If any target compounds are detected above the detection limit (Section 10.3), the associated data is flagged.

9.0 CALCULATIONS

$$\text{Relative Response Factor (RRF)} = \frac{\text{Area of Compound}}{\text{Area of Int. Standard}} \times \frac{\text{Conc. Int. Standard (ng)}}{\text{Conc. of Compound (ng)}}$$

$$\text{Results Calculation (ng on column)} = \frac{\text{Area of Compound in Sample}}{\text{Area of Int. Standard in Sample}} \times \frac{\text{Conc. Int. Standard (ng)}}{\text{ICAL RRF*}}$$

** The average RRF from the initial calibration curve is used to quantitate results.*

$$\mu\text{g/Sample} = \frac{\text{ng On Column} \times 1000\ \mu\text{L Final Volume} \times \text{Dilution Factor}}{1.0\ \mu\text{L Inj. Vol.} \times 1000\ \text{ng}/\mu\text{g}}$$

10.0 SAMPLE ANALYSIS

10.1 Analytical Batch

The analytical batch is defined as a group of no more than 20 field samples. The actual number of samples included in one analytical batch varies depending on the number of samples received and extracted for a particular project, the age of the extracts, and the project-specific QC requirements.

Samples are logged into a work order as noted on the chain-of-custody. As many samples on one work order as physically possible are analyzed within one analytical batch. If samples extend to more than one analytical batch, appropriate QC will be reported.

10.2 Analytical Sequence

Initial 12-Hour Period	*Subsequent 12-Hour Period*
DFTPP Tune Check	DFTPP Tune Check
Initial Calibration	CCV
Independent Calibration Verification	Method or Solvent Blank (Sec. 8.7)
Method Blank	LCS per every 20 samples
Samples	Samples

The "Subsequent 12-hour" sequence is followed each 12-hour period that samples are analyzed, until the system is found to be out of calibration.

10.3 Detection limits

Detection limits are determined by analyzing a low-level standard. In general, the detection limits for Full Scan GC/MS are 1 to 30 µg/sample. For SIM, detection limits typically range from as low 0.05 to 0.20 µg/sample.

An annual MDL study is performed to verify our ability to detect target compounds at or below the detection limits, noted in *Appendix A*. Results of these studies are maintained in the laboratory files.

10.4 Qualitative Target Compound Identification

Full scan: Compounds are qualitatively identified using retention time and comparison with reference mass spectrum generated by the laboratory. The reference spectrum is obtained by analyzing standards on the instrument performing the analysis, using the conditions described in this SOP. The criteria for qualitative analysis are:

- The RRT of the sample component is within ±0.06 RRT units of the RRT of the standard component.
- Relative intensities of major ions in the reference spectrum (ions >10% of the most abundant ion) should be present in the sample spectrum.
- The relative intensities of the major ions should agree within ±20%. (E.g., for an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30 & 70%.)
- Molecular ions present in the reference spectrum should be present in the sample spectrum.
- Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.

- Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting peaks. Data system library reduction programs can sometimes create these discrepancies.

SIM: At least 2 selected ions for target analytes are monitored for identification.

10.5 Quantitative Analysis

Quantitation is based on the integrated abundance of the primary ion for each analyte. If the response for any quantitation ion exceeds the initial calibration range of the GC/MS system, the extract is diluted and reanalyzed.

When interference with the primary quantitation ion occurs, quantitation on a secondary ion is carried out after a new response factor (using the secondary ion) is generated from the calibration. Therefore, the same ion used to establish the response factor is used to quantify target analytes in the sample. This is noted in the laboratory narrative that is included in the report.

The criterion for using the secondary ion for quantitation is a difference in the reported result of 50% or more.

10.6 Tentatively Identified Compounds (TICs)

Based on the computer generated searches, the identification of the ten highest non-target unknown peaks is reported. The spectrum of these peaks is searched against the NIST library of greater than 50,000 compounds.

The total ion current is used for quantitation and calculation of TIC results. The total ion current of the closest (by Retention Time, RT) non-interfered with internal standard is used to calculate results. If all internal standards are interfered with, the method blank's internal standards are used to calculate results. A relative response factor of "1" is assumed.

11.0 CORRECTIVE ACTION PROCEDURES

A request for corrective action (CAR) is initiated any time either the ATL SOPs or client-prescribed QC protocol are not followed, or in any other instance that sample results are adversely affected. The corrective action is documented in ATL's Corrective Action Procedures SOP #61.

12.0 DATA REVIEW

12.1 Initial Data Review

As the analytical sequence is run throughout the day, the data is reviewed by the bench chemist using the following eight steps:

12.1.1 Check for any project-specific requirements.
12.1.2 Verify holding time.
12.1.3 Verify the tuning criteria, CCV, LCS (when applicable), and end check (when applicable)
12.1.4 Verify method blank has no hits above detection limit.
12.1.5 Verify sample results.
a) Verify internal standards, retention time, and surrogates recoveries are acceptable.
b) Verify correct amount of sample analyzed.
c) Verify the reasonableness of the automated peak integration and spectral verification.
d) Verify result concentrations are within linear range of calibration curve (upper 50% for dilutions.)
12.1.6 Initial and date raw data/and or logbook entry to indicate that the data is acceptable.
12.1.7 Apply data appropriate data flags.
12.1.8 Describe unusual events on data review sheet.

Notes:

- *Preparation and review of laboratory narrative are carried out as explained in the SOP # 45.*
- *Compilation of data package by the analyst/scientist is carried out as described in the data review SOP #22.*

12.2 Secondary Data Review

The team leader or a QA-approved peer performs a secondary technical data review on 100% reports. This review follows all the steps mentioned in the initial data review (Section 12.1).

12.3 Tertiary (QA) Data Review

A thorough tertiary data review is performed by the QA department on a randomly chosen 10% of the final data packages. The QA review entails verification that project and QC requirements are met. Failure to meet QC and/or project requirements results in a corrective action report and documentation. Dilution factors, analyte retention times, peak integration areas, concentration calculations, unit conversions, and detection limits are also checked. Field and trip blanks are checked and trends are observed.

12.3 Quaternary Data Review

Some clients requests that 100% of their final data packages undergo a fourth technical review. The quaternary reviews in this case are performed by the team leader, QA-approved peer, or QA personnel.

13.0 INSTRUMENT MAINTENANCE

Instruments are monitored on a daily basis by the bench analyst for any potential failure. The analysis of blanks and control standards at the start of the day and as analysis continues helps to provide real time feedback to the analyst on the condition of the instruments. Routine maintenance includes:

13.1 Mass Spectrometers

- Daily check of vacuum ion gauge (Increase in ion count indicates a potential leak)
- Cleaning of ion source on quarterly basis or as needed
- The oil level and quality is visually checked on a monthly basis to insure proper vacuum pump function, and oil is changed every 6 months.

13.2 Gas Chromatograph

Basic maintenance includes the following: (*Every 6 months or more frequently if needed)*

13.2.1 Clip 3 feet off the front end of the capillary column, and if necessary, the backend as well.

13.2.2 Replace the injection port liner, and gold seal. The liner is replaced by removing the inlet cap using a wrench and releasing the liner from the inlet body using a pair of tweezers. Care should be taken not to get fingerprints on any inside surface.

13.2.3 Change septa on the GC whenever the front-end maintenance is performed. Always use Supelco Thermogreen septa and take care not to leave fingerprints on any inside heated surface. Wear a pair of white cotton gloves or use tweezers to handle the septa. Lower the oven temperature to 40^0C. Remove the inlet cap with a wrench, remove the old septa with a pair of tweezers and insert the new septa.

13.2.4 The column is replaced when chromatography peak shape or resolution degrades. Similarly, if the column bleed profile rises with age then the column needs replacing. Use new black graphite ferrules each time and clip off approximately 1" of column after inserting it through the ferrule. This will remove any graphite

particles that may have scrapped off into the column. Tighten the column nut and ferrule finger tight and one quarter turn with a wrench. Tightening any more only crushes the ferrule and may damage the column.

13.2.5 The bench analyst will document any routine or major maintenance in the bound instrument logbook assigned to each instrument. The date of the maintenance, what work was performed and analyst initials are included.

14.0 DELIVERABLES

Data reporting packages are prepared as described in SOP# 41 – Preparation of Hardcopy Analytical Reports Using ADT.

15.0 REFERENCES

EPA Method TO-13
Methods for Determination of Toxic Organic Compounds in Air, EPA Methods, Revision 1, June, 1988.

SW-846 Method 8270C
Test Methods for Evaluating Solid Waste, SW-846, Third Edition, Final Update III, Revision 1, December, 1996.

List of Appendices

Appendix A. Method TO-13 Compound List and Detection Limits

Table A-1 *Method TO-13 PAH Compound List*
Table A-2 *Method TO-13 Semivolatile Organic Compounds List – Full Scan Mode*
Table A-3 *Surrogates*
Table A-4 *Internal Standards*
Table A-5 *Extracted Laboratory Control*
Table A-6 *Summary of Calibration and QC Procedures for EPA Method TO-13 – Full Scan Mode*

Appendix B. Decafluorotriphenylphosphine (DFTPP) GC/MS Tuning

Appendix A

Table A-1. Method TO-13 PAH Compound List

Analyte	Full Scan Detection Limit (µg)	SIM Detection Limit (µg)	Acceptance Criteria		
			ICAL (%RSD)	ISCV (%R)	CCV (%R)
2-Chloronapthalene	1.0	0.1	≤ 30	± 50	± 30%
2-Methylnapthalene	1.0	0.1	≤ 30	± 50	± 30%
Acenaphthylene	1.0	0.1	≤ 30	± 50	± 30%
Acenapthene	1.0	0.1	≤ 30	± 50	± 30%
Anthracene	1.0	0.1	≤ 30	± 50	± 30%
Benzo(a)anthracene	1.0	0.1	≤ 30	± 50	± 30%
Benzo(a)pyrene	1.0	0.1	≤ 30	± 50	± 30%
Benzo(b)fluoranthene	1.0	0.1	≤ 30	± 50	± 30%
Benzo(g,h,i)perylene	1.0	0.1	≤ 30	± 50	± 30%
Benzo(k)fluoranthene	1.0	0.1	≤ 30	± 50	± 30%
Chrysene	1.0	0.1	≤ 30	± 50	± 30%
Dibenz(a,h)anthracene	1.0	0.1	≤ 30	± 50	± 30%
Fluoranthene	1.0	0.1	≤ 30	± 50	± 30%
Fluorene	1.0	0.1	≤ 30	± 50	± 30%
Indeo(1,2,3-c,d)pyrene	1.0	0.1	≤ 30	± 50	± 30%
Napthalene	1.0	0.1	≤ 30	± 50	± 30%
Phenanthrene	1.0	0.1	≤ 30	± 50	± 30%
Pyrene	1.0	0.1	≤ 30	± 50	± 30%

Table A-2. Method TO-13 Semivolatile Organic Compounds List – Full Scan Mode

Analyte	Detection Limit (µg)	Acceptance Criteria		
		ICAL (%RSD)*	ISCV (%R)	CCV
1,2,4-Trichlorobenzene	1.0	≤ 30	± 50	-
1,2-Dichlorobenzene	1.0	≤ 30	± 50	-
1,3-Dichlorobenzene	1.0	≤ 30	± 50	-
1,4-Dichlorobenzene - CCC	1.0	≤ 30	± 50	%D ≤ 30%
2,4,5-Trichlorophenol	5.0	≤ 30	± 50	-
2,4,6-Trichlorophenol - CCC	5.0	≤ 30	± 50	%D ≤ 30%
2,4-Dichlorophenol - CCC	5.0	≤ 30	± 50	%D ≤ 30%
2,4-Dimethylphenol	5.0	≤ 30	± 50	-
2,4-Dinitrophenol - SPCC	20	≤ 30	± 50	RF ≥ 0.050
2,4-Dinitrotoluene	5.0	≤ 30	± 50	-
2,6-Dinitrotoluene	5.0	≤ 30	± 50	-
2-Chloronapthalene	1.0	≤ 30	± 50	-
2-Chlorophenol	5.0	≤ 30	± 50	-
2-Methylnapthalene	1.0	≤ 30	± 50	-
2-Methylphenol	5.0	≤ 30	± 50	-
2-Nitroaniline	10	≤ 30	± 50	-
2-Nitrophenol – CCC	5.0	≤ 30	± 50	%D ≤ 30%
3,3-Dichlorobenzidine	20	≤ 30	± 50	-
3-Nitroaniline	10	≤ 30	± 50	-
4,6-Dinitro-2-methylphenol	10	≤ 30	± 50	-
4-Bromophenyl-phenyl ether	1.0	≤ 30	± 50	-
4-Chloro-3-methylphenol - CCC	5.0	≤ 30	± 50	%D ≤ 30%
4-Chloroaniline	10	≤ 30	± 50	-
4-Chlorophenyl-phenyl ether	1.0	≤ 30	± 50	-
4-Methylphenol	5.0	≤ 30	± 50	-
4-Nitroaniline	10	≤ 30	± 50	-
4-Nitrophenol – SPCC	20	≤ 30	± 50	RF ≥ 0.050
Acenaphthylene	1.0	≤ 30	± 50	-
Acenapthene – CCC	1.0	≤ 30	± 50	%D ≤ 30%
Anthracene	1.0	≤ 30	± 50	-
Benzo(a)anthracene	1.0	≤ 30	± 50	-
Benzo(a)pyrene - CCC	1.0	≤ 30	± 50	%D ≤ 30%
Benzo(b)fluoranthene	1.0	≤ 30	± 50	-
Benzo(g,h,i)perylene	1.0	≤ 30	± 50	-
Benzo(k)fluoranthene	1.0	≤ 30	± 50	-
Benzoic Acid	30	≤ 30	± 50	-
Bis(2-Chloroethoxy) Methane	1.0	≤ 30	± 50	-
Bis(2-Chloroispropyl) Ether	1.0	≤ 30	± 50	-
Bis(2-Chlroethyl) Ether	1.0	≤ 30	± 50	-
Bis(2-Ethylhexyl)phthalate	5.0	≤ 30	± 50	-
Butylbenzylphthalate	5.0	≤ 30	± 50	-
Chrysene	1.0	≤ 30	± 50	-
di-n-Butylphthalate	5.0	≤ 30	± 50	-
di-n-Octylphthalate - CCC	5.0	≤ 30	± 50	%D ≤ 30%
Dibenz(a,h)anthracene	1.0	≤ 30	± 50	-

continued

Table A-2. Method TO-13 Semivolatile Organic Compounds List – Full Scan Mode (continued)

Analyte	Detection Limit (µg)	Acceptance Criteria		
		ICAL (%RSD)*	ISCV (%R)	CCV
Dibenzofuran	1.0	≤ 30	± 50	-
Diethylphthalate	5.0	≤ 30	± 50	-
Dimethylphthalate	5.0	≤ 30	± 50	-
Fluoranthene – CCC	1.0	≤ 30	± 50	%D ≤ 30%
Fluorene0	1.0	≤ 30	± 50	-
Hexachlorobenzene	1.0	≤ 30	± 50	-
Hexachlorobutadiene - CCC	1.0	≤ 30	± 50	%D ≤ 30%
Hexachlorocylcopentadiene – SPCC	20	≤ 30	± 50	RF ≥ 0.050
Hexachloroethane	1.0	≤ 30	± 50	-
Indeo(1,2,3-c,d)pyrene	1.0	≤ 30	± 50	-
Isophorone	1.0	≤ 30	± 50	
n-Nitroso-di-n-propylamine – SPCC	1.0	≤ 30	± 50	RF ≥ 0.050
n-Nitrosodiphenylamine – CCC	10	≤ 30	± 50	%D ≤ 30%
Napthalene	1.0	≤ 30	± 50	-
Nitrobenzene	1.0	≤ 30	± 50	-
Pentachlorophenol – CCC	20	≤ 30	± 50	%D ≤ 30%
Phenanthrene	1.0	≤ 30	± 50	-
Phenol – CCC	5.0	≤ 30	± 50	%D ≤ 30%
Pyrene	1.0	≤ 30	± 50	-

* Can use the mean RSD criterion of ≤ 30% as noted in par. 7.5.1.2.1 of SW-846, 8000B.

Table A-3. Surrogates

Analyte	Full Scan (%R)**	SIM (%R)
2,4,6-Tribromophenol	9 – 98	NA
2-Fluorobiphenyl	15 – 98	15 – 98
2-Fluorophenol	7 – 85	NA
Nitrobenzene-d_5	14 – 92	NA
Phenol-d_5	2 – 94	NA
p-Terphenyl-d_{14}	19 – 162	19 – 162

NA – Not applicable

Table A-4 Internal Standards

Analyte	(%R)
Acenaphthene-d_{10}	50 – 200
Chrysene-d_{12}	50 – 200
1,4-Dichlorobenzene-d_4	50 - 200
Naphthalene-d_8	50 - 200
Perylene-d_{12}	50 - 200
Phenanthrene-d_{10}	50 - 200

Table A-5. Extracted Laboratory Control

Analyte	Full Scan (%R)**	SIM (%R)
1,2,4-Trichlorobenzene	4 - 115	NA
1,4-Dichlorobenzene	6 - 101	NA
2,4-Dinitrotoluene	24 - 106	NA
2-Chlorophenol	8 - 98	NA
4-Chloro-3-methylphenol	10 - 104	NA
4-Nitrophenol	11 - 125	NA
Acenaphthene	7 - 106	7 - 106
N-Nitroso-di-n-propylamine	10 - 95	NA
Pentachlorophenol	3 - 138	NA
Phenol	7 - 96	NA
Pyrene	48 - 108	48 - 108

** The LCS and surrogate limits are in-house limits that are updated quarterly. These limits are only applied to samples that are extracted by ATL. When sample extracts are sent to ATL, limits of 50 - 150% are applied.

Table A-6. Summary of Calibration and QC Procedures for EPA Method TO-13 – Full Scan Mode

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action
Tuning Criteria	Prior to calibration and at start of every 12 hrs.	SW 846 tuning criteria for Semivolatiles analysis	Correct problem then repeat tune.
Initial 5-Point Calibration	Prior to sample analysis	ICAL criteria in Tables A-1 & A-2	Correct problem then repeat initial calibration.
Independent Source Calib. Ver. (ISCV)	All analytes – Once per initial calibration	At least 90% of the target Compound recoveries must be Between 50 – 150%.	Determine the source of discrepancy between standards. Recalibrate if needed.
Detection Limit Verification (DLV)	With each initial Calibration	± 50% of the expected value	Check the system and reanalyze the standard. Notify QA dept. via a CAR form if the criteria cannot be met.
Continuing Calibration Verification (CCV)	At the start of every clock immediately after the DFTPP tune check	**PAHs list only:** %D ≤ 30% **Extended list:** **SPCCs:** RF≥0.050 **CCCs:** %D ≤ 30%	Investigate and correct the problem, up to and including re-calibration if necessary.
Internal Standards (IS)	As each standard, blank, and sample is being loaded	**For CCVs:** area counts within 50 to 200% and retention Times within 30 seconds of The mid-level standard from The most recent initial Calibration **For blanks, samples and non-CCV QC Checks:** retention Times within ± 0.5 minutes (30 Seconds) and area counts Within 50 to 200% of the CCV	**For CCVs:** Investigate and correct the problem before proceeding with sample analysis. If interferences are present, a secondary ion may be selected **For blanks:** inspect the system and reanalyze the blank **For samples and non-CCV QC:** reanalyze the samples. If the criteria is not met a second time, flag the data to indicate interference.
Surrogates	With all samples and blanks prior to extraction	See Table A-3	Re-aliquot and re-analyze the extract. If within limits, report the re-analysis. Otherwise narrate
Extracted LCS	With each set of up to 20 extracted samples	See LCS Criteria in Table A-5	Re-aliquot and re-analyze the extract. If within limits, report the re-analysis. Otherwise narrate
Laboratory Blank	With each set of up to 20 extracted samples, immediately after the calibration standard	Results less than laboratory Detection limit (Tables A-1 & A-2)	Flag the data.
Solvent Blanks	When samples that are extracted together are analyzed on different analytical shifts	All target compounds below The detection limit (Tables A-1 & A-2)	Flag the data.
Laboratory Duplicates	With each set of up to 20 extracted samples.	RPD < or = 30% for all Detections > 5 X's DLs	Flag the data.

Appendix B

SEMIVOLATILE ORGANIC GC/MS TUNING AND MASS CALIBRATION

Decafluorotriphenylphosphine (DFTPP)

M/e	ION ABUNDANCE CRITERIA
51	30.0 - 80.0% of mass 198
68	Less than 2.0% of mass 69
70	Less than 2.0% of mass 69
127	25.0 - 75.0% of mass 198
197	Less than 1.0% of mass 198
198	Base Peak, 100% relative abundance
199	5.0 - 9.0% of mass 198
275	10.0 - 30.0% of mass 198
365	Greater than 0.75% of mass 198
441	Present, but less than mass 443
442	40.0 – 110% of mass 198
443	15.0 – 24.0% of mass 442

Control Copy #: NA

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STANDARD OPERATING PROCEDURE

EXTRACTION OF AMBIENT AIR & MM5 SAMPLES FOR SEMIVOLATILE ANALYSIS

MODIFIED EPA SW-846 METHODS 3510C/3540C/3542

SOP #15

Revision Date: 9/15/00
Revision #: 2
Reason for Revision: External

	Signature	Print	Title	Date
Updated By:	Lisa M. Bettencourt	Lisa M. Bettencourt	Task Leader	1/16/01
Technical Review:	[illegible]	HEIDI HAYES	Lab Manager	1/16/01
QA Review:	James Parker	James Parker	Quality Assurance Manager	1/16/01
Laboratory Director:	Linda L. Freeman	Linda L. Freeman		01/16/01

1.0 SCOPE AND APPLICATION

This document describes the procedures used to: (1) prepare glassware; (2) perform sample extractions; and (3) concentrate the extracts in preparation for Method TO-13 and 8270C analyses.

2.0 METHOD SUMMARY

2.1 Description

Samples are shipped from the field in a cooler with ice and are stored at 4°C until extraction. Extraction must be performed within seven days of sample collection for TO-13 cartridges and 14 days for MM5 sampling train with extracts stored at 4°C until analysis. Analysis of sample extracts must be performed within 40 days of sample extraction.

2.2 Deviations

Table 1. Summary of Method Modifications

Requirements	EPA Methods 3510C/3540C/3542 and TO-13	ATL Modifications
Separate extractions for MM5 sampling train	**Method 3542:** Three separate extractions 1. Filter (soxhlet) and front half rinse (separatory funnel) + surrogate → combine → concentrate to 5 mL. 2. Condensate + condensate rinse + spike with surrogate → combine (separatory funnel) → concentrate to 5 mL. 3. XAD-trap (soxhlet) back half rinse (separatory funnel) → combine → concentrate to 5 mL.	1. XAD + filter → Soxhlet extraction (A) 2. Front half rinse + back half rinse + condensate → separatory funnel (B) 3. Combine A + B → Concentrate to 1 mL.
Solid sample preparation	**Method 3540C:** Mix solid sample with anhydrous Na_2SO_4 prior to extraction.	Media is PUF/XAD; no Na_2SO_4 needed
Matrix spike	**Method 3540C:** Spike sample with target analyte.	Matrix spike not set up
Kuderna-Danish (K-D) concentrator	**Method 3540C/TO-13:** Use a K-D apparatus and hot water bath to condense extract.	Use a Snyder column with a flat bottom flask on a hot plate for concentration.
Drying extract	**Method 3540C/TO-13:** Extract is dried prior to K-D setup.	Extract is dried prior to final nitrogen blown down.

continued

Table 1. Summary of Method Modifications (continued)

Requirements	EPA Methods 3510C/3540C/3542 and TO-13	ATL Modifications
Extraction solvent	**Method TO-13:** Use of PUF only requires use of 10% ether in hexane; separate extraction of filter in CH_2Cl_2. Use of XAD only requires use of CH_2Cl_2; extract filter with XAD.	Use PUF/XAD cartridge; extract cartridge + filter together in CH_2Cl_2.
Final volume adjustment	**TO-13:** Bring extract to final volume with cyclohexane.	Extract brought to final volume with CH_2Cl_2.

3.0 *HEALTH AND SAFETY*

Normal safety procedures should be followed. Preparation of standard solutions should be handled in a hood or well-ventilated area whenever possible and gloves should always be worn when handling samples or stock solutions. Precautions must be taken to avoid contact with the methylene chloride used during extraction. These precautions include working in a fume hood, wearing eye protection, avoiding skin contact with methylene chloride, and wearing a laboratory coat. Refer to the compound specific MSDS for additional information.

4.0 *SAMPLE PRESERVATION, CONTAINERS, HANDLING, AND STORAGE*

Samples must be stored at 4°C until extraction. Extractions must be performed within 7 days of sample collection and stored at 4°C; analysis within 40 days of sample extraction.

5.0 *INTERFERENCES AND POTENTIAL PROBLEMS*

Interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware. Glassware should be thoroughly cleaned following the glassware preparation protocol outlined in Section 7.1. High purity reagents and solvents are used to minimize interference problems in sample analysis.

Matrix interferences in the analysis may be caused by non-target analytes present in the sample.

6.0 *EQUIPMENT/APPARATUS*

- Hot plate
- 1000 mL flat bottom flasks
- Funnels

- Forceps
- Snyder column
- #41 filter paper
- Fume hood
- Soxhlets
- Anhydrous sodium sulfate
- Reagent-grade methylene chloride
- 1 mL graduated turbo vap vials
- 2000 mL separatory funnels
- 10 M Sulfuric Acid (H_2SO_4)
- 9 M Sodium Hydroxide (NaOH)
- Methanol
- HPLC-grade reagent water
- Wide-range pH paper
- Turbo vap (nitrogen evaporator)
- PFTE boiling chips
- 2-mL screw top vials.
- Surrogate spiking solution - A 4000 µg/mL Surrogate Solution is purchased from Ultra Scientific or equivalent that contains 2-Fluorobiphenyl, 2-Fluorophenol, Nitrobenzene-d_5, Phenol-d_5, Terphenyl-d_{14}, and 2,4,6-Tribromophenol. A 200 µg/mL working solution is prepared by adding 2.5 mL of the purchased solution to a 50 mL volumetric and bringing up to volume with methylene chloride. The surrogate spiking solution is stored at 4 ±2°C and expires 6 months after preparation.
- LCS spiking solution - A 1000 µg/mL Base/Neutral and a 2000 µg/mL Acid Matrix Spiking Solution is purchased from Restek or equivalent. The Base/Neutral Mix contains 1,4-Dichlorobenzene, n-Nitroso-di-n-propylamine, 1,2,4-Trichlorobenzene, Acenaphthene, 2,4-Dinitrotoluene, and Pyrene. The Acid Mix contains Phenol, 2-Chlorophenol, 4-Chloro-3-methylphenol, 4-Nitrophenol, and Pentachlorophenol. A 200 µg/mL working LCS solution is prepared from the purchased mixes by adding 2 mL of the Base/Neutral Mix and 1 mL of the Acid Mix to a 10 mL volumetric and brought to volume with methylene chloride. The LCS solution is stored at 4 ±2°C and expires 6 months after preparation.

7.0 PROCEDURE

7.1 Glassware Preparation

7.1.1 Extraction glassware

Wash with warm soapy water, triple rinse with tap water, triple rinse with de-ionized water, then set to dry. All glassware must be completely dry prior to use. Triple rinse with methylene chloride. If

glassware is not dry, a triple methanol rinse followed by a triple methylene chloride rinse may be used.

7.1.2 Funnels

Set up funnels lined with #41 filter paper in the fume hood using ring stands. Add a small amount of sodium sulfate to the lined funnel and triple rinse it with methylene chloride.

7.2 Soxhlet Set-up

7.2.1 Fill each round bottom flask with approximately 700-800 mL methylene chloride.

7.2.2 Add several methylene chloride-rinsed PTFE boiling chips to each flask and cover with foil.

7.2.3 Triple rinse each soxhlet extraction body with methylene chloride, place on flat bottom flask and cover with foil until use.

7.3 Extraction

7.3.1 Separatory Funnel Extraction

MM-5 train - Condensate and rinse extraction

7.3.1.1 Combine the condensate fraction and the front and back half rinses for each sample in a clean 2000-mL separatory funnel. The method blank is 500 or 1000 mL HPLC-grade water.

7.3.1.2 Add methylene chloride if necessary in order to achieve a methylene chloride volume of approximately 60 mL (or a ratio of 1:3 [DCM:H_2O]).

7.3.1.3 Shake the sample for 2 min venting the funnel as pressure builds up. Let the layers separate and drain the bottom methylene chloride layer into Na_2SO_4 funnel (Section 7.1.2) and collect in a round bottom flask.

7.3.1.4 Repeat the extraction two more times adding the methylene chloride aliquots into the same round bottom flask.

7.3.1.5 Add appropriate amount of 9M NaOH to the separatory funnel to change the pH to 10-11.

7.3.1.6 Perform 3 more extractions each with approximately 60 mL of methylene chloride of 2 min each.

7.3.1.7 Drain each aliquot through Na_2SO_4 into the same round bottom flask.

7.3.1.8 Add appropriate amount of 10M H_2SO_4 to the separatory funnel to change the pH of the aqueous fraction to less than 2.

7.3.1.9 Repeat the 3 X 2 min extraction as described above. Cover the round bottom flask with foil and continue with the extraction concentration step (Section 7.4).

7.3.2 MM-5 Trap Preparation

7.3.2.1 Remove ends of trap and transfer glass wool packing and XAD contents into a clean triple-rinsed extraction thimble.
7.3.2.2 Place the thimble and the sample filter into the soxhlet body.
7.3.2.3 If necessary, place a clean 1" PUF plug over the top of the extraction filter to keep thimble contents from overflowing into the soxhlet and possibly plugging the sidearm.
7.3.2.4 Include a blank and spike sample.

7.3.3 PUF/XAD cartridge extraction preparation

7.3.3.1 Unwrap each sample and place the sample cartridge and its quartz filter into labeled extraction sohxlets. When extracting low volume cartridges, insure that the siphon arm of the extractor is not plugged with the tip of the cartridge. Blockage of the siphon arm may hinder the cycling of solvent to the round bottom flask.
7.3.3.2 Include a blank and spike sample.

7.3.4 Extraction Process

7.3.4.1 Bring chiller to set point temperature of 10 - 15°C.
7.3.4.2 Remove appropriate surrogate and spiking solutions from the freezer to allow them to come to room temperature.
7.3.4.3 Add 500 µL of surrogate solution to each soxhlet, including the blank and spike samples.
7.3.4.4 Add 500 µL of spiking solution to the spike sample.
7.3.4.5 CAREFULLY place the condenser on each soxhlet.
7.3.4.6 Turn on each heating mantle to a set point of 5.5. The orange light flashing indicates the mantle is heating. This setting should result in approximately 4-6 cycles per hour.
7.3.4.7 Complete necessary documentation, including:
- extraction log
- sample log
- Filemaker Pro database

7.3.4.8 Extract samples for a minimum of 18 hours, maintaining a chiller temperature of less than 15°C. (Room temperature may need to be lowered to 65°F in order to maintain

appropriate chiller temperature when running multiple soxhlet extractions.)

7.3.4.9 Turn off heating mantels at the end of the 18-hour period and allow each soxhlet to cool approximately 1 hour before proceeding.

7.3.4.10 CAREFULLY remove the condenser from each soxhlet.

7.3.4.11 Drain all remaining solvent from the extractor body to the flat bottom flask by tilting the soxhlet to start the side arm siphon. Remove the soxhlets from the flat bottom flasks.

7.3.4.12 Flasks are then either transferred to fume hood for heat reduction step (Section 7.4.1), or covered with foil and stored in the refrigerator.

7.3.4.13 Extracted PUF inserts, filters, and XAD are allowed to dry in a plastic tub in the fume hood, and then disposed.

7.3.4.14 The soxhlets are stored flat on the heating mantels.

7.4 Extraction Concentration

The extract is reduced to a volume of 1 mL using heat then nitrogen evaporation as follows.

7.4.1 Heat Reduction

7.4.1.1 Triple rinse each Snyder column with methylene chloride and place the column on the respective flat bottom flask.

7.4.1.2 Place the samples on hot plates using a temperature setting between 5 and 6. Samples will begin to boil and columns will chatter.

7.4.1.3 Allow to boil until sample volume is NEAR dry, then remove from heat. Do not allow samples to go to dryness. This will cause poor recoveries and loss of sample.

7.4.1.4 Add three short squirts of CH_2Cl_2 to rinse column into the flask and set aside to cool.

7.4.1.5 When flask is cool to the touch, again rinse column into the flask with three short squirts of methylene chloride.

7.4.1.6 Remove column and pour sample through a funnel lined with #41 filter paper with anhydrous sodium sulfate (Section 7.1.2) into a turbo vap vial.

7.4.1.7 After all solvent has drained out of the funnel, triple rinse the funnel with methylene chloride in the turbo vap vial.

7.4.1.8 For the MM5 train samples, combine the XAD/Filter extract and the Condensate/Back & Front Half Rinse extract prior to Nitrogen evaporation.

7.4.2 *Nitrogen Evaporation*

7.4.2.1 Evaporate filtered sample to just below 1.0 mL using nitrogen in the turbo vap.

7.4.2.2 Remove sample from turbo vap and adjust the volume to exactly 1 mL using a clean Pasteur pipette and clean methylene chloride.

7.4.2.3 Vortex the sample for five seconds.

7.4.2.4 Using a clean Pasteur pipette, transfer the 1 mL sample to a labeled coarse-threaded screw top vial. Cap each sample with a light blue cap.

7.4.2.5 Store vials in the refrigerator and fill out all appropriate documentation, including:

- Sample/Extract Logbook
- Filemaker Pro database.

8.0 REFERENCES

SW-846 Method 3510C
Test Methods for Evaluating Solid Waste, SW-846, Third Edition, Final Update III, Revision 3, December 1996.

SW-846 Method 3540C
Test Methods for Evaluating Solid Waste, SW-846, Third Edition, Final Update III, Revision 3, December 1996.

SW-846 Method 3542
Test Methods for Evaluating Solid Waste, SW-846, Third Edition, Final Update III, Revision 0, December 1996.

EPA Method TO-13
Methods for Determination of Toxic Organic Compounds in Air, EPA Methods, Revision 1, June 1988.

SOP No.	Revision No.	Date	Page
UWC-SOP-405.1	08	03/15/00	1 of 18

TITLE: WET CHEMISTRY

Biochemical Oxygen Demand (BOD) & Carbonaceous BOD (cBOD)

Updated By:	Signature:	Date
Diane L. Harper Section Manager, Wet Chemistry	_____	_____

Approved by:	Signature:	Date
Diane L. Harper Section Manager, Wet Chemistry	_____	_____
Raymond J. Frederici Quality Manager	_____	_____

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1.0 SCOPE / APPLICATION

This Standard Operating Procedure (SOP) is used to measure the oxygen required for biochemical degradation of organics and oxidation of inorganics in wastewaters, effluents, and other aqueous samples. It may also measure the oxygen used to oxidize reduced forms of nitrogen unless nitrification is prevented by an inhibitor. This SOP was written using EPA 600/4-79-020, Method 405.1 as a reference.

*Equivalent Method: Standard Methods, 18th Edition, Method 5210B.

On occasion, clients request slight modifications to this Standard Operating Procedure (SOP). These modifications are addressed on a case-by-case basis and would be written into a Quality Assurance Plan (QAP).

1.1 Method Sensitivity

1.1.1 Method Detection Limits

The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to Appendix B of 40 CFR 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants". MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains MDL studies for analyses performed; these are verified at least annually.

1.1.2 Reporting Limits

Reporting Limits are defined as the lowest concentration of an analyte determined by a given method in a given matrix that the laboratory feels can be reported with acceptable quantitative error or client requirements, values specified by the EPA methods or other project and client requirements. Because of the high level of quantitative error associated with determinations at the level of the MDL, the laboratory endeavors to keep reporting limits higher than the MDL. Wherever possible, reporting is limited to values approximately 3-5x the respective MDL to ensure confidence in the value reported.

Matrix	Reporting Limit
Waters	2 mg/L

NOTE: The above reporting limit was determined by considering the recommended depletion of 2 mg/L O_2 in an undiluted sample. While statistical MDLs are determined annually, the above reporting limit is used routinely except for projects that require statistical limits. Occasionally, the reporting limit for a sample will vary due to over or under depletion of all dilutions.

1.1.3 Definitions

Refer to Section 9.0 of the laboratory's QAP (UQA-SOP-QAPP).

1.2 Summary of Method

Several different dilutions of the sample are prepared using dilution water which contains nutrients necessary for bacterial growth and a biological seed to provide a microbial population capable of oxidizing biodegradable organic matter. The initial dissolved oxygen (DO) of each sample dilution is recorded. The samples are incubated in the dark, at 20°C, for the specified time period. At the end of the incubation period, the DO of each sample dilution is recorded. After correcting for the oxygen depletion exerted by the seed, the BOD of the sample is calculated.

2.0 INTERFERENCES

- Extremes of pH will kill or prevent normal metabolism of microbes. Adjustment of the pH may be necessary.

- Samples containing chlorine should be treated with sodium sulfite. Chlorine kills or inhibits the growth of the microorganisms necessary for the BOD test. Other toxins may be present, especially in industrial wastewaters, that may inhibit microbial growth. Often, little can be done other than developing a special strain of seeding material. (See Standard Methods, 17th Ed., for additional information).

- Dirty BOD bottles are a common source of laboratory error. See Section 7.5 for Preventive Maintenance

3.0 SAFETY

As always, general laboratory safety practices should always be followed. Waste samples should be handled with care due to the uncertainty of the properties and contents involved.

Refer to the specific MSDS for the hazardous properties of any chemical or reagent involved in this procedure.

4.0 EQUIPMENT AND SUPPLIES

4.1 Equipment

- Hach SensION 6 BOD System with suitable D.O. Probe.
- Incubator; maintained at 20 ± 1°C

4.2 Glassware/Miscellaneous

- 300 mL BOD bottles with stoppers and plastic caps
- tubing
- five-gallon glass water bottles
- 5, 10, 25 mL Seriological pipettes
- 50 mL and 100 mL graduated cylinders
- eppendorf pipettes and tips
- aeration pump and diffusers
- miscellaneous laboratory glassware

5.0 REAGENTS AND STANDARDS

All standards and reagents are prepared with Milli-Q Water, unless otherwise specified, in Class A volumetric flasks.

5.1 Reagents

5.1.1 Miscellaneous

Manganous Sulfate Solution
Alkali-Iodide-Azide Reagent
Sulfuric Acid, concentrated

Purchased from a chemical vendor.

- Life of Reagent: manufacturer's recommendation
- Storage requirements: none

5.1.2 Starch Solution

Dissolve 2 g laboratory grade soluble starch and 0.2 g Salicylic Acid, as a preservative, in 100 mLs hot DI water. Alternatively, this can be purchased from a vendor or a powdered starch form can be used.

- Life of reagent: one year
- Storage requirements: refrigerate

5.1.3 Sodium Thiosulfate Titrant, 0.025 M

Using an analytical balance capable of reading 0.1 mg, dissolve 6.205 g Analytical Reagent Grade Sodium Thiosulfate with DI water in a 1.0 L volumetric flask. Add 1.5 mLs of 6 N sodium hydroxide or 0.4 g solid Sodium Hydroxide pellets and dilute to volume. Standardize with Potassium Bi-iodate Solution.

- Life of reagent: one year
- Storage requirements: none

5.1.3.1 Standardization of Sodium Thiosulfate Titrant

Dissolve ~2 g Potassium Iodide free from iodate in a 500 mL Erlenmeyer flask with 150 mLs DI water. Add a few drops of concentrated Sulfuric Acid and 20 mLs standard Bi-Iodate solution (Rgt. 5.1.5). Dilute to 200 mLs and titrate liberated iodine with Thiosulfate titrant. Add starch indicator toward the end of the titration, when a pale straw color is reached. The solution will turn blue/black upon addition of the starch indicator. Titrate until the first disappearance of the blue color. When the solutions are of equal strength, 20 mLs of 0.025 M Sodium Thiosulfate should be required. If not, adjust the Sodium Thiosulfate solution to 0.025 M by adding either Milli-Q water or Sodium Thiosulfate proportionately.

5.1.4 Potassium Bi-iodate, 0.021 M

Using an analytical balance capable of measuring 0.1 mg, dissolve 8.1240 g of Analytical Reagent Grade Potassium Bi-Iodate in DI water and dilute to 1.0 L in a volumetric flask.

- Life of reagent: one year
- Storage requirements: none

5.1.5 Potassium Bi-iodate, 0.0021 M

Using all class A volumetric glassware, dilute 10.0 mL of Reagent 5.1.4 to 100.0 mLs with Milli-Q water.

- Life of Reagent: 24 hours
- Storage Requirements: none

5.1.6 Sodium Sulfite

Dissolve 1.575 g of Sodium Sulfite anhydrous in 1.0 L of DI water or dissolve 0.16 g of Sodium Sulfite anhydrous in 100 mLs of DI water.

· Life of reagent: 4 hours
· Storage requirements: none

5.1.7 BOD Dilution Water

Just prior to analysis, empty the contents of a HACH BOD nutrient buffer pillow into 19 liters of Milli-Q water that has been aerated for 24 hours, then aged for 24 hours at 20 ± 1°C. **Mix very well** – the nutrient salts are difficult to dissolve and complete dissolution is necessary for consistent results. After an aliquot is removed for the unseeded control, add seed at a 1.0% ratio to the remaining dilution water.

- Life of reagent: 24 hours for buffered dilution water
- Storage requirements: five-gallon glass bottle at 20 ± 1°C

5.1.8 Polyseed BOD Inoculum for Seeding

Empty the contents of polyseed capsule in 250 mLs of dilution water in a glass container. (This volume can be varied to produce the desired seed depletion.) Bran, which acts as a carrier for the bacteria, will neither dissolve nor will it inhibit bacterial activity. Aerate and stir the polyseed for at least one hour. This must be used within 6-hours of preparation. Seed is added to the dilution water at a concentration of 1% after an aliquot of unseeded dilution water for controls has been removed.

- Life of reagent: 6 hours
- Storage requirements: none

5.1.9 Potassium Iodide Solution

Dissolve 10 g KI into 100 mLs DI water in a volumetric flask.

5.1.10 1 + 50 Sulfuric Acid

Dilute 1 mL concentrated Sulfuric Acid (H_2SO_4) to 50 mLs DI Water in a volumetric flask.

5.2 Standards

5.2.1 Glucose/Glutamic Acid Quality Control Solution

Using an analytical balance capable of measuring 0.1 mg, add 0.075 g each of Glucose and Glutamic Acid, which have each been oven dried for 1 hour at 103°C and desiccated, to a 500 mL volumetric flask. Dilute to volume with Milli-Q water.

- Life of reagent: prepare weekly
- Storage requirements: refrigerate

5.2.2 Unseeded Control - Method Blank

300 mLs Dilution Water

5.2.3 Laboratory Control Standard (LCS) / LCS Duplicate (LCSD)

7 mLs Glucose-Glutamic Acid Solution + 293 mLs Seeded Dilution Water. In sets that contain one or more samples for carbonaceous BOD, add nitrification inhibitor to one of the LCS bottles.
Concentration: 198 ± 30.5 mg/L as BOD5

5.2.4 Matrix Spike (MS)

Choose a dilution of the sample to be spiked that is expected to deplete <4 mg/L O_2. Set up a second bottle and add 2 mLs Glucose-Glutamic Acid Solution prior to filling the bottle and dilution water. Concentration: 198 mg/L

5.2.5 Seed Control

Two dilutions are set up, typically using 20 and 30 mLs of Polyseed. Make sure to shake the seed preparation well prior to dispensing. Fill the bottles with unseeded dilution water.

5.2.6 Matrix Duplicate (DUP)

Set up one sample per set of twenty or fewer samples with a duplicate dilution.

5.2.7 Seeded Dilution Water Control

Set up 1 bottle with 300 mLs of seeded Dilution Water.

6.0 CALIBRATION (NON-DAILY)

Not Applicable.

7.0 PROCEDURE

7.1 Quality Control Checks

Quality Controls	Frequency	Control Limit
Method Blank (MB) [1]	1 in 20 or fewer samples	< 0.2 mg/L
LCS	1 in 20 or fewer samples	statistical limits
LCSD	1 in 20 or fewer samples	statistical limits
Matrix Spike	1 in 20 or fewer samples	75 - 125% Recovery
Matrix Duplicate	1 in 20 or fewer samples	≤ 20 RPD
Seed Control [2]	2 in 20 or fewer samples	>50% depletion (recommended)
Seeded Dilution Water Control	1 in 20 or fewer samples	0.6 to 1.0 mg/L

[1] Unseeded Control
[2] The control with the better depletion is used in all correction calculations.

7.2 Sample Preservation and Storage

Sample containers, preservation techniques and holding times may vary and are dependent on sample matrix, method of choice, regulatory compliance and/or specific contract or client request. Listed below are the holding times and the references which include container and preservation requirements for compliance with the Clean Water Act (CWA).

Regulation	Holding Time	Preservation	Reference
CWA	48 hours	Cool 4 ± 2°C	40 CFR Part 136.3

NOTE: BOD analysis is often done on time-composited samples. The 48-hour holding time starts at the beginning of the sampling period.

7.3 Sample Preparation

7.3.1 Sample Size

Great care must be taken in choosing sample dilutions, because if all depletions are out of range after 5 days of incubation, the samples cannot be set up again within the 48 hour holding time.

All samples that require BOD analysis, other than routine samples for which there is historical data, will be set up for COD titration as soon as possible after log-in. No BOD dilutions will be set up without a COD result, without specific written permission of the

Section Manager or a representative of the QC Department. The COD results will be recorded in the BOD data book in the column formatted for that purpose. CODs completed for BOD purposes only, do not need to be done in the context of a prep batch, but do need to be diluted and titrated correctly.

Determine the estimated BOD value either through historical data or a COD result. Normally, the BOD:COD ratio is 1:2 to 2:3. For routine samples, set up a minimum of 3 dilutions, one chosen from Table 1, to bracket the expected value, then a second using ~1/3 as much sample and a third dilution using ~3 times as much volume.

Set up a minimum of 5 BOD dilutions for all new or otherwise unfamiliar samples. Three of the dilutions should "cluster" around the expected BOD based on the COD, and the other 2 should spread the covered range using approximately 1/3 higher and 1/3 lower dilutions as described above.

There are several variations on BODs. See Standard Methods for procedures other than total and carbonaceous 5-day BOD.

7.3.2 Preparation

7.3.2.1 Set up the data book with sample control names and bottle numbers, 1 probe-read unseeded control, 2 probe-read seed controls, 1 probe-read seeded dilution water control and 2 Laboratory Control Standards (LCS). A matrix duplicate and a matrix spike sample must be set up for each analytical set of 20 or fewer samples. A minimum of 3 -dilutions per sample should be made.

7.3.2.2 Check all samples for pH. If <6.5 or >7.5, adjust the pH with sulfuric acid or sodium hydroxide. Do not dilute the sample more than 0.5%.

7.3.2.3 Check the samples for chlorine using a HACH DPD pillow. If chlorine is present, determine the amount of sodium sulfite needed to eliminate the chlorine. To 100 mLs of sample, add 10 mLs of KI and 10 mLs of 1+50 sulfuric acid. A yellow color should appear. Titrate with sodium sulfite solution to a pale straw color. Add a small amount of starch solution and titrate to the first disappearance of the blue color.

Determine the total amount of sample needed for all dilutions and use a titrant/sample ratio to determine how much sodium sulfite will be needed to treat the total amount. Do not dilute the sample more than 10%.

Measure out the amount of sample and mix with the appropriate amount of sodium sulfite. If a large amount of sodium sulfite is used, aerate the treated sample.

7.3.2.4 Determine the dilutions to be made on each sample and place the chosen amounts in the correct BOD bottles. Add nitrification inhibitor to all sample dilutions of any samples that require carbonaceous BOD analysis.

7.3.2.5 Refer to Section 5.2 for the preparation of the QC Samples.

7.3.2.6 Fill the unseeded control bottle and the 2 seed control bottles with buffered dilution water.

7.3.2.7 Add sufficient prepared seed solution to the remaining dilution water in the carboy to make a 1% solution. Mix well. Use the graduations on the carboy and a graduated cylinder.

7.3.2.8 Fill the remaining bottles, including the seeded dilution water control, the LCSs, and the sample bottles by siphoning seeded dilution water up to the middle of the ground glass part of each bottle. Swirl the carboy occasionally to ensure homogeneity of the seeding material. The bottles are now ready to be read for the initial DO content. The meter must first be calibrated.

7.4 Calibration / Standardization

7.4.1 Fill two BOD bottles with water from the same source; one for a Winkler titration and the other for calibrating the probe.

7.4.2 To the Winkler bottle, add 1 mL of manganous sulfate solution and 1 mL alkali-iodine azide reagent. Stopper the bottle and mix thoroughly. Allow the precipitate to settle until ~1 inch thick. Add 1 mL of concentration sulfuric acid and re-stopper the bottle. Mix until all the precipitate has dissolved.

7.4.3 Titrate 201 mLs of this solution with 0.025 M sodium thiosulfate until the solution is a pale yellow color. Add a few drops of 2% starch solution and continue titrating until the first disappearance of the blue color. If the endpoint is overshot, add a measured amount of bi-iodate solution and finish titrating, correcting the final volume of sodium thiosulfate for the amount of bi-iodate added. The amount of titrant used will be used to calibrate the DO probe: mL of titrant = mg/L oxygen.

7.4.4 Place the probe into the BOD bottle being used for calibration. Press the cal button. The CAL icon will appear. Press the read/enter button three times, enter in D.O. determined by the Winkler titration, then press the read/enter button again. This will then return to the read mode.

7.4.5 Remove the probe and re-cap this bottle for re-reading after all the samples have been read to verify that no drift has occurred.

7.5 Preventive Maintenance

7.5.1 Dissolved Oxygen Probe

Membrane cap replacement and refilling are required at scheduled intervals or if the probe does not function properly (due to damage or contamination). The recommended interval between filling solution changes is 1-2 months.

Prior to replacing the membrane cap, rub the outer metallic stem (anode) with the supplied polishing cloth to remove deposits that may interfere with probe function. Cleaning the anode alone may improve probe function.

7.5.2 Probe Storage

Store the probe in the provided storage compartment or a BOD bottle, either filled with DI water.

7.5.3 Incubator

The external coils on the incubators must be cleaned at least yearly for proper function. The incubator must be defrosted every 2 months.

7.5.4 BOD Bottles

Dirty BOD bottles are a common source of laboratory error. Bottles must be routinely rinsed between uses with acid, rinsed 3-times with tap water, then rinsed 3-times with DI water until no trace of the acid remains. Always check wet bottles with pH paper prior to use. Rinse thoroughly if necessary. (pH paper should not indicate a pH of <5.)

7.6 Sample Analysis

7.6.1 Reading Dissolved Oxygen

Read the dissolved oxygen in each bottle, rinsing the probe between each bottle with DI water, and record this as the initial DO in data book. Place the ground glass stoppers in the bottles and then seal them with white plastic caps. After all sample dilutions have been read, re-read the calibration bottle reserved from Section 7.4.6. The reading must be within 10% of the original reading or a corrective action report (CAR) must be written. Document the reading in the data book.

Record the temperature of incubator. Place the bottles in the incubator for 5-days $\pm$ 3 hours. After 5 days, remove the bottles and read the temperature of the incubator. Read and record final DO's, calculate and report the results.

7.7 Documentation

7.7.1 Analysis Logbook

The analysis of samples and standards is documented within the instrument run log. The data book must be completed for each day's analysis. An example of an analysis log page appears in Appendix A.

7.7.2 Reporting Results

Without rounding, enter the raw data on the appropriate Lotus spreadsheet. Carefully print, review and approve the spreadsheet. Have the data book and spreadsheet approved and signed by the designated reviewer before creating a print file and transferring the data to LIMS.

To obtain the result to report:

- Omit any dilutions with < 2 mg/L depletion;
- Omit any dilutions that have a final DO < 1.0 mg/L;
- Average those results which appear to be reasonable based on sample history, appearance, appropriate depletion, and agreement between values to obtain the final result. If the highest dilution volume was 250 mLs of sample and no depletion was over 2 mg/L, report as < reporting limit.

See your Section Manager and/or QA Group if any of the following situations occurred:

- All dilutions have < 2 mg/L drop in DO and volumes of sample are < 250 mLs;
- All final DO's are < 2 mg/L;
- Any or all results are in disagreement.

Less than or greater than values may be calculated or the sample may be analyzed past hold time at the client's request.

7.7.3 Traceability of Standards

Upon receipt or preparation, each chemical salt, solvent, acid, standard, or other reagent is entered into the laboratory's LabNet database and is issued a unique ID# based upon the type and sequential order in which the item was received. Further information entered into the database includes the manufacturer, lot # (if applicable), the date received or prepared, the expiration date, volume/weight received; concentration (if applicable); preparation details (if applicable), initials of the recording analyst, and the description of the item (i.e., Stock Solution – LCS/MS). Once the record is created, a unique label is printed and affixed to the appropriate standard/reagent container. Through a query, the laboratory can print the standards/reagents traceability for any batch of samples.

7.7.4 Data Review

Analytical data goes through a 200% review cycle. The analyst and a trained data reviewer perform the reviews according to the criteria established on the data review

checklist (refer to Appendix B). Upon the first 100% review, the review form is initialed and dated as reviewed. The package, with its review sheet, comments and any CARs is submitted to the section manager or peer reviewer for a second review. Once again, the review form is initialed and dated by the second reviewer. The completed data review form remains on file with the original data.

8.0 QUALITY CONTROL

8.1 QC Summary

8.1.1 At least one MB and the average of two LCSs will be included in each laboratory lot of 20 or fewer samples. One of the LCSs will be cBOD when one or more samples require cBOD.

8.1.2 The MBs, unseeded control, will be examined to determine if contamination is being introduced in the laboratory.

8.1.3 The LCS will be examined to determine both precision and accuracy.

8.1.4 Accuracy will be measured by the percent recovery (%R) of the LCS. The recovery must be in range, as determined by statistical analysis, in order to be considered acceptable. Additionally, %R will be plotted on control charts to monitor method accuracy.

8.1.5 Precision will be measured by the reproducibility of the LCSs

8.2 Corrective Action

When an out of control situation occurs, the analysts must use his/her best analytical judgment and available resources to determine the corrective action to be taken. The out of control situation may be caused by more than one variable. The analyst should seek the assistance of his/her immediate supervisor, QA personnel, or other experienced staff if he/she is uncertain of the cause of the out of control situation. The test must not be resumed until the source of the problem and an in-control status is attained. Out of control data must never be released without approval of the supervisor, QA personnel or the laboratory manager.

Due to short hold-time and 5-day BOD incubation period, out-of-control QC situations will not be discovered until after the sample hold times have expired. **The analyst must notify the Section Manager and/or Project Manager immediately when out-of-control QC situations occur.**

Listed below are steps to be taken when an out of control situation occurs. The analyst must:

- demonstrate that all the problems creating the out of control situation were addressed;

- document the problem and the action which was taken to correct the problem on a CAR;
- document on the CAR that an in control has been achieved; and
- receive approval (signature) of the Section Manager and/or QA personnel, or the Project Manager prior to the release of any analytical data associated with the problem.

9.0 DATA ANALYSIS AND CALCULATIONS

9.1 Sample Calculations

$$mg/L = \frac{[(\text{Initial DO} - \text{Final DO}) - (\text{Initial Seed DO} - \text{Final Seed DO}) \times F]}{P}$$

Where:
F = 0.01 x mLs dilution water / seed control mLs
P = mLs sample used/300

NOTE: Choose the one seed control with the better depletion for use in all BOD5 calculations.

9.2 Accuracy

9.2.1 Matrix Spike

$$\frac{(\text{Depletion of spiked sample bottle} - \text{depletion of original sample bottle})}{2} \times 300 = \text{Observed BOD in mg/L}$$

$$\frac{\text{Observed BOD}}{200} \times 100 = \%\ \text{Recovery}$$

9.2.2 LCS and LCS Duplicate

$$\frac{\text{Observed BOD}}{198^*} \times 100 = \%\ \text{Recovery LCS}$$

*or 164 for cBOD

9.3 Precision

9.3.1 Matrix Dup. and LCS Dup. Relative Percent Difference (RPD)

$$\frac{|\text{Original BOD} - \text{Duplicate BOD}|}{(\text{Original BOD} + \text{Duplicate BOD})/2} \times 100 = \text{RPD}$$

10.0 WASTE MANAGEMENT AND POLLUTION CONTROL

Refer to the SOP entitled "Disposal of Laboratory Waste".

11.0 METHOD PERFORMANCE CRITERIA

Refer to the SOP entitled "Laboratory Training: Skills and Mechanisms".

12.0 REFERENCES

Refer to Section 1.0

13.0 ATTACHMENTS

Table 1: BOD Dilutions
Appendix A: Example: Analysis Run Log
Appendix B: Example: Data Review Form

Historical File:

Revision 00: 07/22/91
Revision 01: 08/20/92
Revision 02: 01/08/93
Revision 03: 04/07/94
Revision 04: 09/14/95
Revision 05: 02/02/96
Revision 06: 10/16/96
Revision 07: 03/01/99
Revision 08: 02/24/00

Reasons for Change, Revision 08:

- Annual review.
- Added Section 1.1.3, Definitions.
- Change meter manufacturer, maintenance, etc.

U:\QC\SOP\WC\4051.DOC

Table 1

BOD Dilutions

Sample Volume (mL) per 300 mL Bottle	Minimum BOD Detected	Maximum BOD Detected
300	2	7
250	2	8
200	3	10
150	4	14
100	6	21
75	8	28
50	12	42
35	17	60
25	24	84
20	30	105
15	40	140
10	60	210
9	67	230
7	86	300
5	120	420
3	200	700
2	300	1,050
1	600	2,100
0.5	1,200	4,200
0.3	2,000	7,000
0.1	6,000	21,000
0.05	12,000	42,000
0.03	20,000	70,000
0.01	60,000	210,000
0.005	120,000	420,000
0.003	200,000	700,000
0.001	600,000	2,100,000

These ranges are determined as follows:

$$\frac{2\ (\text{minimum acceptable depletion}) \times 300}{\text{volume (mLs)}} = \text{minimum BOD detected}$$

$$\frac{7\ (\text{approximate maximum depletion}) \times 300}{\text{volume (mLs)}} = \text{maximum BOD detected}$$

Appendix A.

Example: Analysis Run Log

Appendix B.

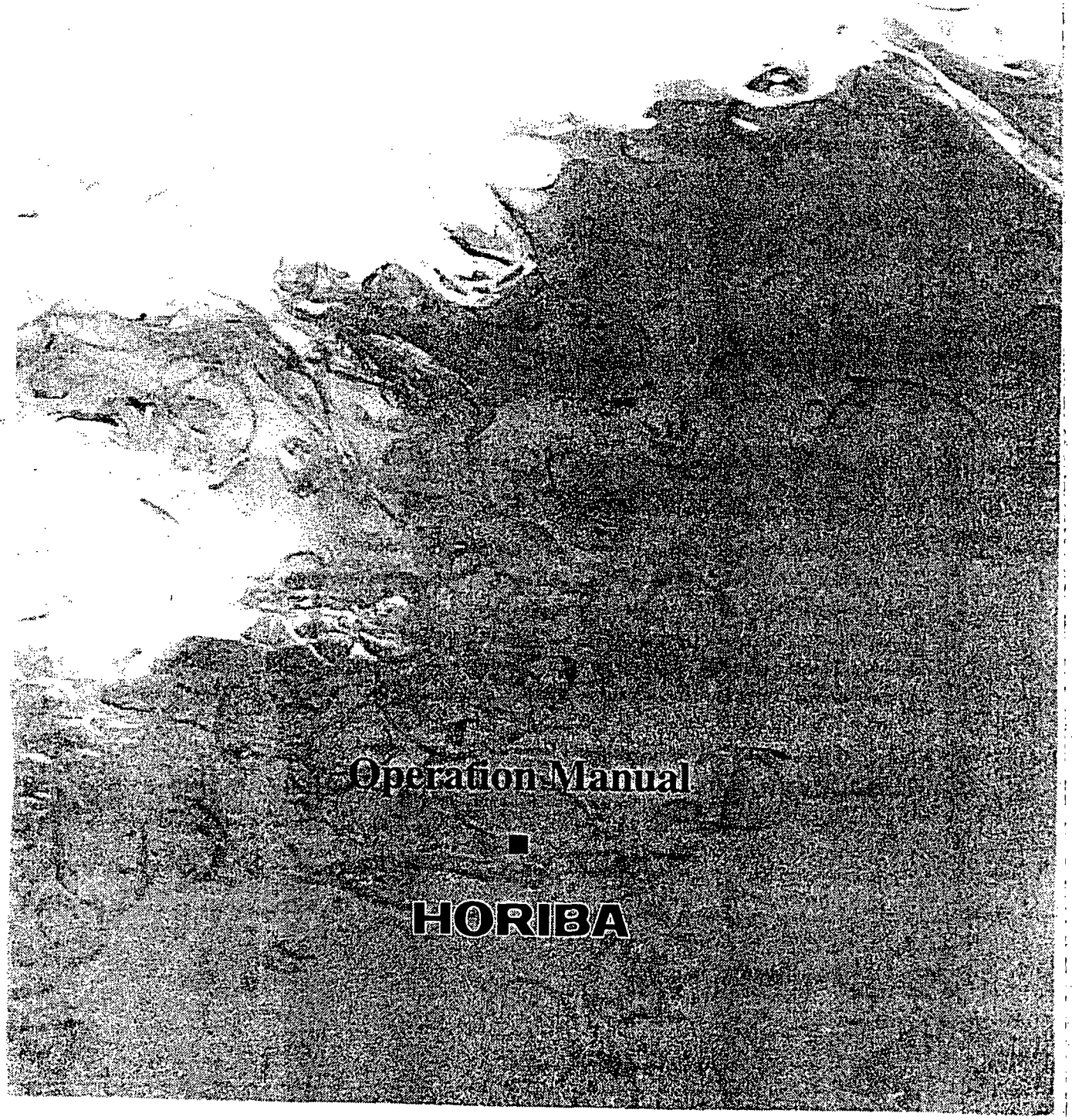
Example: Data Review Checklist

B

MULTI-PARAMETER WATER QUALITY MONITORING SYSTEM

U-20 Series

U-22.23



Operation Manual

HORIBA

HORIBA's Warranty and Responsibility

Your U-20 series multi-parameter water quality monitoring system is covered by HORIBA's warranty for a period of one (1) year, under normal use. Although unlikely, if any trouble attributable to HORIBA should occur during this period, necessary exchange or repairs shall be conducted by HORIBA, free of charge. The warranty does not cover the following:

- Any trouble or damage attributable to actions or conditions specifically mentioned in the operation manuals to be avoided
- Any trouble or damage attributable to use of the multi-parameter water quality monitoring system in ways or for purposes other than those described in the operation manuals
- If any repairs renovations, disassembly, etc. are performed on this multi-parameter water quality monitoring system by any party other than HORIBA or a party authorized by HORIBA
- Any alteration to the external appearance of this multi-parameter water quality monitoring system attributable to scratches, dirt, etc. occurring through normal use
- Wear and tear to parts, the exchange of accessories, or the use of any parts not specified by HORIBA

Conformable Directive

CE

This equipment is in conformity with the following directives and standards:

Directives: The EMC Directives 89/336/EEC as amended by 91/263/EEC, 92/31/EEC and 93/68/EEC, in accordance with the Article 10 (1) of the Directive.

Standards: EN55011: 1991 Class B Group I
EN50082-1: 1992

FCC Warning

This equipment has been tested and found to comply with the limits for a Class A digital device, pursuant to part 15 of the FCC Rules. These limits are designed to provide reasonable protection against harmful interference when the equipment is operated in a commercial environment. This equipment generates, uses, and can radio frequency energy and, if not installed and used in accordance with the instruction manual, may cause harmful interference to radio communications. Operation of this equipment in a residential area is likely to cause harmful interference in which case the user will be required to correct the interference at his own expense.

Unauthorized reprinting or copying of this operation manual

No unauthorized reprinting or copying of all or part of this operation manual is allowed. The utmost care has been used in the preparation of this operation manual. If, however, you have any questions or notice any errors, please contact the HORIBA customer service printed on the back cover of this operation manual.

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Preface

Thank you very much for purchasing HORIBA's "MULTI-PARAMETER WATER QUALITY MONITORING SYSTEM" U-20 Series.

Compact and one-hand-held, our multi-parameter water quality monitoring system makes measurements about a large number of items simultaneously.

The instrument uses a large-sized LCD display and has a variety of functions through easy operation, being useful for use at sites where measurements are to be made.

The water-proof construction of the instrument is compliant with IP-67 of IEC 529, "Water-proof test on electrical and mechanical equipment and tools and protection grade against entry of solids." Please use the instrument by following the information in this Operation Manual to maintain the water-proof construction of the instrument.

IP-67 standards

- Keeping dust and grit out of the instrument
- Up to 5°C difference between water and an instrument employed and no entry of water into the inside of the instrument at a depth of 1 m for 30 minutes

This Operation Manual contains information on the basic way of handling the instrument, notes, etc. for the user. Be sure to read through the Operation Manual before use.

Symbols employed

The symbols employed herein have the following meanings:

⚠ **WARNING** : Improper use can result in serious injury or even death.

⚠ **CAUTION** : The improper use of the instrument may cause the following dangers:

- Danger of injury
- Danger of damage to the instrument, its peripherals, and data

Important : Explanation necessary for the proper operation of the instrument

Note : Explanation that is useful and necessary for handling the instrument

☞ : Refer to the item shown.

Symbols employed in screen description

The symbols and used in screen description have the following meanings:

: The letters and numbers in this symbol are blinking on the screen.

: The letters and numbers in this symbol are lighting up on the screen.

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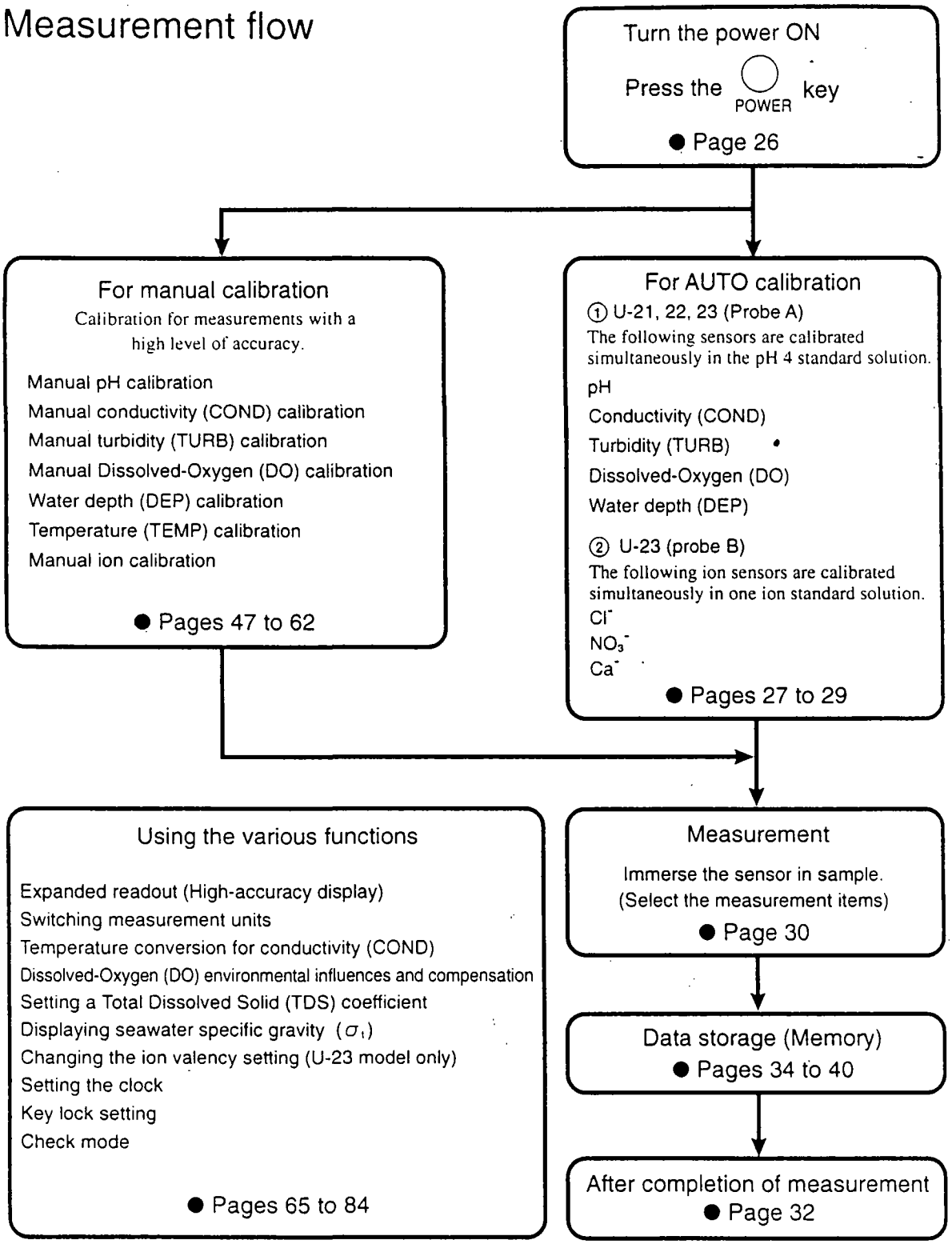
Measurement flow



3. Basic operation

The pH, conductivity (COND), turbidity (TURB), dissolved-oxygen (DO), water depth (DEP) and ion (ION1, 2, 3) sensors can be calibrated automatically. Upon completion of this chapter, even beginners should be able to make measurements easily.

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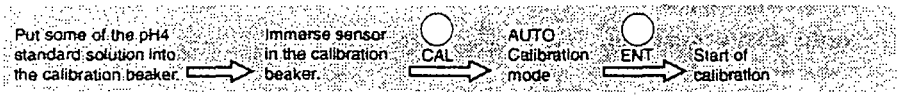
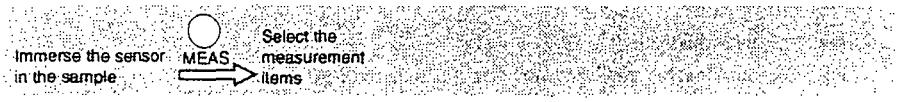


3.2.3 Measurement 30



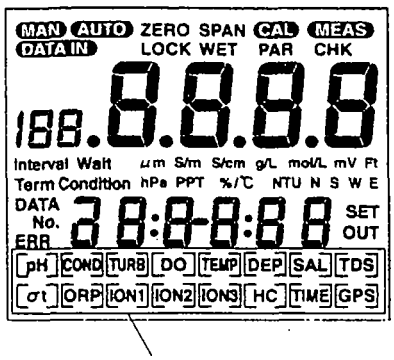
3.2.4 After completion of measurement 32

3.1 Key operations and mode switching

Measuring items and displays which are switched with the MEAS key

The items measurable with individual models are displayed. The items selected with the MEAS key will be indicated with [ ].

Example: In the pH Measurement mode: [pH]



Display block

The symbols displayed and their meanings are as follows:

pH ..... pH
COND ..... Conductivity
TURB ..... Turbidity
DO ..... Dissolved-Oxygen
TEMP ..... Temperature
DEP ..... Depth
SAL ..... Salinity
TDS ..... Total dissolved solids
σ_t ..... Specific gravity of seawater
ORP ..... Oxidation-reduction potential
ION1 ..... Cl^- (Chloride) ion
ION2 ..... NO_3^- (Nitric acid) ion
ION3 ..... Ca^{2+} (Calcium) ion
(ION1, ION2, ION3: if standard attachment ion sensors are used)
TIME ..... Display of date and time
GPS ..... G.P.S. (Global Positioning System) for imformation of position

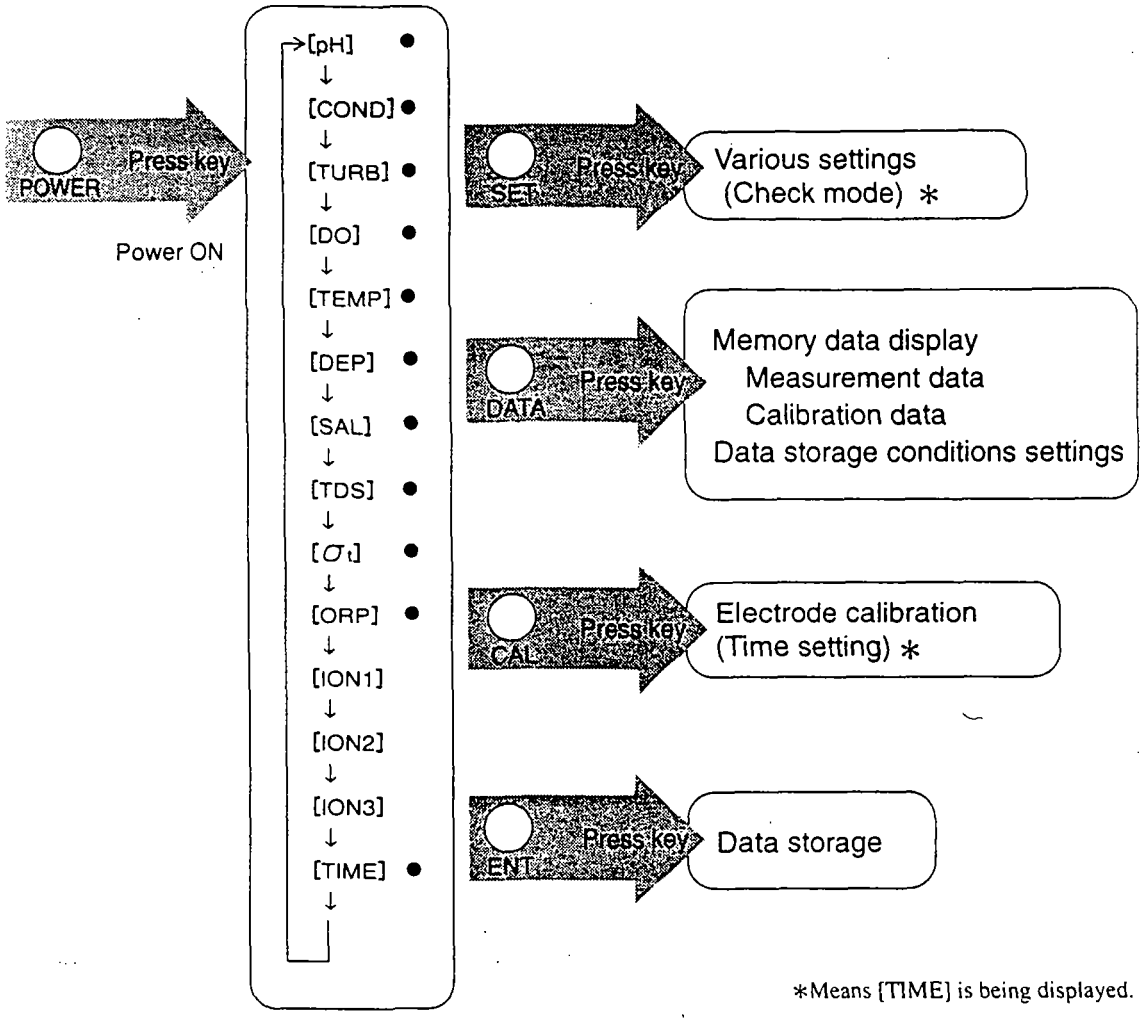
* When optional sensors C1, C2, and C3 are connected to the instrument, ION1, ION2, and ION3 appears for the optional sensors C1, C2, and C3, respectively.

Note

- [GPS] lights up when the optional G.P.S. sensor has been connected to the instrument and position information is received from the G.P.S. sensor during the measurement. For more information, refer to the instruction manual for the expansion units.

U-23 Measurement mode

(MEAS) When the MEAS key is pressed, the next measurement item appears.



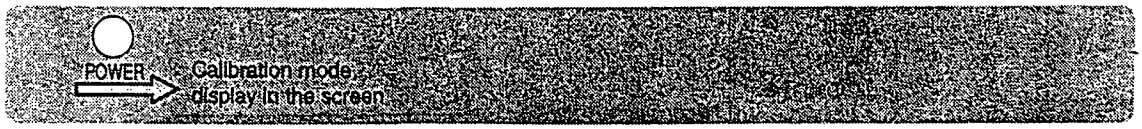
*Means [TIME] is being displayed.

Note

- The measurement items for the U-22 model are indicated with ●, respectively.
- "*Measurement item setting*" on page 79 explains how to set the display so items are not displayed.

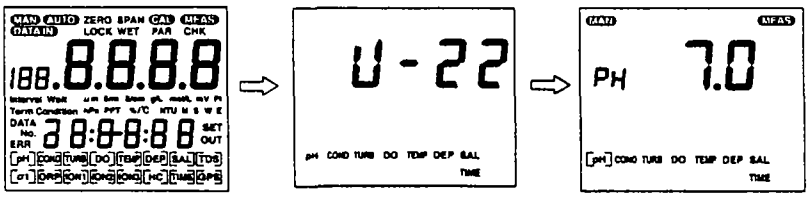
3.2 Operation procedure

3.2.1 Power ON



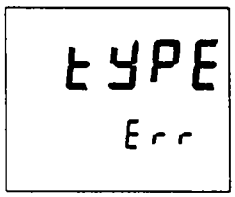
1. Press the **POWER** key.

The display will change in the order of All segment display → Sensor detector display → pH Measurement mode.



For U-22 model

With the sensor probe is not connected,



is displayed.

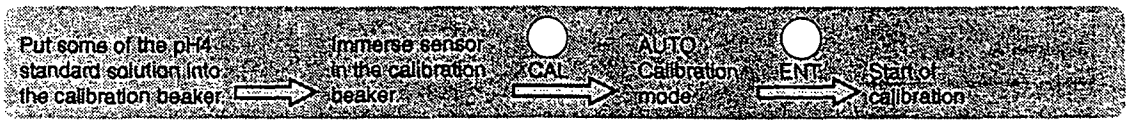
Before turning ON the instrument, connect the sensor probe properly.

3.2.2 AUTO calibration method

To obtain correct measurement, it is necessary to calibrate the sensor using the standard solution before performing measurement.

Note

- In the AUTO calibration mode, the pH, COND, and TURB sensors are calibrated in the pH4 standard solution, and the DO and DEP sensors in the atmosphere simultaneously.
- Values may be unstable if there is temperature fluctuation. Calibrate after waiting for about an hour.

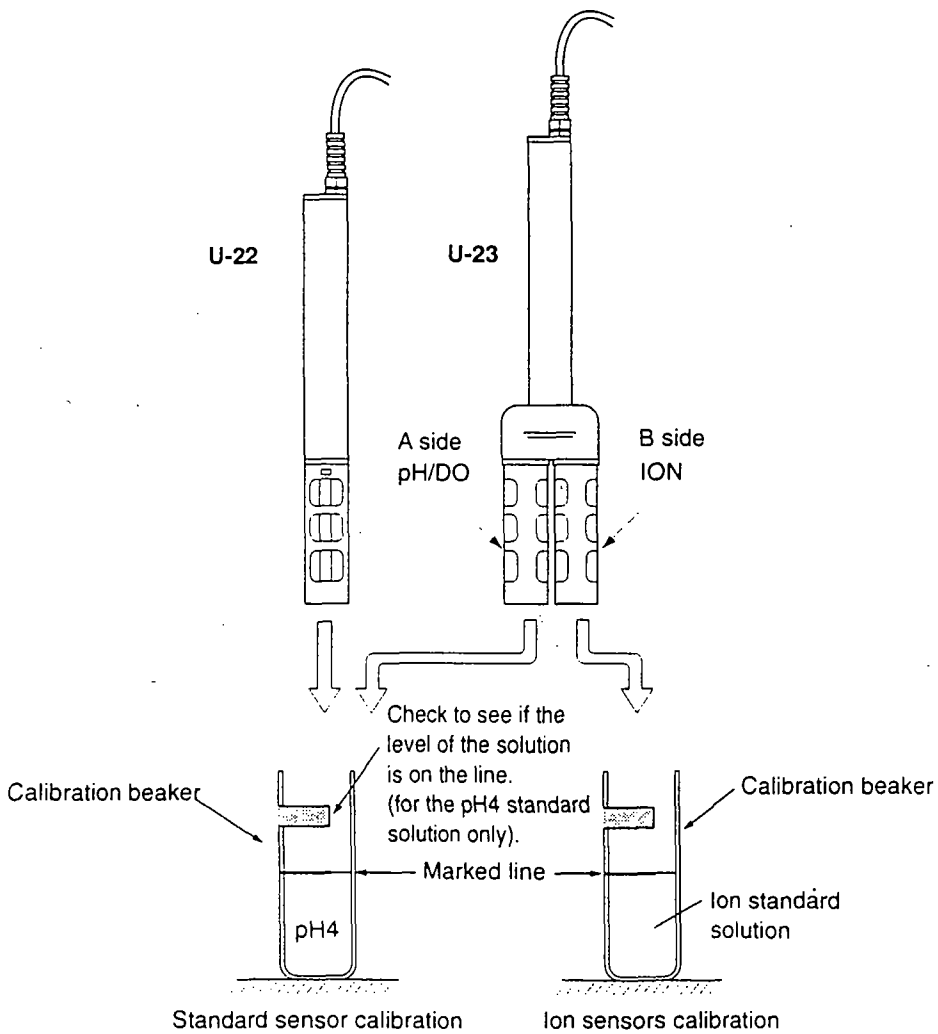


Calibrate using the following procedure.

1. Wash the sensor in distilled water a few times and put some of the pH4 standard solution into the calibration beaker to the marked line. Then immerse the sensor in it.
For the U-23 model, immerse the sensor A side.

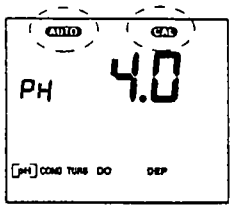
Important

- Use the label on the calibration beaker and check to see if the level of the calibration solution is on the label line.



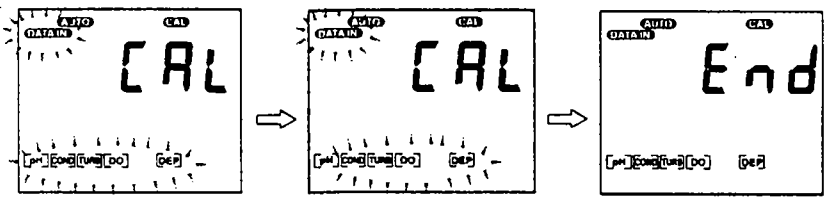
2. Press the **CAL** key in one of the Measurement modes pH, COND, TURB, DO and DEP.

AUTO and **CAL** appear and the instrument enters the AUTO Calibration mode.



3. Press the **ENT** key to start AUTO Calibration.

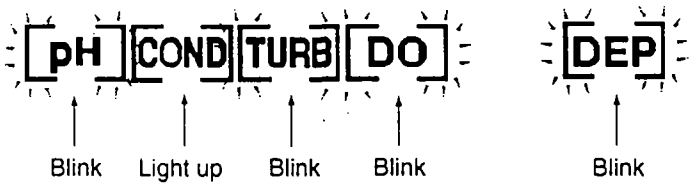
Upon completion of all of the pH, COND, TURB, DO, and DEP modes, End will be displayed.
During calibration, **DATA IN** and [ ] for the selected measurement item blink. [ ] light up for the item of which calibration is finished.



End of calibration

With DATA IN is blinking
To stop calibrating the sensor .... press the CAL key.
To establish the calibration ..... press the ENT key.

Example: When COND calibration is finished:
[ ] for [COND] stops blinking and light up steadily.



Note

- [ ] continues to blink because calibration is not performed for the item for which an error has happened. If two or more errors happen, an error with a smaller number appears. (See pages 89 to 91 for these errors and ways to solve them.) These calibration errors disappear when the sensor is calibrated properly again, or when the instrument is turned ON again.
- Calibration should be performed for maximum three minutes. When the indications become stable, calibration should be finished.

4. Press the **MEAS** key to return to the Measurement mode.

Important

- Neutralize any basic pH 4 fluids before disposal.

AUTO calibration of the ion sensors (U-23 model only)

AUTO calibration of the ion sensors (only for the combination of Cl^-, NO_3^-, Ca^{2+}).
The AUTO calibration function can be performed if the user has selected the combination of Cl^-, NO_3^-, Ca^{2+} ion sensors. For other combination of the ion sensors, be sure to set the ion valency described on page 74 for the manual calibration.

Important

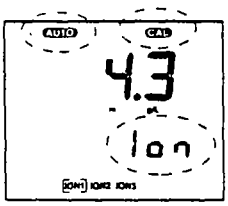
- Ion sensors take time to give stable indications. Therefore, immerse the ion sensors in the sample for approximately one hour. Then calibrate the ion sensors and perfom measurements.

1. Wash the sensor in distilled water a few times and put some of the supplied ion standard solution (#130) into the calibration beaker to the marked line. Then immerse the B side of the sensor in it.

2. Enter ion measurement mode 1, 2 or 3.

3. Press the **CAL** key.

AUTO, **CAL**, and "Ion" below them appear. The instrument then enters the AUTO Calibration mode.

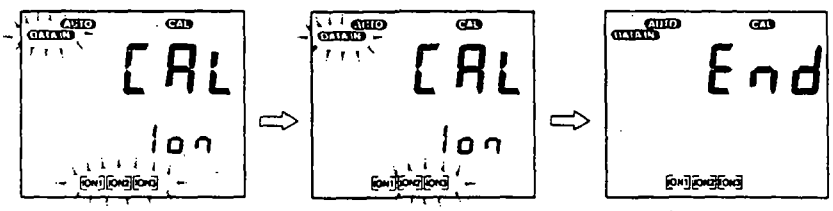


Important

- Only the standard supplied ion sensors (Cl^-, NO_3^-, and Ca^{2+}) can be calibrated automatically in the supplied ion standard solution (#130).

4. Press the **ENT** key to start AUTO calibration.

Upon completion of the AUTO calibration of all the ion sensors ION1, ION2, and ION3, End will be displayed.



End of calibration

With DATA IN is blinking
To stop calibrating the sensor .... press the CAL key.
To establish the calibration ..... press the ENT key.

5. Press the **MEAS** key to return to the Measurement mode.

Important

- When the AUTO calibration is performed on the ion sensors, the data for the ion sensor calibrated manually is erased.

3.2.3 Measurement

1. Immerse the sensor in the sample.

2. Select the measurement item.

Use the MEAS key to switch measurement items in the following order:

For model U-22

pH → COND → TURB → DO → TEMP → DEP → SAL → TDS → σ_t → ORP → TIME ... then back to pH.

For model U-23

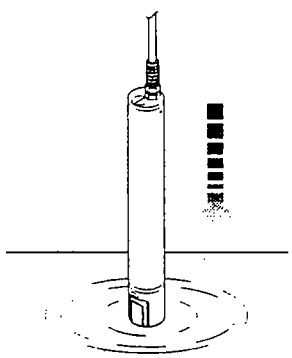
pH → COND → TURB → DO → TEMP → DEP → SAL → TDS → σ_t → ORP → ION1 → ION2 → ION3 → TIME ... then back to pH.

Note

- [GPS] lights up when the optional G.P.S. sensor is connected to the instrument and position information is received from the G.P.S. sensor.
- The above measurement items can be changed by setting "*Measurement item setting*" described on page 79.

Important

- When immersing the sensor probe in the sample, slowly lower the sensor probe into the sample.



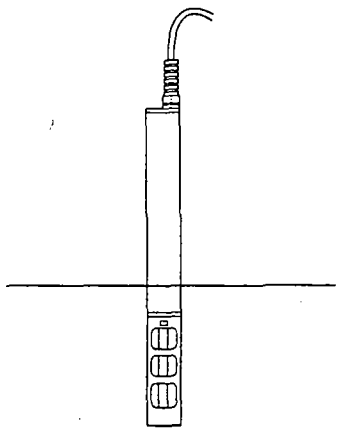
Two useful uses of the U-20 Series models

Making measurements

1. Manually storing the measurement data after checking the indication becomes stable

Example: After switching measurement items with the MEAS key, you can then store the measurement data after checking the indication becomes stable.

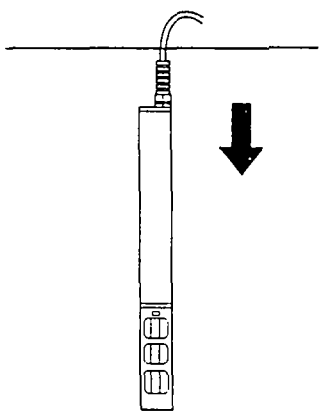
(☞ 4.1 *Manual storage of data while monitoring the measurement data*, page 34.)



2. Storing data

Example: Data can be stored continuously at constant intervals from the start of the automatic data storage. This function is useful in obtaining data in depth direction and in storing data continuously.

(☞ 4.2 *Automatic data storage*, page 36.)



Notes in obtaining data on depth

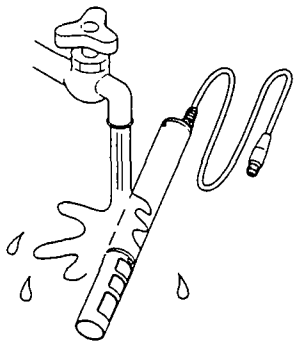
- When the instrument is placed at a depth of 100 m or more, the instrument may be broken.
  In measurements on the model U-23, the Ca^{2+} and NH_4^+ ion sensors can be used only at depth up to 15 m, and the K^+ ion sensor only at depth up to 3 m. This is because of the properties of the responsive membrane.

Notes for reliable measurements

- Any sensor contamination may affect measurements. Use the AUTO calibration mode to check for contamination on sensors about once a day for ion measurements and about once a week for others.

3.2.4 After completion of measurement

1. Turn the power to the instrument off.
2. Use tap water to completely wash off the sample on the sensor and then wipe waterdrops.



3. Put distilled water into the calibration beaker to the marked line with distilled water. Then, attach the calibration beaker to the sensor probe, cover the connector with the rubber cap and store the probe assembly in the carrying case.

Important

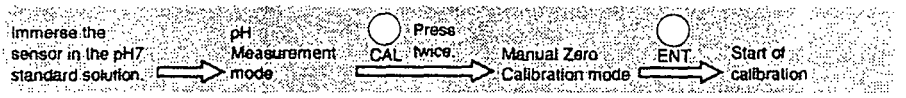
- Do not put water in the calibration beaker before attaching it to the ion sensor end (B side) of U-23.

Now you have read the description for performing measurements. For further information on how to use the instrument, refer to the chapters hereafter.

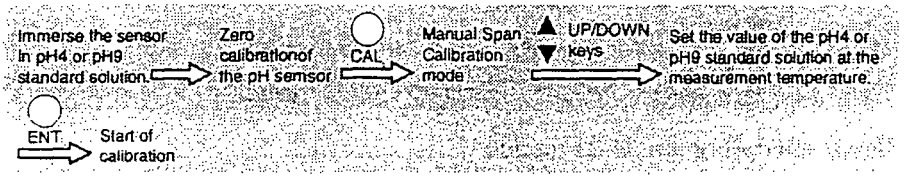
5. Techniques for more accurate measurement

In normal operation, calibration using the AUTO Calibration mode described earlier in the basic operation section provides sufficient accuracy. However, for more accurate measurement, manual calibration is effective. When measurement with high-accuracy extended display is needed, be sure to perform manual calibration.
Attention: The extended display mode is entered automatically when manual calibration is selected.

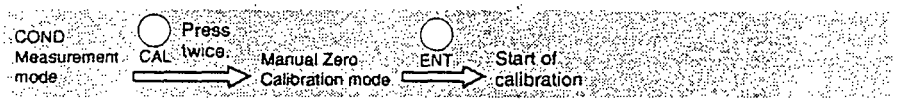
5.1 Manual pH calibration 47
5.1.1 Zero calibration 47



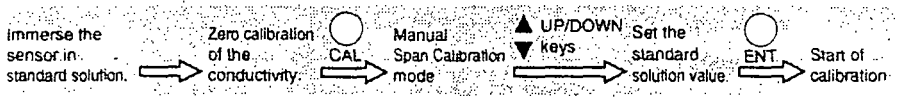
5.1.2 Span calibration 48



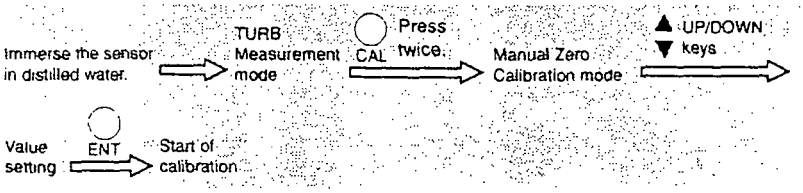
5.2 Manual conductivity (COND) calibration 49
5.2.1 Zero calibration 49



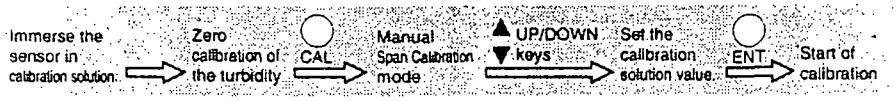
5.2.2 Span calibration 50



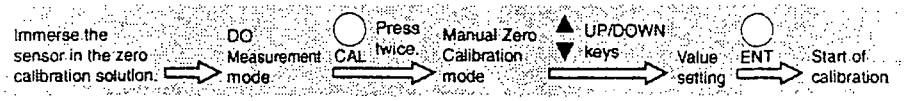
5.3 Manual turbidity (TURB) calibration 52
5.3.1 Zero calibration 52



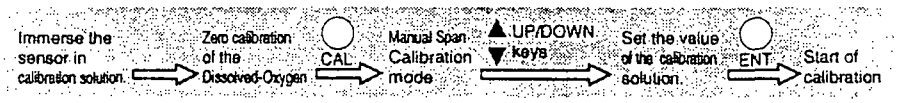
5.3.2 Span calibration 53



5.4 Manual Dissolved-Oxygen (DO) calibration 54
5.4.1 Zero calibration 54

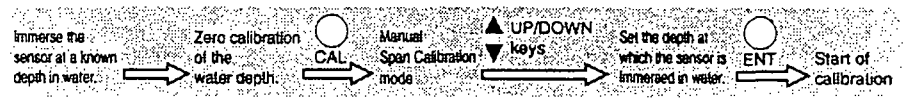


5.4.2 Span calibration 55

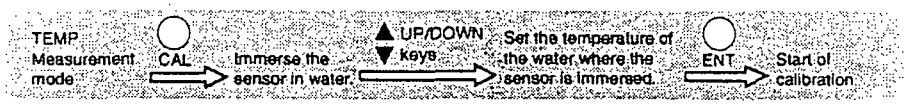


5.5 Water depth (DEP) calibration 57
5.5.1 Zero calibration 57

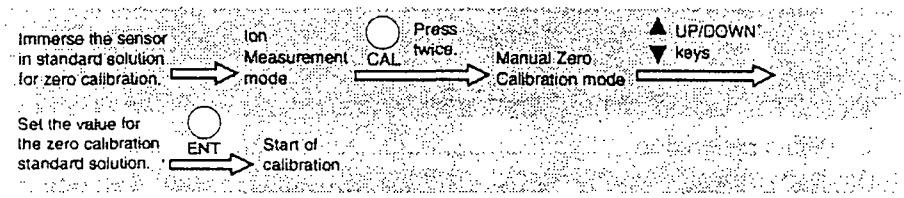
5.5.2 Span calibration 58



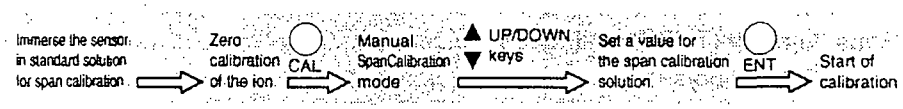
5.6 Temperature (TEMP) calibration 59



5.7 Manual ion calibration (U-23 model) 60
5.7.1 Preparation of calibration solution 60
5.7.2 Zero calibration 61

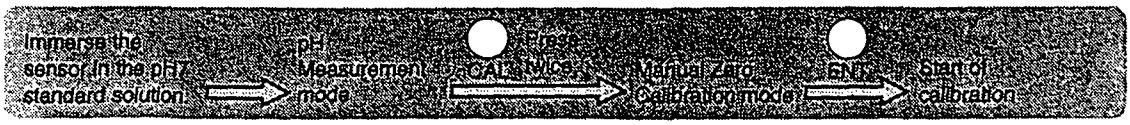


5.7.3 Span calibration 62



5.1 Manual pH calibration

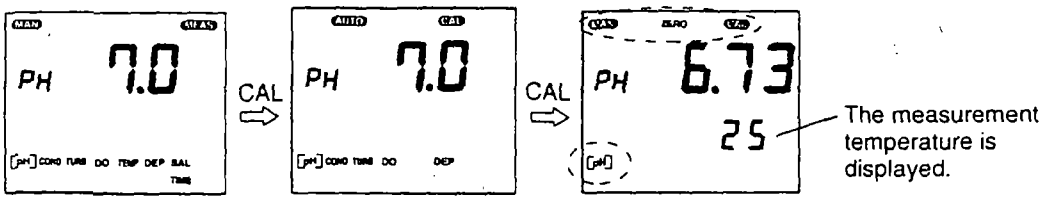
5.1.1 Zero calibration



1. Wash the sensor two or three times using distilled water, then pour some pH7 standard solution into the calibration beaker, and immerse the sensor in it. (For the U-23, immerse the sensor A side.)

2. Press the **CAL** key twice in the pH Measurement mode.

When the instrument enters the Manual Zero Calibration mode, **MAN**, **ZERO** and **CAL** light up.



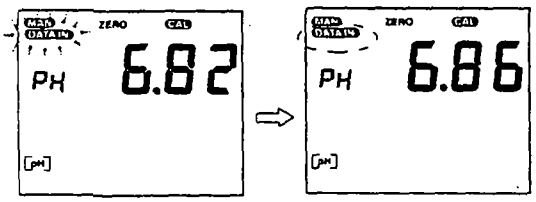
Manual Zero Calibration mode

3. Use the **UP/DOWN** (▲ ▼) keys to input the value for the pH7 standard solution at the measurement temperature.

(☞ *8. Reference data* page 98.)

4. Press the **ENT** key.

The manual zero calibration starts.



End of calibration

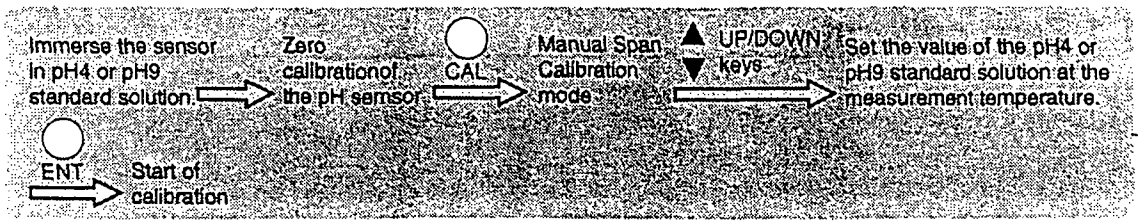
The measured value is displayed during calibration, and **DATA IN** blinks until the indicated value stabilizes. When the indicated value has stabilized, **DATA IN** lights up and the calibration finishes.

With DATA IN is blinking

To stop calibrating the sensor .... Press the CAL key.

To establish the calibration ..... Press the ENT key.

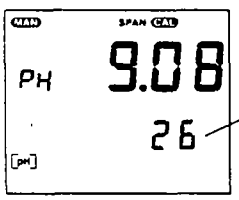
5.1.2 Span calibration



1. Wash the sensor two or three times using distilled water, then pour some pH4 or pH9 standard solution into the calibration beaker, and immerse the sensor in it. (For the U-23, immerse the sensor A side.)

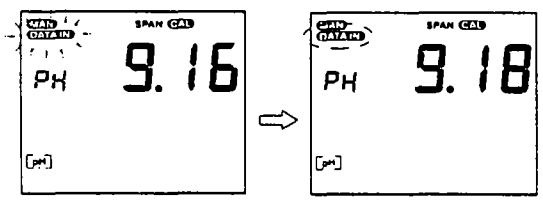
2. After the zero calibration of the pH sensor, press the **CAL** key to make sure that the instrument is in the Manual Span Calibration mode.
   MAN. SPAN and **CAL** light up.

3. Use the **UP/DOWN** (▲ ▼) keys to set the value for the pH4 or pH9 standard solution at the measurement temperature.



The measurement temperature is displayed.

4. Press the **ENT** key.
   The manual span calibration starts.



End of calibration

The measured value is displayed during calibration. and **DATA IN** blinks until the indicated value stabilizes. When the indicated value has stabilized. **DATA IN** lights up and the calibration finishes.

With DATA IN is blinking
To stop calibrating the sensor .... Press the CAL key.
To establish the calibration ..... Press the ENT key.

5. Press the **MEAS** key to return to the Measurement mode.

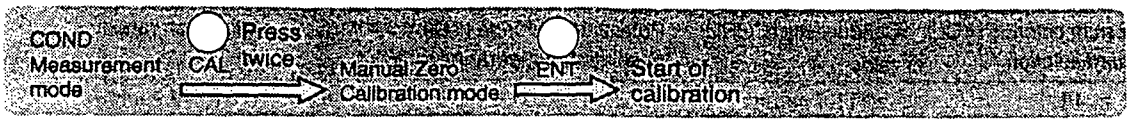
Note

- When the SET and CAL keys are pressed during the manual pH calibration mode, the calibration data for the pH sensor can be deleted.

5.2 Manual conductivity (COND) calibration

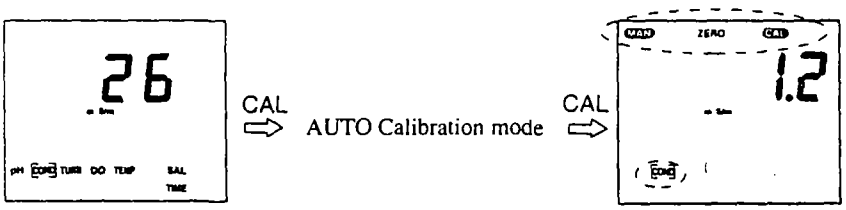
The U-20 series models can measure conductivity (COND) in the range from 0.90 to 9.99 S/m. Depending on the concentration of the sample, these models automatically select the most suitable measuring range from three ranges: 0.0 to 99.9 mS/m, 0.090 to 0.999 S/m, and 0.90 to 9.99 S/m. The zero point is common to the three measuring ranges.

5.2.1 Zero calibration



1. Wash the conductivity (COND) sensor two or three times using distilled water. Completely remove the water on the sensor and calibrate the instrument in the atmosphere.
2. Press the **CAL** key twice in the Conductivity (COND) Measurement mode.

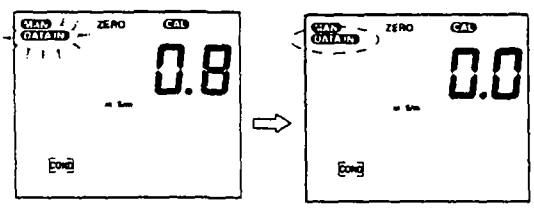
   When the instrument enters the Manual Zero Calibration mode, **MAN**, **ZERO** and **CAL** light up.



Manual Zero Calibration mode

3. Use the **UP/DOWN** (▲ ▼) keys to set the value to 0.0.
4. Press the **ENT** key.

   The manual zero calibration is starts.



End of calibration

The measured value is displayed during calibration, and **DATA IN** blinks until the indicated value stabilizes. When the indicated value has stabilized, **DATA IN** lights up and the calibration finishes.

With DATA IN is blinking
To stop calibrating the sensor .... Press the CAL key.
To establish the calibration ..... Press the ENT key.

5.2.2 Span calibration

Preparation of calibration solution (Potassium chloride (KCl) standard solution)

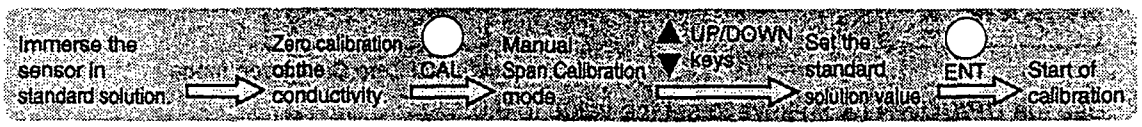
Dry Potassium chloride (KCl) powder (high-grade commercially available) at 105°C for two hours, and leave it to cool in a desiccator.
Consult the following table and measure a portion of potassium chloride (KCl), then prepare standard potassium chloride (KCl) solution following the procedure below.

Potassium chloride (KCL) standard solution	Conductivity (COND) value	Potassium chloride (KCl) weight (g) at solution temperature of 25°C	Calibration range
0.005 mol/L	71.8 mS/m	0.373	0.0 to 99.9 mS/m
0.050 mol/L	0.667 S/m	3.73	0.090 to 0.999 S/m
0.500 mol/L	5.87 S/m	37.2	0.90 to 9.99 S/m

1. Dissolve the weighed Potassium Chloride (KCl) in distilled water.
2. Put the dissolved Potassium Chloride (KCl) into a 1L measuring flask, and fill to the 1L mark with distilled water.

Calibration procedure

Perform the span calibration using the three types of standard solution as follows.

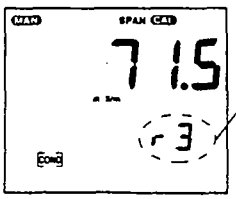


Important

- Set the temperature of the span standard solution to 25 ± 5°C.
- The sensor should be calibrated in the three standard solutions in the order of increasing concentration.

1. Wash the sensor two or three times using distilled water, then pour some standard solution into the calibration beaker, and immerse the sensor in it. (In the case of the U-23 model, immerse the sensor A side.)
2. After the zero calibration of the conductivity (COND) sensor, press the **CAL** key to make sure that the instrument is in the Manual Span Calibration mode.
   MAN, **SPAN** and **CAL** light up.

3. Use the **UP/DOWN** (▲ ▼) keys to set the standard solution value.



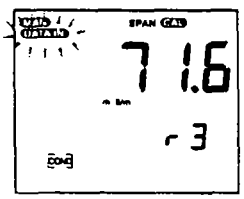
The calibration range is displayed.

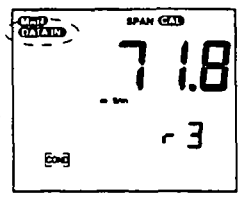
Note

- The sensor automatically identifies the calibration solution and the relevant calibration range is displayed.
  - r 1 : 0.90 to 9.99 S/m
  - r 2 : 0.090 to 0.999 S/m
  - r 3 : 0.0 to 99.9 mS/m

4. Press the **ENT** key.

The manual span calibration is starts.





End of calibration

The measured value is displayed during calibration, and **DATA IN** blinks until the indicated value stabilizes. When the indicated value has stabilized, **DATA IN** lights up and the calibration finishes.

With DATA IN is blinking
To stop calibrating the sensor .... Press the CAL key.
To establish the calibration ..... Press the ENT key.

5. Press the **CAL** key and use each standard solution and perform steps 1 to 4 above for calibration.

6. Press the **MEAS** key to return to the Measurement mode.

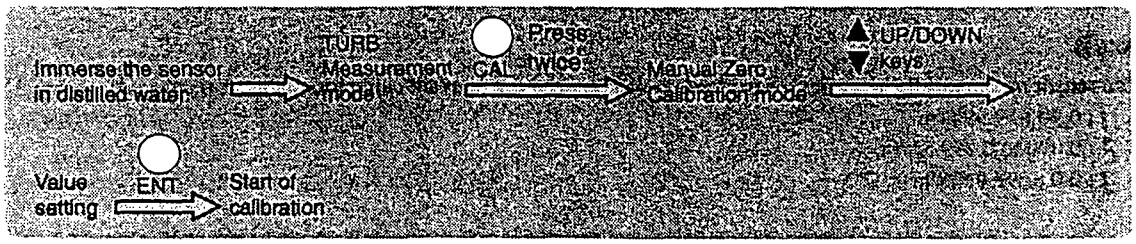
Note

- When the SET and CAL keys are pressed during the manual Conductivity (COND) Calibration mode, the calibration data for the conductivity (COND) sensor can be deleted.

5.3 Manual turbidity (TURB) calibration

5.3.1 Zero calibration

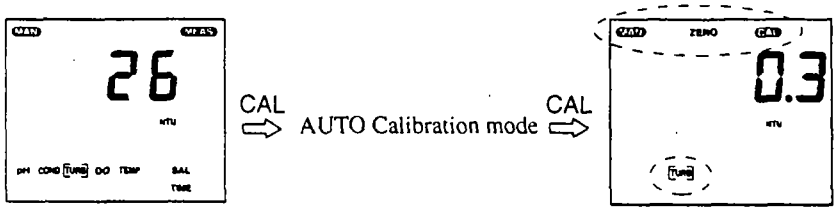
In zero calibration, distilled water is used as a calibration solution. If you cannot obtain distilled water, you may use ion exchange water, which can be considered to have a turbidity of zero.
When the turbidity (TURB) sensor is calibrated, it is particularly important that the probe is completely contamination-free. Do not use a contaminated probe. Otherwise unreliable calibration will result.



1. Wash the sensor two or three times using distilled water, then place some distilled water into the calibration beaker, and immerse the sensor in it. (For the U-23, immerse the sensor A side.)

2. Press the **CAL** key twice in the Turbidity (TURB) Measurement mode.

   When the instrument enters the Manual Zero Calibration mode, **MAN**, **ZERO** and **CAL** light up.

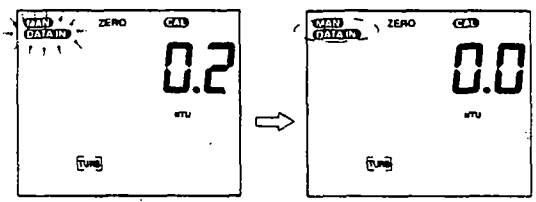


Manual Zero Calibration mode

3. Use the **UP/DOWN** (▲ ▼) keys to set the value to 0.0.

4. Press the **ENT** key.

   The manual zero calibration is started.



End of calibration

The measured value is displayed during calibration, and **DATA IN** blinks until the indicated value stabilizes. When the indicated value has stabilized, **DATA IN** lights up and the calibration finishes.

With DATA IN is blinking
To stop calibrating the sensor .... Press the CAL key.
To establish the calibration ..... Press the ENT key.

5.3.2 Span calibration

Preparation of calibration solution

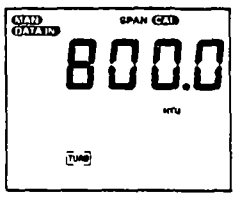
Weigh out 5.0 g of hydrazine sulfate, and dissolve it in 400 mL of distilled water. Next dissolve 50 g of hexamethylene tetramine in 400 mL of distilled water, and mix the two solutions together. Finally add distilled water until the total solution volume is 1000 mL, and mix well. Store this solution at a temperature of 25 ± 3°C for 48 hours. The turbidity value (TURB) of this solution is equivalent to 4000NTU.
Use the solution as span calibration solution for turbidity (TURB) of 800NTU by diluting this solution by a factor of 5 (use a pipette to measure 50 mL of the 4000NTU solution and pour it into a 250 mL measuring flask, and add 200 mL of distilled water).

Calibration procedure

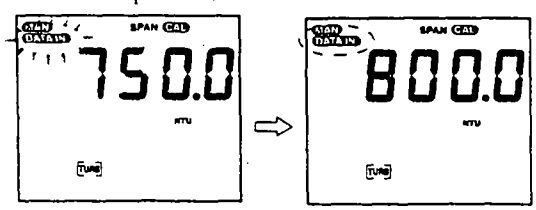
1. Wash the sensor two or three times using distilled water, then pour standard solution into a calibration beaker, and immerse the sensor in it. (For the U-23, immerse the sensor A side.)

2. After the zero calibration of the turbidity (TURB) sensor, press the **CAL** key to make sure that the instrument is in the Manual Span Calibration mode.
MAN, **SPAN** and **CAL** light up.

3. Use the **UP/DOWN** (▲ ▼) keys to set the value to 800.0.



4. Press the **ENT** key.
The manual span calibration is starts.



End of calibration

The measured value is displayed during calibration, and **DATA IN** blinks until the indicated value stabilizes. When the indicated value has stabilized, **DATA IN** lights up and the calibration finishes.

With DATA IN is blinking
To stop calibrating the sensor .... Press the CAL key.
To establish the calibration ..... Press the ENT key.

5. Press the **MEAS** key to return to the Measurement mode.

Important

- When it is known beforehand that the solution for measurement has a low turbidity (0 to 100 NTU), calibrate the sensor in the span calibration solution of 80 NTU. To prepare an 80 NTU calibration solution, dilute the 4,000NTU calibration solution with distilled water by a factor of 50.

Note

- When the SET and CAL keys are pressed during the manual Turbidity (TURB) Calibration mode, the calibration data for the turbidity (TURB) sensor can be deleted.

5.4 Manual Dissolved-Oxygen (DO) calibration

It is necessary to prepare a new calibration solution each time directly before calibration of the Dissolved-Oxygen (DO) sensor.

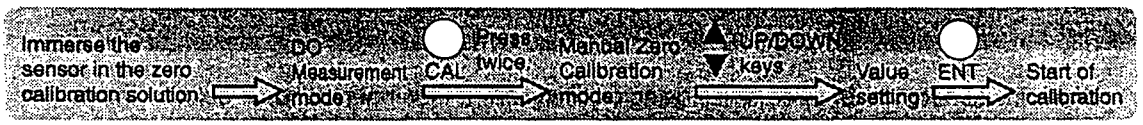
5.4.1 Zero calibration

Use ion exchange water or tap water with sodium sulfite dissolved in it.

Preparation of calibration solution

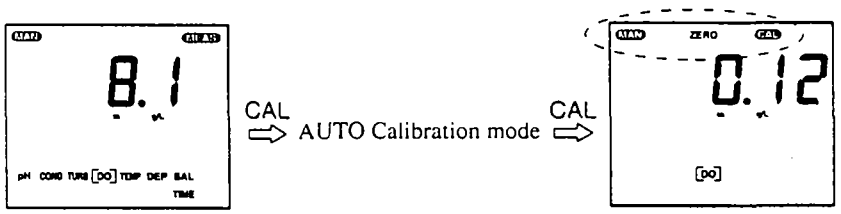
Add approximately 50 g of sodium sulfite to 1,000 ml of water (either ion exchange water or tap water) and stir the mixture to dissolve the sodium sulfite in it.

Calibration procedure



1. Use distilled water to wash the sensor a few times. Then fill the calibration beaker (above the marked line) with the zero calibration solution until the DO sensor can be immersed in the solution. Then immerse the sensor (the A side for the U-23 model) in the solution.
2. Press the **CAL** key twice in the Dissolved-Oxygen (DO) Measurement mode.

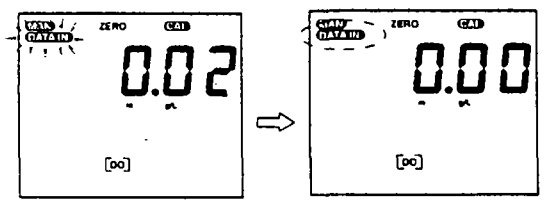
   When the instrument enters the Manual Zero Calibration mode, **MAN**, **ZERO** and **CAL** light up.



Manual Zero Caliburation mode

3. After the display has stabilized, use the **UP/DOWN** (▲ ▼) keys to set the value to 0.0.
4. Press the **ENT** key.

   The manual zero calibration is starts.



End of calibration

The measured value is displayed during calibration, and **DATA IN** blinks until the indicated value stabilizes. When the indicated value has stabilized, **DATA IN** lights up and the calibration finishes.

With DATA IN is blinking

To stop calibrating the sensor .... Press the CAL key.

To establish the calibration ..... Press the ENT key.

Important

- After calibration, use tap water to clean the sensor.

5.4.2 Span calibration

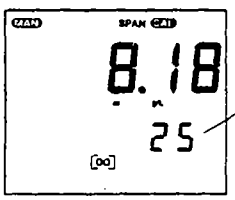
Use ion exchange water or tap water with saturated dissolved oxygen as the span calibration liquid.

Preparation of standard solution for span calibration

Pour 1 to 2 liters of water into a container (either ion exchange water or tap water). Using a pneumatic pump, feed air into the water and froth up the solution until oxygen is saturated.

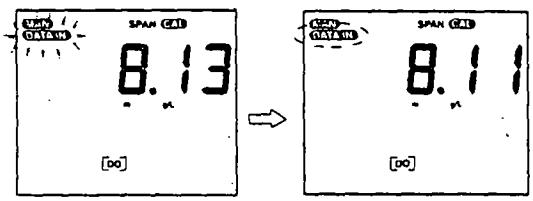
Calibration procedure

1. Wash the sensor twice or three times and immerse the sensor (the A side for the U-23 model) in the span calibration solution.
2. After the zero calibration of the Dissolved-Oxygen (DO) sensor, press the **CAL** key to make sure that the instrument is in the Manual Span Calibration mode.
   MAN, **SPAN** and **CAL** light up.
3. After the display has stabilized, use the **UP/DOWN** (▲ ▼) keys to set the amount of saturated dissolved oxygen in water at the temperature.



The temperature setting is displayed. Refer to the table given on page 56 and set a value equivalent to the amount of saturated dissolved oxygen at the temperature.

4. Press the **ENT** key.
   The manual span calibration is starts.



End of calibration

The measured value is displayed during calibration, and **DATA IN** blinks until the indicated value stabilizes. When the indicated value has stabilized, **DATA IN** lights up and the calibration finishes.

With DATA IN is blinking
To stop calibrating the sensor .... Press the CAL key.
To establish the calibration ..... Press the ENT key.

5. Press the **MEAS** key to return to the Measurement mode.

Note

- When the SET and CAL keys are pressed during the manual Dissolved-Oxygen (DO) calibration mode, the calibration data for the dissolved-oxygen (DO) sensor can be deleted.

Amounts of saturated dissolved oxygen in water at various temperatures (salinity=0.0%)

Temp. (°C)	DO (mg/L)	Temp. (°C)	DO (mg/L)	Temp. (°C)	DO (mg/L)	Temp. (°C)	DO (mg/L)
0	14.16						
1	13.77	11	10.67	21	8.68	31	7.42
2	13.40	12	10.43	22	8.53	32	7.32
3	13.04	13	10.20	23	8.39	33	7.22
4	12.70	14	9.97	24	8.25	34	7.13
5	12.37	15	9.76	25	8.11	35	7.04
6	12.06	16	9.56	26	7.99	36	6.94
7	11.75	17	9.37	27	7.87	37	6.86
8	11.47	18	9.18	28	7.75	38	6.76
9	11.19	19	9.01	29	7.64	39	6.68
10	10.92	20	8.84	30	7.53	40	6.59

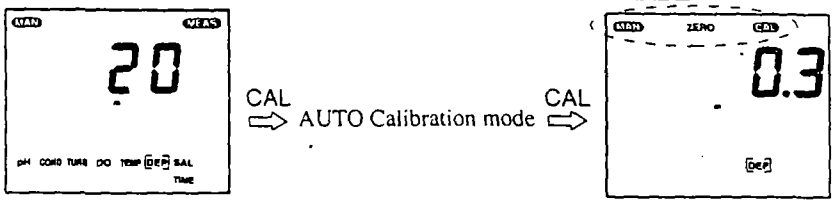
5.5 Water depth (DEP) calibration

5.5.1 Zero calibration

1. Immerse the sensor in the sample water for approximately 30 minutes so that sensor probe and sample temperatures become the same.

2. Press the **CAL** key twice in the Water Depth (DEP) Measurement mode.

When the instrument enters the Manual Zero Calibration mode, **MAN**, **ZERO** and **CAL** light up.



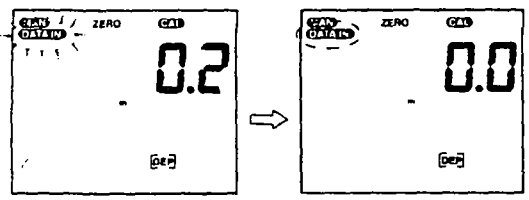
Manual Zero Calibration mode

Immerse the sensor probe so that the storage lid for a memory backup battery is at the water surface. The water surface level is considered as depth 0 m.

3. Use the **UP/DOWN** (▲ ▼) keys to set the value to 0.0.

4. Press the **ENT** key.

The manual zero calibration is starts.



End of calibration

The measured value is displayed during calibration, and **DATA IN** blinks until the indicated value stabilizes. When the indicated value has stabilized, **DATA IN** lights up and the calibration finishes.

With DATA IN is blinking

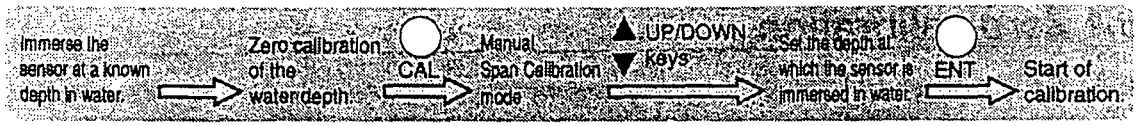
To stop calibrating the sensor .... Press the CAL key.

To establish the calibration ..... Press the ENT key.

Important

- Since the water depth (DEP) sensor depends greatly on temperature, calibrate the sensor at the same temperature as the sample for more accurate measurement.
- Use the AUTO Calibration mode because calibration error becomes large when using in a place with flow velocity or where it is shallow.

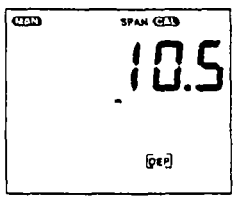
5.5.2 Span calibration



1. Immerse the sensor at a known depth in water. (Set the depth of the lid for memory backup battery as the depth setting.)

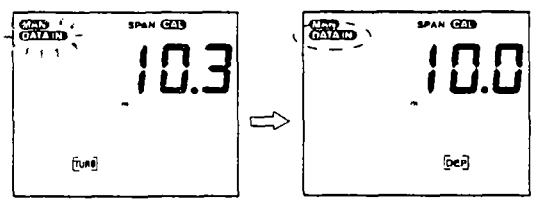
2. After the zero calibration of the water depth (DEP) sensor, press the **CAL** key to make sure that the instrument is in the Manual Span Calibration mode.
MAN, SPAN and **CAL** light up.

3. Use the **UP/DOWN** (▲ ▼) keys to set the depth at which the sensor is immersed in water.



4. Press the **ENT** key.

The manual span calibration is starts.



End of calibration

The measured value is displayed during calibration, and **DATA IN** blinks until the indicated value stabilizes. When the indicated value has stabilized, **DATA IN** lights up and the calibration finishes.

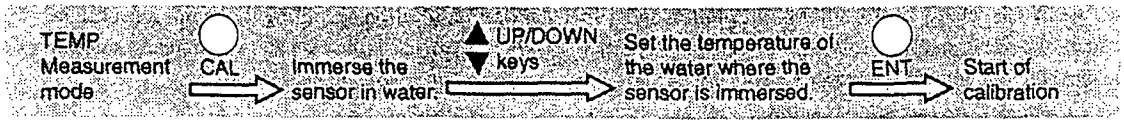
With DATA IN is blinking
To stop calibrating the sensor .... Press the CAL key.
To establish the calibration ..... Press the ENT key.

5. Press the **MEAS** key to return to the Measurement mode.

Note

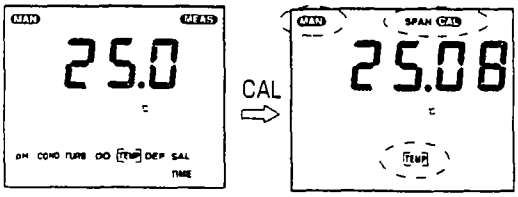
- When the SET and CAL keys are pressed during the manual Water depth (DEP) Calibration mode, the calibration data for the water depth (DEP) sensor can be deleted.

5.6 Temperature (TEMP) calibration



1. Press the **CAL** key in the Temperature (TEMP) Measurement mode.

Select the manual calibration mode.

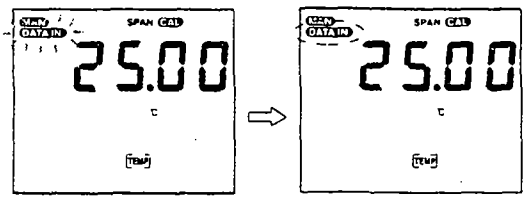


2. Immerse the sensor in water at a known temperature.

3. Use the **UP/DOWN** (▲ ▼) keys to set the temperature of the water where the sensor is immersed as a calibration value.

4. Press the **ENT** key.

The manual calibration is starts.



End of calibration

The measured value is displayed during calibration, and **DATA IN** blinks until the indicated value stabilizes. When the indicated value has stabilized, **DATA IN** lights up and the calibration finishes.

With DATA IN is blinking

To stop calibrating the sensor .... Press the CAL key.

To establish the calibration ..... Press the ENT key.

5. Press the **MEAS** key to return to the Measurement mode.

Note

- When the SET and CAL keys are pressed during the manual Temperature (TEMP) calibration mode, the calibration data for the temperature (TEMP) sensor can be deleted.

5.7 Manual ion calibration (U-23 model)

It is necessary to prepare a zero calibration solution and a span calibration solution according to the ion sensor to be calibrated. When the supplied standard ion sensors (Cl^-, NO_3^-, and Ca^{2+}) are used, the supplied ion standard solution can be used in common. When other sensors are used, it is necessary to set the ion valency first.
(☞ 6.7 *Changing the ion valency setting*)

5.7.1 Preparation of calibration solution

For standard ion sensors

To prepare a zero calibration solution, dilute the supplied ion standard solution (#130) by a factor of 10 with distilled water. The supplied ion standard solution (#130) is used without dilution as a span calibration solution. The supplied ion standard solution (#130) is used without dilution as a span calibration solution. The zero and span calibration values for the individual ion sensors are as follows:

Meter indication	ION	Zero calibration value	Span calibration value
ION1	Cl^-	3.55 mg/L	35.5 mg/L
	Chloride	(0.1m mol/L)	(1m mol/L)
ION2	NO_3^-	3.10 mg/L	31.0 mg/L
	Nitric acid	(50μ mol/L)	(0.5m mol/L)
ION3	Ca^{2+}	2.01 mg/L	20.1 mg/L
	Calcium	(50μ mol/L)	(0.5m mol/L)

For optional ion sensors

When calibrating any optional sensor, prepare a 0.1 mol/L standard solution first. Then dilute the standard solution to prepare a zero and a span calibration solution.

Preparing a 0.1 mol/L standard solution

Weigh out the individual reagents listed below for each ion type and dissolve each reagent in distilled water to obtain one liter of solution.

Ion type	Ion valency	Reagent (Special grade, commercial)	Weight	Concentration (mg/L)
Fluoride F^-	−1	Potassium fluoride	5.81 g	1900 mg/L
Potassium K^+	+1	Potassium chloride	7.46 g	3910 mg/L
Ammonia NH_4	+1	Ammonium chloride	5.35 g	1800 mg/L

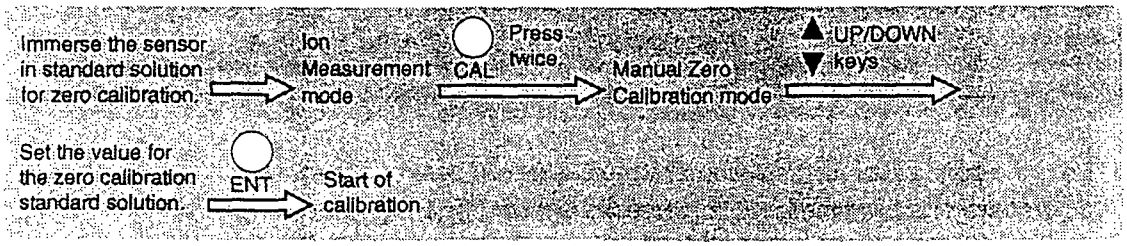
Preparing a calibration solution

To prepare a zero calibration solution and a span calibration solution , dilute the 0.1 mol/L standard solution for each ion type by a factor of 1000 and 100, respectively.

Ion type	Zero calibration solution	Span calibration solution
Fluoride F^-	1.9 mg/L (0.1m mol/L)	19 mg/L (1m mol/L)
Potassium K^+	3.9 mg/L (0.1m mol/L)	39 mg/L (1m mol/L)
Ammonia NH_4	1.8 mg/L (0.1m mol/L) + Sodium hydride*	18 mg/L (1m mol/L) + Sodium hydride*

* To prepare a standard solution for the ammonia ion sensor, place sodium hydride (0.4 g per 100 ml) into a standard solution for ammonium chloride directly before calibrating the ion sensor. A standard solution with sodium hydride changes with time because all of the ammonia content exists as ammonia gas. It is important to use the solution immediately.

5.7.2 Zero calibration



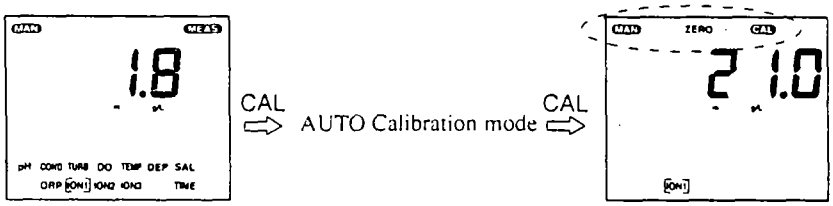
1. Wash the sensor with distilled water a few times. Then pour a zero calibration solution into the calibration beaker and immerse the sensor (the B side) into the solution.

Important

- Error messages are not displayed for ion sensor zero and span calibration. Immerse the sensor in the calibration solution and check the measured reading against the reference value before proceeding.

2. Select the measurement mode for each measurement item (ION1, 2, and 3) and press the **CAL** key twice.

When the instrument enters the Manual Zero Calibration mode, **MAN**, ZERO and **CAL** light up.

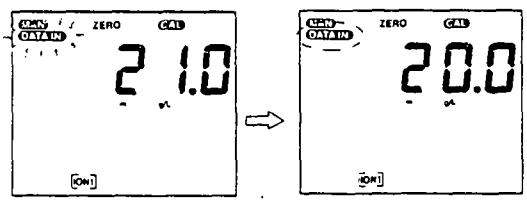


Manual Zero Calibration mode

3. Use the **UP/DOWN** (▲ ▼) keys to set the value for the zero calibration standard solution.

4. Press the **ENT** key.

The manual zero calibration is starts.



End of calibration

The measured value is displayed during calibration, and **DATA IN** blinks until the indicated value stabilizes. When the indicated value has stabilized, **DATA IN** lights up and the calibration finishes.

With DATA IN is blinking

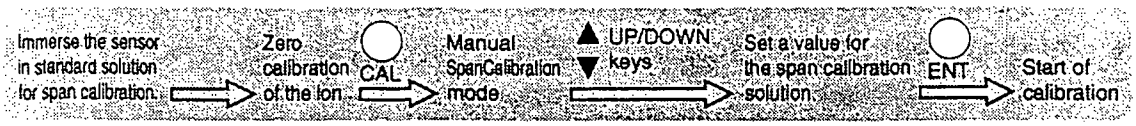
To stop calibrating the sensor .... Press the CAL key.

To establish the calibration ..... Press the ENT key.

Important

- For standard ion sensors, the common zero calibration solution is used. It is necessary to calibrate each of these ion sensors in the solution by performing the above procedure.
- For optional sensors, it is necessary to calibrate each of these ion sensors in the zero calibration solution for each ion sensor.

5.7.3 Span calibration



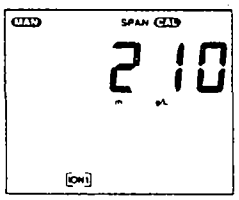
1. Pour the span calibration solution into the calibration beaker. Then wash the sensor with distilled water a few times and immerse the sensor (the B side) into the solution.

Important

- Error messages are not displayed for ion sensor zero and span calibration. Immerse the sensor in the calibration solution and check the measured reading against the reference value before proceeding.

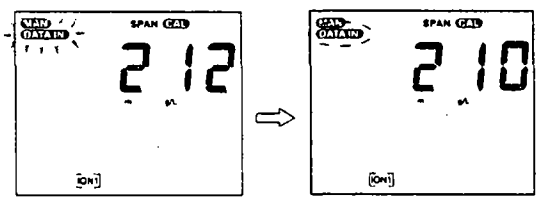
2. After the zero calibration of the ion sensor, press the **CAL** key to make sure that the instrument is in the Manual Span Calibration mode.
MAN. SPAN and **CAL** light up.

3. Use the **UP/DOWN** (▲ ▼) keys to set a value for the span calibration solution according to the ion type.



4. Press the **ENT** key.

The manual span calibration is starts.



End of calibration

The measured value is displayed during calibration, and **DATA IN** blinks until the indicated value stabilizes. When the indicated value has stabilized, **DATA IN** lights up and the calibration finishes.

With DATA IN is blinking
To stop calibrating the sensor .... Press the CAL key.
To establish the calibration ..... Press the ENT key.

5. Press the **MEAS** key to return to the Measurement mode.

Important

- For standard ion sensors, the common span calibration solution is used. It is necessary to calibrate each of these ion sensors in the solution by performing the above procedure.
- For optional sensors, it is necessary to calibrate each of these ion sensors in the span calibration solution for each ion sensor.

Note

- When the SET and CAL keys are pressed during the relevant manual Ion calibration mode, the calibration data for the relevant ion sensor can be deleted.

7.3 Specifications of U-20 series models

NOTE ○: Applicable
—: Unapplicable

		U-22	U-23
Instrument	Water-proof construction	IP67	IP67
	Mass	Approximately 475g (including the grip holder)	Approximately 475g (including the grip holder)
Sensor *1	Use in 2-inch well	○	—
	Measurement temperature	0 to 55°C	0 to 55°C (except ion)
	Storage temperature	-5 to 60°C	-5 to 60°C
	Measurement depth *2	to 100m	to 100m (except ion)
	Maximum sensor outside diameter	46mm	95mm
	Sensor length	380mm	430mm
	Continuous use available *3	30 days	30 days (except ion)
	Automatic data gathering at set time	○	○
	Mass (Cable10m)	Approximately 1.5kg	Approximately 1.8kg
pH ● Two-point calibration ● Automatic temperature compensation	Measuring principle	Glass electrode method	Glass electrode method
	Range	pH0 to 14	pH0 to 14
	Resolution	0.01pH	0.01pH
	Repeatability	±0.05pH	±0.05pH
	Accuracy	±0.1pH	±0.1pH
Dissolved-Oxygen ● Salinity conversion (0 to 40ppt/Auto) ● Automatic temperature compensation	Measuring principle	Diaphragm galvanic battery method	Diaphragm galvanic battery method
	Range	0 to 19.99mg/L	0 to 19.99mg/L
	Resolution	0.01mg/L	0.01mg/L
	Repeatability	±0.1mg/L	±0.1mg/L
	Accuracy	±0.2mg/L	±0.2mg/L
Conductivity ● Auto range ● Automatic temperature conversion (25°C)	Measuring principle	4 AC electrode method	4 AC electrode method
	Range	0 to 9.99S/m	0 to 9.99S/m
	Resolution	0.1%F.S	0.1%F.S
	Repeatability	±1%	±1%
	Accuracy	±3%	±3%
Salinity	Measuring principle	Conductivity conversion	Conductivity conversion
	Range	0 to 4%	0 to 4%
	Resolution	0.01%	0.01%
	Repeatability	±0.1%	±0.1%
	Accuracy	±0.3%	±0.3%
Total Dissolved Solid (TDS) ● Conversion factor setting	Measuring principle	Conductivity conversion	Conductivity conversion
	Range	0 to 99.9 g/L	0 to 99.9 g/L
	Resolution	0.1%F.S	0.1%F.S
	Repeatability	±2 g/L	±2 g/L
	Accuracy	±5 g/L	±5 g/L
Seawater specific gravity ● Display σ_t, σ_0, σ_{15}	Measuring principle	Conductivity conversion	Conductivity conversion
	Range	0 to 50 σ_t	0 to 50 σ_t
	Resolution	0.1 σ_t	0.1 σ_t
	Repeatability	±2 σ_t	±2 σ_t
	Accuracy	±5 σ_t	±5 σ_t
Temperature	Measuring principle	Thermistor method	Thermistor method
	Range	0 to 55°C	0 to 55°C
	Resolution	0.01°C	0.01°C
	Repeatability	±0.3°C	±0.3°C
	Accuracy	±1.0°C	±1.0°C

		U-22	U-23
Turbidity (TURB)	Measuring principle	Penetration and scattering method	Penetration and scattering method
● Unit selection	Range (NTU or mg/L)	0 to 800NTU	0 to 800NTU
	Resolution	0.1NTU	0.1NTU
	Repetability	±3%	±3%
	Accuracy	±5%	±5%
Water depth	Measuring principle	Pressure method	Pressure method
	Range	0 to 100m	0 to 100m
	Resolution	0.1m	0.1m
	Repetability	±3%	±3%
	Accuracy	±5%	±5%
Oxidation-reduction potential (ORP)	Measuring principle	Platinum electrode method	Platinum electrode method
	Range	±1999mV	±1999mV
	Resolution	1mV	1mV
	Repetability	±5mV	±5mV
	Accuracy	±15mV	±15mV
Ion type	Measuring principle		Ion electrode method
● Auto range	Resolution	-	0.1%F.S
	Repetability	-	±5%
	Accuracy	-	±10%
	Range		
	Nitric acid ion	-	NO_3^-: 0.62 to 62000mg/L (pH3 to 7)
	Chloride ion	-	Cl^-: 0.4 to 35000mg/L (pH3 to 11)
	Calcium ion	-	Ca^{2+}: 0.4 to 40080mg/L (pH5 to 11)
	Fluoride ion	-	F^-: 0.02 to 19000mg/L (pH4 to 10: 20mg/L)
	Potassium ion	-	K^+: 0.04 to 39000mg/L (pH5 to 11: 3.9mg/L)
	Ammonia ion	-	NH_3: 0.1 to 1000mg/L (pH12 or more)
Simultaneous measurement items		10	13

Note: The accuracy rating value is obtained from measurements at intermediate point of the standard solution after two-point calibration (at room temperature and pressure). The repeatability and accuracy rating percentages are based on the full scale(except for salinity).

*1: Organic solvents, strong acids, and strong alkaline solvents cannot be measured.

*2: The maximum depth for ion measurements are 100 m for nitric acid ion, chloride ion, fluoride ion, 15 m for calcium ion, ammmonia, and 3 m for potassium ion.

*3: Based on the data measured automatically at 15 minutes intervals. The battery life taken into account. Periodical maintenance and calibration is necessary when a lot of shellfishes and seaweeds exist at the measurement point.