APPENDIX A1

PACE ANALYTICAL SERVICES, INC.

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QUALITY MANUAL

Quality Assurance/Quality Control Policies and Procedures

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Signature Page

This document, with the necessary addenda, has been accepted as the Quality Manual.

Laboratory General Manager	Date 11/1/04	Upper Midwest Region Laboratory
Quality Manager	Date 01 NOV 2004	Includes: Minneapolis Laboratory. EnChem Green Bay Laboratory EnChem Kimberly Laboratory.
Technical Director	Date 11-1-04	
Technical Director	Date 11-1-04	
Technical Director	Date 11/1/04	
Technical Director	Date	
Technical Director	Date	

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1.0 INTRODUCTION & ORGANIZATIONAL STRUCTURE

"To meet the business needs of our customers for high-quality, cost-effective analytical measurements and services"

Pace Analytical Statement of Purpose

1.1 Introduction to Pace

Pace Analytical Services, Inc. is a privately-held, full-service environmental testing firm operating a nationwide system of laboratories. Pace offers extensive services beyond standard environmental testing, including: bioassay for aquatic toxicity, air toxics, industrial hygiene testing, explosives, high resolution mass spectroscopy (including dioxins, furans and coplanar PCB's), radiochemical analyses, product testing, pharmaceutical testing, field services and mobile laboratory capabilities. Pace has implemented a consistent Quality System in each of its laboratories and service centers. In addition, the company utilizes an advanced data management system that is highly efficient and allows for flexible data reporting. Together, these systems ensure data reliability and superior on-time marketing performance. This document defines the Quality System and QA/QC protocols.

Pace Analytical's goal is to continue to combine its expertise in laboratory operations with customized solutions to meet the specific needs of its clients.

1.2 Statement of Purpose

To meet the business needs of our customers for high quality, cost-effective analytical measurements and services.

1.3 Quality Policy Statement and Goals of the Quality System

Pace Analytical is committed to providing the highest quality product to our clients, while maintaining good professional practices.

The management of Pace Analytical is responsible for maintaining the highest possible standard of service for our clients by following a documented quality system. The overall objective of this quality system is to provide reliable data by adhering to rigorous quality assurance policies and quality control procedures as documented in this Quality Manual.

All personnel within the Pace network are required to be familiar with all facets of the quality system and implement these policies and procedures in their daily work. This daily focus on quality is applied with the initial project planning, and is continued through all field and laboratory activities and ultimately, to the final report generation.

The management of Pace demonstrates its commitment to quality by providing the resources, including facilities, equipment and personnel to ensure the adherence to these documented policies and procedures. All Pace personnel comply with all current applicable state, federal, and industry standards (such as the NELAC and ISO 17025 standards).

1.4 Pace Analytical Core Values

- **INTEGRITY**
- **VALUE EMPLOYEES**
- **KNOW OUR CUSTOMERS**
- **HONOR COMMITMENTS**
- **FLEXIBLE RESPONSE TO DEMAND**
- **PURSUE OPPORTUNITIES**
- **CONTINUOUSLY IMPROVE**

1.5 Code of Ethics

Pace Analytical's fundamental ethical principles are as follows:

- Each Pace Analytical employee is responsible for the propriety and consequences of his or her actions.
- Each Pace Analytical employee must conduct all aspects of Company business in an ethical and strictly legal manner, and must obey the laws of the United States and of all localities, states and nations where Pace Analytical does business or seeks to do business.
- Each Pace Analytical employee must reflect the highest standards of honesty, integrity and fairness on behalf of the Company with clients, suppliers, the public, and one another.

Strict adherence by each Pace Analytical employee to this Code of Ethics and to the Standards of Conduct is essential to the continued vitality of Pace Analytical.

Failure to comply with the Code of Ethics and Standards of Conduct will result in disciplinary action up to and including termination and referral for civil or criminal prosecution where appropriate. An employee will be notified of an infraction and given an opportunity to explain, as prescribed under current disciplinary procedures.

1.6 Standards of Conduct

1.6.1 Data Integrity

The accuracy and integrity of the analytical results produced at Pace Analytical are the lifeblood of the company. Lack of data integrity is an assault on our most basic values and puts Pace Analytical and its employees at grave financial and legal risk. Therefore, employees are to accurately prepare and maintain all technical records, scientific notebooks, calculations and databases. Employees are prohibited from making false entries or misrepresentations of data (i.e., dates, calculations, results or conclusions).

Managerial staff must make every effort to ensure that personnel are free from any undue pressures that may affect the quality of their work; including commercial, financial, over-scheduling and working condition pressures.

1.6.2 Confidentiality

Pace Analytical employees must not (directly or indirectly) use or disclose confidential or proprietary information except when in connection with their duties at Pace Analytical. This is effective over the course of employment and for a period of two years thereafter.

Confidential or proprietary information, belonging to either Pace Analytical and/or its clients, includes but is not limited to test results, trade secrets, research and development matters, procedures, methods, processes and standards, company-specific techniques and equipment, marketing and client information, inventions, materials composition, etc.

1.6.3 Financial Responsibility

Pace Analytical employees must accurately keep all books, records and accounts for which they are responsible. Employees are responsible for maintaining and safeguarding all company funds and/or assets in their possession or control. Additionally, all employees are responsible for submission of accurate reporting documents pertaining to payroll (timesheets, etc.) and reimbursement requests (expense reports, tuition reimbursement, etc.).

1.6.4 Drug-free Workplace

Pace Analytical recognizes that alcoholism and other drug dependencies are a significant social problem with a potential for causing severe detriment to the workforce. Employees have the right to work in an alcohol and drug-free environment. Employees are not to report to work under the influence of alcohol or controlled substances as prescribed in the Drug-free Workplace Program. The possession, use and sale of alcohol and controlled substances as well as detailed information regarding drug testing is described in the Drug-Free Workplace Program Policy handout provided to all new employees. Additional copies are available from Human Resources. Employees are obligated to conform to the strict Drug-Free Workplace Program Policy.

1.6.5 Conflict of Interest

Pace Analytical employees must avoid situations that might involve a conflict of interest or appear questionable to others. The employee must be careful in two general areas:

- Participation in activities that conflict or appear to conflict with Pace Analytical responsibilities.
- Offering or accepting anything that might influence the recipient or cause another person to believe that the recipient may be influenced. This includes bribes, kickbacks or illegal payments.

Employees are not to engage in outside business or economic activity relating to a sale or purchase by the Company. Other questionable activities include service on the Board of Directors of a competing or supplier company, significant ownership in a competing or supplier company, employment for a competing or supplier company or participation in any outside business during the employee's work hours.

1.6.6 Non-Harassment

Pace Analytical endeavors to provide a workplace free of both harassment and discrimination. Harassment of an employee or job applicant on the basis of race, color, creed, religion, national origin, sex, disability, age, marital status, sexual orientation, or any characteristic protected by applicable municipal, state, and federal laws is both illegal and a violation of company policy. Pace Analytical maintains a Sexual Harassment Prevention policy that clearly defines the company's stance against sexual harassment and provides a mechanism for reporting infractions. The Sexual Harassment Prevention Policy is addressed in employee orientation, and employees are provided the Policy handbook. Additional copies are available from Human Resources.

1.6.7 Proper and Professional Conduct

Employees are bound to use fairness, honesty and regard for the law in their business relationships with Pace Analytical investors, clients, suppliers, employees, and applicants as well as all local, national and international communities and governments.

1.6.8 Protection of Property

Pace Analytical employees have an obligation to protect all company and client property against loss, theft and misuse. Employees are responsible for maintaining an orderly, clean workplace. Employees are also liable for using company and client property for intended purposes only. Employees are prohibited from using company property for their personal use without the expressed permission of their supervisor or General Manager. No such use of property may be made after termination of employment with Pace Analytical. Employees must also make every effort to prevent the misuse of company and client property by other persons. Misuse includes selling, loaning or giving away company or client property.

1.6.9 Communication

Each employee is responsible for obtaining the information necessary to follow directives in the Code of Ethics and the Standards of Conduct, and for reporting to their management or Human Resources representative any observed deviations from these policies. The identity of the employee reporting the infraction will not be disclosed without his/her permission unless disclosure is unavoidable during an investigation. No adverse action will be taken against a Pace Analytical employee because he/she has reported a suspected impropriety. These reports will be treated in confidence to the maximum extent consistent with the fair and rigorous enforcement of the Code of Ethics and Standards of Conduct.

1.6.10 Compliance

All employees are required to read, understand and comply with the various components of the standards listed in this document. As confirmation that they understand this responsibility, each employee is required to sign an acknowledgment form annually that becomes part of the employee's permanent record.

1.7 Laboratory Organization

The Pace Corporate Office centralizes company-wide accounting, business development, financial management, human resources development, information systems, marketing, quality, safety and training activities. Pace Analytical's Director of Quality, Safety and Training is responsible for assisting the development, implementation and monitoring of quality programs for the company. See Figure 1.1 for the Corporate Organizational structure.

Each laboratory within the system operates with local management, but all share common systems and receives support from the Corporate Office.

A General Manager supervises each regional laboratory. Quality Managers at each lab report directly to their General Manager but receive guidance and direction from the Director of Quality, Safety and Training.

Under the direction of the General Manager, the technical staff of the laboratory is generally organized into the following functional groups:

- Organic Sample Preparation
- Wet Chemistry Analysis
- Metals Analysis
- Volatiles Analysis
- Semi-volatiles Analysis
- Radiochemical Analysis
- Product Testing
- Equipment Maintenance
- Microbiology

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Appropriate support groups are present in each laboratory. Figure 1.2 represents a typical organizational structure for a laboratory operation. The organizational structure for a specific laboratory is part of each laboratory's addendum to this Quality Manual.

1.8 Laboratory Job Descriptions

1.8.1 General Manager

1. Oversees all functions of the operations.
2. Authorizes personnel development including staffing, recruiting, training, workload scheduling, employee retention and motivation.
3. Prepares budgets and staffing plans.
4. Monitors the Quality Systems of the laboratory and advises the Quality Manager accordingly.
5. Ensures compliance with all applicable state, federal and industry standards.

1.8.2 Quality Manager

1. Oversees the laboratory Quality Systems while functioning independently from laboratory operations. Reports directly to the General Manager.
2. Monitors Quality Assurance policies and Quality Control procedures to ensure that the laboratory achieves established standards of quality.
3. Maintains records of quality control data and evaluates data quality.
4. Conducts periodic internal audits and coordinates external audits performed by regulatory agencies or client representatives.
5. Reviews and maintains records of proficiency testing results.
6. Maintains the document control system
7. Assists in development and implementation of appropriate training programs.
8. Provides technical support to laboratory operations regarding methodology and project QA/QC requirements.
9. Maintains certifications from federal and state programs.
10. Ensures compliance with all applicable state, federal and industry standards.

1.8.3 Project Manager

1. Coordinates all aspects of specific projects.
2. Focal point for client contact pertaining to project requirements and project status.
3. Arranges bottle orders and shipment of sample kits to clients.
4. Verifies log-in information relative to project requirements and field sample Chains-of-Custody.
5. Communicates with operations staff to update and set project priorities.
6. Provides results to clients in the requested format (verbal, hardcopy, electronic, etc.).
7. Works with clients, laboratory staff, and other appropriate Pace Analytical staff to develop project statements of work or resolve problems of data quality.

1.8.4 Operations Manager or Department Manager/Supervisor

1. Oversees the day-to-day production and quality activities of the laboratory.
2. Ensures that quality assurance and quality control criteria of analytical methods and projects are satisfied.
3. Assesses data quality and takes corrective action when necessary.
4. Approves and releases technical and data management reports.
5. Ensures compliance with all applicable state, federal and industry standards.

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1.8.5 Group Supervisor/Leader

1. Trains analysts in laboratory operations and analytical procedures.
2. Organizes and schedules analyses with consideration for sample holding times.
3. Implements data verification procedures by assigning data verification duties to appropriate personnel.
4. Evaluates instrument performance and supervises instrument calibration and preventive maintenance programs.
5. Reports non-compliance situations to laboratory management including the Quality Manager.

1.8.6 Analyst

1. Analyzes samples according to published methods and laboratory procedures.
2. Monitors quality control data. This includes examination of raw data such as chromatograms as well as an inspection of reduced data, calibration curves, and laboratory notebooks.

1.8.7 Sample Management Personnel

1. Signs for incoming samples and verifies the data entered on the Chain-of-Custody forms.
2. Enters the sample information into the Laboratory Information Management System (LIMS) for tracking and reporting.
3. Stages samples according to EPA requirements.
4. Assists Project Managers in filling bottle orders and sample shipments.

1.9 Training and Orientation

Each new employee receives a five part orientation: human resources, data integrity ethics, safety, Quality Systems, and departmental.

The human resources orientation includes benefits, salary, and company policies. All records are stored with Human Resources.

The data integrity system of each lab contains four elements:

- Data integrity training
- Signed data integrity documentation for all employees
- In-depth, periodic monitoring of data integrity –including but not limited to:
  - logbook checks
  - raw data review
  - final report review
  - manual integration checks
- Documentation of review and investigations regarding data integrity issues.

The safety orientation includes an in-depth review of the Pace Analytical Chemical Hygiene Plan/Safety Plan, which are consistent with the requirements of OSHA's Hazard Communication Program (29 CFR 1910.1200) and other pertinent regulations.

The Quality Systems orientation provides the new employee with information through an introduction to the Quality Manual and SOPs, acceptable record keeping practices, and the individual's responsibility to data quality.

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The new employee's Department Supervisor provides the employee with a basic understanding of the role of the laboratory within the structure of Pace Analytical and the basic elements of that individual's position.

Supervised training uses the following techniques:

- Hands-on training
- Lectures and training sessions
- Method-specific training packages on PaceNet (WAN)
- Conferences and seminars
- Short courses
- Specialized training by instrument manufacturers
- Quiz
- Proficiency testing programs.

Group Supervisors/Leaders are responsible for providing documentation of training and proficiency for each employee under their supervision. The employee's training file indicates what procedures an analyst or a technician is capable of performing, either independently or with supervision. The files also include documentation of continuing capability (see Section 3.4 for details on Demonstration of Capability requirements). Training documentation files for each person are kept in a central location in each laboratory. The Quality Manager is responsible for maintaining the training files.

All procedures and training records are maintained and available for review during laboratory audits. These procedures are reviewed/updated annually by lab management.

1.10 Laboratory Safety

It is the policy of Pace Analytical to make safety and health an integral part of daily operations and to ensure that all employees are provided with safe working conditions, protective equipment, and requisite training to do their work without injury. Each employee is responsible for his/her own safety by complying with established company rules and procedures.

Sample receiving areas and laboratories are equipped with suitable hoods, protective clothing and eye wear, gloves, barrier creams and any other appropriate measures to prevent or minimize staff contact with hazardous substances. Other appropriate safety equipment such as eyewash stations, drench showers, spill absorbents and neutralizers, fire extinguishers, and first aid materials are available.

Each laboratory has a designated Safety/Chemical Hygiene Officer and Safety Committee that meets regularly and discusses agenda topics and addresses action items. The Safety/Chemical Hygiene Officer facilitates the preparation and maintains the laboratory's Chemical Hygiene Plan/Safety Manual, provides safety and occupational health orientation to new employees, conducts safety training and review sessions as required, and maintains up-to-date familiarity with safety and occupational health issues pertinent to the laboratory.

1.11 Security and Confidentiality

Security is maintained by controlled access to laboratory buildings. Exterior doors to laboratory buildings remain either locked or continuously monitored by Pace Analytical staff. Keyless door-lock combinations (and computer access codes/logins) are changed on a regular basis. Posted signs direct visitors to the reception office and mark all other areas as off limits to unauthorized personnel. All visitors to the facilities must sign the Visitor's Logbook maintained by the receptionist. All visitors are accompanied by a staff member during the duration of their stay on the premises. The staff member escorts the visitor back to the reception area at the end of his/her visit where he/she signs out the Visitor's Logbook. Prior to departure of the last staff member at the close of each day, the facility is checked for security.

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Additional security is provided where necessary, i.e., specific secure areas for sample, data and client report storage, as requested by clients or in cases of national security. These areas are lockable within the facilities, or are in secure offsite storage. Access is limited to specific individuals or their designees. Security of sample storage areas is the responsibility of the Sample Custodian. Security of samples and data during analysis and data reduction is the responsibility of Group Supervisors. Security of client report archive is the responsibility of the Client Services Manager. These secure areas are locked whenever these individuals or their designees are not present in the facility.

Access to designated laboratory sample storage locations is limited to authorized personnel only. Provisions for lock and key access are provided. No samples are to be removed without proper authorization. If requested by client or contract, samples are not to be removed from secure storage areas without filling out the associated Chain-of-Custody records.

Standard business practices of confidentiality are applied to all documents and information regarding client analyses. Specific protocols for handling confidential documents are described in Pace Analytical SOPs. Additional protocols for internal identification of samples and data by number only are implemented as required under contract-specific Quality Assurance Project Plans (QAPPs).

All information pertaining to a particular client, including national security concerns will remain confidential. Data will not be released to outside agencies without written authorization from the client.

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Figure 1.1

Corporate/Management Structure

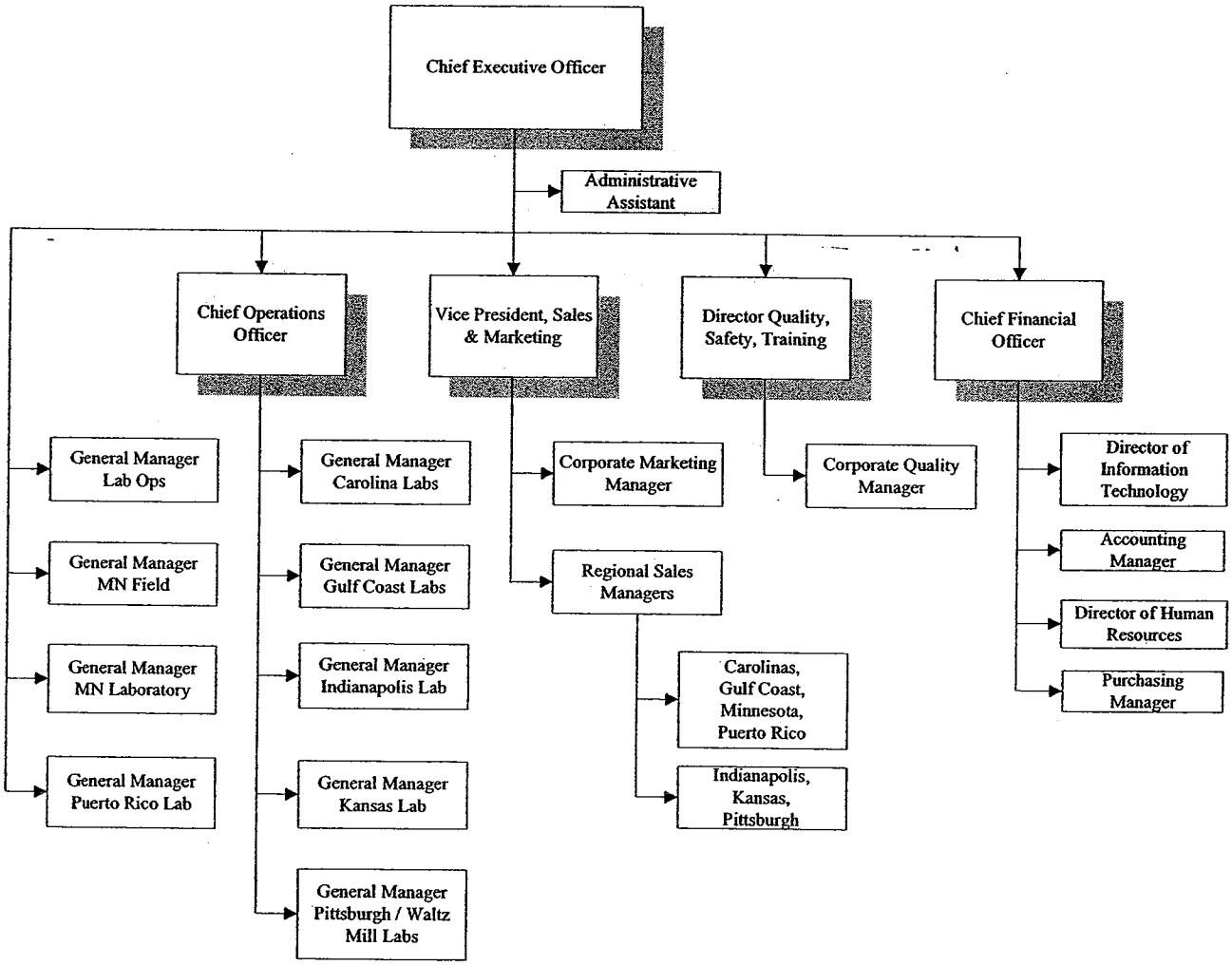
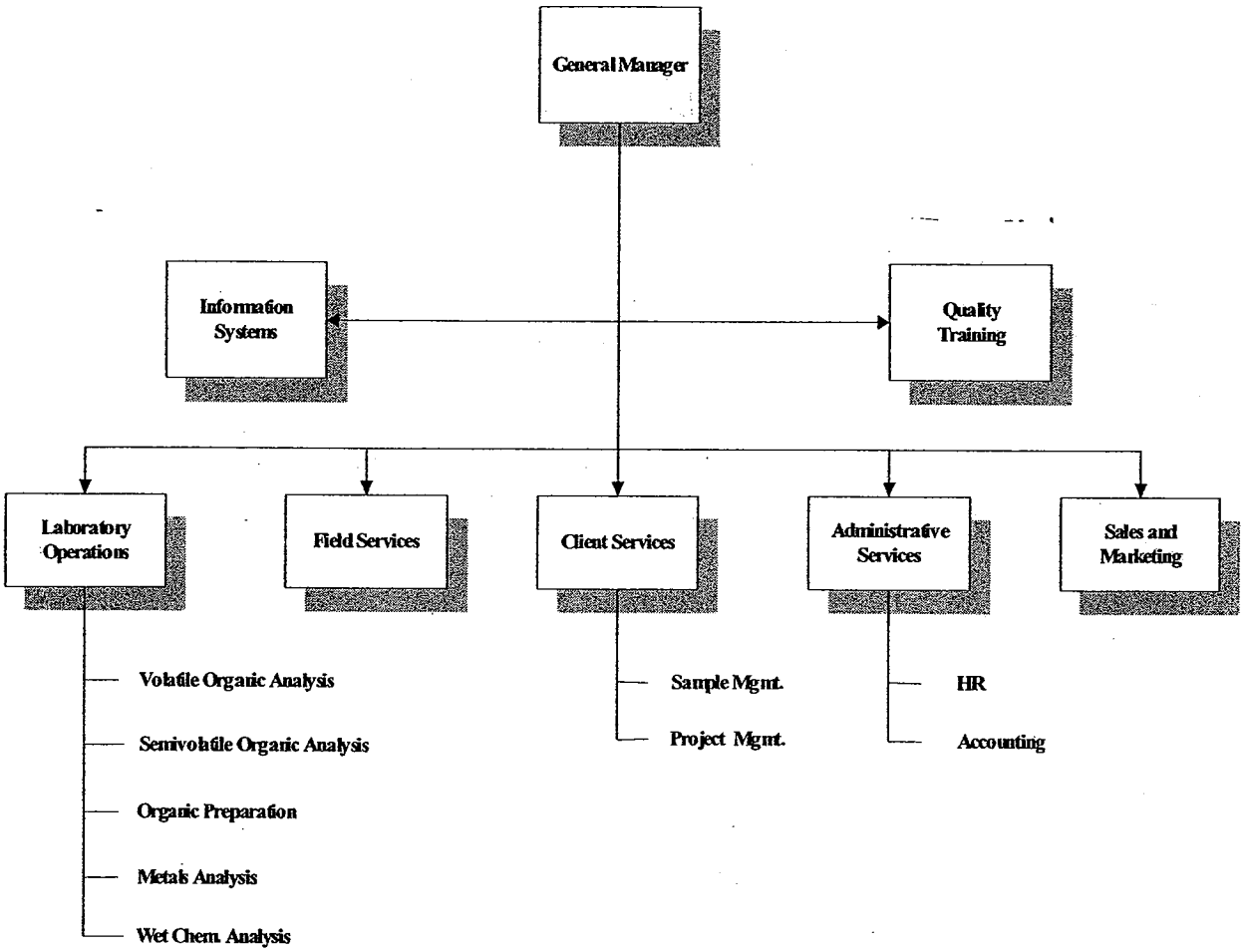


Figure 1.2

Typical Laboratory Organizational Chart



2.0 SAMPLE CUSTODY

2.1 Sampling Support

Each individual Pace Analytical laboratory provides sample containers, shipping containers, sample containers (including applicable chemical preservatives), custody documents, and field quality control samples (i.e., trip blanks) to support field sampling events. Tables 2.1, 2.2, 2.3 and 2.4 list general guidelines for sample container types, preservatives and holding times for a variety of methods. Note that all analyses listed are not necessarily performed at all Pace Analytical locations and there may be additional laboratory analyses performed that are not included in these tables. Pace laboratories provide pick-up and delivery services to their clients when needed.

2.2 Project Initiation

Prior to accepting new work, the lab reviews its capability to perform this work. The purpose of this review is to establish that the lab has sufficient resources (personnel, equipment capacity, analytical method capability, etc.) to complete the required work. Once client needs and data quality objectives are defined, client services personnel or sales representatives contact the laboratory management. Members of the management staff review current instrument capacity, personnel availability and training, analytical procedures capability, laboratory certifications and projected sample load. Management will then inform the sales and client services personnel whether the lab can accept the new projects. This communication is preferably via written correspondence or email, although it may occur during daily operations meetings.

The laboratory maintains records of all such reviews, including discussions with clients. The lab also maintains records of sub-contracted work and keeps a file of all sub-contractor information including current certifications.

2.3 Sample Acceptance Policy

All Pace laboratories have a documented sample acceptance policy that clearly outlines circumstances under which samples will either be accepted or rejected. Documentation of samples rejected under this policy is made on the chain-of-custody or similar document. Results for any sample that does not meet the sample acceptance policy requirements are flagged so that the data user is aware of the nature of the deficiency and the impact on their data. The sample acceptance policy is available to all sample receiving personnel and contains the following requirements:

- Projects must be accompanied by proper documentation including sample identification, location, date and time of sample collection, the sampler's name, preservation types, and any comments made by the sampler.
- Samples must be properly labeled. This includes having a unique field identification written in indelible ink on a durable label.
- The samples must be collected in the appropriate sample containers (See tables 2.1, 2.2, 2.3 and 2.4)
- The samples must be collected and transported to the lab within the required holding times (See tables 2.1, 2.2, 2.3 and 2.4).
- The appropriate sample volume or weight must be available to perform the required tests (including project-specific quality control samples).
- The samples must contain the proper preservative and must not be damaged or contaminated before receipt by the lab.

2.4 Chain-Of-Custody

A chain-of-custody (COC) (see figure 2.1) document provides the legal documentation of samples from time of receipt to completion of analysis. It is important that these documents be as complete as possible. Pace Analytical has implemented standard operating procedures to ensure that sample custody objectives of traceability and responsibility are achieved for every project.

Field personnel or client representatives complete a chain-of-custody form for all samples. Samples are received by the laboratory accompanied by these forms.

If sample shipments are not accompanied by the correct documentation, the Sample Receiving department will notify the Project Manager. The Project Manager is then responsible for obtaining the correct documentation/information from the client so that analysis of samples can proceed.

The sampler is responsible for providing the following information on the chain-of-custody:

- Client project name
- Project location or number
- Field sample number/identification
- Date and time sampled
- Sample type (matrix)
- Preservative
- Requested analyses
- Sampler signature
- Relinquishing signature
- Date and time relinquished
- Sampler remarks
- Custody Seal Number (if applicable)
- Regulatory Program Designation
- The state where the samples were taken to ensure all state requirements are met
- Turnaround time requested
- Purchase order number

The record is filled out completely and legibly with indelible ink. Errors are corrected by drawing a single line through and initialing and dating the change. All transfers of samples must be recorded on the chain-of-custody in the "relinquished" and "received by" sections. All information except signatures should be printed.

2.5 Sample Receipt

Sample receiving personnel inspect each sample shipment upon arrival. The following items are checked:

- Presence of custody seals or tapes on the shipping containers
- Presence of Chain-of-Custody
- Presence of sample tags or labels
- Agreement between the sample tags or labels, Chain-of-Custody, and any client documentation.
- Condition of the samples when received, including:
  - Sample temperature: samples are acceptable if the arrival temperature is within 2°C of the required temperature, except as specified in the applicable test method or other state or federal regulation. Samples that are hand-delivered directly from the field on the same day that they are collected are acceptable if there is evidence that the chilling process has begun (arrival on ice).
  - Sample condition: Intact, broken/leaking
  - Headspace in VOA vials
  - Sample holding time

Sampling

- Sample pH when required
- Adequate sample volume
- Appropriate containers/preservatives

If discrepancies are found, the Pace Analytical Project Manager is contacted immediately. If the Project Manager is not available, the Quality Manager is contacted for further directions. Discrepancies are documented and reported with analytical results.

2.6 Sample Log-in

After the sample inspection, all sample information on the chain-of-custody is entered into the Laboratory Information Management System (LIMS).

Sample data must include, at a minimum:

- Client name and contact
- Client number
- Pace Analytical project number
- Pace Analytical Project Manager
- Sample descriptions
- Due dates
- List of analyses requested

All samples received are logged into the LIMS system within one working day of receipt. Sample log-in may be delayed due to client clarification of analysis needed, corrective actions for sample receipt non-conformance, or other unusual circumstances.

All sample containers are assigned a unique laboratory identification code that is unequivocally linked to the field Identification code. This code is placed on the sample container as a durable label.

Sample Labels are printed from the LIMS system and affixed to each sample container.

Samples with hold times that are near their expiration date/time may be sent directly to the laboratory for analysis at the discretion of the Project Manager and/or General Manager.

2.7 Sample Storage/Staging

2.7.1 Storage Conditions

Samples are stored away from all standards, reagents, food or other potential sources of contamination. Samples are stored in a manner that prevents cross-contamination (i.e. volatile samples are stored separate from other samples). All sample fractions, extracts, leachates and other sample preparation products are stored in the same manner as actual samples.

2.7.2 Temperature Monitoring

Samples are taken to the appropriate storage location immediately after the samples are entered into the LIMS. All sample storage areas are located in limited access areas and are monitored to ensure sample integrity.

The temperature of each storage areas is maintained at 4°C ± 2°C unless state or program requirements differ. The temperature of the storage areas is monitored and recorded each workday. If the temperature falls outside the acceptable limits, the following corrective actions are taken and appropriately documented:

- The temperature is rechecked after two hours to verify temperature exceedance. Initiate corrective action if necessary.

Sampling

- The Quality Manager and/or laboratory management are notified if the problem persists.
- The samples are relocated to a proper environment if the temperature cannot be maintained after corrective actions are implemented.
- The affected clients are notified.
- Documentation is provided on analytical report.

2.7.3 Hazardous Materials

Pure product or potentially heavily contaminated samples are tagged as "hazardous" or "lab pack" and are stored separately from other samples.

2.7.4 Foreign Soils

Depending on the soil disposal practices of the laboratory, foreign soils and soils from USDA regulated areas are segregated. The USDA requires these samples to be incinerated or sterilized by an approved treatment procedure.

2.8 Sample Protection

Pace laboratory facilities are operated under controlled access to ensure sample and data integrity. Only employees are allowed into the laboratory facilities. Visitors must register at the front desk and be properly escorted.

Samples are removed from their proper location by designated personnel and returned the storage area, if necessary, immediately after the required sample quantity has been taken.

Upon client request, additional and more rigorous chain-of-custody protocols for samples and data can be implemented. For example, some projects may require complete documentation of sample custody within the secure laboratory.

2.9 Subcontracting Analytical Services

Every effort is made to perform chemical analyses for Pace Analytical clients within the laboratory that receives the samples. When subcontracting to a laboratory other than the receiving laboratory (inside or outside the Pace network) becomes necessary, a preliminary verbal communication with an appropriate laboratory is undertaken. Clients are notified in writing of the lab's intention to subcontract any portion of the testing to another laboratory. Work performed under specific protocols may involve special considerations.

Prior to subcontracting samples to a laboratory outside Pace Analytical, the laboratory will be qualified by verifying that the subcontractor meets the following criteria:

- All certifications required for the proposed subcontract are in effect,
- Sufficient professional liability and other required insurance coverage is in effect, and
- Is not under investigation by any federal, state, or local government agency for data integrity issues and has not been under such investigation for at any time during the past 5 years.

The contact and preliminary arrangements and terms of agreement are made between the Pace Analytical Project Manager and the appropriate subcontract laboratory personnel. The specific terms of the subcontract laboratory agreement includes the requirement for provision of the following (when applicable):

- Method (EPA or otherwise) of analysis
- Number and type of samples expected
- Project specific QA/QC requirements
- Deliverables required
- Laboratory certification requirement

- Price per analysis
- Turn around time requirements

Chain-of-custody forms are generated for samples requiring subcontracting to other laboratories. The sample receiving personnel re-package the samples for shipment, create a transfer chain-of-custody form and record the following information:

- Pace Analytical Laboratory Number
- Matrix
- Requested analysis
- Special instructions (quick turn-around, required detection or reporting limits, unusual information known about the samples or analytical procedure).
- Signature in "Relinquished By"

All subcontracted sample data reports are sent to the Pace Analytical Project Manager.

Any Pace Analytical work sent to other labs within the Pace network is handled as subcontracted work (also known as inter-regional) and all final reports are labeled clearly with the name of the laboratory performing the work.

2.10 Sample Retention and Disposal

After completion of sample analysis and submission of the analytical report, unused portions of samples are retained by the laboratory for a minimum of 30 days unless otherwise stated by the project contract or client request. After this period expires, non-hazardous samples are properly disposed as non-hazardous waste.

The preferred method for disposition of hazardous samples is to return the excess sample to the client. It may not be feasible to return samples, or the client may require Pace Analytical to dispose of excess samples. In that case, Pace Analytical will arrange for proper disposal by an approved contractor. Pace Analytical will charge a disposal fee to recover costs of this service.

Figure 2.1
Pace Analytical Services, Inc. CHAIN-OF-CUSTODY FORM (EXAMPLE)

Pace Analytical™
www.pacelabs.com

CHAIN-OF-CUSTODY / Analytical Request Document

The Chain-of-Custody is a LEGAL DOCUMENT. All relevant fields must be completed accurately.

Section A — Required Client Information: Company; Address; Phone; Fax

Section B — Required Client Information: Report To; Copy To; Invoice To; P.O.; Project Name; Project Number;

Page: of

Section C — To Be Completed by Pace Analytical and Client: Quote Reference: 830222; Project Manager; Project #; Profile #; Requested Analysis:

Client Information (Check quote/contract): Requested Due Date; TAT:

* Turn around times less than 14 days subject to laboratory and contractual obligations and may result in a Rush Turnaround Surcharge.
Turn Around Time (TAT) in calendar days.

Section D — Required Client Information:

SAMPLE ID
One character per box. (A-Z, 0-9 / -)
Sample IDs MUST BE UNIQUE

Valid Matrix Codes: MATRIX / CODE — WATER WT; SOIL SL; OIL OL; WIPE WP; AIR AR; TISSUE TS; OTHER OT

ITEM #	SAMPLE ID	MATRIX CODE	DATE COLLECTED (mm / dd / yy)	TIME COLLECTED (hh:mm a/p)	# Containers	Unpreserved	H_2SO_4	HNO_3	HCl	NaOH	$Na_2S_2O_3$	Methanol	Other	Remarks / Lab ID
1														
2														
3														
4														
5														
6														
7														
8														
9														
10														
11														
12														

Preservatives

SITE LOCATION: ☐ NC ☐ SC ☐ GA ☐ Other

REGULATORY AGENCY: ☐ NPDES ☐ GROUND WATER ☐ DRINKING WATER ☐ UST ☐ RCRA ☐ Other

SAMPLE CONDITION: Temp in °C; Received on Ice Y/N; Sealed Cooler Y/N; Samples Intact Y/N

SAMPLE NOTES

Additional Comments:

RELINQUISHED BY / AFFILIATION	DATE	TIME	ACCEPTED BY / AFFILIATION	DATE	TIME

SAMPLER NAME AND SIGNATURE
PRINT Name of SAMPLER:
SIGNATURE of SAMPLER: DATE Signed: (MM / DD / YY)

SEE REVERSE SIDE FOR INSTRUCTIONS

Form COC01 Rev. 08/03

TABLE 2.1 List of Containers, Preservatives and Holding Times for Inorganic and Organic Analyses of Aqueous Samples:

NAME	CONTAINER[1]	PRESERVATION[2]	MAXIMUM HOLDING TIME[3]
Inorganic Tests:			
Acidity	P,G	Cool, 4^0C	14 days
Alkalinity	P,G	Cool, 4^0C	14 days
Ammonia	P,G	Cool, 4^0C, H_2SO_4 to pH<2	28 days
Biochemical oxygen demand	P,G	Cool, 4^0C	48 hours
Bromide	P,G	None Required	28 days
Biochemical oxygen demand, carbonaceous	P,G	Cool, 4^0C	48 hours
Chemical oxygen demand	P,G	Cool, 4^0C, H_2SO_4 to pH<2	28 days
Chloride	P,G	None Required	28 days
Chlorine, total residual	P,G	None Required	Analyze immediately
Color	P,G	Cool, 4^0C	48 hours
Cyanide, total amenable to chlorination	P,G	Cool, 4^0C, NaOH to pH>12 0.6g ascorbic acid[4]	14 days
Fluoride	P	None Required	28 days
Hardness	P,G	HNO_3, to pH<2, H_2SO_4 to pH<2	6 months
Hydrogen ion (pH)	P,G	None Required	Analyze immediately
Kjeldahl and organic nitrogen	P,G	Cool, 4^0C, H_2SO_4 to pH<2	28 days
Nitrate	P,G	Cool, 4^0C	48 hours
Nitrate-nitrite	P,G	Cool, 4^0C, H_2SO_4 to pH<2	28 days
Nitrite	P,G	Cool, 4^0C	48 hours
Oil and grease	G	Cool, 4^0C, H_2SO_4 to pH<2	28 days
Organic carbon	P,G	Cool, 4^0C, H_2SO_4 to pH<2	28 days
Orthophosphate	P,G	Filter immediately, Cool, 4^0C	48 hours
Phenols	G only	Cool, 4^0C, H_2SO_4 to pH<2	28 days
Phosphorus (elemental)	G	Cool, 4^0C	48 hours
Phosphorus, total	P,G	Cool, 4^0C, H_2SO_4 to pH<2	28 days
Residue, total	P,G	Cool, 4^0C	7 days
Residue, filterable	P, G	Cool, 4^0C	7 days
Residue, nonfilterable (TSS)	P, G	Cool, 4^0C	7 days
Residue, Settleable	P, G	Cool, 4^0C	48 hours
Residue, volatile	P, G	Cool, 4^0C	7 days
Silica	P	Cool, 4^0C	28 days
Specific conductance	P,G	Cool, 4^0C	28 days
Sulfate	P,G	Cool, 4^0C	28 days
Sulfide	P,G	Cool, 4^0C, add zinc acetate & sodium hydroxide to pH>9	7 days
Sulfite	P,G	None Required	Analyze immediately
Surfactants	P,G	Cool, 4^0C	48 hours
Turbidity	P,G	Cool, 4^0C	48 hours

TABLE 2.1 (cont.) List of Containers, Preservatives and Holding Times for Inorganic and Organic Analyses of Aqueous Samples:

NAME	CONTAINER[1]	PRESERVATION[2]	MAXIMUM HOLDING TIME[3]
Metals:			
Chromium VI	P,G	Cool, 4^0C	24 hours
Mercury (SW846)	P,G	HNO3 to pH<2	28 days in glass
Mercury (CLP, 200 series)	P,G	HNO3 to pH<2	28 days
Metals, except chromiumVI and mercury	P,G	HNO3 to pH<2	6 months
Organic Tests:			
Oil and Grease	G	Cool, 4^0C, HCl or H_2SO_4 to pH<2	28 days
Organic carbon, Total (TOC)	P,G	Cool, 4^0C, HCl or H_2SO_4 to pH<2	28 days
Purgeable Halocarbons	G,Teflon-lined septum	Cool, 4^0C, 0.008% $Na_2S_2O_3$[4], HCl[5,6] to pH<2	14 days
Purgeable Aromatic Hydrocarbons	G,Teflon-lined septum	Cool, 4^0C, 0.008% $Na_2S_2O_3$[4], HCl[5,6] to pH<2	14 days
Acrolein and acrylonitrile	G,Teflon-lined septum	Cool, 4^0C, 0.008% $Na_2S_2O_3$[4] Adjust pH to 4-5	14 days
Phenols	G,Teflon-lined cap	Cool, 4^0C, 0.008% $Na_2S_2O_3$[4]	7 days until extraction, 40 days after extraction
Benzidines	G,Teflon-lined cap	Cool, 4^0C, 0.008% $Na_2S_2O_3$[4]	7 days until extraction, 40 days after extraction
Phthalate esters	G,Teflon-lined cap	Cool, 4^0	7 days until extraction, 40 days after extraction
Nitrosamines	G,Teflon-lined cap	Cool, 4^0C, store in dark, 0.008% $Na_2S_2O_3$[4]	7 days until extraction, 40 days after extraction
PCBs	G,Teflon-lined cap	Cool, 4^0C	7 days until extraction, 40 days after extraction
Nitroaromatics and cyclic ketones	G,Teflon-lined cap	Cool, 4^0C, store in dark, 0.008% $Na_2S_2O_3$[4]	7 days until extraction, 40 days after extraction
Polynuclear aromatic hydrocarbons	G,Teflon-lined cap	Cool, 4^0C, 0.008% $Na_2S_2O_3$[4]	7 days until extraction, 40 days after extraction
Haloethers	G,Teflon-lined cap	Cool, 4^0C, 0.008% $Na_2S_2O_3$[4]	7 days until extraction, 40 days after extraction
Chlorinated Hydrocarbons	G,Teflon-lined cap	Cool, 4^0C, HCl or H_2SO_4	7 days until extraction, 40 days after extraction
Dioxins and Furans	G,Teflon-lined cap	Cool, 4^0C, 0.008% $Na_2S_2O_3$[4]	30 days until extraction, 40 days after extraction
Total organic halides (TOX)	G,Teflon-lined cap	Cool, 4^0C, HCl or H_2SO_4 to pH <2	28 days
Pesticides	G,Teflon-lined cap	Cool, 4^0C pH 5-9	7 days until extraction, 40 days after extraction

Table Footnotes:
[1] Polyethylene (P) or glass (G)
[2] Sample preservation should be performed immediately upon sample collection.
[3] Holding times are based from time of sample collection.
[4] Should only be used in the presence of residual chlorine.
[5] Free chlorine must be removed prior to addition of HCl by the appropriate addition of $Na_2S_2O_3$
[6] Sample receiving no pH adjustment must be analyzed within seven days of sampling.

Table 2.2 Required Containers, Preservation Techniques, and Holding Times for Non-Aqueous, Soil or Solid Matrices (as specified in SW-846):

NAME	CONTAINER	PRESERVATION	MAXIMUM HOLDING TIME[1]
Semivolatile Organics/Organochlorine Pesticides/PCBs and Herbicides			
Concentrated waste samples	8 oz. wide mouth glass w/Teflon liner	None	14 days until extraction, 40 days after extraction
Liquid samples, no residual Chlorine present	1 gal. or 2 1/2 gal. amber glass w/Teflon liner	Cool, 4^0C	Samples must be extracted within 7 days & extracts analyzed within 40 days
Residual Chloride, present	1 gal. or 2 1/2 gal. amber glass w/Teflon liner	Add 3mL 10% sodium thiosulfate	Samples must be extracted within 7 days & extracts analyzed within 40 days
Soil/sediments and sludges	8 oz. wide mouth glass w/Teflonlliner	Cool, 4^0C	14 days until extraction, extracts analyzed within 40 days.
Volatile Organics			
Concentrated waste samples	8 oz. wide mouth glass w/Teflonlliner	None	14 days
Liquid samples, no residual Chlorine present	3x40 mL vials w/Teflon lined septum caps	Cool, 4^0C[2]	14 days
Residual Chlorine, present	3x40 mL vials w/Teflon lined septum caps	Collect sample in a 4 oz. soil VOA container which has been pre-preserved w/4 drops of 10% sodium thiosulfate. Gently mix sample & transfer to a 40mL VOA vial[2]. Cool to 4^0C	14 days
Acrolein & Acrylonitrile	3x40 mL vials w/Teflon lined septum caps	Adjust to pH 4-5, Cool to 4^0C	14 days
Soil/sediments and sludges	4 oz. (120mL), wide mouth glass w/Teflon liner or wide mouth glass container sealed w/a septum	Cool to 4^0C	14 days

[1] Holding times are based from time of sample collection.
[2] Adjust pH<2 w/H_2SO_4, HCl or solid $NaHSO_4$

Table 2.3 Required Containers, Preservation, and Technical Hold Times for Air Methods:

TEST	MEDIA	PRESERVATION	MAXIMUM HOLDING TIME [1]
TO1	Tenax tubes	Freezer -20°C	14 days
TO2	Carbo Sieve	Cool to 4°C	14 days
VOST	Tenaz/Tenaz-charcoal	Cool to 4°C	14 days
TO4	Puf 3" long, 60mm diameter	Freezer - 10°C or below	Extracted 7 days after collection
TO1O	Puf 10cm long, 20mm diameter	Cool to 4°C	Extracted 7 days after collection
TO11	Absorbent cartridge	Cool to 4°C	30 days
TO13	Puf XAD/XAD		Extracted 7 days after collection
TO14	Summa canisters Tedlar bags	Room temperature Room temperature	Not specified 48-72 hours (dependant on client)
T09	PUF XAD/XAD	Cool to 4°C	30 days
Method 3C	Summa canisters Tedlar bags	Room temperature	15 days
Method 23	XAD	Cool to 4°C	30 days

1. Holding times are based from time of sample collection.

Table 2.4 Containers, Preservatives and Hold Time Information for Radioactives

Parameter(s)	Matrix	Container Type and Preservation	Hold Time
All radiochemical parameters except Rn-22, tritium, C14 and Iodine 131	Water Solid/Other	1 L Plastic (2 x 2 L Preferred), HNO_3, pH < 2 250 mL Glass Jar	180 Days 180 Days
Rn-222 Radon 222	Water	3 x 40 mL Amber Glass Vial, None	72 Hours
H-3 Tritium	Water Solid/Other	1 L Glass Sample size will vary with moisture content	180 Days 180 Days
C-14 Carbon 14	Water	1 L Plastic	180 Days
I-131 Iodine 131	Water	1 L Plastic	180 Days
New Jersey Special Requirement(s)			
Gross Alpha (48 hour)	Water	1 L Plastic HNO_3;pH < 2	48 hours

3.0 ANALYTICAL CAPABILITIES

3.1 Analytical Method Sources

Pace Analytical laboratories are capable of analyzing a full range of environmental samples from a variety of matrices, including air surface and groundwater, soil, sediment, tissue, and waste. Methodologies are applied from regulatory and professional sources including EPA, ASTM, USGS, NIOSH and, State agencies. Section 11 is a representative listing of general analytical protocol references. In some situations, Pace Analytical develops and validates methodologies that may be more applicable to a specific problem or objective. Pace Analytical discloses in writing to its clients and regulatory agencies any instances in which modified methods are being used in the analysis of samples.

3.2 Analytical Method Documentation

The primary form of documentation of analytical methods is the Standard Operating Procedure (SOP). SOPs contain pertinent information as to what steps are required by an analyst to successfully perform a procedure. The required contents for the SOPs are specified in the company-wide SOP for Preparation of SOPs (ALL-Q-001). The SOPs are consistent company-wide documents with addenda as needed for individual laboratories.

The SOPs are supplemented by Work Processing and Training Documents that further detail how methods are specifically performed with detailed training information.

3.3 Analytical Method Validation

When non-standard methods (i.e. methods other than EPA, NIOSH, ASTM, AOAC, etc.) are required for specific projects or analytes of interest, or when the laboratory develops a method, or modifies a standard method, the laboratory validates the method prior to applying it to client samples. Method validity is established by meeting criteria for precision and accuracy as established by the data quality objectives specified by the end user of the data. The laboratory records the validation procedure, the results obtained and a statement as to the usability of the method. The minimum requirements for method validation include determination of the limit of detection and limit of quantitation of each analyte of interest.

3.4 Demonstration of Capability (DOC)

Analysts complete an initial demonstration of capability (IDOC) study prior to starting a method or when there is a change in instrument type, personnel or test method (when a defined 'work cell' is in operation, the entire work cell must meet the criteria). The mean recovery and standard deviation of each analyte, taken from 4 replicates of a quality control standard, is calculated and compared to method criteria (if available) or established lab criteria for evaluation of acceptance. Each laboratory maintains copies of all demonstrations of capability for future reference and must document the acceptance criteria prior to the analysis of the DOC. Demonstration of capabilities is renewed on an annual basis.

3.5 Regulatory and Method Compliance

Pace Analytical understands that the expectations of our clients commonly include the assumption that laboratory data will satisfy specific regulatory requirements. Therefore Pace Analytical will attempt to ascertain, prior to beginning a project, what applicable regulatory jurisdiction, agency, or protocols apply to that project. This information is also required on the Chain-of-Custody submitted with samples.

Pace Analytical will make every effort to detect regulatory or project plan inconsistencies as they arise and communicate them to the clients to aid in the decision-making process.

It is Pace Analytical policy to disclose in a forthright manner any detected noncompliance that may affect the usability of data produced by our laboratories.

Analytical

4.0 QUALITY CONTROL PROCEDURES

4.1 Data Integrity System

The data integrity system at Pace Analytical provides assurances to management that a highly ethical approach is being applied to all planning, training and implementation of methods. Data integrity is crucial to the success of our company and Pace is committed to providing a culture of quality throughout the organization. To accomplish this goal, Pace has implemented a data integrity system that encompasses the following four requirements:

- A data integrity training program: standardized training is given to each new employee and a yearly refresher is presented to all employees. Key topics within this training include:
  - Need for honesty in analytical reporting
  - Process for report data integrity issues
  - Specific examples of unethical behavior and improper practices
  - Documentation of non-conforming data that is still useful to the data user
  - Consequences and punishments for unethical behavior
  - Examples of monitoring devices used by management to review data and systems
- Signed data integrity documentation for all employees: this includes the documentation in this Quality Manual and in other Standard Operating Procedures
- In-depth, periodic monitoring of data integrity: including peer data review and validation, internal data audits, proficiency testing studies, etc.
- Documentation of any review or investigation into possible data integrity infractions. This documentation must be available for review for lab assessors.

Pace management makes every effort to ensure that personnel are free from any undue pressures that may affect their quality of work including commercial, financial, over-scheduling, and working condition pressures.

The management also provides a mechanism for confidential reporting of data integrity issues that includes confidentiality and a receptive environment in which all employees are comfortable discussing items of ethical concern.

4.2 Method Blank

A method blank is used to evaluate contamination in the preparation/analysis system. The method blank is processed through all preparation and analytical steps with its associated samples. Any affected sample associated with a contaminated method blank will be re-analyzed or reported with an appropriate data qualifier.

A method blank is processed at a minimum frequency of 1 per preparation batch. In the case of a method that has no separate preparation step (i.e. volatiles), a method blank is processed with no more than 20 samples of a specific matrix performed by the same analyst, in the same method, using the same standards or reagents.

The method blank consists of a matrix similar to the associated samples that is known to be free of the analytes of interest.

Each method blank is evaluated for contamination. The source of any contamination is investigated and documented corrective action is taken when the concentration of any target analyte is detected above the reporting limit and is greater then 1/10 of the amount of that analyte found in any associated sample. Corrective actions may include re-analyzing the samples with a clean blank or reporting the data with the appropriate data qualifiers.

4.3 Laboratory Control Sample/Laboratory Control Sample Duplicate (LCS/LCSD)

The Laboratory Control Sample (LCS) is used to evaluate the performance of the entire analytical system including preparation and analysis. The LCS results are compared to established acceptance criteria and if the results are outside of the criteria, then the system is out-of-control. Any affected sample associated with a failing LCS will be re-analyzed or reported with an appropriate data qualifier.

An LCS is processed at a minimum frequency of 1 per preparation batch. In the case of a method that has no separate preparation step (i.e. volatiles), an LCS will be processed with no more than 20 samples of a specific matrix performed by the same analyst, in the same method, using the same standards or reagents.

The LCS consists of a matrix similar to the associated samples that is known to be free of the analytes of interest that is then spiked with known concentrations of target analytes.

The LCS contains all analytes specified by a specific method or by the client or regulatory agency. In the absence of specified components, the lab will spike with the following compounds:

- For multi-peak analytes (i.e. PCBs), a representative standard will be processed.
- For methods with long lists of analytes, a representative number of target analytes may be chosen. The following criteria is used to determine the number of LCS compounds used:
  - For methods with 1-10 target compounds, the lab will spike with all compounds
  - For methods with 11-20 target compounds, the lab will spike with at least 10 compounds or 80%, whichever is greater
  - For methods with greater than 20 compounds, the lab will spike with at least 16 compounds.

The LCS is evaluated against the method or laboratory-derived criteria. Any compound that is outside of these limits is considered to be 'out of control' and must be qualified appropriately. Any associated sample containing an 'out-of-control' compound must either be re-analyzed with a successful LCS or reported with the appropriate data qualifier.

An LCS/LCSD (duplicate LCS) can be substituted in a batch when sufficient sample volume is not available to prepare a matrix spike/ matrix spike duplicate (MS/MSD) pair according to project specific objectives. However, both the LCS and the LCSD must pass LCS criteria for the batch to be acceptable. A matrix spike can be used in place of a failing LCS in a batch as long as the MS passes the LCS acceptance criteria.

4.4 Matrix Spike/Matrix Spike Duplicate (MS/MSD)

A matrix spike (MS) is used to determine the effect of the sample matrix on the precision and accuracy of the results for a particular method. The information from these spikes is sample or matrix specific and is not used to determine the acceptance of an entire batch (see LCS).

A **Matrix Spike/Matrix Spike Duplicate** (MS/MSD) set is processed at a frequency specified in a particular method or as determined by a specific client. In the absence of such requirements, an MS/MSD set is routinely analyzed once per every 20 client samples per matrix per method.

The MS and MSD consist of the sample matrix that is then spiked with known concentrations of target analytes.

The MS and MSD contain all analytes specified by a specific method or by the client or regulatory agency. In the absence of specified components, the lab will spike with the same number of compounds as previously discussed in the LCS section.

The MS/MSD are evaluated against the method or laboratory-derived criteria. Any compound that is outside of these limits is considered to be 'out of control' and must be qualified appropriately. Batch acceptance, however, is based on method blank and LCS performance, not on MS/MSD recoveries. The spike recoveries give the data user a better understanding of the final results based on their site-specific information.

4.5 Surrogates

Surrogates are compounds that reflect the chemistry of target analytes and are typically added to sample for organic analyses to monitor the effect of the sample matrix on compound recovery.

Surrogates are added to each client sample (for organics), method blank, LCS and MS prior to extraction or analysis. The surrogates are evaluated against the method or laboratory-derived criteria. Any surrogate compound that is outside of these limits is considered to be 'out of control' and must be qualified appropriately. Samples with surrogate failures are typically re-analyzed to confirm that the out-of-control value was caused by the matrix of the sample and not by some other systematic error. An exception to this would be samples that have high surrogate values but no reportable hits for target compounds. These samples would be reported because the implied high bias would not affect the final results.

4.6 Sample Duplicate

A sample duplicate is a second portion of sample that is prepared and analyzed along with the first portion. It measures the precision associated with preparation and analysis. A sample duplicate is processed at a frequency specified by the particular method or as determined by a specific client.

The sample and duplicate are evaluated against the method or laboratory-derived criteria for relative percent difference (RPD). Any duplicate that is outside of these limits is considered to be 'out of control' and must be qualified appropriately.

4.7 Internal Standards

Internal Standards are analytes added to every standard, blank, lab control sample, matrix spike, matrix spike duplicate, and sample at a know concentration, prior to analysis for the purpose of adjusting the response factor used in quantifying target analytes.

4.8 Field Blanks

Field blanks are blanks prepared at the sampling site in order to monitor for contamination that may be present in the environment where samples are collected. These field quality control samples may be referenced as field blanks, rinseate blanks, or equipment blanks. The lab analyzes these field blanks as normal samples and informs the client if there are any target compounds detected above the reporting limits.

4.9 Trip Blanks

Trip blanks are blanks that are prepared in the laboratory before the sampling event and are used to monitor for contamination of samples during transport. These blanks accompany the empty sample containers to the field and then accompany the collected samples back to the lab. These blanks are routinely analyzed for volatile sample methods.

4.10 Limit of Detection

Pace laboratories are required to use a documented procedure to determine a method detection limit (MDL) for each analyte of concern in each matrix reported. All sample processing steps of the analytical method are included in this determination. For any test that does not have a valid MDL, sample results below the lowest calibration standard cannot be reported.

The MDL is initially established for the compounds of interest for each method in a clean matrix with no target analytes present and no interferences at a concentration that would impact the results. The MDL is then determined every time there is a change in the test method that affects how the test is performed or when there has been a change in the instrument that affects the sensitivity. The MDL is verified on an annual basis.

Unless otherwise noted, the method used by Pace laboratories to determine MDLs is based on the Method Detection Limit procedure outlined in 40 CFR Part 136, Appendix B. Where required by regulatory program or client, the above referenced procedure will be followed.

4.11 Limit of Quantitation

A limit of quantitation (LOQ) for every analyte of concern must be determined. For Pace laboratories, this LOQ is referred to as the PRL, or Pace Reporting Limit. This PRL is based on the lowest calibration standard concentration that is used in each initial calibration. No results are allowed to be reported below this level since the results would not be substantiated by a calibration standard. For methods with a determined MDL, results can be reported out below the LOQ but above the MDL if they are properly qualified (J flag).

There must be a sufficient buffer between the MDL and the limit of quantitation (LOQ). The PRL must be higher than the MDL.

4.12 Proficiency Testing (PT) Studies

Pace Analytical laboratories participate in the NELAC-defined proficiency testing program. PT samples are obtained from NIST-approved providers and analyzed and reported at a minimum of two times per year for the relevant fields of testing per matrix.

The lab initiates an investigation whenever PT results are deemed 'unacceptable' by the PT provider. All findings and corrective actions taken are reported to the Quality Manager. A corrective action plan (including re-analysis of similar samples) is initiated and this report is sent to the appropriate state accreditation agencies for their review.

PT samples are treated as typical client samples, utilizing the same staff, methods, equipment, facilities, and frequency of analysis. PT samples are included in the laboratory's normal analytical processes and do not receive extraordinary attention due to their nature.

Comparison of analytical results with anyone participating in the same PT study is prohibited prior to the close of the study.

5.0 DOCUMENT CONTROL AND CHANGE

5.1 Document Control

Pace Analytical Services has established a procedure for controlling documents that are part of the quality system. The list of controlled documents includes, but is not limited to, Standard Operating Procedures, Quality Manuals, quality policy statements, training documents, work-processing documents, charts, posters, memoranda, notices, forms, software, and any other procedures, tables, plans, etc. that has a direct bearing on the quality system.

A master list of all documents is maintained at each facility identifying the current revision status and distribution of the documents. This establishes that there are no invalid or obsolete documents in use in the lab. All documents are reviewed periodically and revised if necessary and obsolete documents are systematically discarded or archived for legal or knowledge preservation purposes.

Each document related to the quality system is uniquely identified to include the date of issue, the revision identification, page numbering, the total number of pages and the issuing authorities. For complete information on document numbering, refer to the company-wide Standard Operating Procedure Document Numbering (ALL-Q-003).

As an alternative to the hard copy system of control, secured electronic copies of controlled documents may be maintained on the local or wide-area network (WAN). These document files must be read-only for all personnel except the Quality Department and system administrator. Other requirements for this system include:

- Ready accessibility to all laboratory staff
- A complete description of the computerized aspects, including security
- A provision to explicitly indicate that all printed copies are uncontrolled and expire on the date printed.

5.1.1 Quality Manual

The Quality Manual is the company-wide document that describes all aspects of the quality system for Pace Analytical laboratories. It is document-controlled by the corporate quality office and signed copies are distributed to each of the regional Quality Managers. The regional management personnel sign the Quality Manual and the local Quality Manager is then in charge of distribution to employees and external clients or regulatory agencies and maintaining a controlled list of distributed copies. Each laboratory may attach a lab-specific addendum to the Quality Manual as needed.

5.1.2 Standard Operating Procedures (SOPs)

SOPs fall into two categories: company-wide documents (starting with the prefix ALL-) or individual lab documents (starting with the individual lab abbreviation). Company-wide SOPs (ALL SOPs) are document-controlled by the corporate quality office and signed copies are distributed to each of the laboratory Quality Managers. The Laboratory management personnel sign the company-wide (ALL) SOPs and the local Quality Manager then distributes to employees and external clients or regulatory agencies and maintains a controlled list of distributed copies. Each laboratory may attach a lab-specific addendum to any of the Company-wide (ALL) SOPs as needed. Individual lab specific SOPs are controlled by the local Quality Manager in the same manner.

SOPs are reviewed every two years at a minimum (a more frequent review may be required by state agencies or clients). Documentation of this review and any applicable revisions is made in the last section of each SOP. This provides a historical record of all revisions.

Documents

All superseded SOPs are removed from general use and are either destroyed by the Quality Manager or archived for audit or knowledge preservation purposes. This ensures that all Pace employees use only the most current version of each SOP.

5.1.3 Work-processing documents

These documents, more commonly in the form of flowcharts, are internal documents intended to aid the analysts in the processing of the work. These documents are controlled by the local Quality Managers in the same manner as the SOPs.

5.1.4 Training documents

The training documents are more detailed documents that describe lab-specific details such as computer and equipment set-up, sample preparation and analysis steps, data validation steps, documentation requirements, and data packet preparation. Documentation that an analyst has completed their training via these training documents, including successfully passing a quiz, is maintained in their training file.

5.2 Document Change

Changes to documents are reviewed and approved in the same manner as the original document control. Any revision to a document requires the approval of the applicable signatories. After revisions are approved, a revision number is assigned and the previous version of the document is officially retired. Copies may be kept for audit or knowledge preservation purposes.

All controlled copies of the previous document are replaced with controlled copies of the revised document and the old copies are destroyed or archived. All affected personnel are advised that there has been a revision and any necessary training can be scheduled.

6.0 EQUIPMENT AND CALIBRATION

Equipment

Each Pace lab is equipped with instrumentation and support equipment to perform the required analyses. Support equipment includes chemical standards, thermometers, balances, pipettes, etc. This section will detail some of this equipment and instrumentation and the procedures necessary for its proper calibration.

6.1 Standards and Traceability

Reference measurement standards are required to provide an assurance that laboratory results are traceable to an acceptable standard. Laboratories document the purchase, receipt, origin, preparation and use of all standards, reagents, and other chemicals.

Upon receipt, all purchased standard reference materials are recorded into a standard logbook or database. The entries include the Pace laboratory's unique identification number, the chemical name, manufacturer name, manufacturers identification numbers, receipt date and expiration date. Vendor's certificates of analysis for all standards, reagents, or chemicals are retained by the lab for future reference.

Subsequent preparations of intermediate or working solutions are also documented in a standard logbook or database. These entries include the stock standard name and lot number, the manufacturer name, the solvents used for preparation, the solvent lot number and manufacturer, the preparation steps, preparation date, preparer's initials, and a unique Pace Analytical lab number. This number is used in any applicable sample preparation or analysis logbook so the standard can be traced back to the standard preparation record.

All prepared standard or reagent containers include the Pace identification number, the standard or chemical name, the date or preparation, the date of expiration, the concentration and units, and the preparer's initials. This ensures traceability back to the standard preparation logbook.

If a second source standard is required to verify an existing calibration or spiking standard, this standard is purchased from a different supplier. If no second source is available, a second standard may be purchased from the same supplier but the lab is required to receive a certificate of warranty noting that both standards were prepared from different raw materials. Obtaining two standards from the same parent material are not acceptable for satisfying this requirement.

6.2 General Calibration Procedures

All types of support equipment and instrumentation are calibrated before use to ensure that they function properly. All calibrations are performed by, or under the supervision of, an experienced analyst at scheduled intervals against either certified standards traceable to recognized national standards, or reference standards whose values have been statistically validated. Instrumentation or support equipment that cannot be calibrated to specifications, or is otherwise defective, are taken out of service. They are clearly labeled as out-of-service until they have been repaired and tested to meet specifications. In the event that recalibration of a piece of test equipment casts doubt on the validity of test results already transmitted to the client, the client is notified promptly by the laboratory. Instrumentation found to be consistently out of calibration is either repaired and positively verified or replaced.

Calibration standards for each parameter are chosen to establish the linear range of the instrument and must bracket the concentrations of those parameters measured in the samples. Samples with analytical results that fall outside the calibration range are either diluted and reanalyzed or reported with an appropriate data qualifier. The lowest calibration standard is normally run at the reporting limit for each analyte.

Calibration standards are prepared at a minimum of three concentration levels for inorganic analyses and a minimum of five concentrations for organic analyses. A calibration blank is also included for

some inorganic analyses. Any specific method requirement for number and type of calibration standards supersedes the general requirement.

Initial calibration curves are evaluated against appropriate statistical models as required by the analytical methods. Curves that do not meet the appropriate criteria require corrective action that may include re-running the initial curve.

During the course of analysis, the calibration curve is verified by the analysis of a calibration verification standard. This verification standard must also pass acceptance criteria for sample analysis to proceed. Concentrations of calibration verification standards must be varied periodically to evaluate the entire range of the initial calibration curve.

6.3 Calibration Procedures for GC/MS (Gas Chromatograph/ Mass Spectrometer)

More detailed calibration information can be obtained from Pace Standard Operating Procedures or other similar documentation.

6.3.1 GC/MS Tuning

The first step in preparing a GC/MS instrument for sample analysis is to tune the instrument. This is accomplished through the analysis of 4-bromofluorobenzene (BFB) for volatile analysis or decafluorotriphenyl-phosphine (DFTPP) for semi-volatile analysis. The tune standard must pass the method acceptance criteria for mass spectral abundance for these compounds before calibration standards are evaluated.

6.3.2 Initial Calibration

The GC/MS system is initially calibrated with standards at multiple concentrations to establish the linearity of the instrument's response. The number of calibration standards used depends on the specific method criteria or client project requirements, although normally a minimum of five standards is used.

The response factor (RF) for each compound at each concentration is calculated and an average RF is obtained for each compound in the initial calibration curve. The percent relative standard deviation (%RSD) is calculated for each compound. This RSD value must be $\leq$ 15% for each reported compound and must be $\leq$ 30% for those compounds in the method identified as calibration check compounds (CCCs). For compounds with an RSD >15%, a least squares regression can be applied (the best fit value must be >0.99 to confirm linearity) or data for these compounds must be reported with the appropriate data qualifiers.

The mean RF from the initial calibration curve is used to calculate the sample concentration of the compound of interest.

6.3.3 Calibration Verification

A calibration verification standard is analyzed with each analytical batch to verify that the initial calibration is still valid. This standard must contain all target analytes and is typically analyzed at a concentration around the midpoint of the initial calibration curve. The RF data from this standard is compared to the average RF from the initial calibration. If the RF from any compound differs from the average RF from the initial calibration by more than 20%, then either the calibration verification standard must be re-analyzed or any data reported for those compounds that exceeded the acceptance criteria are reported with the appropriate data qualifiers.

6.4 Calibration Procedures for GC and HPLC (Gas Chromatograph and High Performance Liquid Chromatograph)

More detailed calibration information can be obtained from Pace Standard Operating Procedures or other similar documentation.

6.4.1 Initial Calibration

The GC or HPLC system is initially calibrated with standards at multiple concentrations to establish the linearity of the instrument's response. The number of calibration standards used depends on the specific method criteria or client project requirements, although normally a minimum of five standards is used.

The initial calibration curve may be evaluated in several different manners. The curve is determined to be linear if the correlation coefficient for each target compound is > 0.99 (unless otherwise stated in the method). Linearity may also be determined using calibration factors or response factors. Response factors are calculated for each compound at each concentration level. These RFs are averaged to generate the mean RF for each compound over the range of the standard curve. The curve is determined to be linear if the RSD of the response factors is ≤ 20% (or as specified by the method).

The mean RF from the initial calibration curve is used to calculate the sample concentration of the compound of interest.

6.4.2 Calibration Verification

A calibration verification standard is analyzed within each analytical batch at method/program specific intervals to verify that the initial calibration is still valid (this standard is also run at the end of each batch). This standard must contain all target analytes and is typically analyzed at a concentration around the midpoint of the initial calibration curve. The RF data from this standard is compared to the average RF from the initial calibration. If the RF from any compound differs from the average RF from the initial calibration by more than ±15%, then either the calibration verification standard must be re-analyzed or any data reported for those compounds that exceeded the acceptance criteria are reported with the appropriate data qualifiers. Reported sample results must be bracketed by acceptable calibration verification standards.

6.5 Calibration Procedures for ICP and AAS (Inductively Coupled Plasma and Atomic Absorption Spectrometer)

More detailed calibration information can be obtained from Pace Standard Operating Procedures or other similar documentation.

6.5.1 Initial Calibration

The ICP or AAS system is initially calibrated with standards at multiple concentrations to establish the linearity of the instrument's response. The number of calibration standards used depends on the specific method criteria or client project requirements, although normally a minimum of three standards is used (ICP calibration can be performed with a single standard and a calibration blank if annual linear range studies are conducted).

6.5.2 Calibration Verification

A calibration verification standard is analyzed within each analytical batch at method/program specific intervals to verify that the initial calibration is still valid (this standard is also run at the end of each batch). If the response from this standard differs from the initial calibration

standard by more than 10% for ICP or by more than 20% for AAS, then the instrument must be re-calibrated before proceeding with sample analysis. A calibration blank is also run with each calibration verification standard to verify the cleanliness of the system.

Interference check standards are also run per method requirements at the beginning and end of each batch and must pass method acceptance criteria.

6.6 General Equipment Calibration Procedures

6.6.1 Analytical Balances

Each analytical balance is checked and (if necessary) calibrated annually by a qualified service technician. The calibration of each balance is checked each day of use with weights traceable to NIST. Calibration weights are ASTM Class 1 (replaces Class S designation) and are re-certified annually against a NIST traceable reference. Some accrediting agencies may require more frequent checks. If balances are calibrated by an external agency, verification of their weights must be provided. All information pertaining to balance maintenance and calibration is recorded in the individual balance logbook and/or is maintained on file in the Quality department.

6.6.2 Thermometers

Certified, or reference, thermometers are maintained for checking calibration of working thermometers. Reference thermometers are provided with NIST traceability for initial calibration and are re-certified, at a minimum, yearly with equipment directly traceable to NIST.

Working thermometers are compared with the reference thermometers annually according to corporate metrology procedures. Each thermometer is individually numbered. In addition, working thermometers are visually inspected by laboratory personnel prior to use and temperatures are documented.

Laboratory thermometer inventory and calibration data are maintained in the Quality department.

6.6.3 pH/Electrometers

The meter is calibrated before use each day, and once after each four hours of continuous use using fresh buffer solutions.

6.6.4 Spectrophotometers

During use, spectrophotometer performance is checked at established frequencies in analysis sequences against initial calibration verification (ICV) with continuing calibration verification (CCV) standards.

6.6.5 Pipettes

Mechanical hand pipettes are calibrated on a quarterly basis.

6.7 Instrument/Equipment Maintenance

The objectives of the Pace Analytical maintenance program are twofold: to establish a system of instrument care that maintains instrumentation and equipment at required levels of calibration and sensitivity, and to minimize loss of productivity due to repairs.

The Laboratory Operations Manager and department manager/supervisors are responsible for providing technical leadership to evaluate new equipment, solve equipment problems and coordinate instrument repair and maintenance. The analysts have a primary responsibility to perform routine maintenance.

To minimize downtime and interruption of analytical work, preventive maintenance is routinely performed on each analytical instrument.

Department manager/supervisors are responsible for maintaining an adequate inventory of spare parts required to minimize equipment downtime. This inventory includes parts and supplies that are subject to frequent failure, have limited lifetimes, or cannot be obtained in a timely manner should a failure occur.

All major equipment and instrumentation items are uniquely identified to allow for traceability. Equipment/instrumentation are, unless otherwise stated, identified as a system and not as individual pieces. The laboratory maintains equipment records that include the following:

- The name of the equipment and its software
- The manufacturer's name, type, and serial number
- Approximate date received and date placed into service
- Current location in the laboratory
- Condition when received (new, used, etc.)
- Copy of any manufacturer's manuals or instructions
- Dates and results of calibrations and next scheduled calibration (if known)
- Details of past maintenance activities, both routine and non-routine
- Details of any damage, modification or major repairs

All routine and non-routine instrument maintenance is documented in maintenance logbooks that are assigned to each particular instrument or system.

When maintenance is performed to repair an instrument problem, depending on the initial problem, demonstration of return to control may be satisfied by the successful analysis of a reagent blank or continuing calibration standard. The entry must include a summary of the results of that analysis and verification by the analyst that the instrument has been returned to an in-control status. In addition, each entry must include the initials of the analyst making the entry, the dates the maintenance actions were performed, and the date the entry was made in the maintenance logbook, if different from the date(s) of the maintenance.

Any equipment that has been subjected to overloading or mishandling, or that gives suspect results, or has been shown to be defective is taken out of service and clearly identified. The equipment shall not be used to analyze client samples until it has been repaired and shown to perform satisfactorily.

6.8 Spare Parts

Department manager/supervisors are responsible for maintaining an adequate inventory of spare parts required to minimize equipment downtime. This inventory includes parts and supplies that:

- Are subject to frequent failure,
- Have limited useful lifetimes, or
- Cannot be obtained in a timely manner should failure occur.

7.0 CONTROL OF DATA

Analytical results processing, verification and reporting are the processes that result in the delivery of defensible analytical data to the data user. These processes include calculation of raw data into final concentration units, reviewing results for accuracy and assembly of the technical report for delivery to the data user.

All analytical data undergo a well-defined, well-documented multi-tier review process before being reported to the client. The following information describes procedures employed at Pace Analytical for translating raw analytical data into accurate, finished sample reports and describes data storage policies.

7.1 Analytical Results Processing

When "raw data" is manually generated by an analyst, it is recorded in either a bound notebook (run logbook), or copies of the computer printouts are appropriately labeled and filed. Logbooks and other bench records are kept in accordance with each laboratory's Standard Operating Procedure on documentation practices (this may also include the use of electronic logbooks). The primary analyst is responsible for the initial reduction and review of the data. This includes confirming compliance with required methodology; checking the calculations used; checking quality control data against known criteria; noting any discrepancies that occurred both in the necessary logbooks and as a footnote or narrative in LIMS; and entering analytical data into the LIMS system. The primary analyst then compiles the initial data package for data verification. This compilation must include sufficient documentation to review the data. It may include chromatograms or strip-chart recordings, other computer printouts, chain-of-custody copies if available, and logbook copies. Some agencies or clients require different levels of data reporting. For these special levels, the primary analyst may also need to compile additional project information such as initial calibration data or extensive spectral data before the data package goes to the verification step.

7.2 Data Verification

Data verification is the process of examining data and accepting or rejecting it based on pre-defined criteria. This review step is designed to ensure that the reported data are free from calculation and transcription errors, that quality control parameters are evaluated, and that any discrepancies are properly documented.

Analysts performing the analysis and subsequent data reduction have the primary responsibility for the quality of the data produced. The primary analyst initiates the data verification process by reviewing and accepting the data provided QC criteria have been met for the samples being reported. Data review checklists are used to document the data review process.

The completed data package is then sent to the Group Supervisor or designated qualified reviewer (this cannot be the primary analyst). This reviewer provides an independent technical assessment of the data package and technical review for accuracy according to methods employed and laboratory protocols. All data that are manually entered into the LIMS is reviewed at a rate of 100%. This involves a quality control review for use of the proper methodology and detection limits, compliance to quality control protocol and criteria, presence and completeness of required deliverables, and accuracy of calculations and data quantitation. The reviewer also reviews analyst-generated calculations.

For results that are processed via computer, calculations are checked by the analyst (or designee) assigned to this task at a frequency designed to assure that the data reductions are valid. The results are either manually transferred to a standard reporting form or reported via computer generation of forms.

Once the data have been technically reviewed and approved, authorization for release of the data from the analytical section is indicated by initialing and dating the data review checklist or otherwise initialing and dating the data.

The Operations or Project Manager examines the report for method appropriateness, detection limits and QC acceptability. Any deviations from the referenced methods are checked for documentation and validity, and QC corrective actions are reviewed for successful resolution.

Use of checklists ensures that all data are systematically handled and no steps are omitted. Checklists are reviewed, retained, and made accessible should they need to be referenced at a later date.

7.3 Data Reporting

All data segments pertaining to a particular Pace Analytical project number are delivered to the Client Services Department (Project Manager) for assembly into the final report. All points mentioned during technical and QC review is included in a case narrative if it is deemed necessary to explain the impact on the quality of the data.

Final reports are prepared according to the level of reporting required by the client. A standard Pace Analytical final report consists of the following components:

1. A title which designates the report as "Final Report", "Laboratory Results", "Certificate of Results", etc.
2. Name and address of laboratory (or subcontracted laboratories, if used).
3. Phone number and name of laboratory contact where questions can be referred.
4. A unique number for the report (project number). The pages of the report shall be numbered and a total number of pages shall be indicated (usually in the cover letter).
5. Name and address of client and name of project (if applicable).
6. Unique identification of samples analyzed (including client sample numbers).
7. Identification of any sample that did not meet acceptable sampling requirements (from NELAC or other governing agency), such as improper sample containers, holding times missed, sample temperature, etc.
8. Date and time of collection of samples, date of sample receipt by the laboratory, dates of sample preparation and analysis, and times of sample preparation and analysis when the holding time for either is 72 hours or less.
9. Identification of the test methods used.
10. Identification of sampling procedures if sampling was conducted by the laboratory.
11. Deviations from, additions to, or exclusions from the test methods. These can include failed quality control parameters, deviations caused by the matrix of the sample, etc., and can be shown as a case narrative or as defined footnotes to the analytical data.
12. Identification of whether calculations were performed on a dry or wet-weight basis.
13. Reporting limits used.
14. Final results or measurements, supported by appropriate chromatograms, charts, tables, spectra, etc.
15. If required, a statement of the estimated uncertainty of the test results.
16. A signature and title of person accepting responsibility for the content of the report (can be an equivalent electronic identification) and date report was issued.
17. A statement clarifying that the results of the report relate only to the samples tested or to the samples as they were received by the laboratory.
18. If necessary, a statement indicating that the report must not be reproduced except in full, without the written approval of the laboratory.
19. Identification of all test results provided by a subcontracted laboratory or other outside source.
20. Identification of results obtained outside of quantitation levels.

Any changes made to a final report shall be designated as a "Supplement" or equivalent wording. For higher levels of data reporting, a copy of all raw data is sent to the client along with a final report of results. When possible, the Pace Analytical laboratory will provide electronic data deliverables (EDD) as required by contracts or upon client request.

Client data that requires transmission by telephone, telex, facsimile or other electronic means undergoes appropriate steps to preserve confidentiality.

7.4 Data Archiving

All records compiled by Pace Analytical labs are maintained, stored and secured by the Quality Manager or by a designated Data Archivist for a minimum of five years unless superseded by federal, contractual, and/or accreditation requirements. These records can include client data reports, certificates pertaining to calibration and maintenance of equipment, raw data from instrumentation, quality control documents and logbooks. These records are retained in order to provide for possible historical reconstruction of data. Access to archived data is kept to a minimum, with the Data Archivist maintaining the archive documentation in a secure, fireproof (if possible) location. Some laboratories archive their data in an off-site facility and the Data Archivist will keep a record of this archival as well. Records that are computer generated have either a hard copy or electronic backup copy.

In the event of a change in ownership, accountability or liability, reports of analyses performed pertaining to accreditation will be maintained by the acquiring entity for a minimum of five years. In the event of bankruptcy, laboratory reports and/or records will be transferred to the client and/or the appropriate regulatory entity.

8.0 QUALITY SYSTEM AUDITS AND REVIEWS

In an effort to assess the effectiveness of the Quality Systems, all Pace Analytical laboratories are subject to internal and external audits and reviews.

8.1 Internal Audits

8.1.1 Responsibilities

The Quality Manager is responsible for designing and/or conducting internal audits. Since internal audits represent an independent assessment of laboratory functions, the auditor must be functionally independent from laboratory operations to ensure objectivity. 'The auditor must be familiar enough with the objectives, principles, and procedures of laboratory operations to be able to perform a thorough and effective evaluation. The Quality Manger evaluates audit observations and verifies the completion of corrective actions. In addition, an annually corporate audit is conducted by the Director of Quality, Safety and Training and/or designee.

8.1.2 Scope and Frequency of Internal Audits

Internal systems audits are conducted yearly at a minimum. The scope of these audits includes evaluation of specific analytical department or a specific quality-related system as applied throughout the laboratory.

Examples of system-wide elements that can be audited include:

- Quality Systems documents, such as standard operating procedures and Quality Manual.
- Personnel and training files.
- General laboratory safety protocols.
- Chemical handling practices, such as labeling of reagents, solutions, standards, and associated documentation.
- Documentation concerning equipment and instrumentation, calibration/maintenance records, operating manuals.
- Sample receipt and management practices.
- Analytical documentation, including any discrepancies and corrective actions.
- General procedures for data security, review, documentation, reporting and archiving.

When the operations of a specific department are evaluated, a number of additional functions are reviewed including:

- Method detection limit studies
- Internal chain-of-custody documentation
- Documentation of standard preparations
- Control charts

Certain projects may require an internal audit to ensure laboratory conformance to site work plans, sampling and analysis plans, QAPPs, etc.

A representative number of data audits are completed annually. The report format of any discrepancy is similar to that of other internal audits. Further information on the internal audit process is documented in the applicable SOPs.

Assessment

8.1.3 Internal Audit Reports and Corrective Action Plans

A full description of the audit, including the identification of the operation audited, the date(s) on which the audit was conducted, the specific systems examined, and the observations noted are summarized in an internal audit report. Although other personnel may assist with the performance of the audit, the Quality Manager writes and issues the internal audit report identifying which audit observations are deficiencies that require corrective action.

Once completed, the internal audit report is issued jointly to the Laboratory General Manager and the manager(s)/supervisor(s) of the audited operation at a minimum. The responsible manager(s)/supervisor(s) responds with a plan to correct all of the deficiencies cited by the due date specified in the audit report. Each response must include timetables for completion of all proposed corrective actions.

The Quality Manager reviews the audit responses. If the response is accepted, the Quality Manager uses the action plan and timetable as a guideline for verifying completion of the corrective action(s). If the Quality Manager determines that the audit response does not adequately address the correction of cited deficiencies, the response will be returned for modification.

To complete the audit process, the Quality Manager performs a re-examination of the areas where deficiencies were found to verify that all proposed corrective actions have been implemented. An audit deficiency is considered closed once implementation of the necessary corrective action has been verified. If corrective action cannot be verified, the associated deficiency remains open until that action is completed.

8.2 External Audits

Pace Analytical laboratories are audited regularly by regulatory agencies, to maintain laboratory certifications, and by clients to maintain appropriate specific protocols.

Audit teams external to the company review the laboratory to assess the existence of systems and degree of technical expertise. The Quality Manager and other QA staff host the audit team and assist in facilitation of the audit process. Generally, the auditors will prepare a formalized audit report listing deficiencies observed and follow-up requirements for the laboratory. In some cases, items of concern are discussed during a debriefing convened at the end of the on-site review process.

The laboratory staff and supervisors develop corrective action plans to address any deficiencies with the guidance of the Quality Manager. The Laboratory General Manager provides the necessary resources for staff to develop and implement the corrective action plans. The Quality Manager collates this information and provides a written report to the audit team. The report contains the corrective action plan and expected completion dates for each element of the plan. The Quality Manager follows-up with the laboratory staff to ensure corrective actions are implemented.

8.3 Quarterly Quality Reports

The Quality Manager is responsible for preparing a quarterly report to management indicating the effectiveness of the laboratory Quality Systems. This status report will include:

- Results of internal systems or performance audits
- Corrective action activities
- Discussion of QA issues raised by clients
- Results of third party or external audits
- Status of laboratory certifications
- Other significant events

- Performance Evaluation/Proficiency Test Sample Results
- Results of internal laboratory review activities
- Summary of holding time overruns and data qualification
- Method detection limit study status
- Training activity summary
- SOP revision summary

The Corporate Director of Quality, Safety and Training utilizes the information from each laboratory to make decisions impacting the Quality Systems of the company as a whole. Each General Manager utilizes the quarterly report information to make decisions impacting Quality Systems and operational systems at a local level.

8.4 Annual Managerial Review

A managerial review of Quality Systems is performed on an annual basis at a minimum. This allows for assessing program effectiveness and introducing changes and/or improvements.

The managerial review must include the following topics of discussion:

- Policy and procedure suitability
- Manager/Supervisor reports
- Internal audit results
- Corrective and preventative actions
- External assessment results
- Proficiency testing studies
- Sample capacity and scope of work changes
- Client feedback, including complaints

This managerial review must be documented for future reference by the Quality Manager and copies of the report are distributed to laboratory staff.

9.0 CORRECTIVE ACTION

During the process of sample handling, preparation and analysis, certain occurrences may warrant the necessity of corrective actions. These occurrences may take the form of analyst errors, deficiencies in quality control, method deviations, or other unusual circumstances. The Quality System of Pace Analytical provides systematic procedures for documentation and completion of corrective actions. This can be done using a Corrective Action Tracking Log which lists the deficiency by ID, along with the deficiency source, responsible party, root cause, resolution, due date, and date resolved.

9.1 Corrective Action Documentation

The following items are examples of occurrences that warrant some form of documented corrective action:

- Quality Control data outside of acceptance criteria
- Sample Acceptance Policy deviations
- Missed holding times
- Instrument failures
- Sample preparation or analysis errors
- Errors in client reports
- Audit findings (internal and external)

Documentation of corrective actions may be in the form of a comment or footnote on the final report that explains the deficiency (i.e. matrix spike recoveries outside of acceptance criteria) or it may be a more formal documentation (either paper system or computerized spreadsheet). This will depend on the extent of the deficiency, the impact on the data, and the method or client requirements for documentation.

Documentation of a corrective action is initiated by the person who discovers the deficiency. Regardless of who initiates the corrective action, the documentation must contain the approval of all affected parties.

Each formal corrective action requires the signature or initials of all affected parties (or electronic equivalent) and the date they reviewed the corrective action documentation. This includes all applicable analysts, technicians, supervisors, Project Managers, Operations Managers, General Manager, and eventually the Quality Manager. Any comments or specific corrective actions taken (including steps taken to return the system to control, if possible) must also be included in this documentation. The Quality Manager is responsible for final signoff on all formal corrective action documentation and is responsible for the archival and maintenance of all corrective action documentation, including any follow-up information.

9.2 Corrective Action Completion (Specific Examples)

9.2.1 **Quality Control outside of acceptance criteria**: the analyst that is generating or validating Analytical data is responsible for checking the results against established acceptance criteria (quality control limits). The analyst must immediately address any deficiencies discovered. Method blank, LCS or matrix spike failures are evaluated against method, program, and client requirements and appropriate footnotes are entered into the LIMS system. Some deficiencies may be caused by matrix interferences. Where possible, matrix interferences are confirmed by re-analysis. Quality control deficiencies must be made known to the client on the final report for their review of the data for usability. If appropriate, the supervisor is alerted to the QC

failure and if necessary a formal corrective action can be initiated. This may involve the input of the Quality Manager or the General Manager. The department supervisor and/or Operations Manager are responsible for evaluating the source of the deficiency and for returning the analytical system to control. This may involve instrument maintenance, analytical standard or reagent evaluation, or an internal audit of the analytical procedure.

9.2.2 **Sample Acceptance Policy deviations:** any deviation from the Sample Acceptance Policy listed in this Manual must be documented on the Chain-of-Custody or other applicable form by the sample receiving personnel or by the Project Manager. The client must be notified of these deviations as soon as possible so they can make decisions on whether to continue with the sample analysis or re-sample. Copies of this documentation must be included in the project file. Analysts or supervisors that discover such deviations must contact the sample receiving personnel or appropriate Project Manager so they can initiate the proper documentation and client contact. If a more formalized corrective action must be documented, the Quality Manager should be made aware of the situation.

9.2.3 **Missed holding times**: in the event that a holding time requirement has been missed, the analyst or supervisor must complete a formal corrective action form. The Project Manager and the Quality Manager must be made aware of these hold time exceedances.

The Project Manager must contact the client for appropriate decisions to be made with the resolution documented and included in the client project file. The Quality Manager includes a list of all missed holding times in their Quarterly Report to the corporate office.

9.2.4 **Instrument Failures**: in the event of an instrument failure that either causes the necessity for re-analysis or questions the validity of generated results, a formal corrective action must be initiated. The analyst and supervisor must evaluate any completed data for validity and usability. They are also responsible for returning the instrument to valid operating condition and for documenting that the system is in control (i.e. acceptable calibration verification).

9.2.5 **Sample Preparation or Analysis errors**: whenever there is an error in the preparation or analysis of samples, the analyst evaluates the impact on the usability of the analytical data with the assistance from their supervisor or manager. The effected samples will be re-processed or re-analyzed under acceptable conditions. In the event that no additional sample is available for re-analysis, the client must be contacted for their decision on how to proceed. Documentation may take the form of footnotes or a formal corrective action form.

9.2.6 **Errors in client reports:** when an error on the client report is discovered, the Project Manager is responsible for initiating a formal corrective action form that describes the failure (i.e. incorrect analysis reported, reporting units are incorrect, reporting limits do not meet objectives). The Project Manager is also responsible for revising the final report if necessary and submitting it to the client.

9.2.7 **Audit findings:** the Quality Manager is responsible for documenting all audit findings and their corrective actions. This documentation must include the initial finding, the persons responsible for the corrective action, the due date for reporting back to the auditing body, the root cause of the issue, and the corrective action taken to resolve the findings. The Quality Manager is also responsible for providing any back-up documentation used to prove that a corrective action has been completed.

10.0 GLOSSARY

Accuracy: The degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components that are due to sampling and analytical operations; a data quality indicator.

Aliquot: A measured portion of a sample taken for analysis.

Analyte: The specific entity an analysis seeks to determine.

Batch: Environmental samples that are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents. A preparation batch is composed of one to 20 environmental samples of the same NELAC-defined matrix, meeting the above-mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be 24 hours. An analytical batch is composed of prepared environmental samples (extracts, digestates or concentrates) that are analyzed together as a group. An analytical batch can include prepared samples originating from various environmental matrices and can exceed 20 samples.

Blank: A sample that has not been exposed to the analyzed sample stream in order to monitor contamination during sampling, transport, storage or analysis. The blank is subjected to the usual analytical and measurement process to establish a zero baseline or background value and is sometimes used to adjust or correct routine analytical results.

Blind Sample: A sub-sample for analysis with a composition known to the submitter. The analyst/laboratory may know the identity of the sample but not its composition. It is used to test analyst or laboratory proficiency in the execution of the measurement process.

CRDL: Contract Required Detection Limit.

CRQL: Contract Required Quantitation Limit.

Calibration: To determine, by measurement or comparison with a standard, the correct value of each scale reading on a meter, instrument, or other device. The levels of the applied calibration standard should bracket the range of planned or expected sample measurements.

Calibration Curve: The graphical relationship between the known values, such as concentrations, or a series of calibration standards and their instrument response.

Chain-of-Custody (COC): A record that documents the possession of samples from the time of collection to receipt in the laboratory. This record generally includes the number and type of containers, the mode of collection, the collector, the time of collection, the preservation, and the requested analyses.

Confirmation: Verification of the identity of a component through the use of an approach with a different scientific principle from the original method. These may include, but are not limited to:

- second-column confirmation
- alternate wavelength
- derivitization
- mass spectral interpretation
- alternative detectors
- additional cleanup procedures

Comparability: Comparability is a qualitative parameter expressing the confidence with which one data set can be compared to another. Comparable data are produced through the use of standardized procedures and techniques.

Completeness: Measure of the amount of valid data obtained from a measurement system compared to the amount of valid data expected under normal conditions. The equation for completeness is:

$$\frac{\text{\# of data points obtained}}{\text{\# of data points expected}} * 100 = \text{\% completeness}$$

Calibration Verification: The process of analyzing standards periodically to verify the maintenance of calibration of the analytical system.

Control Chart: A graphical representation of test results with respect to time or sequence of measurements, together with limits within which they are expected to lie when the system is in a state of statistical control (see Control Limit)

Control Limit: A range within which specified measurement results must fall to signify compliance. Control limits may be mandatory, requiring corrective action if exceeded, or advisory, requiring that nonconforming data be investigated and flagged.

Corrective Action: The action taken to eliminate the causes of an existing nonconformity, defect, or other undesirable situation in order to prevent recurrence.

Data Quality Objective (DQO) Systematic strategic planning tool based on the scientific method that identifies and defines the type, quality, and quantity of data needed to satisfy a specified use or end user.

Data Reduction: The process of transforming raw data by arithmetic or statistical calculations, standard curves, concentration factors, etc., and collation into a more usable form.

Demonstration of Capability: A procedure to establish the ability of the analyst to generate acceptable accuracy.

Detection Limit (DL): The lowest concentration or amount of the target analyte that can be identified, measured and reported with confidence that the analyte concentration is not a false positive value. See Method Detection Limit.

Dry Weight: The weight of a sample based on percent solids. The weight after drying in an oven at a specified temperature.

Duplicate (Replicate)Analysis: The measurement of the variable of interest performed identically on two or more sub-samples of the same sample within a short interval of time.

Environmental Sample: A representative sample of any material (aqueous, non-aqueous, or multimedia) collected from any source for which determination of composition or contamination is requested or required. Environmental samples can generally be classified as follows:

- Surface Water and Ground Water
- Drinking Water - Delivered (treated or untreated) water designated as potable water.
- Water/Wastewater - Raw source waters for public drinking water supplies, ground waters, municipal influents/effluents, and industrial influents/effluents.
- Sludge - Municipal sludges and industrial sludges.
- Soil - Predominately inorganic matter ranging in classification from sands to clays.

- Waste - Aqueous and non-aqueous liquid wastes, chemical solids, and industrial liquid and solid wastes.

Equipment Blank: A sample of analyte-free media used to rinse common sampling equipment to check effectiveness of decontamination procedures.

Field Blank: A blank sample prepared in the field by filling a clean container with reagent water and appropriate preservative, if any, for the specific sampling activity being undertaken.

Holding Time: The maximum time that samples may be held prior to analysis and still be considered valid or not compromised.

Homogeneity: The degree to which a property or substance is evenly distributed throughout a material.

Initial Calibration: (ICAL) The process of analyzing standards, prepared at specified concentrations, to define the quantitative response, linearity and dynamic range of the instrument to the analytes of interest. Initial calibration is performed whenever the results of a continuing calibration do not conform to the requirements of the method in use or at a frequency specified in the method.

Internal Standards: A known amount of standard added to a test portion of a sample as a reference for evaluating and controlling the precision and bias of the applied analytical method.

Laboratory Control Samples (LCS): A blank sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amount of analytes. It is generally used to establish intra-laboratory or analyst-specific precision and bias or to assess the performance of all or a portion of the measurement system.

LIMS: Laboratory Information Management System

Lot: A quantity of bulk material of similar composition processed or manufactured at the same time.

Matrix: The component or substrate that contains the analyte of interest. For purposes of batch and QC requirement determinations, the following matrix distinctions are used:

- **Aqueous**: any aqueous sample excluded from the definition of Drinking Water matrix or Saline/Estuarine source. Includes surface water, groundwater, effluents, and TCLP or other extracts.
- **Drinking Water**: any aqueous sample that has been designated a potable or potentially potable water source.
- **Saline/Estuarine**: any aqueous sample from an ocean or estuary, or other salt water source.
- **Non-aqueous liquid**: any organic liquid with <15% settleable solids.
- **Biological Tissue**: any sample of a biological origin such as fish tissue, shellfish or plant material. Such sample can be grouped according to origin.
- **Solids**: includes soils, sediments, sludges, and other matrices with >15% settleable solids.
- **Chemical Waste**: a product or by-product or an industrial process that results in a matrix not previously defined.
- **Air**: whole gas or vapor samples including those contained in flexible or rigid wall containers and the extracted concentrated analytes of interest from a gas vapor that are collected with a sorbent tube, impinger solution, filter, or other device.

Matrix Spike (MS):	A sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available. Matrix spikes are used to determine the effect of the matrix on a method's recovery efficiency.
Matrix Spike Duplicate (MSD):	A second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of precision of the recovery of each analyte.
Method Blank:	A sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedures: and in which no target analytes or interferences are present at concentrations that impact the analytical results for sample analyses.
Method Detection Limit (MDL):	The minimum concentration of a substance 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.
PBMS:	(Performance Based Measurement System) a set of processes wherein the data quality needs, mandates or limitations of a program or project are specified and serve as criteria for selecting appropriate test methods to meet those needs in a cost-effective manner.
Precision:	A data quality indicator measuring the degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves. Precision is usually expressed as standard deviation, variance or range, in either absolute or relative terms.
Preservation:	Refrigeration and/or reagents added at the time of sample collection (or later) to maintain the chemical and/or biological integrity of the sample.
Proficiency Testing:	A means of evaluating a laboratory's performance under controlled conditions relative to a given set of criteria through analysis of unknown samples provided by an external source.
Protocol:	A detailed written procedure for field and/or laboratory operation that must be strictly followed.
Quality Assurance Project Plan (QAPP):	A formal document describing the detailed quality control procedures by which the quality requirements defined for the data and decisions pertaining to a specific project are to be achieved.
Quality Assurance (QA):	An integrated system of activities involving planning, quality control, quality assessment, reporting and quality improvement to ensure that a product or service meets defined standards of quality with a stated level of confidence.
Quality Control(QC):	The overall system of technical activities whose purpose is to measure and control the quality of a product or service so that it meets the needs of users.
Quality Manual:	A document stating the management policies, objectives, principles, organizational structure and authority, responsibilities, accountability, and implementation of an agency, organization, or laboratory, to ensure the quality of its product and the utility of its product to its users.

Quality System: A structured and documented management system describing the policies, objectives, principles, organizational authority, responsibilities, accountability, and implementation plan of an organization for ensuring quality in its work processes, products (items), and services. The quality system provides the framework for planning, implementing, and assessing work performed by the organization and for carrying out required QA and QC.

Random Error: The EPA has established that there is a 5% probability that the results obtained for any one analyte will exceed the control limits established for the test due to random error. As the number of compounds measured increases in a given sample, the probability for statistical error also increases.

Raw Data: Any original factual information from a measurement activity or study recorded in a laboratory notebook, worksheets, records, memoranda, notes, or exact copies thereof that are necessary for the reconstruction and evaluation of the report of the activity or study. Raw data may include photography, microfilm or microfiche copies, computer printouts, magnetic media, including dictated observations, and recorded data from automated instruments. If exact copies of raw data have been prepared (e.g. tapes which have been transcribed verbatim, dated and verified accurate by signature), the exact copy or exact transcript may be submitted.

Reagent Grade: Analytical reagent (AR) grade, ACS reagent grade, and reagent grade are synonymous terms for reagents that conform to the current specifications of the Committee on Analytical Reagents of the American Chemical Society.

Reporting Limit (RL): The level at which method, permit, regulatory and client specific objectives are met. The reporting limit may never be lower than the statistically determined MDL, but may be higher based on any of the above considerations. Reporting limits are corrected for sample amounts, including the dry weight of solids, unless otherwise specified. There must be a sufficient buffer between the Reporting limit and the MDL.

Representativeness: A quality element related to the ability to collect a sample reflecting the characteristics of the part of the environment to be assessed. Sample representativeness is dependent on the sampling techniques specified in the project work plan.

Sample Delivery Group (SDG): A unit within a single project that is used to identify a group of samples for delivery. An SDG is a group of 20 or fewer field samples within a project, received over a period of up to 14 calendar days. Data from all samples in an SDG are reported concurrently. An SDG is generally defined by one of the following, whichever occurs first: Samples may be assigned to SDGs by matrix (i.e., all soil samples in one SDG, all water samples in another), at the discretion of the laboratory. Clients may establish different SDG classifications to meet project specific requirements. NOTE: The two previous sentences make no sense…what is trying to be defined?

Sensitivity: The capability of a method or instrument to discriminate between measurement responses representing different levels (concentrations) of a variable of interest.

Standard: A substance or material, the properties of which are known with sufficient accuracy, to permit its use to evaluate the same property in a sample.

Standard Blank: A calibration standard consisting of the same solvent/reagent matrix used to prepare the calibration standards without the analytes. It is used to construct the calibration curve by establishing instrument background.

Standard Operating A written document which details the method of an operation, analysis, or action

Procedure (SOP):	whose techniques and procedures are thoroughly prescribed and which is accepted as the method for performing certain routine or repetitive tasks.
Surrogates:	A substance with properties that mimic the analyte of interest. It is unlikely to be found in environmental samples and is added to them for quality control purposes.
Systems Audit:	An on-site inspection or assessment of a laboratory's quality system.
Traceability:	The property of a result of a measurement whereby it can be related to appropriate standards, generally international or national standards, through an unbroken chain of comparisons.
Training/Work Processing Doc.:	A more detailed version of a Standard Operating Procedure that is used for training purposes. This document details exact computer keystrokes, specific instrument controls and laboratory-specific equipment and supplies that assist an analyst with the training for their work area.
Trip Blank:	This blank sample is used to detect sample contamination from the container and preservative during transport and storage of the sample. A cleaned sample container is filled with laboratory pure water; any preservative used in the sample is added and then the blank is stored, shipped, and analyzed with its group of samples.
Validation:	The process of substantiating specified performance criteria.
Verification:	Confirmation by examination and provision of evidence that specified requirements for instruments have been met. The result of verification leads to a decision either to restore in service, to perform adjustment, to repair, to downgrade, or to declare obsolete. In all cases, it is required that a written trace of the verification performed shall be kept on the measuring instrument's individual record.
Warning Limits:	The limits (typically 2 standard deviations either side of the mean) shown on a control chart within which most results are expected to lie (within a 95% probability) while the system remains in a state of statistical control.

11.0 REFERENCES

ANALYTICAL PROTOCOLS

- "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act." Federal Register, 40 CFR Part 136.
- "Test Methods for Evaluating Solid Wastes: Physical/Chemical Methods." SW-846. Most current edition and update.
- "Methods for Chemical Analysis of water and Wastes", EPA 600-4-79-020, 1979 Revised 1983, U.S. EPA.
- U.S. EPA Contract Laboratory Program Statement of Work for Organic Analysis
- U.S. EPA Contract Laboratory Program Statement of Work for Inorganic Analysis
- "Standard Methods for the Examination of Water and Wastewater." Current Edition APHA-AWWA-WPCF
- "Annual Book of ASTM Standards", Section 4: Construction, Volume 04.04: Soil and Rock; Building Stones, American Society of Testing and Materials.
- "Annual Book of ASTM Standards", Section 11: Water and Environmental Technology, American Society of Testing and Materials.
- "NIOSH Manual of Analytical Methods", Third Edition, 1984, U.S. Department of Health and Human Services, National Institute for Occupational Safety and Health.
- "Methods for the Determination of Organic Compounds in Finished Drinking Water and Raw Source Water", U.S. EPA, Environmental Monitoring and Support Laboratory – Cincinnati (September 1986).

ANALYTICAL REFERENCES

- Handbook for Analytical Quality Control in Water and Wastewater Laboratories, U.S. EPA 600/4-79-019, March, 1979.
- Federal Register, 40 CFR Part 136.
- Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846.
- Quality Assurance of Chemical Measurements, Taylor, John K.; Lewis Publishers, Inc. 1987.
- Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WPCF: Current Edition.
- NOISH Manual of Analytical Methods, U. S. Department of Health, Education and Welfare; Current Edition.
- Methods for Non-conventional Pesticides Chemicals Analysis of Industrial and Municipal Wastewater, Test Methods, EPA-440/1-83/079C.
- Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, 1983.
- Environmental Measurements Laboratory (EML) Procedures Manual, HASL-300, US DOE, February, 1992.
- Requirements for Quality Control of Analytical Data, HAZWRAP, DOE/HWP-65/R1, July, 1990.
- Requirements for Quality Control of Analytical Data for the Environmental Restoration Program, Martin Marietta, ES/ER/TM-16, December, 1992.
- Quality Assurance Manual for Industrial Hygiene Chemistry, AIHA, 1988.
- National Environmental Laboratory Accreditation Conference, Constitution, Bylaws, and Standards. Most recent revision.

UPPER MIDWEST REGION
QUALITY MANUAL ADDENDUM

Prepared by Pace Analytical Services, Inc. for

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(Effective date of addendum is the last date signed above)

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1.0 INTRODUCTION & ORGANIZATIONAL STRUCTURE

1.1 Introduction to Pace

The Upper Midwest region of Pace Analytical Services has three analytical laboratories, performing a wide variety of tests. Its capabilities include:

- volatiles and semi-volatiles by Gas Chromatography/Mass Spectrometry (GC/MS);
- metals analysis by Inductively Coupled Plasma spectrometry (ICP) and ICP/MS;
- pesticide, polychlorinated biphenyls (PCB), and volatile (BTEX) analyses by gas chromatography (GC);
- dioxin/furan analysis by high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS) and LRMS
- volatile and semivolatile air analysis by GC and GCMS
- polyaromatic hydrocarbon analysis by High Pressure Liquid Chromatography (HPLC);
- gasoline, diesel and Total Petroleum Hydrocarbon analyses by Gas Chromatography (GC);
- Biota analyses for all major tests
- mercury by cold vapor analysis
- low level mercury analysis by Method 1631E
- and numerous inorganic wet chemical analyses

(All methods are listed in Attachment III and may be subject to change prior to addenda update. The Quality Assurance Office maintains a complete list of each method and analyte approved by NELAC and pertinent state agencies).

The Upper Midwest region is capable of analyzing a variety of environmental and non-environmental samples from different media including surface, drinking and ground waters, air, biota, soils, sediments, waste products, sludge and concretes. All analyses follow written Standard Operating Procedures that are kept on file in the Quality Assurance office. A listing of the major equipment in each facility is available through the quality assurance office in each facility.

The upper Midwest region holds certifications with approximately 40 state and federal agencies. (A complete listing may be obtained through the quality assurance office.) Pace Minneapolis and Enchem Kimberly laboratories hold accreditation by NELAC, the National Environmental Laboratory Accreditation Conference, through the accrediting authority of the Florida Department of Health. The Enchem Green Bay laboratory holds accreditation by NELAC through the accrediting authority of the Illinois Environmental Protection Agency. Copies of the certificates and fields of testing lists may be forwarded to you from the quality assurance department.

This addendum, combined with the preceding corporate quality manual, comprises the complete Laboratory Quality Manual for Upper Midwest region of Pace Analytical Services. This addendum contains information specific to the Upper Midwest region,

whereas the corporate section details practices and policies that are common to all the member Pace laboratories. The addendum is updated by the Regional Quality Manager when necessary.

1.7 Laboratory Organization

The designation for MN laboratory in Figure 1.1 has been expanded to include the Upper Midwest Region. This region and corresponding reporting structure is defined in Attachment I to this addendum.

1.9 Training and Orientation

Refer to the Training Standard Operating Procedure (MN-Q-211) for specific information on acceptable means of documenting initial and continuing demonstrations of capability.

1.10 Laboratory Safety

The designated safety/chemical hygiene officer is Melanie Ollila for the Minneapolis laboratory and Michael Suha for the Enchem Green Bay and Kimberly laboratories. All specific information on laboratory safety is located in each facilities Safety Manual/Chemical Hygiene Plans.

1.11 Security and Confidentiality

All information pertaining to a particular client and their analytical results will remain confidential including national security concerns. Data will not be released to outside agencies without the written authorization from the client.

2.0 SAMPLE CUSTODY

2.1 Sampling Support

Additions to Table 2.1 through 2.4 include but may not be limited to:

Method/Matrix	Container	Preservative	Maximum Hold Time
SM9221D (Fecal-col)	100mL	4°C, 10% sodium thiosulfate	6 hours
SM9223B (Total-col)	100mL	4°C, 10% sodium thiosulfate	24 hours
1653 Water	2 Liter	4°C, pH<2 H_2SO_4	30 Days to Extraction 30 from Ext. to Analysis
1668 Water	1 Liter	4°C	1 Year to Extraction*
1668 Soil	4 or 8 ounce jar	4°C	1 Year to Extraction*
8280 Water	1 Liter	4°C	30 Days to Extraction*
8280 Soil	4 or 8 ounce	4°C	30 Days to Extraction*

Method/Matrix	Container	Preservative	Maximum Hold Time
8290 Solid	4 or 8 ounce	4°C	30 Days to Extraction*
8290 Water	1 Liter	4°C	30 Days to Extraction*
Method 23/TO9	Sampling Head	4°C	30 Days to Extraction*
8290 Waste	2 ounce	4°C	30 Days to Extraction*
1613 Solid	4 or 8 ounce	4°C	1 Year to Extraction*
1613 Water	1 Liter	4°C, 80 mg sodium thiosulfate (if chlorinated source)	1 Year to Extraction (or per state requirements)*
23 XAD	Sampling Head	NA	30 Days to Extraction*
T09/23 PUF	Sampling Head	NA	30 Days to Extraction*
TO-3	Tedlar Bags	NA	48 hrs (client/state specific)
TO-15	Summa Cans	NA	Not specified
Method 3C	Tedlar Bags	NA	48 hrs (client/state specific)
Method 3810 (Mod)	Headspace vials	NA	28 days
TO-4A	PUF Cartridge	NA	7 days (extraction) 40 days (analysis)
TO-13	PUF Cartridge	NA	7 days (extraction) 40 days (analysis)
Method 29	Filter/Impinger	Various (refer to method)	None listed
Method 26	Impinger	Various (refer to method)	None listed
Method 5	Filter	None	None listed
Method 201A (PM10)	Filter, Probe Wash Cyclone wash	None	None listed
Method 202	Organic and Inorganic Wet Catch	None	None listed
Method 1631E	500mL Glass	None	Oxidized in bottle within 28 days

* 40 Days from Extraction to Analysis. (EPA 1613 and 613)
45 Days from Extraction to Analysis (SW8290, 1668, 8280 and Method 23/TO9)

2.4 Chain of Custody

Clarification: The external chain of custody (COC) is signed by the client for relinquishment of samples. The samples may be transported by the client or through the use of a ground or air carrier (e.g. Fed Ex, UPS, SpeeDee) The carrier will assign a tracking number to each cooler and this number may be traced. When the coolers are received at Pace Analytical Services, Inc., the COC is signed by sample management personnel for sample receipt.

2.5 Sample Receipt

All correspondence pertaining to samples which do not meet the acceptance criteria will be fully documented and retained with the project file. All affected data will be footnoted appropriately in the final report.

2.6 Sample Log-in

The Minneapolis laboratory utilizes an "On-Hold" logbook for samples which require further clarification. The logbooks are associated with each sample refrigerator and freezer. The client ID, date, etc are entered into the book, the samples placed into the corresponding refrigerator or freezer, and the project manager associated with the affected client is contacted.

2.7 Sample Storage/Staging

2.7.2 Temperature Monitoring

The Enchem laboratories take the samples to the storage locations after the sample containers have been labeled and prior to entry in the LIMS.

Refrigerators are at $4^{o}C \pm 2^{o}C$ unless state or program requirements differ.

Freezer Area Maintenance

All freezers are maintained at $<0^{o}C$ unless otherwise denoted in analytical method SOPs. The temperature is monitored and recorded each working day. If the temperature is greater than $0^{o}C$, corrective action is taken and appropriately documented.

2.9 Subcontracting Laboratory Services

Unless holding times will be affected and client is not available, the client will be advised in writing prior to shipment of subcontracted samples. All laboratories that perform subcontracted work shall provide documentation regarding certification status with state and federal agencies. This documentation is retained in the Quality Assurance Office.

The chain of custody forms generated will not contain any specific client information to protect client confidentiality.

2.10 Sample Disposal

Air canisters will be retained for 14 days after submission of the analytical report. At that time, the cans will be cleaned and certified per the standard operating procedures unless otherwise stated by the project contract or client request.

3.0 ANALYTICAL CAPABILITIES

3.4 Demonstration of Capability (DOC)

Alternate procedures than those outlined in NELAC Quality System Chapter 5 (most recent version) are referenced in the Minnesota standard operating procedure, MN-Q-211 (*Training Procedures*).

4.0 QUALITY CONTROL PROCEDURES

4.9 Trip Blanks

The collection date of a trip blank is generally the collection date of the associated samples. The closer the collection date of a trip blank is to its preparation date, the more reliable and valuable is the data obtained by analyzing it. In order to ensure the relevancy of trip blank data, Pace confirms that trip blanks are contaminant free prior to shipment to the client and recommends that trip blanks always accompany original bottle orders back to Pace for analysis. Identifications in such trip blanks can probably be ascribed to contamination during collection or transport.

4.10 Limit of Detection

Further information on detection limit studies are outlined in the corporate SOP ALL-P-104 (*Method Detection Limit Studies*) and the relationship to the Limit of Quantitation.

The state of Wisconsin requires a 10/3 relationship between the Limit of Detection (LOD) and the Limit of Quantitation (LOQ).

5.0 DOCUMENT CHANGE CONTROL

The Upper Midwest has no further changes to this section of the corporate quality manual. More detailed information on document change control may be found in MN-Q-229 (*Document Change Control*).

6.0 EQUIPMENT AND CALIBRATION

6.3 Calibration Procedures for GC/MS (Gas Chromatograph/ Mass Spectrometer)

6.3.3 Calibration Verification

Clarification: If the RF from any CCC compound differs from the average RF from the initial calibration by more than 20%, then either the calibration verification standard must be reanalyzed or recalibrate. All non-CCC compounds

should be within 40% from the average RF from the initial calibration unless alternate criteria are specified in the laboratory SOP.

6.4 Calibration Procedures for GC and HPLC (Gas Chromatograph and High Performance Liquid Chromatograph)

6.4.2 Calibration Verification

Method criteria supercede the information in the corporate quality manual.

Table 6.1 Summary of Calibration Requirements

Instrument	Calibration Standard	Acceptance Limit	Corrective Action
Glass Syringes, except autosampler syringes which inject a constant amount.	Prior to use an initial demonstration must be performed, at a minimum	Acceptable based on application	Replace
Automatic Dispensing Devices	Quarterly	Varies	Remove from service and fix, replace
Dial Thermometers	Quarterly	Dependent on Method	Remove from service and fix, replace
Oven	Daily with NIST traceable reference	Acceptable based on application	Remove from service and fix, replace
Refrigerator	Daily with NIST traceable reference	Acceptable based on application	Remove from service and fix, replace
Freezer	Daily with NIST traceable reference	Acceptable based on application	Remove from service and fix, replace
Incubator	Daily with NIST traceable reference	Acceptable based on application	Remove from service and fix, replace
Waterbath	Daily with NIST traceable reference	Acceptable based on application	Remove from service and fix, replace
Bottle Top Dispensers	Biannually when the dispenser is used at variable amounts	Varies, See appropriate SOP	Remove from service and fix, replace

6.6 General Calibration Procedures

6.6.1 Analytical Balances

The Manual for the Certification of Laboratories Analyzing Drinking water specifies that Class 1 or 2 weights may be used in the laboratory.

7.0 CONTROL OF DATA

7.5 Response to Inquiries

The project manager initiates the resolution of customer complaints. A Client Data Review Request Form is used to document complaints, project requests, or comments. The form is forwarded to the laboratory and the actions taken are recorded. When a complaint raises doubt concerning the laboratory policies, procedures, or data quality, the area in question will be internally audited. All records are maintained within the project file or Quality Assurance Office depending on the course of action taken. More detailed information on this process may be found in MN-Q-245 (*Documentation of Client Requests and Complaints*).

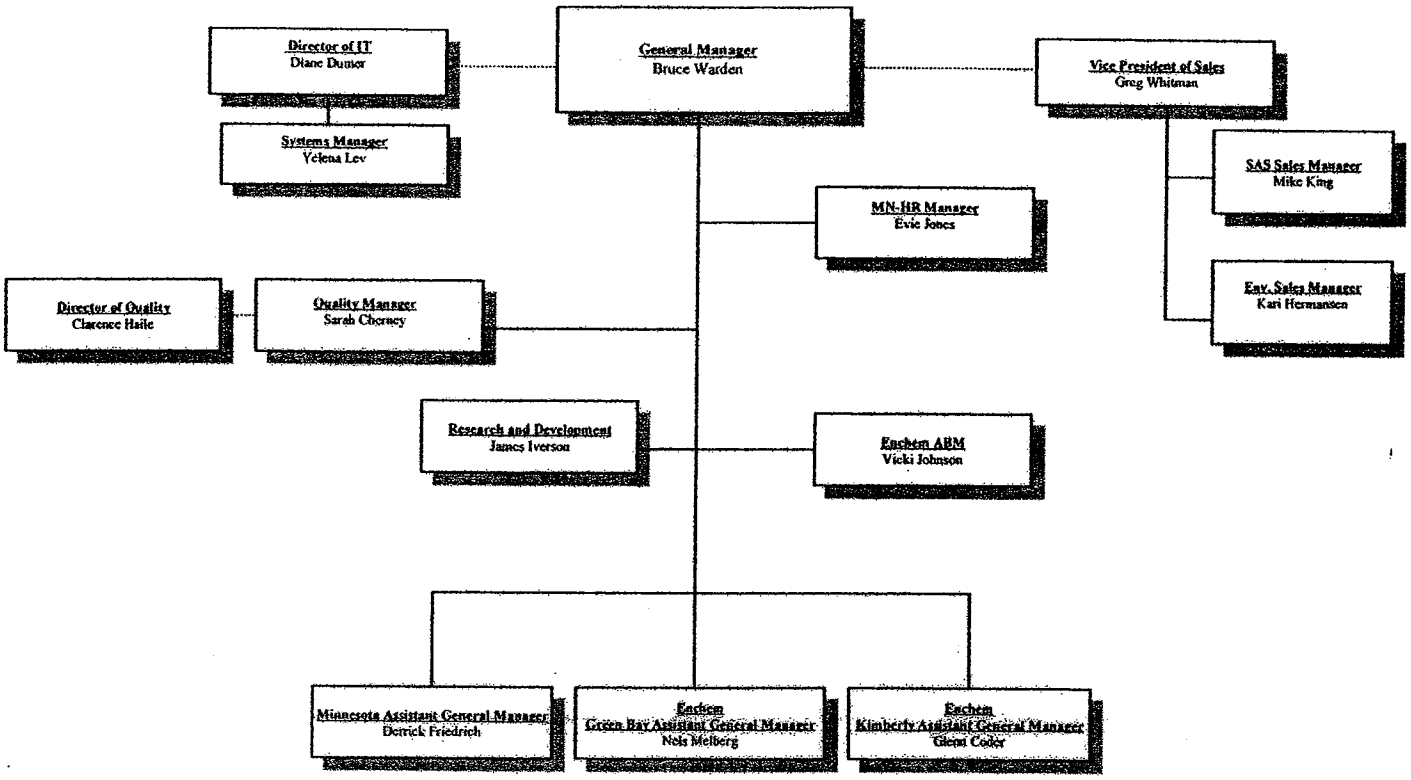
8.0 QUALITY SYSTEM AUDITS AND REVIEWS

The Upper Midwest region has no further changes to this section of the corporate quality manual. More detailed information on internal audits may be found in MN-Q-206 (*Internal Audits and Inspections*) and MN-Q-216 (*Reporting QA Audits*). More detailed information on external audits may be found in MN-Q-223 (*External Audits*).

9.0 CORRECTIVE ACTION

The Upper Midwest region has no further changes to this section of the corporate quality manual. More detailed information on the corrective action and investigation process may be found in MN-L-133 (*Out of Specification Investigation*) and MN-L-136 (*Corrective Action Reports*).

Attachment 1



Attachment 2 (Page 1 of 3)

Pace Analytical™
www.pacelabs.com

Pace Analytical Services, Inc.
1700 Elm Street, Suite 200
Minneapolis, MN 55414
Phone: 612.607.1700
Fax: 612 607 6444

Method ID	Method Name
%MOISTURE	Percent Moisture
Ag-List	Organophosphorus Compounds by Gas Chromatography/Mass Spectrometry: Capillary Column Technique
ASTM D5057	Density by ASTM
CALUF-D	Determination of Diesel Range Organics in water and soil
CALUF-G	Gasoline Range Organics in Water and Soil
EPA 120.1	Physical Properties: Conductance, Specific Conductance
EPA 150.1	Physical Properties: pH, Electrometric
EPA 160.1	Physical Properties: Residue, Filterable, Gravimetric, Dried at 180 C o
EPA 160.2	Physical Properties: Residue, Non-Filterable Gravimetric, Dried at 103-105 C o
EPA 160.3	Physical Properties: Residue, Total Gravimetric, Dried at 103-105 C o
EPA 160.4	Physical Properties: Residue, Volatile, Gravimetric, Ignition at 550 C o
EPA 160.5	Physical Properties: Settleable Matter, Volumetric, Imhoff Cone
EPA 1613	Tetra- through Octa-Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS
EPA 1613B-DW	2,3,7,8-Tetrachlorodibenzo-p-Dioxin in Drinking Water by Isotope Dilution HRGC/HRMS
EPA 1650	Adsorbable Organic Halides
EPA 1653	Chlorinated Phenolics in Wastewater by In Situ Acetylation and GC/MS
EPA 1664, Rev A	N-Hexane Extractable Material (HEM) and Silica Gel Treated N-Hexane Extractable Material (SGT-HEM) by Extraction and Gravimetry (Oil and Grease and Total Petroleum Hydrocarbons)
EPA 1668	Chlorinated Biphenyl Congeners in Water, Soil, sediment, and Tissue by HRGC/HRMS
EPA 170.1	Physical Properties: Temperature, Thermometric
EPA 180.1	Determination of Turbidity by Nephelometry
EPA 200.7	Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma-
EPA 200.8	Determination of Trace Elements in Water and Wastes by Inductively Cuple Plasma-Mass Specrometry
EPA 245.1	Determination of Mercury in Water by Cold Vapor Atomic Absorption Spectrometry
EPA 300.0	Determination of Inorganic Anions by Ion Chromatography - Revision 2.1
EPA 310.1	Inorganic, Non-Metallics: Alkalinity, Titrimetic (pH 4.5)
EPA 310.2	Alkalinity, Colorimetric, Automated Methyl Orange
EPA 330.2	Inorganic, Non-Metallics: Chlorine, Total Residual, Titrimetric, Back, Iodometric
EPA 335.2	Inorganic, Non-Metallics: Cyanide, Total, Titrimetric, Spectrphotometric
EPA 340.2	Inorganic, Non-Metallics: Fluoride, Potentiometric, Ion Selective Electrode
EPA 350.1	Determination of Ammonia Nitrogen by Semi-Automated Colorimetry -Revision 2.0
EPA 351.2	Determination of Total Kjeldahl Nitrogen by Semi-Automated Colorimetry -Revision 2.0
EPA 353.2	Determination of Nitrate-Nitrite by Automated Colorimetry
EPA 354.1	Inorganic, Non-Metallics: Nitrite, Spectrophotometric
EPA 365.2	Inorganic, Non-Metallics: Phosphorus, All Forms, Colorimetric, Ascorbic Acid, Single Reagent
EPA 376.1	Inorganic, Non-Metallics: Sulfide, Titrimetric, Iodine
EPA 3810 (mod)	Methane,Ethane, Ethene in Water by Headspace Analysis
EPA 405.1	Organics: Biochemical Oxygen Demand, 5 day, 20 C o
EPA 410.2	Organics: Chemical Oxygen Demand, Titrimetric, Low-Level
EPA 410.4	Determination of Chemical Oxygen Demand by Semi-Automated Colorimetry - Revision 2.0
EPA 415.1	Total Organic Carbon
EPA 420.1	Organics: Phenolics, Total Recoverable, Spectrophotometric, Manual 4-AAP with Distillation
EPA 420.4	Phenol
EPA 610	Polynuclear Aromatic Hydrocarbons
EPA 613	2,3,7,8-TetraChlorodibenzo-p-dioxin by Low Resolution GC/MS
EPA 624	Chlorinated Hydrocarbons-Purgeables by Low Resolution GC/MS
EPA 625	Base/Neutrals and Acids by Low Resolution GC/MS

Attachment 2 (Page 2 of 3)

Pace Analytical™
www.pacelabs.com

Pace Analytical Services, Inc.
1700 Elm Street, Suite 200
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Phone: 612 607 1700
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Method ID	Method Name
Method 23	Determinatin of Polychlorinated, Polybrominated and Brominated/Chlorinated Dibenzo-p-Dioxins and Dibenzofurans in Ambient Air
Method 26	Determination of Anions and Cations from Ambient Air
Method 29	Determination of Metals Emissions from Stationary Sources
Method 308	Methanol and Ethanol from Stationary Sources
Method 3C	Determination of Carbon Dioxide, Methane, Nitrogen, and Oxygen from Stationary Sources
Method 5	EPA5, Air Filter, Cyclone Wash, Wet Catch, Probe Wash
Molds	Various molds identification
NIOSH 7300 (mod)	Metals, ICP, NIOSH 7300 - MOD
NWTPH-Dx	Semi-volatile Petroleum Products Method for Soil and Water
NWTPH-Gx	Volatile Petroleum Products Method for Soil and Water
OA1	Gasoline Range Organics in Water and Soil
OA2	Diesel Products in Water and Soil
PM10	PM 10, Air Filter, Cyclone Wash, Wet Catch, Probe Wash
REDOX	Oxidation/Reduction Potential
SM 2320B	Alkalinity, Water
SM 2340B	Hardness, Ca & Mg as Carbonates by ICP
SM 3500-Cr-D	Chromium, Hexavalent (Colorimetric)
SM 4500	Chloride (Silver Nitrate)
SM 4500-CN-E	Cyanide (Colorimetric Method)
SM 4500-CN-G	Cyanides Amenable to Chlorination after Distillation
SM 4500-CN-I	Weak Acid Dissociable Cyanide
SM 4500-F-C	Fluoride by Ion-Selective Electrode Mode
SM 4500-P-E	Phosphorous- Ascorbic Acid Method
SM 4500-SO3-B	Sulfide
SM 5210B	5-Day Biochemical Oxygen Demand (BOD) Test
SM 5220C	Chemical Oxygen Demand (COD) by Closed Reflux, Titrimetic Method
SM 5220D	Chemical Oxygen Demand (COD) by Closed Reflux, Colormetric Method
SM 5310C	Total Organic Carbon
SM 9215A	Heterotrophic Plate Count
SM 9222D	Fecal Coliform in Water
SM 9223B	Total Coliform in Water
SM2540C	Total Dissolved Solids
SM2540D	Total Suspended Solids
SPC	Standard Plate Count
SW 1010	Pensky-Martens Closed-Cup Method for Determining Ignitability
SW 1311	Toxicity Characteristic Leaching Procedure
SW 1323	Synthetic Precipitation Leaching Procedure
SW 3010A	Acid Digestion of Aqueous Samples and Extracts for Total Metals for Analysis by FLAA or ICP Spectroscopy
SW 3050B	Acid Digestion of Sediments, Sludges, and Soils
SW 3051	Microwave Assisted Acid Digestion of Sediments, Sludges, Soils, and Oils
SW 3510C	Separatory Funnel Liquid-Liquid Extraction
SW 3520C	Continuous Liquid-Liquid Extraction
SW 3535	Solid-Phase Extraction (SPE)
SW 3540C	Soxhlet Extraction
SW 3541	Automated Soxhlet Extraction
SW 3550B	Ultrasonic Extraction

Attachment 2 (Page 3 of 3)

Pace Analytical™
www.pacelabs.com

Pace Analytical Services, Inc.
1700 Elm Street, Suite 200
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Method ID	Method Name
SW 3580A	Waste Dilution
SW 5030B	Purge-and-Trap for Aqueous Samples
SW 5035	Closed-System Purge-and-Trap and Extraction for Volatile Organics in Soil and Waste Samples
SW 6010B	Inductively Coupled Plasma-Atomic Emission Spectrometry
SW 6020	Determination of Trace Elements in Water and Wastes by Inductively Cuple Plasma-Mass Specrometry
SW 7196A	Chromium, Hexavalent (Colorimetric)
SW 7470A	Mercury in Liquid Waste (Manual Cold-Vapor Technique)
SW 7471A	Mercury in Solid or Semisolid Waste (Manual Cold-Vapor Technique)
SW 8015B	Nonhalogenated Organics Using GC/FID
SW 8021B	Aromatic and Halogenated Volatiles by Gas Chromatography Using Photoionization and/or Electrolytic Conductivity Detectors
SW 8081A	Organochlorine Pesticides by Gas Chromatography
SW 8082	Polychlorinated Biphenyls (PCBs) by Gas Chromatography
SW 8260B	Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS)
SW 8270C	Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS)
SW 8270C SIM	Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS)-utilizing selective ion monitoring
SW 8280A	The Analysis of Polychlorinated Dibenzo-p-Dioxins and Polychlorinated Dibenzofurans by High Resolution Gas Chromatography/Low Resolution Mass Spectrometry (HRGC/LRMS)
SW 8290	Polychlorinated Dibenzodioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs) by High-Resolution Gas Chromatography/High-Resolution Mass Spectrometry (HRGC/HRMS)
SW 8310	Polynuclear Aromatic Hydrocarbons
SW 9010	Total and Amenable Cyanide: Distillation
SW 9030B	Acid-Soluble and Acid-Insoluble Sulfides: Distillation
SW 9045C	Soil and Waste pH
SW 9060	Total Organic Carbon
SW 9095A	Paint Filter Liquids Test
TO-13	Determination of Semi-Volalatile Organics in Ambient Air
TO-14	Determination of Volatile Organic Compounds in Ambient Air utilizing a Summa Canister and GC/MS
TO-15	The Determination of Volatile Organic Compounds in Air Collected in Summa Canisters and Analyzed by GC/MS
TO-15 SIM	The Determination of Volatile Organic Compounds in Air Collected in Summa Canisters and Analyzed by GC/MS utilizing selective ion monitoring
TO-3	TO3, in Air Source
TO-4 (PCB)	Determinatin of Polychlorinated Biphenyl in Ambient Air
TO-4 (Pesticides)	Determinatin of Polychlorinated Pesticide in Ambient Air
TO-9A	Determinatin of Polychlorinated, Polybrominated and Brominated/Chlorinated Dibenzo-p-Dioxins and Dibenzofurans in Ambient Air
WDRO	Determination of Diesel Range Organics in water and soil
WGRO	Determination of Gasoline Range Organics in water and soil

PAHs - Soils

TestName	AnalMethod	CalcEQL	CalcMDL	CalcUnit
1-Methylnaphthalene	8270C-SIM	25	3.0	ug/kg
2-Methylnaphthalene	8270C-SIM	25	3.1	ug/kg
Acenaphthene	8270C-SIM	25	3.0	ug/kg
Acenaphthylene	8270C-SIM	25	3.0	ug/kg
Anthracene	8270C-SIM	25	3.6	ug/kg
Benzo(a)anthracene	8270C-SIM	25	5.3	ug/kg
Benzo(a)pyrene	8270C-SIM	25	2.9	ug/kg
Benzo(b)fluoranthene	8270C-SIM	25	2.8	ug/kg
Benzo(ghi)perylene	8270C-SIM	25	3.6	ug/kg
Benzo(k)fluoranthene	8270C-SIM	25	3.1	ug/kg
Chrysene	8270C-SIM	25	4.4	ug/kg
Dibenz(a,h)anthracene	8270C-SIM	25	2.8	ug/kg
Fluoranthene	8270C-SIM	25	2.9	ug/kg
Fluorene	8270C-SIM	25	3.4	ug/kg
Indeno(1,2,3-cd)pyrene	8270C-SIM	25	2.5	ug/kg
Naphthalene	8270C-SIM	25	4.0	ug/kg
Phenanthrene	8270C-SIM	25	2.9	ug/kg
Pyrene	8270C-SIM	25	2.5	ug/kg

PCBs - Soils

TestName	AnalMethod	CalcEQL	CalcMDL	CalcUnit
Aroclor 1016	SW846 8082	50	15	ug/kg
Aroclor 1221	SW846 8082	50	15	ug/kg
Aroclor 1232	SW846 8082	50	15	ug/kg
Aroclor 1242	SW846 8082	50	15	ug/kg
Aroclor 1248	SW846 8082	50	15	ug/kg
Aroclor 1254	SW846 8082	50	15	ug/kg
Aroclor 1260	SW846 8082	50	15	ug/kg
Total PCBs	SW846 8082	50	15	ug/kg

RCRA Metals - Soils

TestName	AnalMethod	CalcEQL	CalcMDL	CalcUnit
Silver	SW846 6010B	1.0	0.24	mg/kg
Silver	SW846 6020	0.30	0.022	mg/kg
Arsenic	SW846 6010B	2.0	0.84	mg/kg
Arsenic	SW846 6020	0.30	0.11	mg/kg
Barium	SW846 6010B	0.50	0.10	mg/kg
Barium	SW846 6020	0.30	0.092	mg/kg
Cadmium	SW846 6010B	0.50	0.051	mg/kg
Cadmium	SW846 6020	0.10	0.074	mg/kg
Chromium	SW846 6010B	0.50	0.15	mg/kg
Chromium	SW846 6020	0.30	0.14	mg/kg
Mercury	SW846 7471A	0.010	0.0015	mg/kg
Lead	SW846 6010B	1.0	0.34	mg/kg
Lead	SW846 6020	0.25	0.076	mg/kg
Selenium	SW846 6010B	2.0	0.81	mg/kg
Selenium	SW846 6020	1.0	0.35	mg/kg

Metals - Soils

TestName	AnalMethod	CalcEQL	CalcMDL	CalcUnit
Aluminum	SW846 6010B	50	20	mg/kg
Aluminum	SW846 6020	15	1.2	mg/kg
Antimony	SW846 6010B	2.0	0.66	mg/kg
Antimony	SW846 6020	0.30		mg/kg

Copper	SW846 6010B	1.0	0.16	mg/kg
Copper	SW846 6020	1.0	0.077	mg/kg
Iron	SW846 6010B	10	5.0	mg/kg
Iron	SW846 6020	30	3.3	mg/kg
Nickel	SW846 6010B	1.0	0.29	mg/kg
Nickel	SW846 6020	0.30	0.099	mg/kg
Vanadium	SW846 6010B	0.50	0.16	mg/kg
Vanadium	SW846 6020	0.30	0.054	mg/kg
Zinc	SW846 6010B	4.0	2.0	mg/kg
Zinc	SW846 6020	3.0	0.37	mg/kg

Wetchem - Soils

TestName	AnalMethod	CalcEQL	CalcMDL	CalcUnit
TOC as NPOC	SW846 M9060	500	60	mg/kg
Cyanide, Total	SW846 9012A	0.60	0.31	mg/kg
Sulfide	EPA 376.1	5.0	2.5	
COD	EPA M410.4	1000	850	mg/kg
BOD	SM M5210B	200	200	mg/kg

DRO - Soils

TestName	AnalMethod	CalcEQL	CalcMDL	CalcUnit
Diesel Range Organics	WI MOD DRO	5.0	1.7	mg/kg

GRO - Soils

TestName	AnalMethod	CalcEQL	CalcMDL	CalcUnit
Gasoline Range Organics	WI MOD GRO	2500	1300	mg/kg

VOA - Soils

TestName	AnalMethod	CalcEQL	CalcMDL	CalcUnit
1,1,1,2-Tetrachloroethane	SW846 8260B	50	16	ug/kg
1,1,1-Trichloroethane	SW846 8260B	50	19	ug/kg
1,1,2,2-Tetrachloroethane	SW846 8260B	50	21	ug/kg
1,1,2-Trichloroethane	SW846 8260B	50	24	ug/kg
1,1-Dichloroethane	SW846 8260B	50	19	ug/kg
1,1-Dichloroethene	SW846 8260B	50	22	ug/kg
1,1-Dichloropropene	SW846 8260B	50	19	ug/kg
1,2,3-Trichlorobenzene	SW846 8260B	50	17	ug/kg
1,2,3-Trichloropropane	SW846 8260B	50	21	ug/kg
1,2,4-Trichlorobenzene	SW846 8260B	50	16	ug/kg
1,2,4-Trimethylbenzene	SW846 8260B	50	11	ug/kg
1,2-Dibromo-3-chloropropane	SW846 8260B	100	12	ug/kg
1,2-Dibromoethane	SW846 8260B	50	18	ug/kg
1,2-Dichlorobenzene	SW846 8260B	50	12	ug/kg
1,2-Dichloroethane	SW846 8260B	50	21	ug/kg
1,2-Dichloroethene, Total	SW846 8260B	100	27	ug/kg
1,2-Dichloropropane	SW846 8260B	50	22	ug/kg
1,3,5-Trimethylbenzene	SW846 8260B	50	12	ug/kg
1,3-Dichlorobenzene	SW846 8260B	50	16	ug/kg
1,3-Dichloropropane	SW846 8260B	50	12	ug/kg
1,4-Dichlorobenzene	SW846 8260B	50	18	ug/kg
1,1,2-Trichlorotrifluoroethane	SW846 8260B	50	18	ug/kg
1,2,3-Trimethylbenzene	SW846 8260B	50	12	ug/kg
1,4-Dioxane	SW846 8260B	2500	2100	ug/kg
1-Propanol	SW846 8260B	2500	1800	ug/kg
2,2-Dichloropropane	SW846 8260B	50	16	ug/kg
2,3-Dichloropropene	SW846 8260B	50	20	ug/kg
2-Butanone	SW846 8260B	250	72	ug/kg

2-Chloroethylvinylether	SW846 8260B	250	24	ug/kg
2-Chlorotoluene	SW846 8260B	50	18	ug/kg
2-Hexanone	SW846 8260B	250	62	ug/kg
2-Methylnaphthalene	SW846 8260B	250	24	ug/kg
4-Chlorotoluene	SW846 8260B	50	23	ug/kg
4-Methyl-2-pentanone	SW846 8260B	250	26	ug/kg
Acetone	SW846 8260B	250	58	ug/kg
Acetonitrile	SW846 8260B	500	210	ug/kg
Acrolein	SW846 8260B	500	150	ug/kg
Acrylonitrile	SW846 8260B	250	41	ug/kg
Allyl chloride	SW846 8260B	50	20	ug/kg
Amyl acetate	SW846 8260B	250	26	ug/kg
Benzene	SW846 8260B	50	14	ug/kg
Bromochloromethane	SW846 8260B	50	20	ug/kg
Bromodichloromethane	SW846 8260B	50	16	ug/kg
Bromobenzene	SW846 8260B	50	14	ug/kg
Bromoform	SW846 8260B	50	20	ug/kg
Bromomethane	SW846 8260B	50	24	ug/kg
Butyl acetate	SW846 8260B	50	34	ug/kg
cis1,4-Dichloro-2-butene	SW846 8260B	50	42	ug/kg
Carbon disulfide	SW846 8260B	50	20	ug/kg
Carbon tetrachloride	SW846 8260B	50	16	ug/kg
Chlorodibromomethane	SW846 8260B	50	20	ug/kg
Chlorobenzene	SW846 8260B	50	9.5	ug/kg
Chloroethane	SW846 8260B	50	25	ug/kg
Chloroform	SW846 8260B	50	18	ug/kg
Chloromethane	SW846 8260B	50	20	ug/kg
Chloroprene	SW846 8260B	250	30	ug/kg
cis-1,2-Dichloroethene	SW846 8260B	50	20	ug/kg
cis-1,3-Dichloropropene	SW846 8260B	50	14	ug/kg
Cyclohexane	SW846 8260B	250	26	ug/kg
Cyclohexanone	SW846 8260B	12000	580	ug/kg
Dichlorodifluoromethane	SW846 8260B	50	21	ug/kg
Dibromomethane	SW846 8260B	50	18	ug/kg
Dichlorofluoromethane	SW846 8260B	50	24	ug/kg
Diisopropyl ether	SW846 8260B	50	9.5	ug/kg
Ethyl(tert)butylether (ETBE)	SW846 8260B	250	25	ug/kg
Ethyl methacrylate	SW846 8260B	250	19	ug/kg
Ethyl acetate	SW846 8260B	500	430	ug/kg
Ethylbenzene	SW846 8260B	50	15	ug/kg
Diethyl ether	SW846 8260B	50	24	ug/kg
Fluorotrichloromethane	SW846 8260B	50	19	ug/kg
Hexachlorobutadiene	SW846 8260B	50	23	ug/kg
Hexachloroethane	SW846 8260B	50	16	ug/kg
Iodomethane	SW846 8260B	50	30	ug/kg
Isopropyl acetate	SW846 8260B	250	66	ug/kg
Isopropyl alcohol	SW846 8260B	12000	610	ug/kg
Isoamyl acetate	SW846 8260B		66	ug/kg
Isobutanol	SW846 8260B	25000	280	ug/kg
Isopropylbenzene	SW846 8260B	50	11	ug/kg
Methylene chloride	SW846 8260B	50	14	ug/kg
Methyl acetate	SW846 8260B	250	74	ug/kg
Methylcyclohexane	SW846 8260B	250	18	ug/kg
Xylenes, m + p	SW846 8260B	100	22	ug/kg
Methyl-tert-butyl-ether	SW846 8260B	50	15	ug/kg
Methacrylonitrile	SW846 8260B	250	50	ug/kg
Methyl methacrylate	SW846 8260B	250	27	ug/kg
Naphthalene	SW846 8260B	50	15	ug/kg

N-Butanol	SW846 8260B	12000	2600	ug/kg
N-Butylbenzene	SW846 8260B	50	12	ug/kg
N-Heptane	SW846 8260B	250	66	ug/kg
N-Hexane	SW846 8260B	50	16	ug/kg
n-Propyl acetate	SW846 8260B	250	68	ug/kg
n-Propylbenzene	SW846 8260B	50	5.5	ug/kg
Xylene, o	SW846 8260B	50	15	ug/kg
p-Isopropyltoluene	SW846 8260B	50	12	ug/kg
Propionitrile	SW846 8260B	250	46	ug/kg
sec-Butylbenzene	SW846 8260B	50	8.0	ug/kg
Styrene	SW846 8260B	50	12	ug/kg
trans-1,2-Dichloroethene	SW846 8260B	50	14	ug/kg
trans-1,3-Dichloropropene	SW846 8260B	50	15	ug/kg
trans-1,4-Dichloro-2-butene	SW846 8260B	250	21	ug/kg
Tertiaryamylmethylether (TAME)	SW846 8260B	250	27	ug/kg
t-Butyl alcohol (TBA)	SW846 8260B	2500	270	ug/kg
tert-Butylbenzene	SW846 8260B	50	12	ug/kg
Trichloroethene	SW846 8260B	50	20	ug/kg
Tetrachloroethene	SW846 8260B	50	16	ug/kg
Tetrahydrofuran	SW846 8260B	250	75	ug/kg
Toluene	SW846 8260B	50	8.5	ug/kg
Vinyl acetate	SW846 8260B	250	50	ug/kg
Vinyl chloride	SW846 8260B	50	14	ug/kg
Xylene, Total	SW846 8260B	150	21	ug/kg

SVOCs - Soils

TestName	AnalMethod	CalcEQL	CalcMDL	CalcUnit
1,2,4-Trichlorobenzene	SW846 8270C	250	30	ug/kg
1,2-Dichlorobenzene	SW846 8270C	250	41	ug/kg
1,3-Dichlorobenzene	SW846 8270C	250	40	ug/kg
1,4-Dichlorobenzene	SW846 8270C	250	33	ug/kg
Biphenyl	SW846 8270C	250	100	ug/kg
1,2-Diphenylhydrazine	SW846 8270C	250	49	ug/kg
1,4-Dioxane	SW846 8270C	250	180	ug/kg
1-Methylnaphthalene	SW846 8270C	250	33	ug/kg
2,2'-oxybis(1-Chloropropane)	SW846 8270C	250	34	ug/kg
2,4,5-Trichlorophenol	SW846 8270C	250	31	ug/kg
2,4,6-Trichlorophenol	SW846 8270C	250	30	ug/kg
2,4-Dichlorophenol	SW846 8270C	250	39	ug/kg
2,4-Dimethylphenol	SW846 8270C	250	84	ug/kg
2,4-Dinitrophenol	SW846 8270C	500	82	ug/kg
2,4-Dinitrotoluene	SW846 8270C	250	39	ug/kg
2,6-Dinitrotoluene	SW846 8270C	250	41	ug/kg
2-Chloronaphthalene	SW846 8270C	250	34	ug/kg
2-Chlorophenol	SW846 8270C	250	80	ug/kg
2-Methylnaphthalene	SW846 8270C	250	37	ug/kg
2-Methylphenol	SW846 8270C	250	130	ug/kg
2-Nitroaniline	SW846 8270C	250	30	ug/kg
2-Nitrophenol	SW846 8270C	250	28	ug/kg
3,3-Dichlorobenzidine	SW846 8270C	500	120	ug/kg
3 & 4-Methylphenol	SW846 8270C	250	25	ug/kg
3-Nitroaniline	SW846 8270C	250	88	ug/kg
4,6-Dinitro-2-methylphenol	SW846 8270C	250	80	ug/kg
4-Bromophenyl phenyl ether	SW846 8270C	250	29	ug/kg
4-Chloro-3-methylphenol	SW846 8270C	250	31	ug/kg
4-Chloroaniline	SW846 8270C	500	210	ug/kg
4-Chlorophenyl phenyl ether	SW846 8270C	250	35	ug/kg
4-Methylphenol	SW846 8270C	250	25	ug/kg

4-Nitroaniline	SW846 8270C	250	51	ug/kg
4-Nitrophenol	SW846 8270C	500	63	ug/kg
Acenaphthene	SW846 8270C	250	36	ug/kg
Acetophenone	SW846 8270C	250	93	ug/kg
Acenaphthylene	SW846 8270C	250	31	ug/kg
Aniline	SW846 8270C	250	120	ug/kg
Anthracene	SW846 8270C	250	32	ug/kg
Atrazine	SW846 8270C	250	110	ug/kg
bis(2-Chloroethyl)ether	SW846 8270C	250	41	ug/kg
bis(2-Chloroethoxy)methane	SW846 8270C	250	30	ug/kg
bis(2-Ethylhexyl)phthalate	SW846 8270C	250	32	ug/kg
Benzaldehyde	SW846 8270C	250	120	ug/kg
Benzidine	SW846 8270C	2500	1300	ug/kg
Benzoic acid	SW846 8270C	500	120	ug/kg
Benzo(a)anthracene	SW846 8270C	250	29	ug/kg
Benzo(a)pyrene	SW846 8270C	250	34	ug/kg
Benzo(b)fluoranthene	SW846 8270C	250	36	ug/kg
Benzo(ghi)perylene	SW846 8270C	250	44	ug/kg
Benzo(k)fluoranthene	SW846 8270C	250	32	ug/kg
Benzyl alcohol	SW846 8270C	500	47	ug/kg
Butylbenzylphthalate	SW846 8270C	250	31	ug/kg
Caprolactam	SW846 8270C	250	80	ug/kg
Carbazole	SW846 8270C	250	40	ug/kg
Chrysene	SW846 8270C	250	44	ug/kg
Dibenz(a,h)anthracene	SW846 8270C	250	49	ug/kg
Diethylphthalate	SW846 8270C	250	32	ug/kg
Dibenzofuran	SW846 8270C	250	37	ug/kg
Dimethylphthalate	SW846 8270C	250	33	ug/kg
Di-n-butylphthalate	SW846 8270C	250	42	ug/kg
Di-n-octylphthalate	SW846 8270C	250	50	ug/kg
Fluoranthene	SW846 8270C	250	49	ug/kg
Fluorene	SW846 8270C	250	45	ug/kg
Hexachlorobutadiene	SW846 8270C	250	37	ug/kg
Hexachlorobenzene	SW846 8270C	250	27	ug/kg
Hexachlorocyclopentadiene	SW846 8270C	250	28	ug/kg
Hexachloroethane	SW846 8270C	250	33	ug/kg
Indeno(1,2,3-cd)pyrene	SW846 8270C	250	55	ug/kg
Isophorone	SW846 8270C	250	29	ug/kg
Naphthalene	SW846 8270C	250	56	ug/kg
Nitrobenzene	SW846 8270C	250	33	ug/kg
N-Nitrosodimethylamine	SW846 8270C	250	69	ug/kg
N-Nitrosodi-n-propylamine	SW846 8270C	250	33	ug/kg
N-Nitrosodiphenylamine	SW846 8270C	250	77	ug/kg
Pentachlorophenol	SW846 8270C	250	82	ug/kg
Phenanthrene	SW846 8270C	250	28	ug/kg
Phenol	SW846 8270C	250	35	ug/kg
Pyrene	SW846 8270C	250	25	ug/kg
Pyridine	SW846 8270C	500	81	ug/kg

PAHs - Waters

TestName	AnalMethod	CalcEQL	CalcMDL	CalcUnit
1-Methylnaphthalene	8270C-SIM	0.050	0.011	ug/L
2-Methylnaphthalene	8270C-SIM	0.050	0.012	ug/L
Acenaphthene	8270C-SIM	0.050	0.0086	ug/L
Acenaphthylene	8270C-SIM	0.050	0.0086	ug/L
Anthracene	8270C-SIM	0.050	0.012	ug/L
Benzo(a)anthracene	8270C-SIM	0.050	0.017	ug/L
Benzo(a)pyrene	8270C-SIM	0.050	0.019	ug/L
Benzo(b)fluoranthene	8270C-SIM	0.050	0.017	ug/L
Benzo(ghi)perylene	8270C-SIM	0.050	0.020	ug/L
Benzo(k)fluoranthene	8270C-SIM	0.050	0.020	ug/L
Chrysene	8270C-SIM	0.050	0.020	ug/L
Dibenz(a,h)anthracene	8270C-SIM	0.050	0.020	ug/L
Fluoranthene	8270C-SIM	0.050	0.016	ug/L
Fluorene	8270C-SIM	0.050	0.0096	ug/L
Indeno(1,2,3-cd)pyrene	8270C-SIM	0.050	0.020	ug/L
Naphthalene	8270C-SIM	0.050	0.013	ug/L
Phenanthrene	8270C-SIM	0.050	0.012	ug/L
Pyrene	8270C-SIM	0.050	0.015	ug/L

PCBs - Waters

TestName	AnalMethod	CalcEQL	CalcMDL	CalcUnit
Aroclor 1016	SW846 8082	1.0	0.26	ug/L
Aroclor 1221	SW846 8082	1.0	0.26	ug/L
Aroclor 1232	SW846 8082	1.0	0.26	ug/L
Aroclor 1242	SW846 8082	1.0	0.26	ug/L
Aroclor 1248	SW846 8082	1.0	0.26	ug/L
Aroclor 1254	SW846 8082	1.0	0.26	ug/L
Aroclor 1260	SW846 8082	1.0	0.26	ug/L
Total PCBs	SW846 8082	1.0	0.26	ug/L

RCRA Metals - Waters

TestName	PrepMethod	AnalMethod	CalcEQL	CalcMDL	CalcUnit
Silver	SW846 3020A	SW846 6020	2.0	0.40	ug/L
Silver	SW846 6010B	SW846 6010B	10	1.5	ug/L
Silver	SW846 3010A	SW846 6010B	10	2.6	ug/L
Arsenic	SW846 3020A	SW846 6020	2.0	0.40	ug/L
Arsenic	SW846 6010B	SW846 6010B	20	8.2	ug/L
Arsenic	SW846 3010A	SW846 6010B	20	7.6	ug/L
Barium	SW846 3020A	SW846 6020	2.0	0.40	ug/L
Barium	SW846 6010B	SW846 6010B	5.0	1.0	ug/L
Barium	SW846 3010A	SW846 6010B	5.0	1.0	ug/L
Cadmium	SW846 3020A	SW846 6020	2.0	0.40	ug/L
Cadmium	SW846 6010B	SW846 6010B	5.0	0.92	ug/L
Cadmium	SW846 3010A	SW846 6010B	5.0	0.74	ug/L
Chromium	SW846 3020A	SW846 6020	2.0	0.40	ug/L
Chromium	SW846 6010B	SW846 6010B	5.0	1.9	ug/L
Chromium	SW846 3010A	SW846 6010B	5.0	1.3	ug/L
Mercury	SW846 7470A	SW846 7470A	0.20	0.072	ug/L
Mercury	SW846 7470A	SW846 7470A	0.20	0.072	ug/L
Lead	SW846 3020A	SW846 6020	2.0	0.40	ug/L
Lead	SW846 6010B	SW846 6010B	10	2.7	ug/L
Lead	SW846 3010A	SW846 6010B	10	3.4	ug/L
Selenium	SW846 3020A	SW846 6020	20	4.0	ug/L
Selenium	SW846 6010B	SW846 6010B	20	7.4	ug/L
Selenium	SW846 3010A	SW846 6010B	20	8.3	ug/L

Metals - Waters

TestName	PrepMethod	AnalMethod	CalcEQL	CalcMDL	CalcUnit
Aluminum	SW846 3020A	SW846 6020	200	40	ug/L
Aluminum	SW846 6010B	SW846 6010B	500	200	ug/L
Antimony	SW846 3010A	SW846 6010B	20	8.2	ug/L
Antimony	SW846 3020A	SW846 6020	2.0	0.40	ug/L
Copper	SW846 3020A	SW846 6020	10	2.0	ug/L
Copper	SW846 6010B	SW846 6010B	10	1.1	ug/L
Copper	SW846 3010A	SW846 6010B	10	1.5	ug/L
Iron	SW846 3020A	SW846 6020	200	40	ug/L
Iron	SW846 6010B	SW846 6010B	100	50	ug/L
Manganese	SW846 3020A	SW846 6020	2.0	0.40	ug/L
Manganese	SW846 3010A	SW846 6010B	5.0	0.22	ug/L
Manganese	SW846 6010B	SW846 6010B	5.0	0.36	ug/L
Nickel	SW846 3020A	SW846 6020	6.0	1.2	ug/L
Nickel	SW846 6010B	SW846 6010B	10	3.9	ug/L
Nickel	SW846 3010A	SW846 6010B	10	1.6	ug/L
Vanadium	SW846 3020A	SW846 6020	6.0	1.2	ug/L
Vanadium	SW846 6010B	SW846 6010B	5.0	1.7	ug/L
Vanadium	SW846 3010A	SW846 6010B	5.0	0.79	ug/L
Vanadium	SW846 3020A	SW846 6020	10	1.2	ug/L
Zinc	SW846 3020A	SW846 6020	20	4.0	ug/L
Zinc	SW846 6010B	SW846 6010B	40	20	ug/L

Wetchem - Waters

TestName	AnalMethod	CalcEQL	CalcMDL	CalcUnit
Cyanide, Total	EPA 335.4	0.020	0.0094	mg/L
Cyanide, Weak & Dissociable	SM 4500CN	0.020	0.0089	mg/L
Sulfide	EPA 376.1	5.0	2.5	mg/L
Alkalinity as CaCO3	EPA 310.2	20	9.7	mg/L
Nitrogen, NO3 + NO2	EPA 300.0	0.40	0.088	mg/L
Sulfate	EPA 300.0	4.0	0.77	mg/L

DRO - Waters

TestName	AnalMethod	CalcEQL	CalcMDL	CalcUnit
Diesel Range Organics	WI MOD DRO	100	38	ug/L

GRO - Waters

TestName	AnalMethod	CalcEQL	CalcMDL	CalcUnit
Gasoline Range Organics	WI MOD GRO	50	26	ug/L

MEE - Waters

TestName	AnalMethod	CalcEQL	CalcMDL	CalcUnit
Ethane	SW846 M8015B	10	1.6	ug/L
Ethene	SW846 M8015B	10	1.4	ug/L
Methane	SW846 M8015B	10	2.0	ug/L

VOCs - Waters

TestName	AnalMethod	CalcEQL	CalcMDL	CalcUnit
1,1,1,2-Tetrachloroethane	SW846 8260B	1.0	0.92	ug/L
1,1,1-Trichloroethane	SW846 8260B	1.0	0.90	ug/L
1,1,2,2-Tetrachloroethane	SW846 8260B	1.0	0.20	ug/L
1,1,2-Trichloroethane	SW846 8260B	1.0	0.42	ug/L
1,1,2-Trichlorotrifluoroethane	SW846 8260B	1.0	0.54	ug/L
1,1-Dichloroethane	SW846 8260B	1.0	0.75	ug/L
1,1-Dichloroethene	SW846 8260B	1.0	0.57	ug/L

1,1-Dichloropropene	SW846 8260B	1.0	0.75	ug/L
1,2,3-Trichlorobenzene	SW846 8260B	1.0	0.74	ug/L
1,2,3-Trichloropropane	SW846 8260B	1.0	0.99	ug/L
1,2,3-Trimethylbenzene	SW846 8260B	1.0	0.84	ug/L
1,2,4-Trichlorobenzene	SW846 8260B	1.0	0.97	ug/L
1,2,4-Trimethylbenzene	SW846 8260B	1.0	0.97	ug/L
1,2-Dibromo-3-chloropropane	SW846 8260B	1.0	0.87	ug/L
1,2-Dibromoethane	SW846 8260B	1.0	0.56	ug/L
1,2-Dichlorobenzene	SW846 8260B	1.0	0.83	ug/L
1,2-Dichloroethane	SW846 8260B	1.0	0.36	ug/L
1,2-Dichloroethene, Total	SW846 8260B	2.0	1.4	ug/L
1,2-Dichloropropane	SW846 8260B	1.0	0.46	ug/L
1,3,5-Trimethylbenzene	SW846 8260B	1.0	0.83	ug/L
1,3-Dichlorobenzene	SW846 8260B	1.0	0.87	ug/L
1,3-Dichloropropane	SW846 8260B	1.0	0.61	ug/L
1,4-Dichlorobenzene	SW846 8260B	1.0	0.95	ug/L
1,4-Dioxane	SW846 8260B	250	52	ug/L
1-Propanol	SW846 8260B	250	52	ug/L
2,2-Dichloropropane	SW846 8260B	1.0	0.62	ug/L
2,3-Dichloropropene	SW846 8260B	1.0	0.84	ug/L
2-Butanone	SW846 8260B	5.0	4.3	ug/L
2-Chloroethylvinylether	SW846 8260B	1.0	0.95	ug/L
2-Chlorotoluene	SW846 8260B	1.0	0.85	ug/L
2-Hexanone	SW846 8260B	5.0	1.1	ug/L
2-Methylnaphthalene	SW846 8260B	5.0	1.4	ug/L
4-Chlorotoluene	SW846 8260B	1.0	0.74	ug/L
4-Methyl-2-pentanone	SW846 8260B	5.0	1.2	ug/L
Acetone	SW846 8260B	5.0	2.2	ug/L
Acrolein	SW846 8260B	10	10	ug/L
Acrylonitrile	SW846 8260B	5.0	1.3	ug/L
Allyl chloride	SW846 8260B	5.0	2.0	ug/L
Benzene	SW846 8260B	1.0	0.41	ug/L
Bromobenzene	SW846 8260B	1.0	0.82	ug/L
Bromochloromethane	SW846 8260B	1.0	0.97	ug/L
Bromodichloromethane	SW846 8260B	1.0	0.56	ug/L
Bromoform	SW846 8260B	1.0	0.94	ug/L
Bromomethane	SW846 8260B	1.0	0.91	ug/L
Carbon disulfide	SW846 8260B	1.0	0.66	ug/L
Carbon tetrachloride	SW846 8260B	1.0	0.49	ug/L
Chlorobenzene	SW846 8260B	1.0	0.41	ug/L
Chlorodibromomethane	SW846 8260B	1.0	0.81	ug/L
Chloroethane	SW846 8260B	1.0	0.97	ug/L
Chloroform	SW846 8260B	1.0	0.37	ug/L
Chloromethane	SW846 8260B	1.0	0.24	ug/L
Chloroprene	SW846 8260B	5.0	0.67	ug/L
cis-1,2-Dichloroethene	SW846 8260B	1.0	0.83	ug/L
cis-1,3-Dichloropropene	SW846 8260B	1.0	0.19	ug/L
cis1,4-Dichloro-2-butene	SW846 8260B	5.0	1.2	ug/L
Cyclohexane	SW846 8260B	5.0	0.89	ug/L
Dibromomethane	SW846 8260B	1.0	0.60	ug/L
Dichlorodifluoromethane	SW846 8260B	1.0	0.99	ug/L
Dichlorofluoromethane	SW846 8260B	1.0	0.88	ug/L
Diethyl ether	SW846 8260B	1.0	0.98	ug/L
Diisopropyl ether	SW846 8260B	1.0	0.76	ug/L
Ethyl methacrylate	SW846 8260B	5.0	0.80	ug/L
Ethyl(tert)butylether (ETBE)	SW846 8260B	5.0	0.15	ug/L
Ethylbenzene	SW846 8260B	1.0	0.54	ug/L
Fluorotrichloromethane	SW846 8260B	1.0	0.79	ug/L

Hexachlorobutadiene	SW846 8260B	1.0	0.67	ug/L
Hexachloroethane	SW846 8260B	1.0	0.87	ug/L
Iodomethane	SW846 8260B	5.0	0.63	ug/L
Isobutanol	SW846 8260B	500	3.9	ug/L
Isopropylbenzene	SW846 8260B	1.0	0.59	ug/L
Methacrylonitrile	SW846 8260B	5.0	1.2	ug/L
Methyl acetate	SW846 8260B	5.0	2.1	ug/L
Methyl methacrylate	SW846 8260B	5.0	1.1	ug/L
Methylcyclohexane	SW846 8260B	5.0	1.9	ug/L
Methylene chloride	SW846 8260B	1.0	0.43	ug/L
Methyl-tert-butyl-ether	SW846 8260B	1.0	0.61	ug/L
Naphthalene	SW846 8260B	1.0	0.74	ug/L
N-Butanol	SW846 8260B	250	36	ug/L
N-Butylbenzene	SW846 8260B	1.0	0.93	ug/L
N-Heptane	SW846 8260B	5.0	1.4	ug/L
N-Hexane	SW846 8260B	1.0	0.53	ug/L
n-Propylbenzene	SW846 8260B	1.0	0.81	ug/L
p-Isopropyltoluene	SW846 8260B	1.0	0.67	ug/L
Propionitrile	SW846 8260B	5.0	1.6	ug/L
sec-Butylbenzene	SW846 8260B	1.0	0.89	ug/L
Styrene	SW846 8260B	1.0	0.86	ug/L
t-Butyl alcohol (TBA)	SW846 8260B	50	7.3	ug/L
tert-Butylbenzene	SW846 8260B	1.0	0.97	ug/L
Tertiaryamylmethylether (TAME)	SW846 8260B	5.0	0.13	ug/L
Tetrachloroethene	SW846 8260B	1.0	0.45	ug/L
Tetrahydrofuran	SW846 8260B	5.0	1.7	ug/L
Toluene	SW846 8260B	1.0	0.67	ug/L
trans-1,2-Dichloroethene	SW846 8260B	1.0	0.89	ug/L
trans-1,3-Dichloropropene	SW846 8260B	1.0	0.19	ug/L
trans-1,4-Dichloro-2-butene	SW846 8260B	5.0	1.1	ug/L
Trichloroethene	SW846 8260B	1.0	0.48	ug/L
Vinyl acetate	SW846 8260B	5.0	1.6	ug/L
Vinyl chloride	SW846 8260B	1.0	0.18	ug/L
Xylene, o	SW846 8260B	1.0	0.83	ug/L
Xylene, Total	SW846 8260B	3.0	2.6	ug/L
Xylenes, m + p	SW846 8260B	2.0	1.8	ug/L

SVOCs - Waters

TestName	AnalMethod	CalcEQL	CalcMDL	CalcUnit
1,2,4-Trichlorobenzene	SW846 8270C	5.0	2.0	ug/L
1,2-Dichlorobenzene	SW846 8270C	5.0	2.0	ug/L
1,2-Diphenylhydrazine	SW846 8270C	5.0	0.53	ug/L
1,3-Dichlorobenzene	SW846 8270C	5.0	2.0	ug/L
1,4-Dichlorobenzene	SW846 8270C	5.0	2.0	ug/L
1,4-Dioxane	SW846 8270C	5.0	2.6	ug/L
1-Methylnaphthalene	SW846 8270C	5.0	1.3	ug/L
2,2'-oxybis(1-Chloropropane)	SW846 8270C	5.0	0.65	ug/L
2,3,4,6-Tetrachlorophenol	SW846 8270C	5.0	3.3	ug/L
2,4,5-Trichlorophenol	SW846 8270C	5.0	1.3	ug/L
2,4,6-Trichlorophenol	SW846 8270C	5.0	0.92	ug/L
2,4-Dichlorophenol	SW846 8270C	5.0	0.92	ug/L
2,4-Dimethylphenol	SW846 8270C	5.0	0.77	ug/L
2,4-Dinitrophenol	SW846 8270C	10	2.4	ug/L
2,4-Dinitrotoluene	SW846 8270C	5.0	0.99	ug/L
2,6-Dinitrotoluene	SW846 8270C	5.0	0.71	ug/L
2-Chloronaphthalene	SW846 8270C	5.0	1.3	ug/L
2-Chlorophenol	SW846 8270C	5.0	0.90	ug/L
2-Methylnaphthalene	SW846 8270C	5.0	1.6	ug/L

2-Methylphenol	SW846 8270C	5.0	0.77	ug/L
2-Nitroaniline	SW846 8270C	5.0	0.69	ug/L
2-Nitrophenol	SW846 8270C	5.0	1.0	ug/L
3 & 4-Methylphenol	SW846 8270C	5.0	0.75	ug/L
3,3-Dichlorobenzidine	SW846 8270C	10	1.4	ug/L
3-Nitroaniline	SW846 8270C	5.0	0.87	ug/L
4,6-Dinitro-2-methylphenol	SW846 8270C	5.0	1.0	ug/L
4-Bromophenyl phenyl ether	SW846 8270C	5.0	0.84	ug/L
4-Chloro-3-methylphenol	SW846 8270C	5.0	0.96	ug/L
4-Chloroaniline	SW846 8270C	5.0	1.0	ug/L
4-Chlorophenyl phenyl ether	SW846 8270C	5.0	0.99	ug/L
4-Methylphenol	SW846 8270C	5.0	0.75	ug/L
4-Nitroaniline	SW846 8270C	10	0.73	ug/L
4-Nitrophenol	SW846 8270C	10	0.98	ug/L
Acenaphthene	SW846 8270C	5.0	1.1	ug/L
Acenaphthylene	SW846 8270C	5.0	1.1	ug/L
Acetophenone	SW846 8270C	5.0	2.0	ug/L
Aniline	SW846 8270C	5.0	0.83	ug/L
Anthracene	SW846 8270C	5.0	0.82	ug/L
Atrazine	SW846 8270C	5.0	2.0	ug/L
Benzaldehyde	SW846 8270C	5.0	2.1	ug/L
Benzidine	SW846 8270C	50	23	ug/L
Benzo(a)anthracene	SW846 8270C	5.0	1.2	ug/L
Benzo(a)pyrene	SW846 8270C	5.0	1.0	ug/L
Benzo(b)fluoranthene	SW846 8270C	5.0	0.97	ug/L
Benzo(ghi)perylene	SW846 8270C	5.0	2.0	ug/L
Benzo(k)fluoranthene	SW846 8270C	5.0	1.2	ug/L
Benzoic acid	SW846 8270C	10	1.8	ug/L
Benzyl alcohol	SW846 8270C	10	1.1	ug/L
Biphenyl	SW846 8270C	5.0	1.7	ug/L
bis(2-Chloroethoxy)methane	SW846 8270C	5.0	0.81	ug/L
bis(2-Chloroethyl)ether	SW846 8270C	5.0	0.77	ug/L
bis(2-Ethylhexyl)phthalate	SW846 8270C	5.0	1.1	ug/L
Butylbenzylphthalate	SW846 8270C	5.0	1.2	ug/L
Caprolactam	SW846 8270C	5.0	1.5	ug/L
Carbazole	SW846 8270C	5.0	1.0	ug/L
Chrysene	SW846 8270C	5.0	1.6	ug/L
Dibenz(a,h)anthracene	SW846 8270C	5.0	1.9	ug/L
Dibenzofuran	SW846 8270C	5.0	0.84	ug/L
Diethylphthalate	SW846 8270C	5.0	1.0	ug/L
Dimethylphthalate	SW846 8270C	5.0	0.85	ug/L
di-n-Butylphthalate	SW846 8270C	5.0	0.98	ug/L
di-n-Octylphthalate	SW846 8270C	5.0	1.4	ug/L
Fluoranthene	SW846 8270C	5.0	1.3	ug/L
Fluorene	SW846 8270C	5.0	0.88	ug/L
Hexachlorobenzene	SW846 8270C	5.0	0.87	ug/L
Hexachlorobutadiene	SW846 8270C	10	2.8	ug/L
Hexachlorocyclopentadiene	SW846 8270C	5.0	1.1	ug/L
Hexachloroethane	SW846 8270C	5.0	2.2	ug/L
Indeno(1,2,3-cd)pyrene	SW846 8270C	5.0	0.65	ug/L
Isophorone	SW846 8270C	5.0	0.66	ug/L
Naphthalene	SW846 8270C	5.0	1.4	ug/L
Nitrobenzene	SW846 8270C	5.0	0.82	ug/L
N-Nitrosodimethylamine	SW846 8270C	5.0	0.54	ug/L
N-Nitrosodi-n-propylamine	SW846 8270C	5.0	0.64	ug/L
N-Nitrosodiphenylamine	SW846 8270C	10	4.5	ug/L
Pentachlorophenol	SW846 8270C	5.0	1.0	ug/L
Phenanthrene	SW846 8270C	5.0	0.72	ug/L

Phenol	SW846 8270C	5.0	0.60	ug/L
Pyrene	SW846 8270C	5.0	0.95	ug/L
Pyridine	SW846 8270C	10	1.4	ug/L

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STANDARD OPERATING PROCEDURE

Determination of Volatile Organics by GC/MS

Reference Methods: SW-846 Methods 8260B with 5030B and 5035A

SOP NUMBER:	ALL-O-002-rev.1
EFFECTIVE DATE:	Date of Final Signature
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APPROVAL

John P. Dullaghan, COO	11/2/04 Date
Clarence L. Haile, Ph.D., Director of QST	2 Nov 2004 Date
Laboratory General Manager	5/17/05 Date
Laboratory Quality Manager	5/17/05 Date

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1. Purpose

This Standard Operating Procedure (SOP) is used to determine the concentration of volatile organic compounds in a water and soil samples by purge-and-trap GC/MS compliant with SW-846 Methods 5030B, 5035A and 8260B.

2. Scope and Application

2.1. This method is applicable to most organic compounds that have boiling points below 200 °C and that are insoluble or slightly soluble in water. Volatile water-soluble compounds may also be determined, although achievable quantitation limits typically higher because of poor purging efficiency. Ketones are typical examples. A list of applicable compounds and their CAS numbers are shown in the addendum.

2.2. This method is applicable to most water and solid samples, regardless of water content. Common matrices are ground water, wastewater, aqueous sludge, sediment, and soil. Pace Reporting Levels (PRLs) listed for each compound in common matrices are also shown in the addendum. PRLs are subject to change based on current analytical system performance.

2.3. This SOP was prepared for method-compliant use by all Pace Analytical environmental laboratories. Additional lab-specific requirements that may be mandated by individual states or clients are presented in the addendum.

2.4. This procedure is restricted to use by, or under the supervision of, analysts experienced in the use of purge-and-trap GC/MS systems and interpretation of GC/MS data. Each analyst must demonstrate the capability to generate acceptable results with this method to be considered qualified to report sample results.

3. Summary of Method

3.1. The volatile organic compounds are introduced into the gas chromatograph by a purge-and trap method. The analytes are purged from a sample aliquot or extract by sparging with an inert gas (helium). The purged analytes are trapped in a sorbent tube. At the completion of the purge time, the sorbent tube is rapidly heated and back flushed with helium to desorb trapped analytes directly onto the inlet of a capillary gas chromatography column. The carrier gas flow through the column is controlled and the temperature is increased according to a set program to achieve optimum separation of purged analytes. The gas chromatographic detector is a mass spectrometer operated in a repetitive scan mode.

3.2. Analytes are identified by comparison of their mass spectra with spectra of authentic standards. Analytes are quantified by comparing the response of a selected major (quantitation) ion relative to an internal standard using a five-point calibration curve.

4. Interferences

4.1. Major contaminant sources are volatile materials in the laboratory and impurities in the inert purging gas and in the sorbent trap. The use of non-polytetrafluoroethylene (PTFE) thread sealants, plastic tubing, or flow controllers with rubber components should be avoided since such materials can be sources of compounds which can concentrate in the trap during the purging. Analyses of blanks provide information about the presence of contaminants. When potential interfering peaks are noted in blanks, the analyst should investigate the source of contamination and correct it. Subtracting blank values from sample results is not permitted. If the laboratory feels that a sample results is a false positive due to these sources, this should be fully explained in text accompanying the uncorrected data.

4.2. A common source of interfering contamination is carryover. This may occur when a sample containing low concentrations of volatile organic compounds is analyzed immediately after a sample containing high concentrations of volatile organic compounds. The preventive technique is rinsing the purging apparatus and sample syringes with two portions of organic free water between samples. Analyze one or more method blanks to check for cross contamination prior to sample analysis.

4.3. Since methylene chloride and acetone are common laboratory solvents, special precautions must be taken. The volatiles analysis and sample storage area should be isolated from areas where these solvents are used or stored. Where possible, the volatiles analysis and sample storage area should be served by a separate HVAC system. Laboratory clothing previously exposed to methylene chloride fumes during extraction procedures can contribute to sample contamination.

5. Safety

5.1. **Standards and Reagents** - The toxicity and carcinogenicity of standards and reagents used in this method have not been fully defined. Each chemical compound should be treated as a potential health hazard. Reduce exposure by the use of gloves, lab coats and safety glasses. Material Safety Data Sheets (MSDSs) are on file in the laboratory and available to all personnel. Standard solutions should be prepared in a hood.

5.2. **Samples** - Take precautions when handling samples. Samples should always be treated as potentially hazardous "unknowns". The use of personal protective equipment (gloves, lab coats and safety glasses) is required when handling samples.

6. Definitions

6.1. **Batch** – A grouping of 20 samples, or less, of similar matrix which are prepared and/or analyzed together with the same method and the same lots of reagents within the same time frame, as designated by the method.

6.2. **Blank Sample** – A sample analyzed to detect and/or monitor the potential contamination by target analytes and other interferences attributable to

instrumental background and sample handling, including sampling, sample shipping and storage, and analysis.

6.3. **Duplicate Sample** – A second aliquot of the same field sample analyzed in the same manner as the original sample in order to evaluate precision.

6.4. **Environmental Sample** – An environmental sample or field sample is a representative sample of any material (aqueous, non-aqueous, or multimedia) collected from any source for which determination of composition or contamination is requested or required.

6.5. **Internal Standard (IS)** – Analytes added to every standard, blank, lab control sample, matrix spike, matrix spike duplicate, and sample at a known concentration, prior to analysis for the purpose of adjusting the response factor used in quantifying target analytes.

6.6. **Laboratory Control Sample (LCS)** – A blank sample spiked with a known concentration of analytes of interest.

6.7. **Laboratory Information Management System (LIMS)** – A system for transferring, processing, storing, and reporting analysis results. The Pace Analytical LIMS is named EPIC.

6.8. **Lot** – A quantity of bulk material of similar composition processed or manufactured at the same time.

6.9. **Matrix Spike (MS)** – Aliquot of sample spiked with known quantities of specified target compounds and subjected to the entire sample preparation and analysis procedure. The analysis results from a matrix spike sample are compared to results from an unspiked aliquot of the same sample to determine recovery of the spike. Spike recoveries are used to evaluate method accuracy.

6.10. **Matrix Spike Duplicate (MSD)** – A second aliquot of the sample that is treated the same as the original matrix spike sample. The relative percent difference between the matrix spike and matrix spike duplicate is calculated and used to assess method precision.

6.11. **Method Blank (MB)** – A blank sample prepared in the laboratory containing all reagents, internal standards and surrogate standards, that is carried through the entire analytical procedure. The method blank is used to evaluate laboratory background and contamination.

6.12. **Method Detection Limit (MDL)** – The minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero. Method detection limits are determined by analyzing replicate spike samples prepared by the lab and taken through all preparation and analysis steps of the method. The method detection limit is calculated using the appropriate Student's t-parameter times the standard deviation of a series of spiked samples.

6.13. **Reagent Grade** – Analytical reagent (AR) grade, ACS reagent grade, and reagent grade are synonymous terms for reagents that conform to the current specifications of the Committee on Analytical Reagents of the American Chemical Society.

6.14. **Replicate Samples** – Samples collected at the same time, from the same place, for the same analysis, as the original sample in order to determine precision between samples.

6.15. **Pace Reporting Limit (PRL)** – The lowest level that will be reported by this method. Reporting limits are at least two times the MDL. Reporting limits are corrected for sample amounts, including the dry weight of solids, unless otherwise specified.

6.16. **Surrogate Compounds** – These are compounds added to every blank, sample, matrix spike, matrix spike duplicate, lab control sample, and standard prior to any processing or preparation. Surrogate compounds are not expected to be detected in environmental samples, but are similar to the analytes of interest. The percent recoveries of surrogates are used to evaluate accuracy for each sample.

6.17. **Toxicity Characteristic Leaching Procedure (TCLP)** – A test used to determine waste disposal requirements for a waste. If a leachate from a representative sample is shown to contain any contaminant in excess of regulatory levels, the waste is banned for land disposal unless properly treated.

6.18. **Trip Blank** – This blank is used to evaluate sample contamination from the container and preservative during transport and storage of the sample. A cleaned sample container is filled with blank water; any preservative used in the sample is added; and then the blank is stored, shipped, and analyzed with samples.

6.19. **Tune Period** – The 12-hour analysis period between instrument tune checks.

7. Responsibilities and Distribution

7.1. **Analyst** – Any analyst using this procedure is responsible for reading, understanding and following this SOP. Any deviation from this SOP must be reported to the appropriate Supervisor. The analyst must make their recommendations for changing the SOP to their supervisor or the QM in writing.

7.2. **Volatile Organic Supervisor** – The supervisor must ensure that all analysts are properly trained and qualified to use this procedure, and that the SOP is followed.

7.3. **Quality Manager (QM)** – The QM is responsible for monitoring the implementation of the SOPs and the associated good laboratory practice. The QM shall participate in the revision of the SOP and make sure it is current. The QM shall review and approve all SOPs.

7.4. **Laboratory General Manager** – The Laboratory General Manager has overall responsibility for ensuring that SOPs are prepared and implemented for all

activities appropriate to the region. The Laboratory General Manager shall review and approve all SOPs.

7.5. **Director of Quality, Safety, and Training (QST)** – The Director of QST has the oversight responsibility for Pace Analytical's quality programs, including establishing and monitoring compliance with all quality system requirements.

7.6. **Chief Operating Officer (COO)** – The COO has oversight responsibility for Pace Analytical environmental laboratory operations, including compliance with all quality system requirements.

7.7. **Distribution** – The official version of this SOP is the signed hardcopy version found in the laboratory, complete the addendum. A copy of the SOP shall be kept in the appropriate department for reference.

7.8. **Revision** – This SOP will be reviewed every two years at a minimum. Independent of the minimum review frequency, revisions will be incorporated as needed if procedures or methods change.

8. Sample Collection, Preservation, and Handling

8.1. Water Samples

8.1.1. **Sample Collection and Preservation** – Samples are collected in 40-mL vials with PTFE-lined septa and screw cap. Prior to filling the vials with sample, sufficient 1:1 HCl (1-2 drops) is added to each vial to preserve the sample at pH<2. If the sample contains residual chlorine, it should be preserved with a few crystals of sodium thiosulfate ($Na_2S_2O_3$). Each sample vial is carefully filled and capped to eliminate any headspace. Sample vials with bubbles larger than 5 mm should be discarded. It is recommended to collect 3 vials for each sample.

8.1.2. **Sample Storage** - Store all samples at 4 ± 2°C.

8.1.3. **Holding Time** – Properly preserved samples must be analyzed within 14 days of collection.

8.2. Soil/Solid Samples

8.2.1. **Sample Collection and Preservation** – Solid/soil samples are collected in 4 vials for each sample. Two 5-g aliquots for low-level analysis, one 10-g aliquot for high-level analysis, and a fourth container for moisture determination.

8.2.1.1. **Low-Level Aliquots** – Two 5-g aliquots are collected in specially prepared 40-mL vials with PTFE-lined septa and screw cap containing a small magnetic stir bar. The vials may also contain 5.0 mL of blank reagent water or a solution of 1.0 g sodium bisulfate in 5.0 mL of blank reagent water. The vials are

weighed to ±0.01 g and the tare weight is recorded on the vial label. If a sample demonstrates a high level of carbonates by effervescing on contact with the preservative, the sodium bisulfate should be eliminated for that sample.

8.2.1.2. **High-Level Aliquot** – One 10-g aliquot is collected in a 40-mL vial with PTFE-lined septa and screw cap. The vials are prepared by adding 10.0 mL of methanol, weighing to ±0.01 g, and recording and the tare weight on the vial label.

8.2.1.3. **Moisture Aliquot** – One aliquot is collected by filling a 40-mL vial with PTFE-lined septa and screw cap.

8.2.2. **Sample Storage** – High-level aliquots, moisture aliquots, and low-level aliquots preserved with sodium bisulfate are stored at 4±2°C. Non-preserved low-level aliquots may be stored at 4±2°C for up to 48 hours before storing frozen at ≤-7°C. Preserved low-level aliquots may also be stored frozen ≤-7°C. Sample vials should not be frozen at <-20°C.

8.2.3. **Holding Time** – All sample aliquots must be analyzed within 14 days of collection. Low-level aliquots not preserved with sodium bisulfate or stored frozen must be analyzed within 48 hours of collection.

8.2.4. **Alternate Collection of Low-Level Aliquots** – Low-level aliquots may also be collected in Encore™ sampling tubes. Samples collected in Encore™ tubes must be extracted into properly prepared low-level and high-level vials within 48 hours of collection.

8.3 **TCLP Leachates** – Leachates are collected in 40-mL vials with PTFE-lined septa and screw cap. Each sample vial is carefully filled and capped to eliminate any headspace. Sample vials with bubbles larger than 5 mm should be discarded. Store all samples at 4 ± 2°C and analyze within 14 days of initiating the leaching procedure.

9. Equipment and Supplies

9.1. **Purge-Trap GC/MS System** – The complete purge-trap GC/MS system must include an autosampler, sample concentrator, and GC/MS with associated Data System. The specific system components and operating parameters that will be used with this method are shown in the addendum.

9.2. **Glassware and Materials**

9.2.1. **Sample Vials** – 40-mL glass with Teflon-lined septa and screw caps.

9.2.2. **Sample Vials for Soil/Solid Samples** – 40-mL with Teflon-lined septa and screw caps, containing a magnetic stir bar.

9.2.3. **Volumetric Flasks** – 5-mL, 10-mL, 50-mL.

9.2.4. **Glass Vials** – 1-mL, 4-mL, and 12-mL with Teflon-lined screw caps.

9.2.5. **Teflon Mininert Valves** – for 1-mL and 4-mL vials.

9.2.6. **Gas-tight Syringe with Shut-off Valve** – 5-mL.

9.2.7. **Gas-tight Syringes** – 1-µL, 10-µL, 25-µL, 50-µL, 100-µL, 250-µL, 500-µL, and 1000-µL.

9.2.8. **Teflon Dispensing Bottles** – for organic-free water (OFW) and methanol.

9.2.9. **pH Test Strips**

10. Reagents and Standards

10.1. Reagents

10.1.1. **Organic-Free Water (OFW)** – De-ionized. Verify that background levels of volatile compounds are acceptable by analysis.

10.1.2. **Blank Sand** – Heated to 130°C, allowed to cool and stored in a sealed container.

10.1.3. **Methanol** – Purge and trap grade.

10.1.4. **Sodium Bisulfate ($NaHSO_4$)** – ACS grade or equivalent.

10.2. Analytical Standards

Standards are required for mass spectrometer tuning, initial calibration, continuing calibration checks and system performance checks, continuing calibration checks, internal standards, surrogates, and for preparing LCS, MS, and MSD samples. The following describes the contents of each type of solution.

10.2.1. **Tune Standard** – 4-Bromofluorobenzene (BFB).

10.2.2. **Calibration Standards** – At least 5 concentration levels of calibration solutions are prepared containing all target compounds for which the calibration is applied.

10.2.3. **Calibration Verification Standard** – A calibration verification standard is prepared at a mid-level concentration for all target compounds.

10.2.4. **Internal Standards** – This solution contains the following compounds.

Fluorobenzene
1,4-Dichlorobenzene-d_4
Chlorobenzene-d_5

10.2.5. **Surrogate Standards** – This solution contains the following compounds.

Toluene-d_8
4-Bromofluorobenzene
1,2-Dichloroethane-d_4
dibromofluoromethane

10.2.6. **LCS, MS, and MSD Spiking Solutions** – This solution contains, at a minimum, the following compounds. The spiking solution should not be prepared from the same standards as the calibration standards.

1,1-Dichloroethane
Trichloroethene
Chlorobenzene
Toluene
Benzene

10.3. **Preparation of Analytical Standard Solutions**

Standards are prepared from commercially available multi-compound stock solutions and neat materials by multiple dilutions. The sources of the stock solutions and neat materials, recipes for preparing dilutions and working standards, and concentrations for all compounds are presented in the addendum. All standards are prepared using purge and trap methanol and stored in amber vials with Teflon lined screw caps or Mininert valves at 4 °C.

10.4. **Storage and Stability of Analytical Standards**

10.4.1. **Stock Solutions** – Solutions of gas standards must be replaced one month after the ampule is cracked. All other standards must be replaced 6 months after the ampule is cracked. Replace sooner if the standards show signs of degradation. As each standard, from the vendor is opened, record all pertinent information in the stock standard logbook. Record all standard preparations in the working standard logbook.

10.4.2. **Secondary Dilutions and Working Solutions** – Dilution and Working Solutions must be replaced weekly. Working Solutions must be checked frequently and replace if degradation or evaporation is suspected. Concentrations must be with 20% of initial calibration.

11. Calibration

11.1. **Tuning** – At the beginning of each tune period, the mass spectrometer must be tuned with a 50-ng injection of BFB to meet specific ion abundance criteria shown in the following table. The BFB and calibration verification standard may be combined into a single standard as long as both tuning and calibration acceptance criteria can be met without interferences.

Mass (m/z)	Ion Abundance criteria
50	8.0-40.0% of m/z 95
75	30.0-66.0% of m/z 95
95	Base peak, 100% relative abundance
96	5.0-9.0% of m/z 95
173	<2.0% of m/z 95
174	50.0-120.0% of m/z 95
175	4.0-9.0% of m/z 174
176	93.0-101.0% of m/z 174
177	5.0-9.0% of m/z 176

11.2. **Initial Calibration (ICAL)**

11.2.1. **Analysis of Standards** – Analyze at least 5 levels of calibration standards to define the calibration range. The lowest concentration should be at the target PRL.

11.2.2. **Response Factors** – Tabulate the area response of the characteristic ions against concentration for each compound and each internal standard. Calculate response factors (RF) for each compound relative to one of the internal standards. The internal standard selected for the calculation of the RF for a compound should be the internal standard that has a retention time closest to the compound being measured. Response factors are calculated using the following equation.

$$RF = \frac{A_x C_{is}}{A_{is} C_x}$$

where:
A_x = Area of the characteristic ion for the compound being measured.
A_{is} = Area of the characteristic ion for the specific internal standard.
C_{is} = Concentration of the specific internal standard (µg/L).
C_x = Concentration of the compound being measured (µg/L).

11.2.3. **Acceptance Criteria**

11.2.3.1. **System Performance Check Compounds (SPCCs)** – The minimum response factors for volatile SPCCs are as follows.

SPCC	RF Min
Chloromethane	0.10
1,1-Dichloroethane	0.10
Bromoform	0.10
Chlorobenzene	0.30
1,1,2,2-Tetrachloroethane	0.30

If the minimum response factors are not met, the system must be evaluated, and corrective action must be taken before sample analysis begins. Some possible problems are standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, and active sites in the column or chromatographic system.

11.2.3.2. **Calibration Check Compounds (CCCs)** – The percent relative standard deviation (%RSD) for the calibration check compounds (CCC's) must be <30%.

11.2.3.3. **Other Target Compounds** – If the % RSD of any compound is greater than 15%, construct calibration curves using a least squares regression with a correlation coefficient ≥0.99. Note: A quadratic curve requires six standards and a third order polynomial requires seven standards.

11.3. **Calibration Verification**

The calibration must be verified for every tune period by analysis of a calibration verification standard. The percent difference (or % drift, if a linear regression was used) from the calibration for the CCC's must be ≤20% and the minimum response factors for the SPCC's must meet the same criteria listed for initial calibration. Internal Standard areas must be within -50% to +100% from the mid-point standard of the most recent initial calibration. Internal standard retention times must be within 30 seconds from the mid-point standard of the most recent initial calibration.

12. Procedure

12.1. **Sample Preparation** – All samples and standards must be allowed to warm to room temperature before analysis.

12.1.1. **Water Samples** - Water samples do not require any sample preparation unless they require a dilution. Prior to the first analysis of a sample, a decision to dilute may be based on historical results or sample screening.

If dilution is not required, place the sample vial in the autosampler. If dilution is required, follow the following procedure.

12.1.1.1. **Sample Dilution (if required)** – Dilutions should be conducted using volumetric flasks. Select the volumetric flask that will allow for the necessary dilution. Intermediate dilutions may be necessary for extremely high dilutions. Add slightly less OFW to the flask than the volumetric capacity. Inject the proper aliquot of sample into the flask. Aliquots of less than 1 mL are not recommended. Dilute the sample to the mark with OFW. Cap the flask and invert three times. Repeat above procedure for additional dilutions. Fill a clean 40-mL vial with diluted sample and place it in the autosampler for analysis.

12.1.1.2. **Verification of Preservative** – Verify and document that all samples are properly preserved with HCl by testing the remaining sample in the VOA vial with pH paper. For undiluted samples, check the residue in the vial following analysis. The pH should be <2. Document results in the injection log. Footnote any sample not meeting the pH requirement.

12.1.2. **Low Concentration Soil/Solid Samples** – Gently shake the sample vials to ensure that the contents move freely and place the vial in the autosampler for analysis.

12.1.3. **High Concentration Soil/Solid.**

12.1.3.1. **Methanol-Preserved Samples** – Add 100 µL of extract to 4.9 mL OFW in a clean 40-mL vial and place it in the autosampler for analysis.

12.1.3.2. **Unpreserved Samples**

12.1.3.2.1. Weigh 5 g of the unpreserved sample into a clean 40-mL vial.. Add 5 mL MeOH to the vial and shake for 2 minutes.

12.1.3.2.2. Add 100 µL of extract to 4.9 mL OFW in a clean 40-mL vial and place it in the autosampler for analysis.

12.2. **Purge-Trap GC/MS System Preparation**

12.2.1. **Operating Parameters** – Set up the instrument parameters shown in the addendum.

12.2.2. **System Tuning** – The GC/MS system must be hardware-tuned using perfluorotributylamine (PFTBA). In the manual tune program of the instrument, adjust the MS parameters to obtain the following m/z ratios.

m/z	Relative Abundance
69	100%
131	30-40%
219	35-45%

For best results, the abundance of 219 should be slightly higher than the 131. Fragments associated with air and water (m/z 18, 28 & 32) should be less than 10% of m/z 69. Print out a tune report displaying the profile scan and the spectrum scan.

12.3. **Batch Sequence** – Generate a sequence to run a batch of samples.

12.3.1. **Initial Calibration** - The typical batch for initial calibration should include the following.

BFB Tune Standard
Method Blank
Calibration Level 1
Calibration Level 2
Calibration Level 3
Calibration Level 4
Calibration Level 5
Calibration Verification Standard

12.3.2. **Sample Analysis** – The batch for sample analysis must include BFB Tune/SPCC/CCC standard, MB, LCS, MS/MSD, and Duplicate in addition to environmental samples.

12.4 **Load Autosampler** – Load the autosampler with standards and samples for the batch created above. Preparation of BFB/calibration verification standards is described in the addendum. Prepare Method Blank, LCS, MS, and MSD samples for each sample type as described below.

12.4.1 **Method Blank**

12.4.1.1 **Water Samples** – Fill a clean 40-mL vial with OFW.

12.4.1.2 **Low Concentration Soil/Solid Samples** – Place a clean stir bar, 5.0 g of clean sand, 5.0 mL of OFW, and 1.0 g of sodium bisulfate in a clean 40-mL vial.

12.4.1.3 **High Concentration Soil/Solid Samples** – Place a clean stir bar, 4.0 mL of OFW, and 100 µL methanol in a clean 40-mL vial.

12.4.2 **LSC**

12.4.2.1 **Water Samples** – Fill a clean 40-mL vial with OFW. Spike the vial with a mid-level standard.

12.4.2.2 **Low Concentration Soil/Solid Samples** – Place a clean stir bar, 5.0 g of clean sand, 5.0 mL of OFW, and 1.0 g of sodium bisulfate in a clean 40-mL vial. Spike the vial with a mid-level standard.

12.4.2.3 **High Concentration Soil/Solid Samples** – Place a clean stir bar, 4.0 mL of OFW, and 100 µL methanol in a clean 40-mL vial. Spike the vial with a mid-level standard.

12.4.3 **MS and MSD**

12.4.3.1 **Water Samples** – Select an environmental sample. Spike the vial with a mid-level standard.

12.4.3.2 **Low Concentration Soil/Solid Samples** – Select an environmental sample. Spike the vial with a mid-level standard.

12.4.3.3 **High Concentration Soil/Solid Samples** – Select an environmental sample and prepare the sample extract in the normal fashion. Spike the vial with a mid-level standard.

12.5 **Analyze Samples** – Analyze all standards, quality control samples, and environmental samples.

12.6 **Qualitative Analysis of Results** – The following retention time and mass spectra comparison criteria must be met to identify target compounds.

12.6.1 **Retention Time Comparison** – The relative retention time (RRT) of the sample component must be within ±0.06 RRT units of the RRT of the component in the calibration verification standard. Extracted Ion Current Plots (EICPs) may be used to provide a more reliable assignment of retention time in the presence of coeluting components.

12.6.2 **Mass Spectrum Comparison** – The characteristic ions from the reference mass spectrum are defined as the three ions of greatest relative intensity, or any ions over 30% relative intensity if less than three such ions occur in the reference spectrum. Compounds are identified as present when the following criteria are met.

12.6.2.1 The intensities of the characteristic ions of a compound maximize in the same scan or within one scan of each other. Selection of a peak by a data system target compound search routine where the search is based on the presence of a target chromatographic peak containing ions specific for the target compound at a compound-specific retention time will be

accepted as meeting this criterion.

12.6.2.2 The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum.

12.6.2.3 Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

12.6.2.4 Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When gas chromatographic peaks obviously represent more than one sample component (i.e., a broadened peak with shoulder(s) or a valley between two or more maxima), appropriate selection of analyte spectra and background spectra is important.

12.7 Quantitative Analysis of Results

12.7.1 **Concentration** – The GC/MS data system will calculate the concentration of each analyte as µg/L. For water samples, no further calculations are necessary unless a dilution of the sample has been analyzed. If the initial analysis of the sample or a dilution of the sample has a concentration that exceeds the calibration range, the sample must be analyzed at a higher dilution. All dilutions should keep the response of the major constituents in the upper half of the linear range of the curve.

12.7.1.1 Water and Water-Miscible Waste Samples

$$\text{Concentration } (\mu g/L) = \frac{(A_x)(I_s)}{(A_{is})(RF)(V_o)}$$

Where:

A_x= Area of characteristic ion for compound being measured.
I_s = Amount of internal standard injected (ng).
A_{is} = Area of characteristic ion for the internal standard.
RF = Average Relative Response factor for compound being measured.
V_o = Volume of water purged (mL), taking into consideration any dilutions made.

12.7.1.2 **Soil/Solid Samples**

$$High \text{ Conc. (ug/kg)} = \frac{(A_x)(I_s)(V_t)}{(A_{is})(RF)(V_i)(W_s)}$$

$$Low \text{ Conc. (ug/kg)} = \frac{(A_x)(I_s)}{(A_{is})(RF)(W_s)}$$

Where:

A_x, I_s, A_{is}, RF = Same as in water and water-miscible waste above.
V_t = Volume of total extract (mL).
V_i = Volume of extract added (mL) for purging.
S_v = Volume of diluted extract.
W_s = Weight of sample extracted or purged (g). The wet weight or dry weight may be used, depending upon the specific applications of the data.

12.7.2 **Quality Control Results** – Calculate recoveries for surrogate compounds in all samples, spiked compounds in LCS and MS/MSD samples, and Relative Percent Differences (RPD) for duplicate and MS/MSD samples.

12.8 **Tentatively Identified Compounds (TICs)** – For some samples, identification may be desired for non-target compounds. A mass spectral library search may be conducted to attempt assignment of tentative identifications. Only after visual comparison of sample spectra with the nearest library searches may the analyst assign a tentative identification. Use the following guidelines for making tentative identifications.

12.8.1 Relative intensities of major ions in the reference spectrum (ions greater than 10% of the most abundant ion) should be present in the sample spectrum.

12.8.2 The relative intensities of the major ions should agree within ± 20%.

12.8.3 Molecular ions present in the reference spectrum should be present in the sample spectrum.

12.8.4 Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of co-eluting compounds.

12.8.5 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 co-

eluting peaks. Data system library reduction programs can sometimes create these discrepancies.

13. Quality Control

13.1. Calibration Checks

13.1.1. **ICAL** – If initial calibration criteria are not met, check standards preparation procedure for errors. Prepare new standards as required and re-run the calibration.

13.1.2. **System Performance and Calibration Checks** – If the SPCC and CCC criteria are not met, check system parameters, identify and correct likely causes, and re-run the check. An acceptable check is required to report sample results for the applicable batch.

13.1.3. **Internal Standard Responses and Retention Times** – Internal standard areas for calibration checks must be within the range of –50% to +100% and retention times must be within 30 seconds compared to the most recent ICAL. If these criteria are not met, check system parameters, identify and correct likely causes, and re-run the samples. If the IS results appear out of control due to sample matrix, re-run the sample to confirm the matrix interference.

13.2 **Surrogate Recoveries** – Surrogate compounds must be added to all samples, spikes, control samples and method blanks, prior to analysis as indicators of method accuracy. Acceptance criteria for recoveries in water and soil/sediment samples are shown below. Lab-derived limits may be substituted for these criteria. If these criteria are not met, check system parameters, identify and correct likely causes, and re-run the samples. If surrogate recoveries are higher than the acceptance criteria and target compounds are less than the reporting limit, the result may be reported with an appropriate footnote. If recoveries appear out of control due to sample matrix, re-run the samples to confirm the matrix interference and report the results with an appropriate footnote.

Compound	Waters	Soils
Dichloroethane-d_4	80-120	80-120
Dibromofluoromethane	86-118	80-120
Toluene-d_8	88-110	81-117
4-Bromofluorobenzene	86-115	74-121

13.3 **Method Blank** – Must be analyzed daily with each batch of samples. The method blank should not contain any target analytes at or above the reporting limit. If the results are not acceptable, analyze a new method blank. If the problem persists, conduct maintenance to clean the analytical system. An acceptable method blank is required to report sample results for the applicable batch. If a target analyte is present in the method blank at greater than the reporting level, sample results for samples in the batch for which that analyte is less than the reporting level may be reported.

13.4 **LCS Recoveries** – One LCS must be analyzed with each batch of 20 samples. Laboratory-based accuracy limits should be used to for acceptance criteria. If results are not acceptable, analyze a new LCS. If the problem persists, check the spiking solutions, and/or conduct system maintenance prior to running a new LCS. An acceptable LCS is required to report sample results for the applicable batch.

13.5 **MS/MSD Recoveries** – One MS should be analyzed with each batch of 20 samples. Laboratory-based accuracy limits should be used to for acceptance criteria. If the results are not acceptable, re-run the MS and/or MSD. If the problem persists, check the spiking solutions, and/or conduct system maintenance prior to running again. If recoveries appear out of control due to sample matrix, re-run the samples to confirm the matrix interference and report the results with an appropriate footnote.

13.6 **Duplicate and MS/MSD RPDs** – Five percent of all environmental samples should be analyzed in duplicate. A MS/MSD pair is also an acceptable duplicate analysis. Acceptance criteria should not exceed 20% for concentrations at least 10 times the PRL. If results are not acceptable, check for possible sample preparation problems and re-run if needed. Report the results with an appropriate footnote.

14. Method Performance

14.1. **Method Detection Limit (MDL) Study** – An MDL study must be conducted annually. Analyze a minimum of 7 replicates of a low level standard. Calculate the mean and standard deviation of the seven measurements for each analyte. Calculate the MDL for each analyte. The PRL for each analyte must be at least 2 times the MDL.

14.2. **Demonstration of Capability (DOC)** – Every analyst who performs this method must first document acceptable accuracy and precision by passing a demonstration of capability study (DOC). First, analyze 4 replicates of a mid-level standard. Calculate the mean and standard deviation of results for each analyte. All results must be in control to qualify the analyst for reporting sample results. Results of DOC studies for each analyst shall be retained in the lab quality assurance office.

15. Pollution Prevention and Waste Management

15.1. Procedures for handling waste generated during this analysis are addressed in individual laboratory SOPs for waste management.

15.2. In order to minimize the amount of waste generated during this procedure, analyst should prepare reagents in an amount which may be used in a reasonable amount of time (i.e. before a reagent expires)

15.3. The laboratory Chemical Hygiene Plan/Health and Safety Plan contains additional information on pollution prevention.

16. References

16.1. USEPA, SW-846, Method 8260B, "Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS), December 1996.

16.2. USEPA, SW-846, Method 5030B, "Purge and Trap for Aqueous Samples," December 1996.

16.3. USEPA, SW-846, Method 5035A, "Closed-System Purge-and-Trap and Extraction for Volatile Organics in Soil and Waste Samples.

16.4. USEPA, SW-846, Method 8000B, "Determinative Chromatographic Separations", December 1996.

17. Tables, Diagrams, Flowcharts, Attachments, Appendices, etc.

Not Applicable

18. Revisions

Document Number	Reason for Change	Date
ALL-O-002-rev.1	10.2.3. Removed last sentence. 11.1 replaced table with different Ion Abundance Criteria 12.2.2. moved typical batch for initial calibration to 12.3.1 13.2 changed to 13.1.3. 13.3. Changed to 13.2., added lab-derived limits may be substituted for these criteria. Added a sentence for surrogate recoveries that are higher than the acceptance criteria. 13.4. Changed to 13.3., added a sentence for how to handle if a target analyte is present in the method blank at a greater than reporting level. 13.5. Changed to 13.4., removed the acceptance criteria sentence and last sentence. 13.6. Changed to 13.5., removed the acceptance criteria sentence. 13.7. Changed to 13.6., changed ten to five. 16.4. added reference	November 1, 2004

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STANDARD OPERATING PROCEDURE

Green Bay Addendum

Determination of Volatile Organics by GC/MS

Reference Method: SW-846 Method 8260B with 5030B and 5035A/EPA 624

ADDENDUM NUMBER:	ALL-GB-O-002-rev.1
SOP NUMBER:	ALL-O-002-rev.1
EFFECTIVE DATE:	Date of Final Signature
SUPERSEDES:	N/A

APPROVAL

Nils Melberg, Assistant General Manager — Date: 6/15/06

Arthur F. Lautenbach, Quality Manager — Date: 6/15/06

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1. Purpose

This method is also used to determine the concentration of volatile organic compounds in water samples by purge-and-trap GC/MS compliant with EPA Method 624.

2. Scope and Application

See Table 1 for Reporting Limits.

3. Summary of Method

3.2 Pace Analytical Services, Inc. – Green Bay Laboratory is using a five and six-point calibration curve, depending on the compound.

See Table 2 for Chromatographic Retention Times and Characteristic Masses (m/z)

4. Interferences

No Applicable Changes

5. Safety

See Table 3 for required Safety Equipment.

6. Definitions

6.3 No duplicate sample analyzed, unless submitted by the client as a separate sample with duplicate field id.

6.6 Laboratory Control Sample Duplicate (LCSD)

7. Responsibilities and Distribution

No Applicable Changes

8. Sample Collection, Preservation and Handling

8.1.3 Holding Time – Unpreserved samples must be analyzed within 7 days of collection if analyzing for aromatic compounds.

8.2.1 Soil samples are collected for analysis with two-5-g aliquots for low level analysis and one 25-g aliquot for high-level analysis.

8.2.1.2 High-Level Aliquot – One 25-g aliquot is collected in a 2-oz. Jar with PTFE-lined screw cap. The jars are prepared by adding 20-ml of methanol and weighing to 0.01 g, and recording the tare weight on the vial label.

8.2.1.3 Moisture Aliquot – One aliquot is collected by filling a 2 oz. Jar with PTFE-lined screw cap.

See Table 4 for Sample Collection and Preservation

9. Equipment and Supplies

9.2.6 Gas tight syringes – 5 mL, 50 mL.

See Table 5 for Supplies.

10. Reagents and Standards

10.2.4 Internal Standards – This solution contains the following compounds.
Pentafluorobenzene
1,4-Difluorobenzene
Chlorobenzene-d5
1,4-Dichlorobenzene-d4

10.2.5 Surrogate Standards – This solution contains the following compounds.
Dibromofluoromethane
Toluene-d8
4-Bromofluorobenzene

10.3 Standards are stored at –10 C.

10.4.2 Intermediate standards are placed in 1.8 ml amber vials. As the dissolved gas concentrations decrease, a new ampule is used and old one is disgarded when the gas concentrations are below 20% of the initial calibration.

See Table 6, Table 7, Table 8, and Table 9 for Reagents and Standards

11. Calibration

11.1 Tuning-

m/z	ion abundance criteria
50	15-40%
75	30-60%
174	50-99%
175	5-9%

176	95-101%

11.2.3.2 Calibration Check Compounds (CCC) – The percent relative standard deviation (%RSD) for the calibration check compounds (CCC'S) must be <20%.

The following compounds are the Calibration Check Compounds(CCC):

Calibration Check Compounds (CCC)

1,1-Dichloroethene
Chloroform
1,2-Dichloropropane
Toluene
Ethylbenzene
Vinyl Chloride

11.2.3.3 The linear equation regression will produce the slope and intercept in the following form:

$$y = ax + b$$

where:

y = Instrument response
a = Slope of the line
x = Concentration of the calibration standard
b = The intercept

In calculating sample concentration by the internal standard method, the regression equation is as follows:

$$C_s = \frac{\frac{A_s C_{is}}{A_{is}} - b}{a}$$

where:

A_s = Area of the peak for the target analyte in the sample
A_{is} = Area of the peak of the internal standard
C_s = Concentration of the target analyte in the calibration standard
C_{is} = Concentration of the internal standard
a = Slope of the line
b = the intercept

A non-linear calibration model may be employed as in the following equation:

$$y = ax^2 + bx + c$$

See Table 10 for Calibration and Standardization

12. Procedure

12.1.1.1 Sample dilution (if required)-Dilutions are made in 50-ml gastight syringes.

12.1.1.2 The pH should be ≤ 2.

12.1.3.1 Methanol-preserved samples- Add 1ml of extract to 49 ml OFW in a 50 ml gastight syringe and decant into a clean 40-ml vial.

12.1.3.2.1 Weigh 20 g of unpreserved sample into a clean 2 oz. Jar and add 20 ml methanol and shake for 2 min.

12.1.3.2.2 Add 1 ml of extract to 49 ml OFW in a clean 50 ml gastight syringe and decant into a clean 40 ml voa vial.

12.4.1.3 Add 1 ml of methanol to 49 ml OFW in a clean 50 ml gastight syringe and decant into a clean 40 ml voa vial without a stir bar.

12.4.2 LCS

12.4.2.3 Add 1 ml of methanol to 49 ml OFW in a clean 50 ml gastight syringe and decant into a clean 40 ml voa vial without a stir bar.

13. Quality Control

13.4 One LSC/LCSD must be analyzed with each batch of 20 samples.

13.5 No sample duplicate analyses are performed other than the LCS/LCSD and MS/MSD pairs. The sample use for the MS/D pair is either determined by the client or selected at random from client samples as sample volume allows.

See Tables 11, 12, 13, 14, 15, and 16 for Quality Control requirements.

14. Method Performance

No Applicable changes.

15. Pollution Prevention and Waste Management

No Applicable Changes.

16. References

Test Methods for Organic Chemical Analysis of Municipal and Industriasl Wastewater, Appendix A to Part 136, Method 624-Purgeables

17. Tables, Diagrams, Flowcharts, Appendices, Addenda etc.

Table 1
Method 8260B/624 Compounds and Reporting Limits

COMPOUND NAME	AQUEOUS (ug/L)		SOLIDS (ug/Kg)			
			Low Level		Medium Level	
		EQL		EQL	MDL	EQL
Dichlorodifluoromethane		1.0		5.0		50
Chloromethane		1.0		5.0		50
Vinyl Chloride		1.0		5.0		50
Bromomethane		1.0		5.0		50
Chloroethane		1.0		5.0		50
Dichlorofluoromethane		1.0		5.0		50
Trichlorofluoromethane		1.0		5.0		50
Diethyl Ether		1.0		5.0		50
Acrolein		5.0		5.0		50
1 1-Dichloroethene		1.0		5.0		50
1 1 2-Trichlorotrifluoroethane		1.0		5.0		50
Acetone		5.0		5.0		250
Iodomethane		1.0		5.0		50
Carbon Disulfide		1.0		5.0		50
Allyl Chloride		1.0		5.0		50
Methylene Chloride		1.0		5.0		50
Acrylonitrile		5.0		5.0		250
Trans-1 2-Dichloroethene		1.0		5.0		50
Methyl T-Butyl Ether		1.0		5.0		50
N-Hexane		1.0		5.0		50
1 1-Dichloroethane		1.0		5.0		50
Vinyl Acetate		5.0		5.0		250
Diisopropyl Ether		1.0		5.0		50
2 2-Dichloropropane		1.0		5.0		50
Cis-1 2-Dichloroethene		1.0		5.0		50
2-Butanone		5.0		5.0		250
Bromochloromethane		1.0		5.0		50
Tetrahydrofuran		5.0		5.0		250
Chloroform		1.0		5.0		50
1 1 1-Trichloroethane		1.0		5.0		50
Carbon Tetrachloride		1.0		5.0		50
1 1-Dichloropropene		1.0		5.0		50
Benzene		1.0		5.0		50
1 2-Dichloroethane		1.0		5.0		50
Diethoxymethane		1.0		5.0		50
Trichloroethene		1.0		5.0		50
1 2-Dichloropropane		1.0		5.0		50

COMPOUND NAME	AQUEOUS (ug/L)		SOLIDS (ug/Kg)			
			Low Level		Medium Level	
		EQL		EQL		EQL
Dibromomethane		1.0		5.0		50
Bromodichloromethane		1.0		5.0		50
2-Chloroethyl Vinyl Ether		1.0		5.0		50
Cis-1 3-Dichloropropene		1.0		5.0		50
4-Methyl-2-Pentanone		5.0		5.0		250
Toluene		1.0		5.0		50
Trans-1 3-Dichloropropene		1.0		5.0		50
1 1 2-Trichloroethane		1.0		5.0		50
Tetrachloroethene		1.0		5.0		50
1 3-Dichloropropane		1.0		5.0		50
2-Hexanone		5.0		5.0		250
Dibromochloromethane		1.0		5.0		50
1 2-Dibromoethane		1.0		5.0		50
Chlorobenzene		1.0		5.0		50
1 1 1 2-Tetrachloroethane		1.0		5.0		50
Ethyl Benzene		1.0		5.0		50
M- P-Xylene		2.0		10		100
O-Xylene		1.0		5.0		50
Styrene		1.0		5.0		50
Bromoform		1.0		5.0		50
Isopropylbenzene		1.0		5.0		50
Trans-1 4-Dichloro-2-Butene		5.0		5.0		250
Bromobenzene		1.0		5.0		50
1 1 2 2-Tetrachloroethane		1.0		5.0		50
1 2 3-Trichloropropane		1.0		5.0		50
Cis-1 4-Dichloro-2-Butene		5.0		5.0		250
N-Propylbenzene		1.0		5.0		50
2-Chlorotoluene		1.0		5.0		50
4-Chlorotoluene		1.0		5.0		50
1 3 5-Trimethylbenzene		1.0		5.0		50
Tert-Butylbenzene		1.0		5.0		50

COMPOUND NAME	AQUEOUS (ug/L)		SOLIDS (ug/Kg)			
			Low Level		Medium Level	
1 2 4-Trimethylbenzene		1.0		5.0		50
Sec-Butylbenzene		1.0		5.0		50
1 3-Dichlorobenzene		1.0		5.0		50
P-Isopropyltoluene (Cymene)		1.0		5.0		50
1 4-Dichlorobenzene		1.0		5.0		50
1 2-Dichlorobenzene		1.0		5.0		50
N-Butylbenzene		1.0		5.0		50
Hexachloroethane		1.0		5.0		50
1 2-Dibromo-3-Chloropropane		1.0		5.0		50
1 2 4-Trichlorobenzene		1.0		5.0		50
Hexachlorobutadiene		1.0		5.0		50
Naphthalene		1.0		5.0		50
1 2 3-Trichlorobenzene		1.0		5.0		50
2-Methylnaphthalene		5.0		5.0		250
Diisopropyl ether		1.0		5.0		50
Tert Butyl Alcohol		50		_		2500
Tert Amyl Methyl Ether		5.0		_		250
Ethyl Tert Butyl Ether		5.0		_		250

Table 2
Chromatographic Retention Times and Characteristic Masses (m/z)

Compound	Retention Time	Primary Ion	Secondary Ions
Dichlorodifluoromethane	1.64	85	87
Chloromethane	1.85	50	52
Vinyl Chloride	1.98	62	64
Bromomethane	2.39	94	96
Chloroethane	2.53	64	66
Trichlorofluoromethane	2.87	151	101,153
Acrolein	3.47	56	55,58
Iodomethane	3.84	142	127,141
Acetonitrile**	---	41	40,39
Carbon Disulfide	3.93	76	78
Methyl-t-butyl ether	5.05	73	57
Allyl Chloride	4.23	76	41,39,78
Methylene Chloride	4.45	84	86,49
1,1-Dichloroethene	3.63	96	61,63
Diethyl Ether	3.37	74	45,59
Acetone	3.73	58	43
trans-1,2-Dichloroethene	4.93	96	61,98
Acrylonitrile	4.87	53	52,51
1,1-Dichloroethane	3.63	63	65,83
Vinyl Acetate	5.78	43	86
2,2-Dichloropropane	6.60	77	97
2-Butanone	6.66	72	43
cis-1,2-Dichloroethene	6.62	96	61,98
Propionitrile**(ethyl cyanide)	---	54	52,55,40
Chloroform	7.17	83	85
Bromochloromethane	6.99	128	49,130
Methacrylonitrile**	---	41	67,39,52,66
1,1,1-Trichloroethane	7.44	97	99,61
Carbon Tetrachloride	7.71	117	119
1,1-Dichloropropene	7.72	75	110,77
Benzene	8.04	78	-
1,2-Dichloroethane	8.07	62	98
Trichloroethene	9.11	95	97,130,132
1,2-Dichloropropane	8.07	63	112
Bromodichloromethane	9.93	83	85,127
Dibromomethane	9.63	93	95,174
Methyl Methacrylate	9.83	69	41,100,39
1,4-Dioxane**	---	88	58,43,57
2-Chloroethylvinyl ether	10.46	63	65,106
4-Methyl-2-pentanone	10.94	100	43,58,85
Toluene	11.21	92	91
trans-1,3-Dichloropropene	11.60	75	77,39
cis-1,3-Dichloropropene	17.90	75	77,39
1,1,2-Trichloroethane	11.89	83	97,85
Ethyl Methacrylate	11.91	69	41,99,86,114
2-Hexanone	12.34	43	58,57,100
Tetrachloroethene	12.14	164	129,131,166

Compound	Retention Time	Primary Ion	Secondary Ions
1,3-Dichloropropane	12.16	76	78
Dibromochloromethane	12.54	129	127
1,2-Dibromoethane	12.70	107	109,188
Chlorobenzene	13.56	112	77,114
1,1,1,2-Tetrachloroethane	13.72	131	133,119
Ethylbenzene	13.78	91	106
m/p-Xylene	13.99	106	91
o-Xylene	14.66	106	91
Styrene	14.68	104	78
Bromoform	14.97	173	175,254
Isopropylbenzene(Cumene)	15.32	105	120
cis-1,4-Dichloro-2-butene	15.94	75	53,77,124,89
1,1,2,2-Tetrachloroethane	15.84	83	131,85
Bromobenzene	15.80	156	77,158
1,2,3-Trichloropropane	15.89	75	77
n-Propylbenzene	16.05	91	120
2-Chlorotoluene	16.17	91	126
trans-1,4-Dichloro-2-butene	15.42	53	88,75
1,3,5-Trimethylbenzene	16.38	105	120
4-Chlorotoluene	16.36	91	126
Pentachloroethane**	---	167	130,132,165,169
1,2,4-Trimethylbenzene	17.03	105	120
sec-Butylbenzene	17.34	105	134
tert-Butylbenzene	16.94	119	91,134
p-Isopropyltoluene	17.61	119	134,91
1,3-Dichlorobenzene	17.49	146	111,148
1,4-Dichlorobenzene	17.65	146	111,148
n-Butylbenzene	18.34	91	92,134
1,2-Dichlorobenzene	18.30	146	111,148
1,2-Dibromo-3-chloropropane	19.69	75	155,157
1,2,4-Trichlorobenzene	21.21	180	182,145
Hexachlorobutadiene	21.58	225	223,227
Hexachloroethane	18.90	201	166,199,203
Naphthalene	21.63	128	-
1,2,3-Trichlorobenzene	22.08	180	182,145
Diisopropyl ether	4.625	45	87
Tert Butyl Alcohol	3.816	59	41
Tert Amyl Methyl Ether	6.663	73	55, 87
Ethyl Tert Butyl Ether	5.106	59	87, 41
Internal Standards/Surrogates			
Pentafluorobenzene	7.55	168	-
1,4-Difluorobenzene	8.71	114	-
Chlorobenzene-d5	13.51	117	-
1,4-Dichlorobenzene-d4	17.61	152	-
4-Bromofluorobenzene	15.56	95	174,176
Dibromofluoromethane	7.42	113	-
Toluene-d8	11.11	98	-

Table 3
REQUIRED SAFETY EQUIPMENT

Item:	Safety Apparel Description	Mandatory for Procedure	Optional
1	Safety Goggles or Glasses	X	
2	Lab Coat		X
3	Gloves		X
4	Face Shield		X

Table 4
SAMPLE COLLECTION, PRESERVATION, SHIPMENT AND STORAGE

Matrix	Prep Method	Container(s)	Preservation	Shipment Conditions	Lab Storage Conditions
Aqueous	SW846 5030B/EPA 624	40 ml VOC Vials (3)	0.5 ml of 18 % HCL	On ice 4+/- 2° Celsius	Refrigerate 4+/- 2° Celsius
Solid	SW846 5035	Encore samplers (two 5 gram samplers and one 25 gram sampler) or 40 ml unpreserved VOC vial	If sample exhibits effervescence, then 5 mls OFW. Non-effervescence = 5 mls OFW containing 1 g Sodium Bisulfate. Medium level with MeOH	On ice 4+/- 2° Celsius	Refrigerate 4+/- 2° Celsius or Freeze within 48 hours of sampling, thaw, preserve with OFW, then analyze
Solid	SW846 5030B	4 oz ZH packed tight	Water and/or MeOH	On ice 4+/- 2° Celsius	Refrigerate 4+/- 2° Celsius

Table 5
Supplies

Supplies	Manufacturer	Vendor	Catalog #
10ul Gastight 1701	Hamilton	Fisher Scientific	14-815-1
25ul Gastight 1702	Hamilton	Fisher Scientific	14-815-29
50ul Gastight 1705	Hamilton	Fisher Scientific	14-824-30
100ul Gastight 1710	Hamilton	Fisher Scientific	13-684-100
250ul Gastight 1725	Hamilton	Fisher Scientific	13-684-102
500ul Gastight 1750	Hamilton	Fisher Scientific	13-684-106
1ml Gastight 1001	Hamilton	Fisher Scientific	14-824-25
5ml Gastight 1005	Hamilton	Fisher Scientific	13-684-96
50ml Gastight 1050	Hamilton	Fisher Scientific	14-815-195
DB-624 Capillary column, 20mX0.18 mm i.d.X1.0 um	J&W Scientific	VWR Scientific	121-1324
K-Trap, Vocarb3000, Tekmar3000	Supelco	Supelco	24920-U
Fritless 5-ml Sparge Tube	Supelco	Supelco	22780
IceBlue Septa, 11mm	Restek	Restek	22392
Single Gooseneck Injection port liners (4mm)	Restek	Restek	20799
Gold-plated inlet seals	Restek	Restek	21306
Viton O-rings	Restek	Restek	20377
0.4mm Vespel/Graphite ferrules	Restek	Restek	20211
GCMS Filaments	Agilent Technologies	Agilent Technologies	05972-60053
Stir Bar	Fisher Brand	Fisher Brand	14-511-60A
40 ml VOA vials	QEC	QEC	3112-40ml
10 ml volumetric	Kimax Brand	Fisher Scientific	10-212AA
25 ml volumetric	Kimax Brand	Fisher Scientific	10-212BB
50 ml volumetric	Kimax Brand	Fisher Scientific	10-212A
100 ml volumetric	Kimax Brand	Fisher Scientific	10-212B
200 ml volumetric	Kimax Brand	Fisher Scientific	10-212C
500 ml volumetric	Kimax Brand	Fisher Scientific	10-218D
Pasteur Pipettes	Fisher Scientific	Fisher Scientific	13-678-20A
Pipette bulb	Fisher Scientific	Fisher Scientific	14-065B
0.1-2.5 ml Repipetter	Brinkmann	Fisher Scientific	13-688-130
1-5 ml Repipetter	Brinkmann	Fisher Scientific	13-688-131
2-10 ml Repipetter	Brinkmann	Fisher Scientific	13-688-133
5-25 ml Repipetter	Brinkmann	Fisher Scientific	13-688-134
1.8 ml amber vials & caps	Restek	Restek	24637
10 ml graduate cylinder	Kimex Brand	Fisher Scientific	08-554B "to deliver"
40 ml VOA vials HCl preserved	QEC	QEC	3112-40HCL
2 oz. jars with teflon lids	QEC	QEC	2114-0002
spatulas	Fisher Scientific	Fisher Scientific	14-511-60A

Table 6
Reagents

Reagent	Conc.	Purity	Manufacturer	Vendor	Catalog #
Methanol	100%	Purge and Trap grade	Burdick & Jackson	VWR Scientific	232-1
Sodium Bisulfate	granular	Certified grade	Fisher Scientific	Fisher Scientific	S-240-3
Helium gas		99.999%	Michigan Airgas	Michigan Airgas	
OFW		ASTM Type II	Barnstead-Nanopure	VWR Scientific	D8961
4-BFB Tuning Standard	5000 ug/mL	99%	Restek	Restek	30003-520
Ottawa Sand, 20-30 mesh		ASTM C190	Fisher Scientific	Fisher Scientific	S23-3
502.2 Calibration Mix#1	2000 ug/mL	99%	Restek	Restek	30042
502.2 Calibration Mix#1 - ICV	2000 ug/mL	99%	Accustandard	Accustandard	M-502B-10X
502.2 Cal 2000 Megamix	2000 ug/mL	99%	Restek	Restek	30431
502.2 Cal 2000 Megamix - ICV	2000 ug/mL	99%	Accustandard	Accustandard	M-502A-R-10X
Vinyl Acetate	2000 ug/mL	99+%	Restek	Restek	30216
Vinyl Acetate	neat	99+%	Aldrich Chemical	Aldrich Chemical	V150-3
VOA Calibration Mix #1	5000 ug/mL	99%	Restek	Restek	30006
VOA Calibration Mix #1 - ICV	5000 ug/mL	99%	Accustandard	Accustandard	CLP-022K-25X
Pace GB Custom Mix	2000 ug/mL	99+%	Restek	Restek	56230
Pace GB Custom Mix – ICV	2000 ug/mL	99%	Accustandard	Accustandard	S-13659
Pace GB Custom Mix – Cyclohexanes	10000 ug/mL	99+%	Restek	Restek	58314
Pace GB Custom Mix – Cyclohexanes - ICV	10000 ug/mL	99%	Accustandard	Accustandard	S-7134-R1-5X
Pace GB Custom Mix – NELAP	Various	99+%	Restek	Restek	553772
Pace GB Custom Mix – NELAP - ICV	Various	99%	Accustandard	Accustandard	S-13661
Pace GB Custom Mix – Acrolein	20000 ug/mL	99+%	Restek	Restek	52995
Pace GB Custom Mix – Acrolein - ICV	20000 ug/mL	99%	Accustandard	Accustandard	QM-8015B/5031-03-2X
Pace GB Custom Mix – 2-Chloroethylvinyl Ether	2000 ug/mL	99+%	Restek	Restek	30265
Pace GB Custom Mix – 2-Chloroethylvinyl Ether - ICV	2000 ug/mL	99%	Accustandard	Accustandard	M-601C-10X
Pace GB Custom Mix – Appendix IX	Various	99+%	Restek	Restek	58998
Pace GB Custom Mix – Appendix IX - ICV	Various	99%	Accustandard	Accustandard	S-13660
California Oxygenate Mix	Various	99+%	Restek	Restek	30465
California Oxygenate Mix – ICV	Various	99%	Accustandard	Accustandard	OGAD-001
8260 Internal Standard	2500 ug/mL	99%	Restek	Restek	30173
8260 Surrogate Standard	2500 ug/mL	99%	Restek	Restek	30174
Cal 2000 Mix A/B	2000 ug/mL	99%	Restek	Restek	30438
VOA Cal Mix # 5	2000 ug/mL	99%	Restek	Restek	30010
502.2 Mix #1	2000 ug/mL	99%	Restek	Restek	30042
Michigan GRO Mix	2000 ug/mL	99%	Restek	Restek	30468

Table 7
Standards

Standard	Acronym	Concentration	Direction found in Section:	Alias
Level 1 Calibration Standard	VSTD001	1.0 ug/L all compounds except as follows: 10 ug/L acrolein	Table 8	Cal Std
Level 2 Calibration Standard	VSTD005	5.0 ug/L all compounds except as follows: 50 ug/L acrolein	Table 8	Cal Std
Level 3 Calibration Standard	VSTD020	20 ug/L all compounds except as follows: 200 ug/L acrolein	Table 8	Cal Std
Level 4 Calibration Standard	VSTD050	50 ug/L all compounds except as follows: 500 ug/L acrolein	Table 8	Cal Std
Level 5 Calibration Standard	VSTD100	100 ug/L all compounds except as follows: 1000 ug/L acrolein	Table 8	Cal Std
Level 6 Calibration Standard	VSTD200	200 ug/L all compounds except as follows: 2000 ug/L acrolein	Table 8	Cal Std
Independent Calibration Verification Standard	ICV050	50 ug/L all compounds except as follows: 500 ug/l Acrolein	Table 8	ICV
Calibration Verification Standard	VSTD050	50 ug/L all compounds except as follows: 500 ug/l Acrolein	Table 8	CCV
Level 1 Calibration Standard for NELAP/Appx IX Compounds	VSTD001 for NELAP/Appx IX Compounds	1.0 ug/L all compounds except as follows: 10 ug/l cyclohexanone, ethyl acetate, isopropanol, isobutanol. 50 ug/L 1,4-dioxane, 1-propanol, n-butanol	Table 8	Cal Std for NELAP/Appx IX Compounds
Level 2 Calibration Standard for NELAP/Appx IX Compounds	VSTD005 for NELAP/Appx IX Compounds	5.0 ug/L all compounds except as follows: 50 ug/l cyclohexanone, ethyl acetate, isopropanol, isobutanol.	Table 8	Cal Std for NELAP/Appx IX Compounds

		250 ug/L 1,4-dioxane, 1-propanol, n-butanol		
Level 3 Calibration Standard for NELAP/Appx IX Compounds	VSTD020 for NELAP/Appx IX Compounds	20 ug/L all compounds except as follows: 200 ug/l cyclohexanone, ethyl acetate, isopropanol, isobutanol. 1000 ug/L 1,4-dioxane, 1-propanol, n-butanol	Table 8	Cal Std for NELAP/Appx IX Compounds
Level 4 Calibration Standard for NELAP/Appx IX Compounds	VSTD050 for NELAP/Appx IX Compounds	50 ug/L all compounds except as follows: 500 ug/l cyclohexanone, ethyl acetate, isopropanol, isobutanol. 2500 ug/L 1,4-dioxane, 1-propanol, n-butanol	Table 8	Cal Std for NELAP/Appx IX Compounds
Level 5 Calibration Standard for NELAP/Appx IX Compounds	VSTD100 for NELAP/Appx IX Compounds	100 ug/L all compounds except as follows: 1000 ug/l cyclohexanone, ethyl acetate, isopropanol, isobutanol. 5000 ug/L 1,4-dioxane, 1-propanol, n-butanol	Table 8	Cal Std for NELAP/Appx IX Compounds
Level 6 Calibration Standard for NELAP/Appx IX Compounds	VSTD200 for NELAP/Appx IX Compounds	200 ug/L all compounds except as follows: 2000 ug/l cyclohexanone, ethyl acetate, isopropanol, isobutanol. 10000 ug/L 1,4-dioxane, 1-propanol, n-butanol	Table 8	Cal Std for NELAP/Appx IX Compounds
Independent Calibration Verification Standard for NELAP/Appx IX compounds	ICV050 – NELAP/Appx IX	50 ug/L all compounds except as follows: 500 ug/l cyclohexanone, ethyl acetate, isopropanol, isobutanol.	Table 8	ICV for NELAP/Appx IX Compounds

		2500 ug/L 1,4-dioxane, 1-propanol, n-butanol		
Calibration Verification Standard for NELAP/Appx IX compounds	VSTD050 – NELAP/Appx IX	50 ug/L all compounds except as follows: 500 ug/l cyclohexanone, ethyl acetate, isopropanol, isobutanol. 2500 ug/L 1,4-dioxane, 1-propanol, n-butanol	Table 8	CCV for NELAP/Appx IX Compounds
Level 1 Calibration Standard for California Oxygenates	VSTD001 for California Oxygenates	1.0 ug/L all compounds except as follows: 5.0 ug/L tert butyl alcohol	Table 8	Cal Std for California Oxygenates
Level 2 Calibration Standard for California Oxygenates	VSTD005 for California Oxygenates	5.0 ug/L all compounds except as follows: 25 ug/L tert butyl alcohol	Table 8	Cal Std for California Oxygenates
Level 3 Calibration Standard for California Oxygenates	VSTD020 for California Oxygenates	20 ug/L all compounds except as follows: 100 ug/L tert butyl alcohol	Table 8	Cal Std for California Oxygenates
Level 4 Calibration Standard for California Oxygenates	VSTD050 for California Oxygenates	50 ug/L all compounds except as follows: 250 ug/L tert butyl alcohol	Table 8	Cal Std for California Oxygenates
Level 5 Calibration Standard for California Oxygenates	VSTD100 for California Oxygenates	100 ug/L all compounds except as follows: 500 ug/L tert butyl alcohol	Table 8	Cal Std for California Oxygenates
Level 6 Calibration Standard for California Oxygenates	VSTD200 for California Oxygenates	200 ug/L all compounds except as follows: 1000 ug/L tert butyl alcohol	Table 8	Cal Std for California Oxygenates
Independent Calibration Verification Standard	ICV050 for California Oxygenates	50 ug/L all compounds except as follows: 500 ug/L tert butyl alcohol	Table 8	ICV for California Oxygenates
Calibration Verification Standard	VSTD050 for California Oxygenates	50 ug/L all compounds except as follows: 500 ug/L tert butyl alcohol	Table 8	CCV for California Oxygenates
Surrogate Standard	SS	50 ug/L	Table 8	Surrogate

Internal Standard	IS	50 ug/L	Table 8	Internal
Method Blank	MB	< Reporting Limit	Table 8	Reagent Blank
BFB	Vtunxxx	50 ng injection	Table 8	Tune Check
Matrix Spike/Blank Spike Stock Solution - TCL 3.4 List for Water and Low Level Soil Samples	MS/BS TCL 3.4 List Stock Solution for Water and Low Level Soil Samples	100 ug/mL for all comounds	Table 8	TCL 3.4 list for Water and Low Level Soil Samples
Matrix Spike/Blank Spike Stock Solution - TCL 3.4 List for Methanol Preserved Soil Samples	MS/BS TCL 3.4 List Stock Solution for Methanol Preserved Soil Samples	500 ug/mL for all comounds	Table 8	TCL 3.4 list for Methanol Preserved Soil Samples
Matrix Spike/Blank Spike Stock Solution - Full List for Water and Low Level Soil Samples	MS/BS Stock Solution - Full List for Water and Low Level Soil Samples	100 ug/mL all compounds except as follows: 1000 ug/mL Acrolein	Table 8	Full list for Water and Low Level Soil Samples
Matrix Spike/Blank Spike Stock Solution - Full List for Methanol Preserved Soil Samples	MS/BS Stock Solution – Full List for Methanol Preserved Soil Samples	500 ug/mL all compounds except as follows: 5000 ug/mL Acrolein	Table 8	Full list for Methanol Preserved Soil Samples
MS/MSD – BS/BSD Spike for Water Samples	MS/MSD BS/BSD	50 ug/L for most compounds, Various for others.	Table 8	MS/MSD BS/BSD
MS/MSD – BS/BSD Spike for Low Level Soil Samples	MS/MSD BS/BSD	50 ug/kg for most compounds, Various for others.	Table 8	MS/MSD BS/BSD
MS/MSD – BS/BSD Spike for Methanol Preserved Soil Samples	MS/MSD BS/BSD	2500 ug/kg for most compounds, Various for others.	Table 8	MS/MSD BS/BSD
Extraction Blank	EBLK	< Reporting Limit		Extraction Blank (MeOH)

Table 8
Preparation of Standards

Standard	Acronym	Concentration of Intermediate	Reagents Used	Final Volume
4-Bromofluorobenzene	BFB	50 ug/mL	100µL of 5000 ug/mL BFB into methanol	10 mL
Internal Standard	IS	250 ug/mL	5000 µL of 2500 ug/mL IS into methanol	50 mL
Surrogate Standard	SS	250 ug/mL	5000 µL of 2500 ug/mL SS into methanol	50 mL
Internal/Surrogate Std.	IS/SS	250 ug/mL	5000 µL of 2500 ug/mL IS/SS into MeOH	50 mL
100 ug/mL Calibration Std. 1000 ug/mL Acrolein	CAL Stock Standard	100 ug/mL all compounds except as follows: 1000 ug/mL Acrolein	1250 µL of 2000 ug/mL 502.2 Calibration Mix #1 1250 µL of 2000 ug/mL 502.2 Cal 2000 Megamix 1250 µL of 2000 ug/mL Vinyl Acetate 500 µL of 5000 ug/mL VOA Calibration Mix #1 1250 µL of 2000 ug/mL Pace GB Custom Mix 250 µL of 10000 ug/mL Pace GB Custom Mix - Cyclohexanes 1250 µL of 20000 ug/mL Pace GB Custom Mix - Acrolein 1250 µL of 2000 ug/mL Pace GB Custom Mix - 2-Chloroethylvinyl ether Diluted into methanol	25 mL
100 ug/mL Calibration Std. 1000 ug/mL Acrolein	ICV Stock Standard	100 ug/mL all compounds except as follows: 1000 ug/mL Acrolein	1250 µL of 2000 ug/mL 502.2 Calibration Mix #1 - ICV 1250 µL of 2000 ug/mL 502.2 Cal 2000 Megamix - ICV 500 µL of 5000 ug/mL VOA Calibration Mix #1 - ICV 1250 µL of 2000 ug/mL Pace GB Custom Mix - ICV 250 µL of 10000 ug/mL Pace GB Custom Mix – Cyclohexanes - ICV 1250 µL of 20000 ug/mL Pace GB Custom Mix – Acrolein - ICV 1250 µL of 2000 ug/mL Pace GB Custom Mix - 2-Chloroethylvinyl ether - ICV 263 µL of 9520 ug/mL Vinyl Acetate Diluted into methanol	25 mL
Vinyl Acetate	VA	9520 ug/mL	0.238 mg of neat Vinyl Acetate Diluted into methanol	25 mL
Level 1 Calibration Standard	VSTD001	1.0 ug/L all compounds except as follows: 10 ug/L acrolein	Dilute 0.5 uL 100 ug/mL all compounds except as follows: 1000 ug/mL Acrolein CAL Stock Standard into 50 mL reagent water. If for a methanol curve, use 49 mL reagent water and 1 mL methanol.	50 mL
Level 2 Calibration Standard	VSTD005	5.0 ug/L all compounds except as follows: 50 ug/L acrolein	Dilute 2.5 uL 100 ug/mL all compounds except as follows: 1000 ug/mL Acrolein CAL Stock Standard into 50 mL reagent water. If for a methanol curve, use 49 mL reagent water and 1 mL methanol.	50 mL
Level 3 Calibration Standard	VSTD020	20 ug/L all compounds except	Dilute 10 uL 100 ug/mL all compounds except as follows: 1000 ug/mL Acrolein CAL Stock	50 mL

		as follows: 200 ug/L acrolein	Standard into 50 mL reagent water. If for a methanol curve, use 49 mL reagent water and 1 mL methanol.	
Level 4 Calibration Standard	VSTD050	50 ug/L all compounds except as follows: 500 ug/L acrolein	Dilute 25 uL 100 ug/mL all compounds except as follows: 1000 ug/mL Acrolein CAL Stock Standard into 50 mL reagent water. If for a methanol curve, use 49 mL reagent water and 1 mL methanol.	50 mL
Level 5 Calibration Standard	VSTD100	100 ug/L all compounds except as follows: 1000 ug/L acrolein	Dilute 50 uL 100 ug/mL all compounds except as follows: 1000 ug/mL Acrolein CAL Stock Standard into 50 mL reagent water. If for a methanol curve, use 49 mL reagent water and 1 mL methanol.	50 mL
Level 6 Calibration Standard	VSTD200	200 ug/L all compounds except as follows: 2000 ug/L acrolein	Dilute 100 uL 100 ug/mL all compounds except as follows: 1000 ug/mL Acrolein CAL Stock Standard into 50 mL reagent water. If for a methanol curve, use 49 mL reagent water and 1 mL methanol.	50 mL
Independent Calibration Verification Standard	ICV050	50 ug/L all compounds except as follows: 500 ug/l Acrolein	Dilute 25 uL 100 ug/mL all compounds except as follows: 1000 ug/mL Acrolein ICV Stock Standard into 50 mL reagent water. If for a methanol curve, use 49 mL reagent water and 1 mL methanol.	50 mL
Calibration Verification Standard	VSTD050	50 ug/L all compounds except as follows: 500 ug/l Acrolein	Dilute 25 uL 100 ug/mL all compounds except as follows: 1000 ug/mL Acrolein CAL Stock Standard into 50 mL reagent water. If for a methanol curve, use 49 mL reagent water and 1 mL methanol.	50 mL
100 ug/mL Calibration Std. 1000 ug/mL cyclohexanone, ethyl acetate, isopropanol, isobutanol. 5000 ug/mL 1,4-dioxane, 1-propanol, n-butanol for NELAP/Appx IX Compounds	CAL Stock Standard for NELAP/Appx IX Compounds	100 ug/mL all compounds except as follows: 1000 ug/mL cyclohexanone, ethyl acetate, isopropanol, isobutanol. 5000 ug/mL 1,4-dioxane, 1-propanol, n-butanol	1250 µL of Various Concentration Pace GB Custom Mix - NELAP 500 µL of Various Concentration Pace GB Custon Mix – Appendix IX Diluted into methanol	25 mL
100 ug/mL Calibration Std. 1000 ug/mL cyclohexanone, ethyl acetate, isopropanol, isobutanol. 5000 ug/mL 1,4-dioxane, 1-propanol, n-butanol for NELAP/Appx IX Compounds	ICV Stock Standard for NELAP/Appx IX Compounds	100 ug/mL all compounds excepts as follows: 1000 ug/mL cyclohexanone, ethyl acetate, isopropanol, isobutanol. 5000 ug/mL 1,4-dioxane, 1-propanol, n-butanol	1250 µL of Various Concentration Pace GB Custom Mix – NELAP - ICV 500 µL of Various Concentration Pace GB Custon Mix – Appendix IX – ICV Diluted into methanol	25 mL
Level 1 Calibration Standard	VSTD001 for	1.0 ug/L all	Dilute 0.5 uL 100 ug/mL all compounds except	50 mL

for NELAP/Appx IX Compounds	NELAP/Appx IX Compounds	compounds except as follows: 10 ug/l cyclohexanone, ethyl acetate, isopropanol, isobutanol. 50 ug/L 1,4-dioxane, 1-propanol, n-butanol	as follows: 1000 ug/mL cyclohexanone, ethyl acetate, isopropanol, isobutanol. 5000 ug/mL 1,4-dioxane, 1-propanol, n-butanol CAL Stock Standard for NELAP/Appx IX Compounds into reagent water. If for a methanol curve, use 49 mL reagent water and 1 mL methanol.	
Level 2 Calibration Standard for NELAP/Appx IX Compounds	VSTD005 for NELAP/Appx IX Compounds	5.0 ug/L all compounds except as follows: 50 ug/l cyclohexanone, ethyl acetate, isopropanol, isobutanol. 250 ug/L 1,4-dioxane, 1-propanol, n-butanol	Dilute 2.5 uL 100 ug/mL all compounds except as follows: 1000 ug/mL cyclohexanone, ethyl acetate, isopropanol, isobutanol. 5000 ug/mL 1,4-dioxane, 1-propanol, n-butanol CAL Stock Standard for NELAP/Appx IX Compounds into reagent water. If for a methanol curve, use 49 mL reagent water and 1 mL methanol.	50 mL
Level 3 Calibration Standard for NELAP/Appx IX Compounds	VSTD020 for NELAP/Appx IX Compounds	20 ug/L all compounds except as follows: 200 ug/l cyclohexanone, ethyl acetate, isopropanol, isobutanol. 1000 ug/L 1,4-dioxane, 1-propanol, n-butanol	Dilute 10 uL 100 ug/mL all compounds except as follows: 1000 ug/mL cyclohexanone, ethyl acetate, isopropanol, isobutanol. 5000 ug/mL 1,4-dioxane, 1-propanol, n-butanol CAL Stock Standard for NELAP/Appx IX Compounds into reagent water. If for a methanol curve, use 49 mL reagent water and 1 mL methanol.	50 mL
Level 4 Calibration Standard for NELAP/Appx IX Compounds	VSTD050 for NELAP/Appx IX Compounds	50 ug/L all compounds except as follows: 500 ug/l cyclohexanone, ethyl acetate, isopropanol, isobutanol. 2500 ug/L 1,4-dioxane, 1-propanol, n-butanol	Dilute 25 uL 100 ug/mL all compounds except as follows: 1000 ug/mL cyclohexanone, ethyl acetate, isopropanol, isobutanol. 5000 ug/mL 1,4-dioxane, 1-propanol, n-butanol CAL Stock Standard for NELAP/Appx IX Compounds into reagent water. If for a methanol curve, use 49 mL reagent water and 1 mL methanol.	50 mL
Level 5 Calibration Standard for NELAP/Appx IX Compounds	VSTD100 for NELAP/Appx IX Compounds	100 ug/L all compounds except as follows: 1000 ug/l cyclohexanone, ethyl acetate, isopropanol, isobutanol. 5000 ug/L 1,4-	Dilute 50 uL 100 ug/mL all compounds except as follows: 1000 ug/mL cyclohexanone, ethyl acetate, isopropanol, isobutanol. 5000 ug/mL 1,4-dioxane, 1-propanol, n-butanol CAL Stock Standard for NELAP/Appx IX Compounds into reagent water. If for a methanol curve, use 49 mL reagent water and 1 mL methanol.	50 mL

		dioxane, 1-propanol, n-butanol		
Level 6 Calibration Standard for NELAP/Appx IX Compounds	VSTD200 for NELAP/Appx IX Compounds	200 ug/L all compounds except as follows: 2000 ug/l cyclohexanone, ethyl acetate, isopropanol, isobutanol. 10000 ug/L 1,4-dioxane, 1-propanol, n-butanol	Dilute 100 uL 100 ug/mL all compounds except as follows: 1000 ug/mL cyclohexanone, ethyl acetate, isopropanol, isobutanol. 5000 ug/mL 1,4-dioxane, 1-propanol, n-butanol CAL Stock Standard for NELAP/Appx IX Compounds into reagent water. If for a methanol curve, use 49 mL reagent water and 1 mL methanol.	50 mL
Independent Calibration Verification Standard for NELAP/Appx IX compounds	ICV050 – NELAP/Appx IX	50 ug/L all compounds except as follows: 500 ug/l cyclohexanone, ethyl acetate, isopropanol, isobutanol. 2500 ug/L 1,4-dioxane, 1-propanol, n-butanol	Dilute 25 uL 100 ug/mL all compounds except as follows: 1000 ug/mL cyclohexanone, ethyl acetate, isopropanol, isobutanol. 5000 ug/mL 1,4-dioxane, 1-propanol, n-butanol ICV Stock Standard for NELAP/Appx IX Compounds into reagent water. If for a methanol curve, use 49 mL reagent water and 1 mL methanol.	50 mL
Calibration Verification Standard for NELAP/Appx IX compounds	VSTD050 – NELAP/Appx IX	50 ug/L all compounds except as follows: 500 ug/l cyclohexanone, ethyl acetate, isopropanol, isobutanol. 2500 ug/L 1,4-dioxane, 1-propanol, n-butanol	Dilute 25 uL 100 ug/mL all compounds except as follows: 1000 ug/mL cyclohexanone, ethyl acetate, isopropanol, isobutanol. 5000 ug/mL 1,4-dioxane, 1-propanol, n-butanol CAL Stock Standard for NELAP/Appx IX Compounds into reagent water. If for a methanol curve, use 49 mL reagent water and 1 mL methanol.	50 mL
100 ug/mL Calibration Std. 500 ug/mL tert butyl alcohol	CAL Stock Standard for California Oxygenates	100 ug/mL all compounds except as follows: 500 ug/mL tert butyl alcohol	1250 µL of Various Concentration California Oxygenate Mix Diluted into methanol	25 mL
100 ug/mL Calibration Std. 500 ug/mL tert butyl alcohol	ICV Stock Standard for California Oxygenates	100 ug/mL all compounds excepts as follows 500 ug/mL tert butyl alcohol	1250 µL of Various Concentration California Oxygenate Mix – ICV Diluted into methanol	25 mL
Level 1 Calibration Standard for California Oxygenates	VSTD001 for California Oxygenates	1.0 ug/L all compounds except as follows: 5.0 ug/L tert butyl alcohol	Dilute 0.5 uL 100 ug/mL all compounds except as follows: 500 ug/mL tert butyl alcohol CAL Stock Standard for California Oxygenates into reagent water. If for a methanol curve, use 49 mL	50 mL

			reagent water and 1 mL methanol.	
Level 2 Calibration Standard for California Oxygenates	VSTD005 for California Oxygenates	5.0 ug/L all compounds except as follows: 25 ug/L tert butyl alcohol	Dilute 2.5 uL 100 ug/mL all compounds except as follows: 500 ug/mL tert butyl alcohol CAL Stock Standard for California Oxygenates into reagent water. If for a methanol curve, use 49 mL reagent water and 1 mL methanol.	50 mL
Level 3 Calibration Standard for California Oxygenates	VSTD020 for California Oxygenates	20 ug/L all compounds except as follows: 100 ug/L tert butyl alcohol	Dilute 10 uL 100 ug/mL all compounds except as follows: 500 ug/mL tert butyl alcohol CAL Stock Standard for California Oxygenates into reagent water. If for a methanol curve, use 49 mL reagent water and 1 mL methanol.	50 mL
Level 4 Calibration Standard for California Oxygenates	VSTD050 for California Oxygenates	50 ug/L all compounds except as follows: 250 ug/L tert butyl alcohol	Dilute 25 uL 100 ug/mL all compounds except as follows: 500 ug/mL tert butyl alcohol CAL Stock Standard for California Oxygenates into reagent water. If for a methanol curve, use 49 mL reagent water and 1 mL methanol..	50 mL
Level 5 Calibration Standard for California Oxygenates	VSTD100 for California Oxygenates	100 ug/L all compounds except as follows: 500 ug/L tert butyl alcohol	Dilute 50 uL 100 ug/mL all compounds except as follows: 500 ug/mL tert butyl alcohol CAL Stock Standard for California Oxygenates into reagent water. If for a methanol curve, use 49 mL reagent water and 1 mL methanol.	50 mL
Level 6 Calibration Standard for California Oxygenates	VSTD200 for California Oxygenates	200 ug/L all compounds except as follows: 1000 ug/L tert butyl alcohol	Dilute 100 uL 100 ug/mL all compounds except as follows: 500 ug/mL tert butyl alcohol CAL Stock Standard for California Oxygenates into reagent water. If for a methanol curve, use 49 mL reagent water and 1 mL methanol.	50 mL
Independent Calibration Verification Standard	ICV050 for California Oxygenates	50 ug/L all compounds except as follows: 500 ug/L tert butyl alcohol	Dilute 25 uL 100 ug/mL all compounds except as follows: 500 ug/mL tert butyl alcohol ICV Stock Standard for California Oxygenates into reagent water. If for a methanol curve, use 49 mL reagent water and 1 mL methanol.	50 mL
Calibration Verification Standard	VSTD050 for California Oxygenates	50 ug/L all compounds except as follows: 500 ug/L tert butyl alcohol	Dilute 25 uL 100 ug/mL all compounds except as follows: 500 ug/mL tert butyl alcohol CAL Stock Standard for California Oxygenates into reagent water. If for a methanol curve, use 49 mL reagent water and 1 mL methanol.	50 mL
Matrix Spike/Blank Spike Stock Solution - TCL 3.4 List for Water and Low Level Soil Samples	MS/BS TCL 3.4 List Stock Solution for Water and Low Level Soil Samples	100 ug/mL for all comounds	1250 µL of 2000 ug/mL Cal 2000 Mix A/B 1250 µL of 2000 ug/mL VOA Cal Mix #5 1250 µL of 2000 ug/mL 502.2 Cal. Mix #1 Dilute into methanol.	25 mL
Matrix Spike/Blank Spike Stock Solution - TCL 3.4 List for Methanol Preserved Soil Samples	MS/BS TCL 3.4 List Stock Solution for Methanol Preserved Soil	500 ug/mL for all comounds	6250 µL of 2000 ug/mL Cal 2000 Mix A/B 6250 µL of 2000 ug/mL VOA Cal Mix #5 6250 µL of 2000 ug/mL 502.2 Cal. Mix #1 Dilute into methanol.	25 mL

	Samples			
Matrix Spike/Blank Spike Stock Solution - Full List for Water and Low Level Soil Samples	MS/BS Stock Solution - Full List for Water and Low Level Soil Samples	100 ug/mL all compounds except as follows: 1000 ug/mL Acrolein	1250 µL of 2000 ug/mL 502.2 Calibration Mix #1 - ICV 1250 µL of 2000 ug/mL 502.2 Cal 2000 Megamix - ICV 500 µL of 5000 ug/mL VOA Calibration Mix #1 - ICV 1250 µL of 2000 ug/mL Pace GB Custom Mix - ICV 250 µL of 10000 ug/mL Pace GB Custom Mix – Cyclohexanes - ICV 1250 µL of 20000 ug/mL Pace GB Custom Mix – Acrolein - ICV 1250 µL of 2000 ug/mL Pace GB Custom Mix - 2-Chloroethylvinyl ether - ICV 263 µL of 9520 ug/mL Vinyl Acetate Diluted into methanol	25 mL
Matrix Spike/Blank Spike Stock Solution - Full List for Methanol Preserved Soil Samples	MS/BS Stock Solution – Full List for Methanol Preserved Soil Samples	500 ug/mL all compounds except as follows: 5000 ug/mL Acrolein	6250 µL of 2000 ug/mL 502.2 Calibration Mix #1 - ICV 6250 µL of 2000 ug/mL 502.2 Cal 2000 Megamix - ICV 2500 µL of 5000 ug/mL VOA Calibration Mix #1 - ICV 6250 µL of 2000 ug/mL Pace GB Custom Mix - ICV 1250 µL of 10000 ug/mL Pace GB Custom Mix – Cyclohexanes - ICV 6250 µL of 20000 ug/mL Pace GB Custom Mix – Acrolein - ICV 6250 µL of 2000 ug/mL Pace GB Custom Mix - 2-Chloroethylvinyl ether - ICV 1315 µL of 9520 ug/mL Vinyl Acetate Diluted into methanol	25 mL
100 ug/mL Matrix Spike/Blank Spike Solution for Michigan List	MS/BS Stock Solution for Michigan List	100 ug/mL for all compounds	1250 µL of 2000 ug/mL Michigan GRO Mix Dilute into methanol.	25 mL
MS/MSD – BS/BSD Spike for Water Samples	MS/MSD BS/BSD	50 ug/L for most compounds, Various for others.	Add 21 µL of the appropriate Matrix Spike/Blank Spike Solution to 42 mL of sample for MS/MSD, or 42 mL of reagent water for BS/BSD	42 mL
MS/MSD – BS/BSD Spike for Low Level Soil Samples	MS/MSD BS/BSD	50 ug/kg for most compounds, Various for others.	Add 2.5 µL of the appropriate Matrix Spike/Blank Spike Solution to 5.0 g of sample containing 5 mL of reagent water for MS/MSD, or 5.0 g of Ottawa sand containing 5 mL of reagent water for BS/BSD	5 mL
MS/MSD – BS/BSD Spike for Methanol Preserved Soil Samples	MS/MSD BS/BSD	2500 ug/kgL for most compounds, Various for others.	Add 50 µL of the appropriate Matrix Spike/Blank Spike Solution to 10 g of sample containing 10 mL of methanol for MS/MSD, amount of Spike Solution is adjusted according to the initial methanol volume; or 10 g of Ottawa sand containing 10 mL of methanol for BS/BSD	10 mL

Table 9
EPA 624/SW846 8260B Calibration Standard Mixes

Vendor	Standard Name	Catalog#	Compound list	Concentration (ug/mL)
Restek	502.2 Cal Mix 1	30042	Dichlorodifluoromethane	2000
			Chloromethane	2000
			Vinyl Chloride	2000
			Bromomethane	2000
			Chloroethane	2000
			Trichlorofluoromethane	2000
Accustandard	502.2 Cal Mix 1 - ICV	M-502B-10X	Dichlorodifluoromethane	2000
			Chloromethane	2000
			Vinyl Chloride	2000
			Bromomethane	2000
			Chloroethane	2000
			Trichlorofluoromethane	2000
Restek	502.2 MegaMix	30431	1,1-Dichloroethene	2000
			Methylene Chloride	2000
			trans-1,2-Dichloroethene	2000
			1,1-Dichloroethane	2000
			2,2-Dichloropropane	2000
			cis-1,2-Dichloroethene	2000
			Chloroform	2000
			Bromochloromethane	2000
			1,1,1-Trichloroethane	2000
			1,1-Dichloropropene	2000
			Carbon Tetrachloride	2000
			1,2-Dichloroethane	2000
			Benzene	2000
			Trichloroethene	2000
			1,2-Dichloropropane	2000
			Bromodichloromethane	2000
			Dibromomethane	2000
			cis-1,3-Dichloropropene	2000
			Toluene	2000
			trans-1,3-Dichloropropene	2000
			1,1,2-Trichloroethane	2000
			1,3-Dichloropropane	2000
			Tetrachloroethene	2000
			Dibromochloromethane	2000
			1,2-Dibromoethane	2000
			Chlorobenzene	2000
			1,1,1,2-Tetrachloroethane	2000
			Ethylbenzene	2000
			m-Xylene	2000
			p-Xylene	2000
			o-Xylene	2000
			Styrene	2000
			Isopropylbenzene	2000
			Bromoform	2000
			1,1,2,2-Tetrachloroethane	2000
			1,2,3-Trichloropropane	2000
			n-Propylbenzene	2000
			Bromobenzene	2000
			1,3,5-Trimethylbenzene	2000
			2-Chlorotoluene	2000
			4-Chlorotoluene	2000
			1,2,3-Trimethylbenzene	2000
			sec-Butylbenzene	2000
			4-Isopropyltoluene	2000
			1,3-Dichlorobenzene	2000
			1,4-Dichlorobenzene	2000
			n-Butylbenzene	2000
			tert-Butylbenzene	2000
			1,2-Dichlorobenzene	2000
			1,2-Dibromo-3-chloropropa	2000
			1,2,4-Trimethylbenzene	2000
			Hexachloro-1,3-butadiene	2000
			Naphthalene	2000
			1,2,3-Trichlorobenzne	2000

Accustandard	502.2 MegaMix - ICV	M-502A-R-10X	1,1-Dichloroethene	2000
			Methylene Chloride	2000
			trans-1,2-Dichloroethene	2000
			1,1-Dichloroethane	2000
			2,2-Dichloropropane	2000
			cis-1,2-Dichloroethene	2000
			Chloroform	2000
			Bromochloromethane	2000
			1,1,1-Trichloroethane	2000
			1,1-Dichloropropene	2000
			Carbon Tetrachloride	2000
			1,2-Dichloroethane	2000
			Benzene	2000
			Trichloroethene	2000
			1,2-Dichloropropane	2000
			Bromodichloromethane	2000
			Dibromomethane	2000
			cis-1,3-Dichloropropene	2000
			Toluene	2000
			trans-1,3-Dichloropropene	2000
			1,1,2-Trichloroethane	2000
			1,3-Dichloropropane	2000
			Tetrachloroethene	2000
			Dibromochloromethane	2000
			1,2-Dibromoethane	2000
			Chlorobenzene	2000
			1,1,1,2-Tetrachloroethane	2000
			Ethylbenzene	2000
			m-Xylene	2000
			p-Xylene	2000
			o-Xylene	2000
			Styrene	2000
			Isopropylbenzene	2000
			Bromoform	2000
			1,1,2,2-Tetrachloroethane	2000
			1,2,3-Trichloropropane	2000
			n-Propylbenzene	2000
			Bromobenzene	2000
			1,3,5-Trimethylbenzene	2000
			2-Chlorotoluene	2000
			4-Chlorotoluene	2000
			1,2,3-Trimethylbenzene	2000
			sec-Butylbenzene	2000
			4-Isopropyltoluene	2000
			1,3-Dichlorobenzene	2000
			1,4-Dichlorobenzene	2000
			n-Butylbenzene	2000
			tert-Butylbenzene	2000
			1,2-Dichlorobenzene	2000
			1,2-Dibromo-3-chloropropa	2000
			1,2,4-Trimethylbenzene	2000
			Hexachloro-1,3-butadiene	2000
			Naphthalene	2000
			1,2,3-Trichlorobenzene	2000
Restek	Vinyl Acetate	30216	Vinyl Acetate	2000
Aldrich	Vinyl Acetate - ICV	V150-3	Vinyl Acetate	Neat
Restek	VoaCalMix 1	30008	Acetone	5000
			2-Butanone	5000
			4-Methyl-2-pentanone	5000
			2-Hexanone	5000
Accustandard	VoaCalMix 1 - ICV	CLP-022K-25X	Acetone	5000
			2-Butanone	5000
			4-Methyl-2-pentanone	5000
			2-Hexanone	5000
Restek	Pace-GB Custom	56230	1 1 2-TRICHLOROTRIFLUOROETHA	2000

	Mix		1 2 3-TRIMETHYLBENZENE	2000
			2 3-DICHLOROPROPENE	2000
			2-METHYLNAPHTHALENE	2000
			ACRYLONITRILE	2000
			ALLYL CHLORIDE	2000
			CARBON DISULFIDE	2000
			CIS-1 4-DICHLORO-2-BUTENE	2000
			DICHLOROFLUOROMETHANE	2000
			DIETHYL ETHER	2000
			DIISOPROPYL ETHER	2000
			ETHYL METHACRYLATE	2000
			HEXACHLOROETHANE	2000
			IODOMETHANE	2000
			METHYL METHACRYLATE	2000
			METHYL T-BUTYL ETHER	2000
			N-HEXANE	2000
			TETRAHYDROFURAN	2000
			TRANS-1 4-DICHLORO-2-BUTENE	2000
Accustandard	Pace-GB Custom	S-13659	1 1 2-TRICHLOROTRIFLUOROETHAI	2000
	Mix - ICV		1 2 3-TRIMETHYLBENZENE	2000
			2 3-DICHLOROPROPENE	2000
			2-METHYLNAPHTHALENE	2000
			ACRYLONITRILE	2000
			ALLYL CHLORIDE	2000
			CARBON DISULFIDE	2000
			CIS-1 4-DICHLORO-2-BUTENE	2000
			DICHLOROFLUOROMETHANE	2000
			DIETHYL ETHER	2000
			DIISOPROPYL ETHER	2000
			ETHYL METHACRYLATE	2000
			HEXACHLOROETHANE	2000
			IODOMETHANE	2000
			METHYL METHACRYLATE	2000
			METHYL T-BUTYL ETHER	2000
			N-HEXANE	2000
			TETRAHYDROFURAN	2000
			TRANS-1 4-DICHLORO-2-BUTENE	2000
Restek	Pace-GB Custom	58314	CYCLOHEXANE	10000
	Mix - Cyclohexanes		METHYL ACETATE	10000
			METHYLCYCLOHEXANE	10000
Accustandard	Pace-GB Custom	S-7134-R1-5X	CYCLOHEXANE	10000
	Mix - Cyclohexanes - ICV		METHYL ACETATE	10000
			METHYLCYCLOHEXANE	10000
Restek	Pace-GB Custom	553772	1 4-DIOXANE	100000
	Mix - Nelap		1-PROPANOL	100000
			AMYL ACETATE	2000
			BUTYL ACETATE	2000
			CYCLOHEXANONE	20000
			ETHYL ACETATE	20000
			ISOAMYL ACETATE	2000
			ISOPROPANOL	20000
			N-BUTANOL	100000
			N-HEPTANE	2000
			N-PROPYL ACETATE	2000
			ISOPROPYL ACETATE	2000
Accustandard	Pace-GB Custom	S-13661	1 4-DIOXANE	100000
	Mix - Nelap - ICV		1-PROPANOL	100000
			AMYL ACETATE	2000
			BUTYL ACETATE	2000
			CYCLOHEXANONE	20000
			ETHYL ACETATE	20000
			ISOAMYL ACETATE	2000
			ISOPROPANOL	20000
			N-BUTANOL	100000
			N-HEPTANE	2000

			N-PROPYL ACETATE	2000
			ISOPROPYL ACETATE	2000
Restek	Pace-GB Custom	52995	ACROLEIN	20000
	Acrolein			
Accustandard	Pace-GB Custom	QM-8015B/5031-03-2X	ACROLEIN	20000
	Acrolein - ICV			
Restek	Pace-GB Custom	30265	2-CHLOROETHYLVINYL ETHER	2000
	2-chloroethylvinyl ether			
Accustandard	Pace-GB Custom	M-601C-10X	2-CHLOROETHYLVINYL ETHER	2000
	2-chloroethylvinyl ether - ICV			
Restek	Pace-GB Custom	58998	ACETONITRILE	5000
	Mix - Appendix IX		CHLOROPRENE	5000
			PROPIONITRILE	5000
			ISOBUTANOL	20000
			METHACRYLONITRILE	5000
Accustandard	Pace-GB Custom	S-13660	ACETONITRILE	5000
	Mix - Appendix IX - ICV		CHLOROPRENE	5000
			PROPIONITRILE	5000
			ISOBUTANOL	20000
			METHACRYLONITRILE	5000
Restek	California Oxygenates	30465	DIISOPROPYL ETHER	2000
	Mix		ETHYL TERT BUTYL ETHER	2000
			TERT AMYL METHYL ETHER	2000
			TERT BUTYL ALCOHOL	10000
			METHYL TERT BUTYL ETHER	2000
Accustandard	California Oxygenates	OGAD-001	DIISOPROPYL ETHER	2000
	Mix - ICV		ETHYL TERT BUTYL ETHER	2000
			TERT AMYL METHYL ETHER	2000
			TERT BUTYL ALCOHOL	10000
			METHYL TERT BUTYL ETHER	2000

Table 10
Calibration and Standardization

Analytical Method Acceptance Criteria⇨ Calibration Measure ⇩	Frequency	Accpetance Criteria
Initial Calibration	• Installation of new column or trap • Creation of new analytical method • CVS fails criteria • BFB tuning criteria fails and GCMS is retuned • GCMS is retuned	• % RSD ≤ 15% for every compound; 30% for CCCs • RF SPCCs = 0.300 for: Chlorobenzene, 1,1,2,2-Tetrachloroethane • RF= 0.100 for: Chloromethane, 1,1-Dichloroethane, Bromoform • Use of Average Response factors if: %RSD is ≤15% for all reportable compounds or the mean % RSD of all calibrated compounds is ≤15%. Otherwise, use Linear Regression or Quadratic Fit and Correlation Coefficient is ≥ 0.9900.
Independent Calibration Verification Standard	• After every valid initial calibration	• RF of ICVS must be ≤ 20% from initial calibration.
Continuing Calibration Verification	• At the beginning of every 12 hour time clock or analytical sequence.	• RF of CCV must be ≤ 20% from initial calibration.
Laboratory Control Spike and Duplicate	• One pair per batch of samples, up to 20 environmental samples, whichever is more frequent. Fortify with 5 classic spikes	• Recovery must be within 85-115 % for all compounds.
Matrix Spike and Duplicate	• One pair per batch of samples, up to 20 environmental samples, whichever is more frequent. Fortify with all target compounds.	• In house limits determined.
Internal Standards	• Added to every sample.	• Retention Time must be ± 30 seconds from the last CVS • Area of IS must be -50% to +100%
Surrogate Standards	• Added to every sample.	• In house limits determined.

Table 11
Quality Control

Preparation Method ⇨ Quality Control Measure ⇩	SW846 5030	SW846 5030B	SW846 5035	EPA 624
Initial Calibration	Minimum of five levels; lowest level near but above MDL	Minimum of five levels; lowest level near but above MDL	Minimum of five levels; lowest level near but above MDL	Minimum of five levels; lowest level near but above MDL
Method Blank	One per batch of samples, up to 20 environmental samples, whichever is more frequent.	One per batch of samples, up to 20 environmental samples, whichever is more frequent.	One per batch of samples, up to 20 environmental samples, whichever is more frequent.	One per batch of samples, up to 20 environmental samples, whichever is more frequent.
Continuing Calibration Verification	Mid-level calibration standards run at the beginning of each 12 hour time clock.	Mid-level calibration standards run at the beginning of each 12 hour time clock.	Mid-level calibration standards run at the beginning of each 12 hour time clock.	Mid-level calibration standards run at the beginning of each 12 hour time clock.
Independent Calibration Verification	Mid-level calibration standard from an independent source to verify initial calibration curve.	Mid-level calibration standard from an independent source to verify initial calibration curve.	Mid-level calibration standard from an independent source to verify initial calibration curve.	Mid-level calibration standard from an independent source to verify initial calibration curve.
Laboratory Control Spike and Duplicate	One pair per batch of samples, up to 20 environmental samples, whichever is more frequent.	One pair per batch of samples, up to 20 environmental samples, whichever is more frequent.	One pair per batch of samples, up to 20 environmental samples, whichever is more frequent.	One pair per batch of samples, up to 20 environmental samples, whichever is more frequent.
Matrix Spike and Duplicate	One pair per batch of samples, up to 20 environmental samples, whichever is more frequent.	One pair per batch of samples, up to 20 environmental samples, whichever is more frequent.	One pair per batch of samples, up to 20 environmental samples, whichever is more frequent.	One pair per batch of samples, up to 20 environmental samples, whichever is more frequent. .
Internal Standards	Added to every sample.	Added to every sample.	Added to every sample.	Added to every sample.
Surrogate Standards	Added to every sample.	Added to every sample.	Added to every sample.	Added to every sample.

Table 12
ANALYST/TECHNICIAN DATA ASSESSMENT

Analytical Method Acceptance Criteria⇨ Data Assessment Measure ⇩	**Method Citation SW If these conditions are not achieved ⇒**	**Method Citation EPA If these conditions are not achieved ⇒**
Initial Calibration	• 1	• 1
Initial Calibration Verification	• 1	• 1
Calibration Blank	• 1	• 1
Method Blank	• 2	• 2
Internal Standard Area	• 3	• 3
Continuing Calibration Verifications	• 4	• 4
Surrogate Recovery	• 5	• 5
Accuracy & Precision Laboratory Control Spikes	• 6	• 6
Accuracy & Precision Matrix Spikes	• 7	• 7

1. Check instrumentation/equipment condition; enter maintenance in instrument log; perform another initial calibration. No data can be reported. Generate on Non-Conformance Memo.

2. In the absence of project specific requirements, sample detects greater than 20 times the method blank contamination level are reported with those not exceeding 20 times re-analyzed or qualified. Generate on Non-Conformance Memo.

3. In the absence of project specific requirements, check to be sure that there are no errors in the calculations. If errors are found, recalculate the data accordingly. Examine chromatograms for interfering peaks and integrated peak areas. Re analyze sample if volume allows. Generate on Non-Conformance Memo.

4. In the absence of project specific requirements, immediately after the flawed CCV analyze another CCV or re-analyzed all samples set after the last acceptable CCV. Generate on Non-Conformance Memo.

5. In the absence of project specific requirements, check to be sure that there are no errors in the calculations. If errors are found, recalculate the data accordingly. Examine chromatograms for interfering peaks and integrated peak areas. If the program allows report the concentrations noting the surrogate recovery is most likely due to co-elution with target compounds. Some samples may require dilution in order to bring one or more target analytes within the calibration range or to overcome significant interferences with some analytes. Re analyze sample if volume allows. If the surrogate recoveries are available from a less-diluted or undiluted aliquot of the sample or sample extract, those recoveries may be used to demonstrate that the surrogates were within the in-house QC limits, and no further action is required. If, upon re-analysis the recovery is again not within limits, report the data as an "estimated concentration." If the recovery is within the limits in the re-analysis, provide the re-analysis data to the data user. Generate on Non-Conformance Memo.

6. In the absence of project specific requirements, the LCS and LCSD are spiked with the same analytes at the same concentrations as the matrix spike. When the results of the matrix spike analysis indicate a potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix. If the LCS and LCSD recoveries do not meet those limits as required in the method or program, the samples shall be re-analyzed. If sample volume does not allow re-analysis the entire prep/analytical batch of samples shall be flagged to reflect the deficiencies. Generate on Non-Conformance Memo.

7. In the absence of project specific requirements, when the results of the matrix spike analysis indicate a potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix. If sample volume allows re-analysis, it shall be performed to verify the matrix effect. When sample volume does not re-analysis, the parent sample and samples from that project site shall be flagged to reflect the deficiencies. Generate a Non- Conformance Memo.

Table 13
ANALYST/SUPERVISOR DATA ASSESSMENT

Analytical Method Acceptance Criteria⇨ Data Assessment Measure ⇩	**Method Citation SW If these conditions are not achieved ⇒**	**Method Citation EPA If these conditions are not achieved ⇒**
Initial Calibration	• 1	• 1
Initial Calibration Verification	• 1	• 1
Calibration Blank	• 1	• 1
Method Blank	• 2	• 2
Internal Standard Area	• 3	• 3
Continuing Calibration Verifications	• 4	• 4
Surrogate Recovery	• 5	• 5
Accuracy & Precision Laboratory Control Spikes	• 6	• 6
Accuracy & Precision Matrix Spikes	• 7	• 7

1. Check instrumentation/equipment condition; enter maintenance in instrument log; perform another initial calibration. No data can be reported. Generate on Non-Conformance Memo.

2. In the absence of project specific requirements, sample detects greater than 20 times the method blank contamination level are reported with those not exceeding 20 times re-analyzed or qualified. Generate on Non-Conformance Memo.

3. In the absence of project specific requirements, check to be sure that there are no errors in the calculations. If errors are found, recalculate the data accordingly. Examine chromatograms for interfering peaks and integrated peak areas. Re analyze sample if volume allows. Generate on Non-Conformance Memo.

4. In the absence of project specific requirements, immediately after the flawed CCV analyze another CCV or re-analyzed all samples set after the last acceptable CCV. Generate on Non-Conformance Memo.

5. In the absence of project specific requirements, check to be sure that there are no errors in the calculations. If errors are found, recalculate the data accordingly. Examine chromatograms for interfering peaks and integrated peak areas. If the program allows report the concentrations noting the surrogate recovery is most likely due to co-elution with target compounds. Some samples may require dilution in order to bring one or more target analytes within the calibration range or to overcome significant interferences with some analytes. Re analyze sample if volume allows. If the surrogate recoveries are available from a less-diluted or undiluted aliquot of the sample or sample extract, those recoveries may be used to demonstrate that the surrogates were within the in-house QC limits, and no further action is required. If, upon re-analysis the recovery is again not within limits, report the data as an "estimated concentration." If the recovery is within the limits in the re-analysis, provide the re-analysis data to the data user. Generate on Non-Conformance Memo.

6. In the absence of project specific requirements, the LCS and LCSD are spiked with the same analytes at the same concentrations as the matrix spike. When the results of the matrix spike analysis indicate a potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix. If the LCS and LCSD recoveries do not meet those limits as required in the method or program, the samples shall be re-analyzed. If sample volume does not allow re-analysis the entire prep/analytical batch of samples shall be flagged to reflect the deficiencies. Generate on Non-Conformance Memo.

7. In the absence of project specific requirements, when the results of the matrix spike analysis indicate a potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix. If sample volume allows re-analysis, it shall be performed to verify the matrix effect. When sample volume does not re-analysis, the parent sample and samples from that project site shall be flagged to reflect the deficiencies. Generate a Non- Conformance Memo.

Table 14
REPORT REVIEWER/PROJECT MANAGEMENT DATA ASSESSMENT

Analytical Method Acceptance Criteria⇨ Data Assessment Measure ⇩	**Method Citation SW If these conditions are not achieved ⇒**	**Method Citation EPA If these conditions are not achieved ⇒**	**Method Citation EPA If these conditions are not achieved ⇒**
Holding Time Compliance	• 1	• 1	•
Sample Receipt Conditions and Preservation	• 2	• 2	•
Method Citation	• 3	• 3	•
Reasonableness: Field Duplicate	• 4	• 4	•
Reasonableness: Analytical Comments Qualifications	• 5	• 5	•

1. Flag results with an H and the number of days past hold in parenthesis e.g. H(5).
2. In prose describe the receipt conditions as they relate to the acceptance criteria list in Table G
3. Compare to regulatory program in QAPjP or Chain of Custody.
4. Are duplicate with 40% agreement. If not, internally flag for review.
5. Do related suites of tests agree or are reasonable.

Table 15
CORRECTIVE ACTIONS

Analytical Method Acceptance Criteria⇨ Quality Control Measure ⇩	**Method Citation SW If these conditions are not achieved ⇒**	**Corrective Action (Key below)**	**Method Citation EPA If these conditions are not achieved ⇒**	**Corrective Action (Key below)**
Initial Calibration		• 1	•	• 1
Method Blank		• 2	•	• 2
Continuing Calibration Verification		• 3	•	• 3

1. Check instrumentation/equipment condition; enter maintenance in instrument log; perform another initial calibration

2. Samples detects greater than 20 times the method blank contamination level are reported with those not exceeding 20 times re-analyzed or qualified.

3. Immediately after the flawed CCV analyze another CCV or re-analyzed all samples set after the last acceptable CCV.

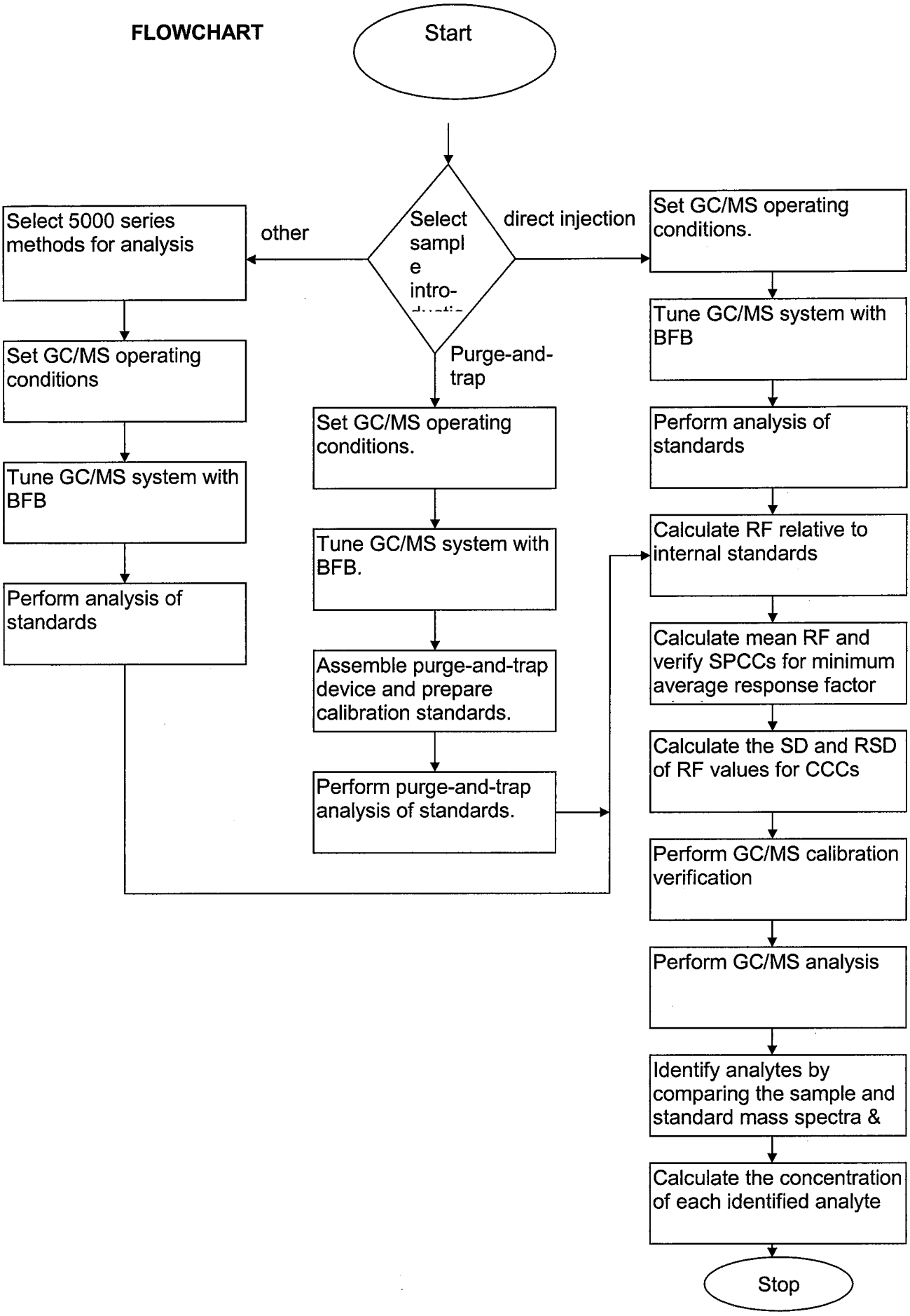
Table 16
CONTINGENCIES FOR HANDLING OUT-OF-CONTROL OR UNACCEPTABLE DATA

Analytical Method Acceptance Criteria⇨ Quality Control Measure ⇩	Method Citation SW If these conditions are not achieved ⇒	Corrective Action (Key below)	Method Citation EPA If these conditions are not achieved ⇒	Corrective Action (Key below)
Matrix Spike and Duplicate	•	• 1	•	• 1
Internal Standards	•	• 2	•	• 2
Surrogate Standards	•	• 2	•	• 2

1. If Lab Control Spikes pass acceptance criteria, flag parent sample and samples from the entire project with a QC batch associated with analysis indicated matrix effects.

2. When sample volume is available reanalyze the samples. If the second analysis indicates the same internal standard recoveries add analytical comments and effects on data.

FLOWCHART


Start
Select sampl e intro-
other
direct injection
Purge-and-trap
Select 5000 series methods for analysis
Set GC/MS operating conditions
Tune GC/MS system with BFB
Perform analysis of standards
Set GC/MS operating conditions.
Tune GC/MS system with BFB.
Assemble purge-and-trap device and prepare calibration standards.
Perform purge-and-trap analysis of standards.
Set GC/MS operating conditions.
Tune GC/MS system with BFB
Perform analysis of standards
Calculate RF relative to internal standards
Calculate mean RF and verify SPCCs for minimum average response factor
Calculate the SD and RSD of RF values for CCCs
Perform GC/MS calibration verification
Perform GC/MS analysis
Identify analytes by comparing the sample and standard mass spectra &
Calculate the concentration of each identified analyte
Stop

18. Revisions

Document Number	Reason for Change	Date
ALL-GB-O-002-rev.1	Added Oxygenates to Tables 1 and 2 Updated Tables 6, 7, and 8 Inserted Table 9 Renumbered Tables 10 through 16 Added EPA 624 to references	**06June2006**

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STANDARD OPERATING PROCEDURE

Determination of Polynuclear Aromatic Hydrocarbons (PAH) in Water by GC/MS SIM

Reference Method: SW-846 Method 8270C

SOP NUMBER:	GB-O-003-rev.1
EFFECTIVE DATE:	Date of Final Signature
SUPERSEDES:	GB-O-003-rev.0

APPROVAL

Nils Melberg, Assistant Laboratory Manager	8/11/05 Date
Bruce Warden, General Manager	7/13/05 Date
Arthur F. Lautenbach, Quality Manager	7/12/05 Date

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1. Purpose

This Standard Operating Procedure (SOP) is used to determine the concentration of Polynuclear Aromatic Hydrocarbon (PAH) compounds in water samples compliant with SW-846 Method 8270C.

2. Scope and Application

2.1. This method may be used to determine concentrations of polynuclear aromatic hydrocarbon compounds in extracts prepared from water samples. Analytes must be soluble in dichloromethane and amenable to capillary gas chromatography. . A list of applicable compounds and their CAS numbers are shown in Table 1. Pace Reporting Levels (PRLs) are also shown for water samples. PRLs are subject to change based on current analytical system performance and actual sample matrices.

2.2. The procedures for extract preparation are described in separate SOPs. The applicable sample preparation method is SW-846 3510C.

2.3. This procedure is restricted to use by, or under the supervision of, analysts experienced in the use of GC/MS systems and interpretation of GC/MS data. Each analyst must demonstrate the capability to generate acceptable results with this method to be considered qualified to report sample results.

3. Summary of Methods

3.1. Sample extracts are prepared for analysis by an appropriate sample preparation method.

3.2. The semivolatile organic compounds are introduced into the gas chromatograph (GC) by injecting an aliquot of the sample extract. The GC column temperature is programmed to separate the analytes. The GC effluent is directly introduced to a mass spectrometer (MS) for both identification and quantification of analytes.

3.3. Analytes are identified by comparison of their mass spectra with spectra of authentic standards. Analytes are quantified by comparing the response of a selected major (quantitation) ion relative to an internal standard using a five-point calibration curve. Major and secondary quantitation ions for each applicable compound are shown in Table 2.

4. Interferences

4.1. Interferences may be introduced into sample extracts by contaminants in solvents, reagents, glassware, and any other material that comes in contact with the sample or extract during extract preparation. These interferences must be closely monitored by analyzing Method Blank samples and taking corrective action as required.

4.2. Matrix interferences may result from materials co-extracted from some samples.

4.3. Contamination by carryover can occur when high concentration extracts are analyzed prior to low concentration extracts. The contamination may also cause degradation of labile analytes. Whenever carryover is suspected, the effected extracts should be re-analyzed. If significant degradation of the GC/MS systems is suspected, system performances samples should be analyzed and corrective action taken as needed.

5. Safety

5.1 The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable. Cautions are included for known extremely hazardous materials.

5.2 A reference file of Material Safety Data Sheets (MSDS) is made available to all personnel involved in the chemical analysis, and is located at the front desk. A formal safety plan has been prepared and is distributed to all personnel with documented training.

6. Definitions

6.1. **Batch** – A grouping of 20 samples, or less, of similar matrix which are prepared and/or analyzed together with the same method and the same lots of reagents within the same time frame, as designated by the method.

6.2. **Blank Sample** – A sample analyzed to detect and/or monitor the potential contamination by target analytes and other interferences attributable to instrumental background and sample handling, including sampling, sample shipping and storage, and analysis.

6.3. **Duplicate Sample** – A second aliquot of the same field sample analyzed in the same manner as the original sample in order to evaluate precision.

6.4. **Environmental Sample** – An environmental sample or field sample is a representative sample of any material (aqueous, non-aqueous, or multimedia) collected from any source for which determination of composition or contamination is requested or required.

6.5. **Extract** – A solution of contaminants extracted and concentrated from a sample.

6.6. **Internal Standard (IS)** – Analytes added to every standard, blank, lab control sample, matrix spike, matrix spike duplicate, and sample at a known concentration, prior to analysis for the purpose of adjusting the response factor used in quantifying target analytes.

6.7. **Laboratory Control Sample (LCS)** – A blank sample spiked with a known concentration of analytes of interest.

6.8. **Laboratory Information Management System (LIMS)** – A system for transferring, processing, storing, and reporting analysis results.

6.9. **Lot** – A quantity of bulk material of similar composition processed or manufactured at the same time.

6.10. **Matrix Spike (MS)** – Aliquot of sample spiked with known quantities of specified target compounds and subjected to the entire sample preparation and analysis procedure. The analysis results from a matrix spike sample is compared to results from an unspiked aliquot of the same sample to determine recovery of the spike. Spike recoveries are used to evaluate method accuracy.

6.11. **Matrix Spike Duplicate (MSD)** – A second aliquot of the sample that is treated the same as the original matrix spike sample. The relative percent difference between the matrix spike and matrix spike duplicate is calculated and used to assess method precision.

6.12. **Method Blank (MB)** – A blank sample prepared in the laboratory containing all reagents, internal standards and surrogate standards, that is carried through the entire analytical procedure. The method blank is used to evaluate laboratory background and contamination.

6.13. **Method Detection Limit (MDL)** – The minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero. Method detection limits are determined by analyzing replicate spike samples prepared by the lab and taken through all preparation and analysis steps of the method. The method detection limit is calculated using the appropriate Student's t-parameter times the standard deviation of a series of spiked samples.

6.14. **Replicate Samples** – Samples collected at the same time, from the same place, for the same analysis, as the original sample in order to determine precision between samples.

6.15. **Pace Reporting Limit (PRL)** – The lowest level that will be reported by this method. Reporting limits are at least two times the MDL. Reporting limits are corrected for sample amounts, including the dry weight of solids, unless otherwise specified.

6.16. **Surrogate Compounds** – These are compounds added to every blank, sample, matrix spike, matrix spike duplicate, lab control sample, and standard prior to any processing or preparation. Surrogate compounds are not expected to be detected in environmental samples, but are similar to the analytes of interest. The percent recoveries of surrogates are used to evaluate accuracy for each sample.

6.17. **Tune Period** – The 12-hour analysis period between instrument tune checks.

7. Responsibilities and Distribution

7.1. **Analyst** – Any analyst using this procedure is responsible for reading, understanding and following this SOP and the associated Work Processing and Training Document. Any deviation from this SOP must be reported to the appropriate Supervisor. The analyst must make their recommendations for changing the SOP to their supervisor or the QM in writing.

7.2. **Semivolatile Organic Supervisor** – The supervisor must ensure that all analysts are properly trained and qualified to use this procedure. The supervisor is also responsible to ensure that the SOP is followed. The supervisor is responsible for reviewing the SOP and communicating recommended changes to the LQM.

7.3. **Quality Manager (QM)** – The QM is responsible for monitoring the implementation of the SOPs and the associated good laboratory practice. The QM shall participate in the revision of the SOP and make sure it is current. The QM shall review and approve all SOPs.

7.4. **Laboratory General Manager (GM)** – The Laboratory General Manager has overall responsibility for ensuring that SOPs are prepared and implemented for all activities appropriate to the region. The Laboratory General Manager shall review and approve all SOPs.

7.5. **Director of Quality, Safety, and Training (QST)** – The Director of QST has oversight responsibility for Pace Analytical's quality programs, including establishing and monitoring compliance with all quality system requirements.

7.6. **Chief Operating Officer (COO)** – The COO has oversight responsibility for Pace Analytical environmental laboratory operations, including compliance with all quality system requirements.

7.7. **Distribution** – The official version of this SOP is the signed hardcopy version found in the laboratory, complete the addendum. A copy of the SOP shall be kept in the appropriate department for reference.

7.8. **Revision** – This SOP will be reviewed every two years at a minimum. Independent of the minimum review frequency, revisions will be incorporated as needed if procedures or methods change.

8. Sample Collection, Preservation, and Handling

8.1. **General Procedures** – Procedures for sample collection, preservation, and handling are described in the separate sample preparation SOPs.

8.2. **Holding Times**

8.2.1. **Water Samples** – Samples must be extracted within 7 days of collection.

8.2.2. **Extracts** – Extracts must be analyzed within 40 days of preparation.

8.3. **Sample Storage** – Store all samples at 4 ± 2°C. Extracts are to be stored at <0C.

9. Equipment and Supplies

9.1. **GC/MS System** – The complete GC/MS system must include an autosampler and GC/MS with associated Data System. The specific system components and operating parameters that will be used with this method are shown in the Table 3.

9.2. **Glassware and Materials**

9.2.1. **Syringes** – 10-µL, 25-µL, 50-µL, 100-µL, 250-µL, 500-µL, and 1,000-µL, as needed, Hamilton or equivalent.

9.2.2. **Clear Vials** – 2-mL with PTFE-lined caps.

10. Reagents and Standards

10.1. **Dichloromethane** – Pesticide quality, or equivalent.

10.2. **Analytical Standards**
Standards are required for mass spectrometer tuning, initial calibration, calibration verification, internal standards, surrogates, and for preparing LCS, MS, and MSD samples. The following describes the contents of each type of solution.

10.2.1. **Tune Standard** – Decafluorotriphenylphosphine (DFTPP) in dichloromethane.

10.2.2. **Calibration Standards** – At least 5 concentration levels of calibration solutions are prepared containing all target compounds for which the calibration is applied.

10.2.3. **Initial Calibration Verification Standard** – This solution contains mid-level concentrations of analytes in dichloromethane and is used to verify the analytical system calibration. The initial calibration verification standard must be prepared from source materials independent of the calibration standards. It must contain all of the PAH compounds that are being analyzed. All compounds are treated as System Performance Check Compounds (SPCC) and Calibration Check Compounds (CCC).

10.2.4. **Continuing Calibration Verification Standard** – This solution contains mid-level concentrations of analytes in dichloromethane and is used to verify the analytical system calibration. It must contain all of the PAH compounds that are being analyzed. All compounds are treated as System Performance Check Compounds (SPCC) and Calibration Check Compounds (CCC).

10.2.5 **Internal Standards** – This solution contains the following compounds in dichloromethane and is spiked into all working standards and sample

extracts.

Naphthalene-d_8
Acenaphthene-d_{10}
Phenanthrene-d_{10}
Chrysene-d_{12}
Perylene-d_{12}

10.2.6 **Surrogate Standards** – This solution contains the following compound in dichloromethane and is spiked into all samples prior to extract preparation.

Nitrobenzene-d_5
2-Fluorobiphenyl
Terphenyl-d_{14}

10.2.7 **LCS, MS, and MSD Spiking Solution** – These solutions must contain all of the target compounds.

10.3 Preparation of Analytical Standard Solutions

Standards are prepared from commercially available multi-compound stock solutions. The sources of materials, recipes for preparing dilutions and working standards, and concentrations for all compounds are presented below. All standards are prepared using dichloromethane and stored in clear vials with PTFE lined caps Storage and Stability of Analytical Standards - All standards must be stored in the dark at less than –10 °C or at a temperature recommended by the manufacturer. They should be replaced every 6 months, or sooner if the standards show signs of degradation. As each standard, from the vendor is opened, record all pertinent information in the stock standard logbook. Record all standard preparations in the working standard logbook.

10.3.1 **DFTPP tuning standard**
A Dichloromethane solution containing 50ng/uL of decafluorotriphenylphosphine(DFTPP) is prepared. A stock solution; Restek cat.# 31001; containing DFTPP at 2500ug/mL, is diluted taking 0.500mL and diluting to 25mL of dichloromethane.

10.3.2 **Internal Standard solution**
Stock solution obtained from Restek cat.#31006 containing 1,4-Dichlorobenzene-d4, Naphthalene-d8, Acenaphthene-d10, Phenanthrene-d10, Chrysene-d12 and Perylene-d12 all at 4000ug/mL in dichloromethane. This intermediate standard is prepared by diluting 50uL upto 10mLs of dichloromethane, producing a solution that is 20ug/mL for each component. 10uL of this standard is added to 1mL of every standard, sample, spike and blank analyzed by this method. Producing a on column concentration of 200ug/L.

10.3.3 **Surrogate Standard solution**
Stock Solution obtained from Restek, cat. #31082 containing 1,2-Dichlorobenzene-d4, Nitrobenzene-d5, 2-Fluorobiphenyl and p-Terphenyl-

d14 all at 5000ug/mL in dichloromethane. An intermediate standard is prepared by diluting 300uL up to 10mLs of dichloromethane, producing a standard that is 150ug/mL of each component. This intermediate is further diluted to produce the daily working standard by diluting 66.7uL of the 150ug/mL intermediate to 50mLs of Dichloromethane. 1.0mL of this daily working standard is spiked into all QC and Samples, producing an on column value of 200ug/L.

10.3.4 **Initial Calibration Intermediate Standard**
Stock solution is obtained from Accustandard, product # M-610-FL-R-5X, containing the 18 PAH compounds, all at 500ug/mL. The intermediate is prepared by diluting 10uL of the 500ug/L PAH stock, along with 33.5uL of the 150ug/L surrogate intermediate(10.3.3) upto 10.0mLs dichloromethane, producing a intermediate calibration standard that is 500ug/L of all components.

10.3.5 **Initial Calibration Working Standards**
The following working calibration standards are prepared by using the intermediate mix listed above (10.3.4):

Standard Concentration (ug/L)	Amount of Intermediate Standard added	Amount of Intermediate Internal Standard added	Final Volume
25	50uL	10uL	1000uL
50	100uL	10uL	1000uL
100	200uL	10uL	1000uL
200	400uL	10ul	1000uL
300	600uL	10uL	1000uL
500	1000uL	10uL	1000uL
Daily Cal 200	400uL	10uL	1000uL

10.3.6 **Initial Calibration Verification Standard**

Stock Solution is obtained from Supelco, cat# 47543-U, containing the 18 PAH compounds all at 2000ug/mL. A working solution is prepared by diluting 5uL of the 2000ug/mL PAH stock, along with 67uL of the 150ug/mL B/N surrogate intermediate(10.3.3) up to 50mLs with dichloromethane. This produces an ICV with a concentration of 200ug/L.

10.3.7 **LCS/MS Spiking Standard**

Stock solution is obtained from Accustandard, product # M-610-FL-R-5X, containing the 18 PAH compounds, all at 500ug/mL. Intermediate standard is prepared by diluting 10uL of the 500ug/mL upto 25.0mLs with Dichloromethane. 1.0 mL of this standard is spiked into all Lab Control and Matrix Spikes, producing a on-column concentration of 200ug/L.

11. Calibration

11.1. **Tuning** – At the beginning of each tune period, the mass spectrometer must be tuned with a solution containing 50 ng of DFTPP to meet specific ion abundance criteria shown in the following table.

Mass Peak (m/z)	Ion Abundance Criteria
51	30.0-80.0% of m/z 198
68	<2.0% of m/z 69
69	Present
70	<2.0% of m/z 69
127	25.0-75.0% of m/z 198
197	<1.0% of m/z 198
198	Base peak, 100% relative abundance
199	5.0-9.0% of m/z 198
275	10.0-30.0% of m/z 198
365	>0.75% of m/z 198
441	Present, but less than m/z 443
442	40.0-110.0% of m/z 198
443	15.0-24.0% of m/z 442

11.2. **Initial Calibration (ICAL)**

11.2.1. **Analysis of Standards** – Analyze at least 5 levels of calibration standards to define the calibration range. The lowest concentration should be at the target PRL.

11.2.2. **Response Factors** – Tabulate the area response of the characteristic ions against concentration for each compound and each internal standard. Calculate response factors (RF's) for each compound relative to the assigned internal standards. The assignments of analytes for each internal standard are shown in Table 4. Response factors are calculated using the

following equation. Also, calculate the mean and relative standard deviation (RSD) of the response factors for all analytes.

$$RF = \frac{A_x C_{is}}{A_{is} C_x}$$

where:
A_x = Area of the characteristic ion for the compound being measured.
A_{is} = Area of the characteristic ion for the specific internal standard.
C_{is} = Concentration of the specific internal standard (ng/µL).
C_x = Concentration of the compound being measured (ng/µL).

11.2.3 **Linear Regression** - The linear equation regression will produce the slope and intercept in the following form:

$$y = ax + b$$

Where:

y = Instrument response
a = Slope of the line
x = Concentration of the calibration standard
b = The intercept

In calculating sample concentration by the internal standard method, the regression equation is as follows:

$$C_s = \frac{\frac{A_s C_{is}}{A_{is}} - b}{a}$$

where:

A_s = Area of the peak for the target analyte in the sample
A_{is} = Area of the peak of the internal standard
C_s = Concentration of the target analyte in the calibration standard
C_{is} = Concentration of the internal standard
a = Slope of the line
b = the intercept

11.2.4 **Acceptance Criteria**

11.2.4.1 **Response Factors** -- The RSD for each analyte must be less than 30% for all compounds. If the average RSD for all analytes is <15%, average RFs may be used to quantitate all analytes. A linear curve maybe used if the RSD is >15%, but <30%. The correlation coefficient of a linear curve must be >0.99.

11.2.4.2 **SPCC's** – The average RF for all compounds must be at ≥0.050. If this criteria is not met, corrective action must be taken.

11.3. **Calibration Verification**

11.3.1. **Analysis of Calibration Verification Standard** – Analyze the Calibration Verification Standard.

11.3.2. **Acceptance Criteria --**

11.3.2.1. **SPCC's** – All compounds are treated as SPCCs therefore the response factor for each compound must ≥0.050. Otherwise, corrective action must be taken and the system re-calibrated.

11.3.2.2. **CCC's** – All compounds are treated as CCCs, therefore if the difference for each compound is ≤20%, the initial calibration is assumed to be valid. Otherwise, corrective action must be taken and the system re-calibrated.

11.3.2.3. **Internal Standard Responses and Retention Times** – Internal standard areas for all CVS's must be within the range of –50% to +100% and retention times must be within 30 seconds compared to the midpoint standard of the most recent ICAL. If these criteria are not met, check system parameters, identify and correct likely causes, and re-analyze the Calibration Verification Standard. If the IS results from the second analysis are out of control, initial calibration must be re-initiated.

12. Procedure

12.1. **Sample Extract Preparation** – All sample extracts and standard solutions must be allowed to warm to room temperature before analysis.

12.2. **Internal Standard Spiking** – Prior to analysis, each sample, MB, LCS, MS, and MSD is spiked with 10uL of the internal standard solution (10.3.2).

12.3. **GC/MS System Preparation**

12.3.1. **Operating Parameters** – Set up the instrument parameters shown in Table 3.

12.3.2. **System Tuning and GC Performance Checks** – Analyze the Tuning Solution and tune the mass spectrometer to meet the criteria shown in Section 11.1. Verify acceptable GC system performance as described in Section 11.2. Print out a tune report.

12.4. **Batch Sequence** – Generate a sequence to run a batch of samples.

12.4.1. Initial Calibration - The typical batch for initial calibration should include:

Tune Standard
Calibration Level 1
Calibration Level 2
Calibration Level 3
Calibration Level 4
Calibration Level 5
Calibration and System Performance Solution

12.4.2. **Sample Analysis** – The typical batch for sample analysis should include the following. Preparation of LCS, MS, MSD, and Duplicate sample extracts is described in the appropriate sample preparation SOP.

Tune Standard
Calibration and System Performance Solution
Instrument Blank
Method Blank
Laboratory Control Sample
Laboratory Control Sample Duplicate
20 samples
Matrix Spike
Matrix Spike Duplicate

12.5. **Autosampler** – Load the autosampler with standards and samples for the batch created above.

12.6. **Analyze Samples** – Analyze all standards, quality control samples, and environmental samples.

12.7. **Qualitative Analysis of Results** – The following retention time criteria must be met to identify target compounds.

12.7.1. **Retention Time Comparison** – The relative retention time (RRT) of the sample component must be within ±0.06 RRT units of the RRT of the component in the calibration verification standard. Extracted Ion Current Plots (EICPs) may be used to provide a more reliable assignment of retention time in the presence of coeluting components.

12.7.2 **Structural isomers** that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the sum of the two peak heights. When daily check standard meet criteria for resolution, nothing will be done. When daily check standard does not meet the method requirement for resolution, samples running under that check standard will be flagged stating the method requirement for resolution was not met for affected compounds.

12.7.3 Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When gas chromatographic peaks obviously represent more than one sample component (i.e., a broadened peak with shoulder(s) or a valley between two or more maxima), appropriate selection of analyte spectra and background spectra is important.

12.8. **Quantitative Analysis of Results**

12.8.1. **Concentration** – The GC/MS data system will calculate the concentration of each analyte as µg/mL in the extract. Concentrations in samples are calculated from the sample size, total volume of the final extract, the concentrations in the extract, and any dilution factor. If the initial analysis of a sample extract results in a concentration that exceeds the calibration range, the extract should be diluted and re-analyzed. All dilutions should keep the response of the major constituents in the upper half of the linear range of the curve. Any sample results outside the calibration range must be reported with a result flagged as an estimated result.

12.8.1.1. **Water and Water-Miscible Waste Samples**

$$\text{Concentration } (\mu g/L) = \frac{(C_x)(V_x)(DF)}{(V_s)}$$

Where:

C_x = Concentration in extract (µg/mL).
V_v = Volume of final extract (mL).
DF = Dilution factor.
V_s = Volume of water sample extracted (mL).

12.8.2 **Quality Control Results** – Calculate recoveries for surrogate compounds

in all samples, spiked compounds in LSC and MS/MSD samples, and Relative Percent Differences (RPD) for duplicate and MS/MSD samples.

12.8.3 ***Tentatively Identified Compounds (TICs)*** *–Not possible from a "SIM" analysis.*

13. Quality Control

13.1. **Calibration**

13.1.1. **ICAL** – If initial calibration criteria are not met, check standards preparation procedure for errors. Prepare new standards as required and re-run the calibration.

13.1.2. **Calibration Verification Checks** – If the SPCC and CCC criteria are not met, check system parameters, identify and correct likely causes, and re-run the check. An acceptable check is required to report sample results for the applicable batch.

13.2. **Internal Standard Responses and Retention Times** – Internal standard areas for all CCV's must be within the range of –50% to +100% and retention times must be within 30 seconds compared to the most recent ICAL. If these criteria are not met, check system parameters, identify and correct likely causes, and re-run the sample extracts. If the IS results appear out of control due to sample matrix re-analyze to confirm the matrix interference.

13.3. **Surrogate Recoveries** – Surrogate compounds must be added to all samples, spikes, control samples and method blanks, prior to extraction as indicators of method accuracy. Laboratory-based accuracy limits should be used to for acceptance criteria. If these criteria are not met, check system parameters, identify and correct likely causes, and re-extract and re-analyze if adequate sample is provided. If surrogate recoveries are higher than the acceptance criteria the results may be reported with an appropriate footnote. If recoveries appear out of control due to sample matrix, report the results with an appropriate footnote.

13.4. **Method Blank** – Must be analyzed daily with each extraction batch. The method blank must not contain any target analytes at or above the PRL. If the results are not acceptable, the entire extraction batch should be re-extracted and re-analyzed if adequate sample is provided, if not the data should be reported with appropriate qualifiers. Whenever sample volume allows, an acceptable method blank is required to report sample results for the applicable batch.

13.5. **LCS Recoveries** – One LCS/LSCD pair must be analyzed with each extraction batch of 20 samples. Laboratory-based accuracy and precision limits should be used for acceptance criteria. If acceptance criteria is not met, the entire extraction batch should be re-extracted and re-analyzed if adequate sample is provided, if not the data should be reported with appropriate qualifiers. Whenever sample volume allows an acceptable LCS/LCSD pair is required to report sample results for the applicable batch.

13.6. **MS/MSD Recoveries** – One MS/MSD pair should be analyzed with each batch of 20 samples. Laboratory-based accuracy and precision limits should be used to for acceptance criteria. If recoveries appear out of control and the batch LCS/LCSD recoveries are acceptable, matrix interference is the likely cause and results for the parent sample should be reported with an appropriate footnote.

13.7. **Duplicate and MS/MSD RPDs** – Five percent of all environmental samples should be analyzed in duplicate. A MS/MSD pair is also an acceptable duplicate analysis. Acceptance criteria should not exceed 20% for concentrations at least 10 times the PRL. If results are not acceptable, check for possible sample preparation problems and re-run if needed. Report the results with an appropriate footnote.

14. Method Performance

14.1 There are several requirements that must be met to insure that this procedure generates accurate and reliable data. A general outline of requirements has been summarized below. Further specifications may be found in the Laboratory Quality Manual.

14.2 The analyst must read and understand this procedure with written documentation maintained in his/her training file.

14.3 An initial demonstration of capability (IDC) must be performed per MN-Q-211, Training Procedures. A record of the IDC will be maintained in his/her QA file with written authorization from the Laboratory Manager and Quality Manager.

14.4 An annual method detection limit (MDL) study will be completed per ALL-Q-004, Method Detection Limit Studies, for this method and whenever there is a major change in personnel or equipment. The results of these studies are retained in the quality assurance office.

14.5 Periodic performance evaluation (PE) samples are analyzed per ALL-Q-010, PE/PT Program, to demonstrate continuing competence. All results are stored in the QA office.

15. Pollution Prevention and Waste Management

15.1 The quantity of chemicals purchased is based on expected usage during its shelf life and disposal cost of unused material. Actual reagent preparation volumes reflect anticipated usage and reagent stability.

15.2 Excess reagents, samples and method process wastes are characterized and disposed of in an acceptable manner. For further information on waste management consult the current version of ALL-C-001, Sample Management.

16. References

16.1. USEPA, SW-846, Method 8270C, "Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS)", December 1996.

16.2. USEPA, SW-846, Method 8000B, "Determinative Chromatographic Separations", December 1996.

17. Tables, Diagrams, Flowcharts, Attachments, Appendices, Etc.

Table 1
Compounds and Reporting Limits

COMPOUND	CAS#	PRL(ug/L)
Naphthalene	91-20-3	0.050
2-Methylnaphthalene	91-57-6	0.050
1-Methylnaphthalene		0.050
Acenaphthylene	208-96-8	0.050
Acenaphthene	83-32-9	0.050
Fluorene	86-73-7	0.050
Phenanthrene	85-01-8	0.050
Anthracene	120-12-7	0.050
Fluoranthene	206-44-0	0.050
Pyrene	129-00-0	0.050
Benzo(a)anthracene	56-55-3	0.050
Chrysene	218-01-9	0.050
Benzo(b)fluoranthene	205-99-2	0.050
Benzo(k)fluoranthene	207-08-9	0.050
Benzo(a)pyrene	50-32-8	0.050
Indeno(1,2,3-cd)pyrene	193-39-5	0.050
Dibenzo(a,h)anthracene	53-70-3	0.050
Benzo(g,h,i)perylene	191-24-2	0.050

Table 2
Ions

Compound	Primary Ion	Secondary Ion
Naphthalene	128	
2-Methylnaphthalene	142	141
1-Methylnaphthalene	142	141
Acenaphthylene	152	
Acenaphthene	154	152
Fluorene	166	165
Phenanthrene	178	
Anthracene	178	
Fluoranthene	202	
Pyrene	202	
Benzo(a)anthracene	228	226
Chrysene	228	226
Benzo(b)fluoranthene	252	
Benzo(k)fluoranthene	252	
Benzo(a)pyrene	252	
Indeno(1,2,3-cd)pyrene	276	
Dibenzo(a,h)anthracene	278	
Benzo(g,h,i)perylene	276	
Nitrobenzene-d(5)-SS	82	
2-Fluorobiphenyl-SS	172	
Terphenyl-d(14)-SS	244	
Naphthalene-d(8)-IS	136	
Acenaphthene-d(10)-IS	164	
Phenanthrene-d(10)-IS	188	
Chrysene-d(12)-IS	240	
Perylene-d(12)-IS	264	

Table 3
Recommended GC/MS Operating Conditions

Parameter	
Instrument	HP6890/5973
Column	Restek XTI-5 w/ Integraguard 30m, 0.25mm ID, 0.25df
Mass Range	50-500AMU
Mode	SIM
Temperature Program	40 C Hold 3 minutes to 130 C at 30 C/min hold 0.01 minutes to 325 C at 20 C/min hold 6.00 minutes
Injector Temp.	310 C
ransfer Line Temp	310 C
Source Temp	310 C
Injector	EPC in Pulsed Splitless Mode 70psi until 0.8min
Volume Injected	1uL
Carrier/Flow	Helium at 1.5mL/min.

Table 4
Internal Standard Assignments

Compound	Internal Standard
Naphthalene	Naphthalene-d(8)-IS
2-Methylnaphthalene	Naphthalene-d(8)-IS
1-Methylnaphthalene	Naphthalene-d(8)-IS
Acenaphthylene	Acenaphthene-d(10)-IS
Acenaphthene	Acenaphthene-d(10)-IS
Fluorene	Acenaphthene-d(10)-IS
Phenanthrene	Phenanthrene-d(10)-IS
Anthracene	Phenanthrene-d(10)-IS
Fluoranthene	Phenanthrene-d(10)-IS
Pyrene	Chrysene-d(12)-IS
Benzo(a)anthracene	Chrysene-d(12)-IS
Chrysene	Chrysene-d(12)-IS
Benzo(b)fluoranthene	Perylene-d(12)-IS
Benzo(k)fluoranthene	Perylene-d(12)-IS
Benzo(a)pyrene	Perylene-d(12)-IS
Indeno(1,2,3-cd)pyrene	Perylene-d(12)-IS
Dibenzo(a,h)anthracene	Perylene-d(12)-IS
Benzo(g,h,i)perylene	Perylene-d(12)-IS
Nitrobenzene-d(5)-SS	Naphthalene-d(8)-IS
2-Fluorobiphenyl-SS	Acenaphthene-d(10)-IS
Terphenyl-d(14)-SS	Chrysene-d(12)-IS

18. Revisions

Document Number	Reason for Change	Date
GB-O-003-rev.0	New Green Bay Laboratory document changed into Pace SOP format and updated.	April 5, 2005
GB-O-003-rev.1	10.2.3 changed to Initial Calibration Verification Standard 10.2.4 created for Continuing Calibration Verification Standard 10.3.6 new source for second source standard. 11.2.4.1 RSD must be less tha 30% and linear model may be employed 12.7.2. structural isomer procedure identified 11.2.3 linear equation for calculation of results added. Headers and formatting updated.	July 11,2005

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STANDARD OPERATING PROCEDURE

Determination of Polynuclear Aromatic Hydrocarbons (PAH) in Soil by GC/MS SIM

Reference Method: SW-846 Method 8270C

SOP NUMBER:	GB-O-020-rev.1
EFFECTIVE DATE:	Date of Final Signature
SUPERSEDES:	GB-O-020-rev.0

APPROVAL

Nils Melberg, Assistant Laboratory Manager	8/11/05 Date
Bruce Warden, General Manager	7/13/05 Date
Arthur F. Lautenbach, Quality Manager	7/12/05 Date

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1. Purpose

1.1 This Standard Operating Procedure (SOP) is used to determine the concentration of Polynuclear Aromatic Hydrocarbon (PAH) compounds in soil and solid waste samples compliant with SW-846 Method 8270C.

2. Scope and Application

2.1 This method may be used to determine concentrations of polynuclear aromatic hydrocarbon compounds in extracts prepared from soil and solid waste samples. Analytes must be soluble in dichloromethane and amenable to capillary gas chromatography. . A list of applicable compounds and their CAS numbers are shown in Table 1. Pace Reporting Levels (PRLs) are also shown for soil samples. PRLs are subject to change based on current analytical system performance and actual sample matrices.

2.2 The procedures for extract preparation are described in separate SOPs. The applicable sample preparation method is SW-846 3545.

2.3 This procedure is restricted to use by, or under the supervision of, analysts experienced in the use of GC/MS systems and interpretation of GC/MS data. Each analyst must demonstrate the capability to generate acceptable results with this method to be considered qualified to report sample results.

3. Summary of Methods

3.1 Sample extracts are prepared for analysis by an appropriate sample preparation method.

3.2 The semivolatile organic compounds are introduced into the gas chromatograph (GC) by injecting an aliquot of the sample extract. The GC column temperature is programmed to separate the analytes. The GC effluent is directly introduced to a mass spectrometer (MS) for both identification and quantification of analytes.

3.3 Analytes are identified by comparison of their mass spectra with spectra of authentic standards. Analytes are quantified by comparing the response of a selected major (quantitation) ion relative to an internal standard using at least a five-point calibration curve. Major and secondary quantitation ions for each applicable compound are shown in Table 2.

4. Interferences

4.1 Raw GC/MS data from all blanks, samples, and spikes must be evaluated for interferences. Determine if the source of interference is in the preparation and/or cleanup of the samples and take corrective action to eliminate the problem.

4.2 Contamination by carryover can occur whenever high-concentration and low-concentration samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed out between samples with solvent. Whenever an unusually concentrated sample is encountered, it should be followed by the analysis of solvent to check for cross contamination.

5. Safety

5.1 The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable. Cautions are included for known extremely hazardous materials.

5.2 A reference file of Material Safety Data Sheets (MSDS) is made available to all personnel involved in the chemical analysis, and is located at the front desk. A formal safety plan has been prepared and is distributed to all personnel with documented training

6. Definitions

6.1 Refer to the most current version of SOP MN-Q-241, *Analytical Definitions,* for the terms used at Pace Analytical.

7. Responsibilities and Distribution

7.1 Personnel

7.1.1 All personnel involved with sample preparation and analysis are responsible for adherence to this SOP. A controlled copy will be available for review and consultation within the area methods manual.

7.1.2 Personnel are responsible for ensuring that any deviations to this SOP are reported to the laboratory manager.

7.2 Laboratory Manager

7.2.1 The laboratory manager is responsible for ensuring adherence to this SOP and will receive a controlled copy of this SOP.

7.2.2 The laboratory manager is responsible for performing a biennial review of the SOP and reporting any required revisions to the Quality Assurance Office.

7.3 Quality Assurance Office

7.3.1 The QA Office is responsible for performing a biennial review of the SOP in conjunction with the purchasing department and revising as needed.

7.3.2 The QA Office is responsible for ensuring that all revisions to the SOP are implemented.

7.4 Revisions

7.4.1 This SOP will be reviewed on a biennial basis at a minimum, and any required revisions will be incorporated.

8. Sample Collection, Preservation and Handling

8.1 Soils must be collected in a teflon lined cap amber glass jar

8.2 Holding Times

8.2.1 Soil Samples – Samples must be extracted within 14 days of collection.

8.2.2 Extracts – Extracts must be analyzed within 40 days of preparation.

8.3 Sample Storage – Store all samples at 4 ± 2°C. Extracts are to be stored at <0C.

9. Equipment and Supplies

9.1 GC/MS System – The complete GC/MS system must include an autosampler and GC/MS with associated Data System. The specific system components and operating parameters that will be used with this method are shown in the Table 3.

9.2 Glassware and Materials

9.2.1 Syringes – 10-µL, 25-µL, 50-µL, 100-µL, 250-µL, 500-µL, and 1,000-µL, as needed, Hamilton or equivalent.

9.2.2 Clear Vials – 2-mL with PTFE-lined caps.

10. Reagents and Standards

10.1 Dichloromethane – Pesticide quality, or equivalent.

10.2 Analytical Standards

Standards are required for mass spectrometer tuning, initial calibration, calibration verification, internal standards, surrogates, and for preparing LCS, LSCD, MS, and MSD samples. The following describes the contents of each type of solution.

10.2.1 Tune Standard – Decafluorotriphenylphosphine (DFTPP) in dichloromethane.

10.2.2 Calibration Standards – At least 5 concentration levels of calibration solutions are prepared containing all target compounds for which the calibration is applied.

10.2.3 Initial Calibration Verification Standard – This solution contains mid-level concentrations of analytes in dichloromethane and is used to verify the analytical system calibration. The initial calibration verification standard must be prepared from source materials independent of the calibration standards. It must contain all of the PAH compounds that are being analyzed. All compounds are treated as System Performance Check Compounds (SPCC) and Calibration Check Compounds (CCC).

10.2.4 Continuing Calibration Verification Standard – This solution contains mid-level concentrations of analytes in dichloromethane and is used to verify the analytical system calibration. It must contain all of the PAH compounds that are being analyzed. All compounds are treated as System Performance Check Compounds (SPCC) and Calibration Check Compounds (CCC).

10.2.5 Internal Standards – This solution contains the following compounds in dichloromethane and is spiked into all working standards and sample extracts.

Naphthalene-d_8
Acenaphthene-d_{10}
Phenanthrene-d_{10}
Chrysene-d_{12}
Perylene-d_{12}

10.2.6 Surrogate Standards – This solution contains the following compounds in dichloromethane and is spiked into all samples prior to extract preparation.

Nitrobenzene-d_5
2-Fluorobiphenyl
Terphenyl-d_{14}

10.2.7 LCS, LCSD, MS, and MSD Spiking Solution – These solutions must contain all of the target compounds.

10.3 Preparation of Analytical Standard Solutions

Standards are prepared from commercially available multi-compound stock solutions. The sources of materials, recipes for preparing dilutions and working standards, and concentrations for all compounds are presented below. All standards are prepared using dichloromethane and

stored in clear vials with PTFE lined caps Storage and Stability of Analytical Standards - All standards must be stored in the dark at less than –10 °C or at a temperature recommended by the manufacturer. They should be replaced every 6 months, or sooner if the standards show signs of degradation. As each standard, from the vendor is opened, record all pertinent information in the stock standard logbook. Record all standard preparations in the working standard logbook.

10.3.1 DFTPP tuning standard

A Dichloromethane solution containing 50ng/uL of decafluorotriphenylphosphine(DFTPP) is prepared. A stock solution; Restek cat.# 31001; containing DFTPP at 2500ug/mL, is diluted taking 0.500mL and diluting to 25mL of dichloromethane.

10.3.2 Internal Standard solution

Stock solution obtained from Restek cat.#31006 containing 1,4-Dichlorobenzene-d4, Naphthalene-d8, Acenaphthene-d10, Phenanthrene-d10, Chrysene-d12 and Perylene-d12 all at 4000ug/mL in dichloromethane. This intermediate standard is prepared by diluting 500uL upto 1mL of dichloromethane, producing a solution that is 2000ug/mL for each component. 10uL of this standard is added to 1mL of every standard, sample, spike and blank analyzed by this method. Producing a on column concentration of 20ug/L.

10.3.3 Surrogate Standard solution

Stock Solution obtained from Restek, cat. #31082 containing 1,2-Dichlorobenzene-d4, Nitrobenzene-d5, 2-Fluorobiphenyl and p-Terphenyl-d14 all at 5000ug/mL in dichloromethane. An intermediate standard is prepared by diluting 300uL up to 10mLs of dichloromethane, producing a standard that is 150ug/mL of each component. 100 uL of the 150 ug/mL intermediate is spiked into all QC and samples, producing an on column value of 15 ug/mL.

10.3.4 Initial Calibration Intermediate Standard

Stock solution is obtained from Accustandard, product # M-610-FL-R-5X, containing the 18 PAH compounds, all at 500ug/mL. The intermediate is prepared by diluting 500 uL of the 500 ug/mL PAH Stock Standard along with 50 uL of the 5000 ug/mL B/N Surrogate Stock Solution to 10.0 mL with methylene chloride producing the the high satandard of 25 ug/mL. This standard is then further diluted to obtain the concentrations used for calibration.

10.3.5 Initial Calibration Working Standards

The following working calibration standards are prepared by further dilution of the high standard prepared above (10.3.4):

Standard Concentration (ug/L)	Amount of Intermediate Standard added	Amount of Intermediate Internal Standard added	Final Volume
0.25	10uL	10uL	1000uL
0.50	20uL	10uL	1000uL
1.0	40uL	10uL	1000uL
4.0	160uL	10uL	1000uL
10.0	400uL	10ul	1000uL
20.0	800uL	10uL	1000uL
25.0	1000uL	10uL	1000uL
Daily Cal 10.0	400uL	10uL	1000uL

10.3.6 Initial Calibration Verification

Stock solution is obtained from Supelco, cat # 47543-U, containing the 18 PAH compounds, all at 2000 ug/mL. An intermediate is prepared by diluting 100 uL of the 2000 ug/mL PAH Stock along with 40 uL of 5000 ug/mL B/N Surrogate Stock Solution to 2.0 mL with dichloromethane.

To produce the working ICV solution, the above intermediate ICV solution is further diluted by taking 100 uL of the intermediate ICV and diluting to 1.0 mL with dichloromethane to produce a 10 ug/mL working ICV standard .

10.3.7 LCS/MS Spiking Standard

Stock solution is obtained from Accustandard, product # M-610-FL-R-5X, containing the 18 PAH compounds, all at 500ug/mL. 20 uL of this solution is spiked into all LCS and MS samples, producing an on column concentration of 10 ug/mL.

11. Calibration

11.1 Tuning – At the beginning of each tune period, the mass spectrometer must be tuned with a solution containing 50 ng of DFTPP to meet specific ion abundance criteria shown in the following table.

Mass Peak (m/z)	Ion Abundance Criteria
51	30.0-80.0% of m/z 198
68	<2.0% of m/z 69
69	Present

70	<2.0% of m/z 69
127	25.0-75.0% of m/z 198
197	<1.0% of m/z 198
198	Base peak, 100% relative abundance
199	5.0-9.0% of m/z 198
275	10.0-30.0% of m/z 198
365	>0.75% of m/z 198
441	Present, but less than m/z 443
442	40.0-110.0% of m/z 198
443	15.0-24.0% of m/z 442

11.2 Initial Calibration (ICAL)

11.2.1 Analysis of Standards – Analyze at least 5 levels of calibration standards to define the calibration range. The lowest concentration should be at the target PRL.

11.2.2 Response Factors – Tabulate the area response of the characteristic ions against concentration for each compound and each internal standard. Calculate response factors (RF's) for each compound relative to the assigned internal standards. The assignments of analytes for each internal standard are shown in Table 4. Response factors are calculated using the following equation. Also, calculate the mean and relative standard deviation (RSD) of the response factors for all analytes.

$$RF = \frac{A_x C_{is}}{A_{is} C_x}$$

where:
A_x = Area of the characteristic ion for the compound being measured.
A_{is} = Area of the characteristic ion for the specific internal standard.
C_{is} = Concentration of the specific internal standard (ng/µL).
C_x = Concentration of the compound being measured (ng/µL).

11.2.3 Linear Regression - The linear equation regression will produce the slope and intercept in the following form:

$$y = ax + b$$

Where:

y = Instrument response
a = Slope of the line
x = Concentration of the calibration standard

b = The intercept

In calculating sample concentration by the internal standard method, the regression equation is as follows:

$$C_s = \frac{\frac{A_s C_{is}}{A_{is}} - b}{a}$$

where:

A_s = Area of the peak for the target analyte in the sample
A_{is} = Area of the peak of the internal standard
C_s = Concentration of the target analyte in the calibration standard
C_{is} = Concentration of the internal standard
a = Slope of the line
b = the intercept

11.2.4 Acceptance Criteria

11.2.4.1 Response Factors -- The RSD for each analyte must be less than 30% for all compounds. If the average RSD for all analytes is <15%, average RFs may be used to quantitate all analytes. A linear curve maybe used if the RSD is >15%, but <30%. The correlation coefficient of a linear curve must be >0.99.

11.2.4.2 SPCC's – The average RF for all compounds must be at ≥0.050. If this criteria is not met, corrective action must be taken.

11.3 Calibration Verification

11.3.1 Analysis of Calibration Verification Standard – Analyze the Calibration Verification Standard.

11.3.2 Acceptance Criteria –

11.3.2.1 SPCC's – All compounds are treated as SPCCs therefore the response factor for each compound must ≥0.050. Otherwise, corrective action must be taken and the system re-calibrated.

11.3.2.2 CCC's – All compounds are treated as CCCs, therefore if the difference for each compound is ≤20%, the initial calibration is assumed to be valid. Otherwise, corrective action must be taken and the system re-calibrated.

11.3.2.3 Internal Standard Responses and Retention Times – Internal standard areas for all CVS's must be within the range of –50% to +100% and retention times must be within 30 seconds compared to the midpoint standard of the most recent ICAL. If these criteria are not met, check system parameters, identify and correct likely causes, and re-analyze the Calibration Verification Standard. If the IS results from the sebsequent analysis are out of control, initial calibration must be re-initiated.

12 Procedure

12.1 Sample Extract Preparation – All sample extracts and standard solutions must be allowed to warm to room temperature before analysis.

12.2 Internal Standard Spiking – Prior to analysis, each sample, MB, LCS, MS, and MSD is spiked with 10uL of the internal standard solution (10.3.2).

11.1 GC/MS System Preparation

12.3.1 Operating Parameters – Set up the instrument parameters shown in Table 3.

12.3.2 System Tuning and GC Performance Checks – Analyze the Tuning Solution and tune the mass spectrometer to meet the criteria shown in Section 11.1. Verify acceptable GC system performance as described in Section 11.2. Print out a tune report.

12.4 Batch Sequence – Generate a sequence to run a batch of samples.

12.4.1 Initial Calibration - The typical batch for initial calibration should include:

Tune Standard
Calibration Level 1
Calibration Level 2
Calibration Level 3
Calibration Level 4
Calibration Level 5
Calibration and System Performance Solution

12.4.2 Sample Analysis – The typical batch for sample analysis should include the following. Preparation of LCS, MS, MSD, and Duplicate sample extracts is described in the appropriate sample preparation SOP.

Tune Standard
Calibration and System Performance Solution
Instrument Blank
Method Blank
Laboratory Control Sample
Laboratory Control Sample Duplicate
20 samples
Matrix Spike
Spike Duplicate

12.5 Autosampler – Load the autosampler with standards and samples for the batch created above.

12.6 Analyze Samples – Analyze all standards, quality control samples, and environmental samples.

12.7 Qualitative Analysis of Results – The following retention time criteria must be met to identify target compounds.

12.7.1 Retention Time Comparison – The relative retention time (RRT) of the sample component must be within ±0.06 RRT units of the RRT of the component in the calibration verification standard. Extracted Ion Current Plots (EICPs) may be used to provide a more reliable assignment of retention time in the presence of coeluting components.

12.7.2 Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the sum of the two peak heights. When daily check standard meet criteria for resolution, nothing will be done. When daily check standard does not meet the method requirement for resolution, samples running under that check standard will be flagged stating the method requirement for resolution was not met for affected compounds.

12.7.3 Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When gas chromatographic peaks obviously represent more than one sample component (i.e., a broadened peak with shoulder(s) or a valley between two or more maxima), appropriate selection of analyte spectra and background spectra is important.

12.8 Quantitative Analysis of Results

12.8.1 Concentration – The GC/MS data system will calculate the concentration of each analyte as µg/mL in the extract. Concentrations in samples are calculated from the sample size, total volume of the final extract, the concentrations in the extract, and any dilution factor. If the initial analysis of a sample extract results in a concentration that exceeds the calibration range, the extract should be diluted and re-analyzed. All dilutions should keep the response of the major constituents in the upper half of the linear range of the curve. Any sample results outside the calibration range must be reported with a result flagged as a estimated result.

12.8.1.1 The concentration of the analyte in the solid phase of the sample is calculated using the concentration of the pollutant in the extract and the weight of the solids, as follows:

$$\text{Concentration in ug/kg} = \frac{(C_{(ex)} * V_{(ex)})}{W_{(s)} * \%TS_{(dec)}}$$

where:

$V_{(ex)}$ = extract volume, in mL
$W_{(s)}$ = sample weight, in kg
$\%TS_{(dec)}$ = sample total solids expressed in decimal form

12.8.2 Quality Control Results – Calculate recoveries for surrogate compounds in all samples, spiked compounds in LSC and MS/MSD samples, and Relative Percent Differences (RPD) for duplicate and MS/MSD samples.

12.8.3 Tentatively Identified Compounds (TICs) –Not possible from a "SIM" analysis.

13 Quality Control

13.1 Calibration

13.1.1 ICAL – If initial calibration criteria are not met, check standards preparation procedure for errors. Prepare new standards as required and re-run the calibration.

13.1.2 Calibration Verification Checks – If the SPCC and CCC criteria are not met, check system parameters, identify and correct likely causes, and re-run the check. An acceptable check is required to report sample results for the applicable batch.

13.2 Internal Standard Responses and Retention Times – Internal standard areas for all CCV's must be within the range of –50% to +100% and retention times must be within 30 seconds compared to the most recent ICAL. If these criteria are not met, check system parameters, identify and correct likely causes, and re-run the sample extracts. If the IS results appear out of control due to sample matrix, the sample may be re-analyzed to confirm the matrix interference.

13.3 Surrogate Recoveries – Surrogate compounds must be added to all samples, spikes, control samples and method blanks, prior to extraction as indicators of method accuracy. Laboratory-based accuracy limits should be used to for acceptance criteria. If these criteria are not met, check system parameters, identify and correct likely causes, and re-extract and re-analyze if adequate sample is provided. If surrogate recoveries are higher than the acceptance criteria the results may be reported with an appropriate footnote. If recoveries appear out of control due to sample matrix, report the results with an appropriate footnote.

13.4 Method Blank – Must be analyzed daily with each extraction batch. The method blank should not contain any target analytes at or above the MDL. When compounds are present in the method blank above the MDL; samples associated with the blank are evaluated for the presence of the compounds. Samples in which those compounds are greater than the MDL or less then 20 times the concentration in the blank are flagged. Samples in which those compounds are less than the MDL or greater than 20 times the concentration in the blanks are reported without flags.

13.5 LCS Recoveries – One LCS/LSCD pair must be analyzed with each extraction batch of 20 samples. Laboratory-based accuracy and precision limits should be used for acceptance criteria. If acceptance criteria is not met, the entire extraction batch should be re-extracted and re-analyzed if adequate sample is provided, if not the data should be reported with appropriate qualifiers. Whenever sample volume allows an acceptable LCS/LCSD pair is required to report sample results for the applicable batch.

13.6 MS/MSD Recoveries – One MS/MSD pair should be analyzed with each batch of 20 samples. The sample use for the MS/D pair is either determined by the client or selected at random from client samples as sample volume allows. Laboratory-based accuracy and precision limits should be used to for acceptance criteria. If recoveries appear out of control and the batch LCS/LCSD recoveries are acceptable, matrix interference is the likely cause and results for the parent sample should be reported with an appropriate footnote.

13.7 Duplicate and MS/MSD RPDs – Five percent of all environmental samples should be analyzed in duplicate. A MS/MSD pair is also an acceptable duplicate analysis. Acceptance criteria should not exceed 20% for concentrations at least 10 times the PRL. If results are not acceptable, check for possible sample preparation problems and re-run if needed. Report the results with an appropriate footnote.

14 Method Performance

14.3 There are several requirements that must be met to insure that this procedure generates accurate and reliable data. A general outline of requirements has been summarized below. Further specifications may be found in the Laboratory Quality Manual.

14.3.1 The analyst must read and understand this procedure with written documentation maintained in his/her training file.

14.3.2 An initial demonstration of capability (IDC) must be performed per MN-Q-211, *Training Procedures*. A record of the IDC will be maintained in his/her QA file with written authorization from the Laboratory Manager and Quality Manager.

14.3.3 An annual method detection limit (MDL) study will be completed per ALL-Q-004, *Method Detection Limit Studies*, for this method and whenever there is a major change in personnel or equipment. The results of these studies are retained in the quality assurance office.

14.3.4 Periodic performance evaluation (PE) samples are analyzed per ALL-Q-010, *PE/PT Program*, to demonstrate continuing competence. All results are stored in the QA office.

15 Pollution Prevention and Waste Management

15.3 The quantity of chemicals purchased is based on expected usage during its shelf life and disposal cost of unused material. Actual reagent preparation volumes reflect anticipated usage and reagent stability.

15.4 Excess reagents, samples and method process wastes are characterized and disposed of in an acceptable manner. For further information on waste management consult the current version of ALL-C-001, *Sample Management*.

16 References

16.1 USEPA, SW-846, Method 8270C, "Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS)", December 1996.

16.2 USEPA, SW-846, Method 8000B, "Determinative Chromatographic Separations", December 1996.

17 Tables, Diagrams, Flowcharts, Appendices, Addenda etc.

Table 1
Compounds and Reporting Limits

COMPOUND	CAS#	PRL(ug/kg)
Naphthalene	91-20-3	25
2-Methylnaphthalene	91-57-6	25
1-Methylnaphthalene		25
Acenaphthylene	208-96-8	25
Acenaphthene	83-32-9	25
Fluorene	86-73-7	25
Phenanthrene	85-01-8	25
Anthracene	120-12-7	25
Fluoranthene	206-44-0	25
Pyrene	129-00-0	25
Benzo(a)anthracene	56-55-3	25
Chrysene	218-01-9	25
Benzo(b)fluoranthene	205-99-2	25
Benzo(k)fluoranthene	207-08-9	25
Benzo(a)pyrene	50-32-8	25
Indeno(1,2,3-cd)pyrene	193-39-5	25
Dibenzo(a,h)anthracene	53-70-3	25
Benzo(g,h,i)perylene	191-24-2	25

Table 2
Ions

Compound	Primary Ion	Secondary Ion
Naphthalene	128	
2-Methylnaphthalene	142	141
1-Methylnaphthalene	142	141
Acenaphthylene	152	
Acenaphthene	154	152
Fluorene	166	165
Phenanthrene	178	
Anthracene	178	
Fluoranthene	202	
Pyrene	202	
Benzo(a)anthracene	228	226
Chrysene	228	226
Benzo(b)fluoranthene	252	
Benzo(k)fluoranthene	252	
Benzo(a)pyrene	252	
Indeno(1,2,3-cd)pyrene	276	
Dibenzo(a,h)anthracene	278	
Benzo(g,h,i)perylene	276	
Nitrobenzene-d(5)-SS	82	
2-Fluorobiphenyl-SS	172	
Terphenyl-d(14)-SS	244	
Naphthalene-d(8)-IS	136	
Acenaphthene-d(10)-IS	164	
Phenanthrene-d(10)-IS	188	
Chrysene-d(12)-IS	240	
Perylene-d(12)-IS	264	

Table 3
Recommended GC/MS Operating Conditions

Parameter	
Instrument	HP6890/5973
Column	Restek XTI-5 w/ Integraguard 30m, 0.25mm ID, 0.25df
Mass Range	50-500AMU
Mode	SIM
Temperature Program	50 C Hold 1 minutes to 100 C at 18 C/min hold 0.01 minutes to 290 C at 15 C/min hold 5.95 minutes to 320 C at 40 C/min hold 3.0 minutes
Injector Temp.	295 C
Transfer Line Temp	310 C
Source Temp	310 C
Injector	EPC in Pulsed Splitless Mode 20psi until 0.3min
Volume Injected	1uL
Carrier/Flow	Helium at 1.5mL/min.

Table 4
Internal Standard Assignments

Compound	Internal Standard
Naphthalene	Naphthalene-d(8)-IS
2-Methylnaphthalene	Naphthalene-d(8)-IS
1-Methylnaphthalene	Naphthalene-d(8)-IS
Acenaphthylene	Acenaphthene-d(10)-IS
Acenaphthene	Acenaphthene-d(10)-IS
Fluorene	Acenaphthene-d(10)-IS
Phenanthrene	Phenanthrene-d(10)-IS
Anthracene	Phenanthrene-d(10)-IS
Fluoranthene	Phenanthrene-d(10)-IS
Pyrene	Chrysene-d(12)-IS
Benzo(a)anthracene	Chrysene-d(12)-IS
Chrysene	Chrysene-d(12)-IS
Benzo(b)fluoranthene	Perylene-d(12)-IS
Benzo(k)fluoranthene	Perylene-d(12)-IS
Benzo(a)pyrene	Perylene-d(12)-IS
Indeno(1,2,3-cd)pyrene	Perylene-d(12)-IS
Dibenzo(a,h)anthracene	Perylene-d(12)-IS
Benzo(g,h,i)perylene	Perylene-d(12)-IS
Nitrobenzene-d(5)-SS	Naphthalene-d(8)-IS
2-Fluorobiphenyl-SS	Acenaphthene-d(10)-IS
Terphenyl-d(14)-SS	Chrysene-d(12)-IS

18 Revisions

Document Number	Reason for Change	Date
GB-O-020-rev.0	New Green Bay Laboratory document changed into Pace SOP format and updated.	19May2005
GB-O-020-rev.1	10.2.3 changed to Initial Calibration Verification Standard 10.2.4 created for Continuing Calibration Verification Standard 10.3.6 new source for second source standard. 11.2.4.1 RSD must be less tha 30% and linear model may be employed 12.7.2. structural isomer procedure identified 11.2.3 linear equation for calculation of results added. Headers and formatting updated.	11Jul2005

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STANDARD OPERATING PROCEDURE

Determination of Semivolatile Organics by GC/MS

Reference Method: SW-846 Method 8270C

SOP NUMBER:	ALL-O-001-rev.1
EFFECTIVE DATE:	Date of Final Signature
SUPERSEDES:	ALL-O-001-rev.0

APPROVAL

John P. Dullaghan, COO	10/4/04 Date
Clarence L. Haile, Ph.D., Director of QST	4 Oct 2004 Date
Laboratory General Manager	3/15/05 Date
Laboratory Quality Manager	3/14/05 Date

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1. Purpose

This Standard Operating Procedure (SOP) is used to determine the concentration of semivolatile organic compounds in water and solid samples compliant with SW-846 Method 8270C.

2. Scope and Application

2.1. This procedure may be used to determine concentrations of neutral, acidic, and basic semivolatile organic compounds in extracts prepared from many types of water samples, soil samples and wastes. Analytes must be soluble in dichloromethane and amenable to capillary gas chromatography. Specific compound classes include polynuclear aromatic hydrocarbons, chlorinated hydrocarbons and pesticides, phthalate esters, organophosphate esters, nitrosamines, haloethers, aldehydes, ethers, ketones, anilines, pyridines, quinolines, aromatic nitro compounds, and phenols. A list of applicable compounds and their CAS numbers are shown in the addendum. Pace Reporting Levels (PRLs) are also shown for water and soil samples. PRLs are subject to change based on current analytical system performance and actual sample matrices.

2.2. The procedures for extract preparation are described in separate SOPs. A list of applicable sample preparation methods is shown in the addendum.

2.3. This SOP was prepared for method-compliant use by all Pace Analytical environmental laboratories. Additional lab-specific requirements that may be mandated by individual states or clients are presented in the addendum.

2.4. This procedure is restricted to use by, or under the supervision of, analysts experienced in the use of GC/MS systems and interpretation of GC/MS data. Each analyst must demonstrate the capability to generate acceptable results with this method to be considered qualified to report sample results.

3. Summary of Methods

3.1. Sample extracts are prepared for analysis by an appropriate sample preparation method.

3.2. The semivolatile organic compounds are introduced into the gas chromatograph (GC) by injecting an aliquot of the sample extract. The GC column temperature is programmed to separate the analytes. The GC effluent is directly introduced to a mass spectrometer (MS) for both identification and quantification of analytes.

3.3. Analytes are identified by comparison of their mass spectra with spectra of authentic standards. Analytes are quantified by comparing the response of a selected major (quantitation) ion relative to an internal standard using a five-point calibration curve. Major and secondary quantitation ions for each applicable compound are shown in the addendum.

4. Interferences

4.1. Interferences may be introduced into sample extracts by contaminants in solvents, reagents, glassware, and any other material that comes in contact with the sample or extract during extract preparation. These interferences must be closely monitored by analyzing Method Blank samples and taking corrective action as required.

4.2. Matrix interferences may result from materials co-extracted from some samples.

4.3. Contamination by carryover can occur when high concentration extracts are analyzed prior to low concentration extracts. The contamination may also cause degradation of labile analytes. Whenever carryover is suspected, the effected extracts should be re-analyzed. If significant degradation of the GC/MS systems is suspected, system performances samples should be analyzed and corrective action taken as needed.

5. Safety

5.1. **Standards and Reagents** - The toxicity and carcinogenicity of standards and reagents used in this method have not been fully defined. Each chemical compound should be treated as a potential health hazard. Reduce exposure by the use of gloves, lab coats and safety glasses. Material Safety Data Sheets (MSDSs) are on file in the laboratory and available to all personnel. Standard solutions should be prepared in a hood.

5.2. **Samples** - Take precautions when handling samples. Samples should always be treated as potentially hazardous "unknowns". The use of personal protective equipment (gloves, lab coats and safety glasses) is required when handling samples.

6. Definitions

6.1. **Batch** – A grouping of 20 samples, or less, of similar matrix which are prepared and/or analyzed together with the same method and the same lots of reagents within the same time frame, as designated by the method.

6.2. **Blank Sample** – A sample analyzed to detect and/or monitor the potential contamination by target analytes and other interferences attributable to instrumental background and sample handling, including sampling, sample shipping and storage, and analysis.

6.3. **Duplicate Sample** – A second aliquot of the same field sample analyzed in the same manner as the original sample in order to evaluate precision.

6.4. **Environmental Sample** – An environmental sample or field sample is a representative sample of any material (aqueous, non-aqueous, or multimedia) collected from any source for which determination of composition or contamination is requested or required.

6.5. **Extract** – A solution of contaminants extracted and concentrated from a sample.

6.6. **Internal Standard (IS)** – Analytes added to every standard, blank, lab control sample, matrix spike, matrix spike duplicate, and sample at a known concentration, prior to analysis for the purpose of adjusting the response factor used in quantifying target analytes.

6.7. **Laboratory Control Sample (LCS)** – A blank sample spiked with a known concentration of analytes of interest.

6.8. **Laboratory Information Management System (LIMS)** – A system for transferring, processing, storing, and reporting analysis results.

6.9. **Lot** – A quantity of bulk material of similar composition processed or manufactured at the same time.

6.10. **Matrix Spike (MS)** – Aliquot of sample spiked with known quantities of specified target compounds and subjected to the entire sample preparation and analysis procedure. The analysis results from a matrix spike sample is compared to results from an unspiked aliquot of the same sample to determine recovery of the spike. Spike recoveries are used to evaluate method accuracy.

6.11. **Matrix Spike Duplicate (MSD)** – A second aliquot of the sample that is treated the same as the original matrix spike sample. The relative percent difference between the matrix spike and matrix spike duplicate is calculated and used to assess method precision.

6.12. **Method Blank (MB)** – A blank sample prepared in the laboratory containing all reagents, internal standards and surrogate standards, that is carried through the entire analytical procedure. The method blank is used to evaluate laboratory background and contamination.

6.13. **Method Detection Limit (MDL)** – The minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero. Method detection limits are determined by analyzing replicate spike samples prepared by the lab and taken through all preparation and analysis steps of the method. The method detection limit is calculated using the appropriate Student's t-parameter times the standard deviation of a series of spiked samples.

6.14. **Replicate Samples** – Samples collected at the same time, from the same place, for the same analysis, as the original sample in order to determine precision between samples.

6.15. **Pace Reporting Limit (PRL)** – The lowest level that will be reported by this method. Reporting limits are at least two times the MDL. Reporting limits are corrected for sample amounts, including the dry weight of solids, unless otherwise specified.

6.16. **Surrogate Compounds** – These are compounds added to every blank, sample, matrix spike, matrix spike duplicate, lab control sample, and standard prior to any processing or preparation. Surrogate compounds are not expected to be detected in environmental samples, but are similar to the analytes of interest. The percent recoveries of surrogates are used to evaluate accuracy for each sample.

6.17. **Tune Period** – The 12-hour analysis period between instrument tune checks.

7. Responsibilities and Distribution

7.1. **Analyst** – Any analyst using this procedure is responsible for reading, understanding and following this SOP and the associated Work Processing and Training Document. Any deviation from this SOP must be reported to the appropriate Supervisor. The analyst must make their recommendations for changing the SOP to their supervisor or the QM in writing.

7.2. **Semivolatile Organic Supervisor** – The supervisor must ensure that all analysts are properly trained and qualified to use this procedure. The supervisor is also responsible to ensure that the SOP is followed. The supervisor is responsible for reviewing the SOP and communicating recommended changes to the LQM.

7.3. **Quality Manager (QM)** – The QM is responsible for monitoring the implementation of the SOPs and the associated good laboratory practice. The QM shall participate in the revision of the SOP and make sure it is current. The QM shall review and approve all SOPs.

7.4. **Laboratory General Manager (GM)** – The Laboratory General Manager has overall responsibility for ensuring that SOPs are prepared and implemented for all activities appropriate to the region. The Laboratory General Manager shall review and approve all SOPs.

7.5. **Director of Quality, Safety, and Training (QST)** – The Director of QST has oversight responsibility for Pace Analytical's quality programs, including establishing and monitoring compliance with all quality system requirements.

7.6. **Chief Operating Officer (COO)** – The COO has oversight responsibility for Pace Analytical environmental laboratory operations, including compliance with all quality system requirements.

7.7. **Distribution** – The official version of this SOP is the signed hardcopy version found in the laboratory, complete with the addendum. A copy of the SOP shall be available in the appropriate department for reference.

7.8. **Revision** – This SOP will be reviewed every two years at a minimum. Independent of the minimum review frequency, revisions will be incorporated as needed if procedures or methods change.

8. Sample Collection, Preservation, and Handling

8.1. **General Procedures** – Procedures for sample collection, preservation, and handling are described in the separate sample preparation SOPs.

8.2. **Holding Times**

8.2.1. **Water Samples** – Samples must be extracted within 7 days of collection.

8.2.2. **Soil, Solid, and Other Waste Samples** – Samples must be extracted within 14 days of collection

8.2.3. **Extracts** – Extracts must be analyzed within 40 days of preparation.

8.3. **Sample Storage** – Store all samples and extracts at 4 ± 2°C.

9. Equipment and Supplies

9.1. **GC/MS System** – The complete GC/MS system must include an autosampler and GC/MS with associated Data System. The specific system components and operating parameters that will be used with this method are shown in the addendum.

9.2. **Glassware and Materials**

9.2.1. **Syringes** – 10-µL, 25-µL, 50-µL, 100-µL, 250-µL, 500-µL, and 1,000-µL, as needed, Hamilton or equivalent.

9.2.2. **Amber Vials** – 2-mL with PTFE-lined caps.

9.2.3. **PTFE Mininert Valves** – for 2-mL vials.

10. Reagents and Standards

10.1. **Dichloromethane** – Pesticide quality, or equivalent.

10.2. **Methanol** – Pesticide quality, or equivalent.

10.3. **Analytical Standards**

Standards are required for mass spectrometer tuning, initial calibration, calibration verification, internal standards, surrogates, and for preparing LCS, MS, and MSD samples. The following describes the contents of each type of solution.

10.3.1. **Tune Standard** – Decafluorotriphenylphosphine (DFTPP), 4,4'-DDT, pentachlorophenol, and benzidine in dichloromethane.

10.3.2. **Calibration Standards** – At least 5 concentration levels of calibration solutions are prepared containing all target compounds for which the calibration is applied.

10.3.3. **Initial Calibration Verification Standard** – This solution contains mid-level concentrations of analytes in dichloromethane and is to verify the analytical system calibration. The calibration verification standard must be prepared from source materials independent of the calibration standards. It must contain, at a minimum, the following Calibration Check Compounds (CCC's) and System Performance Check Compounds (SPCC's).

Calibration Check Compounds

Base/Neutral Compounds	Acidic Compounds
Acenaphthene	4-Chloro-3-methylphenol
1,4-Dichlorobenzene	2,4-Dichlorophenol
Hexachlorobutadiene	2-Nitrophenol
N-Nitrosodiphenylamine	Phenol
Di-n-octylphthalate	Pentachlorophenol
Fluoranthene	2,4,6-Trichlorphenol
Benzo[a]pyrene	

System Performance Check Compounds

N-Nitroso-di-n-propylamine
Hexachlorocyclopentadiene
2,4-Dinitrophenol
4-Nitrophenol

10.3.4. **Internal Standards** – This solution contains the following compounds in dichloromethane and is spiked into all working standards and sample extracts.

1,4 Dichlorobenzene-d_4
Naphthalene-d_8
Acenaphthene-d_{10}
Phenanthrene-d_{10}
Chrysene-d_{12}
Perylene-d_{12}

10.3.5. **Surrogate Standards** – This solution contains the following compounds in methanol and is spiked into all samples prior to extract preparation.

Nitrobenzene-d_5
2-Fluorobiphenyl
Terphenyl-d_{14}
Phenol-d_6
2-Fluorophenol
2,4,6-Tribromophenol

10.3.6. LCS, MS, and MSD Spiking Solutions – This solution must contain the following compounds. In addition, all target compounds must be included in an LCS and MS spike at least once in a 2-year period.

Base/neutrals	Acids
1,2,4-Trichlorobenzene	Pentachlorophenol
Acenaphthene	Phenol
2,4-Dinitrotoluene	2-Chlorophenol
Pyrene	4-Chloro-3-methylphenol
N-Nitroso-di-*n*-propylamine	4-Nitrophenol
1,4-Dichlorobenzene	

10.4. **Preparation of Analytical Standard Solutions**

Standards are prepared from commercially available multi-compound stock solutions and neat materials by multiple dilutions. The sources of materials, recipes for preparing dilutions and working standards, and concentrations for all compounds are presented in the addendum. All standards are prepared using dichloromethane and stored in amber vials with PTFE lined caps or Mininert caps.

10.5. **Storage and Stability of Analytical Standards** - All standards must be stored in the dark at less than –10 °C or at a temperature recommended by the manufacturer. They should be replaced every 6 months, or sooner if the standards show signs of degradation. As each standard, from the vendor is opened, record all pertinent information in the stock standard logbook. Record all standard preparations in the working standard logbook.

11. Calibration

11.1. **Tuning** – At the beginning of each tune period, the mass spectrometer must be tuned with a solution containing 50 ng of DFTPP to meet specific ion abundance criteria shown in the following table.

Mass Peak (m/z)	Ion Abundance Criteria
51	30.0-80.0% of m/z 198
68	<2.0% of m/z 69
69	Present
70	<2.0% of m/z 69
127	25.0-75.0% of m/z 198
197	<1.0% of m/z 198
198	Base peak, 100% relative abundance
199	5.0-9.0% of m/z 198
275	10.0-30.0% of m/z 198
365	>0.75% of m/z 198
441	Present, but less than m/z 443
442	40.0-110.0% of m/z 198
443	15.0-24.0% of m/z 442

11.2. **GC Performance and Inertness** – The tuning solution should be used to assess the GC system performance and inertness. Degradation of DDT to DDE and DDD should be less than 20%. Benzidine and pentachlorophenol should exhibit their normal responses with no apparent peak tailing. Injection port maintenance may be required if unacceptable performance is observed.

11.3. **Initial Calibration (ICAL)**

11.3.1. **Analysis of Standards** – Analyze at least 5 levels of calibration standards to define the calibration range. The lowest concentration should be at the target PRL.

11.3.2. **Response Factors** – Tabulate the area response of the characteristic ions against concentration for each compound and each internal standard. Calculate response factors (RF's) for each compound relative to the assigned internal standards. The assignments of analytes for each internal standard are shown in the addendum. Response factors are calculated using the following equation. Also, calculate the mean and relative standard deviation (RSD) of the response factors for all analytes.

$$RF = \frac{A_x C_{is}}{A_{is} C_x}$$

where:
A_x = Area of the characteristic ion for the compound being measured.
A_{is} = Area of the characteristic ion for the specific internal standard.
C_{is} = Concentration of the specific internal standard (ng/µL).
C_x = Concentration of the compound being measured (ng/µL).

11.3.3. **Acceptance Criteria**

11.3.3.1. **Response Factors --** The RSD for each analyte should be less than 15% and must be less than 30% for CCCs. If the average RSD for all analytes is <15%, average RFs may be used to quantitate all analytes. Otherwise, use calibration curves of internal standard corrected response vs. concentration. Linear curves may be used if r ≥0.99, not forced through the origin. Alternatively, quadratic curves with 6 calibration levels may be used if the coefficient of determination is ≥0.99, not forced through the origin.

11.3.3.2. **SPCC's** – The average RF for each SPCC must be ≥0.050. If this criteria is not met, corrective action must be taken.

11.4. **Calibration Verification**

11.4.1. **Analysis of Calibration Verification Standard** – Analyze the Calibration Verification Standard.

11.4.2. **Acceptance Criteria --**

11.4.2.1. **SPCC's** – The response factor for each SPCC must be ≥0.050. Otherwise, corrective action must be taken and the system re-calibrated.

11.4.2.2. **CCC's** - If the difference for each CCC is ≤20%, the initial calibration is assumed to be valid. Otherwise, corrective action must be taken and the system re-calibrated.

11.4.2.3. **Internal Standard Responses and Retention Times** – Internal standard areas for all CCC's must be within the range of –50% to +100% and retention times must be within 30 seconds compared to the most recent ICAL. If these criteria are not met, check system parameters, identify and correct likely causes, and re-analyze the Calibration Verification Standard. If the IS results from the second analysis are out of control, initial calibration must be re-initiated.

12. Procedure

12.1. **Sample Extract Preparation** – All sample extracts and standard solutions must be allowed to warm to room temperature before analysis.

12.2. **Internal Standard Spiking** – Prior to analysis, each sample, MB, LCS, MS, and MSD is spiked with the internal standard solution. The volume spiked is specified in the addendum.

12.3. **GC/MS System Preparation**

12.3.1. **Operating Parameters** – Set up the instrument parameters shown in the addendum.

12.3.2. **System Tuning and GC Performance Checks** – Analyze the Tuning Solution and tune the mass spectrometer to meet the criteria shown in Section 11.1. Verify acceptable GC system performance for DDT, benzidine, and pentachlorophenol as described in Section 11.2. Print out a tune report.

12.4. **Batch Sequence** – Generate a sequence to run a batch of samples.

12.4.1. Initial Calibration - The typical batch for initial calibration should include:

Tune Standard
Calibration Level 1
Calibration Level 2
Calibration Level 3
Calibration Level 4
Calibration Level 5
Initial Calibration Verification Standard

12.4.2. **Sample Analysis** – The typical batch for sample analysis should include the following. Preparation of LCS, MS, MSD, and Duplicate sample extracts is described in the appropriate sample preparation SOP.

Tune Standard
Mid-Level Calibration Standard
Method Blank
Laboratory Control Sample
20 samples
Matrix Spike/Matrix Spike Duplicate
Duplicate (Sample Duplicate or MSD every 10 samples)

12.5. **Load Autosampler** – Load the autosampler with standards and samples for the batch created above.

12.6. **Analyze Samples** – Analyze all standards, quality control samples, and environmental samples.

12.7. **Qualitative Analysis of Results** – The following retention time and mass spectra comparison criteria must be met to identify target compounds.

12.7.1. **Retention Time Comparison** – The relative retention time (RRT) of the sample component must be within ±0.06 RRT units of the RRT of the component in the calibration verification standard. Extracted Ion Current Plots (EICPs) may be used to provide a more reliable assignment of retention time in the presence of coeluting components.

12.7.2. **Mass Spectrum Comparison** – The characteristic ions from the reference mass spectrum are defined as the three ions of greatest relative intensity, or any ions over 30% relative intensity if less than three such ions occur in the reference spectrum. Compounds are identified as present when the following criteria are met.

12.7.2.1. The intensities of the characteristic ions of a compound maximize in the same scan or within one scan of each other. Selection of a peak by a data system target compound search

routine where the search is based on the presence of a target chromatographic peak containing ions specific for the target compound at a compound-specific retention time will be accepted as meeting this criterion.

12.7.2.2. The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum.

12.7.2.3. Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

12.7.2.4. Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When gas chromatographic peaks obviously represent more than one sample component (i.e., a broadened peak with shoulder(s) or a valley between two or more maxima), appropriate selection of analyte spectra and background spectra is important.

12.8. **Quantitative Analysis of Results**

12.8.1. **Concentration** – The GC/MS data system will calculate the concentration of each analyte as µg/mL in the extract. Concentrations in samples are calculated from the sample size, total volume of the final extract, the concentrations in the extract, and any dilution factor. If the initial analysis of a sample extract results in a concentration that exceeds the calibration range, the extract should be diluted and re-analyzed. All dilutions should keep the response of the major constituents in the upper half of the linear range of the curve. Any sample result reported outside of the established calibration range must be footnoted as an estimated result in the final report.

12.8.1.1. **Water and Water-Miscible Waste Samples**

$$\text{Concentration } (\mu g/L) = \frac{(C_x)(V_x)(DF)}{(V_s)}$$

Where:

C_x = Concentration in extract (µg/mL).
V_v = Volume of final extract (mL).
DF = Dilution factor.
V_s = Volume of water sample extracted (mL).

12.8.1.2. **Soil/Solid Samples**

$$\text{Concentration } (\mu\text{g/kg}) = \frac{(C_x)(V_x)(1000)(DF)}{(W_s)}$$

Where:

C_x = Concentration in extract (µg /mL).
V_v = Volume of final extract (mL).
DF = Dilution factor.
W_s = Weight of sample extracted (g).

12.8.2. **Quality Control Results** – Calculate recoveries for surrogate compounds in all samples, spiked compounds in LSC and MS/MSD samples, and Relative Percent Differences (RPD) for duplicate and MS/MSD samples.

12.9. **Tentatively Identified Compounds (TICs)** – For some samples, identification may be desired for non-target compounds. A mass spectral library search may be conducted to attempt assignment of tentative identifications. Only after visual comparison of sample spectra with the nearest library searches may the analyst assign a tentative identification. Use the following guidelines for making tentative identifications.

12.9.1. Relative intensities of major ions in the reference spectrum (ions greater than 10% of the most abundant ion) should be present in the sample spectrum.

12.9.2. The relative intensities of the major ions should agree within ± 20%.

12.9.3. Molecular ions present in the reference spectrum should be present in the sample spectrum.

12.9.4. Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of co-eluting compounds.

12.9.5. 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 co-eluting peaks. Data system library reduction programs can sometimes create these discrepancies.

12.9.6. Estimated concentrations should be calculated using an average response factor of 1.0.

13. Quality Control

13.1. Calibration

13.1.1. **ICAL** – If initial calibration criteria are not met, check standards preparation procedure for errors. Prepare new standards as required and re-run the calibration.

13.1.2. **Calibration Verification Checks** – If the SPCC and CCC criteria are not met, check system parameters, identify and correct likely causes, and re-run the check. An acceptable check is required to report sample results for the applicable batch.

13.2. **Internal Standard Responses and Retention Times** – Internal standard areas for all CCC's must be within the range of –50% to +100% and retention times must be within 30 seconds compared to the most recent ICAL. If these criteria are not met, check system parameters, identify and correct likely causes, and re-run the sample extracts. If the IS results appear out of control due to sample matrix re-analyze to confirm the matrix interference.

13.3. **Surrogate Recoveries** – Surrogate compounds must be added to all samples, spikes, control samples and method blanks, prior to extraction as indicators of method accuracy. Laboratory-based accuracy limits should be used to for acceptance criteria. If these criteria are not met, check system parameters, identify and correct likely causes, and re-extract and re-analyze. If surrogate recoveries are higher than the acceptance criteria and target compounds are less than the reporting limit, the results may be reported with an appropriate footnote. If recoveries appear out of control due to sample matrix, report the results with an appropriate footnote.

13.4. **Method Blank** – Must be analyzed with each extraction batch. The method blank must not contain any phthalate esters at concentrations exceeding 5 times their PRLs or any target analytes at or above the PRL. If the results are not acceptable, the entire extraction batch should be re-extracted and re-analyzed. An acceptable method blank is required to report sample results for the applicable batch.

13.5. **LCS Recoveries** – One LCS must be analyzed with each extraction batch of 20 samples. Laboratory-based accuracy limits should be used for acceptance criteria. An acceptable LCS is required to report sample results for the applicable batch.

13.6. **MS/MSD Recoveries** – One MS should be analyzed with each batch of 20 samples. Laboratory-based accuracy limits should be used to for acceptance criteria. If recoveries appear out of control and the batch LCS recoveries are acceptable, matrix interference is the likely cause and results should be reported with an appropriate footnote.

13.7. **Duplicate and MS/MSD RPDs** – Five percent of all environmental samples should be analyzed in duplicate. A MS/MSD pair is also an acceptable duplicate analysis. Acceptance criteria should not exceed 20% for concentrations at least 10 times the PRL. If results are not acceptable, check for possible sample

preparation problems and re-run if needed. Report the results with an appropriate footnote.

14. Method Performance

14.1. **Method Detection Limit (MDL) Study** – An MDL study must be conducted annually. Analyze a minimum of 7 replicates of a low level standard. Calculate the mean and standard deviation of the seven measurements for each analyte. Calculate the MDL for each analyte. The PRL for each analyte must be at least 2 times the MDL.

14.2. **Demonstration of Capability (DOC)** – Every analyst who performs this method must first document acceptable accuracy and precision by passing a demonstration of capability study (DOC). First, analyze 4 replicates of a mid-level standard. Calculate the mean and standard deviation of results for each analyte. All results must be in control to qualify the analyst for reporting sample results. Results of DOC studies for each analyst shall be retained in the lab quality assurance office.

15. Pollution Prevention and Waste Management

15.1. Procedures for handling waste generated during this analysis are addressed in individual laboratory SOPs for waste management.

15.2. In order to minimize the amount of waste generated during this procedure, analyst should prepare reagents in an amount which may be used in a reasonable amount of time (i.e. before a reagent expires)

15.3. The laboratory Chemical Hygiene Plan/Health and Safety Plan contains additional information on pollution prevention.

16. References

16.1. USEPA, SW-846, Method 8270C, "Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS)", December 1996.

16.2. USEPA, SW-846, Method 8000B, "Determinative Chromatographic Separations", December 1996.

17. Tables, Diagrams, Flowcharts, Attachments, Appendices, Etc.

Not Applicable

18. Revisions

Document Number	Reason for Change	Date
ALL-O-001-rev.0	New company-wide document	July 26, 2004
ALL-O-001-Rev.1	10.3.6. Changed the verbiage and added a table, modified Ion Abundance Criteria in table 11.1, added 11.4.2.3., and added 16.2.	September 28, 2004

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STANDARD OPERATING PROCEDURE

Green Bay Addendum

Determination of Semivolatile Organics by GC/MS

Reference Method: SW-846 Method 8270C/EPA 625

ADDENDUM NUMBER:	ALL-GB-O-001-rev.2
SOP NUMBER:	ALL-O-001-rev.1
EFFECTIVE DATE:	Date of Final Signature
SUPERSEDES:	ALL-GB-O-001-rev.1

APPROVAL

Nils Melberg, Assistant General Manager — Date: 6/15/06

Arthur F. Lautenbach, Quality Manager — Date: 6/15/06

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1. Purpose

This method is also used to determine the concentration of semi volatile organic compounds in water samples by GC/MS compliant with EPA Method 625.

2. Scope and Application

See Table 1 for Reporting Limits.

2.1 Table 1: Method 625/8270C Compounds and Reporting Limits[1]

Analyte	PRL water (ug/L)	PRL soil (ug/kg)
Phenol	10	330
Bis (2-Chloroethyl) ether	10	330
2-Chlorophenol	10	330
1,3-Dichlorobenzene	10	330
1,4-Dichlorobenzene	10	330
Benzyl Alcohol	10	330
1,2-Dichlorobenzene	10	330
2-Methylphenol	10	330
Bis (2-Chloroisopropyl)ether	10	330
3&4-Methylphenol	10	330
N-Nitroso-di-n-propylamine	10	330
Hexachloroethane	10	330
Nitrobenzene	10	330
Isophorone	10	330
2-Nitrophenol	10	330
2,4-Dimethylphenol	10	330
Benzoic acid	10	330
Bis(2-Chloroethoxy)methane	10	330
2,4-Dichlorophenol	10	330
1,2,4-Trichlorobenzene	10	330
Naphthalene	10	330
4-Chloroaniline	10	330
Hexachlorobutadiene	50	330
4-Chloro-3-methylphenol	10	330
2-Methylnaphthalene	10	330
Hexachlorocyclopentadiene	10	670
2,4,6-Trichlorophenol	10	330
2,4,5-Trichlorophenol	10	330
2-Chloronaphthalene	10	330
2-Nitroaniline	10	330
Acenaphthene	10	830
2,4-Dinitrophenol	10	330
4-Nitrophenol	10	330

Analyte	PRL water (ug/L)	PRL soil (ug/kg)
Dibenzofuran	25	330
2,4-Dinitrotoluene	10	330
2,6-Dinitrotoluene	10	330
Diethylphthalate	10	330
4-Chlorophenyl-phenylether	10	830
Fluorene	25	330
4-Nitroaniline	10	830
4,6-Dinitro-2-methylphenol	10	330
N-Nitrosodiphenylamine	25	330
4-Bromophenyl-phenylether	10	330
Hexachlorobenzene	10	670
Pentachlorophenol	10	330
Phenanthrene	10	330
Anthracene	25	330
Di-n-butylphthalate	10	330
Fluoranthene	10	330
Pyrene	10	330
Butylbenzylphthalate	10	330
3,3'-Dichlorobenzidine	25	330
Benzo(a)anthracene	10	330
Chysene	10	330
Bis(2-ethylhexyl)phthalate	10	330
Di-n-octylphthalate	10	330
Benzo(b)fluoranthene	10	330
Benzo(k)fluoranthene	10	330
Benzo(a)pyrene	10	330
Indeno(1,2,3-cd)pyrene	10	330
Dibenz(a,h)anthracene	10	330
Benzo(g,h,i)perylene	10	330
1,2-Diphenylhydrazine	10	330
N-Nitrosodimethylamine	10	670
Benzidine	10	670
Aniline	10	330
Carbazole	25	330
Dimethylphthalate	10	330
Acenaphthylene	10	830
3-Nitroaniline	25	330
Benzaldehyde	10	830
Pyridine	10	330
Acetophenone	10	330
1-Methylnaphthalene	10	330
Caprolactam	10	330
Biphenyl	10	330
Atrazine	10	330
1,4-Dioxane	10	330

[1] This table contains the basic 625/8270C target compounds reported by the lab. Additional compounds may be added at client request.

2.2 Sample Preparation Methods

The Green Bay laboratory currently processes Methods 625/8270C water samples by automated separatory funnel using Method SW846 3510C, and processes Method 8270C soil samples by Automated Solvent Extraction (ASE) using Method SW846 3545. Standard Operating Procedures ALL-O-003 *Separatory Funnel Extraction of Water Samples for Semivolatile Analysis*, ALL--GBO-003 *Separatory Funnel Extraction of Water Samples for Semivolatile Analysis – Green Bay Addendum*, and GB-O-022 *Solids Sample Preparation for the Analysis of Semivolatile Base/Neutral/Acids-Full Scan* for these extraction techniques are available from the quality office.

3. Summary of Method

3.3 Primary and Secondary quantitation ions for target compounds[2]

Analyte	Primary Ion	Secondary Ions
Phenol	94	65, 66
Bis (2-Chloroethyl) ether	63	93, 95
2-Chlorophenol	128	64, 130
1,3-Dichlorobenzene	146	148, 111
1,4-Dichlorobenzene	146	148, 111
Benzyl Alcohol	108	79, 77,107
1,2-Dichlorobenzene	146	148, 111
2-Methylphenol	108	107, 79
Bis (2-Chloroisopropyl)ether	45	77, 121
3&4-Methylphenol	108	107, 77
N-Nitroso-di-n-propylamine	70	42, 43, 130
Hexachloroethane	117	201, 199
Nitrobenzene	77	123, 199
Isophorone	82	95, 138
2-Nitrophenol	139	109, 65
2,4-Dimethylphenol	107	121
Benzoic acid	122	105
Bis(2-Chloroethoxy)methane	93	95, 123
2,4-Dichlorophenol	162	164, 98
1,2,4-Trichlorobenzene	180	182, 145
Naphthalene	128	129, 127
4-Chloroaniline	127	129, 65
Hexachlorobutadiene	225	223, 227, 113
4-Chloro-3-methylphenol	107	144, 142
2-Methylnaphthalene	142	141
Hexachlorocyclopentadiene	237	235, 272
2,4,6-Trichlorophenol	196	198, 200
2,4,5-Trichlorophenol	196	198, 97
2-Chloronaphthalene	162	164, 127
2-Nitroaniline	65	92, 138
Acenaphthene	154	151, 153
2,4-Dinitrophenol	184	63, 154
4-Nitrophenol	109	39, 65
Dibenzofuran	165	63, 89
2,4-Dinitrotoluene	165	63, 89
2,6-Dinitrotoluene	165	63, 89
Diethylphthalate	149	177, 150
4-Chlorophenyl-phenylether	204	206, 141

[2] The information in this table was taken from Table 1 in Method 8270C. Please refer to the method for additional compounds and their applicable ions.

3.3. Primary and Secondary quantitation ions for target compounds[2] (continued)

Analyte	Primary Ion	Secondary Ions
Fluorene	166	165, 167
4-Nitroaniline	138	65, 108, 92
4,6-Dinitro-2-methylphenol	198	51, 105
N-Nitrosodiphenylamine	169	168, 167
4-Bromophenyl-phenylether	248	250, 141
Hexachlorobenzene	284	142, 249
Pentachlorophenol	266	264, 268
Phenanthrene	178	179, 176
Anthracene	178	176, 179
Di-n-butylphthalate	149	150, 104
Fluoranthene	202	101, 203
Pyrene	202	200, 203
Butylbenzylphthalate	149	91, 206
3,3'-Dichlorobenzidine	252	254, 126
Benzo(a)anthracene	228	229, 226
Chysene	228	226, 229
Bis(2-ethylhexyl)phthalate	149	167, 229
Di-n-octylphthalate	149	167, 43
Benzo(b)fluoranthene	252	253, 125
Benzo(k)fluoranthene	252	253, 125
Benzo(a)pyrene	252	253, 125
Indeno(1,2,3-cd)pyrene	276	138, 227
Dibenz(a,h)anthracene	278	139, 279
Benzo(g,h,i)perylene	276	138, 277
1,2-Diphenylhydrazine	77	105, 182, 51
N-Nitrosodimethylamine	88	42, 43, 56
Benzidine	184	92, 185
Aniline	93	66, 65
Carbazole	167	139, 166
Dimethylphthalate	163	194,164
Acenaphthylene	152	153
3-Nitroaniline	138	108,92
Benzaldehyde	105	106,77
Pyridine	79	52
Acetophenone	105	77,120
1-Methylnaphthalene	142	141
Caprolactam	55	56,113
Biphenyl	154	153,152
Atrazine	200	215,58
1,4-Dioxane	88	58

[2] The information in this table was taken from Table 1 in Method 8270C. Please refer to the method for additional compounds and their applicable ions.

3.3. Primary and Secondary quantitation ions for internals and surrogates[3] (continued)

Analyte	Primary Ion	Secondary Ions
Internals		
1,4-Dichlorobenzene-d_4	152	150, 115
Naphthalene-d_8	136	68
Acenaphthene-d_{10}	164	162, 160
Phenanthrene-d_{10}	188	94, 80
Chrysene-d_{12}	240	120, 236
Perylene-d_{12}	264	260, 265
Surrogates		
Phenol-d_6 (acid)	99	42, 71
2-Fluorophenol (acid)	112	64
Nitrobenzene-d_5 (BN)	82	128, 54
2-Fluorobiphenyl (BN)	172	171
2,4,6-Tribromophenol (acid)	330	332, 141
Terphenyl-d_{14} (BN)	244	122, 212

[2] The information in this table was taken from Method 8270C. Please refer to the method for additional compounds and their applicable ions.

4. Interferences

No Applicable Changes

5. Safety

No Applicable Changes

6. Definitions

6.18 Refer to the most current version section 10 of the Pace Quality Manual

7. Responsibilities and Distribution

No Applicable Changes

8. Sample Collection, Preservation and Handling

8.3 Sample Storage- Samples are stored at 4 ± 2° C. Extracts are stored at less than 0° C.

9. Equipment and Supplies

9.1 Instrumentation and typical operating parameters (operating conditions are subject to change):

GC/MS Instrument SVMS-1	
GC: Hewlett Packard model 5890	MS: Hewlett Packard model 5972A
Operating Parameters:	Operating Parameters:
Initial Temp: 40°C	Acquisition mode: SCAN
Temp Program: hold 1.0 min at 40°C, ramp at 18°C/min to 100°C, then ramp at 15°C/min to 290°C, hold 5.95min, then ramp at 40°C/min to 320°C and hold for 1 min	Mass Range: 35-500
Final Temp: 320°C	
Transfer Line Temp: 300°C	
Column: Restek XTI-5 (30m; 0.25mm ID and 0.25um film thickness)w/Integraguard	
Purge Flow: 40mL/min	

GC/MS Instrument SVMS-5	
GC: Hewlett Packard model 5890	MS: Hewlett Packard model 5972A
Operating Parameters:	Operating Parameters:
Initial Temp: 40°C	Acquisition mode: SCAN
Temp Program: hold 1.0 min at 40°C, ramp at 18°C/min to 100°C, then ramp at 15°C/min to 290°C, hold 5.95min, then ramp at 40°C/min to 320°C and hold for 1 min	Mass Range: 35-500
Final Temp: 320°C	
Transfer Line Temp: 300°C	
Column: Restek XTI-5 (30m; 0.25mm ID and 0.25um film thickness)w/Integraguard	
Purge Flow: 40mL/min	

10. Reagents and Standards

10.3.3 The Initial Calibration Verification standard (ICV) is made from a second-source material that is analyzed directly after an initial calibration curve. The subsequent Calibration Verification Standards (CVS) that are analyzed per 12-hour tune are made from the **same** materials as those used in the construction of the initial calibration curve.

10.4 Standard Preparation

10.4.1. **Internal Standard Stock solution:** Restek brand Internal Standard Mix, 4000ug/mL, catalog # 31006 (contains six internal standards: acenaphthene-d10; chrysene-d12; 1,4-dichlorobenzene-d4; naphthalene-d8; perylene-d12; and phenanthrene-d10).

10.4.2. **Surrogate Standard stock solutions:** Restek brand Base Neutral surrogate mix, 5000ug/mL, catalog # 31082 (contains four surrogate standards: 2-fluorobiphenyl; nitrobenzene-d5; p-terphenyl-d14; 1,2-Dichlorobenzene-d4(advisory)). Restek brand Acid surrogate mix, 7500ug/mL, catalog # 31083 (contains four surrogate standards 2-fluorophenol; phenol-d5; 2,4,6-tribromophenol; 2-chlorophenol-d4(advisory)).

10.4.3. **Surrogate Standard working solution (for extractions):** dilute 5.0mL of both the Restek Base Neutral stock surrogate solution (# 31082) and theRestek Acid stock surrogate solution (#31083) to 50mL with Dichloromethane. This gives a final concentration of 500ug/mL per Base Neutral surrogate compound and 750ug/mL per Acid surrogate compound. The extraction analyst spikes each water and soil sample with 100uL of this working solution.

10.4.4. **DFTPP tuning solution:** dilute 500uL of Supelco DFTPP stock standard (catalog # 47548-U; 1000ug/mL) to a total volume of 10mL with methylene chloride for a final concentration of 50ug/mL. The stock standard also contains 4,4'-DDT, benzidine, and pentachlorophenol for assessing column degradation.

10.4.5. **Initial Calibration curve standards**: the following three stock standards are used to prepare the initial calibration curve:

10.4.5.1. 8270 Custom Mix 1, Supelco, 400ug/mL, Quote# 20447738

10.4.5.2. n-Nitrosodiphenylamine, Supelco, 5000ug/mL, catalog # 46702-U

10.4.5.3. 1,4-Dioxane, Restek, 2000ug/mL, catalog # 30287

10.4.6 **Initial Calibration Intermediate Standard**: 2.5mL of 400ug/mL Supelco 8270 Custom Mix 1 plus 200uL of the 5000ug/mL n-Nitrosodiphenylamine solution plus 500uL of the 2000ug/mL 1,4-Dioxane solution are diluted to 5.0mL with dichloromethane. The resulting intermediate standard has a concentration of 200mg/L for each compound.

10.4.7 **Initial Calibration Working Standards**: The following working calibration standards are prepared by using the intermediate mix listed above (10.4.6):

Standard Concentration*	Amount of Intermediate Standard added	Amount of Stock internal standard added	Final Volume
5ppm	25uL	10uL	1000uL
10ppm	50uL	10uL	1000uL
25ppm	125uL	10uL	1000uL
50ppm	250uL	10uL	1000uL
80ppm	400uL	10uL	1000uL
100ppm	500uL	10uL	1000uL
120ppm	600uL	10uL	1000uL

10.4.8 **Initial Calibration Verification stock standards (second-source):** Restek, custom 8270,catalog # 52939, 200ug/mL per compound. Restek n-nitrosodiphenylamine, catalog# 31429, 1000ug/ml. Supelco 1,4-Dioxane, catalog #48367, 2000ug/mL.

10.4.9 **Initial Calibration Verification working standard (second source):** Dilute 250uL of the custom 8270 second source standard #52939, 50ul of n-Nitrosodiphenylamine #31429, 25uL of 1,4-Dioxane #48367 and 10uL of the stock internal standard solution (10.4.1) to 1mL with methylene chloride. This gives a final concentration of 50ppm.

10.4.10 **LCS/MS Standard working solution**: Supelco 70 Component Custom LCS Mix catalog # 861389-U, 200ug/mL. Supelco n-Nitrosodiphenylamine, catalog # 46702-U, 5000ug/mL. The extraction analyst spikes each LCS/LCSD and matrix spike sample with 250uL of the LCS mix and 10uL of the n-NDPA solution. This produces a concentration of 50ug/mL.

10.4.11 **Other calibrations:** Other compounds are analyzed per client requests. Curves are prepared at levels similar to those of the standards above. The calibration standards and the second source

standards are as follows: Calibration Standards, Benzidine, Supelco, catalog # 40005, 5000ug/mL; EPA CLP SOW OLM4 mix, Supelco. catalog # 47514-U, 2000ug/mL (contains Acetophenone, Atrazine, Benzaldehyde, Biphenyl and Caprolactam). Second Source standards, Benzidine, Restek, catalog# 31441, 1000ug/mL; EPA CLP SOW OLM4 mix, Absolute Standards, catalog #19253, 2000ug/mL.

11. Calibration

11.3 General Comment: When constructing a linear initial calibration curve, the analyst can drop curve points as follows:

- The lowest curve point can be dropped as long as there is a standard that can meet the necessary reporting limits of the associated samples (or the reporting limits would have to be raised accordingly).
- The highest curve point can be dropped but this decreases the upper calibration range, thereby limiting the analyst to reporting data within this new calibration range (this may cause more dilutions).
- Any other curve point can only be deleted if it can be proven that it was a bad injection, instrument failure, etc. A supervisor or the Quality Manager is required to approve any such instance.

11.3.2 Internal Standard Assignment List (from Method SW-846 8270C-Table 5): this section lists the internal standard compounds and all of the target compounds that are assigned to each internal for quantitation:

1,4-Dichlorobenzene-d4

Aniline
Benzyl alcohol
Bis(2-chloroethyl)ether
Bis(2-chloroisopropyl)ether
2-Chlorophenol
1,3-Dichlorobenzene
1,4-Dichlorobenzene
1,2-Dichlorobenzene
2-Fluorophenol (surrogate)
Hexachloroethane
2-Methylphenol
4-Methylphenol
N-Nitroso-dimethylamine
N-Nitroso-di-n-propylamine
Phenol
Phenol-d6 (surrogate)

Naphthalene-d8

Acetophenone
Benzoic acid
Bis(2-chloroethoxy)methane
4-Chloroaniline
4-Chloro-3-methylphenol
2,4-Dichlorophenol
2,6-Dichlorophenol
2,4-Dimethylphenol
Hexachlorobutadiene
Isophorone
2-Methylnaphthalene
Naphthalene
Nitrobenzene
Nitrobenzene-d8 (surrogate)
2-Nitrophenol
1-Methylnaphthalene

1,4-Dioxane
Pyridine
2-Chlorophenol-d4(advisory surrogate)
Benzaldehyde
1,2-Dichlorobenzene-d4(advisory surrogate)
1,2,4-Trichlorobenzene

Acenaphthene-d10

Acenaphthene
Acenaphthylene
1,2-Diphenylhydrazine
2-Chloronaphthalene
4-Chlorophenyl phenyl ether
Dibenzofuran
Diethyl phthalate
Dimethyl phthalate
2,4-Dinitrophenol
2,4-Dinitrotoluene
2,6-Dinitrotoluene
Fluorene
2-Fluorobiphenyl (surrogate)
Hexachlorocyclopentadiene
2-Nitroaniline
3-Nitroaniline
4-Nitroaniline
4-Nitrophenol
Biphenyl
2,4,6-Tribromophenol (surrogate)
2,4,6-Trichlorophenol
2,4,5-Trichlorophenol

Phenanthrene-d10

Atrazine
Anthracene
4-Bromophenyl phenyl ether
Di-n-butyl phthalate
4,6-Dinitro-2-methylphenol
Carbazole
Fluoranthene
Hexachlorobenzene
N-Nitroso-diphenylamine
Pentachlorophenol
Phenanthrene

Chrysene-d12

Benzidine
Benzo(a)anthracene
Bis(2-ethylhexyl)phthalate
Butyl benzyl phthalate
Chrysene
3,3'-Dichlorobenzidine
Pyrene
Terphenyl-d6 (surrogate)
Di-n-octyl phthalate
Indeno(123,cd)pyrene

Perylene-d12

Benzo(b)fluoranthene
Benzo(k)fluoranthene
Benzo(g,h,i)perylene
Benzo(a)pyrene
Dibenz(a,h)anthracene

11.4.2.2 **CCC's** – If the difference for each CCC is <20%, the initial calibration is assumed to be valid. Otherwise corrective action must be taken and the system re-calibrated. All non-CCC compounds must be within 40% from the average RF from the initial calibration.

12. Procedure

12.2 Each sample, blank, LCS and spike extract is spiked with 10uL of internal standard working solution prior to analysis.

13. Quality Control

13.2 Internal standards of all extracts and quality control samples are monitored by the laboratory and impacted samples may be rerun at the laboratory's discretion, but failed internal standard area counts do not automatically require the re-extraction or re-analysis of the samples.

13.4 If a method blank contains compounds above the reporting limits, but all associated samples do not have hits above the reporting limits, or they are at least 20 times greater than the blank value for the same compounds, samples may be reported with appropriate data qualifiers. Samples may also be reported with data qualifiers when there is inadequate sample to reextract, or the reextract would be outside of hold time and the client would prefer the original data.

13.5 If LCS recoveries are above the acceptable quality control limits, and there are no hits for these compounds in the associated samples, the sample data may be reported with appropriate data qualifiers.

13.5 Per client request an LCSD is also extracted with every extraction batch. This spike is used to prove precision in the event of a MS/MSD precision failure, due to a matrix effect. LCSD recoveries are also monitored and must meet the same requirements of the LCS.

14. Method Performance

No Applicable changes.

15. Pollution Prevention and Waste Management

No Applicable Changes.

16. References

Test Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater, Appendix A to Part 136, Method 625 – Base/Neutrals and Acids

17. Tables, Diagrams, Flowcharts, Appendices, Addenda etc.

18. Revisions

Document Number	Reason for Change	Date
ALL-GB-O-001-Rev.2	Added Section 11.4.2.2 Added references for EPA 625	12June2006

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STANDARD OPERATING PROCEDURE

Determination of Trace Metals in Waters and Wastes by Inductively Coupled Plasma Mass Spectroscopy

Reference Methods: EPA SW846 6020

SOP NUMBER:	GB-I-026-Rev.1
EFFECTIVE DATE:	Date of Final Signature
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APPROVAL

Nils Melberg, Laboratory Manager — Date 2/28/06

Arthur F. Lautenbach, Quality Manager — Date 2/28/06

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1. Purpose

1.1 The purpose of this Standard Operating Procedure (SOP) is to provide a consistent format for analyzing samples using the ICPMS.

2. Scope and Application

2.1 Inductively coupled plasma-mass spectrometry (ICP-MS) is applicable to the determination of sub-ppb (ug/L) concentrations of a large number of elements in aqueous samples and in solid extracts or digests. When dissolved constituents are required, samples must be filtered and acid-preserved prior to analysis. Dissolved samples are typically acid digested prior to analysis. Acid digestion prior to filtration and analysis is required for aqueous and solid samples for which total (acid-leachable) elements are required.

2.2 This SOP is applicable to the determination of the following elements, at a minimum:

Analytes									
Aluminum	Al	Cadmium	Cd	Lead	Pb	Selenium	Se	Titanium	Ti
Antimony	Sb	Calcium	Ca	Magnesium	Mg	Silver	Ag	Vanadium	V
Arsenic	As	Chromium	Cr	Manganese	Mn	Sodium	Na	Zinc	Zn
Barium	Ba	Cobalt	Co	Molybdenum	Mo	Strontium	Sr		
Beryllium	Be	Copper	Cu	Nickel	Ni	Thallium	Tl		
Boron	B	Iron	Fe	Potassium	K	Tin	Sn		

2.3 If Method 6020 is used to determine any analytes not listed in above table, it is the responsibility of the analyst to demonstrate the accuracy and precision of the method in the waste to be analyzed. The analyst is always required to monitor potential sources of interferences and take appropriate action to ensure data of known quality.

2.4 Use of this method is restricted to analysts who are knowledgeable in the recognition and in the correction of spectral, chemical, and physical interferences in ICP-MS.

3. Summary of Method

3.1 Prior to analysis, samples which, require total ("acid-leachable") values must be digested using appropriate sample preparation methods including 3020 and 3050B.

3.2 Method 6020 describes the multi-elemental determination of analytes by ICP-MS. The method measures ions produced by a radio frequency inductively coupled argon plasma. Analyte species originating in a liquid are nebulized and the resulting aerosol transported by argon gas into the plasma torch. The ions produced are entrained in the plasma gas and introduced, by means of an interface, into a mass spectrometer. The ions produced in the plasma are sorted according to their mass-to-charge ratios and quantified with a channel electron multiplier. Interferences must be assessed and valid corrections applied or the data flagged to indicate problems. Interference correction must include compensation for background ions contributed by the plasma gas, reagents, and constituents of the sample matrix.

4. Interferences

4.1 Isobaric Elemental Interferences – Isobarice elemental interferences result when isotopes of different elements have the same nominal mass-to-charge ratio and connot be resolved with the instruments spectrometer. One way to solve this problem is to measure a different isotope for which there is no interference. Alternatively, one can monitor another isotope of the element and subtract an appropriate amount from the element being analyzed, using known isotope ratio information. Corrections for most of the common elemental interferences are programmed into the software.

4.2 Isobaric Polyatomic Interferences – Isobaric polyatomic interferences result when ions containing more than one atom have the same nominal mass-to-charge ratio as an analyte of interest and can not be resolved by the instrument's spectrometer. Examples include ArCl+ (mass 75) which interferes with As. ClO+ (mass 51) which interferes with V, which must be corrected by measuring ClO+ at mass 53. When possible an interference free isotope should be chosen, to be measured.

4.3 Physical interferences are associated with the sample nebulization and transport processes as well as with ion-transmission efficiencies. Nebulization and transport processes can be affected if a matrix component causes a change in surface tension or viscosity. Changes in matrix composition can cause significant signal suppression or enhancement. Dissolved solids can deposit on the nebulizer tip of a pneumatic nebulizer and on the interface skimmers (reducing the orifice size and the instrument performance). Total solid levels below 0.2% (2,000 mg/L) have been currently recommended to minimize solid deposition. An internal standard can be used to correct for physical interferences, if it is carefully matched to the analyte so that the two elements are similarly affected by matrix changes.

4.4 Memory interferences can occur when there are large concentration differences between samples or standards, which are analyzed sequentially. Sample deposition on the sampler and skimmer cones, spray chamber design, and the type of nebulizer affects the extent of the memory interferences, which are observed. The rinse period between samples must be long enough to eliminate significant memory interference.

4.5 It is important to note that matrix matching acid concentrations and compositions between standards, blanks and samples cannot be ignored.

4.6 Chromic acid should never be used to clean any container used in ICP-MS analysis.

4.7 Borosilicate glass in sample containers can lead to interference of Boron concentrations in samples.

5. Safety

5.1 The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable. Cautions are included for known extremely hazardous materials.

5.2 A reference file of Material Safety Data Sheets (MSDS) is made available to all personnel involved in the chemical analysis, and is located at the front desk. A formal safety plan has been prepared and is distributed to all personnel with documented training.

5.3 Analysts should take necessary safety precautions when handling chemicals and samples. Proper personal protective equipment may include safety gloves, lab coats, and safety glasses or goggles. Analysts should be familiar with the MSDS sheets for all chemicals and reagents they use for this procedure and the location of the MSDS sheets within the laboratory. Any questions or concerns should be taken to the laboratory Chemical Hygiene/Safety Officer.

6. Definitions

6.1 Refer to the most current version section 10 of the Pace Quality Manual.

7. Responsibilities and Distribution

7.1 Personnel

7.1.1 All personnel involved with sample preparation and analysis are responsible for adherence to this SOP. A controlled copy will be available for review and consultation within the area methods manual.

7.1.2 Personnel are responsible for ensuring that any deviations to this SOP are reported to the laboratory manager.

7.2 Laboratory Manager

7.2.1 The laboratory manager is responsible for ensuring adherence to this SOP and will receive a controlled copy of this SOP.

7.2.2 The laboratory manager is responsible for performing a biennial review of the SOP and reporting any required revisions to the Quality Assurance Office.

7.3 Quality Assurance Office

7.3.1 The QA Office is responsible for performing a biennial review of the SOP in conjunction with the purchasing department and revising as needed.

7.3.2 The QA Office is responsible for ensuring that all revisions to the SOP are implemented.

7.4 Revisions

7.4.1 This SOP will be reviewed on a biennial basis at a minimum, and any required revisions would be incorporated.

8. Sample Collection, Preservation and Handling

8.1 All sample containers must be HDPE, glass, or Teflon. The containers are purchased pre-cleaned and documented to be contaminant free.

8.2 Aqueous Samples

8.2.1 Dissolved samples must be filtered through a 0.45-um pore diameter membrane filter at the time of collection or as soon after as practically possible. The laboratory can perform the filtration if the step was not performed in the field. The filtrate is then preserved to a pH<2 with nitric acid, acid not to exceed 5% of the container capacity.

8.2.2 Total samples are preserved to a pH<2 with nitric acid, acid not to exceed 5% of the container capacity.

NOTE: Aqueous samples that react violently to the addition of acid maybe collected without chemical preservation with proper variances approved by the regulatory authority. The responsibility of requesting this variance lies with the sample collector.

NOTE: Samples may be preserved in the lab. The samples may not be processed until 16 hours after preservation with a pH test of <2.

8.3 Solids samples require no chemical preservation.

8.4 Shipments of samples to the laboratory require thermal preservation in the form of cubed or block ice. At the time of laboratory receipt, proper thermal preservation is checked by measuring the temperature of melt water or when provided the temperature blank. The Pace Analytical acceptable temperature range is 2 to 6^0 C. All QAPjP and regulatory authority requirements become priority over this requirement.

8.5 There are no thermal storage requirements for aqueous samples. Solids samples require storage at 2 to 6^0 C. All QAPjP and regulatory authority requirements become priority over this requirement.

9. Equipment and Supplies

9.1 All reusable labware (glass, quartz, polyethylene, PTEFE, FEP, etc.) should be sufficiently clean for the task objectives.

9.2 ICP/MS System, comprised of the following:

9.2.1 Perkin Elmer Elan 6000 Inductively Coupled Plasma Mass Spectrometer and computer and printer

9.2.2 Perkin Elmer AS 91 Autosampler

9.2.3 Gilson Minipulse3 pereistaltic pump and pump tubing

9.2.4 Neslab CFT-775 Refrigerated Circulator

9.2.5 Argon gas supply (high-purity grade, 99.99%)

9.3 Analytical balance, with capability to measure to 0.1 mg.

9.4 Hot block, variable temperature, capable of maintaining a temp. of 95 ± 5^0C.

9.5 Pipetters, capable of delivering volumes ranging from 10 to 5000 uL, and associated metal-free disposable pipette tips.

9.6 50-mL disposable digestion cups (Environmental Express).

9.7 Glassware – Class A volumetric flasks

9.8 See Tables A and B for summary.

10. Reagents and Standards

10.1 Reagents:

10.1.1 Nano-Pure H_2O (>18 mega ohms)

10.1.2 Concentrated HNO_3 Trace Metals Grade

10.1.3 Concentrated HCL Trace Metals Grade

10.2 Stock Standards

10.2.1 E6000 Dual Detector Solution (200ppb Mg, Cu, Rh, Cd, Pb, 2%HNO_3): Used to optimize between the Pulse stage and Analog Stages.

10.2.2 Elan 5 Calibration 4 Solution (10ppb Be, Co, Ge, In, V, Tl, 2%HNO_3): Used to Optimize the Autolense.

10.2.3 Elan 6100 Setup/Stab/Masscal Solution (10ppb Mg, Cu, Rh, Cd, In, Ba, Ce, Pb, U, 2%HNO_3): Used for tuning and the Daily Performance check

10.2.4 ICP-MS Cal Std Solution A (20ppb As, Ba, Be, B, Cd, Cr, Cu, Pb, Mn, Ni, Pb, Ag, Sr, Tl, V, Zn – 40ppb Se – 250ppb Al, Ca, Fe, Mg, K, Na – HNO_3): Used for calibration.

10.2.5 ICP-MS Cal Std Solution B (20ppb Sb, Mo, Sn, Ti, 10%HCL): Used for calibration.

10.2.6 ICP-MS ICV Std Solution A (20ppb As, Ba, Be, B, Cd, Cr, Cu, Pb, Mn, Ni, Pb, Ag, Sr, Tl, V, Zn – 40ppb Se – 250ppb Al, Ca, Fe, Mg, K, Na – HNO_3): Used for initial calibration verification.

10.2.7 ICP-MS ICV Std Solution B (20ppb Sb, Mo, Sn, Ti, 10%HCL): Used for initial calibration verification.

10.2.8 Multi-element Internal Standard (10mg/L Bi, Ho, In, Li6, Se, Tb, Y, 2%HNO_3): Used for Internal standard.

10.2.9 Single-element Internal Standard (10mg/L Ge): Used for internal standard.

10.2.10Au (1,000ug/mL): Used to stabilize Ag in standards.

10.2.116020ICS-9A (250ug/mL Fe, Na – 1000ug/mL Al, Mg, P, K, S – 20 Mo, Ti – 21215ug/mL CL^- – 3000ug/mL Ca – 2000 C – 1%HNO_3): Used for the ICS-A and ISC-AB solutions.

10.3 Please see Attachment II for directions on making Intermediate and working standards and Attachment I for concentrations of standards.

10.4 All standards, reagents, and spiking solutions are kept at room temperature. Stock standards and reagents can be used until they expire, based on the manufactures expiration data.

10.5 The use of any standard or reagent will be terminated if any contamination or problems arise prior to the expiration date.

10.6 Standards, reagents, and solutions are logged as follows:

Stock standards have a copy of their certificate of analysis logged onto a page in the ICPMS Stock Standard Log. The three-digit logbook number followed by a dash and the page number represent the stock standard number (e.g. 784-64).

Reagents are logged in the same manner, except they are logged into the Metals Reagent Logbook.

Solutions (including standards, intermediates, and spikes) are logged into the ICPMS Standard Reference Log, by describing the directions in which they were made. They are logged as follows:

Logbook # - Page # - Line # (eg. 785-62-08)

11. Calibration

11.1 Calibration Curve: A Blk, 1, 2, 3, 4, and 5 are analyzed after a pre-calibration blank is run. The ICPMS software creates a curve based on this data and the following equation: Y=a(x)+b simple linear forced through zero

11.2 Calibration Levels:

Be, B, Ti, V, Cr, Mn, Co, Ni, Cu, Zn, As, Sr, Mo, Ag, Cd, Sn, Sb, Ba, Tl, Pb	5, 10, 20, 40ppb
Se	10, 20, 40, 80ppb
Na, Mg, Al, K, Ca, Fe	125, 250, 500, 1000ppb

11.3 Internal Standard References:

11.3.1 An internal standard is a non-analyte isotope that is added to the standards and samples before they are analyzed to correct for instrument drift and physical interferences. Internal standards must be present in all samples, standards and blanks at identical levels. This is achieved by directly adding the internal standard stock solution to all samples, standards and blanks by on-line addition prior to nebulization using a second channel of the peristaltic pump and a mixing Y-connector. The concentration of the internal standard should be sufficiently high that good precision is obtained in the measurement of the isotope used for data correction and to minimize the possibility of correction errors if the internal standard is naturally present in the sample.

11.3.2 The following internal standard references are recommended:

Sc	Be - Cu
Ge	Zn - Se
Y	Sr, Mo
In	Ag - Ba
Bi	Tl – Pb

11.4.3 Due to matrix interferences one or more of the internal standards may not be suitable. It is up to the analyst to recognize and correct the problem by selecting another internal standard and rerun the sample/samples or reprocess the data.

11.4.4 During the determination, the software uses the ratio of analyte and internal standard intensities to adjust the final intensity values. Ratios are based on the calibration blank inensities.

11.4 Timing Parameters:

Sweeps/Reading:	10
Readings/Replicate:	1
Number of Replicates:	3
Tuning File:	default.tun
Optimization File:	default.dac
QC Enabled:	Yes
Settling Time:	Normal
Scan Mode:	Peak Hopping
MCA Channels:	1
Dwell Time:	100.0 ms
Integration Time:	1000 ms

11.5 Signal Processing

Detector Mode:	Dual
Measurement Units:	Cps
AutoLens:	On
Spectral Peak Processing:	Average
Signal Profile Processing:	Average
Blank Subtraction:	After Internal Standard
Baseline Readings:	0
Smoothing:	Yes, Factor5

11.6 Equations:

The following interference equations are used to correct for isobaric elemental and polyatomic interferences. All equations must be specified in the method before any other data acquisition or data analysis parameters are set.

Ti (47.948)	- (0.089645*Ca44)
V (50.944)	- (3.1081-Cr53) + (0.353351*Cr52)
Ge(73.922)	- (0.116645-Se77)
As(74.922)	-3.1278*(ArCl77 - (0.815*Se82))
Se(81.917)	- (1.008696*Kr83)
Sr(86.909)	- (0.385713*Rb85)
Cd(110.904)	- (1.073*Cd108) + (7.6398*Cd106)
Cd(113.904)	- (0.027250*Sn118)
In(114.904)	- (0.014032*Sn118)
Pb(207.977)	+ (Pb206) + (Pb207)

11.7 Calibration Information:

Curve Type:	Linear Thru Zero
Sample Units:	ug/L
Std Units:	ug/L
Calibration Levels:	

11.8 Demonstration and documentation of acceptable initial calibration is required before any samples are analyzed and is required periodically throughout sample analysis as dictated by results of continuing calibration checks.

11.8.1 ICV - Initial calibration accuracy must be evaluated before any samples are analyzed through the analysis of an Initial Calibration Verification standard (ICV), which includes all analytes of interest. The ICV should be at or near the midpoint of the calibration range, derived from a source independent of the calibration standards, and must quantitate within +/-10% of the expected value. If these limits are not meet then the analysis must be aborted, the problem corrected, the instrument recalibrated and the run reanalyzed.

11.8.2 CCV - Calibration drift is monitored through the analysis of Continuing Calibration Verification standard (CCV) after every 10 samples and again at the end of the run. It must quantitate within 10% of expected value. Any sample analyzed under out-of-control calibration must be reanalyzed.

11.8.3 ICB/CCB - The Initial Calibration Blank is run to check the accuracy of the curve. The Continuing Calibration Blanks are run to check for calibration drift. In the absence of project specific reporting limits, the results of the calibration blanks must be less than the reporting limit.

12. Procedure

12.1 Instrument Startup:

12.1.1 Verify argon supply and pressure, water chiller is on, adequate amount of internal standard and rinse, and waste container is empty.

12.1.2 Insure that all peristaltic pump tubes are in good condition and correctly clamped into the peristaltic pumps. Verify that the flow of sample and internal standard solutions through the uptake lines and into nebulizer is free from pulsations.

12.1.3 Initiate the plasma and allow at least 15 minutes of warm-up.

12.2 Tuning/Daily Performance Check:

Measured Peak Width:	0.625 to 0.675
Measures Mass:	+/- 0.1 of expected mass
Sensitivity:	Rh >80,000 cps
	Mg >20,000 cps
	Pb >100,000 cps
Precision Mg, Rh, Pb:	< 3.0 Net Intens. RSD
Oxide Ions (CeO/Ce):	< 3.0%
Doubly Charged Ions (Ba++/Ba+):	< 3.0%
Background:	<30 cps @ Mass 220

12.3 Sample Preparation

12.3.1 Water Samples: All water samples must be digested as described in Method 3020A.

12.1.1.1 Turn on the Hot Block and allow it to warm up. Before placing samples in the block to digest, verify that the sample well temperature is in the range of 90-95 ^{0}C, adjust as required. Record the sample well temperature in the prep logbook. Verify that the hood is turned on.

12.1.1.2 Prepare the MB and LCS (an LCSD may also be required) by adding 50.0mL of Nanopure water into digestion vials. One MB and one LCS must be prepared for each batch of 20 samples or less.

12.1.1.3 Prepare the parent sample, duplicate and MS, or the MS and MSD by placing 50.0mL aliquots of a selected sample from each batch into digestion vials. One MS and one duplicate or MSD must be prepared for each analytical batch of 20 samples or less. The parent sample is chosen at random – excluding rinse blanks, equipment blanks, and trip blanks.

12.1.1.4 Place 50.0mL of each sample in a digestion vial.

12.1.1.5 Spike the LCS (LCSD), MS, and MSD with 0.10mL of each: High-Purity Standards SM-1125-005 (Cal B Stk Std) and SM-1125-006 (Cal A Stk Std).

12.1.1.6 Carefully add 3.0mL of concentrated HNO_3 to each sample, MB, LCS (LCSD), MS, and MSD vial. Heat in the hot block for 4 hours or until the sample has been reduced to a minimum volume of approximately 5mLs. Do not let sample go to dryness, low sample recovery will result. If this occurs, discard sample and re-prep.

12.1.1.7 Remove the digestates from the hot block and allow to cool in the hood.

12.1.1.8 Dilute each vial to a final volume of 50.0mL with Nanopure water.

12.1.1.9 Place a screw cap on each vial and shake. Allow to settle before analysis.

12.1.1.10 If any digestate is turbid or there is a concern that insoluble materials may clog the nebulizer, filter the digestate with a 2.0μm plunger or filter paper or centrifuge.

12.1.2 Soil/Solid Samples

12.1.2.1 Soils, Sludges, Sediments, and solids are prepared according to Method 3050B.

12.1.2.2 Turn on the hot block and allow it to warm up. Before placing samples in the block to digest, verify that the sample well temperature is in the range of 90-95 ^{0}C, adjust as required. Record the sample well temperature in the prep logbook. Verify that the hood is turned on.

12.1.2.3 If possible, mix each sample thoroughly to homogenize. If homogenization is not feasible, remove the top layer of the sample from the container and discard. Remove a sample aliquot in the range of 0.495 – 0.505 g and transfer to a digestion vial. See the most current version of Pace ALL SOP on Sub-Sampling (ALL-Q-021-Rev.0.) for more details.

12.1.2.4 Prepare the MB and LCS (an LCSD may also be required) by labeling a digestion vial for each. One MB and one LCS (LCSD) must be prepared for each analytical batch of 20 samples or less.

12.1.2.5 Prepare the parent sample, duplicate and MS, or the MS and MSD by placing aliquots of a selected sample from the batch into digestion vials as described for samples. One MS and one duplicate or MSD must be prepared for each analytical batch of 20 samples or less. The parent sample is chosen at random.

12.1.2.6 Spike the LCS (LCSD), MS, and MSD with 0.50mL of each: High-Purity Standards SM-1125-005 (Cal B Stk Std) and SM-1125-006 (Cal A Stk Std).

12.1.2.7 Add 5.0mL Nanopure water to the sample and mix well.

12.1.2.8 Add 2.5mL of concentrated HNO_3, mix the slurry, and cover with a watch glass. Heat the samples and QC on the hot block to 90 -95 °C and reflux for 15 minutes without boiling.

12.1.2.9 Remove from the hot block and allow the samples and QC to cool, add 2.5mL of concentrated HNO_3, replace the watch glass, and reflux for 30 minutes. If brown fumes are generated, repeat this step until no brown fumes are given off. The release of brown fumes indicates oxidation of the sample is in progress. This step is done to ensure complete oxidation. Remove from the hot block and allow the samples and QC to cool.

12.1.2.10 Heat in the hot block without boiling until the volume is reduced to 5.0mL or for two hours. Remove from the hot block and cool for about 5-7min.

12.1.2.11 Add 1.0mL of Nanopure water and 1.0mL of 30% H_2O_2. Cover with a watch glass and return to the hot block for 15 minutes. Warming will start the peroxide reaction. Care must be taken to ensure that losses do not occur due to vigorous effervescence. Effervescence should subside after 15min. Remove from hot block and let cool for 5-7min.

12.1.2.12 If the effervescence has not subsided, add additional 1-mL aliquots of 30% H_2O_2, cover with a watch glass, and return to the hot block until the effervescence is minimal or until the general sample appearance is unchanged. (Note in the comments section of prep sheet the additional aliquots). Remove from hot block and let cool for 5-7min.

12.1.2.13 **NOTE:** DO NOT add more than a total of 5 mL H_2O_2.

12.1.2.14 **NOTE:** Certain matrices such as sludges and ashes are known to consume more H_2O_2 and as a result 2.5mL may replace the 1.0mL in steps 12.1.2.11 and 12.1.2.12 for H_2O_2.

12.1.2.15 Heat the acid-peroxide mix until the volume is reduced to 5.0mL or for two hours. Remove from the hot block and allow the samples and QC to cool.

12.1.2.16 Dilute the samples and QC to 50mL with Nanopure water. Place a screw cap on each vial and shake. Allow to settle before analysis. Filter or centrifuge if needed. The samples and QC are now ready for analysis.

12.2 Automated Calibration, Quality Control and Sample Analysis:

12.2.1 After a passing Daily Performance Report has been generated, an analytical run can be created. A typical analytical run starts with a pre-calibration blank, Calibration Levels Blank,1 - 5, ICV and ICB, ICSA and ICSAB, a Low level Check and the Daily Linear Dynamic Ranges are entered followed by two instrument blanks. The samples can then be entered with a CCV and CCB bracketing all sample periods. A sample period is not to exceed 10 samples.

12.2.2 Directions to make up the standards can be found in Attachment I.

12.2.3 Concentrations of the standards can be found in Attachment II.

12.3 CALCULATIONS:

12.3.1 The instrument software performs all calculations necessary to convert raw spectral intensity data into quantitative results.

12.3.2 Sample results are calculated from the raw quantitative results. This is based on the method of sample preparation.

Aqueous digested final result (3005A, 3020A) = [final volume/initial volume] * [1/dilution factor] * raw quantitative result

Solid digested final result (3050B,3050B+7.5) = [(final volume)/initial weight)] * [1000g/1kg] * [1mg/1000ug] * [1/dilution factor] * [1/%solids]

Hardness as $CaCO_3$ in mg/L = 2.497 * $[Ca_{\text{in mg/L}}]$ + 4.118 * $[Mg_{\text{in mg/L}}]$

13 Quality Control

13.1 A batch will consist of 20 of fewer samples. Batch Quality Control will include a Method Blank(MB), Laboratory Control Spike(LCS), Matrix Spike(MS), Matrix Spike Duplicate(MSD), Post Spike(PS), and a Serial Dilution(SDL). It may also include an Laboratory Control Spike Duplicate(LCSD)

13.1.1 The Method Blank is used to verify that interferences caused by contaminants in the solvents, reagents, glassware, etc. are known and minimized. The method blank is processed through all clean-ups, etc., which were performed on the samples in the batch. For a method blank to be acceptable, in the absence of project specific criteria, the concentration shall not be higher than the highest of the following:
The reporting limit , or Five percent of the regualtory limit of concern for that analyte, or Five percent of the measured concentration in a particular

sample of interest. See Flowcharts for a visual guide on applying flags to the above conditions. Each sample in the batch is assessed against the above criteria to determine if the sample results are acceptable. Any sample associated with an unacceptable blank is either flagged, re-prepped for analysis, or if re-prepping is not an alternative, the results are reported with the appropriate data qualifying codes.

13.1.2 A laboratory control sample (LCS) consists of a control matrix which has been spiked with the analytes(s) of interest or compounds representative of those analytes. Laboratory Control Samples are analyzed at a minimum of 1 per batch of 20 or fewer samples or preparation method. Results of the LCS are expressed in terms of percent recovery, and are used to determine batch acceptance. Acceptance limits are generated based on laboratory generated data and are not to exceed 75 to 125% of the expected recovery. If these limits are not meet with the instrument in control, then the entire batch will be re-digested and re-analyzed.

13.1.3 An LCS Duplicate may be analyzed to evaluate laboratory precision. The LCSD must also meet the criteria for the LCS. The Relative Percent Difference (RPD) will be calculated between the LCS and LCSD. The RPD is calculated as outlined below:

$$RPD = \frac{|D_1 - D_2|}{(D_1, + D_2,)/2} \times 100$$

where:
RPD = relative percent difference.
D_1 = first sample value.
D_2 = second sample value (duplicate)

The control limit for RPD is based on laboratory generated data and is not to exceed 20%. If outside this limit, all associated results are given a * data qualifier. Data generated with LCS samples that fall outside the established acceptance criteria are judged to be out-of-control. These data are considered suspect and the corresponding samples are reanalyzed or reported with qualifiers.
NOTE: In the event where adequate sample is not supplied by the client to perform a Matrix Spike/ Matrix Spike Duplicate, the LCS and duplicate can lend insight on the precision of the analysis.

13.1.4 Matrix spikes (MS and MSD) are performed to evaluate the effect of the sample matrix upon analytical methodology. A separate aliquot of sample is spiked with the analyte of interest and analyzed with the sample. MS and MSD are performed at a minimum frequency of one pair in 20 samples per matrix type per sample preparation method and is done more frequently where regulations require. Matrix spike recoveries are evaluated against in-house control limits. The recovery must not exceed 75 to 125% of the expected recovery. If outside this recovery, the parent is flagged with an N data qualifier. The RPD between the MS and MSD

must be less than 20 %. If outside this limit, the parent is given a * data qualifier. The parent sample for the MS/MSD is chosen at random. Poor performance in a matrix spike generally indicates a problem with the sample composition, and not the laboratory analysis, and results are used to assist in data assessment. A matrix effect is indicated if the LCS data are within acceptance criteria but the matrix spike data exceed the acceptance criteria. Prior to calculating recovery, the parent sample concentration (results <Reporting MDL = 0) is subtracted from the spike aliquot concentrations.

13.1.5 The Serial Dilution (SDL) is run to check for matrix interferences. If the analyte concentration is within the linear dynamic range (LDR) of the instrument and sufficiently high (minimally, a factor of at least 100 times greater than the IDL) an analysis of a fivefold (1+4) dilution must agree within ± 10% of the original determination. If these limits are not meet then an interference effect must be suspected and the data qualified. If the analytes of interest are > the LDR the sample can be diluted and an SDL done off of the dilution.

13.1.6 The Post Spike (PS) is run to verify matrix interferences. An analyte spike added to a portion of a prepared sample, or its dilution, should be recovered to within 75 to 125 percent of the known value. If the spike is not recovered within the specified limits with the instrument in control, then the sample is diluted and reanalyzed until the recovery falls within the limits. The parent sample is reported from the passing dilution. One PS per batch.

13.2 Instrument Quality Control: Prior to the analysis of samples, and in some cases during the analysis run, the following quality control must be generated and/or within limits: Instrument Detection Limits(IDL), Linear Dynamic Range (LDR), Method Detection Limits(MDL), Daily Performance Report, Internal Standards, Interference Correction Solutions A and B(ICSA and ICSAB), Initial Calibration Verification(ICV), Continuing Calibration Verification(CCV), and Initial and Continuing Calibration Blanks(ICB and CCB).

13.2.1 Instrument Detection Limits (IDLs) in ug/L are estimated by calculating the average of the standard deviations of the three runs on three non-consecutive days from the analysis of a reagent blank solution with seven consecutive measurements per day. Each measurement must be performed as though it were a separate analytical sample (i.e., each measurement must be followed by a rinse and/or any other procedure normally performed between the analysis of separate samples). IDLs must be determined at least every three months.

13.2.2 The Linear Dynamic Range (LDR) is determined daily by analyzing a standard expected to be near the high end of the instruments range. The result must be within +/-10% of the expected concentration, or a lesser concentration tested until acceptable results are obtained.

13.2.3 Method detection limits were obtained by multiplying 3.143 by the standard deviation of seven spikes. The spikes went through the digestion procedures and were spiked at a concentration suspected to be within a factor of ten greater than the MDL. The most current version of the MDL SOP, ALL-Q-004, must be followed when determining MDLs. Note: The MDL determined by the MDL study is the theoretical MDL. The MDL used for reporting purposes may be higher than the theoretical MDL.

13.2.4 A Daily Performance Report is generated to verify that the instrument is in tune. It is generated daily or when maintenance is done on the instrument. The Limits are as follows:

	Measured Mass limits	Measured Peak Limits
He-3.016	3.016 +/- 0.10	0.625 – 0.675
Mg-23.985	23.985 +/- 0.10	0.625 – 0.675
Rh-102.905	102.905 +/- 0.10	0.625 – 0.675
Ce-139.905	139.905 +/- 0.10	0.625 – 0.675
Pb-207.977	207.977 +/- 0.10	0.625 – 0.675
U-238.050	238.050 +/- 0.10	0.625 – 0.675

	Net Intensity Mean	Net Intensity RSD
Mg-24.0	>20,000cps	<5.0
Rh-102.9	>80,000cps	<5.0
In-114.9		<5.0
Pb-208.0	>100,000cps	<5.0
Ba-137.9		
Ba++-69.0	<0.03	
Ce-139.9		
CeO-155.9	<0.03	
Background-220	<30.0cps	

If these limits are not met, then the instrument is re-tuned.

13.2.5 The intensities of all internal standards must be monitored for every analysis. When the intensity of any internal standard fails to fall between 30 and 120 percent of the intensity of that internal standard in the blank of the calibration one of the following procedures is followed. The sample is diluted appropriately and reanalyzed with the addition of appropriate amounts of internal standards. This procedure must be repeated until the internal standard intensities fall within the prescribed window. The internal standard for the element, or elements of interest, can also be changed to an internal standard that is within limits and the run reprocessed. If the supporting quality control pass, then the results can be reported. The internal standard recoveries of ICV and CCVs must be between 80-120%.

13.2.6 The ICSA and ICSAB solution are used to verify the magnitude of elemental and molecular-ion isobaric interferences and the adequacy of any corrections at the beginning of an analytical run, prior to the analysis of any samples. The analyst should be aware that precipitation from solution AB may occur with some elements, specifically silver. The control limits for the elements in the ICSAB solution that are in the linear range must be within 80 to 120% of the expected recovery. If an element of interest does not meet these limits, then the problem must be corrected, the instrument reclibrated, and the run reanalyzed.

13.2.7 The ICV is analyzed to check the accuracy of the curve. It must be evaluated before any samples are analyzed. The ICV should be at or near the midpoint of the calibration curve, derived from a source independent of the calibration standards, and must quantitate within +/-10% of the expected value. If these limits are not meet for an element of interest, the problem must be corrected, the instrument recalibrated, and the run reanalyzed. If the ICV fails high and the samples are non-detects, then they may be reported.

13.2.8 The CCV is analyzed to check for calibration drift. The CCV is run after every 10 samples and again at the end of samples. It must quantitate within 10% of expected value. Any sample analyzed under out-of-control calibration must be reanalyzed, following the successful re-calibration of the instrument. If the CCV fails high and the samples are non-detects, then they may be reported.

13.2.9 The ICB is analyzed to check the accuracy of the curve. The CCBs are analyzed to check for calibration drift. In the absence of project specific reporting limits, the results of the calibration blanks must be less than the Reporting Limit. The ICB is run after the ICV and the CCBs are run after the CCVs. If the ICB or CCB fails high for an analyte and the samples are non-detects, then they may be reported.

14 Method Performance

14.1 There are several requirements that must be met to insure that this procedure generates accurate and reliable data. A general outline of requirements has been summarized below. Further specifications may be found in the Laboratory Quality Manual.

14.1.1 The analyst must read and understand this procedure with written documentation maintained in his/her training file.

14.1.2 An initial demonstration of capability (IDC) must be performed per ALL-Q-020, *Training Procedures*. A record of the IDC will be maintained in his/her QA file with written authorization from the Laboratory Manager and Quality Manager.

14.1.3 An annual method detection limit (MDL) study will be completed per ALL-Q-004, *Method Detection Limit Studies*, for this method and whenever there is a major change in personnel or equipment. The results of these studies are retained in the quality assurance office.

14.1.4 Periodic performance evaluation (PE) samples are analyzed per ALL-Q-010, *PE/PT Program*, to demonstrate continuing competence. All results are stored in the QA office.

15 Pollution Prevention and Waste Management

15.1 The quantity of chemicals purchased is based on expected usage during its shelf life and disposal cost of unused material. Actual reagent preparation volumes reflect anticipated usage and reagent stability.

15.2 Excess reagents, samples and method process wastes are characterized and disposed of in an acceptable manner. For further information on waste management consult the current version of ALL-S-002, *Waste Handling.*

16 References

EPA Manual SW846,3rd Edition, 6020

17 Tables, Diagrams, Flowcharts, Appendices, Addenda etc.

17.1	Attachment I -	ICPMS Standard Reference Logbook
17.2	Attachment II -	ICPMS Standard Concentrations (ppb in Solution)
17.3	Flow Chart A-	ICPMS DETERMINATIVE METHOD
17.4	Flow Chart B-	MDL or LOD FLAGGING and REPORTING
17.5	Flow Chart C-	EQL or PSRL FLAGGING and REPORTING
17.6	Table A-	EQUIPMENT
17.7	Table B-	SUPPLIES
17.8	Table C-	REAGENTS

18 Revisions

Document Number	Reason for Change	Date
GB-I-026-Rev.0	Reformatted SOP to Pace Analytical format	1Dec2005
GB-I-026-Rev 1	Added Water and Soil prep methods. Added IS requirenment for ICV/CCV	28Feb2006

Attachment I ICPMS Standard Reference Logbook

ICPMS Standard Refrence Logbook

Logbook #:	1767
Page #:	
Date:	
Analyst	

Elan 6100 Setup Solution (Tune Soln) Standard #: Expiration Date:

Calibration Blank (Blk): Standard #: 1767- -01 Expiration Date:
200uL of Au (_____) + 30mL of HNO_3 to 1.0L with Nano-Pure H2O.

Internal Standards (ISTD) Standard #: 1767- -02 Expiration Date:
2.5 mL of Multi-element Internal Standard (_____) + 2.5 mL of Germanium Internal Standard (_____) to 100mL with Blk.

Calibration Intermediate (Cal Int)/LDR: Standard #: 1767- -03 Expiration Date:
1.0mL of ICPMS Cal A (_____) and 1.0mL of ICPMS Cal B (_____) to 100mL with Blk.

Calibration Expiration Date:

Calibration Standard 1 (Cal 1): 0.25mL of Cal Int to 10mLwith Blk.	Standard #: 1767- -04	
Calibration Standard 2 (Cal 2): 0.50mL of Cal Int to 10mLwith Blk.	Standard #: 1767- -05	
Calibration Standard 3 (Cal 3): 1.00mL of Cal Int to 10mLwith Blk.	Standard #: 1767- -06	
Calibration Standard 4 (Cal 4): 2.00mL of Cal Int to 10mLwith Blk.	Standard #: 1767- -07	
Calibration Standard 5 (Cal 5): 4.00mL of Cal Int to 10mLwith Blk.	Standard #: 1767- -08	
Continuing Calibration Verification (CCV) 10.0mL of Cal Int to 50mLwith Blk.	Standard #: 1767- -09	

Initial Calibration Verification (ICV) Int / Spike (Spk) Standard #: 1767- -10 Expiration Date:
110uL of ICPMS ICV/Spk A (_____) and 110uL of ICPMS ICV/Spk B (_____) + to 100mL with Blk.

Low Level Check (LLC) Standard #: 1767- -11 Expiration Date:
0.5mL of LLC-1 (_____) to 10mL with Blk.

Interference Check A (ICSA) Standard #: 1767- -12 Expiration Date:
0.25mL of 6020ICS-9A (_____) to 10 mL with Blk.

Interference Check AB (ICSAB) Standard #: 1767- -13 Expiration Date:
0.25mL of 6020ICS-9A (_____) + 2.0 mL of Cal Int to 10 mL with Blk.

Linear Dynamic Range Standard 2 (LDR 2) Standard #: Expiration Date:

Other Standards

Standard #:	Standard Name:	Directions:	Expiration Date:

HNO_3:

H_2O: NanoPure

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Attachment II - ICPMS Standard Concentrations (ppb in Solution)

ICPMS Standard Concentrations (ppb in soulution)

	Analyte	Au	ICPMS Cal A	ICPMS Cal B	ICPMS ICV/Spk A	ICPMS ICV/Spk B	6020ICS-9A	LLC-1	Germanium ISTD	Multi-Element ISTD	Cal Int / LDR 1	Cal Blk	Cal 1	Cal 2	Cal 3	Cal 4/ CCV	Cal 5	ICV	ICSA	ICSAB	LLC	LDR 2	ISTD	Tune Soln	Lense Voltage	Analyte
Analytes Tested For	Be		20,000		20,000			20			200	0	5	10	20	40	"80"	22		40	1				10	Be
	B		20,000		20,000			200			200	0	5	10	20	40	"80"	22		40	10					B
	Na		250,000		250,000		2,500,000	2,000			2,500	0	"62.5"	125	250	500	1000	275	62500	62500	100	25000				Na
	Mg		250,000		250,000		1,000,000	2,000			2,500	0	"62.5"	125	250	500	1000	275	12500	12500	100	25000		10		Mg
	Al		250,000		250,000		1,000,000	2,000			2,500	0	"62.5"	125	250	500	1000	275	25000	25000	100	25000				Al
	K		250,000		250,000		1,000,000	2,000			2,500	0	"62.5"	125	250	500	1000	275	25000	25000	100	25000				K
	Ca		250,000		250,000		3,000,000	2,000			2,500	0	"62.5"	125	250	500	1000	275	125000	125000	100	25000				Ca
	Ti			20,000		20,000	20,000	100			200	0	5	10	20	40	"80"	22	500	500	5					Ti
	V		20,000		20,000			60			200	0	5	10	20	40	"80"	22		40	3					V
	Cr		20,000		20,000			20			200	0	5	10	20	40	"80"	22		40	1					Cr
	Mn		20,000		20,000			20			200	0	5	10	20	40	"80"	22		40	1					Mn
	Fe		250,000		250,000		2,500,000	2,000			2,500	0	"62.5"	125	250	500	1000	275	62500	62500	100	25000				Fe
	Co		20,000		20,000			20			200	0	5	10	20	40	"80"	22		40	1				10	Co
	Ni		20,000		20,000			60			200	0	5	10	20	40	"80"	22		40	3					Ni
	Cu		20,000		20,000			100			200	0	5	10	20	40	"80"	22		40	5			10		Cu
	Zn		20,000		20,000			200			200	0	5	10	20	40	"80"	22		40	10					Zn
	As		20,000		20,000			20			200	0	5	10	20	40	"80"	22		40	1					As
	Se		40,000		40,000			200			400	0	10	20	40	80	"160"	44		80	10					Se
	Sr		20,000		20,000			20			200	0	5	10	20	40	"80"	22		40	1					Sr
	Mo			20,000		20,000	20,000	200			200	0	5	10	20	40	"80"	22	500	500	10					Mo
	Ag		20,000		20,000			20			200	0	5	10	20	40	"80"	22		40	1					Ag
	Cd		20,000		20,000			20			200	0	5	10	20	40	"80"	22		40	1			10		Cd
	Sn			20,000		20,000		100			200	0	5	10	20	40	"80"	22		40	5					Sn
	Sb			20,000		20,000		20			200	0	5	10	20	40	"80"	22		40	1					Sb
	Ba		20,000		20,000			20			200	0	5	10	20	40	"80"	22		40	1			10		Ba
	Tl		20,000		20,000			20			200	0	5	10	20	40	"80"	22		40	1				10	Tl
	Pb		20,000		20,000			20			200	0	5	10	20	40	"80"	22		40	1			10		Pb
Other Analytes	C						2,000,000																			C
	P						1,000,000																			P
	S						1,000,000																			S
	Sc									10,000																Sc
	Ge								10,000														250			Ge
	Y									10,000													250			Y
	Rh																						250	10		Rh
	In									10,000													250	10	10	In
	Ce																							10		Ce
	Tb									10,000													250			Tb
	Ho									10,000													250			Ho
	Au	1,000,000																								Au
	Bi									10,000													250			Bi
	U																							10	10	U

Notes:

-All working standards are made up daily unless otherwise noted.
-"-" is the concentration in solution, but is not used in the calibration.
-The LDRs for each analyte are determined for each calibration using the LDR solutions and the high point of the curve.
- Stock Standards

Stock Standards	Vendor Name	Item #	Volume	Other Names
Au	Inorganic Ventures	CGAU1-1	250mL	Gold
ICPMS Cal A	Inorganic Ventures	PACEWI-CAL-1	250mL	
ICPMS Cal B	Inorganic Ventures	PACEWI-CAL-2	250mL	
ICPMS ICV/Spk A	High Purity Standards	SM-1125-006	250mL	Sp Mix Cal A Stk Std
ICPMS ICV/Spk B	High Purity Standards	SM-1125-005	250mL	Sp Mix Cal B Stk Std
6020ICS-9A	Inorganic Ventures	6020ICS-9A	1.0L	
LLC-1	Inorganic Ventures	PACEWI-LLC-1	250mL	Low Level Check Stock
Germanium ISTD	SPEX	CLGE9-1AY	250mL	
Multi-Element ISTD	SPEX	CLISS-1	250mL	
LDR 2	Inorganic Ventures	PACEWI-LDR-1	1.0L	Linear Dynamic Range 2
Tune Solution	Perkin Elmer	N8125030	1.0L	Elan 6100/Setup/Stab/Masscal Solution
Lense Voltage	Perkin Elmer	N8122017	250mL	Elan 5 Calibration 4 Solution

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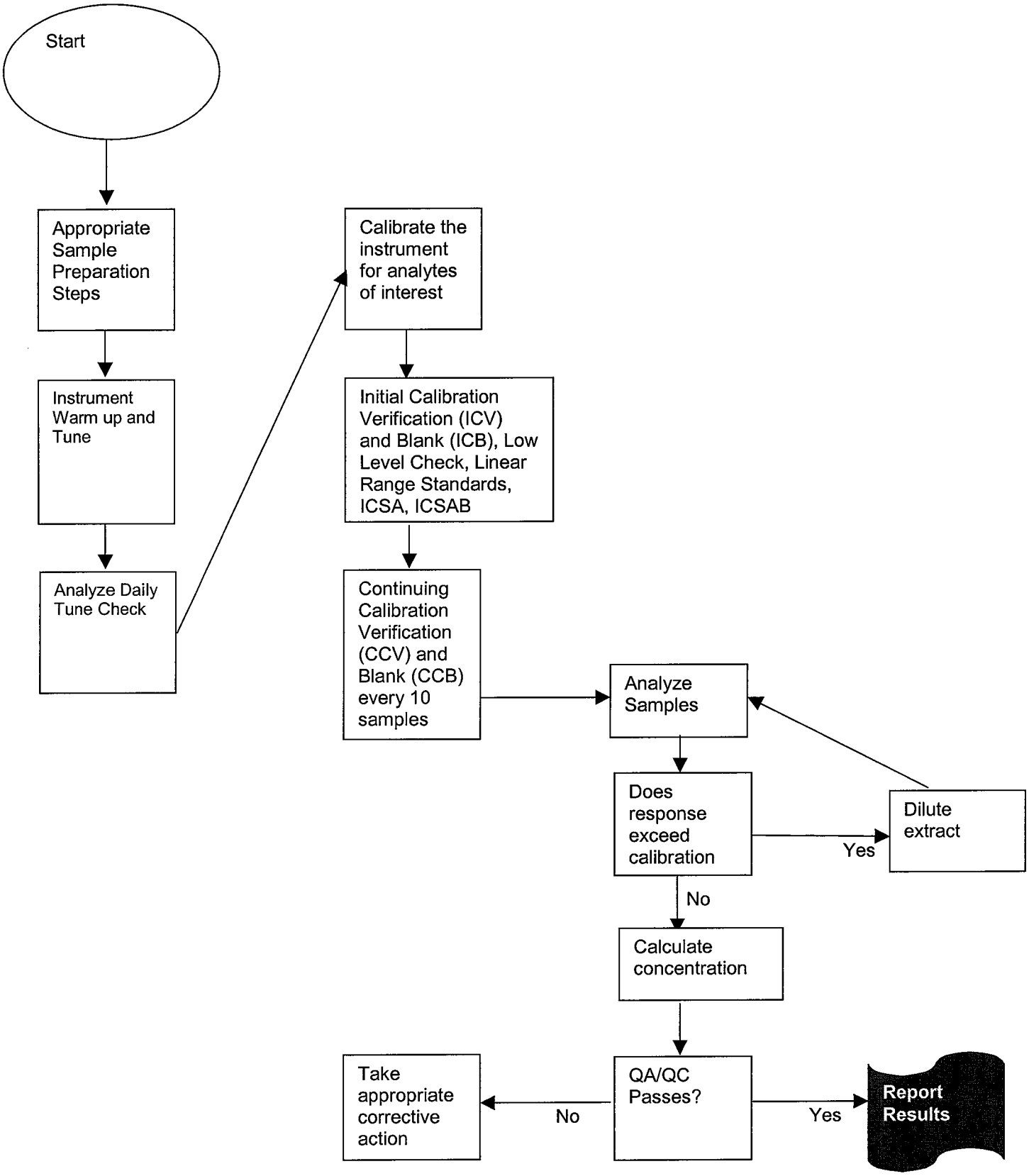
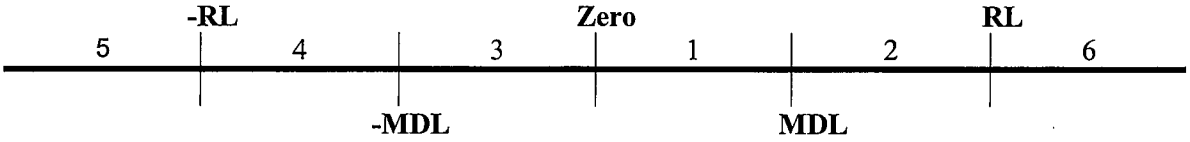
Flowchart A
ICPMS DETERMINATIVE METHOD



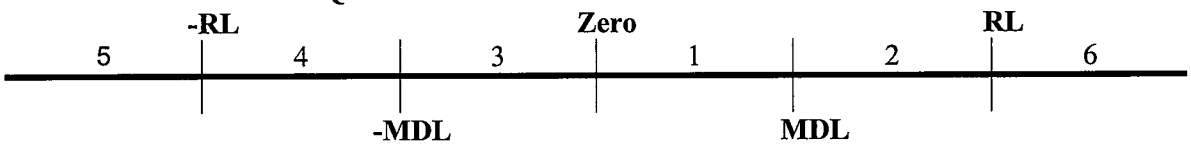
Flowchart B
MDL or LOD FLAGGING and REPORTING



BLANK POSITION> Sample Position⇓	5	4	3	1	2	6
1	R	A Flag Report < MDL	Report < MDL	Report < MDL	Report < MDL	Report < MDL
2	R	A Flag Report result w/20X Rule	Report result	Report result	A Flag Report result w/20X Rule	R
3	R	A Flag Report < MDL	Report < MDL	Report <MDL	Report < MDL	Report <MDL
4	R	A Flag Report <MDL	Report <MDL	Report <MDL	A Flag Report result w/20X Rule	Report <MDL
5	R	R	R	R	R	R
6	R	A Flag Report result w/20X Rule	Report result	Report result	A Flag Report result w/20X Rule	Report result w/20X Rule -or- R if result is not 20XMB

R= Analyst discretion to Re-run, Re-calculate, or Re-digest
X= Value in Method Blank (MB).

Flowchart C
EQL or PRSL FLAGGING and REPORTING



BLANK POSITION> **Sample Position⇓**	5	4	3	1	2	6
1	R	Report < RL	Report < RL	Report < RL	Report < RL	Report < RL
2	R	Report < RL	Report < RL	Report result	Report < RL	Report < RL
3	R	Report < RL	Report < RL	Report <RL	Report < RL	Report < RL
4	R	Report < RL	Report < RL	Report < RL	Report < RL	Report < RL
5	R	R	R	R	R	R
6	R	Report result	Report result	Report result	Report result	Report result w/20X Rule -or- R if result is not 20XMB

R= Analyst discretion to Re-run, Re-calculate, or Re-digest
RL= Reporting Limit

Table A
EQUIPMENT

Equipment	Manufacturer	Model(s)	Serial #	Date In Service
ICPMS	Perkin Elmer	Elan 6000	4349711	5-05
Auto-sampler	Perkin Elmer	AS 91		5-05
Peristaltic Pump	Gilson	Mini pulse 3	610F5298	7-05
Refrigerated Chiller	Neslab	CFT-75	197289060	5-05

Table B
SUPPLIES

Supplies	Vendor	Catalog #
Sample Peri-Pump Tubing	Analytical West	PT-2130P
Internal Standard Peri-Pump Tubing	Analytical West	PT-2030P
Waste Peri-Pump Tubing	Analytical West	PT-2300P
Rinse Peri-Pump Tubing	Analytical West	PT-2180P
Y Connectors	Hewlett-Packard	G1820-65106
Work Coil	Analytical West	70-900-2006C
Sample Cone (Nickel)	Analytical West	SC2011-Ni
Skimmer Cone (Nickel)	Analytical West	SC2012-Ni
Sample Cone (Platinum)	Analytical West	SC2013-Pt
Skimmer Cone(Platinum)	Analytical West	SC2014-Pt
Electron Multiplier	Analytical West	AF210
17X100 Culture Tubes	Fisher Scientific	14-956-8J
50 mL Polypropylene Centrifuge Tubes	Fisher Scientific	14-375-150
Calibrated Pipette 1000 ul	Fisher Scientific	21-371-13
Calibrated Pipette 100-1000 ul	Fisher Scientific	05-402-50
Calibrated Pipette 1000-5000 ul	Fisher Scientific	05-402-91
Eppendorf Pipette Tips 1 mL	Fisher Scientific	05-403-60
Finntip Pipette Tips 5 mL	Fisher Scientific	21-377-305
N-DEX Nitrile Gloves	MG Scientific	G303-13
pH Indicating Strips	Gallard	921-10

Table C
REAGENTS

Reagent/Stock Std	Used In	Purity	Vendor	Order #
Hydrochloric Acid, HCL	Std.s	Trace Metals Grade	Fischer Scientific	A508
Nitric Acid, HNO_3	Std.	Trace Metals Grade	JT Baker	9598-34
Nano-Pure Water	all	18 Meg Ohms	On-Site	On-Site

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STANDARD OPERATING PROCEDURE

The Determination of Mercury by Cold Vapor Atomic Absorption Spectroscopy

Reference Methods: EPA SW-846 Methods 7470A and 7471A

SOP NUMBER:	GB-I-036-Rev.0
EFFECTIVE DATE:	Date of Final Signature
SUPERSEDES:	G2-MET-17 Rev.2, G2-MET-18 Rev.1

APPROVAL

Nils Melberg, Assistant General Manager — Date 8/31/06

Arthur F. Lautenbach, Quality Manager — Date 8/28/06

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1. Purpose

1.1 The purpose of this Standard Operating Procedure (SOP) is to describe the determination of mercury in water, soil/solid samples, and biological tissue.

2. Scope and Application

2.1. This method is applicable to water samples (including drinking water, surface water, and domestic and industrial wastewaters), solid samples (including soils, sediments, sludges, and solid wastes), TCLP leachates, and biological tissue samples.

2.2. This procedure is restricted to use by, or under the supervision of, analysts experienced in the digestion of samples for metals analysis and analysis of digestates by atomic absorption spectrometry. Each analyst must demonstrate the capability to generate acceptable results with this method to be considered qualified to report sample results.

3. Summary of Methods

3.1. Cold vapor atomic absorption utilizes the volatile property of elemental mercury at the 253.7 nm wavelength. To release mercury from organic complexes, the sample is digested with oxidizing reagents and acids in a hot block digester. After digestion, the oxidizing reagents are neutralized. Stannous chloride is added to reduce ionic mercury to the ground state. The Flow Injection Analysis System sweeps the volatile elemental mercury out of the sample and into the cell of an atomic adsorption spectrophotometer. The absorbance signal is proportional to the amount of mercury in the sample.

4. Interferences

4.1. Biota samples can contain diverse matrix types, each of which may present analytical challenges. Spiked samples and Laboratory Control Samples are important for determining digestion efficiency.

4.2 Potassium permanganate is added to eliminate possible interference from sulfide. Concentrations as high as 20 mg/L of sulfide, as NaS, do not interfere with recovery of added inorganic Mercury from D.I. water.

4.3 Copper has also been reported to interfere; however, copper concentrations as high as 10mg/L had no effect on recovery of Mercury from spiked samples.

4.4 Samples high in chlorides require up to 7.5 mls of additional potassium permanganate. During the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation at 253.7 nm. Care must therefore be taken to ensure that free chlorine is absent before the Mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine hydrochloride reagent.

4.5 Certain volatile organic materials that absorb at this wavelength may also interfere. A preliminary run without reagents would determine if this type of interference is present.

5. Safety

5.1. **Standards and Reagents** - The toxicity and carcinogenicity of standards and reagents used in this method have not been fully defined. Each chemical compound should be treated as a potential health hazard. Reduce exposure by the use of gloves, lab coats and safety glasses.

5.2. **Material Safety Data Sheets (MSDSs)** – A reference file of MSDS are on file in the laboratory and available to all personnel. A formal safety plan has been prepared and distributed to a personnel with documented training.

5.3. **Special care should be taken when handling the high concentration acids and oxidizing reagents used for sample digestion. All digestions must be conducted in a properly functioning fume hood.**

5.4. **Samples** - Take precautions when handling samples. Samples should always be treated as potentially hazardous "unknowns". The use of personal protective equipment (gloves, lab coats and safety glasses) is required when handling samples.

5.4.1 Extreme caution must be used when preparing rodents for digestion. The samples must undergo a special procedure to destroy any Hantavirus, which may be present. Refer to the most recent version of SOP KM-L-002 for details.

5.5 Analysts should take necessary safety precautions when handling chemicals and samples. Proper personal protective equipment may include safety gloves, lab coats, and safety glasses or goggles. Analysts should be familiar with the MSDS sheets for all chemicals and reagents they use for this procedure and the location of the MSDS sheets within the laboratory. Any questions or concerns should be taken to the laboratory Chemical Hygiene/Safety Officer.

6. Definitions

6.1. Definitions of terms found in this SOP can also be found in the Pace Quality Manual. When definitions are not consistent with NELAC defined terms, an explanation will be provided in this SOP or the Pace Analytical Services' Quality Manual Glossary, Section 10.0.

6.2 **Fish Control Blank (Matrix Blank)** - A sample of a matrix that is used for the control spike. The fish blank will either be catfish or tilapia which ever is available at the time of analysis. The fish blank must be "farm-raised" to minimize background mercury levels. The concentration in the fish blank will be

subtracted from the concentration of the laboratory control spike. This is done because the fish blank is known to have some contamination. This SOP will reference catfish blank for ease. Note: For plant material analysis, alfalfa can be used as the control blank matrix.

6.3 **Reagent Grade** – Analytical reagent (AR) grade, ACS reagent grade, and reagent grade are synonymous terms for reagents, which conform to the current specifications of the Committee on Analytical Reagents of the American Chemical Society.

6.4 **Standardized Reference Material (SRM)** – A certified reference material produce by the U.S. National Institute of Standards and Technology or other equivalent organization and characterized for absolute content, independent of analytical method. A SRM is analyzed with each analytical batch of biota samples.

6.5 **Pace Reporting Limit (PRL)** – The level at which method, permit, regulatory and client specific objectives are met. The reporting limit may never be lower than the Limit of Detection (i.e statistically determined MDL). Reporting limits are corrected for sample amounts, including the dry weight of solids, unless otherwise specified.

7. Responsibilities and Distribution

7.1 Personnel

7.1.1 All personnel involved with sample preparation and analysis are responsible for adherence to this SOP. A controlled copy will be available for review and consultation within the area methods manual.

7.1.2 Personnel are responsible for ensuring that any deviations to this SOP are reported to the laboratory manager.

7.2 Laboratory Manager

7.2.1 The laboratory manager is responsible for ensuring adherence to this SOP and will receive a controlled copy of this SOP.

7.2.2 The laboratory manager is responsible for performing a biennial review of the SOP and reporting any required revisions to the Quality Assurance Office.

7.3 Quality Assurance Office

7.3.1 The QA Office is responsible for performing a biennial review of the SOP in conjunction with the purchasing department and revising as needed.

7.3.2 The QA Office is responsible for ensuring that all revisions to the SOP are implemented.

7.4 Revisions

7.4.1 This SOP will be reviewed on a biennial basis at a minimum, and any required revisions would be incorporated.

8. Sample Collection, Preservation, and Handling

8.1. Biota Samples

8.1.1. Biota samples can be collected in clean plastic or glass containers or plastic baggies.

8.1.2. Biota samples are kept frozen until time of preparation to preserve integrity. Hold time is 28 days from removal from freezer.

8.2. Soil Samples

8.2.1. Soil and waste samples should be collected in clean wide-mouth glass containers to facilitate obtaining representative aliquots for measurement.

8.2.2. Samples should be stored at 4±2°C and analyzed as soon as possible to minimize microbiological decomposition of organic solids. Samples must be analyzed within 28 days of collection.

8.3 Water samples

8.3.1 Water samples may be collected in plastic or glass containers and must be preserved with HNO_3 to pH <2 and stored at room temp, acid not to exceed 5% of the container capacity.

NOTE: Aqueous samples that react violently to the addition of acid maybe collected without chemical preservation with proper variances approved by the regulatory authority. The responsibility of requesting this variance lies with the sample collector.

NOTE: Samples may be preserved in the lab. The samples may not be processed until 16 hours after preservation with a pH test of <2.

8.3.2 Samples must be analyzed within 28 days of collection.

9. Equipment and Supplies

9.1. Heating Block – Operated at 95 ± 5°C. Heating block should be Environmental Express "Hot Block", or equivalent.

9.2. Digestion Vials – Pre-cleaned 68- mL screw cap vials, Environmental Express (SC475), or equivalent.

9.3. Analytical Balance – Capable of weighing to 0.01g.

9.4. Volumetric Flasks – Assorted, Class A

9.5. Graduated Cylinder – 50-mL

9.6. Mechanical Pipettes – Assorted adjustable air-displacement pipettes with disposable tips (Eppendorf or equivalent).

9.7. pH Strips

9.8. CVAA-FIMS with autosampler

9.9. Inert Sparging and Carrier Gas - Argon

9.10. Autosampler vials

9.11. Autosampler Pump Tubing

9.12. Specimen Cups

9.13. DOLT-3

9.14. Analytical Balance – Capable of weighing to 0.0001g.

10. Reagents and Standards

10.1. Trace Metals Water

10.2. Nitric Acid (HNO_3) – Trace metals grade

10.3. Hydrochloric Acid (HCl) – Trace metals grade

10.4. Sulfuric Acid (H_2SO_4) – Trace metals grade

10.5. Sodium Chloride (NaCl)

10.6. Potassium Permanganate ($KMnO_4$) solution (5%) – Dissolve 50.0 g of $KMnO_4$ into ~800 mL of trace metals water. Dilute to 1000 mL. Prepare fresh each month.

10.7. Potassium Persulfate Solution ($K_2S_2O_8$) solution (5%) – Dissolve 50.0 g of $K_2S_2O_8$ into ~800 mL of trace metals water. Dilute to 1000 mL. Warm to dissolve. Prepare fresh each month.

10.8. Hydroxylamine Hydrochloride ($NH_2OH \bullet HCl$) Solution (12%) – Dissolve 120 g NaCl and 120g $NH_2OH \bullet HCL$ in ~800 mL of trace metals water. Dilute to 1000 mL. Prepare fresh each month.

10.9. Stannous Chloride Solution ($SnCl_2$) - Dissolve 11.0 g of SnCl in ~ 800 mL of trace metals water. Add 30 mL of HCL. Dilute to 1000 mL. Prepare fresh every

other day.

10.10. Analytical Standards – Standard solutions are required calibration, calibration checks, and sample spiking solutions. The following describes the contents of each type of solution. The commercial sources for stock solutions, recipes for preparing dilutions and working standards, and concentrations in standard solutions are presented in Table 1, Table 2, and Table 3.

Table 1
Stock Standards

Standard	Concentration	Vendor	Catalog #
Hg Calibration Stock	1000µg/mL	Inorganic Ventures, Inc.	CGHG1-1
ICV Calibration Stock	1000µg/mL	High-Purity Standards	100033-1

Standards are used until they expire based on the manufacturer's expiration date.

Table 2
Intermediate and Calibration Standards
Waters

Standard	Stock Standard	Conc.	Amount Used	Amount of conc. HNO_3 used	Final Volume (with trace metals water)	Final Conc.
Hg ICV Stock	-	1000µg/mL	-	-	-	1000 µg/mL
Hg Calibration Intermediate	Hg Calibration Stock	1000µg/mL	10 µL	2.0 mL	100 mL	100 ppb
Hg ICV Intermediate	Hg ICV Stock	1000 µg/ml	10 µL	2.0 mL	100 mL	100 ppb
Hg Cal. 1	-	-	-	-	20 mL	0.0 ppb
Hg Cal. 2	Hg Cal. Intermediate	100 ppb	40 µL	-	20 mL	0.2 ppb
Hg Cal. 3	Hg Cal. Intermediate	100 ppb	200 µL	-	20 mL	1.0 ppb
Hg Cal. 4	Hg Cal. Intermediate	100 ppb	500 µL	-	20 mL	2.5 ppb
Hg Cal. 5	Hg Cal. Intermediate	100 ppb	1000 µL	-	20 mL	5.0 ppb
Hg Cal. 6	Hg Cal. Intermediate	100 ppb	2000 µL	-	20 mL	10.0 ppb
Hg ICV	Hg ICV Intermediate	100 ppb	800 µL	-	20 mL	4.0 ppb
Hg CCV	Hg ICV Intermediate	100 ppb	1000 µL	-	20 mL	5.0 ppb
Hg ICB/CCB	-	-	-	-	20 mL	0.0 ppb

All intermediate dilution solutions must be prepared as needed, or at least every 7 days. Working solutions must be prepared fresh daily. Solutions may be stored at room temperature.

Table 3
Intermediate and Calibration Standards
Soils/Biota

Standard	Stock Standard	Conc.	Amount Used	Amount of conc. HNO_3 used	Final Volume (with trace metals water)	Final Conc.
Hg ICV Stock	-	1000µg/mL	-	-	-	1000 µg/mL
Hg Calibration Intermediate	Hg Calibration Stock	1000µg/mL	10 µL	2.0 mL	100 mL	100 ppb
Hg ICV Intermediate	Hg ICV Stock	1000 µg/ml	10 µL	2.0 mL	100 mL	100 ppb
Hg Cal. 1	-	-	-	-	30 mL	0.0 ppb
Hg Cal. 2	Hg Cal. Intermediate	100 ppb	60 µL	-	30 mL	0.2 ppb
Hg Cal. 3	Hg Cal. Intermediate	100 ppb	300 µL	-	30 mL	1.0 ppb
Hg Cal. 4	Hg Cal. Intermediate	100 ppb	750 µL	-	30 mL	2.5 ppb
Hg Cal. 5	Hg Cal. Intermediate	100 ppb	1500 µL	-	30 mL	5.0 ppb
Hg Cal. 6	Hg Cal. Intermediate	100 ppb	3000 µL	-	30 mL	10.0 ppb
Hg ICV	Hg ICV Intermediate	100 ppb	1200 µL	-	30 mL	4.0 ppb
Hg CCV	Hg ICV Intermediate	100 ppb	1500 µL	-	30 mL	5.0 ppb

Hg ICB/CCB	-	-	-	-	30 mL	0.0 ppb

All intermediate dilution solutions must be prepared as needed, or at least every 7 days. Working solutions must be prepared fresh daily. Solutions may be stored at room temperature.

11. Calibration

11.1 A digested calibration curve is made up every time there are samples prepared. The curve is associated to the sample batch it is prepped with. Calibration requires analysis of a calibration blank and at least five levels of calibration solutions. The lowest calibration concentration is the Pace Reporting Limit.

11.2 The resultant correlation coefficient must be greater than 0.995. If this does not occur, then the instrument must be recalibrated and or the calibration curve and the associated samples must be re-prepped.

11.3 The calibration curve must pass an Initial Calibration Verification (ICV) that is analyzed after the calibration standards and before any samples. The ICV concentration is near the midpoint of the calibration curve and is made from a source other than the one used to make the calibration standards.

11.4 Every ten samples or less must be bracketed by Continuing Calibration Verifications (CCV). The CCV concentration is near the midpoint of the calibration curve.

11.5 The ICV and CCV limits are +/- 10% of their expected values. If one fails, then the instrument must be re-calibrated and any samples after the failure or not bracketed by an acceptable CCV, must be reanalyzed.

11.6 An acceptable Initial Calibration Blank (ICB), must be analyzed after the ICV.

11.7 Continuing Calibration Blanks (CCB) are analyzed after the CCVs.

11.8 The control limit for the ICB and CCB is less than the Pace Reporting Limit. If one fails, then the instrument must be re-calibrated and any samples, after the failure or not bracketed by an acceptable CCB, must be reanalyzed.

12. Procedure

12.1. Sample Preparation

12.1.1. Water samples

12.1.1.1 Verify preservation in the samples by checking their pH with a test strip (done in Sample Receiving). Record on prep log that the pH was checked and is correct.

12.1.1.2 Prior to analysis the samples and the calibration curve must be digested.

12.1.1.3 Turn on the heating block and set the temperature to maintain a sample temperature of 95±5°C. Before placing samples in the block to digest, verify that the sample well temperature is correct and adjust as required. Record the temperature in the sample logbook. Verify that the hood is functioning.

12.1.1.4 Add 20 mL of trace metals water and the appropriate amounts (as shown in Table 2) of Hg Calibration Intermediate and Hg ICV Intermediate to digestion vials for the curve, ICV, CCV, ICB, and CCB.

12.1.1.5 Add 20 mL of trace metals water to a digestion vial for the Method Blank.

12.1.1.6 Add 20 mL of trace metals water and 1.0 mL of Hg ICV Intermediate to two digestion vials for the Laboratory Control Spike and Laboratory Control Spike Duplicate. Only prep LCSD if requested by client or there is not enough sample to run an MS/MSD.

12.1.1.7 Add 20 mL of each well-mixed sample to digestion vials.

12.1.1.8 To prepare a Matrix Spike and Matrix Spike Duplicate, a sample with sufficient volume is chosen at random or assigned by the client. An additional 20 mL of this sample along with 1.0 mL of Hg ICV Intermediate is added to two digestion vials.

12.1.1.9 To each digestion vial add 0.5 mL of concentrated nitric acid. Swirl the digestion vials gently.

12.1.1.10 To each digestion vial add 1.0 mL of concentrated sulfuric acid. Swirl the digestion vials gently.

12.1.1.11 Add 1.6 mL of 5% Persulfate solution. Swirl the digestion vials gently.

12.1.1.12 Add 3 mL of 5% $KMnO_4$, place lid or cap on tube so as to allow pressure to vent but minimizing evaporation, swirl the digestion vials gently, and let stand for 15 minutes. If a sample does not maintain a purple or brown color, an additional 3 mL of $KMnO_4$ solution is added to all samples, QC, and standards. **Note: If the sample still does not maintain color, discard applicable samples and dilute the samples prior to digestion.**

12.1.1.13 Digest samples for 2 hours at 95±5°C.

12.1.1.14 Remove samples and let cool to room temperature.

12.1.1.15 Add 1 mL of 12% sodium chloride/hydroxide solution. Swirl the digestion vials gently.

12.1.1.16 Samples are now ready for analysis.

12.1.2. **Soil/Solid/Biota Samples**

12.1.2.1 Prior to analysis the samples and calibration curve must be digested.

12.1.2.2 Turn on the heating block and set the temperature to maintain a sample temperature of 95±5°C. Before placing samples in the block to digest, verify that the sample well temperature is correct and adjust as required. Record the temperature in the sample logbook. Verify that the hood is functioning.

12.1.2.3 Add 30 mL of 3% HNO_3 and the appropriate amounts (as shown in Table 2) of Hg Calibration Intermediate and Hg ICV Intermediate to digestion vials for the curve, ICV, CCV, ICB, and CCB.

12.1.2.4 Prepare one Method Blank by leaving one digestion vial blank. For biota analysis, a fish control blank consisting of catfish or tilapia is also prepared by weighing 0.6 g of homogenized fish control blank (either catfish or tilapia) into a digestion vial.

12.1.2.5 Prepare the Laboratory Control Spike and Laboratory Control Spike Duplicate (LCS/LCSD) for soils and wastes by adding 1.5 mL of Hg ICV Intermediate to two digestion vials. Prepare the LCS/LCSD for biota samples by weighing 0.6 g of homogenized fish control blank (either catfish or tilapia) into two digestion vials. Add 1.5 mL of Hg ICV Intermediate to each vial. Only prep LCSD if requested by client or there is not enough sample to run an MS/MSD.

12.1.2.6 For biota samples weigh approximately 0.05 g of Standard Reference Material on an analytical balance (must read to at least 4 places past the decimal) into a labeled digestion vial.

12.1.2.7 Weigh 0.6 g of homogenized sample into a labeled digestion vial. Record the weight to the nearest 0.01 g in the digestion logbook. For samples with high liquid content, a larger sample size may be used, as long as the digestion is complete.

12.1.2.8 To prepare a Matrix Spike and Matrix Spike Duplicate, a sample with sufficient volume is chosen at random. Weigh 2 additional 0.6 g aliquots into digestion vials. Add 1.5 mL of Hg ICV Intermediate to each vial.

12.1.2.9 Add 30 mL of 3% HNO_3 solution to all QC and samples. Swirl digestion vials to gently mix.

12.1.2.10 To each digestion vial add 0.5 mL of concentrated nitric acid. Swirl digestion vials to gently mix.

12.1.2.11 To each digestion vial add 2.0 mL of concentrated hydrochloric acid. Swirl digestion vials to gently mix.

12.1.2.12 Add 3 mL of 5% $KMnO_4$, place lid or cap on tube so as to allow pressure to vent but minimizing evaporation, swirl the digestion vials gently, and let stand for 15 minutes. If a sample does not maintain a purple or brown color, an additional 3 mL of $KMnO_4$ solution is added to all samples, QC, and standards. **Note: If the sample still does not maintain color, discard set and dilute the sample prior to digestion.** For Biota samples, add 6ml of KMnO4 to start with.

12.1.2.13 Digest samples for 30 minutes at 95±5°C.

12.1.2.14 Remove samples and let cool to room temperature.

12.1.2.15 Add 3 mL of 12% hydroxylamine hydrochloride solution. Swirl digestion vials to gently mix.

12.1.2.16 Samples are now ready for analysis.

12.2. **Basic System Operation – Analytical**

This portion of the SOP is designed to allow the user to set up and run a method, print a sample report, then shut down using the more basic software functions. For a more detailed explanation of the many other options, the user should refer to the Reference Manual.

12.2.1. Turn on the carrier argon gas supply.

12.2.2. Switch on the FIMS 100.

12.2.3. Switch on the computer and enter network password and click on Start.

12.2.4. Click on the AA WinLab Analyst. To use previously defined workspace click "wkspace" icon, otherwise click "Auto" icon.

12.2.5 To select previously defined method:
Under File name highlight: AUTO.fms and click on OK.
Four windows will automatically open:
1. Results
2. Examine Peak
3. Examine Calibration
4. Automated Analysis, within this window double-click on method entry field to display the Methods. Highlight HgtestRun or HG-MSA and click on OK.

12.2.6 Under "Sample Information File" click on Browse and choose **hgidfile.sif** file. A sample information file is created with the Sample Information Editor window.

12.2.7 Enter sample information starting with Autosample Location #10. Enter the LIMS ID numbers under sample ID columns.

12.2.8 Column Fill, in the Edit menu, allows you to clear one or more entries, or make entries in increments. Edit also allows you to delete or insert lines. The sample information Parameter File supplies the computer with all the information needed to convert the concentration of the analyte in the sample solution (solution concentration or result) to the corrected concentration (final result).

12.2.9 In the menu click on Print and sample information to get a copy of the sample information you just entered to check for errors.

12.2.10 Save the completed file by using Save As in the File menu.

12.2.11 Close the window by clicking on the X in the upper right-hand corner.

NOTE: Only sample information should be entered in this file. Information on blanks, standards and QC samples is entered in the QC page of Method Editor.

Under the QC page you set up the QC sample ID, i.e. ICV's and CCV's and the autosampler location. Set the QC concentration and the control limits.

On the Schedule Timing page set up when the QC will be analyzed, i.e. after calibration, after 10 samples, and at the end. IF re-calibration occurs the QC must be analyzed at the same frequency.

Under the Actions Calib. And Periodic page, specify what to do if calibration QC fails, for example recalibrate, recalibrate and rerun, or stop.

On the Actions: End and Retry page, specify what QC to run at the end of a run and corrective action if QC fails.

Under the Options page, set how you want data printed (usually default). It is also possible to specify saving the peaks and add comments about the run.

In the Automated Analysis Window there are 2 pages: Set UP, and Analyze.

12.2.12 Under "Use Autosampler Locations listed Below", type in the numbers or range of numbers to be analyzed.

12.2.13 Select the name of the Results Data Set to save the results. Naming example: HG092800A, denotes the element, month, day and year. A letter is used for describing each run within a day's output.

12.2.14 The Save Data box and Print Log box should already be selected.

12.2.15 Off After Analysis. Pumps should be checked.

12.3. **Starting the Analysis**

12.3.1 Prepare the required reagents: Carrier solution and reducing agent.

Clamp down the tubes by swinging the pressure levers until they lock. Place inlets of each solution in proper container: Yellow/blue in the carrier and red/red in the reductant. Click on the Fias icon to turn on the pump to draw solutions through the tubing. Check on the flow.

12.3.2 Click on the Analyze All button. The system will run the blank and standards specified in the Element Parameter file, then the entire sample specified in the Sample Info. File. Check the calibration curve by clicking on Calibration icon on the tool bar.

12.3.3 To run the blank and standards only: In order to check the calibration curve before running any samples:

Click on Calibration, the system will run the blank and standards specified in the Element File and complete the calibration curve. To check the calibration curve, click on the Calibration icon on the toolbar.

To continue the run, click on the Auto control window then click on Analyze sample. The system will run the samples specific in the Sample Info. file.

12.3.4 To change or stop the element file that has already started: Click on Analyze. A dialogue box will appear with these options:

Stop immediately

Stop after current replicate

Stop after completing all replicates for current sample

12.3.5 To restart the analysis from the beginning: In the Automated Analysis Control window, click on RESET. Start the analysis as usual.

12.3.6 To continue the analysis where it was interrupted or continue with a specific sample: In the Automated analysis Control window, click on Analyze All or Analyze Samples. A dialog box appear, elect one of the options. Click on OK.

12.3.7 Performing a recalibration: You define the type and frequency of automatic recalibration on the Checks page of the Method.

Stop the analysis.

In the Automated Analysis Control window, click on Reset.

In the Automated Analysis Control window, click on Calibrate.

12.3.8 Analyzing One or More Selected Samples: IN the Automated Analysis Control window, click on Select Location – a dialog box appears. Select the Analyze Samples In Locations option. Enter the autosampler locations of the solutions to analyze in the test box: Enter individual locations or a range of locations. Use comas to separate the locations and ranges, e.g. 10-15,18,20,25-30. Click OK.

12.3.9 Resetting the Autosampler: In the Automated Analysis Control window, click on Reset. Analyze the sample; the system will begin with the first sample in the sample list on the Set Up page of the Automated Analysis Control window.

12.3.10 Raising or Lower Sample Probe: In the Automated Analysis Control window, click on Probe Up/Down. The sample probe moves up or down but remains at the sample autosampler locations.

12.3.11 Rinsing the Sampling Probe and Sampling Tube: In the Automated Analysis Control window, select Location – a dialog box appears. Select "Go to Wash." Click on OK. The sampling probe moves to the wash location. In the FIAS Control window: Make sure the FIAS-valve is in the correct position to rinse the sample channel. Click on the Pump.

12.3.12 The sample pump feeds the rinse fluid from the wash container through the sample channel. Click on Pump again to stop it. Click on Move Probe Up/Down to raise the probe out of the wash container in the automated analysis Control window.

12.4 System Shutdown

12.4.1 Place inlets of the carrier and reagent lines in a container of DI water. Rinse the sample, carrier, and reagent tubing with DI water. In the FIAS Control window, click on Valve Fill/Inject a number of times while the pump is running. This ensures that the sample channel and the inside of the FIAS-valve are rinsed effectively.

12.4.2 After adequate time, remove, all the tubes from the rinse containers. Click on Move Probe Up/Down to raise the sampling probe.

12.4.3 Allow the pump to run until all the tubes and the gas/liquid separator are empty. Then click on the Pump button to stop the pump.

12.4.4 Make sure that the FIAS-valve is in the Fill position.

12.4.5 Swing all the pressure levers away from the pump tube magazines.

12.4.6 Turn off the carrier gas supply at the regulator valve.

12.4.7 Exit the AA WinLab application.

12.4.8 Switch off the FIMS spectrometer.

12.4.9 Switch off the computer.

13. Calculations

13.1 **Water Samples** – Since initial sample aliquot and final digestate volumes are the same, the mercury analyzer data system will calculate the concentration directly. No further calculations are necessary unless the sample was diluted.

13.2 **Soil/Solid/Biota Samples -**

Final Result (mg/kg dry weight corrected) =

$$\frac{\text{Raw data result (ug/L) * Final Volume (L) * Dilution Factor}}{\text{Sample weight (g) * Dry weight for soil/solid (decimal form)}}$$

Biota results are reported on an as is/wet weight basis. The dry weight correction in the formula is not applicable.

13.3 **Accuracy-**

$$\text{Spike Percent Recovery} = \frac{\text{Spike Sample Result} - \text{Sample Result}}{\text{Spike Added}} \times 100$$

13.4 **Precision-**

Relative Percent Difference =

$$\frac{\text{Spike Sample Result} - \text{Spike Sample Duplicate Result}}{(\text{Spike Sample Result} + \text{Spike Sample Duplicate Result})/2} \times 100$$

14. Quality Control

14.1 **Calibration Blanks** – Calibration blanks (ICB and CCB) may not contain concentrations in excess of the Pace Reporting Limit. If blank results are not acceptable, analysis of the batch should be halted. Corrective actions could include preparation of fresh calibration standards and blanks.

14.2 **Calibration Checks**- Calibration checks (ICV and CCV) must agree within 10% of the true value. If the results are unacceptable, re-calibrate the system and then re-analyze the check solution and samples.

14.3 **Laboratory Control Spike** – A Laboratory Control Spike (LCS) must be prepared and analyzed with every sample batch or every 20 samples, whichever is more frequent. A Laboratory Control Spike Duplicate (LCSD) is performed if there is insufficient sample available for a MS/MSD or if requested by the client. The LCS and LCSD must meet criteria 85-115% recovery or all the samples

prepared in the batch must be re-prepped and re-analyzed. The accpetance criteria for precision if 20% RPD. If insufficient sample remains to re-prep and re-analyze, the "&" (for accuracy) and/or "*" (for precision) data qualifier is given to all associated samples.

14.4 **Method Blank** – A Method Blank (MB) must be prepared and analyzed with every sample batch or every 20 samples, whichever is more frequent. The MB must not contain mercury at a concentration at or above the Pace Reporting Limit. Any samples digested with an unacceptable method blank must be re-prepped and analyzed unless the sample concentrations are less than the reporting limit or more than 20 times the value found in the method blank. If those cases that MDL reporting is required, the MB must be evaluated to the MDL. For MDL reporting, an "A" data qualifier is given to samples associated with +/-MB hits between the +/-MDL and +/-PRL where the sample results are less than 20 times the value found in the method blank. Please refer to the attachment section for the A-flagging charts.

14.5 **Matrix Spike/ Matrix Spike Duplicate** – A Matrix Spike/Matrix Spike Duplicate (MS/MSD) must be prepared and analyzed for each group of samples that are similar in matrix at a frequency of 5%. The sample used for MS/MSD pair is either determined by the client or selected at random from client samples as sample volume allows. No field, filter, trip or equipment blanks can be used for MS/MSD. If one or both spike recoveries are outside 85-115% recovery acceptance criteria, the parent sample is given the "N" data qualifier. If the RPD is outside 20% RPD criteria the parent sample is given the "*" data qualifier. Parent sample is chosen at random or assigned by the client.

14.6 All reported results must be within the range of the calibration curve. Dilute when results are greater than the high standard in the curve.

15 Method Performance

15.1 There are several requirements that must be met to insure that this procedure generates accurate and reliable data. A general outline of requirements has been summarized below. Further specifications may be found in the Laboratory Quality Manual.

15.1.1 The analyst must read and understand this procedure with written documentation maintained in his/her training file.

15.1.2 An initial demonstration of capability (IDC) must be performed per ALL-Q-020, *Training Procedures*. A record of the IDC will be maintained in his/her QA file with written authorization from the Laboratory Manager and Quality Manager.

15.1.3 An annual method detection limit (MDL) study will be completed per ALL-Q-004, *Method Detection Limit Studies*, for this method and whenever there is a major change in personnel or equipment. The results of these studies are retained in the quality assurance office.

15.1.4 Periodic performance evaluation (PE) samples are analyzed per ALL-Q-010, *PE/PT Program*, to demonstrate continuing competence. All results are stored in the QA office.

16 Pollution Prevention and Waste Management

16.1 The quantity of chemicals purchased is based on expected usage during its shelf life and disposal cost of unused material. Actual reagent preparation volumes reflect anticipated usage and reagent stability.

16.2 Excess reagents, samples and method process wastes are characterized and disposed of in an acceptable manner. For further information on waste management consult the current version of ALL-S-002, *Waste Handling.*

17 References

17.1 SW-846 7470A, Revision 1, September 1994

17.2 SW-846 7471A, Revision 1, September 1994

17.3 PASI Quality Manual, current revision

17.4 National Environmental Laboratory Accreditation Conference (NELAC), July 2003 Standards

18 Tables, Diagrams, Flowcharts, Appendices, etc.

18.1 Mercury Process Flow Chart

18.2 A-flagging chart A: LOD/LOQ Blank Flagging and Reporting

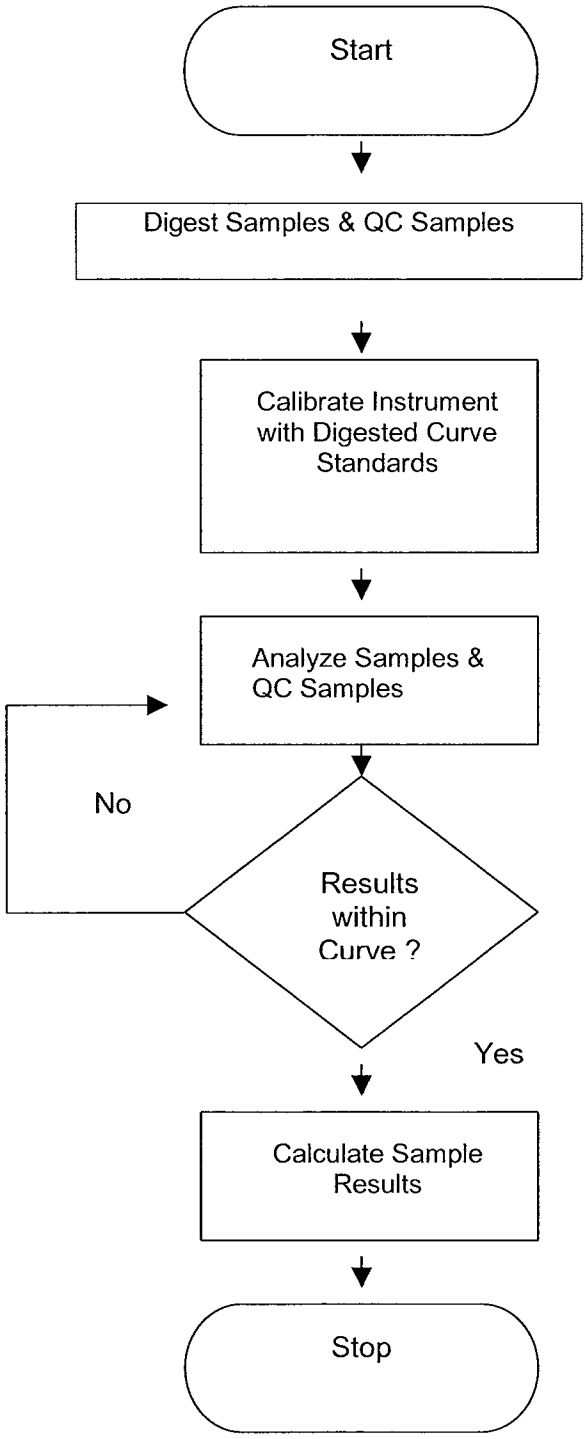
18.3 A-flagging chart B: PRL or PSRL Blank Flagging and Reporting

18.4 A-flagging chart C: MDL Blank Flagging and Reporting

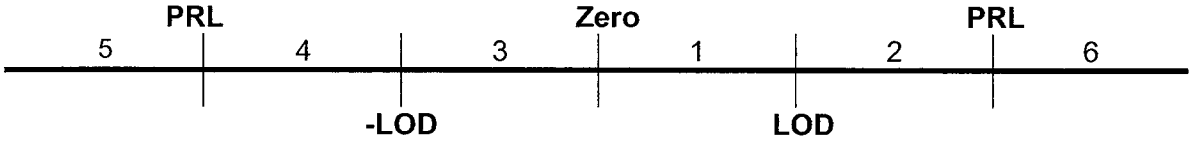
19 Revisions

Document Number	Reason for Change	Date
GB-I-036-Rev.0	Combined G2-MET-17 Rev.2 and G2-MET-Rev1 into 1 SOP in new format.	August 28, 2006

18.1 Mercury Process Flow Chart



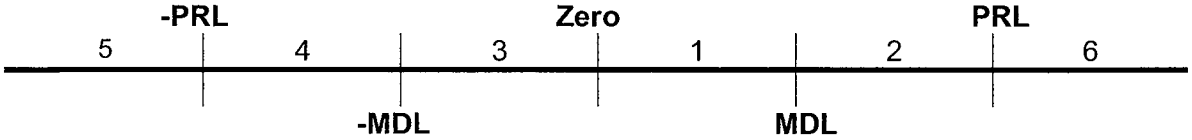
18.2 A-Flagging Chart A: LOD/LOQ Blank Flagging and Reporting



Blank Position → Sample Position↓	5	4	3	1	2	6
1	R	A Flag Report < LOD Comment	Report < LOD	Report < LOD	Report < LOD	Report < LOD
2	R	A Flag Report result w/20X Rule Comment	Report result	Report result	A Flag Report result w/20X Rule Comment	R
3	R	A Flag Report <LOD Comment	Report <LOD	Report <LOD	Report <LOD	Report <LOD
4	R	A Flag Report <LOD Comment	Report <LOD	Report <LOD	A Flag Report result w/20X Rule Comment	Report <LOD
5	R	R	R	R	R	R
6	R	A Flag Report result w/20X Rule Comment	Report result	Report result	A Flag Report result w/20X Rule Comment	Report result w/20X Rule -or- R if result is not 20XMB

R= Analyst discretion to Re-run, Re-calculate, or Re-digest
X= Value in Method Blank (MB).

18.3 A Flagging Chart B: PRL or PSRL Blank Flagging and Reporting

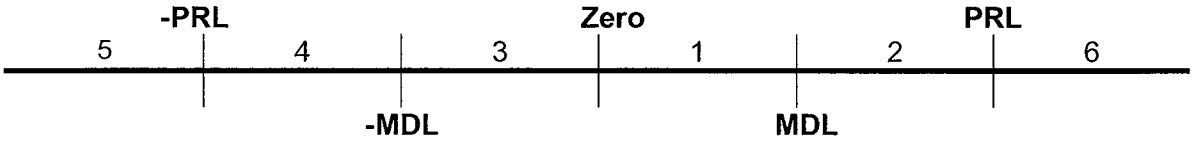


Blank Position → Sample Position↓	5	4	3	1	2	6
1	R	Report < PRL	Report < PRL	Report < MDL	Report < PRL	Report < PRL
2	R	Report < PRL	Report < PRL	Report result	Report < PRL	Report < PRL
3	R	Report < PRL	Report < PRL	Report <MDL	Report < PRL	Report PRL
4	R	Report < PRL	Report < PRL	Report < PRL	Report < PRL	Report < PRL
5	R	R	R	R	R	R
6	R	Report result	Report result	Report result	Report result	Report result w/20X Rule -or- R if result is not 20XMB

R= Analyst discretion to Re-run, Re-calculate, or Re-digest
X= Value in Method Blank (MB).
PRL= Pace Reporting Limit

18.4 A-Flagging Chart C: MDL Blank Flagging and Reporting

PRL or PRSL "B" FLAGGING and REPORTING



Blank Position→ Sample Position↓	5	4	3	1	2	6
1	R	Report < PRL	Report < PRL	Report < PRL	Report < PRL	Report < PRL
2	R	Report Result A Flag W/ 20X Rule Comment	Report Result	Report Result	Report Result A Flag W/ 20X Rule Comment	R
3	R	Report < PRL	Report < PRL	Report < PRL	Report < PRL	Report < PRL
4	R	Report < PRL	Report < PRL	Report < PRL	Report < PRL	Report < PRL
5	R	R	R	R	R	R
6	R	Report result A Flag W/ 20X Rule Comment	Report result	Report result	Report Result A Flag W/ 20X Rule Comment	Report result A Flag w/20X Rule -or- R if result is not 20XMB

R= Analyst discretion to Re-run, Re-calculate, or Re-digest
X= Value in Method Blank (MB).
PRL= Reporting Limit

TITLE: Total Cyanide using Micro-Distillation and Analyzed by Lachat 8000 Flow Injection following SW846 9012A and EPA Method 335.4

MATRICES:

This SOP pertains to drinking, ground, surface, and saline waters, domestic and industrial wastes, soils, and TCLP extracts.

DETECTION LIMITS:

Reporting Limits are used in the absence of Project or State Specific Required Detection Limits. The determinative method contains the current method detection limits (MDL) and Reporting Limits. See Table A for summary.

1.0 **SCOPE AND APPLICATION:**

1.1 This SOP is applicable to drinking, ground, surface, and saline waters, domestic and industrial wastes, soils, and TCLP extracts. The applicable range is 1.6 – 500 ug/L.

1.2 This SOP utilizes the Lachat 8000 analyzer.

2.0 **SUMMARY OF THE TEST METHOD:**

2.1 By means of a passive miniature distillation device, MICRO DIST, cyanide in the sample is released by digesting and acidifying cyanide complexes, and converting them to hydrocyanic acid (HCN). The cyanide ion is trapped in a 1.0 M sodium hydroxide absorbing solution which is diluted to 0.25M solution during distillation. By means of flow injection analysis, the 0.25M NaOH distillate is converted to cyanogens chloride by reaction with chloramines-T, pyridine and barbituric acid to give a red-colored complex. The absorbance of this complex is measured at 570 nm by measuring the peak area resulting from the sample. The peak area is proportional to the concentration of the cyanide in the sample.

2.2 All samples must be distilled before analysis.

3.0 **DEFINITIONS**:

3.1 Calibration Blank: A volume of reagent water. The calibration blank is used to zero the instrument.

3.2 Calibration Standard: A solution prepared from the dilution of a stock standard. The calibration solutions are used to calibrate the instrument response with respect to analyte concentration.

3.3 Calibration Verification Solution (ICV/CCV): A solution of method analytes, used to evaluate the performance of the instrument system with respect to a defined set of method criteria. The ICV is distilled along with the samples. The ICV is analyzed at two different concentrations after the calibration curve and before samples are analyzed. The

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CCV is not distilled along with the samples. The CCV is analyzed after every 10 samples.

3.4 Calibration Verification Blank (ICB/CCB): A solution of blank reagent water, used to evaluate the performance of the instrument system with respect to a defined set of method criteria. The ICB is analyzed after the calibration curve and before samples are analyzed. The CCB is analyzed after every 10 samples. The ICB/CCB are not distilled along with the samples.

3.5 Method Blank: a sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest, which is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedures, and in which no target analytes or interferences are present at concentrations that impact the analytical results for sample analyses. The Method Blank is distilled and analyzed exactly like a sample.

3.6 Matrix Spike (MS) and Matrix Spike Duplicate (MSD): Aliquots of an environmental sample to which known quantities of the analyte(s) of interest are added in the laboratory. The MS and MSD are distilled and analyzed exactly like a sample. Their purpose is to quantify the bias and precision caused by the sample matrix.

3.7 Method Detection Limit (MDL): The minimum concentration of an analyte that can be identified, measured and reported with 99% confidence that the analyte concentration is greater than zero.

3.8 Lab Control Spike (LCS) and Lab Control Spike Duplicate (LCSD): Reagent water to which known quantities of the analytes(s) of interest is added. The LCS and LCSD are distilled and analyzed exactly like a sample. Their purpose is to show complete digestion technique.

3.9 Standard Stock Solution: A concentrated solution containing one or more method analytes prepared in the laboratory using assayed reference material or purchase from a reputable commercial source.

3.10 Estimated Quantitation Limits: The EQL is based upon the low standard in the calibration curve, taking into account the weight/volume of the sample distilled and dilutions.

3.11 Leach Blank: Blank associated with the TCLP, SPLP, ASTM, and Neutral leach procedures. The appropriate leach blank must be distilled and analyzed along with the appropriate samples as leached on the same leach date.

4.0 INTERFERENCES:

4.1 Most non-volatile interferences are eliminated or minimized by the distillation procedure. Some of the known interferences are aldehyde, nitrate-nitrite, and oxidizing agents, such as chlorine, thiosulfate, and sulfide.

4.2 Oxidizing agents such as chlorine decompose most cyanide. Test a drop of the sample with potassium iodine-starch paper (KI-starch paper) at time of collection; a blue color

indicates need for treatment. Add ascorbic acid, a few crystals at a time, until a drop of sample produces no color changes; then add an additional 0.06 g ascorbic acid per liter of sample.

4.3 False positive results may be obtained by samples that contain nitrate and/or nitrite. Sulfamic acid is added to all samples prior to distillation to eliminate this interference.

4.4 Sulfides adversely affect the procedure by producing hydrogen sulfide during distillation. If a drop of sample on lead acetate paper indicated the presence of sulfide, treat the stabilized sample (pH >12) with bismuth nitrate. Repeat until a drop on the lead acetate paper does not darken. Filter sample to remove precipitate and use filtrate as sample to be distilled.

5.0 **SAFETY:**

5.1 Safety is everyone's business at En Chem, Inc. and everyone is responsible for assisting in reducing unsafe and unhealthy working conditions or potential hazards. The company provides you with a safe place to work, but we need your cooperation to keep it safe. When you see something that does not look safe, or you see someone working in an unsafe manner, mention it to your Supervisor.

5.2 All samples should be treated as hazardous. Safety glasses, gloves, and lab coats are to be worn. The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined. However, each chemical compound should be treated as a potential health hazard. Exposure to these chemicals must be reduced to the lowest possible level by a safe technique. A reference file of material safety data sheets should also be made available to all personnel involved in the chemical analysis.

5.3 Required Safety Equipment is listed in Table B

6.0 **EQUIPMENT AND SUPPLIES:**

6.1 See Table C and Table D for a summary.

7.0 **REAGENTS AND STANDARDS:**

7.1 See Table E and F for a summary.

8.0 **SAMPLE COLLECTION, PRESERVATION, SHIPMENT AND STORAGE:**

8.1 Samples are collected either in glass or plastic bottles.

8.2 Samples are preserved with NaOH to a pH $\geq$12 and cooled to 4°C at time of collection.

8.3 Hold time is 14 days.

8.4 See Table G for a summary.

9.0 QUALITY CONTROL:

9.1 Demonstration of Capability - The initial demonstration of capability is used to characterize instrument performance (determination of linear range and laboratory control sample) and laboratory performance (determination of MDLs) prior to performing analyses by this method. The analyst must perform an IDC before they are allowed to analyze samples.

9.1.1 Initial Demonstration of Capability (IDC) – Analysts must perform initial demonstration of capability before analyzing samples.

9.1.1 The analyst will distill and analyze four replicates of the LCS solution.

9.1.2 Calculate the mean, average recovery (x), and the standard deviation of the recovery (s). The recovery of each compound must fall within 90 – 110% of true value. If IDC is outside acceptable limits, corrective action must be taken.

9.1.2 Linear Calibration Range - The linear calibration range must be determined initially and verified whenever a significant change in instrument response is observed or expected. The initial demonstration of linearity must use sufficient standards to determine the upper range limit. The upper range limit is an observed signal no more than 10% below the level extrapolated from lowers standards. The verification of linearity must use a minimum of a blank and three standards. If any verification data exceeds the initial values by ± 10%, linearity must be reestablished. If any portion of the range is shown to be nonlinear, sufficient standards must be used to clearly define the nonlinear portion.

9.1.3 Laboratory Control Sample- When beginning the use of this method and on a continuing basis, verify the calibration standards and acceptable instrument performance with the preparation of a LCS. If the determined concentrations are not within ±10% of the true values, performance of the determinative step is unacceptable. The source of the problem must be identified and corrected before either proceeding on with the initial demonstration or MDLs or continuing with on-going analyses.

9.1.4 Method Detection Limits- MDLs must be established for all analytes; using reagent water (blank) fortified at a concentration of 2-3 times the estimated instrument detection limit. To determine MDL values, take a minimum of seven replicate aliquots of the fortified reagent water and process through the entire analytical method. Perform all calculations defined in the method and report the concentration values in the appropriate units. Calculate the MDL as follows:

$$MDL = (t) \times (S)$$

Where,

t = student's t value for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom [t = 3.14 for seven replicates]. If more than seven reps are used the t-value changes accordingly.

S= standard deviation of the replicate analyses

MDLs are determined annually or whenever there is a significant change in the background or instrument response.

9.2 A Method Blank (MB) must be prepared, distilled, and analyzed with every sample batch or every 20 samples whichever is more frequent. The Method Blank is analyte-free DI water, or washed sea sand, which is carried through the entire procedure.

9.3 A Laboratory Control Sample and Laboratory Control Sample Duplicate (LCS and LCSD) must be prepared, distilled, and analyzed with every sample batch or every 20 samples whichever is more frequent. A LCS is reagent water, or washed sea sand, which has a known amount of analyte of interest added.

9.4 A Matrix spike and Matrix spike duplicate (MS and MSD) must be analyzed least every 10 samples and for each matrix whichever is more frequent. A MS/MSD is an aliquot of environmental sample to which known quantities of the method analytes are added. The MS and MSD are processed along with the samples.

9.5 See Tables H and I for a summary.

10.0 **CALIBRATION AND STANDARDIZATION**:

10.1 **Instrument Settings**

Sample throughput:	80 samples/h, 45s/sample
Pump and Speed:	35
Cycle Period:	45
Peak Base Width:	39 S
% Width Tolerance:	100
Threshold:	25000
Inject to start of peak:	24 s
Chemistry:	Direct

10.2 Follow steps 11.2 –11.2.30 to run calibration curve.

10.3 Calibration Criteria

Calibration Rep Handling:	Replace
Calibration Fit Type:	1st Order Polynomial
Weighting Method:	None
Force through zero:	No

10.3.1 The instrument must be calibrated every time it is set up. The working linear range is from 0.010 to 0.50 mg/L. The correlation coefficient must be at least 0.995.

10.3.2 Place working standards in decreasing concentration.

10.4 Stock Standard verification

The stock standard must be standardized weekly to verify the concentration. **This standardization must be documented in the logbook.**

10.4.1 Standardize the stock standard against 0.01920 N silver nitrate ($AgNO_3$) at the time of preparation and on a weekly basis. Using a buret, titrate a 1.0 mL aliquot of the cyanide stock diluted to 100 ml standard with 0.25 N NaOH and 0.5 mL indicator solution, with $AgNO_3$ solution to a salmon colored endpoint. **Record the volume of titrant used in the logbook**.

10.4.2 Perform the titration in triplicate along with a blank of 100 mL 0.25 N NaOH with 0.5 mL indicator solution. Subtract the volume of titrant used on the blank from the amount used to titrate the sample and calculate the concentration of the Stock Standard. **Record the concentration of the stock cyanide solution in the logbook. 1 mL $AgNO_3$ = 1 mg CN. If after performing the titration in triplicate, 1 mL $AgNO_3$ does not equal 1 mg CN, the CN stock standard needs to be discarded and reprepared.**

11.0 **PROCEDURE:**

11.1 Distillation Procedure

NOTE: Document all sample volumes, standards and reagents used in the distillation on the prep log.

This section of the SOP details the steps in distilling the samples before analysis. Samples must be checked for sulfides before distilling. If sulfides are present and the samples treated with bismuth nitrate, the entire calibration curve must be similarly treated and distilled. Refer to section 4.4 for procedure. In the following procedure, **D** and **M** refer to the marks on the collector tube. **D** means "distillation" end, and **M** means "measuring" end.

11.1.1 Set the controller to 120°C, allow the heater to warm up. The operating temperature of the distillation block needs to be verified annually.

11.1.2 Label tubes with the **M** end up, place as many properly labeled collector tubes as you have samples into the collector tube rack.

11.1.3 For liquid samples, place a drop of sample on lead acetate paper. If the paper darkens this indicate the presence of sulfide. Treat the stabilized sample (pH >12) with bismuth nitrate. Repeat until a drop on the lead acetate paper does not darken. Filter sample to remove precipitate and use filtrate as sample to be distilled. Place 6 ml of sample into each properly labeled sample tube using a calibrated automatic pipette. Add ~ 0.1 g sulfamic acid.

NOTE: If samples contain and are treated for sulfide, the entire calibration curve must also be similarly treated and distilled along with the samples.

11.1.4 For soil samples, weigh out 0.20 g of soil or sludge to the nearest 100th on a calibrated balance and dilute to 6 ml with deionized water tube with a calibrated automatic pipette into each properly labeled sample tube. Add ~ 0.1 g sulfamic acid.

11.1.5 For liquid samples, prepare one method blank by adding 6 mls of DI water to properly labeled sample tube using a calibrated automatic pipette. Add ~ 0.1 g sulfamic acid.

11.1.6 For soil samples, prepare one method blank by weighing out 0.20 g of washed sea sand to the nearest 100th on a calibrated balance and dilute to 6 ml with deionized water tube with a calibrated automatic pipette into a properly labeled sample tube. Add ~ 0.1 g sulfamic acid.

11.1.7 For liquid samples, prepare one LCS/LCSD pair by pipetting 6.0 ml of deionized water, ~ 0.1 g sulfamic acid, and 0.25 ml of 2.4 mg/L CN standard into two properly labeled sample tubes using a calibrated automatic pipette. See Table J2.

11.1.8 For soil samples, prepare one LCS/LCSD pair by weighing out 0.20 g of washed sea sand to the nearest 100th on a calibrated balance. Bring to 6 ml volume with deionized water. Add ~ 0.1 g sulfamic acid and 0.50 ml of 2.4 mg/L CN standard using a calibrated automatic pipette into each properly labeled sample tube. See Table J2.

11.1.9 For liquid samples, select one parent sample and prepare one MS/MSD pair per 10 samples by adding 6.0 ml of sample, ~ 0.1 g sulfamic acid, and 0.25 ml of 2.4 mg/L CN standard into two properly labeled sample tubes using a calibrated automatic pipette. See Table J2.

11.1.10 For soil samples, select one parent sample and prepare one MS/MSD pair by weighing out 0.20 g of sample to the nearest 100th on a calibrated balance. Bring to 6 ml volume with deionized water. Add ~ 0.1 g sulfamic acid and 0.5 ml of 2.4 mg/L CN standard using a calibrated automatic pipette into each properly labeled sample tube. See Table J2.

11.1.11 Prime the re-pipettor several times into the waste container. Then, add 0.75 ml of 7.111 M sulfuric acid / 0.79 M magnesium chloride solution to the sample tube using the supplied automatic pipet.

11.1.12 Immediately push the **D** end of a Cyanide-1 collector tube over the open end of each sample tube to start the seal.

11.1.13 Place the assembly in the press, putting the sample tube through the hole in the white base. Before pressing, the user should grip the collector tube firmly at the breakaway point to keep the tube from shifting during the pressing procedure.

11.1.14 The pressing motion should be a smooth constant pressure, which is just enough to slide the sample tube inside the collector tube. A jerky, forced motion may cause added strain to the tube and could potentially crack it. Press down on the handle until the stop ring on the sample tube hits the **D** end of the collector tube.

11.1.15 Put on heat-resistant gloves. Push the sample tube and **D** end of each tube all the way into the preheated block so that the collector tube stop ring touches the block. Placing 21 tubes should take less than one minute.

11.1.16 Set the timer for 30 minutes.

11.1.17 When 30 minutes is up, remove the first tube, use heat-resistant gloves, from the block and immediately pull its sample tube using a downward twisting motion as opposed to a sideways motion. You must remove the sample tube within 4 seconds of removing it for the block or suck-back of the sample will occur. Dispose of the sample tube and the hot solution.

11.1.18 Invert each collector tube and place it into the collector tube rack, now with the **D** end up. It should take less than two minutes to pull and separate all 21 tubes.

11.1.19 Parafilm the **M** end and allow tubes to cool for at least 10 minutes.

11.1.20 Hold collector tube horizontally and rinse its walls with the distillate in order to homogenize it. Roll tube in order to collect all droplets from the walls of the tube. Return the tube to an upright position so the **D** end is up.

11.1.21 With the **D** end up, break the collector tube in half by pulling the **D** end hard toward yourself to break it, the twisting and tearing off the **D** end. Discard the **D** end.

11.1.22 In the **M** end of the tube dilute to the 6.0 ml mark with DI water. This results in the original sample volume, but now in 0.25 M NaOH.

11.1.23Push the second cap onto the open end of the tube as far as it will go. Shake the tube so it mixes with the diluent. Do not invert the sample. With the M end down; place the tube into the collector tube rack.

11.1.24 Seal both ends of the tube with Parafilm if sample determination is not done immediately.

11.2 Basic System Operation - Analytical

This portion of the SOP is designed to allow the user to set up and run a method, print a sample report, then shut down using the more basic software functions. For a more detailed explanation of the many other options, the user should refer to the Lachat Software Reference Manual. It is assumed that a method program has already been created for the chemistries you wish to run.

11.2.1 Turn on computer with ON/OFF button. Turn on printer. The power to the monitor, autosampler and reaction module is controlled with a multi-outlet noise filter and surge suppresser located behind the reaction module. Turn the red switch to "ON".

11.2.2 Allow the autosampler to perform its startup routine and wait until the autosampler stops with the probe above the wash bath.

11.2.3 Log into the Network with your Login name and password. Windows program will be activated. Program Manager screen will appear. Click twice on Lachat Instruments. Click twice on the Omnion FIA icon on the Lachat Instruments window. The startup box will come up, and then click on **'OK'**. The autosampler probe will go into the wash bath and dilutor activity may be heard. The injection valves may turn to the Inject state if they were not already there.

11.2.4 To encourage GALP (Good Automated Laboratory Practice), Omnion requires that the operator "Log-in" every time with name and password. Enter your assigned name and password in the correct case in the spaces indicated and then click on the **'OK'** button.

11.2.5 After you have logged in, the Omnion FIA Main Menu will appear on the screen. The header should contain the serial number of the software key. No messages should be seen about the SS420 boards, or any serial port failures. Click on the Instrument button labeled 'FIA Instrument 1'.

11.2.6 Each valve allocated to this instrument will be cycled from Load to Inject and Load to Inject again. This is a test of the valves and if no messages are received about failing valves, then they are OK.

11.2.7 If a valve fails, a box will tell you which channel's valve failed. You can press OK and continue. You should arrange for service for the failing valve by calling Lachat Instruments.

11.2.8 After the injection valves are tested, an instrument window for FIA Instrument 1 will appear. Omnion will automatically open the last Method, Tray, DQM Plan and Data File used. Arrow up to 'File" and click. When window appears click on '**Open Method**'.

Under Open Method File Directories, click on **c:\omnion\methods** and then click on the method you will be running. A list of methods will appear. Highlight the appropriate one in the **File Name** box and click on **'OK'**.

11.2.9 The Method will open and the **Analyte Table** will appear. It will show the Analyte Name and which Channel it is run on. The concentration Units and concentration of the calibration standards will be listed. To the far right will be the timing periods, which the instrument uses to detect the peaks.

11.2.10 Click on **'File'** again and then **'Open Tray'**. The **'Open Tray File'** window will come up. Directories will be **c:\omnion\trays\method**. Click on the method you will be running. A list of previous trays for that particular method will appear.

Click on a recent **tray file name and** the on **'OK'** to call it up. Edit this tray below the Calibration Standards with the sample numbers you will be running. Also edit any dilutions that will be required.

11.2.11 Click on **Save Tray As** and edit name of tray to reflect toady's' date and letter to reflect which run: YYMMDDL. L is the sequence of the tray that day i.e., a=first tray, b=second tray and so on. Example: 960730a.

11.2.12 Click on **File** again and then on **Open DQM**. The Open DQM File window will come up. Directories will be **c:\omnion\DQM\method**. Click on the method you will be running and then on the method **DQM File Name**. Click on **OK** and the DQM (Data Quality Management) Plan will appear.

This DQM Plan supplements the tray table itself and acts as a standard operating procedure to be used when running this tray. Check the DQM to make sure it will apply to this tray, or edit it if necessary. If any changes were necessary then the DQM should be saved, and then replace the DQM in the tray, to make the changes permanent. If no changes were necessary, then minimize this window.

11.2.13 Click on the **Run Tray** button. The Tray Run Window will appear. Leave the **Method** and **Tray** spaces blank to run the currently loaded Method and tray. You must fill in the **Data File** space so that Omnion knows where to put the data it will generate. Click on **Catalog** after the **Data File** space to see a list of previous data files. Click on an old file name and then edit it to match today's tray name. Click on **OK**.

11.2.14 Follow Section 17.3 of Lachat QuikChem Method 10-204-00-1-A for proper setup of manifold. Insert the proper manifold for the desired analysis to the proper channel specified in the Analyte Table. The load/inject valve for each channel has six connections with the following designations:

Port #	Function
1	Sample Loop Inlet
2	Carrier Stream Inlet (From Pump)
(Short section of plastic tubing remains port #2 at all times)	
3	Outlet to reaction manifold
4	Sample loop outlet
5	Sample loop waste line
6	Sample source line (from sampler, pump)

Each reaction manifold has a line with pump tubing attached labeled "carrier". Disconnect the pump tubing from this line and reconnect it to the section of line that comes from port #2. Connect the section of tubing coming from the reaction manifold to port #3.

11.2.15 Connect the outlet line from the manifold, located top right, to the bottom inlet of the flow cell.

11.2.16 Insert 0.55 mm i.d. x 200 cm backpressure loop between top outlet of flow cell and the waste line.

11.2.17 Place waste line into proper cyanide waste collection container.

11.2.18 Install proper 570 interference filter.

11.2.19 Allow 15 minutes for heating unit to warm up to 60°C.

11.2.20 Install micro-sample loop in ports #1 and # 4.

11.2.21 Install the pump tubing onto pump cartridges. Check for wear on the pump tubing by rolling between thumb and fingers when stretched across a pump cartridge. Replace tubing if "flat" spots are felt.

11.2.22 Move tension levers to left to provide proper tension.

11.2.23 Check all connections for leakage and proper flow. Make sure waste lines are routed to proper container.

11.2.24 Fill standard, check standard and blank vials with proper solutions. Fill sample tubes with proper samples.

11.2.25 When ready, click on **RUN** on the Tray Run Window and the analysis will start. The symbol for the tray on the toolbar will turn to a **STOP** sign until analysis is complete.

11.2.26 If necessary to stop the run anytime, click on the **STOP** sign. A window will come down with the options to RESUME or ABORT TRAY.

11.2.27 After instrument has calibrated, click on the **Review Calibration** button on the toolbar. The graph of the calibration will be displayed along with the area of each standard. If the r-value of the calibration is 0.995 or better, print the calibration graph and allow the analysis to continue.

11.2.28 After analysis is completed the **STOP** sign in the Toolbar will be replaced with **Run Tray.** Click on File and the window will come down. Click on Export Data. Export data window will appear. Highlight whatever Data Items and Channel Dependent Data Items you want exported to EXCEL Save Export Data As window will appear. Directories should be g:\data\inorgani\lachat\archives.

Highlight the text file you have just run in the File Name box. Click on **OK** and data will be exported to EXCEL. Then go back and click on File again. When window comes down, click on Open Runtime Rpt. Open Runtime Report File window will appear. It should have current data, method and file name of analysis just completed, or if going back at a later date, then highlight the one that you want. Click on **OK** and the Runtime Report will appear on the screen. Click on File and then on Print/Export Runtime Rpt. Runtime Report window will appear.

Click on **OK** to print. On Print window choose the Print Range you want. **ALL** is normally highlighted. Click on **OK**.

11.2.29 Samples that have results greater than the highest standard in the calibration curve need to be diluted appropriately so the result falls within the calibration curve, and reanalyzed. Document all dilutions on prep log.

11.2.30 Document all standards and reagents used in analysis in raw data. Sign and date raw data.

11.2.31 After analysis is complete, place reagent lines in D.I. water and rinse several minutes. Remove lines from water and pump air through the lines until dry.

11.2.32 Turn off pump, release tension levers on pump cartridges and remove pump tubing from cartridges.

11.2.33 Disconnect pump tubing to port #2 at the pump tubing connector, disconnect line to port #3 at port #3 connector and connect pump tubing from #2 to line from manifold.

11.2.34 Disconnect manifold outlet line from flow cell inlet connector.

11.2.35 Wrap pump tubing lightly around manifold panel and store in appropriate box, with sample loop and interference filter.

NOTE: Any daily or periodic maintenance must be recorded in the instrument daily logbook.

11.3 SHUTDOWN:

11.3.1 Click on **EXIT** icon

11.3.2 Omnion FIA Data System Window appears. Click on **Logoff**.

11.3.3 Window listing **User** Name and question: **Logoff Current Session?** Click on **YES**.

11.3.4 Window for User Name and Password comes up. Click on **EXIT**.

11.3.5 Window comes up with: **Terminate Data System?** Click on **YES.**

11.3.6 Turn off computer, printer and switch on surge suppresser.

12.0 **CALCULATIONS:**

12.1 The instrument provides calculated sample results in ug/L. Calculations are only necessary if a dilution was used.

Liquid Calculation

Raw Data Value (ug/L) x Dilution Factor / 1000 = Cyanide (mg/L)

Soil Calculation

$$\frac{\text{Raw Data Value (ug/L) X 0.006 L X Dilution Factor}}{\text{(0.00020 Kg x \% solids in decimal form x 1000)}} = \text{Cyanide(mg/Kg)}$$

12.2 Accuracy:

A matrix spike / matrix spike duplicate is analyzed for each analytical batch of 10 or fewer samples.

MS/MSD calculation

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

SSR = Spike sample result
SR = Sample result
SA = Spike added

12.3 Precision:

The precision is calculated based on the concentration of the matrix spike / matrix spike duplicate result.

Relative percent difference (RPD) calculation:

$$\% \text{ RPD} = \frac{|MS-MSD|}{(MS+MSD)/2} \times 100$$

MS = Matrix spike value
MSD =Matrix spike duplicate Value

12.4 See Table I for summary of limits. Control limits of 90-110% is set by the method.

13.0 METHOD PERFORMANCE:

13.1 The method performance is validated through the Method Detection Limit Study, Initial Validations and the Performance Testing Samples taken through this procedure.

13.2 See Tables A and K for a summary

14.0 POLLUTION PREVENTION:

14.1 Pollution prevention encompasses any technique or procedure that reduces or eliminates the quantity or toxicity of waste at the point of generation. Laboratory staff should order where possible acceptable non-toxic alternative supplies and prepare only those quantities of reagents or standards that will be used prior to the expiration date. Other appropriate measures to minimize waste generation should be brought to the attention of

laboratory management. All laboratory waste shall be handled as directed by the Laboratory Waste Management Plan and Hazardous Waste Contingency Plan.

15.0 DATA ASSESSMENT AND ACCEPTANCE CRITERIA FOR QUALITY CONTROL MEASURES:

15.1 At a minimum there are three levels of data review:

15.2 Analyst/Technician verification at the bench top are looking at instrument performance as it relates to initial calibration, calibration verification, cleanliness.

15.3 Supervisor/Analyst verification after analysis are looking for sample concentration versus linear range of the instrument, typical patterns resulting from the compounds or elements in question, and quality control measure criteria. Data is accepted without qualification, accepted with qualification, or rejected with samples reprocessed.

15.4 Report Reviewer/Project Management personnel look at the presentation of the data on final reports. The reports are verified for holding time compliance, receipt conditions, method citation and reasonableness, which may include field duplicate analysis, analytical comments and qualifications presented by the previous reviews, and comparing results of similar analytical techniques as it relates to the project site information when available.

15.5 A fourth level of review, data validation is determined from a project or program scope of laboratory services and encompasses the generation Quality Control summaries in the media of "Form Generation".

15.6 See Table L and M for a summary.

16.0 CORRECTIVE ACTIONS FOR OUT-OF-CONTROL DATA

16.1 Assessment of Quality Control measures is done to provide a level of confidence in the data generated. The measures provide documentation that the instrument conditions were reliable during the analysis.

16.2 See Table L for summary.

17.0 CONTINGENCIES FOR HANDLING OUT-OF-CONTROL OR UNACCEPTABLE DATA

17.1 During analysis, events occur specific to the physical and chemical characteristics of the environmental sample. When possible, with received sample volumes, data generated along with measures that do not meet statistical goals are re-analyzed again to see if the statistical goal can be achieved. When environmental samples do not meet statistical unacceptable data is generated. These events are different from those pertaining to instrument operating conditions these events occur when the instruments are operating under ideal conditions.

17.2 See Table L for a summary.

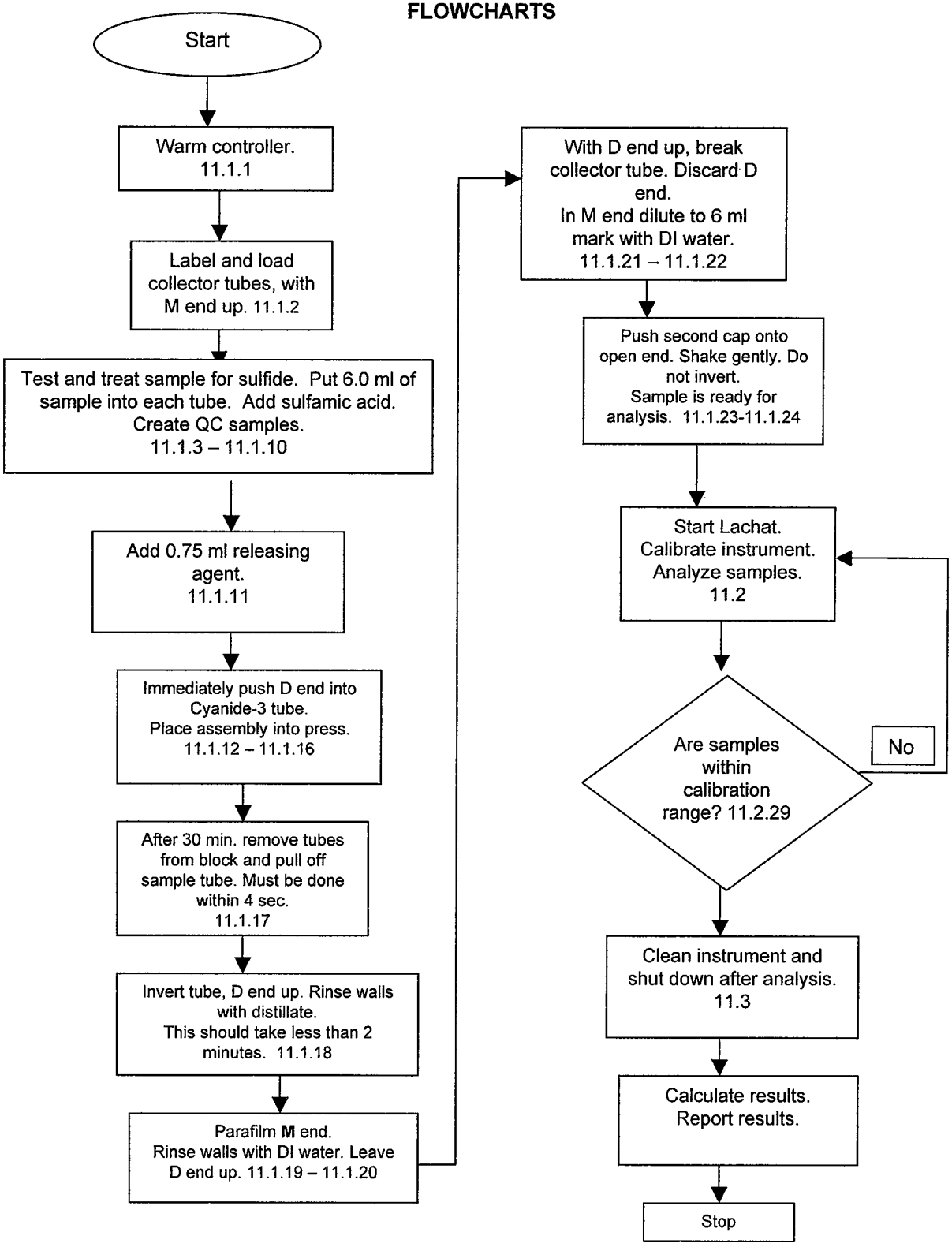
18.0 WASTE MANAGEMENT

18.1 To minimize waste during sample preparation has two benefits. The first benefit is a cost savings to the lab in materials and supplies. The second is a benefit to the environment, as fewer materials need to be disposed.

REFERENCES:

QuikChem Method 10-204-00-1-A, Lachat Instruments, August 28, 2000
Micro Dist Method Cyanide-1, Lachat Instruments, October 12, 2000
SW846 9012A, Revision 1.0, December 1996
EPA 600 R-93-100, Revised August 1993, Method 335.4
Standard Methods for the Examination of Water and Wastewater, 18th Edition, p. 4-18, Methods 4500-CN^- A, B, C, and D (1992)
40CFR Part 136
National Environmental Laboratory Accreditation Conference (NELAC), July 1998 Standards
US EPA Quality Assurance Division (QAD)

FLOWCHARTS


Start
Warm controller. 11.1.1
Label and load collector tubes, with M end up. 11.1.2
Test and treat sample for sulfide. Put 6.0 ml of sample into each tube. Add sulfamic acid. Create QC samples. 11.1.3 – 11.1.10
Add 0.75 ml releasing agent. 11.1.11
Immediately push D end into Cyanide-3 tube. Place assembly into press. 11.1.12 – 11.1.16
After 30 min. remove tubes from block and pull off sample tube. Must be done within 4 sec. 11.1.17
Invert tube, D end up. Rinse walls with distillate. This should take less than 2 minutes. 11.1.18
Parafilm M end. Rinse walls with DI water. Leave D end up. 11.1.19 – 11.1.20
With D end up, break collector tube. Discard D end. In M end dilute to 6 ml mark with DI water. 11.1.21 – 11.1.22
Push second cap onto open end. Shake gently. Do not invert. Sample is ready for analysis. 11.1.23-11.1.24
Start Lachat. Calibrate instrument. Analyze samples. 11.2
Are samples within calibration range? 11.2.29
No
Clean instrument and shut down after analysis. 11.3
Calculate results. Report results.
Stop

VALIDATION DATA:

The laboratory must demonstrate initial proficiency with each combination of sample preparation and determinative methods utilized, by generating data of acceptable accuracy and precision for a reference sample containing the target parameters in a clean matrix. The laboratory must also repeat this demonstration whenever new staff is trained or significant changes in instrumentation are made. Analysts previously trained shall perform a continued demonstration of proficiency annually by performing "Yearly Demonstration of Capability" (YDC).

The values from the determinative method are presented as guidance only and are not intended as absolute acceptance criteria. Accuracy of parameters routinely analyzed by En Chem can be found in Initial Demonstration Data Table K. Blind studies are available upon request from the QC Manager.

MANAGEMENT APPROVAL AND REVIEW OF SOPS - POLICY AND DOCUMENTATION

REVIEWED BY: _____ 1/20/04
Alexandria Wolf
Inorganics Group Leader — Date

_____ 1/20/04
Arthur F. Lautenbach
Quality Assurance Officer — Date

APPROVED BY: _____ 1/20/04
Nils Melberg
Laboratory Manager — Date

Periodic Review Record

Review Date					
Initials					

MANAGEMENT APPROVAL AND REVIEW OF SOPS - POLICY AND DOCUMENTATION

REVIEWED BY: _____ 1/20/04
Alexandria Wolf
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Review Date					
Initials					

Tables

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Table A
REPORTING LIMITS

Compound Name	Aqueous		Solid	
	MDL (µg/L)	EQL (µg/L)	MDL (µg/Kg)	EQL (ug/Kg)
Total Cyanide	1.6	10	170	300

Table B
REQUIRED SAFETY EQUIPMENT

Safety Apparel Description	Mandatory for Procedure	Optional
Safety Goggles or Glasses	√	
Lab Coat	√	
Gloves	√	
Face Shield		√

Table C

EQUIPMENT

Equipment	Manufacturer	Model(s)/Catalog number •
Lachat 8000	Lachat	Lachat
Micro-Distillation	Lachat	Micro Distillation
Top loading Analytical Balance	Mettler	BA310P
1000 µL Pipette	Eppendorf	05-402-76 (Fisher Cat#)
500 µL Pipette	Eppendorf	05-402-72 (Fisher Cat#)
250 µL Pipette	Eppendorf	05-402-69 (Fisher Cat#)
Repipetors (0.5 - 5.0mL)	Barnstead/Thermolyne	13-687-33 (Fisher Cat#)
Vented Hood	Hamilton	
Spoonula (Lab Spoon)	FisherBrand or equivalent	14-375-10 (Fisher Cat#)
Gloves – Heat Resistant		
Cyanide Manifold	Lachat	10204-00-1-A
Interference filter – 570 nm	Lachat	

- Or equivalent

Table D
SUPPLIES

Supplies	Manufacturer	Catalog #
Distillation tubes	Lachat	A17001
Culture Tubes 13X100	Fisher	71500 13100
Volumetric Flasks	Fisher	Various
Parafilm	Fisher	
Sea Sand	Fisher	S25-3

Table E

REAGENTS

Reagent	Alias	Concentration	Directions found in:
Potassium Cyanide	Stock Standard	Neat	
Potassium Cyanide	Second Source Stock Standard	Neat	
Potassium Hydroxide		Neat	
Sodium Hydroxide		Neat	
NaOH – 0.25 N	Carrier Solution	0.25 N	Table J
Deionized Water			
Potassium Phosphate, Monobasic, (KH_2PO_4)		Neat	
Phosphate Buffer	Buffer Solution	0.71 M	Table J
Chloramine-T hydrate		Neat	
Chloramine-T Reagent	Color Reagent		Table J
Barbituric Acid		Neat	
Pyridine		Neat	
Hydrochloric Acid		12 M	
Pyridine-Barbituric Acid Reagent	Pyridine-Barbituric Acid Reagent		Table J
p-dimethylaminobenzalrhodanine	Indicating solution		Table J
Standard Silver Nitrate Solution		0.0192 N	
Magnesium Chloride Hexahydrate		Neat	
Sulfuric Acid		Concentrated	
Sulfuric Acid (50% v/v)	Washing Solution		Table J
Sulfuric Acid/Magnesium Chloride Solution	Releasing Agent	7.11 M H_2SO_4 0.79 M MgCl	Table J
Nitrate Bismuth		Neat	
Lead Acetate Paper		Neat	
Sulfamic Acid		Neat	
Sea Sand (Washed)*		Neat	

* Washed with 50% sulfuric acid (v/v) solution and then dried.

Table F

STANDARDS

Standard	Concentration	Direction found in Section:	Alias
Potassium Cyanide	1000 mg/L	Table J2	Stock Standard
Potassium Cyanide Must be different Lot # than Stock	1000 mg/L	Table J2	Second Source Stock Standard
Level 1 Calibration Standard	0.50 mg/L	Table J2	Cal Std. 1
Level 2 Calibration Standard	0.10 mg/L	Table J2	Cal Std. 2
Level 3 Calibration Standard	0.050 mg/L	Table J2	Cal Std. 3
Level 4 Calibration Standard	0.010 mg/L	Table J2	Cal Std. 4
Level 5 Calibration Standard	0.00 mg/L	Table J2	Cal Std. 5
Initial Calibration Verification – 1	0.05 mg/L	Table J2	ICV – 1
Initial Calibration Verification – 2	0.20 mg/	Table J2	ICV – 2
Continuing Calibration Verification	0.10 mg/L	Table J2	CCV
Working Standard (1)	10 mg/L	Table J2	Working Standard (1)
Working Standard (2)	1.0 mg/L	Table J2	Working Standard (2)
Secondary Working Standard (1)	100 mg/L	Table J2	Secondary Working Standard (1)
Secondary Working Standard (2)	10 mg/L	Table J2	Secondary Working Standard (2)
Secondary Working Standard (3)	1.0 mg/L	Table J2	Secondary Working Standard (3)
Secondary Working Standard (4)	2.4 mg/L	Table J2	Secondary Working Standard (4)
Matrix Spike/Matrix Spike Duplicate – Liquid	0.10 mg/L	Table J2	MS/MSD-Liquid
Matrix Spike/Matrix Spike Duplicate – Solid	0.20 mg/L	Table J2	MS/MSD-Solid
Laboratory Control Spike/Laboratory Control Spike Duplicate - Liquid	0.10 mg/L	Table J2	LCS/LCSD-Liquid
Laboratory Control Spike/Laboratory Control Spike Duplicate - Solid	0.20 mg/L	Table J2	LCS/LCSD-Solid

Table G

SAMPLE COLLECTION, PRESERVATION, HOLDTIME, SHIPMENT, AND STORAGE

Matrix	Prep Method	Container(s)	Preservation Hold Time	Shipment Conditions	Lab Storage Conditions
Aqueous	SW-846 9012A EPA 335.4	250 ml plastic containers	pH >12; NaOH 14 days	On ice 4+/- 2° Celsius	4°C
Solid	SW-846 9012A	125 ml plastic containers	None 14 days	On ice 4+/- 2° Celsius	4°C

Table H

QUALITY CONTROL

Preparation Method ⇨ Quality Control Measure ⇩	**EPA 335.4 SW846 9012A**
Method Blank	One per batch of samples, up to 20 environmental samples, whichever is more frequent. Must be distilled with batch.
Laboratory Control Spike and Duplicate	One per batch of samples, up to 20 environmental samples, whichever is more frequent. A LCSD is required if MS/MSD is not performed. Must be distilled with batch.
Matrix Spike / Matrix Spike Duplicate	One pair per batch of samples, up to 10 environmental samples, whichever is more frequent. Must be distilled with batch.
Initial Calibration	Minimum of 3 standards plus blank. Must be performed every time before samples are analyzed.
Calibration Verification (ICV/CCV)	ICV – analyzed after calibration but before samples. **The ICV is distilled with batch.** CCV – analyzed after every 10 samples. **The CCV is not distilled with batch.**
Calibration Blank (ICB/CCB)	ICB – analyzed after ICV. **The ICB is not distilled with batch.** CCB – analyzed after every CCV pair. **The CCB is not distilled with batch.**
Leach Blank	The appropriate leach blank must be distilled and analyzed along with the appropriate samples as leached on the same leach date.

Table I
CALIBRATION AND STANDARDIZATION

Analytical Method Acceptance Criteria⇨ Calibration Measure ⇩	SW846 9012A EPA 335.4 Frequency	Acceptance Criteria
Laboratory Control Spike and Duplicate	• One pair per batch of samples, up to 20 environmental samples, whichever is more frequent.	• Project Specific or • For water method specific 90 –110% with 20% RPD. • For soil 81-119% with 20% RPD.
Matrix Spike / Matrix Spike Duplicate (MS/MSD)	• One pair per batch of samples, up to 10 environmental samples, whichever is more frequent.	• Project Specific or • For water method specific 90 –110% with 20% RPD. • For soil 70-122% with 20% RPD.
Method Blank	• One per batch of samples, up to 20 environmental samples, whichever is more frequent.	• Project Specific or • Less than the EQL
Initial Calibration	• Analyzed daily before samples	• Correlation coefficient must be 0.995 or greater
Initial Calibration Verification (ICV)	• Distilled with samples and analyzed after calibration at two different concentrations to verify distillation, but before samples.	• Recovery must be between 90 – 110%
Initial Calibration Blank (ICB)	• Analyzed after ICV, but before samples.	• Project specific or • Less than EQL
Continuing Calibration Verification (CCV)	• Analyzed after every 10 samples.	• Project specific or • Recovery between 90 – 110%
Continuing Calibration Blank (CCB)	• After each CCV.	• Project specific or • Less than EQL

TABLE J

PREPARATION OF REAGENTS

Standard	Alias	Final Concentration	Directions	Final Volume
NaOH – 0.25 N	Carrier Solution	0.25 N	Weigh 10 g of neat NaOH into ~ 500 ml DI water in 1 L plastic container. Dilute to volume. Prepare fresh daily.	1000 ml
Phosphate Buffer	Buffer Solution	0.71 M	Weigh 97 g of neat KH_2PO_4 into ~ 500 ml DI water in 1 L volumetric flask. Dilute to volume. Shelf life = 1 month.	1000 ml
Chloramine-T Reagent	Color Reagent		Weigh 2 g of neat Chloramine-T hydrate into ~ 250 ml DI water in 500 ml volumetric flask. Dilute to volume. PREPARE DAILY!	500 ml
Pyridine-Barbituric Acid Reagent	Pyridine-Barbituric Acid Reagent		MAKE UNDER HOOD!!!!!!! Weigh 15 g barbituric acid into a 1 L beaker Add 100 ml DI. Add 75 ml pyridine, mix to dissolve Add 15 ml conc. HCL. Transfer to 1 L volumetric flask and dilute to volume. Shelf life = 1 week.	1000 ml
p-dimethylaminobenzalrhodanine	Indicator Solution		Weigh 20 mg of neat p-dimethylaminobenzalrhodanine into a 100 ml volumetric flask. Dilute into 100 ml acetone. Shelf life = 1 year.	100 ml
Sulfuric Acid/Magnesium Chloride Solution	Releasing Agent	7.11 M H_2SO_4 0.79 M MgCl	Weigh 110.8 g DI water in beaker. Add 32.2 g Magnesium Chloride Hexahydrate ($MgCl_2.6H_2O$). Slowly add 139 g concentrated H_2SO_4. Transfer to automatic pipet container. Cool. Shelf life = 1 year.	200 g
Sulfuric Acid (50% v/v)	Washing Solution	50% v/v	Slowly add 50 ml concentrated H_2SO_4 to~ 50 ml DI water in 100 mL volumetric flask.. Dilute to volume with DI water.	100 ml

TABLE J2

PREPARATION OF STANDARDS

Standard	Alias	Final Concentration	Directions	Final Volume
Potassium Cyanide	Stock Standard.	1000 mg/L	POISON!!!!! Weigh 2.51 g of neat KCN and 2 g of neat KOH into ~900 ml DI water in 1 L volumetric flask. Dilute to volume. Shelf life = 1 month. Standardize against AgNO3. If concentration of stock standard is between 995 – 1005 mg/L then use 1ml of stock solution. If concentration is outside this range use the following formula to determine the amount of stock to use. 5000/Stock Std. Conc. (mg/L).	1000 ml
Potassium Cyanide	Second Source Stock Standard	1000 mg/L	POISON!!!!! Weigh 2.51 g of neat second source KCN and 2 g of neat KOH into ~900 ml DI water in 1 L volumetric flask. Dilute to volume. Shelf life = 1 month. Standardize against AgNO3. If concentration of stock standard is between 995 – 1005 mg/L then use 1ml of stock solution. If concentration is outside this range use the following formula to determine the amount of stock to use. 5000/Stock Std. Conc. (mg/L).	1000 ml
Working Standard (1)	Working Standard (1)	10 mg/L	Pipette 1.0 ml stock standard into 100 ml volumetric flask. Dilute to volume. PREPARE DAILY!	100 ml
Secondary Working Standard (1	Secondary Working Standard (1)	100 mg/L	Pipette 10 mL second source stock standard into 100 ml volumetric flask. Dilute to volume. PREPARE DAILY!	100 ml
Working Standard (2)	Working Standard (2)	1.0 mg/L	Pipette 10 mls of working standard (1) into 100 ml volumetric flask. Dilute to volume. PREPARE DAILY!	100 ml
Secondary Working Standard (2)	Secondary Working Standard (2)	10 mg/L	Pipette 1.0 ml second source stock standard into 100 ml volumetric flask. Dilute to volume. PREPARE DAILY!	1000 ml
Secondary Working Standard (3)	Secondary Working Standard (3)	1.0 mg/L	Pipette 10 mls of secondary working standard (2) into 100 ml volumetric flask. Dilute to volume. PREPARE DAILY!	100 ml
Secondary Working Standard (4)	Secondary Working Standard (4)	2.4 mg/L	Pipette 2.4 mls of secondary working standard (1) into 100 ml volumetric flask. Dilute to volume. PREPARE DAILY!	100 ml
Level 1 Calibration standard	Cal. Std. 1	0.50 mg/L	Pipette 5.0 mls of working standard (1) into 100 ml volumetric flask. Dilute to volume with 0.25N NaOH. PREPARE DAILY!	100 ml
Level 2 Calibration Standard	Cal. Std. 2	0.10 mg/L	Pipette 1.0 mls of working standard (1) into 100 ml volumetric flask. Dilute to volume with 0.25N NaOH. PREPARE DAILY!	100ml
Level 3 Calibration Standard	Cal. Std. 3	0.050 mg/L	Pipette 0.50 mls of working standard (1) into 100 ml volumetric flask. Dilute to volume with 0.25N NaOH. PREPARE DAILY!	100 ml
Level 4 Calibration Standard	Cal. Std. 4	0.010 mg/L	Pipette 1.0 mls of working standard (2) into 100 ml volumetric flask. Dilute to volume with 0.25N NaOH. PREPARE DAILY!	100 ml
Level 5 Calibration Standard	Cal. Std. 5	0.00 mg/L	Use 0.25N NaOH only.	100 ml
Continuing Calibration Verification	CCV – 1	0.10 mg/L	Pipette 1.0 mls of working standard (1) solution into 100 ml volumetric flask. Dilute to volume with 0.25N NaOH. PREPARE DAILY!	100 ml
Initial Calibration Verification –1	ICV – 1	0.05 mg/L	Pipette 2.5 mls of secondary working standard (3) solution into 50 ml volumetric flask. Dilute to volume with 0.25N NaOH. PREPARE DAILY!	50 ml
Initial Calibration Verification –2	ICV – 2	0.20 mg/L	Pipette 10 mls of secondary working standard (3) solution into 50 ml volumetric flask. Dilute to volume with 0.25N NaOH. PREPARE DAILY!	50 ml
Matrix Spike/Matrix Spike Duplicate – Liquid	MS/MSD - Liquid	0.10 mg/L	Pipette 0.25 mls of secondary working standard (4) into sample tubes.	6 ml
Matrix Spike/Matrix Spike Duplicate – Solid	MS/MSD-Solid	0.20 mg/L	Pipette 0.50 mls of secondary working standard (4) into sample tubes.	6 ml
Laboratory Control Spike/Laboratory Control Spike Duplicate – Liquid	LCS/LCSD-Liquid	0.10 mg/L	Pipette 0.25 mls of secondary working standard (4) into sample tubes.	6 ml
Laboratory Control Spike/Laboratory Control Spike Duplicate – Solid	LCS/LCSD-Solid	0.20 mg/L	Pipette 0.50 mls of secondary working standard (4) into sample tubes.	6 ml

Table K

En Chem Initial Demonstration of Capability

Compound	Conc. µg/L	IDC-1 µg/L	IDC-2 µg/L	IDC-3 µg/L	IDC-4 µg/L	Average µg/L	% Recovery	SD	RSD
Cyanide	100	103.4	104.6	104.0	104.1	104.0	104.0	0.492	0.473

Table L

ANALYST/TECHNICIAN DATA ASSESSMENT

Analytical Method Acceptance Criteria⇨ Data Assessment Measure ⇩	Method Citation EPA 335.4 SW846 9012A If these conditions are not achieved ⇒
Method Blank	• 1
Accuracy & Precision Matrix Spike Samples	• 2
Accuracy & Precision Laboratory Control Spikes	• 3
Initial Calibration	• 4
Initial / Continuing Calibration Verification	• 5
Initial / Continuing Calibration Blank	• 6

1. In the absence of project specific requirements, sample detects less than 20 times the method blank contamination level is reported with the "A" data qualifier. Sample detects greater than 20 times the method blank contamination are reported without qualification.

2. In the absence of project specific or method requirements, in-house generated limits will be used. If the concentration of the spike is less than 25% of the concentration of the parent, no further action is needed unless the parent, MS or MSD concentrations are greater than the top standard in the calibration curve. If the parent, MS or MSD is greater than the top standard of the calibration curve, dilute the parent, MS, and MSD to concentrations that are within the curve. The MS and MSD recoveries do not need to be evaluated. If the concentration of the spike is greater than 25% of the concentration of the parent , "N" flag the parent sample if either the MS or MSD fails. If the MS and MSD fails precision control limits flag the parent with the "*" (precision) data qualifier. Generate a Non-Conformance Memo.

3. If sample volume does not allow re-analysis the entire prep/analytical batch of samples shall be flagged with the "&" (accuracy) and "*" (precision) qualifier to reflect the deficiencies. Generate a Non-Conformance Memo.

4. If correlation coefficient is less than 0.995 perform maintenance and recalibrate.

5. If ICV/CCV is outside the control limits reanalyze the ICV/CCV to verify the instrument is out of control. If the 2nd analysis is outside control limits, perform maintenance and recalibrate. Samples that bracket the out of control standards must be reanalyzed.

6. If ICB/CCB is outside the control limits reanalyze the ICB/CCB to verify the instrument is out of control. If the 2nd analysis is outside control limits, perform maintenance and recalibrate. Samples that bracket the out of control standards must be reanalyzed. Samples that are > 10X the concentration in the CCB the samples do not have to be reanalyzed.

Table M

REPORT REVIEWER/PROJECT MANAGEMENT DATA ASSESSMENT

Analytical Method Acceptance Criteria⇨ Data Assessment Measure ⇩	**Method Citation EPA 335.4 SW846 9012A If these conditions are not achieved ⇒**
Holding Time Compliance	• 1
Sample Receipt Conditions and Preservation	• 2
Method Citation	• 3
Reasonableness: Field Duplicate	• 4
Reasonableness: Analytical Comments Qualifications	• 5

1. Flag results with the H data qualifier. The number of dates past hold is addressed in the comments section of the report. Dates past hold will be addressed in the case narrative for Level III and IV.

2. In prose describe the receipt conditions as they relate to the acceptance criteria list in Table G

3. Compare to regulatory program in QAPjP or Chain of Custody.

4. Are duplicates within 20% agreement? If not, internally flag for review.

5. Do related suites of tests agree or are reasonable.

Table N
DATA QUALIFIERS

Qualifier Codes

Flag	Applies To	Explanation
A	Inorganic	Analyte is detected in the method blank. Method blank criteria are evaluated to the laboratory method detection limit. Additionally, method blank acceptance may be based on project specific criteria or determined from analyte concentrations in the sample and are evaluated on a sample-by-sample basis.
B	Inorganic	The analyte has been detected between the method detection limit and the reporting limit.
B	Organic	Analyte is present in the method blank. Method blank criteria are evaluated to the laboratory method detection limit. Additionally, method blank acceptance may be based on project specific criteria or determined from analyte concentrations in the sample and are evaluated on a sample-by-sample basis.
C	All	Elevated detection limit.
D	All	Analyte value from diluted analysis or surrogate result not applicable due to sample dilution.
E	Inorganic	Estimated concentration due to matrix interferences. During the metals analysis using the inductively coupled plasma (ICP), the serial dilution failed to meet the established control limits of 0-10% and the sample concentration is greater than 50 times the IDL (100 times the IDL for analysis done on the ICP-MS). The result was flagged with the E qualifier to indicate that a physical interference was observed.
E	Organic	Analyte concentration exceeds calibration range.
F	Inorganic	Due to potential interferences for this analysis by Inductively Coupled Plasma techniques (SW-846 Method 6010), this analyte has been confirmed by and reported from an alternate method.
F	Organic	Surrogate results outside control criteria.
H	All	Preservation, extraction or analysis performed past holding time.
J	Inorganic	The analyte has been detected between the method detection limit and the reporting limit.
J	Organic	Concentration detected is greater than the method detection limit but less than the reporting limit.
K	Inorganic	Sample received unpreserved. Sample was either preserved at the time of receipt or at the time of sample preparation.
K	Organic	Detection limit may be elevated due to the presence of an un-requested analyte.
L	All	Elevated detection limit due to low sample volume.
N	All	Spiked sample recovery not within control limits.
P	Organic	The relative percent difference between the two columns for detected concentrations was greater than 40%.
Q	All	The analyte has been detected between the limit of detection (LOD) and limit of quantitation (LOQ). The results are qualified due to the uncertainty of analyte concentrations within this range.
S	Organic	The relative percent difference between quantitation and confirmation columns exceeds internal quality control criteria. Because the result is unconfirmed, it has been reported as a non-detect with an elevated detection limit.
U	All	The analyte was not detected at or above the reporting limit.
V	All	Sample received with headspace.
W	All	A second aliquot of sample was analyzed from a container with headspace.
X	All	See Sample Narrative.

&	All	Laboratory Control Spike recovery not within control limits.
*	All	Precision not within control limits.
<	All	The analyte was not detected at or above the reporting limit.
1	Inorganic	Dissolved analyte or filtered analyte greater than total analyte; analyses passed QC based on precision criteria.
2	Inorganic	Dissolved analyte or filtered analyte greater than total analyte; analyses failed QC based on precision criteria.
3	Inorganic	BOD result is estimated due to the BOD blank exceeding the allowable oxygen depletion.
4	Inorganic	BOD duplicate precision not within control limits. Due to the 48 hour holding time for this test, it is not practical to reanalyze and try to correct the deficiency.
5	Inorganic	BOD result is estimated due to insufficient oxygen depletion. Due to the 48 hour holding time for this test, it is not practical to reanalyze and try to correct the deficiency.
6	Inorganic	BOD laboratory control sample not within control limits. Due to the 48 hour holding time for this test, it is not practical to reanalyze and try to correct the deficiency.
7	Inorganic	BOD result is estimated due to complete oxygen depletion. Due to the 48 hour holding time for this test, it is not practical to reanalyze and try to correct the deficiency.

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STANDARD OPERATING PROCEDURE

Determination of Total Organic Carbon Using the DC-80 Instrument

Reference Methods: SM 5310 C and SW846 9060

SOP NUMBER:	GB-I-031-Rev.0
EFFECTIVE DATE:	Date of Final Signature
SUPERSEDES:	First Issue

APPROVAL

Nils Melberg, Assistant Laboratory Manager — Date: 5/26/06

Arthur F. Lautenbach, Quality Manager — Date: 5/25/06

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1. Purpose

1.1 The purpose of this Standard Operating Procedure (SOP) is to describe the procedures used to determine the concentration of Total Organic Carbon (TOC) in water and soil samples compliant with methods SM 5310 C and SW846 9060.

2. Scope and Application

2.1 This SOP pertains to drinking waters, ground waters, surface waters, domestic and industrial wastes, sediment, and soil samples. This SOP includes TOC analysis using the run types: Duplicate, Quadruplicate and a modified version of Quadruplicate (using two injections).

3. Summary of Method

3.1 When running water samples, the sample is injected into a reactor filled with a persulfate solution where it is oxidized by means of ultra-violet light. When running soil samples the sample is placed in a combustion furnace where it heats up and reacts with the catalyst that is contained in the furnace. The product of both reactions is CO_2 gas, which is then blown into the nondispersive infrared detector (NDIR). The NDIR uses electromagnetic radiation or infrared energy to measure the CO_2. This measurement is proportional to the carbon in the sample. In order to analyze for TOC the sample must first have the Inorganic Carbon (IC) taken out by either being purged with acid for a water matrix, or prepped with acid and heat for a soil matrix.

4. Interferences

4.1 Carbonate and bicarbonate carbon represent interferences under the terms of this test and must be removed or accounted for in the final calculation.

4.2 When dealing with a water matrix, this SOP is applicable only to homogenous samples which can be injected into the apparatus reproducibly by means of a micro-liter type syringe or pipette. For soil matrix, this SOP is applicable only to those samples that can be adequately ground with mortar and pestle to result in a fairly homogenous sample.

5. Safety

5.1 Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable. Cautions are included for known extremely hazardous materials.

5.2 A reference file of Material Safety Data Sheets (MSDS) is made available to all personnel involved in the chemical analysis, and is located at the front desk. A formal safety plan has been prepared and is distributed to all personnel with documented training.

5.3 Analysts should take necessary safety precautions when handling chemicals and samples. Proper personal protective equipment may include safety gloves, lab coats, and safety glasses or goggles. Analysts should be familiar with the MSDS sheets for all chemicals and reagents they use for this procedure and the location of the MSDS sheets within the laboratory. Any questions or concerns should be taken to the laboratory Chemical Hygiene/Safety Officer.

6. Definitions

6.1 Total Carbon (TC): The measurement of all the carbon in the sample, both inorganic and organic.

6.2 Total Organic Carbon (TOC): All carbon atoms covalently bonded in organic molecules. To measure TOC, all the inorganic carbon is removed by addition of acid and purging: the result is that only organic carbon is left. Dissolved TOC is filtered through 0.45 um pore filter prior to analysis.

6.3 Total Inorganic Carbon (TIC): The measurement of the total inorganic carbon is found by subtracting the Total Organic Carbon from the Total Carbon. TIC= TC – TOC.

6.4 Additional definitions can be found in Section 10 of the Pace Analytical Services, Inc. Quality Manual.

7. Responsibilities and Distribution

7.1 Analyst - Any analyst using this procedure is responsible for reading, understanding, and following this SOP. Any deviation from this SOP must be reported to the appropriate supervisor. The analyst must make their recommendations for changing the SOP to their supervisor or the QM in writing.

7.2 Assistant General Manager – The Assistant General Manager must ensure that all analysts are properly trained and qualified to use this procedure. The Assistant General Manager is also responsible to ensure that the SOP is followed. The Assistant General Manager is responsible for reviewing the SOP and communicating recommended changes to the QM.

7.3 Quality Manager (QM) – The QM is responsible for monitoring the implementation of the SOPs. The QM shall participate in the revision of the SOP and make sure it is current. The QM shall review and approve all SOPs.

7.4 General Manager – The General Manager has overall responsibility for ensuring that SOPs are prepared and implemented for all activities appropriate to the laboratory. The General Manager shall review and approve all SOPs.

7.5 Distribution– The official version of this SOP is the signed hardcopy version found in the laboratory. A copy of the SOP shall be kept in the department for reference.

7.6 Revision – This SOP shall be reviewed every two years at a minimum. Independent of the minimum review frequency, revisions shall be incorporated as needed if procedures or methods change.

8. Sample Collection, Preservation and Handling

8.1 Water samples are collected in glass 40 mL VOA vials or 4 oz glass jars, which are acidified with H_2SO_4 to a pH of <2. Samples are shipped to the lab on ice and stored at 4°C until time of analysis. Analysis must occur within 28 days of sample collection.

8.2 Soil samples are collected in 4 oz glass jars. Samples are shipped to the lab on ice and stored at 4°C until time of analysis. Analysis must occur within 28 days of sample collection.

9. Equipment and Supplies

9.1 Equipment

9.1.1 DC-80 TOC analyzer with NDIR detector

9.1.2 TOC Boat Analyzer – Rosemount/Dohrmann

9.1.3 Calibrated Mechanical Pipettes –Assorted adjustable air displacement pipettes with disposable tips - Eppendorf or equivalent

9.1.4 Analytical syringe – 500 uL

9.1.5 Analytical syringe – 50 uL

9.1.6 Hot Block

9.1.7 Analytical balance – accurate to 0.0001 gram

9.1.8 Mortar & Pestle

9.1.9 Spatula

9.1.10 Volumetric flasks

9.2 Supplies

9.2.1 Aluminum dishes

9.2.2 40 mL Voa vials

9.2.3 Digestion Tubes

9.2.4 Data printout paper

10. Reagents and Standards

10.1 Reagents

10.1.1 Sulfuric Acid (H_2SO_4) – concentrated

10.1.2 Sulfuric Acid (H_2SO_4) – 10%
To make: Fill 2000mL volumetric flask with 1000mL of DI Water. Measure out 200mL of concentrated Sulfuric Acid and add to volumetric flask. Dilute to volume. Shelf life = 1 year.

10.1.3 Phosphoric Acid (H_3PO_4) – 85%

10.1.4 Phosphoric Acid (H_3PO_4) – 42.5%
To make: Fill 100mL graduate cylinder with 20mL of DI Water. Pour 20mL phosphoric acid into the graduate. Transfer to 40mL Vial and label. Shelf life = 1 year.

10.1.5 Deionized water (DI water)

10.1.6 Purified Compressed Air

10.1.7 Potassium Persulfate – Neat

10.1.8 Persulfate Solution, 2.0% w/v – Dissolve 20 g of potassium persulfate in one liter of deionized water.

10.2 Standards

10.2.1 Potassium hydrogen phthalate (KHP) – 4000 mg/L calibration stock solution
To make: Fill a 100 mL volumetric flask with approximately 50 mL of DI water. Dissolve 850 mg of KHP in the DI water. Dilute to volume. Shelf life = 1 month.

10.2.2 Water 1 Point Calibration Standard – 400 mg/L

Fill a 100 mL volumetric flask with approximately 50 mL of DI water. Pipet 10.0 mL of calibration stock solution into the flask. Dilute to volume. Shelf life = 1 month.

10.2.3 Water Calibration Standard 1 – 0 mg/L

100 mL DI water

10.2.4 Water Calibration Standard 2 – 2 mg/L

Fill a 100 mL volumetric flask with approximately 50 mL of DI water. Pipet 50 uL of calibration stock solution into the flask. Dilute to volume. Shelf life = 1 month.

10.2.5 Water Calibration Standard 3 – 4 mg/L

Fill a 100 mL volumetric flask with approximately 50 mL of DI water. Pipet 100 uL of calibration stock solution into the flask. Dilute to volume. Shelf life = 1 month.

10.2.6 Water Calibration Standard 4 – 10 mg/L

Fill a 100 mL volumetric flask with approximately 50 mL of DI water. Pipet 250 uL of calibration stock solution into the flask. Dilute to volume. Shelf life = 1 month.

10.2.7 Water Calibration Standard 5 – 100 mg/L

Fill a 100 mL volumetric flask with approximately 50 mL of DI water. Pipet 2.50 mL of calibration stock solution into the flask. Dilute to volume. Shelf life = 1 month.

10.2.8 Water Calibration Standard 6 – 150 mg/L

Fill a 100 mL volumetric flask with approximately 50 mL of DI water. Pipet 3.75 mL of calibration stock solution into the flask. Dilute to volume. Shelf life = 1 month.

10.2.9 Water Calibration Standard 7 –200 mg/L

Fill a 100 mL volumetric flask with approximately 50 mL of DI water. Pipet 5.0 mL of calibration stock solution into the flask. Dilute to volume. Shelf life = 1 month.

10.2.10 Soil 1 Point Calibration Standard – 2000 mg/Kg

Fill a 10 mL volumetric flask with approximately 5 mL of DI water. Pipet 5.0 mL of calibration stock solution into the flask. Dilute to volume. Shelf life = 1 month.

10.2.11 Soil Calibration Standard 1 – 0 mg/Kg

10 mL DI water.

10.2.12 Soil Calibration Standard 2 – 500 mg/Kg

Fill a 10 mL volumetric flask with approximately 5 mL of DI water. Pipet 1.25 mL of calibration stock solution into the flask. Dilute to volume. Shelf life = 1 month.

10.2.13 Soil Calibration Standard 3 – 1000 mg/Kg

Fill a 10 mL volumetric flask with approximately 5 mL of DI water. Pipet 2.5 mL of calibration stock solution into the flask. Dilute to volume. Shelf life = 1 month.

10.2.14 Soil Calibration Standard 4 – 2000 mg/Kg

Fill a 10 mL volumetric flask with approximately 5 mL of DI water. Pipet 5.0 mL of calibration stock solution into the flask. Dilute to volume. Shelf life = 1 month.

10.2.15 Potassium hydrogen phthalate (KHP) – 4000 mg/L ICV stock solution

Fill a 100 mL volumetric flask with approximately 50 mL of DI water. Dissolve 850 mg of KHP in the DI water. Dilute to volume. Shelf life = 1 month.

Note: The KHP used to prepare the ICV stock solution must be from another source than the KHP used to prepare the calibration stock solution.

10.2.16 Water Initial Calibration Verification (ICV) –100 mg/L

Fill a 10 mL volumetric flask with approximately 5 mL of DI water. Pipet 250 uL of ICV stock solution into the flask. Dilute to volume. Shelf life = 1 month.

10.2.17 Soil Initial Calibration Verification (ICV) –1000 mg/Kg

Fill a 10 mL volumetric flask with approximately 5 mL of DI water. Pipet 2.5 mL of ICV stock solution into the flask. Dilute to volume. Shelf life = 1 month.

10.2.18 Laboratory Control Spike (LCS) – An independently prepared certified solution of Potassium hydrogen phthalate (KHP) at a concentration equal to the mid-range calibration standard. Shelf life = manufacture's expiration date.

10.2.19 Water Continuing Calibration Verification (CCV) –100 mg/L

Fill a 50 mL volumetric flask with approximately 25 mL of DI water. Pipet 1.25 mL of calibration stock solution into the flask. Dilute to volume. Shelf life = 1 month.

10.2.20 Soil Continuing Calibration Verification (CCV) –1000 mg/Kg

Fill a 10 mL volumetric flask with approximately 5 mL of DI water. Pipet 2.5 mL of calibration stock solution into the flask. Dilute to volume. Shelf life = 1 month.

11. Calibration

11.1 Water calibration

11.1.1 Water 1 Point Calibration: Prior to initial calibration of the instrument, a single point standard is run to verify factory settings.

11.1.1.1 Reset the calibration by holding down the calibration button for 2 seconds until the calibration light turns off.

11.1.1.2 Make sure the baseline is stable, and inject 200 µL of the Water 1 Point Calibration Standard into the injection port using a 500-µL syringe. Immediately press the start button on the detector module.

11.1.1.3 Repeat step 11.1.1.1 two more times. After 3 reps, press the calibration button quickly. The calc light will turn on. The instrument uses the average of the three reps to reset the instrument calibration factor.

Note: Run one replicate of the Water 1 point calibration standard to update the calibration factor when gas flow rates change.

11.1.2 Prepare all of the curve standards as indicated in section 10.2. Make sure the baseline is stable, and inject 200 µL of the Water Calibration Standard mg/L into the injection port using a 500-µL syringe. Immediately press the start button on the detector module.

11.1.3 Once the instrument beeps and prints out the result from the injection, inject 200 µL of the next Water Calibration Standard and press the start button.

11.1.4 Repeat step 11.1.2 and 11.1.3 until all of the standards have been run.

11.1.5 Enter the curve data into an excel spreadsheet to determine the slope, y-intercept, and r squared value. The r squared value must be greater than 0.995, if it isn't recalibrate.

11.1.6 Make sure the baseline is stable, and inject 200 µL of the 100 mg/L Water Initial Calibration Verification (ICV) solution into the injection port using a 500-µL syringe. Immediately press the start button on the detector module.

11.1.7 Once the instrument beeps and prints out the result from the injection, inject 200 µL of DI H_2O (ICB).

11.1.8 The lowest standard in the curve is the EQL.

11.2 Soil Calibration

11.2.1 Soil 1 Point Calibration: Prior to initial calibration of the instrument, a single point standard is run to verify factory settings.

11.2.1.1 Reset the calibration by holding down the calibration button for 2 seconds until the calibration light turns off.

11.2.1.2 Make sure the baseline is stable and inject 40 µL of the Soil 1 Point Calibration Standard through the septa into the boat using a 50 uL syringe. Slide the boat into the oven. Immediately press the start button on the detector module.

11.2.1.3 Repeat step 11.2.1.1 2 more times. After 3 reps, press the calibration button quickly. The calc light will turn on. The instrument uses the average of the three replicates to reset the instrument calibration factor.

11.2.2 Prepare all of the curve standards as indicated in section 10.2. First, make sure the baseline is stable and the boat has cooled down from being in the oven. Next, inject 40 uL of the Soil Calibration Standard through the septa into the boat and slide the boat into the oven. Immediately press the start button on the detector module.

11.2.3 Once the instrument has beeped and the standard result has printed out, you may now pull the boat back out of the furnace and wait for 1 minute to let the boat cool down. Repeat step 11.2.2 using the next Soil Calibration Standard until all of the standards have been run. If at any time when standard is injected into the boat and mist is generated, the boat is too hot. If injected the standard will be inaccurate, so you must burn off the boat, wait for it to cool off and then you can re-inject the same sample. As long as the start button is not pressed the instrument will not record any results.

11.2.4 Enter the curve data into an excel spreadsheet to determine the slope, y-intercept, and r squared value. The r squared value must be greater than 0.995, if it isn't recalibrate.

11.2.5 Make sure the baseline is stable, and inject 40 µL of the 1000 mg/Kg Soil Initial Calibration Verification (ICV) solution into the injection port using a 50-µL syringe. Immediately press the start button on the detector module.

11.2.6 Once the instrument beeps and prints out the result from the injection, inject 40 µL of DI H_2O (ICB).

11.2.7 The lowest standard in the curve is the EQL.

12. Procedure

12.1 There are three different method by which to analyze TOC: SW846 9060, SW846 M9060 and SM 5310 C.

12.1.1 When referencing Method SW846 9060, quadruplicate analysis is required for all samples – water and soil. Each sample will be composed of 4 individual injections. Report all four individual injection readings and the average of the four readings.

12.1.2 If the client desires to have SW846 9060 cited, but does not want quadruplicate analyses performed, the modified procedure for analysis will be followed: two replicates will be performed with the results averaged, the average of two injections is reported with a citation of SW846 M9060.

12.1.3 When referencing Method SM 5310 C, two injections of the sample within 10% RPD is a valid analysis. The first injection reading that is within 10% RPD of the next injection reading is reported. If the first two injection readings are at or below the EQL, precision is NOT calculated and the first injection reading is reported. If no injection reading is within 10% RPD of the next injection reading and the injection readings are above the EQL, the sample must be rerun. This is used for water matrix only.

12.1.4 No injections can be used if they are above the curve. The sample must be diluted and rerun.

12.2 The DC-80 TOC Analyzer must be set up in different ways to accommodate the analysis of waters or soils: Water TOC configuration (12.3) and Soil TOC configuration (12.5). Analysis for these two matrices will be dealt with in 12.4 (water) and 12.6 (soil).

12.3 Water TOC configuration

12.3.1 Routine operation

12.3.1.1 Place the Reagent Tubing in the 2.0% Persulfate Solution, check to for sufficient persulfate solution for the run. If low on solution make some more up and fill the extra Amber bottle. Assign and record traceability of solutions in the standard logbook and on the bottle label.

12.3.1.2 Make sure the Waste Tubing is in the waste container and the container is not full. If the waste container is full, empty it and place the Tubing back in the container.

12.3.1.3 Rinse and fill the DI containers with fresh DI water.

12.3.1.4 Place the tube coming out of the top of the reactor (labeled "Waters") into the "U" Tube Liquid Trap. The tube should be pushed down into the wider area of the Liquid Trap to prevent moisture from entering the permeation dryer tube.

12.3.1.5 Check and record the airflow with an air flow meter. If the flow is lower than 180 mL/min or higher than 210 mL/min adjust regulator on tank until the airflow is within the desired amount.

12.3.1.6 Turn the "Power" on to the Reactor Module and the Detector. Make sure that the Volume knob on the Detector is set to 200uL (liquids) and the Mode knob is set to TOC.

12.3.1.7 Wait until the baseline is stable before analyzing samples. Sample baseline should be between 0.03 and 0.045. If it is closer to 0.045 adjust the Baseline Zero knob to lower the baseline. If this cannot be done ask primary analyst.

WARNING: DO NOT TOUCH SPAN KNOB

12.3.1.8 The unit is now ready to calibrate or run for aqueous TOC samples.

12.4 Water sample analysis

12.4.1 Prepare water samples as follows:

12.4.1.1 Shake sample vigorously to suspend sediment.

12.4.1.2 Pour 20 mLs into a clean 40 mL vial.

12.4.1.3 Add 4-6 drops of 42.5% Phosphoric Acid to all samples including Method Blank and MS/MSD. Purge with compressed air for at least 10 minutes.

12.4.1.4 Prepare Method Blank (MB) by pouring 20 mLs DI water into clean 40 mL VOA vials and add 4-6 drops of 42.5% Phosphoric Acid. Purge with compressed air for at least 10 minutes.

12.4.1.5 Prepare the Laboratory Control Spike (LCS) according to the manufacturer's directions.

12.4.1.6 Prepare Matrix Spike / Matrix Spike Duplicate (MS/MSD) by randomly selecting one sample as the parent. Add 0.5 mL of 4000-mg/L stock solution into 19.5 mL of sample. Known spike value is 100 mg/L.

12.4.2 Sample analysis

12.4.2.1 Make sure the baseline is stable, and inject 200 µL of the 100 mg/L Water Continuing Calibration (CCV) standard into the injection port using a 500-µL syringe. Immediately press the start button on the detector module.

12.4.2.2 Once the instrument beeps and prints out the result from the injection, inject 200 µL of DI H_2O (CCB) and immediately press the start button on the detector module.

12.4.2.3 For each field and QC samples in an analytical batch, inject 200 µL and immediately press the start button on the detector module. Wait for the instrument to beep before injecting the next sample. Run a CCV/CCB every 10 samples and at the end of the run.

12.4.3 Shutdown

12.4.3.1 Turn the compressed air off.

12.4.3.2 Empty and rinse out vials. Check and dump waste collection carboy if necessary.

12.4.3.3 Turn off both Detector and Reactor modules. Take the tube out of the persulfate solution, cap the persulfate solution and place the tube so it is pointing up and the persulfate solution can't drip out of it.

12.4.3.4 Remove data tape and process run data.

12.5 Soil TOC configuration

12.5.1 Routine operation – Beginning with unit in Shutdown mode

12.5.1.1 Open the door and take the tube labeled "Waters" out of the U-tube and replace it with the tube labeled "Soils". This will now connect the boat analyzer to the detector.

12.5.1.2 Look at the tubes connecting the detector with the reactor. There is a glass tube that is half full of copper granules, and half full of Tin granules separated by quartz wool. If the copper looks oxidized (dark/black), replace with new copper granules. If regular analysis is done, copper will last about one month. The tin is replaced every 6 to 12 months.

12.5.1.3 Turn the power on the boat analyzer (black switch). Indicator light shows when the boat sampler furnace is warmed up. Make sure that the current boat in the analyzer is in the oven when it is turned on.

12.5.1.4 Turn on the Air tank. Verify and record that the flow is between 180 and 210 mL/min. If it is not, adjust the regulator on the tank.

12.5.1.5 Check to see that the baseline is stable. If so, the instrument is ready to begin analysis.

12.5.1.6 Using a clean forceps take out the current boat, put a different boat in the boat analyzer and slide the boat into the oven until the baseline comes down and becomes stable. This will insure the boats are both residual and CO2 free. This process is called "baking the boats". When taking the boats out of the boat analyzer they are going to be very hot. Make sure not to burn yourself or put the hot boat on something that will melt. (i.e. rubber, plastic, etc.).

12.5.1.7 Rinse and fill the DI containers.

12.5.1.8 Wait until the baseline is stable before analyzing. Sample baseline should be between 0.03 and 0.045. If it is closer to 0.045 adjust the baseline zero knob to lower the baseline. If this cannot be done ask primary analyst.

WARNING: DO NOT TOUCH SPAN KNOB

12.5.1.9 The unit is now ready to calibrate or run for soil TOC samples.

12.6 Soil sample analysis

12.6.1 Prepare soil samples as follows:

12.6.1.1 Weigh 10 g of soil into a clean beaker, add approximately 25 mL 10% Sulfuric Acid and place in a digestion block at 70°C. After sample ceases to react with acid, the sample is filtered through a glass fiber and rinsed of all traces of acid using deionized water. Filter. The sample is then dried in an oven at 103°C a minimum of 18 hours.

12.6.1.1 Once the sample is dried, crush with a mortar & pestle.

12.6.2 Sample analysis.

12.6.2.1 Make sure the baseline is stable, and inject 40 µL of the 1000 mg/Kg Soil Continuing Calibration Verification (CCV) standard through the septa into the boat using a 50-µL syringe. Immediately press the start button on the detector module and slide the boat into the oven.

12.6.2.2 Once the instrument beeps and prints out the result from the injection, slide the boat out of the oven and wait at least one minute for the boat to cool down. Then inject 40 µL of DI H_2O (CCB) into the boat and slide it into the oven pressing the start button on the detector immediately afterward.

12.6.2.3 When running a Method Blank (MB), 40 uL of DI water is injected into the boat. A Laboratory Control Spike (LCS) is run by injecting 40 uL of the prepared LCS standard. Matrix Spike / Matrix Spike Duplicate (MS/MSD) are run by injecting 20 uL of the 4000 mg/L calibration stock standard along with a variable weight of the parent sample for each the MS and MSD.

12.6.2.4 For each field sample in an analytical batch, weigh 0.04g or less into the boat. Immediately press the start button on the detector module and slide the boat into the oven. Once the instrument beeps and prints out the result from the injection, slide the boat out of the oven and wait at least one minute for the boat to cool down. Run a CCV/CCB every 10 samples and at the end of the run.

12.6.2.5 While running samples, no injections can be used if they are above the curve. If an injection is above the curve, weigh out a smaller amount of the sample and rerun that injection.

12.6.2.6 For Quadruplicate analysis: If the first injection of a sample is below the EQL, more sample must be weighed out unless the weight exceeds 0.04g. Once the weight of 0.04g has been surpassed, the results will be reported even if they are below the EQL. If the first injection is above the EQL and one or two of the other injections is below the EQL it can be used only if it is within 0.0002g of the first injection. However, if three of the injections are under the EQL, four more injections must be run at a higher weight that satisfies these conditions. For Modified quadruplicate analysis: Make injections until you get two injections that are either greater than 0.04 g in weight or greater than the EQL.

12.6.3 Shutdown

12.6.3.1 Slide boat into oven and switch off the boat analyzer (black switch).

12.6.3.2 Then turn off the compressed air.

12.6.3.3 Remove data tape and process run data.

12.7 Calculations:

12.7.1 The instrument provides raw data results in mg/L for waters and mg/kg for soils. All data produced by the DC-80 must be processed through the appropriate curve.

12.7.2 SW846 9060 Sample Calculations:

Injection 1:
Soil:

$$\text{Raw Data Value (mg/L)} \times \frac{0.04\ (\text{ml})}{\text{Injection weight (g)}} \times \frac{1000\ (\text{g})}{1\ (\text{Kg})} \times \frac{1\ (\text{L})}{1000\ (\text{ml})} = \text{TOC (mg/Kg) (TOC1)}$$

Water:

$$\text{Raw Data Value (mg/L)} \times \frac{0.2\ (\text{ml})}{\text{Injection volume (ml)}} \times \text{Dilution} = \text{TOC (mg/L) (TOC1)}$$

Injection 2:
Soil:

$$\text{Raw Data Value (mg/L)} \times \frac{0.04\ (\text{ml})}{\text{Injection weight (g)}} \times \frac{1000\ (\text{g})}{1\ (\text{Kg})} \times \frac{1\ (\text{L})}{1000\ (\text{ml})} = \text{TOC (mg/Kg) (TOC2)}$$

Water:

$$\text{Raw Data Value (mg/L)} \times \frac{0.2\ (\text{ml})}{\text{Injection volume (ml)}} \times \text{Dilution} = \text{TOC (mg/L) (TOC2)}$$

Injection 3 (Quad only):
Soil:

$$\text{Raw Data Value (mg/L)} \times \frac{0.04\ (ml)}{\text{Injection weight (g)}} \times \frac{1000\ (g)}{1\ (Kg)} \times \frac{1\ (L)}{1000\ (ml)} = \text{TOC (mg/Kg) (TOC3)}$$

Water:

$$\text{Raw Data Value (mg/L)} \times \frac{0.2\ (ml)}{\text{Injection volume (ml)}} \times \text{Dilution} = \text{TOC (mg/L) (TOC3)}$$

Injection 4 (Quad only):
Soil:

$$\text{Raw Data Value (mg/L)} \times \frac{0.04\ (ml)}{\text{Injection weight (g)}} \times \frac{1000\ (g)}{1\ (Kg)} \times \frac{1\ (L)}{1000\ (ml)} = \text{TOC (mg/Kg) (TOC4)}$$

Water:

$$\text{Raw Data Value (mg/L)} \times \frac{0.2\ (ml)}{\text{Injection volume (ml)}} \times \text{Dilution} = \text{TOC (mg/L) (TOC4)}$$

12.7.3 Dry weight correction:

$$\frac{\text{Final result (mg/Kg)}}{\text{Dry solids \{in decimal i.e. 0.85\}}} = \text{TOC mg/Kg dry weight}$$

Please note that soils are dried to 100% dry weight before analysis - therefore no dry weight correction is needed. The above formula would be used ONLY if the samples were not dried before analysis.

12.7.4 Average sample result (quadruplicate)

$$\text{Quad Average result} = \frac{(TOC1) + (TOC2) + (TOC3) + (TOC4)}{4\{\text{number of injections}\}}$$

12.7.5 Average sample result (modified)

$$\text{Average result} = \frac{(TOC1) + (TOC2)}{2\{\text{number of injections}\}}$$

12.7.6 For samples run in Quadruplicate (SW846 9060): each injection is calculated using the appropriate injection equation according to 12.7.2. The average final result is acquired using 12.7.4. The final average result (from 12.7.4) is reported as well as each individual injection's final result.

12.7.7 For Modified Quadruplicate (two injections – SW846 M9060): Each injection is calculated using 12.7.2. The average of the final results is acquired using 12.7.5. Report the average result only.

12.7.8 The accuracy is calculated based on the average and not the individual injections.

12.7.8 MS/MSD calculation

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

SSR = Spike sample result
SR = Sample result
SA = Spike added

12.7.9 Precision (for QC samples):

The precision is calculated based on the % recovery of the matrix spike / matrix spike duplicate (MS/MSD) result.

Relative percent difference (RPD) calculation:

$$\% \text{ RPD} = \frac{|MS-MSD|}{(MS+MSD)/2} \times 100$$

For SW846 9060 or SW846 M9060: precision is only calculated on the final average – not each injection.

12.7.10 Water precision calculation (for SM 5310-C):

Relative percent difference (RPD) must be less than 10%

$$\% \text{ RPD} = \frac{|\text{Rep. 1} - \text{Rep. 2}|}{(\text{Rep. 1} + \text{Rep. 2})/2} \times 100$$

Rep. 1 = raw amount of first replicate
Rep. 2 = raw amount of second replicate

The first injection reading that is within 10% RPD of the next injection reading is reported. If the first two injection readings are at or below the EQL, precision is NOT calculated and the first injection reading is reported. If no injection reading is within 10% RPD of the next injection reading and the injection readings are above the EQL, the sample must be rerun.

13 Quality Control

13.1 An Initial Calibration Verification (ICV) must be run immediately following the instrument calibration. The ICV must be prepared from stock standard obtained from a different source than the stock standard used to prepare the initial calibration and must be prepared at a level at or near the mid range of the calibration curve. The result of the ICV must fall within the range of 90%-110% - if not rerun or recalibrate.

13.2 Initial Calibration Blank (ICB) – An ICB is analyzed after the ICV and must meet the acceptance criteria before samples are analyzed. The absolute value of the ICB result must be less than the laboratory EQL – if not rerun or recalibrate.

13.3 Continuing Calibration Verification (CCV) - Each analytical run must begin and end with a CCV and a CCV must be run every 10 samples. The CCV must be prepared from the same solution as the mid-point calibration standard and the result must fall within the range of 90%-110%. If outside the range, rerun 1X. If still outside the range, the problem must be corrected before continuing and the affected samples reanalyzed.

13.4 The Continuing Calibration Blank (CCB) – A CCB is analyzed after the CCV and must meet the acceptance criteria before samples are analyzed. The absolute value of the CCB result must be less than the laboratory EQL. If outside the range, rerun 1 time. If still outside the range, correct the problem and rerun all samples back to the last passing CCB.

13.5 Method Blank - A Method Blank (MB) must be prepared and analyzed with every sample batch or every 15 samples whichever is more frequent. The data obtained is used to assess contamination from the laboratory environment. Values that exceed the EQL indicate laboratory or reagent contamination should be suspected and corrective actions must be taken before continuing the analysis. Values that are between the MDL and EQL are evaluated based on the concentration in the samples compared to the concentration in the blank.

13.6 Laboratory Control Sample (LCS) - A LCS prepared from an independent source must be performed with every batch or every 15 environmental samples, which ever is more frequent. The LCS must be evaluated for accuracy and must meet the laboratory generated control limits before samples are analyzed. If no in-house limits are in use, then a range of 80 - 120% will be used. If the LCS recovery does not meet the acceptance criteria corrective action must be taken and the LCS recovery must be acceptable before proceeding with sample analysis. A LCSD is performed when requested by the client or when there is insufficient sample volume to perform a matrix spike / matrix spike duplicate. The LCS/LCSD must be evaluated for precision and must meet the laboratory generated control criteria.

13.7 Matrix spike/Matrix spike duplicate - A MS/MSD pair must be prepared and analyzed every 10 samples. The MS must be a duplicate of the aliquot used for sample analysis. Calculate the percent recovery, corrected for concentration measured in the parent sample, and compare to the in-house generated limits. If no in-house limits are in used then a range of 80 - 120% will be used. Calculate the precision between the MS and MSD and compare to the in-house generated limits. If no in-house limits are in use, then an upper limit of 20% will be used.

14 Method Performance

14.1 There are several requirements that must be met to insure that this procedure generates accurate and reliable data. A general outline of requirements has been summarized below. Further specifications may be found in the Laboratory Quality Manual.

14.1.1 The analyst must read and understand this procedure with written documentation maintained in his/her training file.

14.1.2 An initial demonstration of capability (IDC) must be performed per ALL-Q-020, *Training Procedures*. A record of the IDC will be maintained in his/her QA file with written authorization from the Laboratory Manager and Quality Manager.

14.1.3 An annual method detection limit (MDL) study will be completed per ALL-Q-004, *Method Detection Limit Studies*, for this method and whenever there is a major change in personnel or equipment. The results of these studies are retained in the quality assurance office.

14.1.4 Periodic performance evaluation (PE) samples are analyzed per ALL-Q-010, *PE/PT Program*, to demonstrate continuing competence. All results are stored in the QA office.

14.2 Linear Calibration Range - The linear calibration range must be determined initially and verified whenever a significant change in instrument response is observed or expected. The initial demonstration of linearity must use sufficient standards to insure that the resulting curve is linear. If any verification data exceeds the initial values by $\pm$ 10%, linearity must be reestablished. If any portion of the range is shown to be nonlinear, sufficient standards must be used to clearly define the nonlinear portion.

15 Pollution Prevention and Waste Management

15.1 All sample residues from this analysis process must be handled as hazardous waste and disposed of in the proper hazardous waste barrel bound for incineration. For further information on waste management consult the current version of WI-S-001, *Regulated Soil Handling*.

15.2 Excess samples and method process wastes are characterized and disposed of in an acceptable manner. For further information on waste management consult the current version of ALL-S-002, *Waste Handling*.

16 References

16.1 40CFR Part 136 National Institute of Standards and Technology (NIST).

16.2 Standard Methods for the Examination of Water and Wastes , 20th edition – Method 5310 C.

16.3 USEPA Test Methods for Evaluating Solid Wastes, SW 846, 3rd Edition, Methods 9060.

16.4 PASI Quality Manual, current revision

16.5 DC-80 TOC Combustion Analyzer User Manual.

17 Tables, Diagrams, Flowcharts, Appendices, Addenda etc.

17.1 None

18 Revisions

Revision Number	Reason for Change	Date
GB-I-031.Rev.0	First Issue.	24May2006

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STANDARD OPERATING PROCEDURE

Alkalinity
Standard Methods for the Examination of Water and Wastewater, 2320B

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APPROVALS

Nils Melberg — **Date** 7/26/05
Laboratory Manager

Arthur Lautenbach — **Date** 7/26/05
Quality Manager

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1. PURPOSE

1.1 This procedure is used to measure alkalinity in aqueous samples. The procedure references Standard Method for the Examination of Water and Wastewater, 18th Edition, 1992, Method 2320B.

2. SCOPE AND APPLICATION

2.1 This SOP is applicable to drinking water, surface water, sewage, and industrial wastes.

2.2 Drinking waters must be analyzed by this method.

3. SUMMARY OF METHOD

3.1 Alkalinity of water is its acid-neutralization capacity. Alkalinity is a measure of an aggregate property of water and can be interpreted in terms of specific substances when titrated to different end points. These pH end points indicate a function of carbonate, bicarbonate, and hydroxide content in the water. A sample is titrated first to a pH of 8.3, then to a final pH of 4.5. Total Alkalinity, Hydroxide Alkalinity, Carbonate Alkalinity, and Bicarbonate Alkalinity can be determined by titration. Two concentrations of titrants can be used to determine high or low alkalinity. For Drinking Water Alkalinity determination, only Total Alkalinity is determined.

4. INTERFERENCES

4.1 Dissolved gases contributing to acidity or alkalinity, such as CO_2, hydrogen sulfide, or ammonia, may be lost or gained during storage to titration. Minimize such effects by titrating promptly after opening sample container, avoiding vigorous shaking. Do not remove interferences from sample because they contribute to the alkalinity.

4.2 Soaps, oily matter, suspended solids, or precipitates may coat the glass electrode and cause a sluggish response. Allow a pause between Titrant additions nearer to the endpoint.

4.3 Substances such as salts of weak organic and inorganic acids in large amount may cause interference.

5. SAFETY

5.1 The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable. Cautions are included for known extremely hazardous materials.

5.2 Common sense safety practices must be adhered to at all times. It is necessary for proper personal protective equipment to be used around all chemicals and equipment, especially safety glasses, lab coats and gloves.

5.3 Each laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of Material Safety Data Sheets (MSDS) should be made available to all personnel involved in the chemical analysis. The preparation of a formal safety plan is also advised.

5.4 MSDS sheets are located in the laboratory sections and should be consulted prior to handling samples and standards.

6. DEFINITIONS

6.1 See SOP MN-Q-241, Analytical Definitions

7. RESPONSIBILITIES AND DISTRIBUTION

7.1 Personnel

7.1.1 All personnel involved with sample preparation and analysis are responsible for adherence to this SOP. A controlled copy will be available for review and consultation within the area methods manual.

7.1.2 Personnel are responsible for ensuring that any deviations to this SOP are reported to the laboratory manager.

7.2 Laboratory Manager

7.2.1 The laboratory manager is responsible for ensuring adherence to this SOP and will receive a controlled copy of this SOP.

7.2.2 The laboratory manager is responsible for performing a biennial review of the SOP and reporting any required revisions to the Quality Assurance Office.

7.3 Quality Manager

7.3.1 The Quality Manager is responsible for conducting laboratory audits to monitor adherence to this and other SOPs. Results of the audit will be reported to management.

7.3.2 The Quality Manager is responsible for ensuring that all revisions to the SOP are implemented.

7.3.3 The Quality Manager is responsible for maintaining the original and complete distribution records.

7.4 Revisions

7.4.1 This SOP will be reviewed on a biennial basis at a minimum and any required revisions would be incorporated. Any revisions made to an SOP prior to biennial review date

will either be incorporated into a new revision with a new review date or included on a revision summary sheet to be included into the SOP on the original review date.

8. SAMPLE COLLECTION/PRESERVATION AND HANDLING

8.1 Samples are collected in polyethylene or borosilicate glass. The bottle is to be filled completely and capped tightly because samples may subject to microbial action and to loss or gain of CO_2 or other gases when exposed to air.

8.2 Ship samples to the laboratory on ice.

8.3 Samples are stored at 4°C $\pm$ 2°C.

8.4 Holding time is 14 days from date of collection.

9. EQUIPMENT AND SUPPLIES

9.1 Burette, class A- 50ml capacity, 0.1 ml increment.

9.2 pH meter (Corning 320 or equivalent).

9.3 Magnetic stirrer w/ PTFE-coated magnetic stir bars.

9.4 Specimen cups

9.5 Pipettes, glass

9.6 Volumetric flasks, 100 ml, 1L class A

9.7 Analytical Balance

9.8 Oven, 250° C

10. REAGENTS AND STANDARDS

Purchased reagents or standards are recorded in the alkalinity logbook. All prepared standards or reagents are recorded in the alkalinity logbook. Each container must be labeled with a PASI ID#, date prepared or received, initials, and expiration date. Reagents and standards are given an expiration date of one year unless otherwise noted by vendor or procedure.

10.1 Carbon dioxide - free water: Prepare all stock and standard solutions and dilution water for the standardization procedure with distilled or deionized water that has been freshly boiled for 15 minutes and cooled to room temperature. The final pH of the water should be $\geq$ 6.0 and its conductivity should be < 2 umhos/cm.

10.2 1000 mg/L Alkalinity Standard –Sodium Carbonate (Na_2CO_3) 1000 mg/L. In a 1 L volumetric flask, dissolve 1.06 grams Na_2CO_3 (dried a 250°C for 4 hours) in about 900 ml DI water.

Dilute to the mark and invert 3 times. Shelf life is 1 year. Do not keep standard longer than 1 year.

10.3 10000 mg/L Alkalinity Standard – Sodium Carbonate (Na_2CO_3) 10000 mg/L. In a 1 L volumetric flask, dissolve 10.6 grams Na_2CO_3 (dried at250°C for 4 hours) in about 900 ml DI water. Dilute to the mark and invert 3 times. Shelf life is 1 year. Do not keep standard longer than 1 year.

10.4 Working standards

10.4.1 20 mg/L (low level check) – Pipette 1 ml of 1,000 mg/L Alkalinity Standard into a 50 ml volumetric flask. Dilute to volume. Shelf life is 1 week.

10.4.2 500 mg/L (mid level check) – Pipette 25 ml of 1,000 mg/L Alkalinity Standard into a 50 ml volumetric flask. Dilute to volume. Shelf life is 1 week.

10.4.3 2500 mg/L (high level check) – Pipette 25 mls of 10,000 mg/L Alkalinity Standard into a 100 ml volumetric flask. Dilute to volume. Shelf life is 1 week.

10.5 High Level Sulfuric Acid Titrant, 0.1N – purchased commercially or prepare from concentrated H_2SO_4. Shelf life is 1 year.

10.5.1 To prepare 0.1 N High Level Sulfuric Acid Titrant from concentrated H_2SO_4 – Pipet 3 mls concentrated H_2SO_4 into ~500 mls Nanopure water in a 1000 mls volumetric flask. Dilute to volume and mix well. Shelf life – 1 year. Standardize against 0.05N Sodium Carbonate solution. See section 10.7.

10.6 Low Level Sulfuric Acid Titrant, 0.02N – Pipet 100 mls of 0.1 N H_2SO_4 into 500 ml volumetric flask. Dilute to volume. Standardize against 0.05N Sodium Carbonate solution. See section 10.7.

10.7 Standardization of Titrant

10.7.1 Prepare 0.05 N Na_2CO_3 (Standardizing Solution) – Dissolve 1.25 g Na_2CO_3 (dried at 250°C for 4 hours) into 500 mls of DI water. Shelf life is 1 week.

10.7.2 Low Level Sulfuric Acid Titrant – 0.02N H_2SO_4

10.7.2.1 Fill burette with Titrant Low Level Sulfuric Acid Titrant, 0.02N.

10.7.2.2 Pipet 15 mls of 0.05 N Na_2CO_3 (Standardizing Solution) into 100 ml volumetric flask. Dilute to volume.

10.7.2.3 Titrate to an approximate pH of 5.0. Cover with watch glass and gently boil solution 3-5 minutes.

10.7.2.4 Allow solution to cool. Continue titration to pH of 4.5.

10.7.2.5 Calculate Normality of sulfuric acid - see step 10.8.

10.7.2.6 Record amount of Titrant used and the calculated normality in Alkalinity Logbook.

10.7.3 High Level Sulfuric Acid Titrant – 0.1N H_2SO_4

10.7.3.1 Fill burette with 0.1 N H_2SO_4.

10.7.3.2 Pipet 40 mls of 0.05N Na_2CO_3 (Standardizing Solution) into 100 ml volumetric flask. Dilute to volume.

10.7.3.3 Titrate to an approximate pH of 5.0. Cover with watch glass and gently boil solution 3-5 minutes.

10.7.3.4 Allow solution to cool. Continue titration to pH of 4.5.

10.7.3.5 Calculate Normality of sulfuric acid – see step 10.8.

10.7.3.6 Record amount of Titrant used and the calculated normality in Alkalinity Logbook.

10.8 Calculate Normality of sulfuric acid as follows:

$$N = \frac{A \times B}{53 \times C}$$

A = g Na_2CO_3 (for calculation purposes use 2.5*) B = mls Na_2CO_3
C = mls acid used to Titrant pH 4.5
* 2.5 grams is used because the calculation assumes that 1L of Standardization solution was made. This SOP cuts the volume in half but the concentration stays the same.

11. CALIBRATION

11.1 Calibrate pH meter as follows. pH meter must be calibrated on a daily basis.

11.1.1 Place pH probe into 4.0 buffer, Press "Cal." Meter automatically endpoints when calibrating. At the measurement endpoint, the appropriate buffer indicator appears on the display.

11.1.2 Rinse and dry probe with Kimwipes.

1.1.1.3 Repeat steps 11.1.1 – 11.1.2 for pH buffer 10.0. When display freezes, the electrode slope will be displayed. Record slope in pH calibration logbook.

11.2 After calibration, record the reading of ICV that consists pH buffer 7.0. The reading must within 0.10 units of the true value.

11.3 Record calibration information in the pH calibration logbook for that meter.

12. PROCEDURE

12.1 Set up run on Alkalinity Bench sheet (See Attachment I and II).

12.2 Use a graduated cylinder to measure 100 ml sample for drinking waters or 50 ml of sample for non-drinking waters into specimen cup.

12.3 Add a stir bar and place on stir plate.

12.4 Measure pH of the sample and record on the bench sheet.

12.5 Fill burette with Low Level Sulfuric Acid Titrant, 0.02 N H_2SO_4. Record initial volume of burette. Begin titration, being careful to stir thoroughly but gently to allow meter to obtain equilibrium, titrate to pH of 8.3. If performing drinking water alkalinity, do not stop at pH 8.3 and continue to step 12.7.

12.6 Record the volume of Titrant used. Do NOT refill the burette.

12.7 Continue titration to a final pH 4.5. Record the volume of Titrant used. Calculate the results using the equation in 12.11.1.

12.8 For samples exceeding an Alkalinity concentration of 1000 mg/L, take a fresh aliquot of sample and titrate with High Level Sulfuric Acid Titrant, 0.1 N H_2SO_4 instead of Low Level Sulfuric Acid Titrant, 0.02 N H_2SO_4 starting at section 12.5.

12.9 For samples equal to or less than an Alkalinity concentration of 20 mg/L, take a fresh 100 mL aliquot of sample and proceed to 12.9.1.

12.9.1 Fill burette with Low Level Sulfuric Acid Titrant, 0.02 N H_2SO_4.

12.9.2 Titrate to pH range 4.3 to 4.7. Record volume of Titrant and exact pH.

12.9.3 Carefully add additional Titrant to reduce the pH exactly 0.3 pH units. Record volume of Titrant and exact pH.

12.9.4 Calculate using equation in 12.11.2.

12.10 Every 10 samples the pH buffer 7.0 must be read. Record pH on alkalinity bench sheet.

12.11 Data Calculations

12.11.1 Potentiometric titration to pH 4.5:

$$\text{Total Alkalinity, as mg } CaCO_3/L = \frac{A \times N \times 50{,}000}{\text{mL sample}}$$

where: **A** = volume of Titrant used
N = normality of H_2SO_4

Report as "The alkalinity to pH ___ = ___ mg $CaCO_3$/L."

To report as milliequivalents per liter, divide the above result by 50.
This calculation is used to determined Total Alkalinity using the Low Level Sulfuric Acid Titrant, 0.02 N H_2SO_4 and the High Level Sulfuric Acid Titrant, 0.1 N H_2SO_4.

12.11.2 Potentiometric titration of low alkalinity:

$$\text{Total Alkalinity, mg } CaCO_3/L = \frac{(2B-C) \times N \times 50{,}000}{\text{mL sample}}$$

where: **B** = mL Titrant to first recorded pH
C = total mL Titrant to reach pH 0.3 unit lower
N = normality of H_2SO_4

Use this calculation for result titrated using step 12.9

12.11.3 "Phenolphthalein Alkalinity" (P) is the term traditionally used for the quantity measured by the titration to pH 8.3. Calculation of Alkalinity relationships. The results obtained from the phenolphthalein (pH 8.3) and total (pH 4.5) alkalinity determinations offer a means for stochiometric classification of the three principle forms of alkalinity present in many waters. The classification ascribes the entire alkalinity to bicarbonate, carbonate, and hydroxide according to this scheme:

12.11.3.1 Carbonate (CO_3^{2-}) alkalinity (C) is present when phenol alkalinity is not zero but is less than total alkalinity.

12.11.3.2 Hydroxide (OH^-) alkalinity (H) is present if phenol alkalinity is more than half of the total alkalinity.

12.11.3.3 Bicarbonate (HCO_3^-) alkalinity (B) is present if the phenol alkalinity is less than half of the total alkalinity.

12.11.3.4 These relationships may be calculated using the following chart:

Result of Titration	Hydroxide (H)	Carbonate (C)	Bicarbonate (B)
P = 0	0	0	T
P < 1/2T	0	2P	T-2P
P = 1/2T	0	2P	0
P > 1/2T	2P-T	2(T-P)	0
P = T	T	0	0

13. QUALITY CONTROL

13.1 Method Blank (MB) - An aliquot of laboratory reagent water. The MB is analyzed exactly like a sample. The MB is used to determine whether the methodology is in control.

13.1.1 A MB must be analyzed with each batch of samples or every 20 samples, whichever more frequent.

13.1.2 Acceptance Criteria: The MB must be less than the reporting limit (RL).

13.1.3 If the MB is not within control limits, perform the following:

13.1.3.1 Check for errors in calculations. If an error or problem is found and can be corrected by amending the calculations and the result falls within the limits, accept the data and report without a qualifier flag.

13.1.3.2 If sufficient sample is available, re-prepare the MB and all associated samples if an error in procedure is discovered which cannot be corrected. If the MB is within the RL in this analysis, accept the second set of data. If the MB is still outside the RL after re-analysis, contact the PM to determine the resolution. If the client does not require additional work, report the data, applying an appropriate flag to the samples associated with the non-compliant MB.

13.1.3.3 If sufficient sample volume is not available, report the sample data with a qualifier flag on each of the samples associated with the non-compliant MB. Contact the project manager regarding the occurrence.

13.2 Laboratory Control Sample (LCS) for Ongoing Precision and Recovery (OPR) – A standard purchased from Analytical Products Group is used for the LCS. The LCS is analyzed exactly like a sample. The LCS is used to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurement.

13.2.1 An LCS must be analyzed with each batch of samples or every 20 samples, whichever more frequent.

13.2.2 Percent Recovery is calculated as follows:

$$\% \text{ Recovery: } \frac{\text{LCS calculated value}}{\text{LCS true value}} \times 100$$

13.2.3 Acceptance Criteria: The true value is obtained from the vendor. The LCS recovery must be within the control limits of 80 - 120%.

13.2.4 If the recovery is not within control limits, perform the following:

13.2.4.1 Check for errors in calculations, standards preparation and spiking of the LCS solution. If an error or problem is found and can be corrected by amending the calculations and the result falls within the limits, accept the data and report without a qualifier flag.

13.2.4.2 If sufficient sample is available, re-prepare the LCS and all associated samples if an error in procedure is discovered which cannot be corrected. If the recovery is

within the limits in this analysis, accept the second set of data. If the recovery is still outside the limits after re-analysis, contact the PM to determine the resolution. If the client does not require additional work, report the data, applying an "&" data qualifier flag to the samples associated with the non-compliant LCS.

13.2.4.3 If sufficient sample volume is not available, report the sample data with an "&" data qualifier flag on each of the samples associated with the non-compliant LCS. Contact the project manager regarding the occurrence.

13.3 Matrix Spike / Matrix Spike Duplicate (MS/MSD) – Aliquots of an environmental sample to which known quantities of the analyte(s) of interest are added in the laboratory. Their purpose is to quantify the bias and precision caused by the sample matrix. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the MS/MSD corrected for background concentrations.

13.3.1 A matrix spike / matrix spike duplicate will be performed on a 5% basis if sample volume permits.

13.3.2 The percent recovery is calculated as follows:

$$\% \text{ Recovery: } \frac{(SSR - SR)}{SA} \times 100$$

SSR - Spiked sample result
SR - Sample result
SA - Spike amount

13.3.3 Acceptance limits: The % recovery must be between 80 – 120% of the true value.

13.3.4 If the % Recovery is exceeded, then:

13.3.4.1 Check for errors in calculations and sample preparation. If an error or problem is found and can be corrected by amending the calculations and the result falls within the limits, accept the data and report without a qualifier flag.

13.3.4.2 If no errors are found in calculation or sample preparation, report the parent sample with the "N" data qualifier.

13.3.5 The precision of the MS/MSD must calculated. See section 13.4.4 for calculation of Relative Percent Difference.

13.4 Duplicate sample (D) –A duplicate aliquot of a sample to be analyzed along with the original sample. Duplicate analyses indicates the precision associated with the sample collection, preservation and storage, as well as, laboratory procedures.

13.4.1 Duplicate sample analysis will be performed at a frequency of 5% if requested by the client.

13.4.2 The relative percent difference (RPD) is calculated as:

$$\mathbf{RPD} = \frac{|S - D| \ * 100}{(S + D)/2}$$

where **S** = sample value, mg/L
D = duplicate value, mg/L

If MS/MSD is used to calculate RPD use SSR and SR in place of S and D. See section 13.3.2.

13.4.3 Acceptance limits: The RPD must be within 0-20% between the original sample and the duplicate.

13.4.4 If the RPD is exceeded, then:

13.4.4.1 Check for errors in calculations and sample preparation. If an error or problem is found and can be corrected by amending the calculations and the result falls within the limits, accept the data and report without a qualifier flag.

13.4.4.2 If no errors are found in calculations or sample preparation report the parent sample with the "*" data qualifier.

13.4.5 A matrix spike duplicate can be performed in place of the sample duplicate to calculate the relative percent difference.

13.5 Check Standard

13.5.1 At least two standards are titrated at the beginning of each analysis day. A 20 mg/L and 500 mg/L are used when titrating with the Low Level Sulfuric Acid Titrant, 0.02N H_2SO_4. If it is determined that the High Level Sulfuric Acid Titrant 0.1 N H_2SO_4 should be used, a 2500 mg/L standard is also titrated.

13.5.2 Acceptance criteria: The % recovery of the check standards must be between 90 –110%.

13.5.3 If acceptance criteria are not met, do not proceed with analysis. Analyze a second set of check standards. If the second set of check standards do not meet acceptance criteria, the standards will be remade and analyzed before analysis of samples.

13.6 Documentation

13.6.1 Draw a single-line strike through for any unacceptable or changed data, then DATE and INITIAL and provide a written explanation of the reason for the change.

13.6.2 Any discrepancies and issues occurring with each batch should be included in a non-conformance, which is submitted to the QA manager for review, and incorporated into a narrative.

14. METHOD PERFORMANCE

14.1 There are several requirements that must be met to insure that this procedure generates accurate and reliable data. A general outline of requirements has been summarized below. Further specifications may be found in the Laboratory Quality Manual.

14.1.1 The analyst must read and understand this procedure with written documentation maintained in his/her training file.

14.1.2 An initial demonstration of capability (IDC) must be performed per MN-Q-211, *Training Procedures*. A record of the IDC will be maintained in his/her QA file with written authorization from the Laboratory Manager and Quality Manager.

14.1.3 An annual method detection limit (MDL) study will be completed per ALL-Q-004, *Method Detection Limit Studies*, for this method and whenever there is a major change in personnel or equipment. The results of these studies are retained in the quality assurance office.

14.1.4 Periodic performance evaluation (PE) samples are analyzed per ALL-Q-010, *PE/PT Program*, to demonstrate continuing competence. All results are stored in the QA office.

15. POLLUTION PREVENTION AND WASTE MANAGEMENT

15.1 The quantity of chemicals purchased is based on expected usage during its shelf life and disposal cost of unused material. Actual reagent preparation volumes reflect anticipated usage and reagent stability.

15.2 Excess reagents, samples and method process wastes are characterized and disposed of in an acceptable manner. For further information on waste management consult the current version of ALL-C-001, *Sample Management.*

16. REFERENCES

16.1 Standard Methods for the Examination of Water and Wastewater, 18th Edition, 2320B. 1992.
16.2 Methods for Chemical Analysis of Water and Wastes. U.S. EPA – 600/4-79-020, 1983. Method 310.1.

17. TABLES, DIAGRAMS, FLOWCHARTS, APPENDICES, ETC.

17.1 Alkalinity bench sheet – Attachment 1

17.2 Alkalinity bench sheet (drinking water) – Attachment 2

17.3 Electronic Alkalinity Calc Sheet (drinking water) – Attachment 3

17.4 Flow chart

18. REVISIONS

Document Number	Reason for Change	Date
GB-I-014 Rev. 0	New Issue	18July2005

Attachment I

ALKALINITY BENCHSHEET
(Method SM2320B)

Alk-2
PAGE ___ OF ___
SM 2320B

DATE/INIT _____
WS# _____
QA/QC CKD BY_____ON_____

STANDARDS:
STD1 –
STD2 –
LCS Std –
Spiking Std –

Titrant: H2SO4 (N)
0.02
0.1

pH Meter Serial Number

Result of Titration

	Hydroxide (H)	Carbonate (C)	Bicarb (B)
P=0	0	0	T
P<1/2T	0	2P	T-2P
P=1/2T	0	2P	0
P>1/2T	2P-T	2(T-P)	0
P=T	T	0	0

Sample ID	Vol (ml)	Matrix	Starting pH	(A) Titrant to pH 8.3 (ml)	(B) Titrant to pH 4.5 (ml)	Total alk (T) ml sample mg/L as $CaCO_3$ B x N x 50000 / Vol in mL	Phenol alk (P) ml sample mg/L as $CaCO_3$ A x N x 50000 / Vol in mL	Alk (H) Hydroxide Alk– mg/L as CaCO3	Alk (C) Carbonate Alk– mg/L as CaCO3	Alk (B) Bicarbonate Alk –mg/L as CaCO3	
pH Buffer Check 7.0											
STD1 (100mg/L)											STD1 % Recovery =
STD2 (500mg/L)											STD2 % Recovery =
											LCS
											LCS RESULT (mg/L):
											LCS TRUE VALUE (mg/L):
											% RECOVERY:
pH Buffer Check 7.0											SAMPLE ID:
											SPIKED RESULT mg/L:
											SAMPLE RESULT:
											SPIKE AMOUNT:
											% RECOVERY:
											MSD
											SAMPLE ID:
											SAMPLE RESULT:
											DUP RESULT:
											RPD/AD:
pH Buffer Check 7.0											% RECOVERY:
pH Buffer Check 7.0											

GBI061b (18May2005)

Attachment II

Drinking water Alkalinity
PAGE ___ OF ___
SM 2320B

DATE/INIT _____
WS# _____
QA/QC CKD BY_____ON_____

STANDARDS:
STD1 --
STD2 --
LCS Std --
Spiking Std --

pH Meter Serial Number

Sample Number	Volume (mL)	Initial pH	Low Acid Titrant Normality: Starting	Mid	Ending	Total	High Acid Titrant Normality: Starting	Ending	Total	Total mg/L	% Recovery
pH buffer check 7.0											
STD1 (100 mg/L)											
STD2 (500 mg/L)											
pH buffer check 7.0											
pH buffer check 7.0											

Alkalinity, mg/L CaCO3 = $\frac{(A \times N \times 50000)}{\text{mL sample}}$ A = mL of titrant used
N = Normality of titrant

Alkalinity (<20), mg/L CaCO3 = $\frac{((2B - C) \times N \times 50000}{\text{mL sample}}$ B = mL titrant to first recorded pH
C = total mL titrant used to reach pH 0.3 units lower

Attachment III

Analyst : _____

Date : _____ Low Acid Titrant : _____ Normality : _____

Worksheet Number : _____

Data File Name : _____ High Acid Titrant : _____ Normality : _____

Sample Number	Matrix	Volume (mL)	Titrant Low/High	Low Acid Titrant				High Acid Titrant			Total (mg/L)
				Start	Mid.	End	Total	Start	End	Total	
				N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
				N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
				N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
				N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
				N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
				N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
				N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
				N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
				N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
				N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
				N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
				N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
				N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
				N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
				N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
				N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
				N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
				N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
				N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
				N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
				N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
				N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A

Sample Calculations

For Low Alkalinity (< 20 mg/L)

$$\text{Alkalinity, mg/L } CaCO_3 = \frac{((2B - C) \times N) \times 50000}{\text{mL Sample}}$$

B = mL standard acid used to first recorded pH,

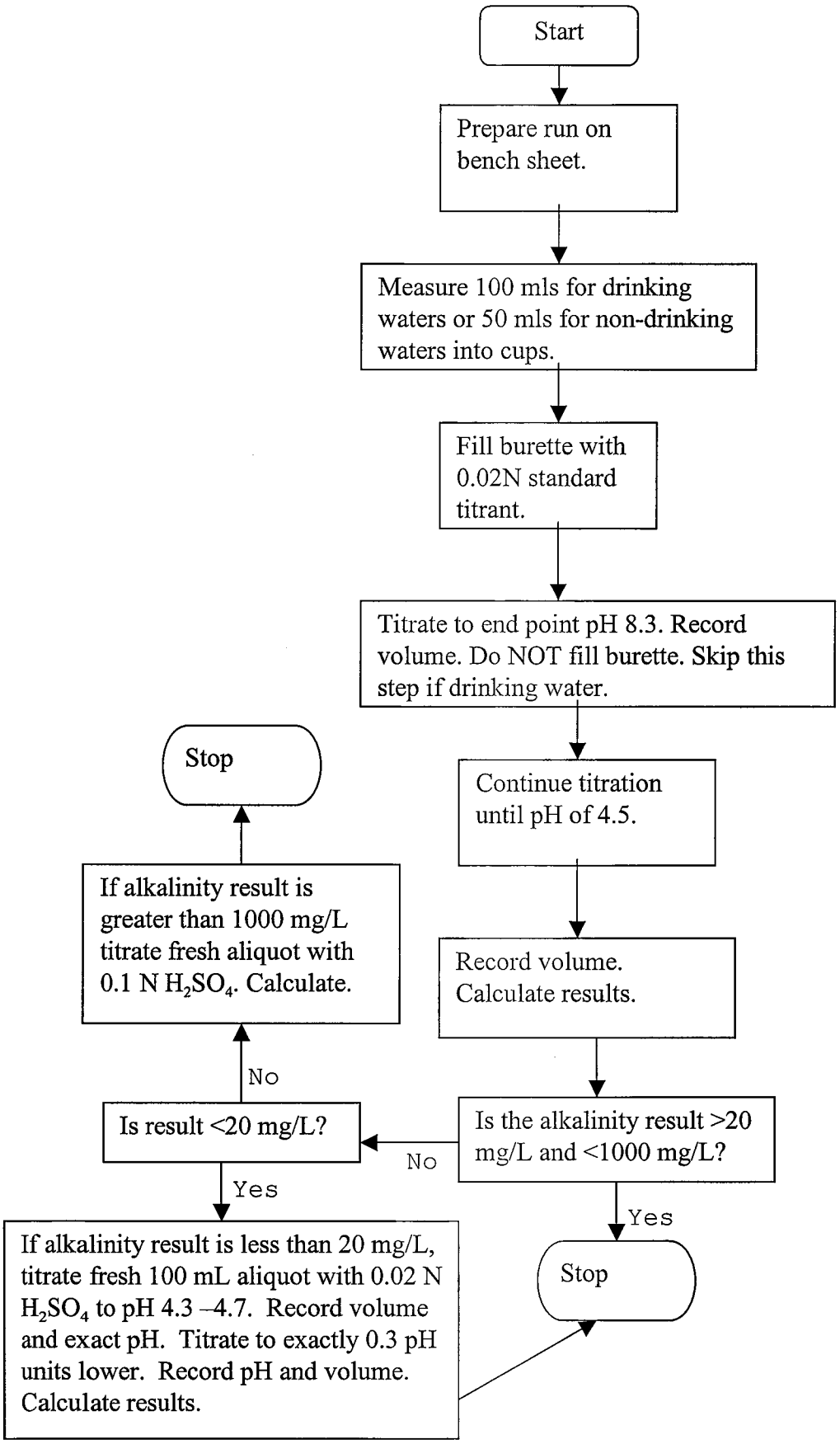
C = total mL standard acid used, N = normality of standard acid

For High Alkalinity (>20 mg/L)

$$\text{Alkalinity, mg/L } CaCO_3 = \frac{(A \times N \times 50000)}{\text{mL Sample}}$$

A = mL standard acid used, N = normality of standard acid

FLOW CHART


Start
Prepare run on bench sheet.
Measure 100 mls for drinking waters or 50 mls for non-drinking waters into cups.
Fill burette with 0.02N standard titrant.
Titrate to end point pH 8.3. Record volume. Do NOT fill burette. Skip this step if drinking water.
Continue titration until pH of 4.5.
Record volume. Calculate results.
Is the alkalinity result >20 mg/L and <1000 mg/L?
Yes
Stop
No
Is result <20 mg/L?
No
If alkalinity result is greater than 1000 mg/L titrate fresh aliquot with 0.1 N H_2SO_4. Calculate.
Stop
Yes
If alkalinity result is less than 20 mg/L, titrate fresh 100 mL aliquot with 0.02 N H_2SO_4 to pH 4.3 –4.7. Record volume and exact pH. Titrate to exactly 0.3 pH units lower. Record pH and volume. Calculate results.

TITLE: Ammonia using Micro-Distillation and Analyzed by Lachat 8000 Flow Injection following EPA Method 350.1

MATRICES:

This SOP pertains to drinking, ground, surface, and saline waters; soils, domestic and industrial wastes.

DETECTION LIMITS:

Reporting Limits are used in the absence of Project or State Specific Required Detection Limits. The determinative method contains the current method detection limits (MDL) and Reporting Limits. See Table A for summary.

1.0 **SCOPE AND APPLICATION:**

1.1 This SOP is for the determination of total cyanide in drinking, ground, surface, and saline waters; soils, domestic and industrial wastes. The applicable range is 0.11-20 mg/L as NH_3.

1.2 This SOP utilizes the Lachat 8000 analyzer.

2.0 **SUMMARY OF THE TEST METHOD:**

2.1 The sample is buffered at a pH of 9.5 with a borate buffer in order to decrease hydrolysis of cyanates and organic nitrogen compounds, and is distilled into a solution of boric acid. Alkaline phenol and hydrochlorite react with ammonia to form indophenol blue that is proportional to the ammonia concentration measured at 630 nm. The blue color formed is intensified with sodium nitroprusside and measured on the auto-analyzer.

2.2 Wisconsin groundwater samples do not need to be distilled before analysis. All other samples must be distilled before analysis.

3.0 **DEFINITIONS**:

3.1 Calibration Blank: A volume of reagent water. The calibration blank is used to zero the instrument.

3.2 Calibration Standard: A solution prepared from the dilution of a stock standard. The calibration solutions are used to calibrate the instrument response with respect to analyte concentration.

3.3 Calibration Verification Solution (ICV/CCV): A solution of method analytes, used to evaluate the performance of the instrument system with respect to a defined set of method criteria. The ICV is not distilled along with the samples. The ICV is analyzed after the calibration curve and before samples are analyzed. The CCV is not distilled along with the samples. The CCV is analyzed after every 10 samples.

3.4 Calibration Verification Blank (ICB/CCB): A solution of blank reagent water, used to evaluate the performance of the instrument system with respect to a defined set of

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method criteria. The ICB is analyzed after the calibration curve and before samples are analyzed. The CCB is analyzed after every 10 samples. The ICB/CCB are not distilled along with the samples.

3.5 Method Blank: a sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest, which is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedures, and in which no target analytes or interferences are present at concentrations that impact the analytical results for sample analyses. The Method Blank is distilled and analyzed exactly like a sample.

3.6 Matrix Spike (MS) and Matrix Spike Duplicate (MSD): Aliquots of an environmental sample to which known quantities of the analyte(s) of interest are added in the laboratory. The MS and MSD are distilled and analyzed exactly like a sample. Their purpose is to quantify the bias and precision caused by the sample matrix. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the MS/MSD corrected for background concentrations.

3.7 Method Detection Limit (MDL): The minimum concentration of an analyte that can be identified, measured and reported with 99% confidence that the analyte concentration is greater than zero.

3.8 Lab Control Spike (LCS) and Lab Control Spike Duplicate (LCSD): An aliquot of reagent water or other blank matrices (Ottawa sand for solid) to which known quantities of the method analytes are added. The LCS and LCSD are distilled and analyzed exactly like a samples. Their purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements.

3.9 Standard Stock Solution: A concentrated solution containing one or more method analytes prepared in the laboratory using assayed reference material or purchase from a reputable commercial source.

3.10 Estimated Quantitation Limits: The EQL is based upon the low standard in the calibration curve, taking into account the weight/volume of the sample distilled and dilutions.

4.0 INTERFERENCES:

4.1 Ammonia in the laboratory may become a contaminant in this test. Care should be taken that ammonium hydroxide, either as a reagent or as a cleaning substance is not in the same room as the instrument.

4.2 Calcium and magnesium ions may be present in concentrations sufficient to cause precipitation problems during analysis. A 5% EDTA solution is used to prevent the precipitation of calcium and magnesium ions in river water and industrial wastes.

4.3 Sample turbidity and color may interfere with this method. Turbidity must be removed by filtration prior to analysis. Sample color that absorbs in the photometric range used will also interfere.

4.4 Residual chlorine must be removed by pretreatment of the sample with sodium thiosulfate before distillation.

4.5 Cyanate, which may be encountered in certain industrial effluents, will hydrolyze to some extent even at pH of 9.5 at which distillation is carried out.

5.0 **SAFETY:**

5.1 Safety is everyone's business at En Chem, Inc. and everyone is responsible for assisting in reducing unsafe and unhealthy working conditions or potential hazards. The company provides you with a safe place to work, but we need your cooperation to keep it safe. When you see something that does not look safe, or you see someone working in an unsafe manner, mention it to your Supervisor.

5.2 All samples should be treated as hazardous. Safety glasses, gloves, and lab coats are to be worn. The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined. However, each chemical compound should be treated as a potential health hazard. Exposure to these chemicals must be reduced to the lowest possible level by a safe technique. A reference file of material safety data sheets should also be made available to all personnel involved in the chemical analysis.

5.3 Required Safety Equipment is listed in Table B

6.0 **EQUIPMENT AND SUPPLIES:**

6.1 See Table C and Table D for a summary.

7.0 **REAGENTS AND STANDARDS:**

7.1 See Table E and F for a summary.

8.0 **SAMPLE COLLECTION, PRESERVATION, SHIPMENT AND STORAGE:**

8.1 See Table G for a summary.

9.0 **QUALITY CONTROL:**

9.1 Demonstration of Capability - The initial demonstration of capability is used to characterize instrument performance (determination of linear range and laboratory control sample) and laboratory performance (determination of MDLs) prior to performing analyses by this method. The analyst must perform an IDC before they are allowed to analyze samples.

9.1.1 Initial Demonstration of Capability (IDC) – Analysts must perform initial demonstration of capability before analyzing samples.

9.1.1.1 The analyst will distill and analyze four replicates of the LCS solution.

9.1.1.2 Calculate the mean, average recovery (x), and the standard deviation of the recovery (s). The recovery of each compound must fall within 90 – 110% of true value. If IDC is outside acceptable limits, corrective action must be taken.

9.1.2 Linear Calibration Range - The linear calibration range must be determined initially and verified whenever a significant change in instrument response is observed or expected. The initial demonstration of linearity must use sufficient standards to determine the upper range limit. The upper range limit is an observed signal no more than 10% below the level extrapolated from lowers standards. The verification of linearity must use a minimum of a blank and three standards. If any verification data exceeds the initial values by ± 10%, linearity must be reestablished. If any portion of the range is shown to be nonlinear, sufficient standards must be used to clearly define the nonlinear portion.

9.1.3 Laboratory Control Sample- When beginning the use of this method and on a continuing basis, verify the calibration standards and acceptable instrument performance with the preparation of a LCS. If the determined concentrations are not within ±10% of the true values, performance of the determinative step is unacceptable. The source of the problem must be identified and corrected before either proceeding on with the initial demonstration or MDLs or continuing with on-going analyses.

9.1.4 Method Detection Limits- MDLs must be established for all analytes; using reagent water (blank) fortified at a concentration of 2-3 times the estimated instrument detection limit. To determine MDL values, take a minimum of seven replicate aliquots of the fortified reagent water and process through the entire analytical method. Perform all calculations defined in the method and report the concentration values in the appropriate units. Calculate the MDL as follows:

MDL = (t) x (S)

Where,

t = student's t value for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom [t = 3.14 for seven replicates]. If more than seven reps are used the t-value changes accordingly.

S= standard deviation of the replicate analyses

MDLs are determined annually or whenever there is a significant change in the background or instrument response.

9.2 A Method Blank (MB) must be prepared, distilled, and analyzed with every sample batch or every 20 samples whichever is more frequent. The Method Blank is analyte-free DI water, which is carried through the entire procedure.

9.3 A Laboratory Control Sample and Laboratory Control Sample Duplicate (LCS and LCSD) must be prepared, distilled, and analyzed with every sample batch or every 20 samples whichever is more frequent. A LCS is reagent water, which has a known amount of analyte of interest added.

9.4 A Matrix spike and Matrix spike duplicate (MS and MSD) must be analyzed least every 10 samples and for each matrix whichever is more frequent. A MS/MSD is an aliquot of environmental sample to which known quantities of the method analytes are added. The MS and MSD are processed along with the samples.

9.5 See Tables H and I for a summary.

10.0 **CALIBRATION AND STANDARDIZATION:**

10.1 **Instrument Settings**

Sample throughput:	80 samples/h, 45s/sample
Pump and Speed:	35
Cycle Period:	45
Peak Base Width:	24 s
% Width Tolerance:	100
Threshold:	10000
Inject to start of peak:	28 s
Chemistry:	Direct

10.2 Follow steps 11.2 –11.3 to run calibration procedure.

10.3 Calibration Criteria

Calibration Rep Handling:	Replace
Calibration Fit Type:	1st Order Polynomial
Weighting Method:	None
Force through zero:	No

10.3.1 The instrument must be calibrated every time it is set up. The working linear range is from 0.11 to 20 mg/L. The correlation coefficient must be at least 0.995.

10.3.2 Place working standards in decreasing concentration.

11.0. **PROCEDURE:**

11.1 Sample Preparation

NOTE: Document all sample volumes, standards and reagents used in the distillation on the prep log.

11.1.1 Wisconsin groundwater samples are analyzed directly and do not need to be distilled or pH adjusted before analysis. All other samples must be distilled before analysis. All other water samples must be pH adjusted before distillation. If a Wisconsin groundwater sample contains turbidity, the sample is filtered before analysis via a syringe and 25 mm filter.

11.1.2 Check all samples for residual chlorine with potassium iodine-starch paper by placing several drop of sample on the paper with a disposable pipette. If the potassium iodine-starch paper turns purple or black, residual chlorine is present. Add as much sodium thiosulfate solution as necessary to remove all residual chlorine.

11.1.3 Place 30 mL of water sample into 50 mL disposable beakers labeled with sample numbers. Using a calibrated pH meter, adjust water sample to between pH 5 to 9 with 3 N NaOH before distillation. Note pH adjustment on prep log.

11.2 Distillation Procedure

This section of the SOP details the steps in distilling the samples before analysis. In the following procedure, **D** and **M** refer to the marks on the collector tube. **D** means "distillation" end, and **M** means "measuring" end.

11.2.1 Set the controller to 120°C, allow the heater to warm up. This will take about 40 minutes. The operating temperature of the distillation block needs to be verified annually.

11.2.2 Label tubes with the **M** end up, place as many tubes as you have samples into the collector tube rack. Fill the tubes with 1 ml of 0.016 M H_2SO_4 trapping solution, add Teflon liner and cap.

11.2.3 For liquid samples place 6 ml of prepared sample into each sample tube with a calibrated automatic pipette.

11.2.4 For soil samples weigh out 0.20 g of soil or sludge to the nearest 100th on a calibrated balance and dilute to 6 ml with deionized water tube with a calibrated automatic pipette into each sample tube. If the sample is high in organics use smaller sample size.

11.2.5 For liquid prepare one method blank by adding 6 mls of DI water to sample tube using a calibrated automatic pipette.

11.2.6 For soil samples, prepare one method blank by weighing out 0.20 g of washed sea sand to the nearest 100th on a calibrated balance and dilute to 6 ml with deionized water tube with a calibrated automatic pipette.

11.2.7 For liquid samples, prepare one LCS/LCSD pair by adding 6.0 ml 0.016 M sulfuric acid solution and 0.6 ml of 100 mg/L secondary spiking solution into sample tubes using a calibrated automatic pipette.

11.2.8 For soil samples, prepare one LCS/LCSD pair by weighing out 0.20 g of washed sea sand to the nearest 100th on a calibrated balance. Bring to 6 ml volume with deionized water. Add 0.6 ml of 100 mg/L secondary spiking solution using a calibrated automatic pipette into each sample tube.

11.2.9 For liquid samples, prepare one MS/MSD pair per 10 samples by adding 6.0 ml of sample and 0.6 ml of 100 mg/L secondary spiking solution using a calibrated automatic pipette into each sample tube.

11.2.10 For soil samples, prepare one MS/MSD pair by weighing out 0.20 g of sample to the nearest 100th on a calibrated balance. Bring to 6 ml volume with deionized water. Add 0.6 ml of 100 mg/L secondary spiking solution using a calibrated automatic pipette into each sample tube.

11.2.11 Add 1.0 ml of 0.55 M borate buffer solution to all samples.

11.2.12 Immediately push the **D** end of an Ammonia-1 collector tube over the open end of each sample tube to start the seal.

11.2.13 Place the assembly in the press, putting the sample tube through the hole in the white base. Before pressing, the user should grip the collector tube firmly at the breakaway point to keep the tube from shifting during the pressing procedure.

11.2.14 The pressing motion should be a smooth constant pressure, which is just enough to slide the sample tube inside the collector tube. A jerky, forced motion may cause added strain to the tube and could potentially crack it. Press down on the handle until the stop ring on the sample tube hits the **D** end of the collector tube.

11.2.15 Put on heat-resistant gloves. Push the sample tube and **D** end of each tube all the way into the preheated block so that the collector tube stop ring touches the block. Placing 21 tubes should take less than one minute.

11.2.16 Set the timer for 30 minutes.

11.2.17 When 30 minutes is up, remove the first tube, use heat-resistant gloves, from the block and immediately pull its sample tube using a downward twisting motion as opposed to a sideways motion. You must remove the sample tube within 4 seconds of removing it for the block or suck-back of the sample will occur. Dispose of the sample tube and the hot solution.

11.2.18 Invert each collector tube and place it into the collector tube rack, now with the **D** end up. It should take less than two minutes to pull and separate all 21 tubes.

11.2.19 Parafilm the **M** end and allow tubes to cool for at least 10 minutes.

11.2.20 Hold collector tube horizontally and rinse its walls with the distillate in order to homogenize it. Roll tube in order to collect all droplets from the walls of the tube. Return the tube to an upright position so the **D** end is up.

11.2.21 With the **D** end up, break the collector tube in half by pulling the **D** end hard toward yourself to break it, the twisting and tearing off the **D** end. Discard the **D** end.

11.2.22 In the **M** end of the tube dilute to the 6.0 ml mark with DI water. This results in the original sample volume, but now in 0.003 M sulfuric acid.

11.2.23 Push the second cap onto the open end of the tube as far as it will go. Shake the tube so it mixes with the diluent. Do not invert the sample. With the M end down; place the tube into the collector tube rack.

11.2.24 Seal both ends of the tube with Parafilm and refrigerate distillates if ammonia determination is not done immediately.

11.3 Basic System Operation - Analytical

This portion of the SOP is designed to allow the user to set up and run a method, print a sample report, then shut down using the more basic software functions. For a more detailed explanation of the many other options, the user should refer to the Lachat Software Reference Manual. It is assumed that a method program has already been created for the chemistries you wish to run.

11.3.1 Create calibration curve standards, ICV/CCV standards and ICB/CCB samples as per Tables H and J2. A new calibration curve is prepared and run each analytical day.

11.3.2 Turn on computer with ON/OFF button. Turn on printer. The power to the monitor, autosampler and reaction module is controlled with a multi-outlet noise filter and surge suppresser located behind the reaction module. Turn the red switch to "ON".

11.3.3 Allow the autosampler to perform its startup routine and wait until the autosampler stops with the probe above the wash bath.

11.3.4 Log into the Network with your Login name and password. Windows program will be activated. Program Manager screen will appear. Click twice on Lachat Instruments. Click twice on the Omnion FIA icon on the Lachat Instruments window. The startup box will come up, and then click on **'OK'**. The autosampler probe will go into the wash bath and dilutor activity may be heard. The injection valves may turn to the Inject state if they were not already there.

11.3.5 To encourage GALP (Good Automated Laboratory Practice), Omnion requires that the operator "Log-in" every time with name and password. Enter your assigned name and password in the correct case in the spaces indicated and then click on the **'OK'** button.

11.3.6 After you have logged in, the Omnion FIA Main Menu will appear on the screen. The header should contain the serial number of the software key. No messages should be seen about the SS420 boards, or any serial port failures. Click on the Instrument button labeled 'FIA Instrument 1'.

11.3.7 Each valve allocated to this instrument will be cycled from Load to Inject and Load to Inject again. This is a test of the valves and if no messages are received about failing valves, then they are OK.

11.3.8 If a valve fails, a box will tell you which channel's valve failed. You can press OK and continue. You should arrange for service for the failing valve by calling Lachat Instruments.

11.3.9 After the injection valves are tested, an instrument window for FIA Instrument 1 will appear. Omnion will automatically open the last Method, Tray, DQM Plan and Data File used. Arrow up to 'File" and click. When window appears click on **'Open Method'**.

Under Open Method File Directories, click on **c:\omnion\methods** and then click on the method you will be running. A list of methods will appear. Highlight the appropriate one in the **File Name** box and click on **'OK'**.

11.3.10 The Method will open and the **Analyte Table** will appear. It will show the Analyte Name and which Channel it is run on. The concentration Units and concentration of the calibration standards will be listed. To the far right will be the timing periods, which the instrument uses to detect the peaks.

11.3.11 Click on **'File'** again and then **'Open Tray'**. The **'Open Tray File'** window will come up. Directories will be **c:\omnion\trays\method**. Click on the method you will be running. A list of previous trays for that particular method will appear. Click on a recent **tray file name and** the on **'OK'** to call it up. Edit this tray below the Calibration Standards with the sample numbers you will be running. Also edit any dilutions that will be required.

11.3.12 Click on **Save Tray As** and edit name of tray to reflect toady's' date and letter to reflect which run: YYMMDDL. L is the sequence of the tray that day i.e., a=first tray, b=second tray and so on. Example: 960730a.

11.3.13 Click on **File** again and then on **Open DQM**. The Open DQM File window will come up. Directories will be **c:\omnion\DQM\method**. Click on the method you will be running and then on the method **DQM File Name**. Click on **OK** and the DQM (Data Quality Management) Plan will appear.

This DQM Plan supplements the tray table itself and acts as a standard operating procedure to be used when running this tray. Check the DQM to make sure it will apply to this tray, or edit it if necessary. If any changes were necessary then the DQM should be saved, and then replace the DQM in the tray, to make the changes permanent. If no changes were necessary, then minimize this window.

11.3.14 Click on the **Run Tray** button. The Tray Run Window will appear. Leave the **Method** and **Tray** spaces blank to run the currently loaded Method and tray. You must fill in the **Data File** space so that Omnion knows where to put the data it will generate. Click on **Catalog** after the **Data File** space to see a list of previous data files. Click on an old file name and then edit it to match today's tray name. Click on **OK**.

11.3.15 Follow Section 17.3 of Lachat QuikChem Method 10-107-06-1-A for proper manifold setup. Insert the proper manifold for the desired analysis to the proper channel specified in the Analyte Table. The load/inject valve for each channel has six connections with the following designations:

Port #	Function
1	Sample Loop Inlet
2	Carrier Stream Inlet (From Pump)
(Short section of plastic tubing remains port #2 at all times)	
3	Outlet to reaction manifold
4	Sample loop outlet
5	Sample loop waste line
6	Sample source line (from sampler, pump)

Each reaction manifold has a line with pump tubing attached labeled "carrier". Disconnect the pump tubing from this line and reconnect it to the section of line that comes from port #2. Connect the section of tubing coming from the reaction manifold to port #3.

11.3.16 Connect the outlet line from the manifold, located top right, to the bottom inlet of the flow cell.

11.3.17 Insert backpressure loop of 200 cm of 0.022" i.d. tubing, between top outlet of flow cell and the waste line.

11.3.18 Place waste line into phenol waste collection container.

11.3.19 Install proper 630 interference filter.

11.3.20 If required, allow heating unit to heat to correct temperature.

11.3.21 Install 13 cm x 0.022 i.d. sample loop in ports #1 and # 4.

11.3.22 Install the pump tubing onto pump cartridges. Check for wear on the pump tubing by rolling between thumb and fingers when stretched across a pump cartridge. Replace tubing if "flat" spots are felt.

11.3.23 Move tension levers to left to provide proper tension.

11.3.24 Check all connections for leakage and proper flow. Make sure waste lines are routed to proper container.

11.3.25 Properly label and fill calibration standard, ICV/CCV standard and ICB/CCB vials with proper solutions. Properly label and fill sample tubes with proper samples.

11.3.26 When ready, click on **RUN** on the Tray Run Window and the analysis will start. The symbol for the tray on the toolbar will turn to a **STOP** sign until analysis is complete.

11.3.27 If necessary to stop the run anytime, click on the **STOP** sign. A window will come down with the options to RESUME or ABORT TRAY.

11.3.28 After instrument has calibrated, click on the **Review Calibration** button on the toolbar. The graph of the calibration will be displayed along with the area of each standard. If the r-value of the calibration is 0.995 or better, print the calibration graph and allow the analysis to continue.

11.3.29 After analysis is completed the **STOP** sign in the Toolbar will be replaced with **Run Tray.** Click on File and the window will come down. Click on Export Data. Export data window will appear. Highlight whatever Data Items and Channel Dependent Data Items you want exported to EXCEL Save Export Data As window will appear. Directories should be g:\data\inorgani\lachat\archives.

Highlight the text file you have just run in the File Name box. Click on **OK** and data will be exported to EXCEL. Then go back and click on File again. When window comes down, click on Open Runtime Rpt. Open Runtime Report File window will appear. It should have current data, method and file name of analysis just completed, or if going back at a later date, then highlight the one that you want. Click on **OK** and the Runtime Report will appear on the screen. Click on File and then on Print/Export Runtime Rpt. Runtime Report window will appear.

Click on **OK** to print. On Print window choose the Print Range you want. **ALL** is normally highlighted. Click on **OK**.

11.3.30 Samples that have results greater than the highest standard in the calibration curve need to be diluted appropriately so the result falls within the calibration curve, and reanalyzed. Document all dilutions on prep log.

11.3.31 Document all standards and reagents used in analysis in raw data. Sign and Date raw data.

11.3.32 After analysis is complete, place reagent lines in D.I. water and rinse several minutes. Remove lines from water and pump air through the lines until dry.

11.3.33 Turn off pump, release tension levers on pump cartridges and remove pump tubing from cartridges.

11.3.34 Disconnect pump tubing to port #2 at the pump tubing connector, disconnect line to port #3 at port #3 connector and connect pump tubing from #2 to line from manifold.

11.3.35 Disconnect manifold outlet line from flow cell inlet connector.

11.3.36 Wrap pump tubing lightly around manifold panel and store in appropriate box, with sample loop and interference filter.

NOTE: Any daily or periodic maintenance must be recorded in the instrument daily logbook.

11.4 SHUTDOWN:

11.4.1 Click on **EXIT** icon

11.4.2 Omnion FIA Data System Window appears. Click on **Logoff**.

11.4.3 Window listing **User** Name and question: **Logoff Current Session?** Click on **YES**.

11.4.4 Window for User Name and Password comes up. Click on **EXIT**.

11.4.5 Window comes up with: **Terminate Data System?** Click on **YES.**

11.4.6 Turn off computer, printer and switch on surge suppresser.

12.0 **CALCULATIONS:**

12.1 The instrument provides calculated sample results in mg/L. Calculations are only necessary if a dilution was used.

Liquid Calculation

Raw Data Value (mg/L) x Dilution Factor = Ammonia (mg/L)

Soil Calculation

$$\frac{\text{Raw Data Value (mg/L) X 0.006 L X Dilution Factor}}{} = \text{Ammonia (mg/Kg)}$$

(0.0002 Kg x % solids in decimal form)

12.2 Accuracy:

A matrix spike / matrix spike duplicate is analyzed for each analytical batch of 10 or fewer samples.

MS/MSD calculation

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

SSR = Spike sample result
SR = Sample result
SA = Spike added

12.3 Precision:

The precision is calculated based on the concentration of the matrix spike / matrix spike duplicate result.

Relative percent difference (RPD) calculation:

$$\% \text{ RPD} = \frac{|MS-MSD| \times 100}{(MS+MSD)/2}$$

MS = Matrix spike value
MSD =Matrix spike duplicate value

12.4 See Table I for summary of limits. For waters control limits of 90-110% is set by the method.

13.0 **METHOD PERFORMANCE:**

13.1 The method performance is validated through the Method Detection Limit Study, Initial Validations and the Performance Testing Samples taken through this procedure.

13.2 See Tables A and K for a summary

14.0 **POLLUTION PREVENTION:**

14.1 Pollution prevention encompasses any technique or procedure that reduces or eliminates the quantity or toxicity of waste at the point of generation. Laboratory staff should order where possible acceptable non-toxic alternative supplies and prepare only those quantities of reagents or standards that will be used prior to the expiration date. Other appropriate measures to minimize waste generation should be brought to the attention of laboratory management. All laboratory waste shall be handled as directed by the Laboratory Waste Management Plan and Hazardous Waste Contingency Plan.

15.0 **DATA ASSESSMENT AND ACCEPTANCE CRITERIA FOR QUALITY CONTROL MEASURES:**

15.1 At a minimum there are three levels of data review:

15.2 Analyst/Technician verification at the bench top are looking at instrument performance as it relates to initial calibration, calibration verification, cleanliness.

15.3 Supervisor/Analyst verification after analysis are looking for sample concentration versus linear range of the instrument, typical patterns resulting from the compounds or elements in question, and quality control measure criteria. Data is accepted without qualification, accepted with qualification, or rejected with samples reprocessed.

15.4 Report Reviewer/Project Management personnel look at the presentation of the data on final reports. The reports are verified for holding time compliance, receipt conditions, method citation and reasonableness, which may include field duplicate analysis, analytical comments and qualifications presented by the previous reviews, and comparing results of similar analytical techniques as it relates to the project site information when available.

15.5 A fourth level of review, data validation is determined from a project or program scope of laboratory services and encompasses the generation Quality Control summaries in the media of "Form Generation",

15.6 See Table L and M for a summary.

16.0 CORRECTIVE ACTIONS FOR OUT-OF-CONTROL DATA

16.1 Assessment of Quality Control measures is done to provide a level of confidence in the data generated. The measures provide documentation that the instrument conditions were reliable during the analysis.

16.2 See Table L for summary.

17.0 CONTINGENCIES FOR HANDLING OUT-OF-CONTROL OR UNACCEPTABLE DATA

17.1 During analysis, events occur specific to the physical and chemical characteristics of the environmental sample. When possible, with received sample volumes, data generated along with measures that do not meet statistical goals are re-analyzed again to see if the statistical goal can be achieved. When environmental samples do not meet statistical unacceptable data is generated. These events are different from those pertaining to instrument operating conditions these events occur when the instruments are operating under ideal conditions.

17.2 See Table L for a summary.

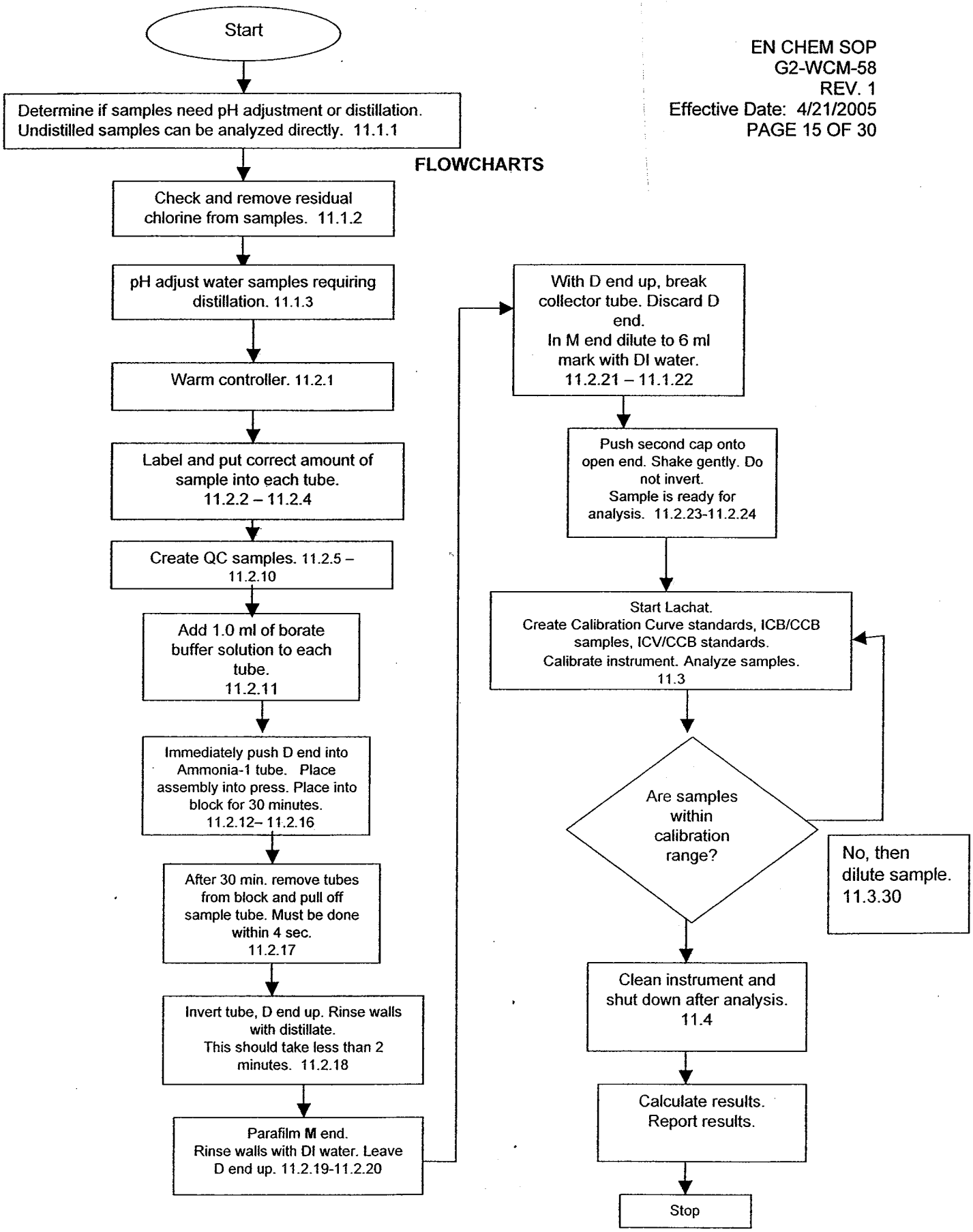
18.0 WASTE MANAGEMENT

18.1 To minimize waste during sample preparation has two benefits. The first benefit is a cost savings to the lab in materials and supplies. The second is a benefit to the environment, as fewer materials need to be disposed.

REFERENCES:

Quikchem Method 10-107-06-1-A, Lachat Instruments, March 29, 1988
Micro Dist Method Ammonia-1: Phenate Method, Lachat Instruments, April 27, 2000
EPA 600 R-93-100, Revised August 1993, Method 350.1
Standard Methods for the Examination of Water and Wastewater, 18th Edition, p. 4-77, Methods 4500 NH3 B and H (1992)
40CFR Part 136
National Environmental Laboratory Accreditation Conference (NELAC), July 1998 Standards
US EPA Quality Assurance Division (QAD)

FLOWCHARTS


Start
Determine if samples need pH adjustment or distillation. Undistilled samples can be analyzed directly. 11.1.1
Check and remove residual chlorine from samples. 11.1.2
pH adjust water samples requiring distillation. 11.1.3
Warm controller. 11.2.1
Label and put correct amount of sample into each tube. 11.2.2 – 11.2.4
Create QC samples. 11.2.5 – 11.2.10
Add 1.0 ml of borate buffer solution to each tube. 11.2.11
Immediately push D end into Ammonia-1 tube. Place assembly into press. Place into block for 30 minutes. 11.2.12– 11.2.16
After 30 min. remove tubes from block and pull off sample tube. Must be done within 4 sec. 11.2.17
Invert tube, D end up. Rinse walls with distillate. This should take less than 2 minutes. 11.2.18
Parafilm M end. Rinse walls with DI water. Leave D end up. 11.2.19-11.2.20
With D end up, break collector tube. Discard D end. In M end dilute to 6 ml mark with DI water. 11.2.21 – 11.1.22
Push second cap onto open end. Shake gently. Do not invert. Sample is ready for analysis. 11.2.23-11.2.24
Start Lachat. Create Calibration Curve standards, ICB/CCB samples, ICV/CCB standards. Calibrate instrument. Analyze samples. 11.3
Are samples within calibration range?
No, then dilute sample. 11.3.30
Clean instrument and shut down after analysis. 11.4
Calculate results. Report results.
Stop

VALIDATION DATA:

The laboratory must demonstrate initial proficiency with each combination of sample preparation and determinative methods utilized, by generating data of acceptable accuracy and precision for a reference sample containing the target parameters in a clean matrix. The laboratory must also repeat this demonstration whenever new staff is trained or significant changes in instrumentation are made. Analysts previously trained shall perform a continued demonstration of proficiency annually by performing "Yearly Demonstration of Capability" (YDC). The YDC shall be performed following Section 9.1.1.

The values from the determinative method are presented as guidance only and are not intended as absolute acceptance criteria. Accuracy of parameters routinely analyzed by En Chem can be found in Initial Demonstration Data Table K. Blind studies are available upon request from the QC Manager.

MANAGEMENT APPROVAL AND REVIEW OF SOPS - POLICY AND DOCUMENTATION

REVIEWED BY: _____ 4-25-05
Alexandria Wolf
Inorganics Group Leader — Date

_____ 4-25-05
Arthur F. Lautenbach
Quality Assurance Officer — Date

APPROVED BY: _____ 4/25/05
Nils Melberg
Laboratory Manager — Date

Periodic Review Record

Review Date					
Initials					

Tables

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Table A
REPORTING LIMITS

Compound Name	Aqueous		Solid	
	MDL (mg/L)	EQL (mg/L)	MDL (mg/Kg)	EQL (mg/Kg)
Ammonia	0.11	0.25	5.7	15

Table B
REQUIRED SAFETY EQUIPMENT

Safety Apparel Description	Mandatory for Procedure	Optional
Safety Goggles or Glasses	√	
Lab Coat	√	
Gloves	√	
Face Shield		√

Table C

EQUIPMENT

Equipment	Manufacturer	Model(s)/Catalog Number •
Lachat 8000	Lachat	Lachat
Micro-Distillation Unit	Lachat	Micro Distillation
Top loading Analytical Balance	Mettler	BA310P
1000 µL Pipette	Eppendorf	05-402-76 (Fisher Cat#)
500 µL Pipette	Eppendorf	05-402-72 (Fisher Cat#)
250 µL Pipette	Eppendorf	05-402-69 (Fisher Cat#)
Bottle Top Dispenser (0.5 - 5.0mL)	Brinkman Dispensette	13-688-221 (Fisher Cat#)
Repipetors (0.5 - 5.0mL)	Barnstead/Thermolyne	13-687-33 (Fisher Cat#)
Vented Hood	Hamilton	
Spoonula (Lab Spoon)	FisherBrand or equivalent	14-375-10 (Fisher Cat#)
Super Colonna Tube Press	Lachat	
Buret – 20 ml	Kimax	03-700-22C
Ammonia Manifold	Lachat	10-107-06-1-B
Interference filter – 630 nm	Lachat	
13 cm x 0.022 i.d. sample loop	Lachat	
pH Meter	Orion	
Gloves – Heat Resistant		

- Or equivalent

Table D

SUPPLIES

Supplies	Manufacturer	Catalog #
Distillation tubes	Lachat	A17117A
Culture Tubes 13X100	Fisher	71500 13100
Volumetric Flasks	Fisher	Various
Syringe – 20 mL	Bectin Dickenson	309661
Syringe Prefilter – 25 mm	Nalogene	F271-21
Potassium Iodine Starch Paper	Fisher Scietific	V260
Disposable Beakers	MG Scientific	B250-50-INV
Parafilm		
Pipettes – Transfer		

Table E

REAGENTS

Reagent	Alias	Concentration	Directions found in:
Ammonium Chloride - Need from two sources		Neat	
Deionized Water	Carrier		
Sodium Hydroxide (NaOH)		Neat	
Sodium Borate ($Na_2B_4O_7$)		Neat	
Borate Buffer	Releasing Solution	0.55 M	Table J
Sulfuric Acid		Concentrated	
Sulfuric Acid	Trapping Solution	0.016 M	Table J
Phenol	88% liquefied phenol	88%	
Sodium Phenolate Solution	Reagent 1		Table J
Sodium Hypochlorite	Chlorox Bleach	5.25%	
Sodium Hypochlorite Solution	Reagent 2		Table J
Disodium Ethylenediamine Tetraacetate (Na_2EDTA)		Neat	
Buffer	Reagent 3		Table J
Sodium Nitroprisside [$Na_2Fe(CN)_5NO.2H_20$]		Neat	
Sodium Nitroprusside Solution	Reagent 4		Table J
Sodium Thiosulfate		Neat	
Sodium Thiosulfate Solution	Dechlorinating Agent		Table J
Sodium Hydroxide Solution	3 N	3 N	Table J
Sodium Hydroxide		Neat	

Table F

STANDARDS

Standard	Concentration	Direction found in Section:	Alias
Ammonium Chloride	100 mg/L	Table J2	Stock Standard
Ammonium Chloride Must be different Lot # than Stock	100 mg/L	Table J2	Second Source Stock Standard
Level 1 Calibration Standard	20 mg/L	Table J2	Cal Std. 1
Level 2 Calibration Standard	8.0 mg/L	Table J2	Cal Std. 2
Level 3 Calibration Standard	4.0 mg/L	Table J2	Cal Std. 3
Level 4 Calibration Standard	2.0 mg/L	Table J2	Cal Std. 4
Level 5 Calibration Standard	1.0 mg/L	Table J2	Cal Std. 5
Level 6 Calibration Standard	0.50 mg/L	Table J2	Cal Std. 6
Level 7 Calibration Standard	0.25 mg/L	Table J2	Cal Std. 7
Level 8 Calibration Standard	0.0 mg/L	Table J2	Cal Std. 8
Initial Check Verification	10 mg/L	Table J2	ICV
Continuing Check Verification	10 mg/L	Table J2	CCV
Matrix Spike/Matrix Spike Duplicate	10 mg/L	Table J2	MS/MSD
Laboratory Control Spike/Laboratory Control Spike Duplicate	10 mg/L	Table J2	LCS/LCSD

Table G

SAMPLE COLLECTION, PRESERVATION, HOLDTIME, SHIPMENT, AND STORAGE

Matrix	Prep Method	Container(s)	Preservation Hold Time	Shipment Conditions	Lab Storage Conditions
Aqueous	EPA 350.1	250 ml plastic containers	H_2SO_4 28 days	On ice 4+/- 2° Celsius	4°C
Solid	EPA 350.1	125 ml plastic containers	None 28 days	On ice 4+/- 2° Celsius	4°C

Table H

QUALITY CONTROL

Preparation Method ⇨ Quality Control Measure ⇩	**EPA 350.1**
Method Blank	One per batch of samples, up to 20 environmental samples, whichever is more frequent. Must be distilled with batch.
Laboratory Control Spike and Duplicate	One per batch of samples, up to 20 environmental samples, whichever is more frequent. A LCSD is required if MS/MSD is not performed. Must be distilled with batch.
Matrix Spike / Matrix Spike Duplicate	One pair per batch of samples, up to 10 environmental samples, whichever is more frequent. Must be distilled with batch.
Initial Calibration	Minimum of 3 standards plus blank. Must be performed every time before samples are analyzed. **The calibration curve is not distilled.**
Calibration Verification (ICV/CCV)	ICV – analyzed after calibration. **The ICV is not distilled with batch.** CCV – analyzed after every 10 samples. **The CCV is not distilled with batch.**
Calibration Blank (ICB/CCB)	ICB – analyzed after ICV. **The ICB is not distilled with batch.** CCB – analyzed after every CCV. **The CCB is not distilled with batch. These are prepared from the 0.016 M Sulfuric Acid Solution.**

Table I

CALIBRATION AND STANDARDIZATION

Analytical Method Acceptance Criteria⇨ Calibration Measure ⇩	EPA 350.1 Frequency	Acceptance Criteria
Laboratory Control Spike and Duplicate	• One pair per batch of samples, up to 20 environmental samples, whichever is more frequent.	• Project Specific or • For water method specific 90 –110% and 20% RPD. • For soil 77-121% with 20% RPD.
Matrix Spike / Matrix Spike Duplicate (MS/MSD)	• One pair per batch of samples, up to 10 environmental samples, whichever is more frequent.	• Project Specific or • For water method specific 90 –110% with 20% RPD. • For soil 75-123% with 20% RPD.
Method Blank	• One per batch of samples, up to 20 environmental samples, whichever is more frequent.	• Project Specific or • Less than the EQL
Initial Calibration	• Analyzed daily before samples	• Correlation coefficient must be 0.995 or greater
Initial Calibration Verification (ICV)	• Analyzed after calibration but before samples	• Recovery must be between 90 – 110%
Initial Calibration Blank (ICB)	• Analyzed after ICV but before samples	• Project specific or • Less than EQL
Continuing Calibration Verification (CCV)	• Analyzed after every 10 samples	• Project specific or • Recovery between 90 – 110%
Continuing Calibration Blank (CCB)	• After each CCV.	• Project specific or • Less than EQL

TABLE J

PREPARATION OF REAGENTS

Standard	Alias	Final Concentration	Directions	Final Volume
Borate Buffer	Releasing Solution	0.55 M	Weigh 5 g of neat sodium borate ($Na_2B_4O_7$) into 964 g DI water. Add 22 g sodium hydroxide (NaOH). Shelf life = 1 year.	1000 ml
Sulfuric Acid Solution	Trapping Solution	0.016 M	Add 0.40 mL of concentrated sulfuric acid ~ 900 ml DI water. Dilute to volume. Shelf life = 1 year.	1000 ml
Sodium Phenolate	Reagent 1		Dissolve 88 mL of 88% liquefied phenol into ~ 600 ml DI water. Slowly add 32 g sodium hydroxide while stirring. Dilute to volume. PREPARE FRESH EVERY 3 TO 5 DAYS!	1000 ml
Sodium Hypochlorite Solution	Reagent 2		Dilute 250 ml of 5.25% sodium hypochlorite to mark with DI water. MAKE FRESH DAILY.	500 ml
Buffer	Reagent 3		Dissolve 50.0 g disodium ethylenediamine tetraacetate and 5.5 g sodium hydroxide in ~ 900 ml DI water. Dilute to volume. Shelf life = 1 month.	1000 ml
Sodium Nitroprusside Solution	Reagent 4		Dissolve 3.5 g sodium nitroprusside in ~ 900 ml DI water. Dilute to volume. Shelf life = 1 week.	1000 ml
Sodium Thiosulfate Solution	Dechlorinating Agent		Dissolve 3.5 g sodium thiosulfate in ~ 900 ml DI water. Dilute to volume. Shelf life = 1 year.	1000 ml
Sodium Hydroxide Solution	3 N	3 N	Dissolve 120 g sodium hydroxide in ~ 900 ml DI water. Dilute to volume. Shelf life = 1 year.	1000 ml

TABLE J2

PREPARATION OF STANDARDS

Standard	Alias	Final Concentration	Directions	Final Volume
Primary Stock Standard	Stock Standard	100 mg/L	Weigh 0.382 g of neat ammonium chloride into ~500 ml DI water. Dilute to volume. Shelf life = 1 year.	1000 ml
Secondary Stock Standard	Second Source Stock Standard	100 mg/L	Weigh 0.382 g of neat second source ammonium chloride into ~500 ml DI water. Dilute to volume. Shelf life = 1 year.	1000 ml
Level 1 Calibration Standard	Cal. Std. 1	20 mg/L	Pipette 20 ml of primary stock standard into 100 ml volumetric flask. Dilute to volume with 0.016 M Sulfuric Acid Solution. Prepare monthly.	100 ml
Level 2 Calibration Standard	Cal. Std. 2	8.0 mg/L	Pipette 8.0 ml of primary stock standard into 100 ml volumetric flask. Dilute to volume with 0.016 M Sulfuric Acid Solution. Prepare monthly.	100 ml
Level 3 Calibration Standard	Cal. Std. 3	4.0 mg/L	Pipette 4.0 ml of primary stock standard into 100 ml volumetric flask. Dilute to volume with 0.016 M Sulfuric Acid Solution. Prepare monthly.	100 ml
Level 4 Calibration Standard	Cal. Std. 4	2.0 mg/L	Pipette 2.0 ml of primary stock standard into 100 ml volumetric flask. Dilute to volume with 0.016 M Sulfuric Acid Solution. Prepare monthly.	100 ml
Level 5 Calibration Standard	Cal. Std. 5	1.0 mg/L	Pipette 1.0 ml of primary stock standard into 100 ml volumetric flask. Dilute to volume with 0.016 M Sulfuric Acid Solution. Prepare monthly.	100 ml
Level 6 Calibration Standard	Cal. Std. 6	0.50 mg/L	Pipette 0.50 ml of primary stock standard into 100 ml volumetric flask. Dilute to volume with 0.016 M Sulfuric Acid Solution. Prepare monthly.	100 ml
Level 7 Calibration Standard	Cal. Std. 7	0.25 mg/L	Pipette 0.25 ml of primary stock standard into 100 ml volumetric flask. Dilute to volume with 0.016 M Sulfuric Acid Solution. Prepare monthly.	100 ml
Level 8 Calibration Standard - Used also for ICB/CCB	Cal. Std. 8	0.0 mg/L	Pipette 0.0 ml of primary stock standard into 100 ml volumetric flask. Dilute to volume with 0.016 M Sulfuric Acid Solution. Prepare monthly.	100 ml
Initial Check Verification	ICV	10 mg/L	Pipette 10 ml of secondary stock standard into 100 ml volumetric flask. Dilute to volume with 0.016 M Sulfuric Acid Solution. Prepare daily.	100 ml
Continuing Check Verification	CCV	10 mg/L	Pipette 10 ml of primary stock standard into 100 ml volumetric flask. Dilute to volume with 0.016 M Sulfuric Acid Solution. Prepare daily.	100 ml
Matrix Spike/ Matrix Spike Duplicate	MS/MSD	10 mg/L	Pipette 0.6 ml of secondary stock standard into sample tubes. Add 6.0 ml of sample. Prepare daily.	6 ml
Laboratory Control Spike/ Laboratory Control Spike Duplicate	LCS/LCSD	10 mg/L	Pipette 0.6 ml of secondary stock standard into sample tubes. Add 6.0 ml of 0.016 M Sulfuric Acid Solution. Prepare daily.	6 ml

Table K
En Chem Initial Demonstration of Capability

Compound	Conc. mg/L	IDC-1 mg/L	IDC-2 mg/L	IDC-3 mg/L	IDC-4 mg/L	Average mg/L	% Recovery	SD
Ammonia	5.0	5.13	5.17	5.13	5.18	5.15	103.2	0.499

Table L

ANALYST/TECHNICIAN DATA ASSESSMENT

Analytical Method Acceptance Criteria⇨ Data Assessment Measure ⇩	Method Citation: EPA 350.1 If these conditions are not achieved ⇒
Method Blank	• 1
Accuracy & Precision Matrix Spike Samples	• 2
Accuracy & Precision Laboratory Control Spikes	• 3
Initial Calibration	• 4
Initial / Continuing Calibration Verification	• 5
Initial / Continuing Calibration Blank	• 6

1. In the absence of project specific requirements, sample detects less than 20 times the method blank contamination level is reported with the "A" data qualifier. Sample detects greater than 20 times the method blank contamination are reported without qualification.

2. In the absence of project specific or method requirements, in-house generated limits will be used. For undistilled samples if the concentration of the spike is less than 25% of the concentration of the parent, dilute parent to a level that the subsequent spike concentration will be greater than 25% the parent and so the parent concentration is above the EQL. Rerun the parent, MS, and MSD at this new dilution. If the MS and/or MSD fails at the diluted concentration, "N" flag the parent sample. If the parent, MS, or MSD is greater than the top standard in the curve, dilute and reanalyze the parent, MS, and MSD following the above guidance. If the concentration of the spike is greater than 25% of the concentration of the parent, "N" flag the parent sample if either the MS and/or MSD fails. For distilled samples, if the concentration of the spike is less than 25% of the concentration of the parent, no further action is needed unless the parent, MS or MSD concentrations are greater than the top standard in the calibration curve. If the parent, MS or MSD is greater than the top standard of the calibration curve, dilute the parent, MS, and MSD to concentrations that are within the curve. The MS and MSD recoveries do not need to be evaluated. If the concentration of the spike is greater than 25% of the concentration of the parent , "N" flag the parent sample if either the MS or MSD fails. If the MS and MSD fails precision control limits flag the parent with the "*" (precision) data qualifier. Generate a Non-Conformance Memo.

3. If sample volume does not allow re-analysis the entire prep/analytical batch of samples shall be flagged with the "&" (accuracy) and "*" (precision) qualifier to reflect the deficiencies. Generate a Non-Conformance Memo.

4. If correlation coefficient is less than 0.995 perform maintenance and recalibrate.

5. If ICV/CCV is outside the control limits reanalyze the ICV/CCV to verify the instrument is out of control. If the 2nd analysis is outside control limits, perform maintenance and recalibrate. Samples that bracket the out of control standards must be reanalyzed.

6. If ICB/CCB is outside the control limits reanalyze the ICB/CCB to verify the instrument is out of control. If the 2nd analysis is outside control limits, perform maintenance and recalibrate. Samples that bracket the out of control standards must be reanalyzed. Samples that are > 10X the concentration in the CCB the samples do not have to be reanalyzed.

Table M

REPORT REVIEWER/PROJECT MANAGEMENT DATA ASSESSMENT

Analytical Method Acceptance Criteria⇨ Data Assessment Measure ⇩	Method Citation EPA 350.1 If these conditions are not achieved ⇒
Holding Time Compliance	• 1
Sample Receipt Conditions and Preservation	• 2
Method Citation	• 3
Reasonableness: Field Duplicate	• 4
Reasonableness: Analytical Comments Qualifications	• 5

1. Flag results with the H data qualifier. The number of dates past hold is addressed in the comments section of the report. Dates past hold will be addressed in the case narrative for Level III and IV.

2. In prose describe the receipt conditions as they relate to the acceptance criteria list in Table G

3. Compare to regulatory program in QAPjP or Chain of Custody.

4. Are duplicates within 20% agreement? If not, internally flag for review.

5. Do related suites of tests agree or are reasonable.

Table N
DATA QUALIFIERS

Qualifier Codes

Flag	Applies To	Explanation
A	Inorganic	Analyte is detected in the method blank. Method blank criteria are evaluated to the laboratory method detection limit. Additionally, method blank acceptance may be based on project specific criteria or determined from analyte concentrations in the sample and are evaluated on a sample-by-sample basis.
B	Inorganic	The analyte has been detected between the method detection limit and the reporting limit.
B	Organic	Analyte is present in the method blank. Method blank criteria are evaluated to the laboratory method detection limit. Additionally, method blank acceptance may be based on project specific criteria or determined from analyte concentrations in the sample and are evaluated on a sample-by-sample basis.
C	All	Elevated detection limit.
D	All	Analyte value from diluted analysis or surrogate result not applicable due to sample dilution.
E	Inorganic	Estimated concentration due to matrix interferences. During the metals analysis using the inductively coupled plasma (ICP), the serial dilution failed to meet the established control limits of 0-10% and the sample concentration is greater than 50 times the IDL (100 times the IDL for analysis done on the ICP-MS). The result was flagged with the E qualifier to indicate that a physical interference was observed.
E	Organic	Analyte concentration exceeds calibration range.
F	Inorganic	Due to potential interferences for this analysis by Inductively Coupled Plasma techniques (SW-846 Method 6010), this analyte has been confirmed by and reported from an alternate method.
F	Organic	Surrogate results outside control criteria.
H	All	Preservation, extraction or analysis performed past holding time.
J	Inorganic	The analyte has been detected between the method detection limit and the reporting limit.
J	Organic	Concentration detected is greater than the method detection limit but less than the reporting limit.
K	Inorganic	Sample received unpreserved. Sample was either preserved at the time of receipt or at the time of sample preparation.
K	Organic	Detection limit may be elevated due to the presence of an un-requested analyte.
L	All	Elevated detection limit due to low sample volume.
N	All	Spiked sample recovery not within control limits.
P	Organic	The relative percent difference between the two columns for detected concentrations was greater than 40%.
Q	All	The analyte has been detected between the limit of detection (LOD) and limit of quantitation (LOQ). The results are qualified due to the uncertainty of analyte concentrations within this range.
S	Organic	The relative percent difference between quantitation and confirmation columns exceeds internal quality control criteria. Because the result is unconfirmed, it has been reported as a non-detect with an elevated detection limit.
U	All	The analyte was not detected at or above the reporting limit.
V	All	Sample received with headspace.
W	All	A second aliquot of sample was analyzed from a container with headspace.
X	All	See Sample Narrative.
&	All	Laboratory Control Spike recovery not within control limits.
*	All	Precision not within control limits.

<	All	The analyte was not detected at or above the reporting limit.
1	Inorganic	Dissolved analyte or filtered analyte greater than total analyte; analyses passed QC based on precision criteria.
2	Inorganic	Dissolved analyte or filtered analyte greater than total analyte; analyses failed QC based on precision criteria.
3	Inorganic	BOD result is estimated due to the BOD blank exceeding the allowable oxygen depletion.
4	Inorganic	BOD duplicate precision not within control limits. Due to the 48 hour holding time for this test, it is not practical to reanalyze and try to correct the deficiency.
5	Inorganic	BOD result is estimated due to insufficient oxygen depletion. Due to the 48 hour holding time for this test, it is not practical to reanalyze and try to correct the deficiency.
6	Inorganic	BOD laboratory control sample not within control limits. Due to the 48 hour holding time for this test, it is not practical to reanalyze and try to correct the deficiency.
7	Inorganic	BOD result is estimated due to complete oxygen depletion. Due to the 48 hour holding time for this test, it is not practical to reanalyze and try to correct the deficiency.

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STANDARD OPERATING PROCEDURE

Ion Chromatography

Referenced Methods:

EPA 300.0, SW-846 9056

SOP NUMBER:	GB-I-009-Rev.1
EFFECTIVE DATE:	Date of Final Signature
SUPERSEDES:	GB-I-009-Rev.0

APPROVAL

Nils Melberg, Laboratory Manager — Date: 2/22/06

Arthur F. Lautenbach, Quality Manager — Date: 2/22/2006

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1. Purpose

1.1 The purpose of this Standard Operating Procedure (SOP) is to provide a consistent procedure in the determination of Bromide, Fluoride, Chloride, Nitrite, Nitrate, and Sulfate ions using Ion Chromatograph following analytical methods EPA 300.0 and SW-846 9056.

2. Scope and Application

2.1 This method is used to determine Bromide, Fluoride, Chloride, Nitrite, Nitrate and Sulfate in drinking water, surface water, mixed domestic and industrial wastewaters, groundwater, reagent waters, soils, and leachates (when no acetic acid is used by use of an Ion Chromatograph.

2.2 Reporting Limits are used in the absence of Project or State Specific Required Detection Limits. Current MDL can be found in Conifer2K or in the Green Bay Wet Chemistry Method Detection limit Summary.

3. Summary of Method

3.1 A small volume of sample, typically 25-100µl, is introduced into an ion chromatograph. The anions of interest are separated and measured, using a system comprised of a guard column, analytical column, suppressor device and conductivity detector.

4. Interferences

4.1 Interferences can be caused by substances with retention times that are similar to and overlap those of the anion of interest. Large amounts of an anion can interfere with the peak resolution of an adjacent anion. Sample dilution and/or fortification can be used to solve most interference problems associated with retention times.

4.2 The water dip or negative peak that elutes near, and can interfere with, the fluoride peak can usually be eliminated by the addition of the equivalent of 1 mL of daily eluent to 5 mL of each standard and sample.

4.3 Method interferences may be caused by contaminants in the reagent water, reagents, glassware, and other sample processing apparatus that lead to discrete artifacts or elevated baseline in ion chromatograms.

4.4 Samples that contain particles larger than 0.45 microns and reagents solutions that contain particles larger than 0.20 microns require filtration to prevent damage to the instrument column or flow system.

4.5 Any anion that is not retained by the column or only slightly retained will elute in the area or fluoride and interfere. Known coelution is caused by carbonate and other small organic anions. At concentrations above 1.5 mg/L, this interference may not be significant, however, it is the responsibility of the user to generate precision and accuracy information in each sample matrix.

4.6 The acetate anion elutes early during the chromatographic run. The retention times of the anions also seem to differ when large amounts of acetates are present. Therefore, this method is not recommended for leachates of solid samples when acetic acid is used for pH adjustment.

4.7 The quantitation of unretained peaks should be avoided, such as low molecular weight organic acids, which are conductive and coelute with or near fluoride and would bias the fluoride quantitation in some drinking and most waste waters.

4.8 Any residual chlorine dioxide present in the sample will result in the formation of additional chlorite prior to analysis. If any concentration of chlorine dioxide is suspected in the sample purge the sample with an inert gas (argon or nitrogen) for about five minutes or until no chlorine dioxide remains.

5. Safety

5.1 The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable. Cautions are included for known extremely hazardous materials.

5.2 The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. Reference files of Material Safety Data Sheets (MSDS) are available to all personnel involved in the chemical analysis, and are located at the front desk. A formal safety plan has been prepared and is distributed to all personnel with documented training.

5.3 Required Safety Equipment is listed in Table A..

6. Definitions

6.1 Refer to Section 10 of the most current version of the Pace Quality Manual for the terms used at Pace Analytical.

7. Responsibilities and Distribution

7.1 Personnel

7.1.1 All personnel involved with sample preparation and analysis are responsible for adherence to this SOP. A controlled copy will be available for review and consultation within the area methods manual.

7.1.2 Personnel are responsible for ensuring that any deviations to this SOP are reported to the laboratory manager.

7.2 Laboratory Manager

7.2.1 The laboratory manager is responsible for ensuring adherence to this SOP and will receive a controlled copy of this SOP.

7.2.2 The laboratory manager is responsible for performing a biennial review of the SOP and reporting any required revisions to the Quality Assurance Office.

7.3 Quality Assurance Office

7.3.1 The QA Office is responsible for performing a biennial review of the SOP in conjunction with the purchasing department and revising as needed.

7.3.2 The QA Office is responsible for ensuring that all revisions to the SOP are implemented.

7.4 Revisions

7.4.1 This SOP will be reviewed on a biennial basis at a minimum, and any required revisions will be incorporated.

8. Sample Collection, Preservation and Handling

8.1 See Table G for a summary.

9. Equipment and Supplies

9.1 See Table B and Table C for a summary.

10. Reagents and Standards

10.1 See Table D and Table E for a summary.

11. Calibration

11.1 Perform calibration using the standards listed in Table F. For those anions exhibiting a linear calibration (bromide, chloride, fluoride, nitrite, nitrate and sulfate), these standards define the linear range for the analysis. The correlation coefficient must be 0.995 or greater. If correlation coefficient is less than 0.995 corrective action must be taken and re-calibration must occur before samples are analyzed.

11.2 See Table F for summary.

12. Procedure

12.1 Sample Preparation and Analysis.

12.1.1 Make fresh Eluent daily by diluting X100Eluent Concentrate (10mL to 1L or 20mL to 2L).

12.1.2 Fill Daily Eluent containers on IC's and container for samples. Place cap with eluent and helium lines and screw hand tight.

12.1.3 Switch IC to local mode; Turn on Eluent Pressure and Pump.

12.1.4 Open Waste Valve for about 10 seconds to get bubbles out of eluent lines.

12.1.5 Turn on SRS.

12.1.6 Flow setting is 1.30 mL/min. Wait for about 15 minutes for flow to stabilize, adjust if needed. Output conductivity will be close to 0 μS.

12.1.7 Check historical data for dilutions.

12.1.8 To prepare soils: Weigh 10 grams of soil into a specimen cup. Add 100 mL DI water. Sonicate or Stir on stir plate for 1 hour. Filter and/or centrifuge as appropriate. Dispose of soil residue as per Section 15.2.

12.1.9 Transfer 5 mL of sample to vial. Add 1 ml of Daily eluent to each vial. Place cap on the top of vial; shake cassettes and using sample insertion tool push cap into the vial.

12.1.10 Create schedule file for each instrument and save it as yymmddX, where yy-year, mm-month, dd-day and X-instrument. After last CCB enter sample "shutdown" with Method shutdown.met. It will turn of IC.

12.1.11 Click on first Data File field. Go up to *Data* folder and create new folder yymmddX. Open created folder and save file as yymmddX. Rename all other files on run. Sample ID's – everything in Capital letters.

12.1.12 Open RUN from Peak Net Main Menu, Select Instrument, Click on Load Schedule. Select schedule file., Push Hold/Run on Autosampler.

12.1.13 Sample vials are placed in Cassettes. Load them in Autosampler with black dots to the right. Press run/hold button of autosampler.

12.1.14 Once analytical run has completed, go to PeakNet main menu and open "Optimize".

12.1.15 Each sample produces it's own .dxd file with chromatograph and analytes amounts. Open each file in the optimize window, check and correct, if necessary, peak naming and void volumes. If necessary manual integration can be performed following procedures as described in SOP ALL-Q-016 "Manual integration". Note necessary dilutions.

12.1.16 Once all samples have been optimized, open "Batch" from PeakNet main menu. Open *EXPORT.bch* file, Select file to be printed and uploaded, Process batch. Type in name of upload file, e.g.: R:\WETCHEM\DATA\IC\OUTPUT\YYMMDD A or B.

12.1.17 Using IC program print results summary and upload results into Conifer 2K.

12.2 Calculations:

12.2.1 The instrument provides uncalculated (raw) sample results in mg/l. Raw results will be processed by IC program during result upload.

12.2.2 Liquid Calculation

Raw Data Value (mg/L) x Dilution Factor = Desired Anion (mg/L)

12.2.3 Soil Calculation

$$\frac{\text{Raw Data Value (mg/L) X Final Volume (L) X Dilution Factor X 1000g}}{\text{(Amount used (g) x \% Solids in decimal formX1Kg)}} = \text{Desired Anion (mg/Kg)}$$

12.2.4 Accuracy:

A matrix spike / matrix spike duplicate is analyzed for each analytical batch of 10 or fewer samples.

MS/MSD calculation:

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

SSR = Spike sample result
SR = Sample result
SA = Spike added

12.2.5 Precision:

The precision is calculated based on the concentration of the matrix spike / matrix spike duplicate result.

Relative percent difference (RPD) calculation:

$$\% \text{ RPD} = \frac{|MS-MSD| \times 100}{(MS+MSD)/2}$$

MS = Matrix spike value
MSD =Matrix spike duplicate Value

12.2.6 A Laboratory Control Sample (LCS) must be prepared and analyzed with every sample batch or every 20 samples whichever is more frequent. A LCS is reagent water, which has a known amount of analyte of interest added. A Laboratory Control Spike Duplicate (LCSD) must be analyzed if there is insufficient sample volume to perform a matrix spike/matrix spike duplicate or if the client requests one.

$$\% \text{ Recovery} = \frac{\text{Control Spike Result X 100}}{\text{Known concentration}}$$

If an LCS or/and LCSD fails, it can be rerun once. Rerun results needs to be associated with original bath.
If either the LCS or LCSD is outside the control limits all samples associated to the control spikes are flagged with the "&" data qualifier if the batch can not be rerun. If the precision fails, "*" flag all samples associated to the control spikes.

12.2.7 See Table I for summary of limits. Control limits of 90-110% is set by the method EPA 300.0.

13. Quality Control

13.1 See Table H for summary of Quality Control Measures. Current list of Data Qualifiers can be found in Conifer 2K. The following Quality control measures are in place:

13.1.1 **Method Blank** One per batch of samples, up to 20 environmental samples, whichever is more frequent. Method Specific or Less than the PRL. If analyte is detected in the method blank, method blank criteria is evaluated to the laboratory method detection limit. Additionally, method blank acceptance may be based on project specific criteria or determined from analyte concentrations in the sample and are evaluated on a sample by sample basis.

13.1.2 **Laboratory Control Spike and Duplicate**. One LCS per batch of samples, up to 20 environmental samples, whichever is more frequent. An LCSD is run per client request or when there is insufficient sample for MS/MSD. LCS/LCSD spike recoveries for all analytes of interest are 90 – 110 %.

13.1.3 **Matrix Spike / Matrix Spike Duplicate** One pair per batch of samples, up to 10 environmental samples, whichever is more frequent. The sample used for MS/MSD pair is either determined by the client or selected at random from client samples as sample volume allows. No field, filter, trip or equipment blanks can be used for MS/MSD. MS/MSD spike recoveries for all analytes of interest are 90 – 110 % (80-120% for soil samples).

13.1.4 **Initial Calibration** Minimum of 5 standards. Must be performed before samples are analyzed. Correlation coefficient must be greater than 0.995.

13.1.5 **Initial Calibration Verification (ICV)** - analyzed immediately after calibration; recovery 90 – 110% of true value.

13.1.6 **Continuing Calibration Verification (CCV)** - analyzed after every 10 samples; recovery 90 – 110% of true value.

13.1.7 **Initial Calibration Blank (ICB)** - analyzed after ICV. Method Specific or ± PRL depending on requirements.

13.1.8 **Continuing Calibration Blank (CCB)** - analyzed after every CCV. Method Specific or ±PRL depending on requirements.

13.1.9 For samples analyzed by method SW-846 9056 some additional requirements are in place:

13.1.9.1 The working calibration curve must be verified on each working day, or whenever the anion eluent strength is changed, and for every batch of samples. If the response or retention time for any analyte varies from the expected values by more than +/- 10%, the test must be repeated, using fresh calibration standards. If the results are still more than +/- 10%, an entirely new calibration curve must be prepared for that analyte.

13.1.9.2 After a stable baseline is obtained, inject a midrange standard. If the peak height deviates by more than 10% from that of the previous run, prepare fresh standards.

13.1.9.3 After every 10 injections, analyze a midrange calibration standard. If the instrument response has changed by more than 5%, recalibrate.

14. Method Performance

14.1 There are several requirements that must be met to insure that this procedure generates accurate and reliable data. A general outline of requirements has been summarized below. Further specifications may be found in the Laboratory Quality Manual and specific Standard Operating Procedures.

14.1.1 The analyst must read and understand this procedure with written documentation maintained in his/her training file.

14.1.2 An initial demonstration of capability (IDC) must be performed. A record of the IDC will be maintained in his/her file with written authorization from the Laboratory Manager and Quality Manager.

14.1.3 An annual minimum detection limit (MDL) study will be completed for this method and whenever there is a major change in personnel or equipment. The results are stored in the Quality Assurance Office.

15. Pollution Prevention and Waste Management

15.1 The quantity of chemicals purchased is based on expected usage during its shelf life and disposal cost of unused material. Actual reagent preparation volumes reflect anticipated usage and reagent stability.

15.2 The Environmental Protection Agency (USEPA) requires that laboratory waste management practice be conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are characterized and disposed of in an acceptable manner. For further information on waste management consult SOP ALL-S-002 *Waste Handling* and WI-S-001 *Regulated Soil Handling*.

16. References

SW-846 9056
EPA 300.0
40CFR Part 136
PASI Quality Manual, current revision

17. Tables, Diagrams, Flowcharts, Appendices, Addenda etc.

17.1 **FLOWCHART**

17.2 **TABLES**

18. Revisions

Revision Number	Reason for Change	Date
GB-I-009-Rev.0	Converted SOP to new corporate format. Added bromide and Soil information.	07Febl2005
GB-I-009-Rev.1	Added chapter "Purpose". Chapter "Matrices" in and "Detection limits" are incorporated in "Scope and Application". Updated "Safety". Updated "Definitions." Added "Responsibilities and Distribution" Updated "Procedures" Updated "Quality Control" Updated "Pollution Prevention and Waste Handling" Updated "Appendix B - Tables" Updated bromide, sulfate and Soil information. Updated ICV/CCV information. Added Procedure for selecting MS/MSD. Added 9056 CCV acceptance requirements.	21Febl2006

FLOWCHART

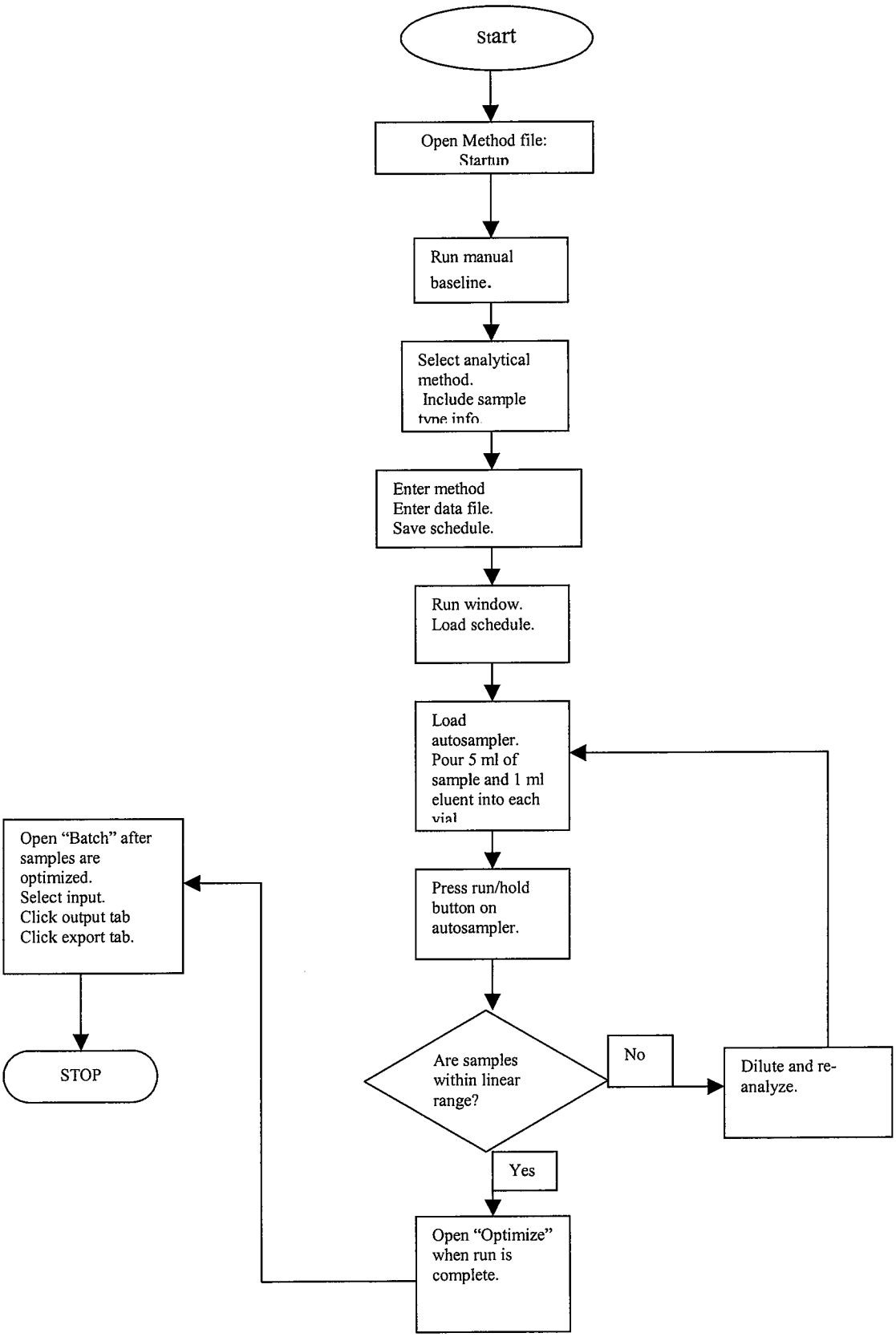
Start
Open Method file:
Startup
Run manual
baseline.
Select analytical
method.
Include sample
type info.
Enter method
Enter data file.
Save schedule.
Run window.
Load schedule.
Load
autosampler.
Pour 5 ml of
sample and 1 ml
eluent into each
vial
Press run/hold
button on
autosampler.
Are samples
within linear
range?
No
Dilute and re-
analyze.
Yes
Open "Optimize"
when run is
complete.
Open "Batch" after
samples are
optimized.
Select input.
Click output tab
Click export tab.
STOP

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Table A
REQUIRED SAFETY EQUIPMENT

Item:	Safety Apparel Description	Mandatory for Procedure	Optional
1	Safety Goggles or Glasses	√	
2	Lab Coat	√	
3	Gloves	√	
4	Face Shield		√

Table B
EQUIPMENT

Equipment	Manufacturer	Model(s)	Serial #	Date In Service
DX – 120 Ion Chromatograph	Dionex	DX-120	97040612	9/27/02
Automated Sampler	Dionex	AS40-1	97060050	9/27/02
DX – 120 Ion Chromatograph	Dionex	DX-120	98070244	2/19/03
Automated Sampler	Dionex	AS40-1	99080800	2/19/03
Stirplate				
Centrifuge				
Balance*	OHAUS	Analytical Plus	1113242960	--

* Or equivalent

Table C
SUPPLIES

Supplies	Manufacturer	Vendor	Catalog #
5.0 mL sample vials with Filter Caps	DIONEX	DIONEX	038141
5.0 mL sample vials	DIONEX	DIONEX	038008
Filter Caps for 5 ml Vial	DIONEX	DIONEX	038009
Stir Bar	N/a	N/a	N/a
Specimen Cups *	Fisher Scientific	Fisher Scientific	
Syringe, 10mL, Disposable (Pack of 20) *	DB	Fisher Scientific	14-829-22A
0.45μm Filter*	Enviromental Express	Enviromental Express	SF045N
50 mL Disposable PP Beaker*	Fisher Scientific	Fisher Scientific	01-291-10
100 – 5000 µL Pipetter, Variable Volume*	Gilson	VWR	40000-210
1000 µL Pipet, Fixed Volume*	Labsystems	Fisher Scientific	21-377-111K
500 µL Pipet, Fixed Volume*	Labsystems	Fisher Scientific	21-377-111J
250 µL Pipet, Fixed Volume*	Labsystems	Fisher Scientific	21-377-111H
200 µL Pipet, Fixed Volume*	Labsystems	Fisher Scientific	21-377-111G
100 µL Pipet, Fixed Volume*	Labsystems	Fisher Scientific	21-377-111F
50 µL Pipet, Fixed Volume*	Labsystems	Fisher Scientific	21-377-111E

* Or equivalent

Table D
REAGENTS

Reagent	Conc.	Acronym	Manufacturer	Catalog #	Directions found in:
Deionized water		Millipore Water			
Sodium Bromide (NaBr)	Neat	Bromide Stock Standard	Fisher Scientific	S255-500	
Sodium Fluoride (NaF)	Neat	Fluoride Stock Standard	Fisher Scientific	S299-100	
Sodium Chloride (NaCl)	Neat	Chloride Stock Standard	Fisher Scientific	S271-500	
Sodium Nitrite ($NaNO_2$)	Neat	Nitrite Stock Standard	Fisher Scientific	S347-250	
Sodium Nitrate ($NaNO_3$)	Neat	Nitrate Stock Standard	Fisher Scientific	S343-500	
Potassium Sulfate (K_2SO_4)	Neat	Sulfate Stock Standard	Fisher Scientific	S304-500	
Sodium Bromide (NaBr)*	Neat	Bromide Second Source Stock Standard	Fisher Scientific	S255-500	
Sodium Fluoride (NaF)*	Neat	Fluoride Second Source Stock Standard	Fisher Scientific	S299-100	
Sodium Chloride (NaCl)*	Neat	Chloride Second Source Stock Standard	Fisher Scientific	S271-500	
Sodium Nitrite ($NaNO_2$)*	Neat	Nitrite Second Source Stock Standard	Fisher Scientific	S347-250	
Sodium Nitrate ($NaNO_3$)*	Neat	Nitrate Second Source Stock Standard	Fisher Scientific	S343-500	
Potassium Sulfate (K_2SO_4)*	Neat	Sulfate Second Source Stock Standard	Fisher Scientific	S304-500	
Br CAL/CCV 1000	1000 mg/L Br	Calibration and CCV Standard			Table J
Br ICV/SPK 1000	1000 mg/L Br	ICV and Spike Standard			Table J
CAL/CCV 2000	Per Anion, F, Cl, NO_2, NO_3, SO_4	Calibration and CCV Standard			Table J
ICV/SPK 2000	Per Anion, F, Cl, NO_2, NO_3, SO_4	ICV and Spike Standard			Table J
Sodium Carbonate (Na_2CO_3)	Neat		Fisher Scientific	S263-500	
Sodium Bicarbonate ($NaHCO_3$)	Neat		Fisher Scientific	S233-500	
100x Eluent Concentrate	0.500 M Na_2CO_3 0.125 M $NaHCO_3$	Eluent Concentrate			Table J
Eluent	5.00 mM Na_2CO_3 1.25 mM $NaHCO_3$	Daily Eluent			Table J

* Must be from different Lot # than Stock Standard

Table E
STANDARDS

Standard	Concentration	Direction found in Section:	Acronym
Calibration and Continuing Calibration Verification Stock Standard	200 mg/L F, 2000 mg/L Cl, 80 mg/L NO_2, 160 mg/L NO_3, 1600 mg/L SO_4	Table J	CAL/CCV 2000
Initial Calibration Verification and Spike Stock Standard	200 mg/L F, 2000 mg/L Cl, 80 mg/L NO_2, 160 mg/L NO_3 1600 mg/L SO_4	Table J	ICV/SPK 2000
Calibration and Continuing Calibration Verification Stock Standard	1000 mg/L Br	Table J	Br CAL/CCV 1000
Initial Calibration Verification and Spike Stock Standard	1000 mg/L Br	Table J	Br ICV/SPK 1000
Level 1 Calibration Standard	0.25 mg/L F, 2.5 mg/L Cl, 0.25 mg/L Br, 0.1 mg/L NO_2, 0.2 mg/L NO_3, 2 mg/L SO_4	Table J	CCS2.5
Level 2 Calibration Standard	0.5 mg/L F, 5 mg/L Cl, 0.5 mg/L Br, 0.2 mg/L NO_2, 0.4 mg/L NO_3, 4 mg/L SO_4	Table J	CCS5
Level 3 Calibration Standard	1 mg/L F, 10 mg/L Cl, 1 mg/L Br, 0.4 mg/L NO_2, 0.8 mg/L NO_3, 8 mg/L SO_4	Table J	CCS10
Level 4 Calibration Standard	2 mg/L F, 20 mg/L Cl, 2 mg/L Br, 0.8 mg/L NO_2, 1.6 mg/L NO_3, 16 mg/L SO_4	Table J	CCS20
Level 5 Calibration Standard	4 mg/L F, 40 mg/L Cl, 4 mg/L Br, 1.6 mg/L NO_2, 3.2 mg/L NO_3, 32 mg/L SO_4	Table J	CCS40
Level 6 Calibration Standard	6 mg/L F, 60 mg/L Cl, 6 mg/L Br, 2.4 mg/L NO_2, 4.8 mg/L NO_3, 48 mg/L SO_4	Table J	CCS60
Level 7 Calibration Standard	8 mg/L F, 80 mg/L Cl, 8 mg/L Br, 3.2 mg/L NO_2, 6.4 mg/L NO_3, 64 mg/L SO_4	Table J	CCS80
Level 8 Calibration Standard	10 mg/L F, 100 mg/L Cl, 10 mg/L Br, 4.0 mg/L NO_2, 8.0 mg/L NO_3, 80 mg/L SO_4	Table J	CCS100
Initial Calibration Verification Standard	5 mg/L F, 50 mg/L Cl, 5 mg/L Br, 2 mg/L NO_2, 4 mg/L NO_3,40 mg/L SO_4	Table J	ICV 50
Continuing Calibration Verification Standard	5 mg/L F, 50 mg/L Cl, 5 mg/L Br, 2 mg/L NO_2, 4 mg/L NO_3, 40 mg/L SO_4	Table J	CCV 50

Table F
CALIBRATION STANDARD CONCENTRATIONS

Component Name / Level	Bromide (mg/L)	Fluoride (mg/L)	Chloride (mg/L)	Nitrite (mg/L)	Nitrate (mg/L)	Sulfate (mg/L)
8	10	10	100	4	8	80
7	8	8	80	3.2	6.4	64
6	6	6	60	2.4	4.8	48
5	4	4	40	1.6	3.2	32
4	2	2	20	0.8	1.6	16
3	1	1	10	0.4	0.8	8
2	0.5	0.5	5	0.2	0.4	4
1	0.25	0.25	2.5	0.1	0.2	2

Table G
SAMPLE COLLECTION, PRESERVATION, HOLD TIME SHIPMENT AND STORAGE

Matrix	Analytical Method	Container(s)	Preservation / Hold Time	Shipment Conditions	Lab Storage Conditions
Aqueous	EPA 300.0 SW-846 9056	Clean Plastic or glass containers	None / 48 hrs – NO_2, NO_3 28 days – Br, Cl, F, SO_4	On ice 4+/- 2° Celsius	Walk-in cooler 4± 2° C
Soils	EPA M300.0	Clean Plastic or glass containers	None / After extraction: 48 hrs – NO_2, NO_3 28 days – Br, Cl, F, SO_4	On ice 4+/- 2° Celsius	Walk-in cooler 4± 2° C

Table H
QUALITY CONTROL

Quality Control Measure	Requirements
Method Blank	One per batch of samples, up to 20 environmental samples, whichever is more frequent.
Laboratory Control Spike and Duplicate	One LCS per batch of samples, up to 20 environmental samples, whichever is more frequent. An LCSD is run per client request or when there is insufficient sample for MS/MSD.
Matrix Spike / Matrix Spike Duplicate	One pair per batch of samples, up to 10 environmental samples, whichever is more frequent. The sample used for MS/MSD pair is either determined by the client or selected at random from client samples as sample volume allows. No field, filter, trip or equipment blanks can be used for MS/MSD. MS/MSD spike recoveries for all analytes of interest are 90 – 110 % (80-120% for soil samples).
Initial Calibration	Minimum of 5 standards. Must be performed before samples are analyzed. Correlation coefficient must be greater than 0.995
Calibration Verification (ICV/CCV)	ICV - analyzed immediately after calibration. CCV - analyzed after every 10 samples.
Calibration Blank (ICB/CCB)	ICB - analyzed after ICV. CCB - analyzed after every CCV.

Table I
CALIBRATION AND STANDARDIZATION

Calibration Measure	Frequency	Acceptance Criteria
Laboratory Control Spike and Duplicate	• One pair per batch of samples, up to 20 environmental samples, whichever is more frequent.	• 90-110%, RPD 20 (80-120%, RPD 20 for soils)
Matrix Spike / Matrix Spike Duplicate	• One pair per batch of samples, up to 10 environmental samples, whichever is more frequent.	• 90-110%, RPD 20 (80-120%, RPD 20 for soils)
Method Blank	• One per batch of samples, up to 20 environmental samples, whichever is more frequent.	• Method Specific or Less than the PRL
Initial Calibration	• Before analysis of samples	• Correlation coefficient must be greater than 0.995.
Initial Calibration Verification (ICV)	• After initial calibration and before samples	• 90 – 110% of true value
Initial Calibration Blank	• After ICV and before samples	• ± PRL
Continuing Calibration Verification	• After 10 samples	• 90 – 110 % of true value (EPA 300.0) • For SW-846 9056, see footnotes
Continuing Calibration Blank	• After CCV	• ± PRL

For samples analyzed by method SW-846 9056 some additional requirements are in place:
The working calibration curve must be verified on each working day, or whenever the anion eluent strength is changed, and for every batch of samples. If the response or retention time for any analyte varies from the expected values by more than +/- 10%, the test must be repeated, using fresh calibration standards. If the results are still more than +/- 10%, an entirely new calibration curve must be prepared for that analyte.
After a stable baseline is obtained, inject a midrange standard. If the peak height deviates by more than 10% from that of the previous run, prepare fresh standards.
After every 10 injections, analyze a midrange calibration standard. If the instrument response has changed by more than 5%, recalibrate.

Table J
PREPARATION OF STANDARDS AND REAGENTS

Standard	Acronym	Concentration	Directions	Final Volume
CAL/CCV 2000	Calibration and CCV Stock Standard	200 mg/L F, 2000 mg/L Cl, 80 mg/L NO_2, 160 mg/L NO_3 1600 mg/L SO_4	0.4420 g of NaF, 3.2970 g of NaCl, 0.3940 g of NaNO2, 0.9708 g og NaNO3, and 2.9026 g of K2SO4 Stock Standards into DI water.	1000 ml
ICV/SPK 2000	ICV and Spike Stock Standard	200 mg/L F, 2000 mg/L Cl, 80 mg/L NO_2, 160 mg/L NO_3 1600 mg/L SO_4	0.4420 g of NaF, 3.2970 g of NaCl, 0.3940 g of NaNO2, 0.9708 g og NaNO3, and 2.9026 g of K2SO4 Second Source Stock Standards into DI water.	1000 ml
Br CAL/CCV 1000	Calibration and CCV Stock Standard	1000 mg/L Br	1.2875 g of NaBr Stock Standards into DI water.	1000 ml
Br ICV/SPK 1000	ICV and Spike Stock Standard	1000 mg/L Br	1.2875 g of NaBr Second Source Stock Standards into DI water.	1000 ml
ICV 50	ICV	5 mg/L F, 50 mg/L Cl, 2 mg/L NO_2, 4 mg/L NO_3 40 mg/L SO_4, 5 mg/L Br	5.0 mL of ICV/SPK 2000 and 1.0 mL of Br ICV/SPK 1000 diluted into DI water.	200 ml
CCV 50	CCV	5 mg/L F, 50 mg/L Cl, 2 mg/L NO_2, 4 mg/L NO_3 40 mg/L SO_4, 5 mg/L Br	5.0 mL of CAL/CCV 2000 and 1.0 mL of Br CAL/CCV 1000 diluted into DI water.	200 ml
LCS/LCSD	Laboratory Control Spike/ Laboratory Control Spike Duplicate	2 mg/L F, 20 mg/L Cl, 0.8 mg/L NO_2, 1.6 mg/L NO_3 16 mg/L SO_4	0.05 mL of ICV/SPK 2000 added to 4.95 mL of DI Water	5.0 mL
MS/MSD	Matrix Spike/ Matrix Spike Duplicate	2 mg/L F, 20 mg/L Cl, 0.8 mg/L NO_2, 1.6 mg/L NO_3 16 mg/L SO_4	0.05 mL of ICV/SPK 2000 added to 4.95 mL of Sample	5.0 mL
LCS/LCSD	Laboratory Control Spike/ Laboratory Control Spike Duplicate	2 mg/L Br	0.1 mL of BR ICV/SPK 1000 added to 4.9 mL of DI Water	5.0 mL
MS/MSD	Matrix Spike/ Matrix Spike Duplicate	2 mg/L Br	0.1 mL of BR ICV/SPK 1000 added to 4.9 mL of Sample	5.0 mL
CCS100	Level 8	10 mg/L F, 100 mg/L Cl, 4.0 mg/L NO_2, 8.0 mg/L NO_3 80 mg/L SO_4, 10 mg/L Br.	5 mL of CAL/CCV 2000 and 1.0 mL of Br CAL/CCV 1000 in DI water	100 mL
CCS80	Level 7	8 mg/L F, 80 mg/L Cl, 3.2 mg/L NO_2, 6.4 mg/L NO_3 64 mg/L SO_4, 8 mg/L Br	4 mL of CAL/CCV 2000 and 0.8 mL of Br CAL/CCV 1000 in DI water	100 mL
CCS60	Level 6	6 mg/L F, 60 mg/L Cl, 2.4 mg/L NO_2, 4.8 mg/L NO_3 48 mg/L SO_4, 6 mg/L Br	3 mL of CAL/CCV 2000 and 0.6 mL of Br CAL/CCV 1000 in DI water	100 mL
CCS40	Level 5	4 mg/L F, 40 mg/L Cl, 1.6 mg/L NO_2, 3.2 mg/L NO_3 32 mg/L SO_4, 4 mg/L Br	2 mL of CAL/CCV and 0.4 mL of Br CAL/CCV 1000 2000 in DI water	100 mL
CCS20	Level 4	2 mg/L F, 20 mg/L Cl, 0.8 mg/L NO_2, 1.6 mg/L NO_3 16 mg/L SO_4, 2 mg/L Br	1 mL of CAL/CCV and 0.2 mL of Br CAL/CCV 1000 2000 in DI water	100 mL
CCS10	Level 3	1 mg/L F, 10 mg/L Cl, 0.4 mg/L NO_2, 0.8 mg/L NO_3 8 mg/L SO_4, 1 mg/L Br	0.5 mL of CAL/CCV 2000 and 0.1 mL of Br CAL/CCV 1000 in DI water	100 mL
CCS5	Level 2	0.5 mg/L F, 5 mg/L Cl, 0.2 mg/L NO_2, 0.4 mg/L NO_3 4 mg/L SO_4, 0.5 mg/L Br	0.25 mL of CAL/CCV 2000 and 0.05 mL of Br CAL/CCV 1000 in DI water	100 mL
CCS2.5	Level 1	0.25 mg/L F, 2.5 mg/L Cl, 0.1 mg/L NO_2, 0.2 mg/L NO_3 2 mg/L SO_4, 0.25 mg/L Br	0.25 mL of CAL/CCV 2000 and 0.05 mL of Br CAL/CCV 1000 in DI water	200 mL
Eluent	Daily Eluent	5.00 mM Na_2CO_3 1.25 mM $NaHCO_3$	10 mL 100x Eluent Concentrate diluted in DI water	1000 ml

Table K
ANALYST/TECHNICIAN DATA ASSESSMENT

Data Assessment Measure	If these conditions are not achieved
Method Blank	• 1
Accuracy & Precision Matrix Spike Samples	• 2
Accuracy & Precision Laboratory Control Spikes	• 3
Initial Calibration	• 4
Initial / Continuing Calibration Verification	• 5
Initial / Continuing Calibration Blank	• 6

1. In the absence of project specific requirements, sample detects less than 20 times the method blank contamination level is reported with the "A" data qualifier. Sample detects greater than 20 times the method blank contamination are reported without qualification.

2. In the absence of project specific or method requirements, in-house generated limits will be used. If the concentration of the spike is less than 25% of the concentration of the parent, no further action is needed unless the parent, MS or MSD concentrations are greater than the top standard in the calibration curve. If the parent, MS or MSD is greater than the top standard of the calibration curve, dilute the parent, MS, and MSD to concentrations that are within the curve. The MS and MSD recoveries do not need to be evaluated. If the concentration of the spike is greater than 25% of the concentration of the parent, "N" flag the parent sample if either the MS or MSD fails. If the MS and MSD fails precision control limits flag the parent with the "*" (precision) data qualifier. Generate a Non-Conformance Memo.

3. If sample volume does not allow re-analysis the entire prep/analytical batch of samples shall be flagged with the "&" (accuracy) and "*" (precision) qualifier to reflect the deficiencies. Generate a Non-Conformance Memo.

4. If correlation coefficient is less than 0.995 perform maintenance and recalibrate.

5. If ICV/CCV is outside the control limits reanalyze the ICV/CCV to verify the instrument is out of control. If the 2nd analysis is outside control limits, perform maintenance and recalibrate. Samples that bracket the out of control standards must be reanalyzed.

6. If ICB/CCB is outside the control limits reanalyze the ICB/CCB to verify the instrument is out of control. If the 2nd analysis is outside control limits, perform maintenance and recalibrate. Samples that bracket the out of control standards must be reanalyzed. Samples that are > 10X the concentration in the CCB the samples do not have to be reanalyzed.

Table L
REPORT REVIEWER/PROJECT MANAGEMENT DATA ASSESSMENT

Analytical Method Acceptance Criteria⇨ Data Assessment Measure ⇩	Method Citation EPA If these conditions are not achieved ⇒	Method Citation SW 846 If these conditions are not achieved ⇒
Holding Time Compliance	• 1	• 1
Sample Receipt Conditions and Preservation	• 2	• 2
Method Citation	• 3	• 3
Reasonableness: Field Duplicate	• 4	• 4
Reasonableness: Analytical Comment Qualifications	• 5	• 5

1. Flag results with the H data qualifier. The number of dates past hold is addressed in the comments section of the report. Dates past hold will be addressed in the case narrative for Level III and IV.

2. In prose describe the receipt conditions as they relate to the acceptance criteria list in Table G

3. Compare to regulatory program in QAPjP or Chain of Custody.

4. Are duplicates within limits of method citation? If not, internally flag for review.

5. Do related suites of tests agree or are reasonable.

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STANDARD OPERATING PROCEDURE

Total Sulfide, Iodometric Titration

Reference Methods: EPA 376.1, SW846 9034

SOP NUMBER:	GB-I-001-Rev.2
EFFECTIVE DATE:	Date of Final Signature
SUPERSEDES:	GB-I-001-Rev. 1

APPROVAL

Nils Melberg, Laboratory Manager — Date 4/14/06

Arthur F. Lautenbach, Quality Manager — Date 4/13/06

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1. Purpose

1.1 The purpose of this SOP is to determine the concentration of sulfide in potable and surface waters, domestic and industrial wastewaters, and saline waters as delineated in Method SW-846 9034 and EPA Method 376.1.

2. Scope and Application

2.1 This method determines sulfide in waters and wastewaters. The current MDL and PRL can be found in Conifer2K or in the Green Bay Wet Chemistry Method Detection Limit Summary.

3. Summary of Method

3.1 Iodine reacts with sulfide in an acid solution, oxidizing it to sulfur. A titration based on this reaction is an accurate method for determining sulfide at concentrations above the current MDL if interferences are absent and if loss of H_2S is avoided. The iodometric method is suitable for analyzing samples freshly taken from wells or springs. The method can be used for wastewater and partly oxidized water from sulfur springs if interfering substances are removed by precipitation.

4. Interferences

4.1 Sulfur reducing substances that decompose in acid, including thiosulfate, sulfite, and various organic compounds, interfere with the iodometric titration. Volatile iodine consuming substances will give high results. Most interference can be removed by the addition of zinc acetate and sodium hydroxide, which precipitates sulfide as zinc sulfide (ZnS).

5. Safety

5.1 Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable. Cautions are included for known extremely hazardous materials.

5.2 A reference file of Material Safety Data Sheets (MSDS) is made available to all personnel involved in the chemical analysis, and is located at the front desk. A formal safety plan has been prepared and is distributed to all personnel with documented training.

5.3 Analysts should take necessary safety precautions when handling chemicals and samples. Proper personal protective equipment may include safety gloves, lab coats, and safety glasses or goggles. Analysts should be familiar with the MSDS sheets for all chemicals and reagents they use for this procedure and the location of the MSDS sheets within the laboratory. Any questions or concerns should be taken to the laboratory Chemical Hygiene/Safety Officer.

6. Definitions

6.1 **Batch** – A grouping of 20 environmental samples, or less, or similar matrix which are prepared and/or analyzed together with the same method.

6.2 **Duplicate Sample** – A second aliquot of the same environmental sample analyzed in the same manner as the original sample in order to evaluate precision.

6.3 **Environmental Sample** – An environmental sample or field sample is a representative sample of any material (aqueous, non-aqueous, or multimedia) collected from any source for which determination of composition or contamination is requested or required.

6.4 **Laboratory Information Management System (LIMS)** – A system for transferring, processing, storing, and reporting analytical results. The Pace Analytical Services, Inc. Green Bay Laboratory's LIMS is named Conifer.

6.5 **Replicate Samples** – Samples collected at the same time, from the same place, for the same analysis, as the original sample in order to determine precision between samples.

6.6 **Pace Reporting Limit (PRL)** – The lowest level that will be reported by this method. Reporting limits are corrected for sample amounts, including the dry weight of solids, unless otherwise specified.

6.7 **Aqueous** – matrix such as water, ground water, surface water, drinking water, and aqueous samples with less than 10% settleable solids.

6.8 Refer to Section 10 of the Pace Quality Manual for additional terms used in this SOP.

7. Responsibilities and Distribution

7.1 Personnel

7.1.1 All personnel involved with sample preparation and analysis are responsible for adherence to this SOP. A controlled copy will be available for review and consultation within the area methods manual.

7.1.2 Personnel are responsible for ensuring that any deviations to this SOP are reported to the laboratory manager.

7.2 Laboratory Manager

7.2.1 The laboratory manager is responsible for ensuring adherence to this SOP and will receive a controlled copy of this SOP.

7.2.2 The laboratory manager is responsible for performing a biennial review of the SOP and reporting any required revisions to the Quality Assurance Office.

7.3 Quality Assurance Office

7.3.1 The QA Office is responsible for performing a biennial review of the SOP in conjunction with the purchasing department and revising as needed.

7.3.2 The QA Office is responsible for ensuring that all revisions to the SOP are implemented.

7.4 Revisions

7.4.1 This SOP will be reviewed on a biennial basis at a minimum, and any required revisions would be incorporated.

8. Sample Collection, Preservation and Handling

8.1 Samples should be collected, with minimum aeration, in glass or polyethylene bottles. If the analysis is not started immediately, the sample should be preserved with 2 mL zinc acetate and NaOH to pH > 9 and refrigerated at 4 ± 2°C. When preserved, the maximum holding time is 7 days. Samples analyzed after 7 days of collections must be qualified with the "H" qualifier.

9. Equipment and Supplies

9.1 Volumetric flasks (various Class A).

9.2 Volumetric pipettes (various Class A).

9.3 Mechanical pipettes, various sizes.

9.4 Analytical balance.

9.5 Magnetic stir plate.

9.6 Micro burette, 10 mL, class A.

9.7 Erlenmeyer flasks, 500 mL.

9.8 Suction filtration apparatus including a vacuum pump and a Buchner funnel.

9.9 Glass microfiber, Ahlstrom Grade 151 or equivalent.

9.10 Miscellaneous laboratory glassware.

10. Reagents and Standards

10.1 DI water

10.2 Hydrochloric acid, 6N - Slowly add 500 mL of concentrated hydrochloric acid, HCl, to 500 mL DI water in a 1000 mL beaker. Store at room temperature in a plastic or glass container. Expires in 6 months.

10.3 Standard Iodine solution, 0.0250 N -Purchased premade. Store at room temperature. Expires as specified by manufacturer or 5 years from received date – whichever is earlier.

10.4 Standardizing Sodium thiosulfate solution, 0.0250 N - Purchased premade. Expires as specified by manufacturer. Store at room temperature in a glass or plastic container. Expires as per the manufacturer or 5 years from received date – whichever is earlier.

10.5 Standard Sulfide Solution – Primary Source, 500 mg/L - Dissolve 2.01g sodium sulfide, $Na_2S{\bullet}9H_2O$, in a 500 ml volumetric flask containing about 400 ml of DI water. Dilute to volume. Store at room temperature in a glass or plastic container. Expires in 1 day.

10.6 Standard Sulfide Solution - Second Source, 500 mg/L - Dissolve 2.01g sodium sulfide, $Na_2S{\bullet}9H_2O$, in a 500 ml volumetric flask containing about 400 ml of DI water. Dilute to volume. Store at room temperature in a glass or plastic container. Expires in 1 day.

10.7 Starch indicator. Dissolve 2.0 g salicylic acid and 2.0 g soluble starch into 100 ml hot D.I. water. Store at room temperature. Expires at one year.

11. Calibration

11.1 Not Applicable.

12. Procedure

12.1 Set up run on benchsheet (See Attachment I).

12.2 If the sample was pretreated with zinc acetate, filter 200 mL of sample through a glass fiber filter into a waste flask. Retain the fiber filter.

12.3 Pipet 5.0 mL of standard iodine solution into a clean 500 mL Erlenmeyer flask.

12.4 Add 2 mL of 6N HCl.

12.5 Add about 100 mL of DI water along with the fiber filter to the flask.

12.6 If the sample was not pretreated, add 200 mL of the sample and precipitate to the flask.

12.7 If the iodine color disappears, add more iodine, in increments of 5.0 mL, so that the color remains. Record the total volume of iodine on the benchsheet if other than 5mL.

12.8 Titrate with purchased standardized sodium thiosulfate solution to a light straw color. Add a few (typically three) drops of starch solution and continue the titration until the blue color disappears.

12.9 Calculation

12.9.1 One milliliter 0.0250N iodine solution reacts with 0.4 mg S^{-2}

$$\text{mg } S^{-2}/L = \frac{[\,(A \times B) - (C \times D)\,]}{\text{ml sample}} \times 16000$$

Where:

A	=	ml iodine solution
B	=	normality of iodine solution
C	=	ml Na S_2O3 solution
D	=	normality of NaS_2O_2 solution

13. Quality Control

13.1 Control Samples

13.1.1 Calibration Verification Standard (CVS)

13.1.1.1 Prepare a CVS (Primary Source) by pipetting 10 mL of Standard Sulfide Solution – Primary Source, into a clean 100 mL Class A volumetric flask and diluting to volume with reagent water. Transfer to a 500 mL Erlenmeyer flask and analyze per Section 12.2. True value of this CVS is approximately 50 mg/L. The determined CVS concentrated is used as the true value for the ICV, and MS/MSD.

13.1.2 Initial Calibration Verification

13.1.2.1 Prepare an ICV by pipetting 10 mL of Standard Sulfide Solution – Second Source, into a clean 100 mL Class A volumetric flask and diluting to volume with reagent water. Transfer to a 500 mL Erlenmeyer flask and analyze per Section 12.2. True value of ICV is approximately 50 mg/L.

13.1.2.2 The ICV is analyzed to verify that the titration procedure is accurate. The result must be ±10% of the calculated value. If not, the analysis must be terminated, the problem corrected, and the calibration reverified.

13.1.3 Laboratory Control Sample (LCS)

13.1.3.1 Prepare an LCS by pipetting 10 mL of Standard Sulfide Solution – Second Source, into a clean 100 mL Class A volumetric flask and diluting to volume with reagent water. The LCS can also be purchase directly from vendor. Transfer to a 500 mL Erlenmeyer flask and analyze per Section 12.2. True value of a internally made LCS is approximately 50 mg/L. If purchased from vendor, the true value is the value assigned by vendor.

13.1.3.2 The LCS is analyzed to verify that the titration procedure is accurate. The result must be ±20% of the calculated value. If not, the analysis must be terminated, the problem corrected, and the calibration reverified. It is necessary to analyze a LCSD only per client/project requirement.

13.1.4 Method Blank (MB)

13.1.4.1 A MB must be analyzed immediately after ICV.

13.1.4.2 The MB must be less than the PRL. If between PRL and EQL, the data is "A" footnoted.

13.1.5 Matrix Spike/ Matrix Spike Duplicate Analysis (MS/MSD)

13.1.5.1 The spike sample analysis is designed to provide information about the effect of the sample matrix on the measurement procedures. The MS/MSD spikes are performed at a minimum frequency of 5%. Samples identified as field blanks cannot be used for spike sample analysis. The sample used for MS/MSD pair is either determined by the client or selected at random from client samples as sample volume allows.

13.1.5.2 The MS/MSD spikes are added to the sample by pipetting 10 mL of the 500 mg/L Sulfide Standard Solution – Second Source directly into 100 mL Class A volumetric flasks and diluting to volume with 90 mL of sample. Transfer to 500 mL Erlenmeyer flasks and analyze per Section 12.2. True value is approximately 50 mg/L.

13.1.5.3 MS/MSD recovery is calculated as follows:

$$\% \text{ Recovery} = \frac{(SSR - (SR(9/10)))}{SA}$$

Where SSR = Spike sample result, mg/L
SR = Sample result, mg/L
SA = Spike added, mg/L

When the sample concentration is less than the MDL, use SR = 0 for the purpose of calculating spike recovery. The control limits for MS/MSD recovery is 80 – 120%.

13.1.5.4 The relative percent difference (RPD) is calculated as:

$$RPD = \frac{[MS-MSD](100)}{(MS + MSD)/2}$$

Where: MS = Matrix Spike sample value, mg/L
MSD = Matrix Spike Duplicate sample value, mg/L

The control limit for duplicate analysis is <20%.

13.2 Documentation

13.2.1 Calculate results using an electronic spreadsheet. See Attachment II for an example. Report sample results to two significant.

14. Method Performance

14.1 There are several requirements that must be met to insure that this procedure generates accurate and reliable data. A general outline of requirements has been summarized below. Further specifications may be found in the Laboratory Quality Manual.

14.1.1 The analyst must read and understand this procedure with written documentation maintained in his/her training file.

14.1.2 An initial demonstration of capability (IDC) must be performed per ALL-Q-020, *Training Procedures*. A record of the IDC will be maintained in his/her QA file with written authorization from the Laboratory Manager and Quality Manager.

14.1.3 An annual method detection limit (MDL) study will be completed per ALL-Q-004, *Method Detection Limit Studies*, for this method and whenever there is a major change in personnel or equipment. The results of these studies are retained in the quality assurance office.

14.1.4 Periodic performance evaluation (PE) samples are analyzed per ALL-Q-010, *PE/PT Program*, to demonstrate continuing competence. All results are stored in the QA office.

15. Pollution Prevention and Waste Management

15.1 All sample residues from this analysis process must be handled as hazardous waste and disposed of in the proper hazardous waste barrel bound for incineration. For further information on waste management consult the current version of WI-S-001, *Regulated Soil Handling*.

15.2 Excess samples and method process wastes are characterized and disposed of in an acceptable manner. For further information on waste management consult the current version of ALL-S-002, *Waste Handling*.

16. References

16.1 U.S. Environmental Protection Agency, Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, (March 1983). Method 376.1.

16.2 USEPA Test Methods for Evaluating Solid Wastes, SW 846, 3rd Edition, Methods 9034.

17. Tables, Diagrams, Flowcharts, Appendices, Addenda, etc.

17.1 Attachment I – Sulfide Benchsheet.

17.2 Attachment II – Sulfide Benchsheet Example

18. Revisions

Document Number	Reason for Change	Date
GB-I-001-Rev. 0	▪ New Issue	1/26/2005
GB-I-001-Rev.1	▪ Updated method references from SW-846 9030B to SW-846 9034 where needed throughout document. ▪ Update SOP references in Section XIV.	9/21/2005
GB-I-001-Rev.2	▪ Updated Scope and Application to include reference to current MDL ▪ Added Chose random parent for MS/MSD	4/11/06

	into section 5a. ▪ Changes LCS control limit to 20% in section 3b. ▪ Change reference from "reporting limit" to "PRL"	

de

Attachment I

SULFIDE BENCHSHEET

EPA 376.1

Digest Date: _____

Analyst: _____

Lab #	Sample Date	Thio start	Thio end	Sample vol	Iodine vol	Sod Thio vol
CVS						
ICV						
MB						
LCS						
LCSD						

CVS: _____ Amount: _____

ICV: _____ Amount: _____

LCS/LCSD: _____ Amount: _____

MS/MSD: _____ Amount: _____

Reagents: _____

GBI006a (27Jan2005)

Total Sulfide, Iodometric Titration
Pace Analytical Services, Inc. – Green Bay Laboratory
GB-I-001-Rev.2

ATTACHMENT II (example)

Sulfide Benchsheet

MDL (mg/L): 0.87

Data File Name: _____

Method: EPA 376.1
Sod Thiosulfate Normality: 0.025
Iodine Normality: 0.025

Analysis Date: _____
Analyst: _____

Run #: 1
Approved: _____
WS#: _____

Lab #	Sample Date	Matrix	Samp Vol ml	Iodine Vol ml	Thio start ml	Thio end ml	Thio Vol ml	use absol value Sulfide mg/l	% RPD	% RECOV	Comments				
CVS		W	100	20			0	80							
ICV		W	100	20			0	80		100.00%					
MB		W	200	5			0	0							
LCS		W	100	20			0	80		100.00%					
LCSD		W	100	20			0	80	0.00	100.00%					
							0	#DIV/0!							
							0	#DIV/0!							
MS		W					0	#DIV/0!		#DIV/0!					
MSD		W					0	#DIV/0!	#DIV/0!	#DIV/0!					
							0	#DIV/0!							
							0	#DIV/0!							
							0	#DIV/0!							
							0	#DIV/0!							
							0	#DIV/0!							
							0	#DIV/0!							
							0	#DIV/0!							
							0	#DIV/0!							
							0	#DIV/0!							
							0	#DIV/0!							
							0	#DIV/0!							

mg/L Sulfide = [((A*B)-(C*D)*16000)]/E

A = vol Thio
B = Norm Thio
C = vol Iodine
D = Norm Iodine
E = ml sample

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STANDARD OPERATING PROCEDURE

Ferrous Iron

Reference Methods: HACH: Ferrous Iron, 1,10-Phenathroline Method 8146

SOP NUMBER:	GB-I-017-Rev.0
EFFECTIVE DATE:	Date of Final Signature
SUPERSEDES:	WCM-48Rev.2

APPROVAL

Nils Melberg, Laboratory Manager — Date: 9/8/05

Arthur F. Lautenbach, Quality Manager — Date: 8/30/05

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1. Purpose

1.1 The purpose of this Standard Operating Procedure (SOP) is to provide a consistent format for performing Ferrous Iron analysis.

2. Scope and Application

2.1 This SOP is applicable to drinking, ground, and surface waters and domestic and industrial wastes.

3. Summary of Method

3.1 The 1,10 phenanthroline indicator in Ferrous Iron reagents reacts with Ferrous Iron in the sample to form an orange color in proportion to the Iron concentration. Ferric Iron (+3) does not react. The Ferric Iron concentration can be determined by subtracting the ferrous iron concentration from the total iron result. Total iron is determined on Inductively Coupled Plasma or Inductively Coupled Plasma Mass Spec.

4. Interferences

4.1 Samples should be analyzed as soon as possible to avoid oxidation of ferrous iron to ferric iron.

5. Safety

5.1 The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable. Cautions are included for known extremely hazardous materials.

5.2 A reference file of Material Safety Data Sheets (MSDS) is made available to all personnel involved in the chemical analysis, and is located at the front desk. A formal safety plan has been prepared and is distributed to all personnel with documented training

6. Definitions

6.1 Refer to the most current version of SOP MN-Q-241, *Analytical Definitions,* for the terms used at Pace Analytical.

7. Responsibilities and Distribution

7.1 Personnel

7.1.1 All personnel involved with sample preparation and analysis are responsible for adherence to this SOP. A controlled copy will be available for review and consultation within the area methods manual.

7.1.2 Personnel are responsible for ensuring that any deviations to this SOP are reported to the laboratory manager.

7.2 Laboratory Manager

7.2.1 The laboratory manager is responsible for ensuring adherence to this SOP and will receive a controlled copy of this SOP.

7.2.2 The laboratory manager is responsible for performing a biennial review of the SOP and reporting any required revisions to the Quality Assurance Office.

7.3 Quality Assurance Office

7.3.1 The QA Office is responsible for performing a biennial review of the SOP in conjunction with the purchasing department and revising as needed.

7.3.2 The QA Office is responsible for ensuring that all revisions to the SOP are implemented.

7.4 Revisions

7.4.1 This SOP will be reviewed on a biennial basis at a minimum, and any required revisions would be incorporated.

8. Sample Collection, Preservation and Handling

8.1 Water samples are collected in glass or plastic sample bottles.

8.2 Samples are shipped to the lab on ice without preservation. Store samples at 4°C.

8.3 Analyzed samples as soon as possible since this is considered a field test. Samples analyzed in the lab are reported as "HF".

9. Equipment and Supplies

9.1 HACH DR2000 Spectrophotometer

9.2 25 ml cells

9.3 100 ml volumetric flasks

9.4 500 ml volumetric flasks

9.5 Pipettors, fixed and adjustable

9.6 25 ml graduated cylinders

10. Reagents and Standards

10.1 HACH Ferrous Iron Reagent Powder Pillows

10.2 Ferrous Ammonium Sulfate: $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$

10.2.1 Stock Ferrous Iron Standard (100 mg/L)

10.1.2.1 Primary Source: Dilute 0.3511 g Ferrous Ammonium Sulfate in ~400 ml DI water in a 500 ml volumetric flask. Dilute to volume. Prepare fresh daily. This primary source standard will be diluted to make the calibration standards and the Continuing Calibration Verification (CCV) Standards.

10.1.2.2 Second Source: Using a Lot of Ferrous Ammonium Sulfate different from the primary source, dilute 0.3511 g Ferrous Ammonium Sulfate in ~400 ml DI water in a 500 ml volumetric flask. Dilute to volume. Prepare fresh daily. This second source standard will be diluted to make the Initial Calibration Verification (ICV) Standard.

10.2.2 Working Standards – Prepare fresh daily

10.2.2.1 50 µg/L Calibration Standard: Pipet 0.05 ml of Primary Source stock standard into ~90 mls of DI water in 100 ml volumetric flask. Dilute to volume. Final concentration is 50 µg/L.

10.2.2.2 100 µg/L Calibration Standard: Pipet 0.1 ml of Primary Source stock standard into ~90 mls of DI water in 100 ml volumetric flask. Dilute to volume. Final concentration is 100 µg/L.

10.2.2.3 250 µg/L Calibration Standard: Pipet 0.25 ml of Primary Source stock standard into ~90 mls of DI water in 100 ml volumetric flask. Dilute to volume. Final concentration is 250 µg/L.

10.2.2.4 500µg/L Calibration Standard: Pipet 0.5 ml of Primary Source stock standard into ~90 mls of DI water in 100 ml volumetric flask. Dilute to volume. Final concentration is 500 µg/L.

10.2.2.5 1000 µg/L Calibration Standard: Pipet 1.0 ml of Primary Source stock standard into ~90 mls of DI water in 100 ml volumetric flask. Dilute to volume. Final concentration is 1000 µg/L.

10.2.2.6 Initial Calibration Verification Standard (ICV): Pipet 0.15 ml of Second Source stock standard into 24.85 mls of DI water in a 25 mL sample cell. Final concentration is 600 µg/L.

10.2.2.7 Continuing Calibration Verification Standard (CCV): Pipet 0.15 ml of Primary Source stock standard into 24.85 mls of DI water in a 25 mLsample cell. Final concentration is 600 µg/L.

10.2.2.8 Quality Control Samples: For LCS/LCSD, MS/MSD pipet 0.15 ml of Primary Source stock standard into 24.85 mls of DI water in a 25 mL sample cell. Final concentration is 600 µg/L.

10.3 Deionized Water used for method blanks and Initial and Continuing Calibration Blanks (ICB/CCB).

11. Calibration

11.1 Turn on the spectrophotometer and let warm up for 20 minutes.

11.2 Prepare Bench sheet.

11.3 On the spectrophotometer, press "0" then "Read/enter". The display will show: "Abs".

11.4 Rotate the wavelength dial until the small display shows: 510 nm.

11.5 Measure 25 mLs of Deionized water with graduated cylinder and pour into 25 ml cell with blank.

11.6 Place cell in spectrophotometer and press "zero".

11.7 Measure 25 mLs of each calibration standard (50 µg/L Calibration Standard, 100 µg/L Calibration Standard, 250 µg/L Calibration Standard, 500 µg/L Calibration Standard, 1000 µg/L Calibration Standard) and pour each standard into separate, clean 25 ml cells. Read and record each standard's absorbance on bench sheet.

11.8 Plot absorbance versus concentration.

11.9 The correlation coefficient must be 0.995 or higher and the y-intercept less than ½ the PRL of 0.1 mg/L. If these criteria are not met, repeat the calibration steps. If these criteria still are not met, remake standards and recalibrate. If these criteria still are not met, perform maintenance on the spectrophotometer.

11.10 The spectrophotometer must be calibrated at least yearly.

12. Procedure

12.1 Turn on the spectrophotometer and let warm up for 20 minutes.

12.2 Prepare Bench sheet.

12.3 On the spectrophotometer, press "0" then "Read/enter". The display will show: "Abs".

12.4 Rotate the wavelength dial until the small display shows: 510 nm.

12.5 Measure 25 ml of Sample, ICV, CCV, ICB, MB into 25 mL sample cell using a graduated cylinder. Prepare LCS/LCSD and MS/MSD as stated in section 10.2.

12.6 Zero the spectrophotometer for Initial Absorbance reading.

12.6.1 Place 25 mL cell ICB into spectrophotometer.

12.6.2 Press "zero" to zero the instrument.

12.6.3 Remove ICB from spectrophotometer.

12.7 Measure Initial Absorbance.

12.7.1 One at a time, place samples and QC in spectrophotometer.

12.7.2 Record the initial absorbance on the bench sheet.

12.7.3 Remove cells from spectrophotometer.

12.8 React Samples.

12.8.1 Add one reagent powder pillow to ICB, all QC and samples.

12.8.2 Invert cell several times to mix.

12.8.3 Set and run timer for three minutes to measure the reaction period.

12.9 Zero the spectrophotometer for Final Absorbance reading.

12.9.1 Place 25 mL ICB into spectrophotometer.

12.9.2 Press "zero" to zero instrument.

12.9.3 Remove ICB from spectrophotometer.

12.10 Measure Final Absorbance.

12.10.1 One at a time, place samples and QC in spectrophotometer.

12.10.2 Record the final absorbance on the bench sheet.

12.10.3 Remove cells from spectrophotometer.

12.10.4 If samples are above the high standard, dilute unreacted sample and repeat steps 12.6 –12.11.3.

12.11 Calculations: Data is entered into excel spreadsheet. Calculations are performed automatically.

13. Quality Control

13.1 Initial Calibration Verification (ICV)

13.1.1 Prepare a ICV from a different source than the calibration standards.

13.1.2 After the instrument has been calibrated and before samples are run, the accuracy of the initial calibration shall be verified and documented by the analysis of the ICV. When measurements exceed the control limits of +/- 10%, the analysis must be terminated, the problem corrected and the calibration reverified.

13.2 Continuing Calibration Verification (CCV)

13.2.1 A CCV standard must be analyzed and reported at a frequency of 10% to ensure calibration accuracy during the analytical run. The CCV is made from the same source as the calibration.

13.2.2 If the deviation of the CCV is greater than +/- 10% of the true value, the analysis must be terminated, the problem corrected, the calibration verified and all analytical samples since the last compliant CCV must be reanalyzed.

13.2.3 Only one CCV needs to be reacted; the same CCV can be read multiple times on the spectrophotometer.

13.3 Initial Calibration (ICB) and Continuing Calibration Blank (CCB)

13.3.1 A calibration blank must be analyzed immediately after every ICV and CCV.

13.3.2 The ICB and CCB must be less than the PRL.

13.3.3 The same 25 mL sample cell with DI water can be used for zeroing the instrument, as the ICB, and as the CCBs.

13.4 Method Blank (MB) - An aliquot of laboratory reagent water. The MB is analyzed exactly like a sample. The MB is used to determine whether the methodology is in control.

13.4.1 A MB must be analyzed with each batch of samples or every 20 samples, whichever is more frequent.

13.4.2 Acceptance Criteria: The MB must be less than the PRL.

13.4.3 If the MB is not within control limits, perform the following:

13.3.4.1 Check for errors in calculations. If an error or problem is found and can be corrected by amending the calculations and the result falls within the limits, accept the data and report without a qualifier flag.

13.3.4.2 If sufficient sample is available, re-prepare the MB and all associated samples if an error in procedure is discovered which cannot be corrected. If the MB is within the RL in this analysis, accept the second set of data. If the MB is still outside the RL after re-analysis, contact the PM to determine the resolution. If the client does not require additional work, report the data, applying an appropriate flag to the samples associated with the non-compliant MB.

13.3.4.3 If sufficient sample volume is not available, report the sample data with a qualifier flag on each of the samples associated with the non-compliant MB. Contact the project manager regarding the occurrence.

13.5 Laboratory Control Sample (LCS) – A primary source standard is prepared for use as the LCS. The LCS is analyzed exactly like a sample. The LCS is used to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurement.

13.5.1 An LCS must be analyzed with each batch of samples or every 20 samples, whichever more frequent.

13.5.2 Percent Recovery is calculated as follows:

$$\% \text{ Recovery} = \frac{\text{LCS concentration}}{\text{LCS known concentration}} \times 100$$

13.5.3 Acceptance Criteria: The LCS recovery must be within the control limits of 80-120%.

13.5.4 If the recovery is not within control limits, perform the following:

13.4.5.1 Check for errors in calculations, standards preparation and spiking of the LCS solution. If an error or problem is found and can be corrected by amending the calculations and the result falls within the limits, accept the data and report without a qualifier flag.

13.4.5.2 If sufficient sample is available, re-prepare the LCS and all associated samples if an error in procedure is discovered which cannot be corrected. If the recovery is within the limits in this analysis, accept the second set of data. If the recovery is still outside the limits after re-analysis, contact the PM to determine the resolution. If the client does not require additional work, report the data, applying an appropriate flag to the samples associated with the non-compliant LCS.

13.4.5.3 If sufficient sample volume is not available, report the sample data with a qualifier an "&" data qualifier on each of the samples associated with the non-compliant LCS. Contact the project manager regarding the occurrence.

13.6 Matrix Spike / Matrix Spike Duplicate (MS/MSD) – Aliquots of an environmental sample to which known quantities of the analyte(s) of interest are added in the laboratory. Their purpose is to quantify the bias and precision caused by the sample matrix. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the MS/MSD corrected for background concentrations.

13.6.1 A matrix spike / matrix spike duplicate will be performed on a 5% basis if sample volume permits.

13.6.2 The percent recovery is calculated as follows:

$$\% \text{ Recovery: } \frac{(SSR - SR)}{SA} \times 100$$

where SSR = spiked sample result, mg/L
SR =sample result, mg/L
SA = spike amount, mg/L

13.6.3 Acceptance limits: The percent recovery must be within 80 - 120% of the true value.

13.6.4 If the percent recovery is exceeded, then:

13.4.6.1 Check for errors in calculations and sample preparation. If an error or problem is found and can be corrected by amending the calculations and the result falls within the limits, accept the data and report without a qualifier flag.

13.4.6.2 If no errors are found in the calculations report the parent sample with the "N" data qualifier.

13.7 Duplicate sample (D) –A duplicate aliquot of a sample to be analyzed along with the original sample. Duplicate analyses indicates the precision associated with the sample collection, preservation and storage, as well as, laboratory procedures. An MSD is normally performed instead of a Duplicate Sample.

13.7.1 Duplicate sample analysis will be performed at a frequency of 5% if requested by the client.

13.7.2 The relative percent difference (RPD) is calculated as:

$$\mathbf{RPD} = \frac{|S - D| * 100}{(S + D)/2}$$

where **S** = sample value, mg/L
D = duplicate value, mg/L

If MS/MSD is used to calculate RPD use SSR and SR in place of S and D. See section 13.3.2.

13.7.3 Acceptance limits: The RPD must be within 0-20% between the original sample and the duplicate.

13.7.4 If the RPD is exceeded, then:

13.4.7.1 Check for errors in calculations and sample preparation. If an error or problem is found and can be corrected by amending the calculations and the result falls within the limits, accept the data and report without a qualifier flag.

13.4.7.2 If no errors are found in calculations report the parent sample with the "*" data qualifier.

13.7.5 A matrix spike duplicate can be performed in place of the sample duplicate to calculate the relative percent difference.

13.8 Documentation

13.8.1 Draw a single-line strike through for any unacceptable or changed data, then DATE and INITIAL and provide a written explanation of the reason for the change.

13.8.2 Any discrepancies and issues occurring with each batch should be included in a non-conformance, which is submitted to the QA manager for review, and incorporated into a narrative.

14. Method Performance

14.1 There are several requirements that must be met to insure that this procedure generates accurate and reliable data. A general outline of requirements has been summarized below. Further specifications may be found in the Laboratory Quality Manual.

14.1.1 The analyst must read and understand this procedure with written documentation maintained in his/her training file.

14.1.2 An initial demonstration of capability (IDC) must be performed per ALL-Q-020, *Training Procedures*. A record of the IDC will be maintained in his/her QA file with written authorization from the Laboratory Manager and Quality Manager.

14.1.3 An annual method detection limit (MDL) study will be completed per ALL-Q-004, *Method Detection Limit Studies*, for this method and whenever there is a major change in personnel or equipment. The results of these studies are retained in the quality assurance office.

14.1.4 Periodic performance evaluation (PE) samples are analyzed per ALL-Q-010, *PE/PT Program*, to demonstrate continuing competence. All results are stored in the QA office.

15. Pollution Prevention and Waste Management

15.1 The quantity of chemicals purchased is based on expected usage during its shelf life and disposal cost of unused material. Actual reagent preparation volumes reflect anticipated usage and reagent stability.

15.2 Excess reagents, samples and method process wastes are characterized and disposed of in an acceptable manner. For further information on waste management consult the current version of ALL-C-001, *Sample Management*.

16. References

16.1 HACH Water Analysis Handbook: Ferrous Iron, 1,10 Phenathroline Method - Method 8146.

17. Tables, Diagrams, Flowcharts, Appendices, Addenda etc.

17.1 Flow Chart

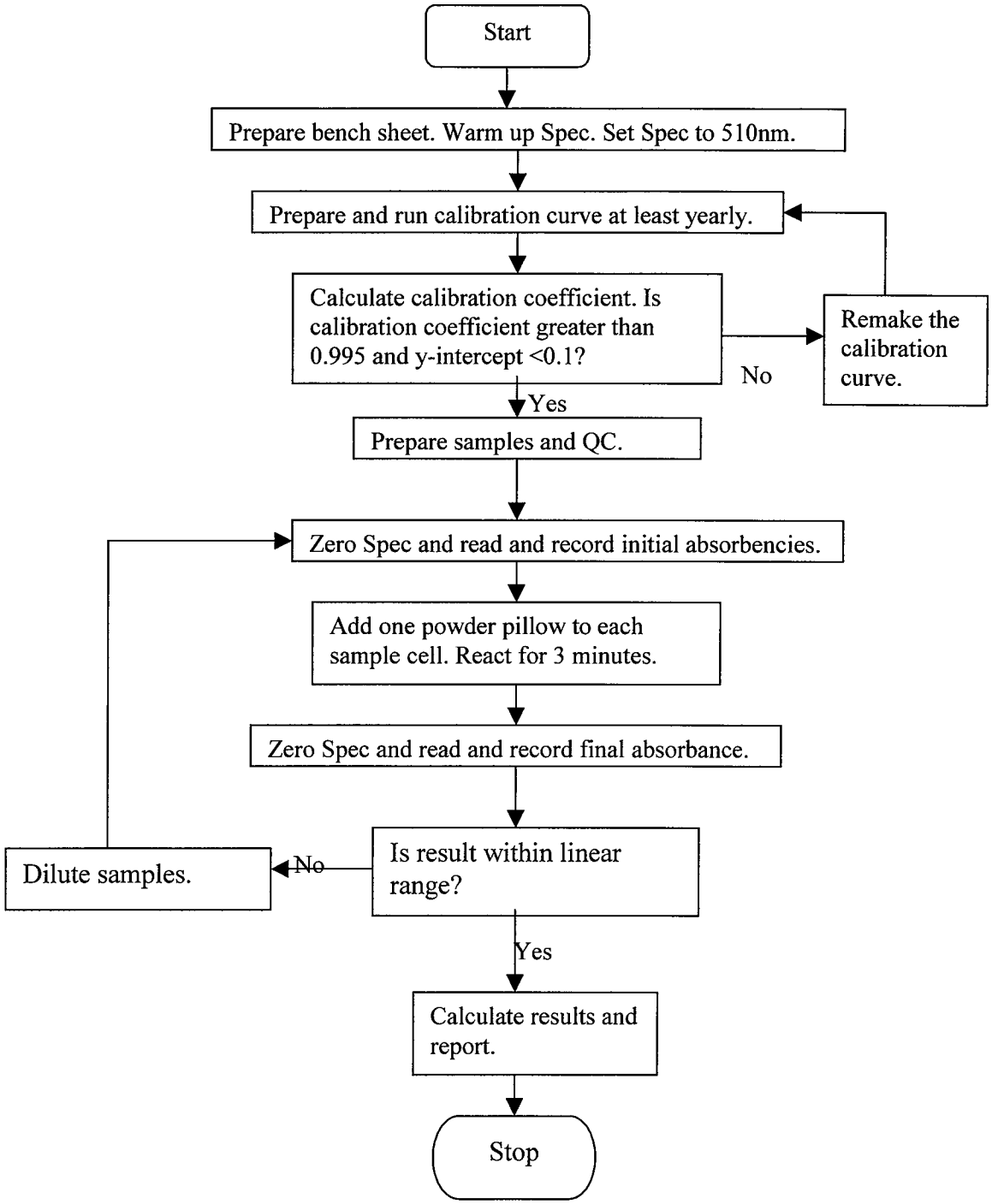
17.2 Attachment I Ferrous Iron Benchsheet

17.3 Attachment II Ferrous Iron Calibration Curve

18. Revisions

Document Number	Reason for Change	Date
GB-I-017-Rev.0	Reformatted body from En Chem to Pace Analytical format.	30 August2005

FLOW CHART


Start
Prepare bench sheet. Warm up Spec. Set Spec to 510nm.
Prepare and run calibration curve at least yearly.
Calculate calibration coefficient. Is calibration coefficient greater than 0.995 and y-intercept <0.1?
No
Remake the calibration curve.
Yes
Prepare samples and QC.
Zero Spec and read and record initial absorbencies.
Add one powder pillow to each sample cell. React for 3 minutes.
Zero Spec and read and record final absorbance.
Is result within linear range?
No
Dilute samples.
Yes
Calculate results and report.
Stop

Attachment I Ferrous Iron Benchsheet

Ferrous Iron Benchsheet

MDL(ug/L): 34
Curve Date: 6/3/04
Method: Hach 8146
Data File Name: Ferrous Iron master3

MATRIX W
Stock std SSR# 1229-23- LCS SSR# 1229-31-
Fe2 Iron reagent SSR# 1229-3-2 CCV SSR# 1229-41-
ICV SSR# 1229-29- MS SSR#: 1229-51-

Analysis Date:
Analyst: DEY
MSD SSR# 1229-51-

WS #:
QC:

Lab #	Sample Date	Prep Time	Sample Vol (mL)	Final Vol (mL)	Absorbances Initial	Absorbances Final	% Solids	Spike Conc. (ug/L)	Net Absorb.	Conc. (ug/L)	Dilution Factor	% RPD	Recovery (%)	Final Conc.	Units	Sample MDL	Flag	Comments
ICV			25	25				600	0.000	8.22	1.00		1.4	8.22	ug/L	34.00		
ICB			25	25					0.000	8.22	1.00			8.22	ug/L	34.00		
MB			25	25					0.000	8.22	1.00			8.22	ug/L	34.00		
LCS			25	25				600	0.000	8.22	1.00		1.4	8.22	ug/L	34.00		
			25	25					0.000	8.22	1.00			8.22	ug/L	34.00		
			25	25					0.000	8.22	1.00			8.22	ug/L	34.00		
			25	25					0.000	8.22	1.00			8.22	ug/L	34.00		
			25	25					0.000	8.22	1.00			8.22	ug/L	34.00		
			25	25				600	0.000	8.22	1.00		1.4	8.22	ug/L	34.00		
			25	25					0.000	8.22	1.00			8.22	ug/L	34.00		
			25	25					0.000	8.22	1.00			8.22	ug/L	34.00		
			25	25					0.000	8.22	1.00			8.22	ug/L	34.00		
CCV			25	25				600	0.000	8.22	1.00		1.4	8.22	ug/L	34.00		
CCB			25	25					0.000	8.22	1.00			8.22	ug/L	34.00		
			24.85	25					0.000	8.22	1.01			8.27	ug/L	34.21		
MS			24.85	25				600	0.000	8.22	1.01		1.4	8.27	ug/L	34.21		
MSD			24.85	25				600	0.000	8.22	1.01	0.00	1.4	8.27	ug/L	34.21		
			25	25					0.000	8.22	1.00			8.22	ug/L	34.00		
			25	25					0.000	8.22	1.00	0.00		8.22	ug/L	34.00		
			25	25					0.000	8.22	1.00			8.22	ug/L	34.00		
			25	25					0.000	8.22	1.00			8.22	ug/L	34.00		
			25	25					0.000	8.22	1.00			8.22	ug/L	34.00		
			25	25					0.000	8.22	1.00			8.22	ug/L	34.00		
			25	25					0.000	8.22	1.00			8.22	ug/L	34.00		
			25	25					0.000	8.22	1.00			8.22	ug/L	34.00		
CCV			25	25					0.000	8.22	1.00			8.22	ug/L	34.00		
CCB			25	25					0.000	8.22	1.00			8.22	ug/L	34.00		
			25	25					0.000	8.22	1.00			8.22	ug/L	34.00		
			25	25					0.000	8.22	1.00			8.22	ug/L	34.00		
			25	25					0.000	8.22	1.00			8.22	ug/L	34.00		
			25	25					0.000	8.22	1.00			8.22	ug/L	34.00		
CCV			25	25					0.000	8.22	1.00			8.22	ug/L	34.00		
CCB			25	25					0.000	8.22	1.00			8.22	ug/L	34.00		
			25	25					0.000	8.22	1.00			8.22	ug/L	34.00		
			25	25					0.000	8.22	1.00			8.22	ug/L	34.00		
			25	25					0.000	8.22	1.00	0.00		8.22	ug/L	34.00		
			25	25					0.000	8.22	1.00	0.00		8.22	ug/L	34.00		
			25	25					0.000	8.22	1.00	0.00		8.22	ug/L	34.00		
			25	25					0.000	8.22	1.00	0.00		8.22	ug/L	34.00		
			25	25					0.000	8.22	1.00	0.00		8.22	ug/L	34.00		

GBI028a (17Feb2005)

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GBI028a (17Feb2005) Ferrous Iron master3

Attachment II Ferrous Iron Calibration Curve

Ferrous Iron Benchsheet

Ferrous Iron Calibration Curve

Date: 6/3/2004
Analyst: DEY

Corr. Coefficient: 0.999776432
Y-Intercept: -0.00307373
Slope: 0.000373917

Log book Number	Concentration (ug/L)	Net Absorbance		Recovery
1229-20-1	0.00	0.000	8.220359872	#DIV/0!
1229-20-3	50.00	0.013	42.98742913	86.0
1229-20-4	100.00	0.037	107.1727678	107.2
1229-20-5	250.00	0.089	246.2410648	98.5
1229-20-6	500.00	0.180	489.6105497	97.9
1229-20-7	1000.00	0.373	1005.767809	100.6

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STANDARD OPERATING PROCEDURE

Measurement of Solids in Water and Wastewater

Reference Methods: 160.1, 160.2, 160.3, 160.4 and
Standard Methods 2540-B, -C, and –D

SOP NUMBER:	ALL-I-014-rev.1
EFFECTIVE DATE:	Date of Final Signature
SUPERSEDES:	ALL-L-002-rev.0

APPROVAL

John P. Dullaghan, COO	7/1/05 Date
Sarah Cherney, Director of Quality and Safety	05 JUL 2005 Date
Laboratory General Manager	7/13/05 Date
Laboratory Quality Manager	7/12/05 Date

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1. Purpose

This Standard Operating Procedure (SOP) describes operations used to measure Total Solids (TS), Total Suspended Solids (TSS), Total Dissolved Solids (TDS), and Total Volatile Solids (TVS) in water samples, based on EPA Methods 160.1, 160.2, 160.3, and 160.4, and Standard Methods 2540-B, 2540-C, and 2540-D.

2. Scope and Application

2.1. This method is applicable to water samples, including drinking water, groundwater, and municipal and industrial wastewater.

2.2. This SOP was prepared for method-compliant use by all Pace Analytical environmental laboratories. Any additional lab-specific requirements that may be mandated by individual states or clients are presented in an addendum.

2.3. This procedure is restricted to use by, or under the supervision of, analysts experienced with the used of laboratory filtration systems, balances, desiccators, and ovens. Each analyst must demonstrate the capability to generate acceptable results with this method to be considered qualified to report sample results.

3. Summary of Methods

3.1. **Total Solids (TS)** – A well-mixed sample is evaporated to dryness and the residue solids are measured gravimetrically.

3.2. **Total Suspended Solids (TSS)** – A well-mixed sample is filtered. The residue collected by the filter is dried and measured gravimetrically.

3.3. **Total Dissolved Solids (TDS)** – A well-mixed sample is filtered. The filtrate passing through the filter is evaporated to dryness and the residual solids are measured gravimetrically.

3.4. **Total Volatile Solids (TVS, TVSS, or TVDS)** – Residue obtained from the determination of TS, TSS, or TDS is ignited at 550 °C in a muffle furnace. The loss of weight on ignition is reported as mg/L volatile solid (TVS if the result was obtained from ashing a TS sample, TVSS if the result was from a TSS sample, or TVDS if the result was obtained from a TDS sample).

4. Interferences

4.1. Non-representative materials, e.g., leaves and sticks should be removed from the sample prior to measurement unless it is determined that their inclusion is desired. If floating oil and grease are present, the sample should

be dispersed by blending prior to analysis.

4.2. Measurements are subject to negative bias for samples containing significant quantities of ammonium carbonate, volatile organics, or other volatile materials that could be lost during drying.

4.3. The residue of samples for TS and TDS that are highly mineralized, especially containing significant concentrations of calcium, magnesium, chloride, and/or sulfate may be hydroscopic and will require longer drying, desiccation, and rapid weighing.

4.4. Samples for TS and TDS containing high concentrations of bicarbonate will require careful, and possibly prolonged, drying to ensure that all bicarbonate is converted to carbonate.

4.5. The volumes of aliquots for TS and TDS should be selected to limit the total residue to 200 mg to prevent the residue from crusting over and trapping water during drying.

4.6. Samples for TSS with high TDS, such as saline waters, brines, and some wastes, may be subject to positive bias. Care must be taken to properly rinse the filter to minimize the bias.

5. Safety

5.1. **Samples** - Although sample check-in should be notified of any hazardous samples, samples shall always be considered as "unknowns". The use of personal protective equipment (gloves, lab coats and safety glasses) is required when handling samples.

6. Definitions

6.1. **Batch** – A grouping of 20 environmental samples, or less, of similar matrix which are prepared and/or analyzed together with the same method.

6.2. **Blank Sample** -- A sample analyzed to determine potential contamination attributable to sample handling and analysis.

6.3. **Duplicate Sample** – A second aliquot of the same environmental sample analyzed in the same manner as the original sample in order to evaluate precision.

6.4. **Environmental Sample** – An environmental sample or field sample is a representative sample of any material (aqueous, non-aqueous, or multimedia) collected from any source for which determination of composition or contamination is requested or required.

6.5. **Laboratory Control Sample (LCS)** – A blank matrix sample spiked with a known concentration of analytes of interest. Laboratory accuracy is evaluated using the LCS.

6.6. **Laboratory Information Management System (LIMS)** – A system for transferring, processing, storing, and reporting analysis results. The Pace Analytical LIMS is named EPIC.

6.7. **Replicate Samples** – Samples collected at the same time, from the same place, for the same analysis, as the original sample in order to determine precision between samples.

6.8. **Pace Reporting Limit (PRL)** – The lowest level that will be reported by this method. Reporting limits are corrected for sample amounts, including the dry weight of solids, unless otherwise specified.

7. Responsibilities and Distribution

7.1. **Director of Quality and Safety** - has oversight responsibility for Pace Analytical's quality programs, including establishing and monitoring compliance with all quality system requirements.

7.2. **Chief Operating Officer (COO)** – The COO has oversight responsibility for Pace Analytical environmental laboratory operations, including compliance with all quality system requirements.

7.3. **Analyst** – Analysts using this procedure are responsible for reading, understanding and following this SOP. Any deviation from this SOP must be reported to the supervisor. The analyst must make their recommendations for changing the SOP to their supervisor or the QM in writing.

7.4. **Inorganic Supervisor** – The supervisor must ensure that all analysts are properly trained and qualified to use this procedure, and that the SOP is followed. The supervisor is responsible for reviewing the SOP and communicating recommended changes to the QM.

7.5. **Quality Manager (QM)** – The QM is responsible for monitoring the implementation of the SOPs and the associated good laboratory practice. The QM shall participate in the revision of the SOP and make sure it is current. The QM shall review and approve all SOPs.

7.6. **Laboratory General Manager** – The Laboratory General Manager has overall responsibility for ensuring that SOPs are prepared and implemented for all activities appropriate to the region. The Laboratory General Manager shall review and approve all SOPs.

7.7. **Distribution** – A copy of the SOP shall be kept in the inorganic department.

7.8. **Revision** – This SOP shall be reviewed every two years at a minimum. Independent of the minimum review frequency, revisions shall be incorporated as needed if procedures or methods change.

8. Sample Collection, Preservation, and Handling

8.1. Samples should be collected in plastic or glass containers.

8.2. Samples should be stored at 4±2 °C and analyzed as soon as possible to minimize microbiological decomposition of organic solids.

8.3. Samples should be analyzed as soon as possible and the holding time should not exceed 7 days.

9. Equipment and Supplies

9.1. **Vacuum Filtration System** – including filter holder, membrane filter funnel, vacuum flask and vacuum pump.

9.2. **Glass Fiber Filters (for TDS)** – Gelman type A/E, Whatman 934-H, or equivalent.

9.3. **Glass Fiber Filters (for TSS)** - pre-weighed with matched aluminum evaporating dishes.

9.4. **Analytical Balance** – Electronic with RS-232 output, capable of weighing 0.1 mg.

9.5. **Desiccator**

9.6. **Indicating Desiccant** – Fisher p/n 07-578-3B, or equivalent

9.7. **Non-indicating Desiccant** – Fisher p/n 07-577-3B, or equivalent.

9.8. **Graduated Cylinders** – 100-mL and 1000-mL.

9.9. **Drying Oven** – Capable of maintaining temperature at 103-105°C.

9.10. **Drying Oven (for TDS)** – Capable of holding temperature at 178-182 °C.

9.11. **Muffle Furnace (for volatile solids)** - Capable of maintaining temperature at 550 °C.

9.12. **Disposable Aluminum Evaporating Dishes** (TSS)

9.13. Ceramic Evaporating Dishes (TVS)

9.14. Evaporating Dish or Beaker (TDS/TS)

9.14. **Wash Bottle** – One-piece stem, Nalgene or equivalent

9.15. **Steam Bath** – to assist in evaporation (optional).

10. Reagents and Standards

10.1. **Deionized Reagent Water (DI)** – ASTM Type II, or equivalent.

10.2. Alpha-Trol™ Solution, or equivalent.

11. Calibration

11.1. The only required calibration is the analytical balance. The balance must be calibrated at least annually by an outside agency and checked before each use using Class 1 or 2 weights.

12. Procedure

12.1. **Total Solids (TS)**

12.1.1. Choose a sample volume to yield a residue of at least 25 mg. If there is not reliable indication of solids content, choose 100 mL if the sample appears clean or, as little as 10 mL if the sample appears to have high solids.

12.1.2. Weigh and label an empty aluminum evaporating dish for each sample.

12.1.3. Shake the sample thoroughly and measure the chosen aliquot volume in to the evaporating dish using a graduated cylinder.

12.1.4. Lower the temperature in the drying oven to 98 °C. Place the samples in the oven to evaporate most of the water. Alternatively, most of the water can be evaporated on a steam bath.

12.1.5. After most of the water has evaporated, place the samples in an oven at 103 - 105 °C and heat for at least an additional 60 minutes to dry the samples.

12.1.6. Remove the samples from the oven and allow to cool in the desiccator.

12.1.7. Weigh the samples after they have cooled and them place them back in the 103 – 105 °C oven for 15 minutes.

12.1.8. Remove the samples from the oven, allow to cool in the desiccator and weigh the samples a second time.

12.1.9. If the first and second weights agree within 0.5 mg, the analysis is complete. If not, place them back in the oven for an additional 15 minutes, cool in the desiccator, and weigh a third time.

12.1.10. If the third weight is within 0.5 mg of either the first or second weight, or if the weight loss between the second and third weighing is less than 4%, the analysis is complete.

12.1.11. If the weight loss between the second and third weighing is more than 4%, heat, cool, and weigh the sample a fourth time and use the fourth weight to calculate the result.

12.1.12. Calculate the TS result by the following equation:

$$TS\ (mg/L) = (A-B)*1000/V$$

Where A = Weight of residue and dish (mg)
B = Tare weight of dish (mg)
V = Volume of sample aliquot (mL)

12.2. **Total Suspended Solids (TSS)**

12.2.1. Choose a sample volume to yield a residue of at least 1 mg. For drinking water and very clean surface waters, use 1000 mL. For wastewaters, choose 100 mL if the sample appears clean or as little as 10 mL if the sample appears to have high solids.

12.2.2. Prepare the filter system with a fresh, tared glass fiber filter. Handle the filter with forceps only. Wet the filter with a small volume of DI water to seat it. Discard the rinsates if the sample is also being analyzed for TDS.

12.2.3. Shake the sample thoroughly and measure the chosen aliquot volume using a graduated cylinder.

12.2.4. Filter the sample and wash the filter 3 times with approximately 10-mL of DI water. Maintain the filter vacuum for about 3 minutes after filtration is complete.

12.2.4.1. If the sample is also being analyzed for TDS, retain the filtrate. Transfer the filtrate to an evaporating

dish or beaker and complete analysis for TDS as described in Section 12.3.

12.2.4.2. If volatile solids (TVS) are also to be performed, the filtrate should be transferred to a ceramic evaporating dish and proceed to Section 12.4.

12.2.5. Remove the filter with forceps and place it back into the evaporating dish.

12.2.6. Place the sample dishes in oven at 103-105°C for at least 1 hour.

12.2.7. Remove the sample dishes from the oven and allow them to cool at least 30 minutes in the desiccator.

12.2.8. Weigh the dishes and place them back in the oven for 15 minutes.

12.2.9. Remove the samples from the oven, allow to cool in the desiccator and weigh the samples a second time.

12.2.10. If the first and second weights agree within 0.5 mg, the analysis is complete. If not, place them back in the oven for an additional 15 minutes, cool in the desiccator, and weigh a third time.

12.2.11. If the third weight is within 0.05 mg of either the first or second weight or if the weight loss between the second and third weighings is less than 4%, the analysis is complete.

12.2.12. If the weight loss between the second and third weighings is more than 4%, heat, cool, and weigh the sample a fourth time and use the fourth weight to calculate the result.

12.2.13. Calculate the TSS result by the following equation:

$$TSS\ (mg/L) = (A-B)*1000/V$$

Where A = Weight of residue, filter, and dish (mg)
B = Tare weight of filter and dish (mg)
V = Volume of sample aliquot (mL)

12.3. **Total Dissolved Solids (TDS)**

12.3.1. Choose a sample volume to yield a residue of at least 25 mg. If there is not reliable indication of solids content, choose 100 mL if the sample appears clean or, as little as 10 mL if the sample appears to have high solids.

12.3.2. Prepare the filter system with a fresh glass fiber filter. If the sample will also be analyzed for TSS, use a tared filter with matched evaporating dish and handle the filter with forceps only. Wet the filter with a small volume of DI water to seat it. Discard the rinse water.

12.3.3. Shake the sample thoroughly and measure the chosen aliquot volume using a graduated cylinder.

12.3.4. Filter the sample and transfer the filtrate to a tared evaporating dish or beaker.

12.3.4.1. If the sample will also be analyzed for TSS, transfer the filter to the matching evaporating dish with forceps. Complete analysis of TSS is described in Section 12.2.

12.3.4.2. If volatile solids (TVS) are also to be performed, the filtrate should be transferred to a ceramic evaporating dish and proceed to Section 12.4.

12.3.5. Lower the temperature in the drying oven to 98 °C. Place the samples in the oven to evaporate most of the water. Alternatively, most of the water can be evaporated on a steam bath.

12.3.6. After most of the water has evaporated, place the samples in an oven at 178 – 182 °C and heat for at least an additional 60 minutes to dry the samples.

12.3.7. Remove the samples from the oven and allow to cool in the desiccator.

12.3.8. Weigh the samples after they have cooled and them place them back in the 178 - 182°C oven for 15 minutes.

12.3.9. Remove the samples from the oven, allow to cool in the desiccator and weigh the samples a second time.

12.3.10. If the first and second weights agree within 0.5 mg, the analysis is complete. If not, place them back in the oven for an additional 15 minutes, cool in the desiccator, and weigh a third time.

12.3.11. If the third weight is within 0.5 mg of either the first or second weight or if the weight loss between the second and third weighing is less than 4%, the analysis is complete.

12.3.12. If the weight loss between the second and third weighing is more than 4%, heat, cool, and weigh the sample a fourth time and use

the fourth weight to calculate the result.

12.3.13. Calculate the TDS result by the following equation:

$$TDS\ (mg/L) = (A-B)*1000/V$$

Where A = Weight of residue and dish (mg)
B = Tare weight of dish (mg)
V = Volume of sample aliquot (mL)

12.4. **Volatile Solids (TVS, TVDS, or TVSS)**

12.4.1. Obtain the dry solid residue sample from a TS, TDS, or TSS determination.

12.4.2. Place the ceramic evaporating dishes (with filter from TSS samples) into the muffle furnace at 550 °C muffle furnace for 30 minutes.

12.4.3. Remove, cool for approximately 10 minutes, and transfer to a desiccator, and allow to cool to room temperature.

12.4.4. Obtain the final weight of residue.

12.4.5. Calculate the TVS, TVDS, or TVSS result by the following equation:

$$Volatile\ Solids\ (mg/L) = (A-B)*1000/V$$

Where A = Initial weight of dry sample (mg)
B = Final weight of ashed sample (mg)
V = Volume of sample aliquot (mL)

13. Quality Control

13.1. **Duplicate Sample** – Measure one duplicate sample with each batch of 10 samples. The Relative Percent Difference (RPD) for duplicate results must be $\leq$ 20%. If the results are unacceptable, re-analyze all samples in the batch.

13.2. **Method Blank** – One blank sample consisting of a 100-mL aliquot of DI water must be analyzed with each batch of 20 samples. The method blank results must be within 50% of the PRL. If the results are unacceptable, re-analyze all samples in the batch.

13.3. **Documentation of Equipment Operation and Calibration** - The balance calibration check and oven temperature should be recorded on the lab

datasheet for each sample batch. In addition, the oven temperature should be read each day that it contains active samples. The temperature should be recorded in the oven log. If balance checks and oven temperatures are not within acceptable limits, all effected samples must be re-analyzed.

14. Method Performance

14.1. **Demonstration of Capability (DOC)** – Every analyst who performs this method must first document acceptable accuracy and precision by passing a demonstration of capability study (DOC). DOCs must be repeated annually. Analyze 4 replicate volumes of Apha-Trol™ Solution for TS, TSS, TDS, and TVS. Calculate the mean and standard deviation of the results. All results must be in control to qualify the analyst for reporting sample results. Results of DOC studies for each analyst shall be retained in the lab quality assurance office.

15. Pollution Prevention and Waste Management

15.1. Procedures for handling waste generated during this analysis are addressed in ALL-S-002, Waste Handling and the individual laboratory SOP addenda for waste management.

15.2. In order to minimize the amount of waste generated during this procedure, analyst should prepare reagents in an amount which may be used in a reasonable amount of time (i.e. before a reagent expires)

15.3. The company-wide Chemical Hygiene / Safety Manual contains additional information on pollution prevention.

16. References

16.1. USEPA Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, March 1983.

16.2. Methods 2540-B, 2540-C, and 2540-D, Standard Methods for the Examination of Water and Wastewater, 19th Edition, 1995.

17. Tables, Diagrams, Flowcharts, Attachments, Appendices, etc.

Not Applicable

18. Revisions

Document Number	Reason for Change	Date
ALL-I-014-rev.1	Renumbered document for consistency with other documents Incorporated the correct evaporating dishes and equipment based on the test. Removed LCS requirement as it is not specified in the methods. Any laboratory requiring these QC will incorporate into their addenda.	30Jun2005

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STANDARD OPERATING PROCEDURE

Green Bay Addendum

Measurement of Solids in Water and Wastewater

Reference Methods: 160.1, 160.2, 160.3, 160.4, and Standard Methods 2540-B, -C, -D, and -E

ADDENDUM NUMBER:	ALL-GB-I-014-rev.1
SOP NUMBER:	ALL-I-014-rev.1
EFFECTIVE DATE:	Date of Final Signature
SUPERSEDES:	ALL-L-002-rev.0

APPROVAL

Nils Melberg, Assistant General Manager	7/25/05 Date
Bruce Warden, General Manager	7/13/05 Date
Arthur F. Lautenbach, Quality Manager	7/12/05 Date

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1. Purpose

This Standard Operating Procedure (SOP) describes operations used to measure Total Solids (TS), Total Suspended Solids (TSS), Total Dissolved Solids (TDS), and Total Volatile Solids (TVS) in water samples, based on EPA Methods 160.1, 160.2, 160.3, 160.4, and Standard Methods 2540-B, 2540-C, 2540-D, 2540-E.

2. Scope and Application

No Applicable Changes

3. Summary of Method

No Applicable Changes

4. Interferences

No Applicable Changes

5. Safety

No Applicable Changes.

6. Definitions

No Applicable Changes

7. Responsibilities and Distribution

No Applicable Changes

8. Sample Collection, Preservation and Handling

No Applicable Changes

9. Equipment and Supplies

9.3 Glass fiber Filters (for TSS) – pre-weighed from Environmental Express, with matched aluminum evaporating dishes.

9.4 Analytical Balance – Electronic with RS-232 output, capable of weighing 0.1 mg. The Pace Analytical Services, Inc. – Green Bay Laboratory currently has in use two analytical balances capable of weighing to 0.1 mg. One of these balances does not have a RS-232 port. The analyst hand records the weigh obtained from the balance onto the laboratory benchsheet.

10. Reagents and Standards

10.2 The Pace Analytical Services, Inc. – Green Bay Laboratory uses APG Solids APGplus QC Standard, Cat. # 4033 for TS, TDS, and TSS analyses; and ERA DataPacK Total Volatile Solids Standard, Cat. # 913 for TVS analyses.

11. Calibration

11.1 The Pace Analytical Services, Inc. – Green Bay Laboratory has all balances calibrated semi-annually by an outside agency. The balances are checked daily using a range of Class 1 weights as per SOP ALL-Q-013-Rev.0. Before and after each weighing session, the balances used for these analyses are checked with a mid-level Class 1 weight.

12. Procedure

12.1 Total Solids (TS)

12.1.1 The Pace Analytical Services, Inc. – Green Bay Laboratory uses 50 mL sample volume or less for total solids analysis.

12.1.4 The samples are placed directly into an oven set at 103-105°C.

12.2 Total Suspended Solids (TSS)

12.2.1 For wastewater, the Pace Analytical Services, Inc. – Green Bay Laboratory uses 500 mL in order to meet Wisconsin Reporting Limit requirement of 2.0 mg/L.

12.2.2 Prepare the filter system with a fresh, tared glass fiber or preweighed filter.

12.2.11 If the third weight is within 0.5 mg of either the first or second weight or if the weight loss between the second and third weighings is less than 4%, the analysis is complete.

12.3 Total Dissolved Solids (TDS)

12.3.1 The Pace Analytical Services, Inc. – Green Bay Laboratory uses 50 mL sample volume or less for total dissolved solids analysis.

12.3.5 The samples are placed directly into an oven set at 178-182°C.

12.4 Volatile Solids (TVS, TDVS, or TVSS)

12.4.2 Place the evaporating dishes (with filter from TSS samples) into the muffle furnace at 550°C for 1 hour.

12.4.4 Obtain the weigh of the samples after they have cooled and place back into the muffle furnace at 550°C for 15 minutes.

12.4.4.1 Remove the samples from the muffle furnace, allow to cool in the desiccator and weigh the samples a second time.

12.4.4.2 If the first and second weights agree within 0.5 mg, the analysis is complete. If not, place them back into the muffle furnace for ana additional 15 minutes. Cool in the desiccator, and weigh a third time.

12.4.4.3 If the third weigh is within 0.5 mg of either the first or second weight, or if the weight loss between the second and third weighing is less than 4%, the analysis is complete.

12.4.4.4 If the weight loss between the second and third weighing is more than 4%, heat, cool, and weigh the sample a fourth time and use the fourth weight to calculate the result.

13. Quality Control

13.2 **Method Blank** - The method blanks is analyzed using 1000 mL for TSS analysis. For all other tests use the same size aliquot as is used for the samples. The method blank results must be less than the PRL.

13.4 **Laboratory Control Sample (LCS)** – At a minimum one LCS is analyzed with each batch of 20 samples. For TS, TDS, and TSS, APG Solids APGplus QC Standard, Cat. # 4033 is used. For TVS, ERA DataPacK Total Volatile Solids Standard, Cat. # 913 is used. An aliquot the same size as the method blank is used.

14. Method Performance

14.1 **Demonstration of Capability (DOC)** - For TS, TDS, and TSS, four replicates of the APG Solids APGplus QC Standard, Cat. # 4033 is used for the annual DOC. For TVS, four replicates of the ERA DataPacK Total Volatile Solids Standard, Cat. # 913 is used for the annual DOC.

15. Pollution Prevention and Waste Management

No Applicable Changes.

16. References

16.2 Methods 2540-B, 2540-C, 2540-D, and 2540-E, Standard Methods for the Examination of Water and Wastewater, 20th Edition, 1998

17. Tables, Diagrams, Flowcharts, Appendices, Addenda etc.

No Applicable Changes.