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WARZYN

Plan
Project No. 60251

Quality Assurance Project Plan
Remedial Investigation/ Feasibility Study
Volume 1 of 2
American Chemical Services, Inc.
Griffith, Indiana

Prepared for:

American Chemical Services
Steering Committee
Chicago, Illinois

Prepared by:

Warzyn Engineering Inc.
Chicago, Illinois

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QUALITY ASSURANCE PROJECT PLAN (QAPP) FOR

AMERICAN CHEMICAL SERVICES, INC.
REMEDIAL INVESTIGATION/FEASIBILITY STUDY

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1.0 INTRODUCTION

The United States Environmental Protection Agency requires that PRP-lead investigations under CERCLA have an approved Quality Assurance Project Plan (QAPP) covering environmental measurements. It is the responsibility of the Respondents or their representatives to implement minimum procedures so that the accuracy, precision, completeness and representativeness of data collected are known and documented.

This QAPP presents the organization, objectives, functional activities and specific quality assurance (QA) and quality control (QC) activities associated with the Remedial Investigation/Feasibility Study (RI/FS) at American Chemical Services, Inc. in Griffith, Indiana. The QAPP is designed to achieve the specific quality goals of the RI/FS.

The QAPP has been prepared using the following guidance documents:

- U.S. EPA, Region V, December 1985, Preparation of Federal-Lead Remedial Investigation Quality Assurance Project Plans for Region V.
- U.S. EPA, December 1980, Interim Guidelines and Specifications for Preparing Quality Assurance Project Plans, QAMS-005/80.
- U.S. EPA, June 1986, Data Quality Objectives for the RI/FS Process, Doc. No. 9355.0-7A.
- U.S. EPA, Region V, Content Requirements for Quality Assurance Project Plans prepared by Cheng-Wen Tsai, QAS (Received 3/2/88).

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3.0 PROJECT DESCRIPTION

The objectives of this Remedial Investigation/Feasibility Study (RI/FS) are to evaluate the existence and magnitude of contamination, and recommend a cost effective, viable remedial action alternative(s) for mitigating the potential hazard posed by the site. Tasks are directed toward accomplishing these primary objectives. The American Chemical Services, Inc. (ACS) RI/FS is a Potentially Responsible Party (PRP) lead investigation.

3.1 BACKGROUND

The ACS site is located at 420 South Colfax Avenue, 1/2 mile southeast of Griffith, Indiana, in the northeast 1/4 of the southeast 1/4, Section 2, Township 35 North, Range 9 West, Lake County Indiana (Figure 1). Although the site name is ACS, the United States Environmental Protection Agency (U.S. EPA) has defined the site as including the inactive portion of the 31-acre Griffith Landfill, the 2-acre Pazmey Corporation site (formerly Kapica Drum, Inc), and the ACS property (19 acres).

On the ACS property is an active hazardous waste storage and treatment facility operating under RCRA interim status. From 1955 to at least 1975, ACS disposed of hazardous wastes on its property, primarily from on-site chemical manufacturing and solvent reclamation operations. Some wastes were accepted from off-site sources for incineration in the ACS on-site incinerator. The incinerator-generated ash was disposed of on ACS property.

The Griffith Landfill is an active sanitary landfill operation. Inactive portions were reported to have received hazardous wastes from ACS and Kapica Drum, Inc. prior to RCRA. Kapica Drum, Inc. was a drum reconditioning facility which generated drum residues and rinse water from cleaning drums that contained hazardous wastes. Figure 2 summarizes the interrelationship between ACS, Kapica Drum, Inc., and the Griffith Landfill based on a review of available information. For a more detailed site history, refer to the ACS Initial Site Evaluation Report (document number 160-WP1-RT-AUJD-1).

Previous investigations have detected contaminants in the groundwater, surface water/leachate, and soil at some level. The contaminants encompass a broad spectrum of volatile organics, extractable organics, and heavy metals. The highest reported concentrations of the specific constituents are listed in Tables 1, 2 and 3.

The topography at the site is almost level in the portion north of the railroad and rises slowly from 630 to 645 feet above MSL in the southern half of the site. Griffith Landfill has excavated about 30 feet of soil to the west of the ACS Off-Site Drum Containment Area near the southeast boundary of the ACS property, thus modifying the gently sloping topography. A marsh to the north of the landfill and west of the ACS property has a surface elevation of about 625 feet. The two major soils in the area are the Plainfield fine sand and the Maumee loamy fine sand with average hydraulic conductivities of 1.42×10^{-2} cm/sec.

There are no natural streams in the area of the site, but a marsh does exist immediately to the west of the northern half of the site. Man-made drainage ditches form the western border of the site and eventually enter Turkey Creek one mile to the south. A natural surface water drainage pond is located just to the west of the western boundary of the site, and a fire pond, in which rainwater is collected to be used in case of a fire at the facility, is located about 200 feet to the east. Turkey Creek, a small stream, flows about 1 mile south of the site and the Little Calumet River is located three miles to the north. Because of these natural and man-made features, the groundwater flow patterns at the site are not well defined, but the regional groundwater flow is reported to be to the northeast in the vicinity of the ACS site.

Based on existing data, the hydrostratigraphy at the site appears to consist of:

- An upper aquifer composed of fine to coarse-grained sand with fine to coarse gravel, and small amounts of peat and silt, about 20-feet thick.
- An intervening silty clay to clay unit containing discontinuous lenses of gravel, 15 to 30-feet thick.
- A lower sand and gravel aquifer, 90-feet thick.

A fourth soil unit consisting of thick, stiff clay is reported in the area, but borings indicate it is absent on-site. The deeper sand and gravel unit is the major water supply aquifer in the area. The depth to bedrock, which consists of interbedded shales and dolomites, is about 130 feet.

3.2 PROJECT OBJECTIVES AND USE OF DATA

The RI/FS will be performed to gather and assess information needed to accomplish the following objectives:

- Determining if the ACS site poses a risk to public health, welfare, or the environment.
- Determining the characteristics, extent and magnitude of contamination at the site.
- Defining the pathways of contaminant migration from the site.
- Defining on-site physical features and facilities that could affect contaminant migration, containment, or cleanup.
- Developing viable remedial action alternatives.
- Evaluating and screening remedial action alternatives.
- Recommending the cost-effective remedial action alternative which adequately protects health, welfare and the environment.

All tasks, subtasks, and activities are directed toward the accomplishment of these primary objectives.

Under the Superfund Amendments and Reauthorization Act of 1986 (SARA), it is recommended that the RI/FS are integrated so that parts of each are conducted concurrently. Therefore, the project will be conducted in several phases of investigation. Each phase will be designed to make optimal use of information as it is derived and to produce the information which is necessary to complete the FS. Because this approach makes use of the most current information, data overlaps and data gaps are minimized. The phased approach allows "mid-course" corrections to be made so that the investigation will develop in the most efficient and cost-effective sequence.

3.3 SPECIFIC PROJECT SUBTASKS AND ACTIVITIES

The activities and subtasks related to the field work are listed below. For a complete itemization of all tasks, see the Work Plan.

Phase I:

- Subtask 1B Survey Site Boundaries
- Subtask 1C Geophysical Survey
- Subtask 1D Surface Water Survey

- Subtask 2A Characterize Flow System
- Subtask 2B Initial Shallow Sampling
- Subtask 3A Waste Characterization

Phase II:

- Subtask 4A Groundwater Characterization
- Subtask 4B Soil Contamination
- Subtask 4C Groundwater Transport Model

Phase III:

- Subtask A Install Wells as Necessary
- Subtask B Collect Additional Samples as Necessary

The QAPP is limited to applicable activities within Phases I and II; additional phases and the associated QAPP would be developed if and when it were to be determined that additional information would be required which had not been developed in Phases I and II. The project schedule is shown in Figure 3.

Specific procedures to be used in sample collection for the various sample matrixes are outlined in the Sampling Plan (Appendix A). A summary of sample numbers and matrices is given in Tables 4 and 5. A summary of sample containers, sample volumes, preservation and shipment methods to be used is given in Table 6.

Subtask 1B Survey Site Boundaries

Activity 1B.1 Establish Site Grid Boundaries

The grid will be based upon two perpendicular baselines with a maximum grid interval of 100 feet. Elevation data will be collected at selected grid points. Grid locations will be surveyed to ±1.0 foot using an electronic "total station" instrument, which uses an infrared light source to determine distances. Ground elevations will be obtained to an accuracy of ±0.1 foot. Elevations will also be obtained using the "total station" system. All "total station" output is received as LED output. The instrument is calibrated on a monthly basis.

Activity 1B.2 Survey Site Boundaries

All boundary surveys will be conducted by a licensed Indiana surveyor. Temporary boundary markers will be installed as necessary in order to easily distinguish individual pieces of property. These boundary markers shall be marked with a sign so they will be easy to locate in heavy vegetation.

Subtask 1C Geophysical Survey

A test shall be conducted to determine if geophysical surveys will be feasible, due to the presence of railroads, powerlines, metal buildings and metal process tanks across and surrounding the site. If feasible, a magnetometer survey will be conducted as it has the best probability of yielding meaningful data.

Subtask 1D Surface Water Survey

A series of 12 bench marks will be established across the site to serve as reference points for surface water elevation measurements. The bench marks will be referenced to USGS elevations to an accuracy of ±.01 foot.

Subtask 2A Characterize Flow System

Activity 2A.1 Monitor ACS Hydraulics

A water budget will be conducted to account for the total water usage within the ACS operation. The total water extracted from on-site wells, or obtained from off-site sources will be compared to the water volume discharged to sewers. A system may be established to monitor the volume of the effluent discharged from plan operations.

Activity 2A.2a Install Leachate Wells

Four leachate sampling wells will be installed in the Griffith Landfill. Wells will intersect the first saturated layer, and will not penetrate the base of the landfill.

Activity 2A.2b Monitor De-Watering Pumpage

A system will be installed to monitor the pumpage from the dewatering activities at the Griffith Landfill excavation. Water that collects in this low area is periodically pumped into a municipal sanitary sewer.

Activity 2A.3 Install Perimeter Monitoring Wells

Six monitoring wells will be installed around the perimeter of the ACS site. The wells will be constructed with 10-foot screens located to intersect the water table. Continuous samples will be obtained from each of these boreholes.

Activity 2A.3a Test Near Surface Hydraulic Properties
Three wells will be selected for aquifer testing (slug test, bail tests, or pump tests) to provide estimates of the upper aquifer hydraulic properties. Criteria to select representative aquifer conditions will include saturated thickness and grain size.

Subtask 2A.4 Install Piezometer Grid
A series of about 40 temporary piezometers will be installed by jetting to provide additional data on the groundwater elevation. Piezometers will be located on approximately a rectangular grid. It is anticipated that water levels will be measured at least twice during the course of Phase I and at least once during Phase II. No water quality samples will be obtained.

Activity 2A.5 Model Groundwater Flow System
Since two aquifers will ultimately be analyzed, it is anticipated that the USGS Three-Dimensional Groundwater Flow Model (Modflow) will be used. The model can simulate stresses to the aquifer(s) by actions such as: flow from external sources, flow to wells, areal recharge, evapotranspiration, flow to drains, and flow through river beds. At this point in the investigation, the modeling effort will be limited to the upper aquifer system.

Subtask 2B Initial Shallow Sampling

Activity 2B.1 Effluent Sampling
It is anticipated that four samples of the effluent waste streams will be collected using a timed sampling device or a device activated by portable detection equipment, such as pH meters or Organic Vapor Analyzers (OVAs).

Activity 2B.2 Groundwater Sampling for the Perimeter Wells and Leachate Wells
A water sample will be obtained from each of the six perimeter wells, and four leachate wells. Additional samples from two perimeter wells and the leachate well samples will not be filtered prior to analysis for metals and cyanide.

Activity 2B.3 Surface Water and Sediment Sampling
Eleven samples of surface water and sediments will be collected. Sampling will proceed from the furthest downstream location to the furthest upstream location, as applicable, to minimize contamination from sediments disturbed in the sampling process. The water sample will be obtained first at a given location for the same reasons.

Subtask 3A Waste Characterization

Activity 3A.1 Soil Borings, Test Pits and Surface Soil Sampling
The source characterization activities include surface soil sampling, drilling of 14 soil and waste borings and excavation of six waste pits. Chemical analysis will be performed on 48 investigative samples.

Subtask 4A Groundwater Characterization

Activity 4A.1 and 4A.2 Well Installation and Aquifer Testing
It is anticipated to at least eight, and up to 12 new monitoring wells will be installed. Four wells will be completed in the upper portion of the lower aquifer and at least four wells (up to eight) will be installed in the lower portion of the shallow aquifer. The location and number of wells will be determined based on the results of Tasks 2 and 3. Slug tests will be performed on the four lower aquifer wells and four of the new upper aquifer wells. If indicated, a pump test might be performed.

Activity 4A.3 On-Site Well Sampling and Private Well Sampling
A water sample will be obtained from all of the on-site wells (up to 18 wells total) and ten private water supply wells. All private well samples and up to five additional on-site well samples will not be filtered prior to analysis for metals and cyanide. Another round of sampling of on-site wells is anticipated with up to 9 wells being sampled for the complete TCL and the remaining being sampled for a reduced parameter list approved by the U.S. EPA.

Subtask 4B Soil Contamination
Based on the results of work conducted in Task 3, it is anticipated that additional drilling and sampling will be conducted. Up to 20 samples may be collected for analysis of those compounds detected at each location in Phase I sampling.

Subtask 4C Groundwater Transport Model
The flow model developed under Activity 2A.5 may be expanded to include the lower aquifer and contaminant transport. If modeling is conducted, the proposed model and associated assumptions will be submitted to the U.S. EPA for review and approval.

3.4 SCHEDULE

A schedule of activities of deliverables for the ACS RI is presented in Figure 3. The final RI report should be complete within 12 months after the project begins.

4.0 PROJECT ORGANIZATION AND RESPONSIBILITY

4.1 OVERALL RESPONSIBILITY

Authorized PRP Representatives
- Andrew Perellis, Esq.
  ACS Steering Committee
- Barbara Magel, Esq.
  ACS Steering Committee

PRP Project Coordinator
- Joseph D. Adams, Jr., PE
  Warzyn Engineering, Inc.

Principle Investigator
- Peter Vagt, Ph.D.
  Warzyn Engineering Inc.

U.S. EPA Remedial Project Manager
- Karen Waldvogel
  U.S. EPA, Region V

- RI/FS Reports and technical memoranda prepared by Warzyn Engineering Inc.

4.2 MONITORING AND SAMPLING OPERATIONS AND QC

- Principal Engineering Firm - Warzyn Engineering Inc.
- Drilling - to be determined through bidding process
- Sampling, Monitoring and Survey - Warzyn Engineering Inc.
- Quality Control

  - Richard W. Maurer, Warzyn Engineering Inc.
    (Quality Assurance Officer or his designate)

4.3 LABORATORY ANALYSIS AND QC

- Analysis of groundwater, soils, and leachate samples for Target Compound List (TCL) organics (see Appendix B for analyte list)

  - Hazleton Laboratory
    3301 Kinsman Blvd.
    Madison, WI 53704

- Analysis of groundwater, and leachate samples for Target Compound List (TCL) inorganics (see Appendix B for analyte list) and general water quality indicator parameters including COD, TOC, total suspended solids, total dissolved solids, nitrate - nitrite, alkalinity, chloride, sulfate and ammonia.

- Warzyn Engineering Inc.
  One Science Court
  Madison, WI 53711

· Analyses of soil samples collected during Activity 2A.3, 4A.1, 4A.2 will be evaluated for Atterberg limits, grain size, permeability and moisture content, and cation exchange capacity.

- Warzyn Engineering Inc.
  One Science Court
  Madison, WI 53711

4.4 SPECIALIZED RESPONSIBILITIES FOR LABORATORY SERVICES

· Hazleton Laboratory Data

- Analytical protocol specified - Warzyn Engineering Inc.
- Review of analytical protocol - Hazleton
- Review of analytical protocol - U.S. EPA Region V Quality Assurance Section (QAS) and Central Regional Laboratory (CRL), Contract Program Management Section (CPMS).
- Review and approval of performing laboratory - U.S. EPA Region V, CRL, CPMS
- Internal QA/QC-Hazleton staff
- Final data review and validation - Warzyn Engineering Inc.
- Review of tentatively identified compounds and assessment of need for confirmation - Warzyn Engineering Inc.

· Warzyn Data

- Review of analytical specifications - U.S. EPA Region V QAS and CRL, CPMS
- Review and approval of performing laboratory - U.S. EPA Region V CRL, CPMS
- Internal QA/QC - Warzyn Engineering Inc.
- Final data review and validation - Warzyn Engineering Inc.

4.5 QUALITY ASSURANCE

· Overall QA Responsibility
  - Warzyn Quality Assurance Officer

· QA for Warzyn Subcontracted Activities
  - Warzyn Engineering Inc.

· Review of QAPP
  - U.S. EPA Region V QAS and CPMS, CRL

- Field Analyses
  - Warzyn Engineering Inc.

4.6 PERFORMANCE AND SYSTEMS AUDITS

- Field Operations
  - QAO, Warzyn Engineering Inc.
  - U.S. EPA Oversite Contractor

- Analytical Laboratories
  - U.S. EPA CPMS, CRL

- Final Evidence File Audits
  - QAO, Warzyn Engineering Inc.

An organizational chart is shown in Figure 4.

5.0 QUALITY ASSURANCE OBJECTIVES

The overall quality assurance objectives are to implement field sampling, chain-of-custody, and quality control reporting procedures that will provide legally defensible data from laboratory analyses in a court of law. Field analyses, including screening of samples for VOCs with an HNu and non-intrusive geophysical measurements, are being made primarily to aid in site selection for more detailed observations and analyses. Quality control objectives for these data, as well as those collected for health and safety purposes, are to obtain reproducible data consistent with limitations imposed by measurement methods used.

Specific procedures to be used for sampling, chain-of-custody, calibration, laboratory analyses, data reporting, internal quality control, audits, preventative maintenance, and corrective actions are described in other sections of this QAPP. This section (5.0) defines goals for the QC effort (accuracy, precision, and sensitivity of analyses and completeness, representativeness, and comparability) for data from analytical laboratories and presents quality control objectives for field measurements.

5.1 LEVEL OF QUALITY CONTROL EFFORT

5.1.1 Field Sampling Program

The quality of data from the field sampling program for laboratory analyses will be evaluated through the collection of field duplicates, field and trip blanks. Duplicates will be used to assess the combined effects of sample collection, handling and analysis on data precision. The general level of effort for all matrices will be one field duplicate per 10 investigative samples. Where appropriate, field blanks will be collected at a frequency of one per group of 10 or fewer samples per sample matrix per day. Blank samples will serve to check for procedural contamination or ambient conditions at the site that may result in apparent contamination of samples. Field blanks for leachate and groundwater samples will consist of deionized water passed through decontaminated sampling equipment. Field blanks for groundwater samples requiring filtration (TCL inorganics and indicator parameters) will consist of deionized water passed through a decontaminated filtering apparatus.

A trip blank (consisting of two 40 ml VOA vials filled with DI water and preservative) will be included with each shipment of samples for volatile analysis. The purpose of a trip blank is to assess cross contamination in the

shipment cooler of samples targeted for volatile organic analysis. Trip blanks will not be analyzed unless the field blank shows contamination. The trip blank will not be opened, but remain sealed from the time it is taken from the laboratory. A shipment is to be considered a shipping unit, i.e. a single cooler.

5.1.2 Laboratory Analyses

Analyses of leachate, groundwater, and soil samples for EPA Target Compound List (TCL) organics (see Appendix B for analyte list) will be performed based on Contract Laboratory Program (CLP) protocols. Levels of QC effort for these analyses are described in CLP Statement of Work SOW-7/87 or most recent. Additional volume of samples will be collected to perform the matrix spike and matrix spike duplicate at a frequency of one per twenty investigative samples. Levels of QC effort for TCL inorganics and general water quality indicators are described with methods in Appendix D. Quality control samples for these analyses include laboratory blanks, laboratory duplicates, calibration, and verification standards. Performance criteria for these analyses are included with the method descriptions.

Samples collected from private water supply wells will be analyzed for EPA TCL (Appendix B). These samples will be analyzed using methods described in Appendices C and D which provide lower detection limits. The level of laboratory QC is described in the individual methods in Appendices C and D.

Levels of QC effort for physical analyses of soil samples for Atterberg limits, grain size, moisture content and permeability are given with methods descriptions in Appendix D.

5.1.3 Field Measurements

pH

Level of QC effort for field measurement of pH will consist of precalibration using two buffer solutions and calibration verification at regular intervals (at least every ten samples), as outlined in Appendix E.

Specific Conductance

Level of QC effort for specific conductance measurements will consist of initial and continuing calibration verification (at least every ten samples) using a standard solution of known conductivity, as outlined in Appendix F.

Geophysical Measurements

Level of QC effort for geophysical measurements will be limited to duplication of measurements to assure consistent response and periodic calibration verification, if applicable. If response of repeated measurement is inconsistent, data will be considered unusable.

Water Elevation

Water elevations will be measured using an electronic water level indicator or sounding device and fiberglass tape. Both devices make an audible sound in contact with liquid and will be used as a basis for measuring depth to groundwater. Quality control effort will be limited to averaging repeated measures at each measurement location.

Air Monitoring

Level of QC effort for air monitoring and sample screening for the photoionization meter (HNU PI-101) and the Monitox unit will be limited to daily calibration. Method of calibration for both instruments are specified in Appendices G and M.

5.2 ACCURACY, PRECISION AND SENSITIVITY OF ANALYSIS

The QA objectives of analyses with respect to accuracy, precision and sensitivity are to achieve acceptable data based on specified performance criteria. Accuracy and precision requirements and method detection limits for CLP-based analyses to be performed on leachate, groundwater, soil and waste samples are described in CLP Statement of Work SOW-7/87 (or most recent version) for TCL organics and are described in Appendix D for TCL inorganics. Accuracy and precision definitions and stated performance criteria for analysis of water and leachate samples for general water quality indicator parameters are included with method descriptions in Appendix D. The accuracy, precision, and sensitivity criteria for analysis of samples from private water supply wells are located with the individual methods in Appendices C and D.

Accuracy of field measured pH will be judged from agreement of instrument readings with standard buffer solutions. Agreement with standards will be within 5% of expected value and field measurements will be made to 0.01 unit. Measurement precision will be estimated by periodically (1 per 10 samples) making duplicate readings of samples. If the unit fails to calibrate it will be replaced.

Accuracy of the conductivity meter will be assured by daily calibration verification with a check standard. If readings vary more than 5% from expected values, the unit will be replaced.

Data needs for geophysical measurements require the ability to detect differences on a consistent relative scale. Hence, in most cases an absolute calibration is not required. However, where applicable, instruments will be calibrated prior to use or be checked using manufacturer's suggested test procedures to assure proper and consistent operation.

Accuracy of field instruments (HNu, Monitox) used for sample screening and health and safety purposes will be assured by daily calibration. If units fail to calibrate, they will be replaced.

5.3 COMPLETENESS, REPRESENTATIVENESS AND COMPARABILITY

It is anticipated that at least 95% of the analyses will provide results meeting acceptance criteria. If required performance criteria are not met by performing laboratories, they will re-analyze samples if holding times permit. If holding times are exceeded, the performing laboratory will inform the Warzyn project manager as soon as possible, so that a decision whether to re-sample or to accept data with limitations noted can be made.

Sampling, preservation and analysis methods are designed to provide results representative of the matrix at the sampling point. Analytical methods used will provide comparable data with respect to both analytical methodology and level of QC effort which will supplement prior data collected at the site.

6.0 SAMPLING PROCEDURES

Specific sampling procedures to be used are documented in the Sampling Plan (Appendix A). Containers, preservatives, holding times, transport and storage methods are summarized in Table 6 of the QAPP and Table 3 of the Sampling Plan.

Documentation of use of specific procedures in the Sampling Plan will be made by initialed entries in the field logs book by the sampling team leader. These shall include, but not be limited to, such operations as decontamination of sampling equipment between sampling locations.

7.0 SAMPLE CUSTODY AND DOCUMENTATION

Sample documentation for field samples will follow chain-of-custody procedures including the use of chain-of-custody forms, sample container tags, custody seals, sample identification records and field notebooks. All samples will be collected under chain-of-custody procedures. The latter will include sampling time, location, tag numbers, samplers, pertinent PID readings, weather conditions, and any field modifications of sampling strategy. Standard forms including chain-of-custody record forms, sample labels, sample identification record forms, and chain-of-custody seals will be maintained throughout the RI/FS sampling activities.

A copy of the chain-of-custody form to be used is shown in Figure 5. Form requirements:

- One form per shipping container
- Carrier service does not need to sign form is custody seals remain intact during shipment.
- Use for all samples.

An example of the chain-of-custody seal to be used for sample shipping is shown in Figure 6. Seal requirements:

- Two (2) chain-of-custody seals per shipping container attached to the cooler lid to provide evidence that samples within have not been tampered with.
- Cover seals with clear tape prior to shipping sample containers.
- Record chain-of-custody seal numbers on chain-of-custody forms as well as sample identification record forms.

A copy of the sample label to be used is shown in Figure 7. Label requirements:

- Each sample container must have a sample label affixed to it. Label will specify sample date, parameters for analysis and preservative used.
- Record sample label numbers on the chain-of-custody form and sample identification record form.
- Use for all samples.

An example of the Sample Identification Record Form to be used is shown in Figure 8. The form is to provide the means of recording shipping and tracking information. The form will include information such as:

- Sample number
- Sample matrix
- Sample location code
- Sample round
- Chain-of-custody number
- Lab code
- Date sampled
- Date shipped
- Airbill number
- Sample label number

The documentation accompanying the samples shipped to the laboratory will be sealed in a plastic bag taped to the inside of the cooler lid. The lid of the sample cooler will be securely taped shut prior to shipment. Once in the laboratory's possession, sample custody will be the responsibility of the laboratory sample custodian.

Original field notes and field documents will be maintained by Warzyn in a final evidence file. Original deliverables for analyses performed by Hazleton and Warzyn will also be contained in this file. Format and maintenance of the Warzyn's final evidence file are given in Appendix I.

Internal chain-of-custody procedures for Hazleton Laboratories will follow those described in Appendix J.

Internal chain-of-custody procedures for Warzyn's laboratory are as follows. Samples are delivered to Warzyn's laboratory under chain-of-custody. A designated sample custodian accepts custody of the shipped samples and verifies that the chain-of-custody seals have not been broken. The sample custodian reviews the information on the sample tags/labels with that on the chain of custody records. Pertinent information as to shipment, pickup, courier, etc., is entered in the remarks section. The custodian then enters that sample tag/label data into a bound logbook which is arranged by project code and station number. The sample custodian must acknowledge receipt on the chain-of-custody form. Any comments pertaining to the shipment should be made under "Remarks".

The sample custodian will use the sample tag/label as identification information to assign a unique sequential laboratory number to each sample. This laboratory number is entered on the chain-of-custody form. The information is logged on to the laboratory logbook. The sample custodian

will transfer samples to the proper analyst or store the sample in the appropriate refrigerator. The chain-of-custody and testing request forms are forwarded to the laboratory supervisor.

The laboratory is a secured area with strict limited access. Data files and doors are locked daily. Laboratory personnel are responsible for the care and custody of samples from the time they are received until the sample is returned to the custodian or refrigerated.

When sample analyses and necessary quality assurance checks have been completed by the laboratory or after a 3-month time period, whichever is longer, the unused portion of the sample will be disposed of properly. Identifying tags, data sheets, and laboratory records shall be retained as part of the permanent documentation of the project and forwarded to the Warzyn Engineering Inc. Project Manager for inclusion in the evidentiary file.

8.0 CALIBRATION PROCEDURES AND FREQUENCY

Calibration of pH and specific conductance meters are detailed in Appendices E and F, respectively. Standard solutions will be used to calibrate the instruments at least every ten samples.

Calibration of the HNu PI-10 (photoionization meter), will follow procedures recommended by the manufacturer (see Appendix G). The HNu will be calibrated to read in benzene equivalents at the beginning of each working day using calibration gas (isobutylene) supplied by HNu.

Calibration of the Organic Vapor Analyzer (OVA) will follow the procedures outlined in Appendix H at the beginning of each day of use.

HCN Monotox detectors will be checked for accuracy each working day prior to use (Appendix M). If the detector fails to calibrate, it will be replaced.

Instruments used for geophysical survey will be calibrated or will undergo internal systems checks, as appropriate, prior to use using methods recommended by the manufacturer.

Procedures and frequency of calibration of laboratory instruments are detailed in Appendices C, D, and the CLP Statement of Work SOW 7/87 (or most recent version.)

9.0 ANALYTICAL SERVICES

9.1 HAZLETON

9.1.1 Analytical and Calibration Procedures

Samples analyzed by Hazleton for TCL volatiles, semi-volatiles, and pesticides (see Appendix B for analyte list) will follow CLP protocols outlined in the CLP Statement of Work SOW 7/87 (or most recent version). Samples from private water supply wells analyzed by Hazleton for organic parameters will follow the procedures outlined in Appendix C for analysis and calibration.

9.2 WARZYN

9.2.1 Analytical and Calibration Procedures

Samples analyzed by Warzyn for TCL inorganic parameters (see Appendix B for analyte list) will follow the CLP protocols outlined in the CLP Statement of Work SOW 7/87 (or most recent version).

Samples analyzed by Warzyn for indicator parameters will follow the procedures outlined in appendix D.

Samples analyzed by Warzyn from private wells for inorganic parameters will follow the procedures outlined in Appendix D.

Samples for geotechnical analysis analyzed by Warzyn will follow the procedures outlined in Appendix D.

10.0 INTERNAL QUALITY CONTROL CHECK

Internal quality control procedures are an integral part of the analytical methods and are, therefore, discussed in detail in the descriptions of the analytical procedures (CLP Statement of Work SOW-7/87 (or most recent version) and Appendices C and D).

The overall objectives of the internal quality control checks are to verify the established precision, accuracy and integrity of the methodology and to support the technical validity of the data. Where appropriate, internal quality control checks for other than CLP-based analyses will include method blanks, laboratory duplicates, laboratory control spikes, and matrix spike analyses. Required frequency and performance criteria for these analyses are listed with method descriptions in Appendices C, D, and in the CLP SOW-7/87 (or most recent version).

11.0 DATA REDUCTION, VALIDATION AND REPORTING

Specific procedures for the identification and quantification of sample parameters for EPA TCL constituents are covered in CLP Statement of Work SOW-7/87 (or most recent version). Data reduction for non-CLP parameters are covered in the method descriptions found in Appendices C and D.

Data validation will be performed by Warzyn. Assessment of organics data will be performed using guidelines developed in Technical Directive Document No. HQ-8410-01, Laboratory Data Validation, Functional Guidelines for Evaluating Organic Analyses, February 1988. Inorganics data assessment will be performed based on guidelines in Laboratory Data Validation, Functional Guidelines for Evaluating Inorganics Analyses, November, 1985.

Data validation for the non-CLP based analyses is based on the guidelines cited above and on comparisons with the QC levels and criteria specified with the methods (Appendices C and D).

Deliverables are as specified in the CLP Statement of Work (SOW-7/87) for the TCL organics. Deliverables are stated in the methods descriptions in Appendices C and D for inorganics, general water quality parameters, and private water supply well parameters.

12.0 PERFORMANCE AND SYSTEM AUDITS

The Region V CPMS, CRL will audit the performing laboratories as a basis for approval or disapproval of the laboratory for the requested analyses. Performance audits are to be made as specified in the appropriate CLP SOW for analyses by CLP protocols.

Performance audits with independent QC samples are to be performed as specified in methods descriptions in Appendices C and D for TCL parameters, general water quality indicator parameters, and private water supply well parameters.

Evidence audits are the responsibility of the Warzyn Quality Assurance Officer (QAO) or his designate and are described in Appendix I. Field audits will be the responsibility of the EPA oversite contractor.

13.0 PREVENTATIVE MAINTENANCE

Preventative maintenance procedures for field instrumentation are detailed in instrument manuals in Appendices E through H, K, L and M.

Maintenance procedures for laboratory instrumentation and equipment associated with CLP protocols are referenced in the CLP Statement of Work SOW-7/87 (or most recent version). The method descriptions found in Appendices C and D contain preventive maintenance procedures for instrumentation and equipment associated with the laboratory analysis.

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

Assessment of accuracy, precision and completeness for analyses based on CLP protocols will follow specifications stated in the CLP Statement of Work SOW-7/87. Accuracy and precision definitions for analysis of water samples for general water quality and private water supply well parameters are specified in the method descriptions found in Appendices C and D.

Assessment of accuracy, precision and completeness of analytical data is based on the acceptable result of QC samples. Where appropriate these include blanks, duplicate samples, laboratory control spikes and matrix spike duplicates.

Method, field and trip blank results are expected to provide a measured value that is less than or equal to the reported detection limit.

Field and laboratory duplicate sample results are assessed based on relative percent difference (RPD) between values, using the following equation:

$$RPD = \frac{D_1 - D_2}{(D_1 + D_2)/2} \times 100\%$$

D_1 = first sample value
D_2 = second sample value (duplicate)

Laboratory control spikes results are assessed based on the percent recovery (%R) of fortified analytes. Percent recovery is calculated using the following equation:

$$\%R = \frac{Qd \times 100\%}{Q_a}$$

Q_d = Quantity determined by analysis
Q_a = Quantity added to sample

Matrix spike/matrix spike duplicate data are assessed based on recovery of fortified analytes using the following equation:

$$\text{Matrix Spike Percent Recovery} = \frac{(SSR - SR)}{SA} \times 100\%$$

SSR = Spike Sample Results
SR = Sample Result
SA = Spike Added

Relative percent difference (RPD) between the matrix spike and matrix spike duplicate is calculated using the following equation:

$$RPD = \frac{D_1 - D_2}{(D_1 + D_2)/2} \times 100\%$$

D_1 = first sample value
D_2 = second sample value (duplicate)

15.0 CORRECTIVE ACTION

If quality control audits result in detection of unacceptable conditions or data, the Warzyn QAO will be responsible for developing and initiating corrective action. Corrective action may include:

- Re-analysis of the samples, if holding time criteria permits;
- Resampling and re-analysis;
- Evaluating and amending sampling and analytical procedures; and
- Accepting data, acknowledging level of uncertainty.

16.0 QUALITY ASSURANCE REPORTS TO MANAGEMENT

Separate QA reports are not anticipated. The final RI report will contain separate sections that summarize data quality.

TABLE 1
GROUNDWATER CHARACTERISTICS

Compound	Range (mg/l)
Benzene	<0.005-29[1,2]
Toluene	ND-35[1]
Vinyl Chloride	<0.005-36[2]
Chloroethane	<0.005-980[1]
Ethyl benzene	ND-10[1]
1,2 Transdichloroethylene	<0.005-34[1]
Methylene Chloride	<0.005-2.2[2]
1,1 Dichloroethane	<0.005-1.3[2]
1,2 Dichloroethane	ND-0.67[2]
1,2 Dichloropropane	ND-0.74[2]
Trichloroethylene	ND-0.039[2]
Phenol	ND-0.75[1]
2,4 Dimethylphenol	ND-0.14[1]
bis (2-Chloroethyl) ether	ND-327[1]
1,1,1-Trichloroethane	<0.005-1.1[1,2]

Notes

1 Ecology and Environment Well Sampling Results, November 3, 1982.

2 Phase I Report, Preliminary Hydrogeological Assessment, American Chemical Services, Colfax Avenue, Griffith, Indiana, ATEC Associates, 1/15/86.

3 ND = Not Detected
mg/l = milligrams per liter

TABLE 2
LEACHATE/SURFACE WATER CHARACTERISTICS

Compound	Range (ug/l)
Naphalene	<0.1 - 29[1]
Phenol	1.1 - 35[1]
Diethylphthalate	<0.4 - 10[1]
Phenenthrene and Anthracene	<1 - 0.1[1]
Di-n-butylphthalate	0.4 - 21[1]
bis (2-ethylhexyl) phthalate	5.4 - 510[1]
bis (2-chloroethyl) ether	<0.1 - 300[1]
Dimethylphthalate	<0.1 - 2,300[1]
(2-ethhoxy) ethyl acetate	ND - 17,000[1,3]
2-(hydroxymethyl)-1-pentanol	ND - 40,000[1,3]
trimethyl-2-cyclohexen-1-one	ND - 36,000[1,3]
n-methyl-2-pyrrolidone	ND - 11,000[1,3]
1-(2-but oxyethoxy) ethanol	ND - 6,800[1,3]
2-ethylhexanoic acid	ND - 4,100[1,3]
methylphenol (2)	ND - 57,000[1,3]
ethylphenols (3)	ND - 58,000[1,3]
dimethylphenols (3)	ND - 15,000[1,3]
pentylphenol	ND - 4,100[1,3]
methoxytrimethylphenol	ND - 11,000[1,3]
dimethyl benzenedicarboxylate	ND - 5,300[1,3]
2,2,4-Trimethyl-3-cyclohexene -1-methanol	ND - 1,700[1,3]
2-(2-methoxy-1-methylethoxy) -1-propanol	ND - 500[1,3]
1,1-oxybis-2-chloroethane	ND - 53[1,3]
3,3-5-trimethylcyclohexene	ND - 460[1,3]
Benzene	1650[1,3]
Ethylbenzene	30[2]
Toluene	1340[2]
TOX	5740[2]

TABLE 2 (Continued)
SURFACE WATER/LEACHATE CHARACTERISTICS

Metal/Cyanide	Range (ug/l)
Cadmium	< - 184[1]
Chromium	<5 - 254[1]
Nickel	<30 - 544[1]
Lead	<30 - 282[1]
Mercury	<0.1 - 0.8[1]
Cyanide	<5 - 96[1]

Notes

1 Organic Analytical Results for samples collected at American Chemical Services and Griffith Landfill, Griffith Park, Indiana, May 9, 1980, U.S. EPA, CRL, Organic Laboratory section, 6/13.80.

2 Letter: ATEC Associates to L. Rundio, May 2, 1986 transmitting results from March 1986 Sampling.

3 Tentatively Identified Compounds (TIC)

4 ug/l = micrograms per liter

TABLE 3
SEDIMENT CHARACTERISTICS

Compound	Range[1] (ug/kg)
Phenol	<1400 - 26
Isophorone	<700 - 6.2
Napthalene	21 - 12,000
Flourene	<7,400 - 1,000
Phenanthrene and Anthracene	26 - 1,400
Di-n-butylphthalate	11 - 1,100
bis (2-ethylhexyl) phtholate	71 - 110,000
butylbenzylphthalate	117 - 8,300
methylnapthalenes	ND - 32,000[2]
dimethylnaphalenes	ND - 22,000[2]
dipheylenther	ND - 3,800[2]

Metals/Cyanide	Range[1] (ug/g)
Cadmium	<0.2
Chromium	8 - 11
Nickel	5 - 9
Lead	14 - 15
Mercury	.036 - .049
Cyanide	<0.3

Notes

ug/kg = micrograms per kilogram
ug/g = micrograms per gram

1 Organic Analytical Results from samples collected at American Chemical Services and Griffith Landfill, Griffith Park, Indiana, May 9, 1980. U.S. EPA, CRL, Organic Laboratory Section 6/13/80)

2 Tentatively Identified Compounds (TIC)

TABLE 4
SUMMARY OF PHASE I SOURCE CHARACTERIZATION
SAMPLING AND ANALYSIS PROGRAM

Sample Matrix[1]	Laboratory	Laboratory Parameters[2]	No. of Investigative Samples	No. of Field Duplicates	No. of Matrix Spike/[3] Matrix Spike Duplicates	Total No. of Samples
Waste Pits	Hazleton	TCL Volatiles	6	1	1	8
	Hazleton	TCL Semi-Volatiles	6	1	1	8
	Hazleton	TCL PCB/Pesticides	6	1	1	8
	Warzyn	TCL Metals	6	1	0	7
	Warzyn	Cyanide	6	1	0	7
Natural Soils	Hazleton	TCL Volatiles	6	1	0	7
-Waste Pit	Hazleton	TCL Semi-Volatiles	6	1	0	7
	Hazleton	TCL PCB/Pesticides	6	1	0	7
	Warzyn	TCL metals	6	1	0	7
	Warzyn	Cyanide	6	1	0	7
	Warzyn	Volatile Residue	6	1	0	7
Waste Borings	Hazleton	TCL Volatiles	8	1	0	9
	Hazleton	TCL Semi-Volatiles	8	1	0	9
	Hazleton	TCL PCB/Pesticides	8	1	0	9
	Warzyn	TCL Metals	8	1	0	9
	Warzyn	Cyanide	8	1	0	9
Natural Soils	Hazleton	TCL Volatiles	8	1	1	10
-Waste Borings	Hazleton	TCL Semi-Volatiles	8	1	1	10
	Hazleton	TCL PCB/Pesticides	8	1	1	10
	Warzyn	TCL Metals	8	1	0	9
	Warzyn	Cyanide	8	1	0	9
	Warzyn	Volatile Residue	8	1	0	9
Soil Areas	Hazleton	TCL Volatiles	8	1	1	10
	Hazleton	TCL Semi-Volatiles	8	1	1	10
	Hazleton	TCL PCB/Pesticides	8	1	1	10
	Warzyn	TCL Metals	8	1	0	9
	Warzyn	Cyanide	8	1	0	9
Soil Borings	Hazleton	TCL Volatiles	12	2	0	14
	Hazleton	TCL Semi-Volatiles	12	2	0	14
	Hazleton	TCL PCB/Pesticides	12	2	0	14
	Warzyn	TCL metals	12	2	0	14
	Warzyn	Cyanide	12	2	0	14

Notes
1 Samples will be considered low or medium concentration.
2 See Appendix B for TCL Analyte lists - also up to 30 tentatively identified compounds.
3 Sample numbers do not reflect the additional volumes required for matrix spike/matrix spike duplicate analysis.
4 Field and trip blanks are not required for soil/waste samples.
5 Qualitative screening with HNu or OVA will be done for investigative and duplicate samples only.

TABLE 5
SUMMARY OF SITE CHARACTERIZATION SAMPLING AND ANALYSIS PROGRAM

Sample(1) Matrix	Laboratory	Laboratory Parameters(2,5)	Study(3) Phase	No. of Investigative Samples	No. of Field Duplicates	No. of Field Blanks	Matrix Spike/(4) Matrix Spike Duplicate	Total No. of Samples
Groundwater	Hazleton	TCL Volatiles	1	6	1	1	1	9
			2A	18	2	2	1	23
			2B	*				*
	Hazleton	TCL Semi-Volatiles	1	6	1	1	1	9
			2A	18	2	2	1	23
			2B	*				*
	Hazleton	TCL PCB/Pesticides	1	6	1	1	1	9
			2A	18	2	2	1	23
			2B	*				*
	Warzyn	TCL Metals (Dissolved)	1	6	1	1	0	8
			2A	18	2	2	0	22
			2B	*				*
	Warzyn	TCL Metals (Total), TSS	1	2	1	1	0	4
			2A	5	1	1	0	7
			2B	*				*
	Warzyn	Cyanide (Filtered)	1	6	1	1	0	8
			2A	18	2	2	0	22
			2B	*				*
	Warzyn	Chloride, Alkalinity, Sulfate	1	6	1	1	0	8
			2A	18	2	2	0	22
			2B	*				*
	Warzyn	Ammonia, Nitrate-Nitrite, TOC, COD	1	6	1	1	0	8
			2A	18	2	2	0	22
			2B	*				*
	Warzyn	Total Dissolved Solids	1	6	1	1	0	8
			2A	18	2	2	0	22
			2B	*				*
Surface Water	Hazleton	TCL Volatiles	1	11	2	2	1	16
	Hazleton	TCL Semi-Volatiles	1	11	2	2	1	16
	Hazleton	TCL PCB/Pesticides	1	11	2	2	1	16
	Warzyn	TCL Metals (Total)	1	11	2	2	0	15
	Warzyn	Cyanide (Unfiltered)	1	11	2	2	0	15
	Warzyn	Chloride, Alkalinity, Sulfate	1	11	2	2	0	15
	Warzyn	Ammonia, Nitrate-Nitrite, COD	1	11	2	2	0	15
Sediment	Hazleton	TCL Volatiles	1	11	2	2	1	16
	Hazleton	TCL Semi-Volatiles	1	11	2	2	1	16

TABLE 5 (Continued)
SUMMARY OF SITE CHARACTERIZATION SAMPLING AND ANALYSIS PROGRAM

Sample(1) Matrix	Laboratory	Laboratory Parameters(2,5)	Study(3) Phase	No. of Investigative Samples	No. of Field Duplicates	No. of Field Blanks	Matrix Spike/(4) Matrix Spike Duplicate	Total No. of Samples
	Hazleton	TCL PCB/Pesticides	1	11	2	2	1	16
	Warzyn	TCL Metals	1	11	2	2	0	15
	Warzyn	Cyanide	1	11	2	2	0	15
Private	Hazleton	TCL Volatiles	2	10	1	1	1	13
Wells	Hazleton	TCL Semi-Volatiles	2	10	1	1	1	13
(Low	Hazleton	TCL PCB/Pesticides	2	10	1	1	1	13
Detection	Warzyn	TCL Metals (Total)	2	10	1	1	0	12
Limits)	Warzyn	Cyanide (Unfiltered)	2	10	1	1	0	12
	Warzyn	Chloride, Alkalinity, Sulfate,	2	10	1	1	0	12
	Warzyn	Ammonia, Nitrate-Nitrite, COD	2	10	1	1	0	12
Leachate	Hazleton	TCL Volatiles	1	4	1	1	1	7
Wells	Hazleton	TCL Semi-Volatiles	1	4	1	1	1	7
	Hazleton	TCL PCB/Pesticides	1	4	1	1	1	7
	Warzyn	TCL Metals (Total)	1	4	1	1	0	6
	Warzyn	Cyanide (Unfiltered)	1	4	1	1	0	6
	Warzyn	Chloride, Alkalinity, Sulfate	1	4	1	1	0	6
	Warzyn	Ammonia, Nitrate-Nitrite, COD, TOC	1	4	1	1	0	6
	Warzyn	TDS, TSS	1	4	1	1	0	6
ACS Effluent	Hazleton	TCL Volatiles	1	4	1	1	1	7
	Hazleton	TCL Semi-Volatiles	1	4	1	1	1	7
	Hazleton	TCL PCB/Pesticides	1	4	1	1	1	7
	Warzyn	TCL Metals (Total)	1	4	1	1	0	6
	Warzyn	Cyanide (Unfiltered	1	4	1	1	0	6
	Warzyn	Chloride, Alkalinity, Sulfate	1	4	1	1	0	6
	Warzyn	Ammonia, Nitrate-Nitrite, COD, TOC	1	4	1	1	0	6
	Warzyn	TSS, TDS	1	4	1	1	0	6
Geotechnical	Warzyn	Atterberg limits	'	18	0	0	0	18
Samples-Wells	Warzyn	Particle Size	1	18	0	0	0	18
	Warzyn	Coefficient of Permeability	1	18	0	0	0	18
	Warzyn	Cation Exchange Capacity	1	18	0	0	0	18
	Warzyn	Moisture Content	1	18	0	0	0	18

TABLE 5 (Continued)
SUMMARY OF SITE CHARACTERIZATION SAMPLING AND ANALYSIS PROGRAM

Notes

1 Samples will be considered low or medium concentration.

2 See Appendix B for TCL analyte lists, also up to 30 tentatively identified compounds.

3 The star (*) indicates that the number of samples and specific parameters will be determined from Phase 1 and 2A results. Preliminary assessment indicates that up to 9 wells will be sampled for the complete TCL, and the remaining number will be sampled for a reduced parameter list. Also note that Phase 2A sample number is given as the expected maximum.

4 Sample numbers do not reflect the additional volume of samples required for matrix spikes and matrix spike duplicate analysis.

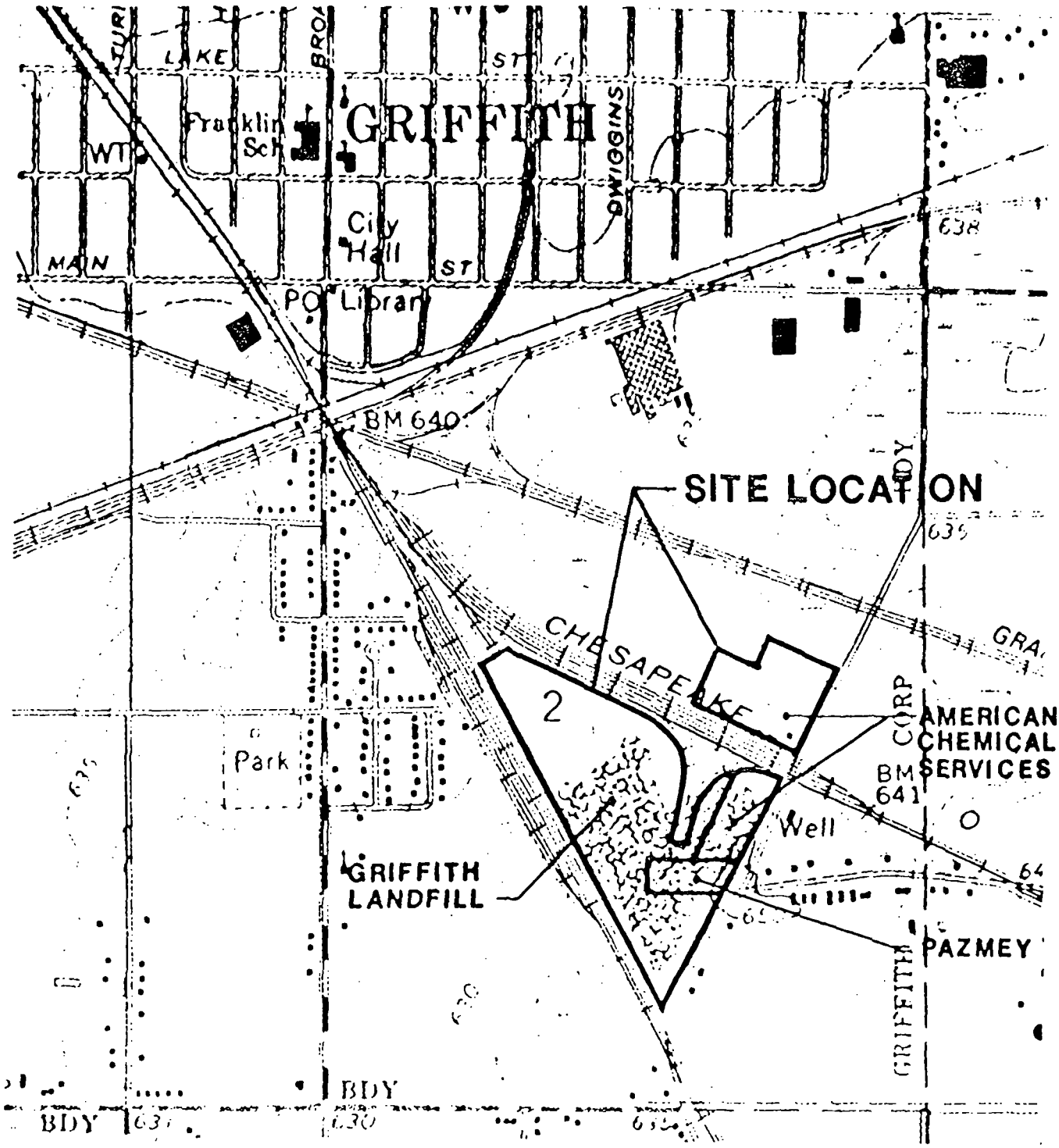
5 Temperature, pH and specific conductance measurements will be taken in the field for aqueous samples. Qualitative screening with the HNu or OVA will be performed on solid samples.

TABLE 6
SAMPLE QUANTITIES, BOTTLES, PRESERVATIVES AND PACKAGING
FOR WATER, SEDIMENT AND LEACHATE SAMPLES

Analysis	Bottles and Jars	Preservation	Holding Time	Volume of Sample	Shipping	Normal Packaging
WATER AND LEACHATE						
Low Concentration (Organics)						
Semi-Volatiles	One 1-liter amber bottle (teflon-lined cap)	Iced to 4°C	5 days until extraction, 40 days after extraction	Fill bottle to neck	Shipped Daily by Overnight Carrier	No. 1 foam liner or vermiculite
Pesticides/PCBs	One 1-liter amber bottle (teflon-lined caps)	Iced to 4°C	5 days until extraction, 40 days after extraction	Fill bottle to neck	Shipped Daily by Overnight Carrier	No. 1 foam liner or vermiculite
Volatiles	Two 40-ml volatile organic analysis (VOA vials)	Iced to 4°C HCL to pH <2	7 days (48 hours for surface water)	Fill completely no headspace	Shipped Daily by Overnight Carrier	No. 1 foam liner or vermiculite
Low Concentration (Inorganics)						
Metals (groundwater)	One 1-liter high density polyethylene bottle	Filter through 0.45 um filter, HNO_3, to pH <2 Iced to 4°C Optional	6 months (Hg, 26 days)	Fill to shoulder of bottle	Shipped Daily by Overnight Carrier	No. 2 foam liner or vermiculite
Metals (leachate, surface water and private water supply wells)	One 1-liter high density polyethylene bottle	HNO_3 to pH <2 Iced to 4°C	28 days	Fill to shoulder of bottle	Shipped Daily by Overnight Carrier	No. 2 foam liner or vermiculite
Cyanide	One 1-liter high density polyethylene bottle	NaOH to pH >12 Iced to 4°C	14 days	Fill to shoulder of bottle	Shipped Daily by Overnight Carrier	No. 2 foam liner or vermiculite
Other Analysis						
Chlorides, Alkalinity Sulfate	One 1-liter high density polyethylene	Iced to 4°C	28 days (14 days for alkalinity)	Fill to shoulder of bottle	Shipped Daily by Overnight Carrier	No. 2 foam liner or vermiculite
Total Organic Carbon, Ammonia, Nitrate-Nitrite, Chemical Oxygen Demand	One 1-liter polyethylene high density bottle	Iced to 4°C H_4SO_4 to pH <2	28 days	Fill to shoulder	Shipped Daily by Overnight Carrier	No. 2 foam liner or vermiculite
Total Dissolved Solids Total Suspended Solids	One 1-liter polyethylene high density bottle	Iced to 4°C	7 days (filter upon receipt at lab)	Fill to shoulder	Shipped Daily by Overnight Carrier	No. 2 foam liner or vermiculite

TABLE 6 (Continued)

SOIL/SEDIMENT						
Low or Med Concentration (Organics)						
Acid extractables, base/neutral extractables, pesticides/PCBs	One 8-oz wide mouth glass jar	Iced to 4°C	10 days until extraction, 40 days after extraction	Fill 3/4 full	Shipped Daily by Overnight Carrier	Foam liner No. 3 (Med in cans/ vermiculite)
Volatiles	Two 120-ml VOA vials	Iced to 4°C	10 days	Fill completely no headspace	Shipped Daily by Overnight Carrier	Vermiculite (Med in cans/ vermiculite)
Low or Med Concentration (Inorganics)						
Metals and Cyanide	One 8-oz wide mouth glass jar	Iced to 4°C	6 months (14 days for cyanide)	Fill 3/4 full	Shipped Daily by Overnight Carrier	Foam liner No. 3 (Med in cans/ vermiculite)
Physical Analyses						
Grain Size, moisture content	One 8-oz wide mouth glass jar	None	not established	Fill 3/4 full	Shipped Daily by Overnight Carrier	Vermiculite
Atterberg Limits	One 8-oz wide mouth glass jar	None	not established	Fill 3/4 full	Shipped Daily by Overnight Carrier	Vermiculite
Permeability	3-in Shelby Tubes	4°C	not established	Fill 3/4 full	Shipped Daily by Overnight Carrier	Vermiculite



NOTE:

1. SITE LOCATION MAP WAS DEVELOPED FROM U.S.G.S. 7½ MINUTE QUADRANGLE MAP ENTITLED HIGHLAND, INDIANA 1968, PHOTOREVISED 1980.

north

SCALE: 1"= 1000'

FIGURE 1

DWN SJP	APP'D RSV	DATE 9/23/88	60251-A2	WARZYN	SITE LOCATION MAP RI/FS AMERICAN CHEMICAL SERVICES SITE GRIFFITH, INDIANA

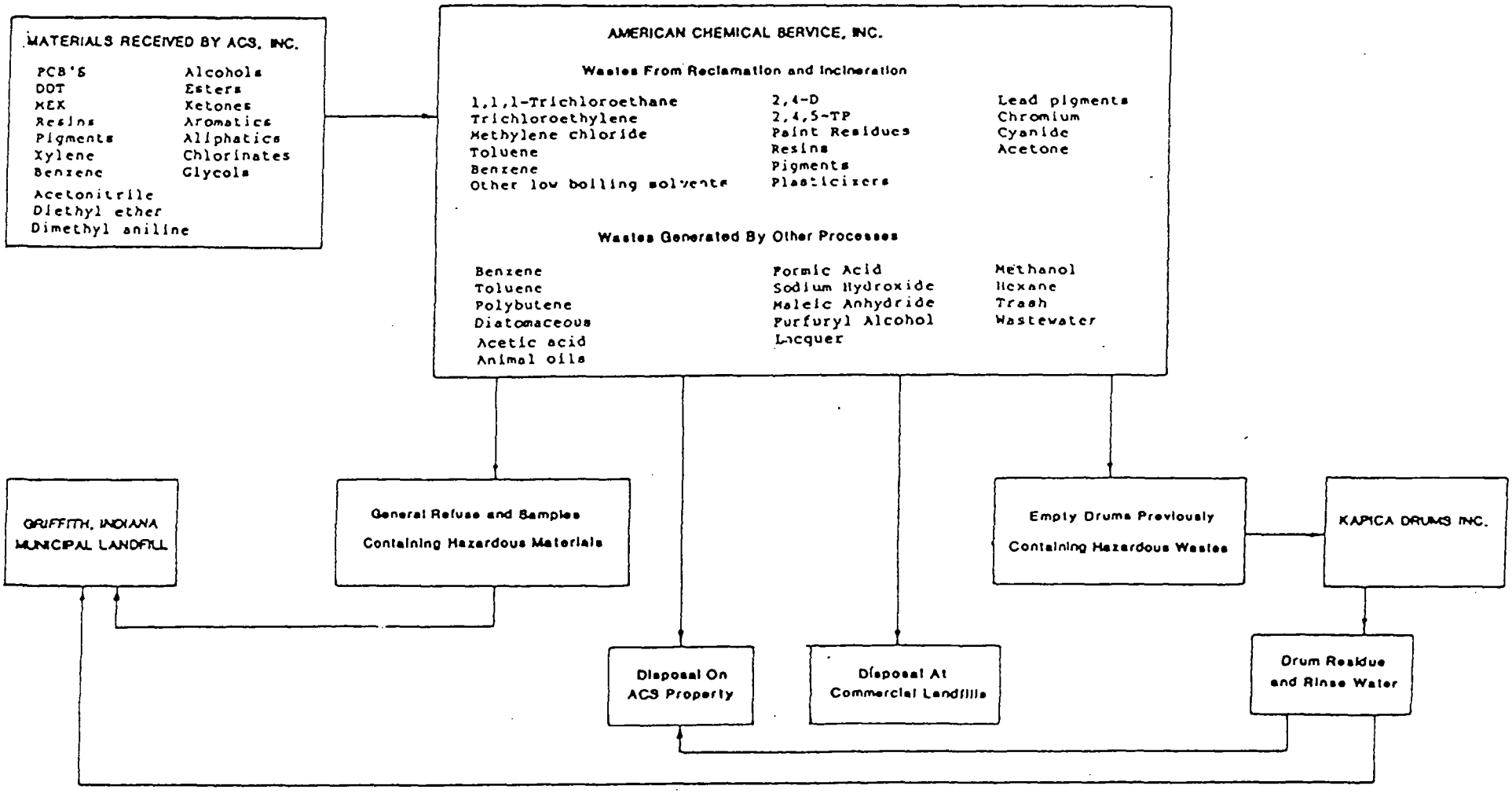
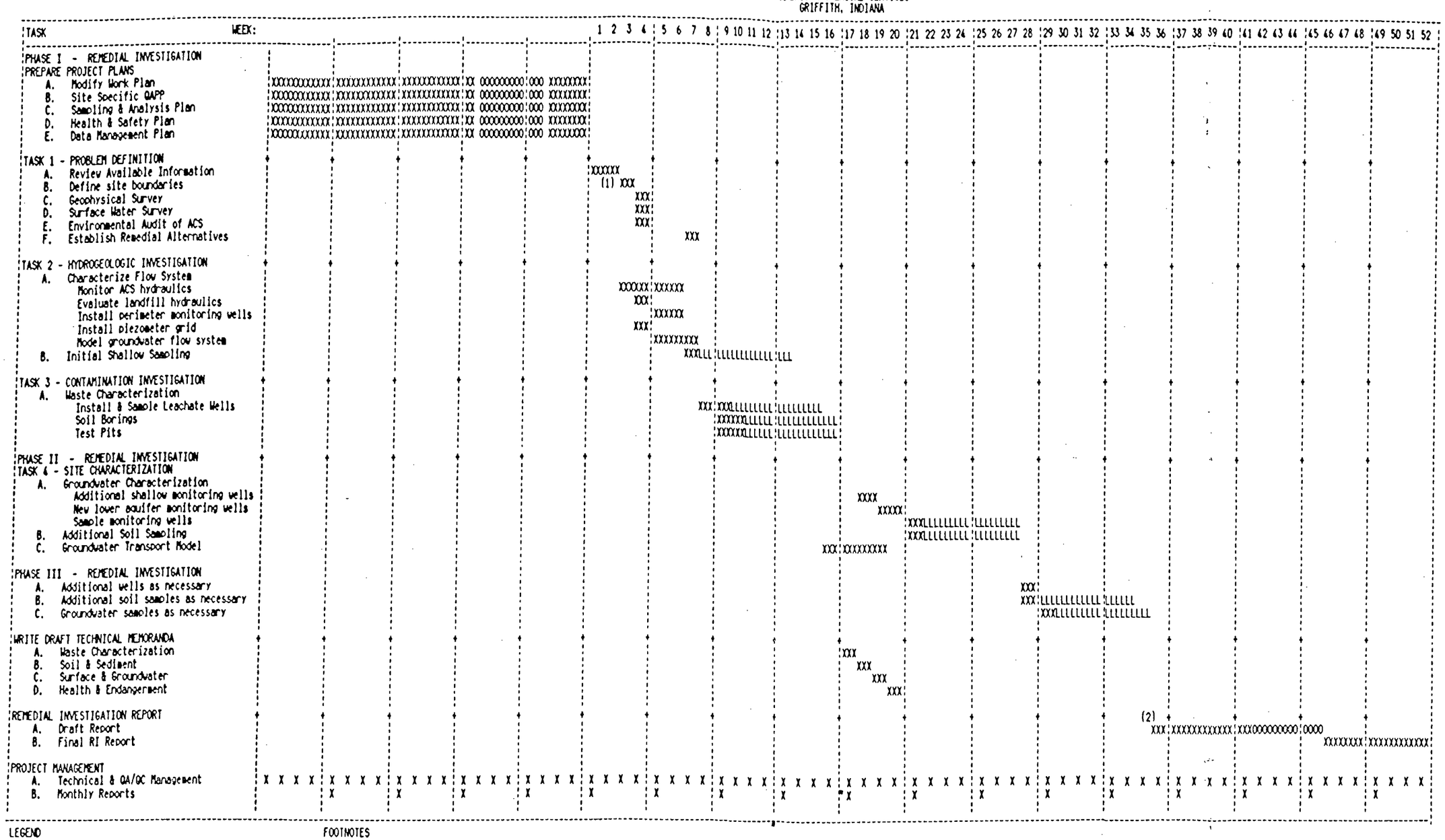


Figure 2. Waste Disposal Flow Chart

FIGURE 3

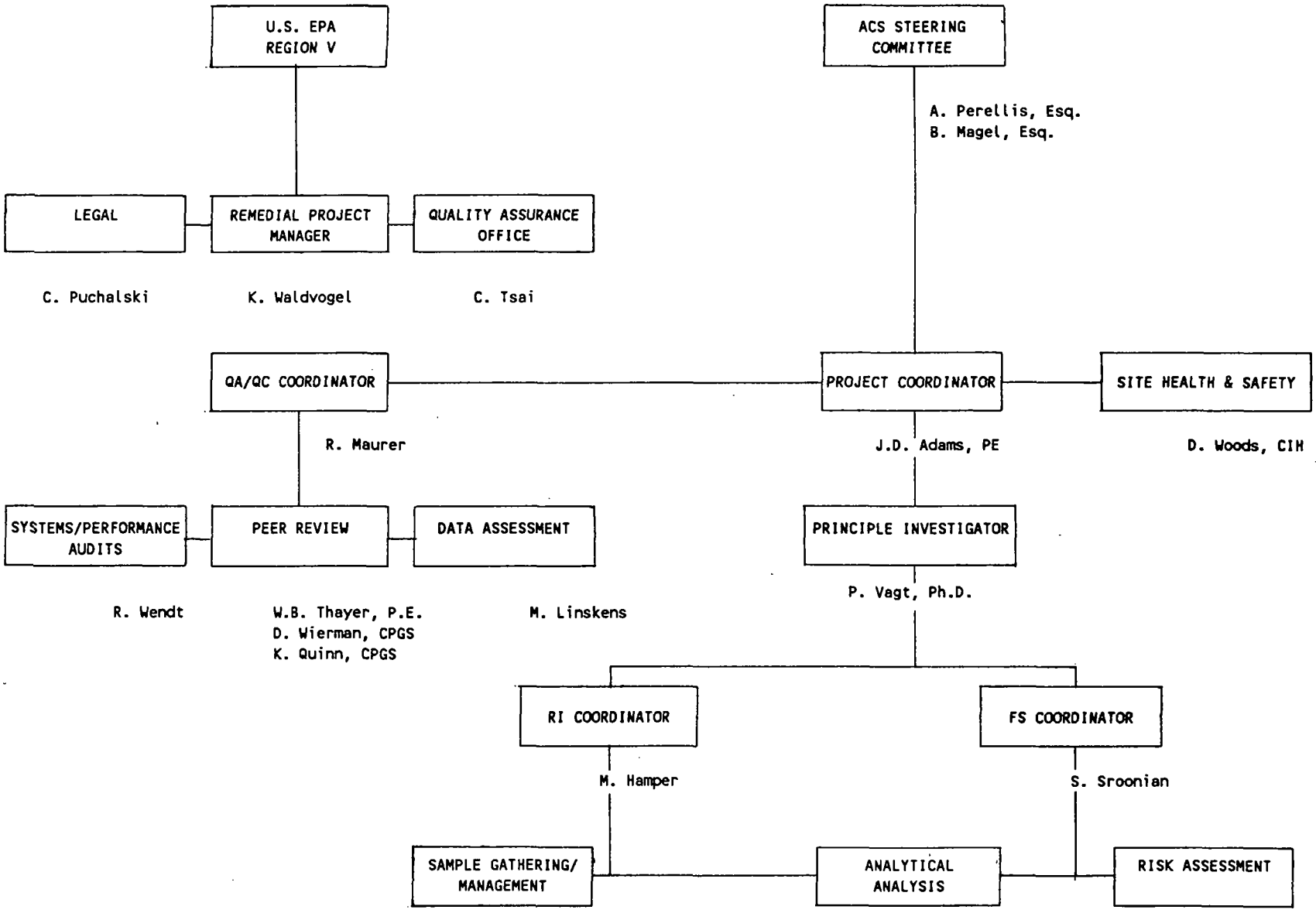
PROPOSED REMEDIAL INVESTIGATION SCHEDULE
AMERICAN CHEMICAL SERVICES
GRIFFITH, INDIANA



LEGEND
=======
XXX WARZYN
OOO REVIEW BY EPA
LLL LAB TURN-AROUND

FOOTNOTES
=========
(1) Task 1.B, defining site boundaries, cannot be completed without authorization of site access from American Chemical Services.
(2) Draft RI will be submitted 10 weeks after completion of Phase II, which will be contingent upon the findings from Phase I.

Figure 4
PROJECT ORGANIZATION CHART



WARZYN

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CHAIN OF CUSTODY RECORD

PROJ. NO.	PROJECT NAME
SAMPLERS: *(Signature)*	

LAB NO.	DATE	TIME	COMP.	GRAB	STATION LOCATION	NO. OF CONTAINERS							REMARKS

Relinquished by: *(Signature)*	Date / Time	Received by: *(Signature)*	Relinquished by: *(Signature)*	Date / Time	Received by: *(Signature)*
Relinquished by: *(Signature)*	Date / Time	Received by: *(Signature)*	Relinquished by: *(Signature)*	Date / Time	Received by: *(Signature)*
Relinquished by: *(Signature)*	Date / Time	Received for Laboratory by: *(Signature)*		Date / Time	

Remarks

Figure 5. Chain-of-Custody Record

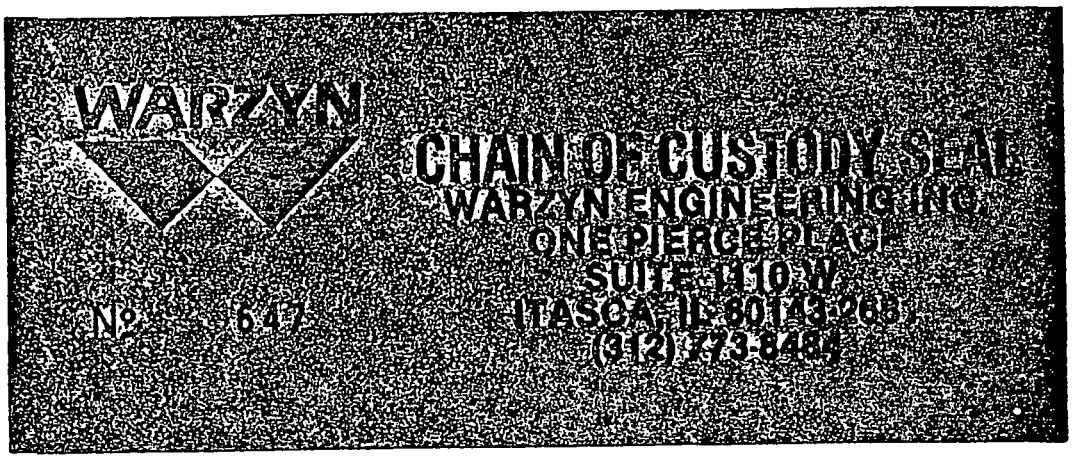

Figure 6. Chain-of-Custody Seal

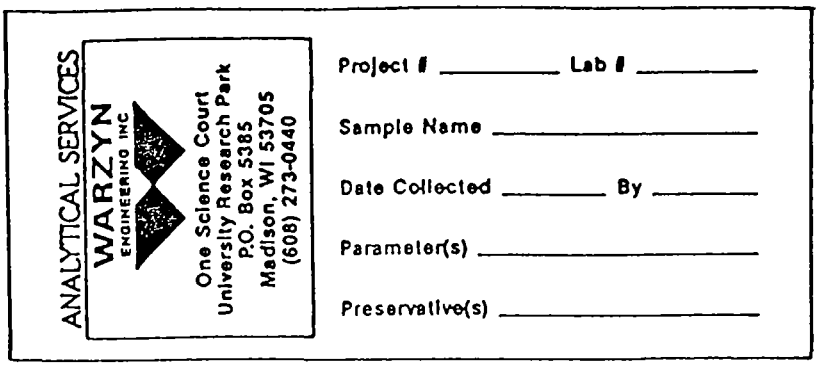

Figure 7. Sample label

SAMPLE IDENTIFICATION RECORD

CASE/JOB NUMBER	MATRIX	SAMPLE NUMBER	LAB	LAB NUMBER	CHAIN OF CUSTODY	DATE SAMPLED	DATE SHIPPED	AIRBILL NUMBER

Figure 8. Sample Identification Record.

APPENDIX A

SAMPLING PLAN
FOR
AMERICAN CHEMICAL SERVICES, INC.
RI/FS

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SAMPLING PLAN
AMERICAN CHEMICAL SERVICES, INC.
RI/FS

1.0 OBJECTIVES

The primary objective of the sampling activities described below is to obtain representative data to be used for the Remedial Investigation/Feasibility Study (RI/FS) analysis. Sampling activities described in this plan will be performed to complete the Site Investigation subtasks of the RI.

Data use objectives of the Site Investigation subtask include:

- Evaluate the details of on-site soil stratigraphy and the stratigraphy in adjacent off-site areas
- Determine the hydrogeologic conditions in the upper aquifer, including vertical and horizontal groundwater flow conditions on-site and in adjacent off-site areas.
- Determine the configuration of the water table in the upper aquifer on-site and in adjacent areas off-site.
- Identify surficial drainage features and flow patterns, and characterize the relationship of surface water to groundwater on-site and in adjacent off-site areas.
- Characterize the extent of surface water and sediment contamination on-site and in adjacent off-site areas.

2.0 SCOPE

The RI will be conducted in three phases in order to make optimal use of the information as it is derived and to produce the information necessary to complete the FS. The phased approach allows "mid-course" corrections to be made so that the investigation will develop in the most efficient and cost-effective sequence. This sampling plan addresses the first two phases. Additional phases would be developed if and when it were determined that additional information would be required. Phase I incudes three major tasks: Problem Definition, Hydrogeologic Investigation, and Near Surface Contamination Investigation. The major task under Phase II is Site Characterization. Additional tasks which may be performed under Phase III are Additional Contamination Investigation and Endangerment Assessment. Review the work plan for specific details.

This Sampling Plan describes the procedures and practices to be used in obtaining Site Investigation data for use in the RI/FS. These procedures include a description of the sample designation system, personnel and their responsibilities, and the sampling methods to be employed. These methods include:

- Soil borings and soil sampling
- Shallow piezometer installation
- Monitoring well installation
- Geophysical Survey
- Leachate well installation
- Groundwater sampling
- Leachate sampling
- Surface water and sediment sampling
- Water level monitoring in piezometers and surface water
- Aquifer tests
- Private well sampling
- Test pits

3.0 SAMPLING LOCATIONS AND NUMBER OF SAMPLES

3.1 HYDROGEOLOGIC INVESTIGATION

The hydrogeologic investigation will include groundwater sampling, water level measurements, aquifer tests, continuously sampled and logged borings, well installations, and piezometer installations.

3.1.1 Groundwater Sampling

One round of groundwater samples will be obtained during Phase I from each of the 6 perimeter wells. The locations proposed for these wells are depicted on Figure 1.

During Phase II of the investigation, two rounds of groundwater samples will be obtained from all of the Phase I perimeter wells, and from all of the wells installed during Phase II. It is anticipated that 8 to 12 wells may be installed during Phase II. During the second round, it is anticipated that only 9 wells will be sampled for the complete TCL, and the remaining number sampled for a reduced parameter test approved by the U.S. EPA.

Off-site, one upgradient and nine downgradient private water supply wells will be sampled during Phase II. The locations of the known private wells are shown on Figure 2. The specific wells to be sampled will be identified based on the results of the Phase I study.

3.1.2 Water Level Measurements

Water levels will be measured at least twice during the Phase I field effort and at least once during the Phase II field effort. Measurements will be obtained from each of the shallow piezometers and each of the surface water locations depicted in Figure 1. The first set of measurements will be made within a week after installations are completed for both the piezometers and the surface water reference locations. If possible, measurements will also be made during dry and wet periods. Also, immediately after a major precipitation event, closely-spaced measurements may be made to determine the response of the system to such an occurrence.

3.1.3 Aquifer Tests

Slug tests will be conducted in three of the six new Phase I wells to determine the hydraulic properties of the upper aquifer. A total of eight slug tests will be conducted during Phase II. All of the four lower aquifer wells will be tested, and four of the Phase II shallow aquifer wells will be tested.

The wells to be used in the aquifer testing will be those best representing the aquifers. Criteria for selection will include saturated thickness and grain size. If indicated, a pumping test might be conducted. In addition, up to 90 laboratory geotechnical tests will be performed on aquifer and aquitard materials. These tests will include hydraulic conductivity, grain size, Atterberg limits, cation exchange capacity, and moisture content.

3.1.4 Monitoring Well Installations

Six wells will be installed during Phase I at the locations shown in Figure 1. These wells will be completed with the ten-foot screen intersecting the water table in the upper aquifer.

It is anticipated that eight to twelve wells will be installed during Phase II. Four wells will be screened in the upper aquifer and the remaining number in the upper part of the lower aquifer. The screen locations for the Phase II upper aquifer wells will be determined based on the Phase I results, as will the horizontal locations of all the wells.

3.1.5 Piezometer Installation

Piezometers, designed to only collect water level data, will be installed at approximately 40 locations as depicted in Figure 1, during Phase I. Piezometers will be located throughout the site including in the landfill. Under no circumstances would piezometers be installed through the base of the landfill. Piezometer screens will intersect the top of the first saturated layer.

3.2 CONTAMINANT INVESTIGATION

The Phase I Contaminant Investigation will involve sampling of the surface soil, the drilling of 14 soil and waste borings, a geophysical survey, surface water and sediment sampling and excavation of 6 waste test pits. A total of 48 investigative samples will be submitted for analysis (Table 2).

Four leachate wells will be installed and sampled during Phase I. Sampling of the ACS effluent may also be done at selected locations. It is anticipated that additional drilling, sampling, and analysis will be conducted under Phase II with up to 20 samples collected for analysis. The locations will be determined based on Phase I results.

3.2.1 Surficial Soil Area Sampling

The On-Site Containment Area will be divided into four sampling areas, and the former Kapica Drum property will be divided into two sampling areas. Within each of these areas, a soil sample will be collected at the depth interval of 6-18 inches at five discrete locations and then composited (volatile organic samples will be grab only) for a total of 6 samples. One grab sample will be collected near the former fume incinerator, and one grab sample at the site of a previous spill/fire. These samples will also be collected from the 6 to 18 inch depth interval. The approximate locations for these eight investigative samples are shown in Figure 3.

3.2.2 Geophysical Survey

A field test will be conducted to determine if a magnetometer survey will provide meaningful data. Because of the presence of railroads, power lines, metal buildings, metal process tanks, geophysical methods may be of limited utility. If feasible, the method would be used to located buried drums in the ACS Off-Site Containment Area, On-Site Containment Area, Old Still Bottoms Pond, Treatment Pond No. 1, and the Kapica Drum draining area.

3.2.3 Test Pits

Six waste test pits will be excavated at approximately the locations identified in Figure 4. These are the On-site Drum Containment Area, the Still Bottoms Pond and Treatment Pond No. 1. If a liner is encountered, excavation will cease. In each test pit one composite waste sample (volatile organic samples will be grab only), consisting of five discrete samples, and one natural subsoil sample will be collected.

3.2.4 Soil and Waste Borings

Five waste borings will be drilled in the Off-Site Drum Containment Area with one composite waste sample (volatile organic samples will be grab only), consisting of five discrete samples, and one natural soil sample being collected from each boring. Three borings are planned for the Kapica Drum site with one composite waste sample and one natural subsoil sample collected from each boring. The approximate locations of these eight borings are located in Figure 4.

Six soil borings will be drilled in the Old Drum Storage Area. Two grab samples will be collected from each boring at the depth intervals of 2 to 2.5 feet and 4 to 4.5 feet, for a total of 12 samples submitted for analysis. The approximate locations of these borings are depicted in Figure 3.

3.2.5 Leachate Well Installation and Sampling

Four leachate wells will be installed approximately as shown in Figure 1. The borings for the wells will not penetrate the base of the landfill. One round of samples will be collected during Phase I.

3.2.6 Surface Water and Sediment Sampling

A surface water and sediment sample will be collected from each of the 11 locations shown in Figure 1. Sampling locations include: Treatment Pond No. 2, the ACS Retention Pond, a drainage ditch at the southwest corner of the ACS plant, the marsh, ponded water near the Off-Site Drum Containment Area, the Griffith Landfill excavation, three sites along a drainage ditch connecting the marsh to Turkey Creek, a drainage ditch that is parallel to Colfax Avenue south of intersection of Colfax Avenue and Reder Road, and a drainage ditch 1,800 feet southeast of the ACS site (beyond limits of Figure 1).

3.2.7 Effluent Sampling

It is anticipated that sampling of ACS waste effluent will be performed. Up to four samples will be collected at locations to be determined based on results of the ACS Environmental Audit.

4.0 SAMPLE DESIGNATION

A sample numbering system will be used to identify each investigative and quality control sample. Each sample identifier will include the project identifier code, sample type and location code, and a sampling event code. The sampler will maintain a log book containing the sample identification listings.

4.1 PROJECT IDENTIFIER CODE

A 3-letter designation will be implemented to identify the sampling site. The project identifier will be "ACS" to signify this site investigation.

4.2 SAMPLE TYPE AND LOCATION CODE

Each sample location will be identified by a 2-letter code corresponding to the sample type. Sample type codes to be utilized for the subtasks covered in this Sampling Plan include:

- GW - groundwater sample from monitoring well
- LE - leachate sample
- SS - split spoon or soil boring sample
- SD - sediment sample
- SW - surface water sample
- PW - groundwater from a private well
- WP - waste sample from test pit
- NP - soil sample from test pit
- AE - ACS effluent sample
- WB - waste boring sample
- NB - natural soil boring sample
- SA - soil area sample
- SB - soil boring sample
- FB - field blank
- TB - trip blank
- MS(D) - matrix spike (duplicate)

Other letter designators may be added for sample activities of later subtasks.

The location code will follow the sample type code. The location code consists of a two- to five-digit numeric or alpha-numeric code that indicates the sample location. Surface water, sediment, field blanks, and trip blanks will use a consecutive numbering system, starting at 01, assigned in the field.

4.3 SAMPLING ROUND CODE/DUPLICATE CODE

A two-digit numerical code will be used to designate additional information. The round code will indicate the groundwater sampling round. Duplicate samples will be designated by the round code preceded by a 9. For boring samples, the round code will represent the depth of the sample in feet below the ground surface.

4.4 EXAMPLES OF SAMPLE NUMBERS

Examples of sample number codes are as follows:

- ACS-SSMW03A-25 = ACS, split spoon sample from Monitoring Well MW03A at a depth of 25 feet
- ACS-GWMW03A-01 = ACS, groundwater sample from Monitoring Well MW03A, first sampling round
- ACS-GWMW03A-91 = ACS, duplicate groundwater sample from Monitoring Well MW03A, first sampling round
- ACS-SD10-01 = ACS, sediment sample from location number 10, first sampling round

5.0 SAMPLING EQUIPMENT AND PROCEDURES

5.1 GROUNDWATER SAMPLING

5.1.1 Monitoring Wells

Groundwater sampling will proceed from wells thought to have the lowest contaminant concentrations to wells suspected to have the highest contaminant concentrations. A clean work area will be set up at the well before sampling begins at that well. Prior to purging the well, a water level measurement will be made using an electronic water level indicator or a tape with a sounding device. Total depth of the well will also be measured. The reference point for these measurements is the top of the inner well casing (when protective casing present). Measurements will be made to the nearest 0.01 foot and recorded in the field notebook along with the purge volume.

Each well will be purged immediately prior to sampling, using a submersible bladder pump. The pump will be constructed of stainless steel and teflon. Dedicated teflon tubing will be used to purge and sample each well. The volume of water removed shall be measured using a calibrated bucket to ensure that a minimum of three well volumes are removed. The pH, specific conductance and temperature will be measured to determine that these parameters have stabilized prior to sample collection. The conductivity meter will be zeroed according to the procedures specified by the manufacturer prior to measurement. Buffer solutions will be used to calibrate the pH meter and conductivity meter at the beginning of each day and after every ten samples. A sample of water will be placed into a beaker into which the probes are inserted. After the readings are made, the water sample is then added to the collected purge water. Purge water will be collected and containerized.

After well purging is completed, the discharge of the pump will be reduced to 100 ml/min or less to fill the sample containers. Sample containers shall be filled in the following order: volatiles, semi-volatile, PCB/pesticides, total organic carbon, metals, cyanide, sulfate-chloride-alkalinity, ammonia-nitrate-nitrite, and total suspended solids-total dissolved solids.

For volatile organic analysis (VOA) samples, the preservative shall be added to the vial prior to collecting the sample. The VOA sample vial will be carefully filled until the proper meniscus forms. The cap shall be carefully placed on the vial, after which the vial will be inverted to inspect for air

bubbles. If air bubbles are present, the cap will be removed and more sample will be added. The cap will be replaced and inspected again for bubbles. Repeat if necessary.

The remainder of the sample bottles will then be filled in the order outlined above according to the specifications listed in Table 3. Groundwater samples requiring field filtering will be filtered using a positive-pressure filtration device. After filtering is completed, preservative may be added to those sample containers as specified in Table 3. The pH of the preserved sample shall be tested by pouring a small amount of sample into a watch glass or beaker and then testing the aliquot with pH paper (except VOA which will not be disturbed). Samples will be iced immediately after collection.

Duplicate samples will be prepared by alternatively filling each vial or bottle (i.e. one investigative sample vial or bottle), then one duplicate sample vial or bottle, etc.).

The trip blank will consist of two 40-ml VOA vials filled with deionized water and preservative at the laboratory or office, transported to the field and shipped to the laboratory with the investigative VOA vials. The vial will not be opened in the field and will be handled and documented using the standard procedures.

Field blanks will be prepared by pumping deionized water through the bladder pump and tubing and filling the sample containers in the same manner as for investigative samples. The field blank for constituents requiring filtering shall require the additional step of passing the aliquot through the field filtering apparatus.

The semi-volatile organics matrix spike/matrix spike duplicate (MS/MSD) for water samples must be collected at double the volume normally required. The PCB/Pesticide MS/MSD for water samples must also be collected at double the volume normally required and the volatile sample MS/MSD must be collected at triple the normal volume.

The sampling equipment shall be cleaned and handled between wells following the procedures outlined in Section 6.

5.1.2 Private Water Supply Well

It is anticipated that these wells will be in constant use and so the purge volume will be limited to that volume between the well head and sampling point. Temperature, pH, and conductivity shall also be monitored to determine stabilization of these parameters. The sampling point will be as close as possible to the well head, before any treatment occurs (i.e. water softeners, filters, etc.). The sampling port may require cleaning prior to purging and sampling. After purging, reduce the discharge rate and follow the same collection and handling procedures outlined under 4.1.1 for groundwater samples. The field blank will be prepared by pouring deionized water directly into the sample containers. The trip blank will be prepared as described in 5.1.1. Water samples will not be filtered. These private water supply samples will be analyzed by different methods with lower detection limits. See Appendices C and D of QAPP for methods and detection limits.

5.1.3 Water Level Measurements

Water level measurements will be obtained from the shallow piezometer system, and monitoring wells, using an electronic water level indicator or a tape and sounding device. The measurement shall be made to the nearest 0.01 foot. The reference point shall be the top of the inner casing. If the top of the inner casing is not level, the reference point will be the highest side of the casing.

5.2 AQUIFER TESTING

5.2.1 Field Testing

The hydraulic conductivity of the penetrated aquifer will be estimated by conducting slug tests. The basic concept behind these tests is that the rate of rise or fall of the water level in a well after "instantaneous" displacement of a "slug" of water is a function of aquifer hydraulic conductivity.

Hydraulic conductivity testing will be performed as follows:

- An initial measurement of static water level will be made.
- A volume of water will then be displaced as rapidly as possibly using a calibrated solid cylinder or compressed air. Highly permeable conditions ($K > 10^{-3}$ cm/sec) are anticipated.

- Water level changes in the well will be sensed and recorded by a pressure transducer connected to an electronic data logger. Water level measurements will be collected automatically on logarithmically increasing time steps, starting at 0.003 minutes (i.e., the first 10 measurements will be taken at the following elapsed time: 0, 0.003, 0.007, 0.010, 0.013, 0.017, 0.020, 0.0233, 0.026, 0.030). The total test time could last from several minutes to several hours for each well.

- The data will be plotted in the field (water level vs. log time) using semi-log paper to determine if the data are sufficient to establish a reasonable straight-line relationship.

Analysis of test data should use appropriate computational methods such as that presented by Bouwer, H. and R.C. Rice, 1977, "A Slug Test for Determining Hydraulic Conductivity of Unconfined Aquifers with Completely or Partially Penetrating Wells," Water Resources Research, Vol, 12, No. 3, pp. 423-428, or Nguyen, V., and G. F. Pinder, 1984, "Direct Calculation of Aquifer Parameters in a Slug Test Analysis", Groundwater Hydraulics, Water Resources Monograph No. 9, American Geophysical Union, pp. 222-240. If indicated, a pumping test might be conducted.

5.2.2 Laboratory Testing

Samples will be collected in 3-inch diameter Shelby tubes, capped, taped to seal and stored at 4 degrees centigrade until analyzed. Samples expected to have a saturated hydraulic conductivity of 1×10^{-3} cm/sec or less will be tested using a falling head test and those expected to be greater than 1×10^{-3} cm/sec will be tested using a constant head test, using a flexible wall permeameter.

Grain size analysis will be accomplished using ASTM Methods D421, D422, and D2217. Samples for grain size analysis will be collected from split-spoon samplers and placed into glass jars. Soil samples will also be tested for Atterberg limits, cation exchange capacity and moisture content.

5.3 MONITORING WELL INSTALLATION

Borings will be drilled using a 4 1/4-inch ID hollow stem auger. Formation samples will be collected continuously from the surface to the end of the borehole. Split-spoon (ASTM D1586-84) formation samples will be visually classified in the field by a geologist. Representative samples of units

encountered will be placed into glass jars for laboratory analysis. Three-inch ID Shelby tube samples (ASTM D1587) will also be collected for laboratory hydraulic conductivity testing of the units encountered. These samples will be handled and stored as described above (Section 5.2.2).

Drilling equipment and tools will be decontaminated between boreholes as outlined in Section 6. Well casing and screens will be cleaned and stored as outlined in Section 6. Well casing and screen will be constructed of 2-inch ID threaded flush-joint stainless steel 316 and will have vented locking caps. Ten foot screens with 0.01-inch openings and a No. 30 flint sand or natural cave-in will be used for the sand pack.

Because Phase I and II upper aquifer wells are expected to be screened at shallow depths in coarse grained deposits, a surface seal will be unnecessary. Phase II lower aquifer wells will be constructed using a telescoping casing. The outer casing will be set 5-feet into the aquitard and sealed. Split-spoon samples (ASTM D1586-84) will be obtained every five feet in the upper aquifer and continuously through the aquitard and lower aquifer to the end of the borehole. The screen of the inner casing will be set 12 feet into the lower aquifer. Two-foot bentonite seal will be placed 2-feet above the screen and then the annular space will be filled with bentonite grout to within three-feet of the surface. The remainder wil be filled with cement-bentonite grout.

A concrete apron will be placed around each well. All wells will be developed using a surge block and/or pumping. Well casing elevation will be surveyed to the accuracy of ±0.01 foot, and ground elevation and horizontal location will be surveyed to the accuracy of ±0.1 foot. Well casings will be permanently marked with the well number.

5.4 PIEZOMETER INSTALLATION

The piezometers will be installed by jetting them into the ground. The piezometers placed within the landfill may have to be installed with a drill rig. Screens for the piezometers will be set at the top of the first saturated layer. Caps will be pop-riveted in place to seal the piezometer and avoid tampering. Piezometer casing elevation will be surveyed to the accuracy of ±0.01 foot, and ground surface elevation and horizontal location will be surveyed to the accuracy of 1.0 foot. Piezometers will be permanently marked with the piezometer number.

5.5 SURFICIAL SOIL SAMPLING

A hand-auger or shovel will be used to remove the upper six inches of material. The bucket auger will then be inserted into the hole and the sample brought to surface and placed into a stainless steel pan. This is repeated to obtain sample from the 6 to 18 inch depth interval.

Grab samples will be placed into the sample containers with a stainless steel scoop. Composite samples (except volatiles) will be obtained by homogenizing the subsamples in the stainless steel pan with a scoop or trowel. A sample will then be placed into the appropriate sample containers. Samples for volatile organic parameters will be grab samples selected from the five discrete samples from each sampling area on the basis of HNu results and/or other evidence of contamination (e.g. visual). One duplicate sample will be collected. No blanks will be prepared. Equipment and tools will be decontaminated as outlined in Section 6.

5.6 GEOPHYSICAL SURVEY

A feasibility test will be conducted to determine if the magnetometer will provide meaningful data. The instrument will be calibrated according to the manufacturer's instructions. Anomalous areas will be marked by pin flags in the field. Selected points will be duplicated to examine equipment response. If response is inconsistent, data will be considered unusable.

5.7 TEST PITS

Waste test pits will be excavated with a backhoe. The backhoe operator will remain in the cab during all excavation activities and be prepared to fill the pit quickly in the event of an emergency. Excavated materials will be placed on the downwind end of the pit for inspection. All pits will be filled prior to starting a new excavation and at the end of each work day. No pit will be left open and unattended at any time. Personnel will not enter test pits. Pits will be marked to enable future location. Samples will be taken from representative layers of waste and then composited (except volatiles). The excavation will extend at least one foot into natural subsoils. A sample of the natural subsoil will be obtained. Hand tools will be used to collect samples. Composite samples will be prepared in the field. Samples for volatile organics will be grab samples selected from one of the five discrete samples on the basis of HNu results and/or other evidence of

contamination (e.g. visual). The material excavated will be used as backfill for the test pit. Samples will be placed into the appropriate containers. No blanks will be prepared. One natural soil and one waste duplicate sample will be collected.

5.8 SOIL AND WASTE BORINGS

Waste borings will be continuously sampled with a split-spoon (ASTM D1586-84) to a depth of approximately 1 1/2 feet below the waste. Waste samples will be homogenized in a stainless steel pan with hand tools and a representative sample placed into the appropriate containers (except volatiles). Samples for volatile organics will be grab samples selected from one of the five discrete samples on the basis of HNu results and/or other evidence of contamination (e.g. visual). A 1-foot grab sample of the natural subsoil will be obtained from each boring using the split-spoon.

Soil borings will be advanced to a depth of two feet, below which a 6-inch split spoon sample will be obtained. The auger will be advanced to a depth of 4 feet and another sample obtained from the interval 4 to 4.5 feet. Each of these 6-inch samples will be a grab sample.

Samples will be placed in the appropriate containers and boreholes will be filled with bentonite grout to the surface. All drilling equipment and tools will be cleaned between sampling locations according to procedures in Section 6.

5.9 LEACHATE WELL INSTALLATION AND SAMPLING

A hollow-stem auger will be used to advance the borehole up to 15 feet below the first saturated zone encountered; in no event shall any liner present be penetrated. The entire saturated zone penetrated shall be screened using threaded flush-joint PVC with PVC riser pipe to the surface. The screen openings shall be 0.01 inch with a No. 30 flint sand (or equivalent) filter. The filter shall extend to 2-feet above the screen, above which a two-foot bentonite pellet seal will be placed. The remaining annular space to within 3-feet of the surface will be filled with bentonite grout. A concrete seal will then be placed to the surface, forming an apron at the surface. Concrete barrier posts shall be placed around the concrete apron.

The well shall be developed and sampled using a stainless steel bailer. All purge and development water shall be collected and containerized. Sampling

will be conducted as for the groundwater wells under 5.1.1 except that a bailer will be used. Trip blanks will be prepared as described in 5.1.1. The field blank will be prepared by pouring deionized water into a clean bailer and filling sample bottles in the same manner as for an investigative sample. The drilling and sampling equipment shall be cleaned and stored between wells using the procedures outlined in Section 6.

5.10 SEDIMENT AND WATER SAMPLING

The surface water grab sample will be collected prior to collecting the sediment (grab) sample at a given location. Where appropriate, the samples will be taken from the most distal downstream location to the furthest upstream location. Samples will be obtained with stainless steel equipment which will be decontaminated between sample locations using the procedures outlined in Section 6. A bucket auger will be used to collect a sample from the depth interval 0 to 6 inches. Samples will be placed into the appropriate containers. Duplicates will be collected for both sediment and water samples, but field blanks will only be prepared for water samples. Water samples will not be filtered. Trip blanks will be prepared as outlined under 5.1.1.

5.11 EFFLUENT SAMPLING

This effort will be designed after the Environmental Audit of ACS.

5.12 PERSONNEL AND RESPONSIBILITIES

All personnel working at the ACS site on the RI will have been trained in health and safety matters relating to hazardous waste site investigations. Efforts will be made to use the same personnel throughout the course of the field work to optimize familiarity with site conditions. The boundary survey will be done by an Indiana licensed land surveyor. All other surveys will be conducted by a two-person team.

A two-person drilling crew and two field technicians will be supervised by a geologist or engineer. The geologist or engineer will also serve as the Safety Officer. A geologist will conduct the slug tests and log the soil samples. Samples will be collected by or under the supervision of the geologist in the various media: groundwater, surface water, leachate and waste. Also water levels will be collected by the geologist or engineer, and a field technician. An earth moving subcontractor will operate the backhoe.

6.0 DECONTAMINATION PROCEDURES

Procedures to be followed to decontaminate equipment and personnel are described in the Site Health and Safety Plan. The procedures are summarized below.

Site Personnel Decontamination Procedure:

- Dispose of outer latex booties
- Wash boots in TSP bootwash
- Clean outer gloves in TSP wash solution (discard if too soiled to clean thoroughly)
- Dispose of polycoated tyvek suits
- Dispose of surgical gloves
- Wash hands in hand wash
- Wash face and neck in face wash
- Clean and sanitize face mask

Site personnel will perform the above mentioned decontamination procedure prior to leaving the site. Personnel will shower immediately after arriving at their residences.

Discarded clothing and other articles will be collected in double-lined, heavy duty garbage bags.

Equipment and vehicle decontamination procedure:

- Decontamination will be performed prior to site entry
- Decontamination will be performed on-site
- Gross contamination will be removed with a brush and TSP solution
- Steam cleaning will follow

The drilling equipment and the backhoe will be steam cleaned prior to exiting the site at an area designated for equipment and vehicle decontamination. Another area, located away from the equipment decon area, will be designated as a site personnel decon area.

Decontamination will include steam cleaning the drilling equipment, backhoe and tools between boreholes and test pits, and detergent washing and deionized water rinsing the split spoon samplers after each collected sample.

Well casing and screens will also be steam cleaned and wrapped in plastic until installed. Sampling equipment such as the bailer cable, trowels, spatulas, stainless steel bucket, pump, bailer, etc. will be cleaned with a trisodium phosphate (TSP) detergent solution, and rinsed with deionized water between sampling locations and stored to prevent contamination before use.

Equipment remaining at the site may not be decontaminated, but will be stored on the contaminated side of the equipment and vehicle decon area at the end of each work day.

7.0 SAMPLE HANDLING AND ANALYSIS

7.1 PARAMETERS

Samples to be analyzed for TCL organics (both standard CLP detection limit, and low detection limit) will be sent to Hazleton Laboratories America, Inc. Samples to be analyzed for TCL metals, cyanide, and indicator parameters will be sent to Warzyn Engineering Inc. (for both standard CLP detection limit and low detection limit). Samples to be analyzed for geotechnical parameter will be sent to Warzyn Engineering Inc. Parameters for which groundwater, surface water, private water supply wells, soil, sediment, ACS effluent and waste are to be analyzed are summarized in Tables 4, 5, 6, 7 and 8.

Measurement of pH, specific conductance and temperature will be performed in the field as will vapor screening with OVA or HNu.

7.2 SAMPLE PRESERVATION

Samples will be collected and preserved in a manner appropriate for the analyses they receive (Table 3). The portion of groundwater samples requiring field filtering prior to analysis (Table 3) will be filtered using a pressure filtration device, through a 0.45 micron filter, as soon as possible after collection. Filtered portions of the samples will be preserved, as appropriate, immediately after filtration. Sample fractions will be preserved before shipment according to the procedures shown in Table 3. Preservatives added to the samples will be prepared using reagent grade chemicals.

8.0 SAMPLE DOCUMENTATION

Samples will be collected under chain-of-custody procedures. Standard forms including sample labels, sample tags, chain-of-custody forms, and custody seals used for sample tracking will be maintained. A brief description of sample documents follow:

A. Chain-of-Custody Form (Figure 5)

1. One Form per shipping container (cooler).
2. Carrier service does not need to sign form, if custody seals remain intact.
3. Use for all samples

B. Chain-of-Custody Seals (Figure 6)

1. Two seals per shipping container to secure the lid and provide evidence that samples have not been tampered with.
2. Cover seals with clear tape.
3. Record seal numbers on Chain-of-Custody Form.
4. Use for all samples.

C. Sample Tags (Figure 7)

1. Each sample container must have a sample tag affixed to it.
2. Sample tag numbers are recorded on the Chain-of-Custody Forms.
3. Use for all samples.

D. Sample Identification Record Form (Figure 8) will:

1. Provide means of recording crucial sample shipping and tracking information.
2. Contain information such as:

   - Sample number
   - Sample matrix
   - Sample location code
   - Sample round

- Chain-of-custody number
- Lab code
- Date sampled
- Date shipped
- Airbill number
- Sampling tag number

Paperwork accompanying the samples being shipped to the laboratory will be sealed in a plastic bag that is taped to the inside of the cooler lid. Copies of the chain-of-custody forms, and other paperwork (if possible), will be retained for the field files.

Two sample seals will be placed on opposite sides of the lid and extending down the sides of the cooler. The lid will be securely taped shut prior to shipment.

Representative photographs will be taken of sampling stations to show surrounding area and used to locate the station. The picture number and roll number will be logged in the field log book to identify which sampling site is depicted in the photograph. The film roll number will be identified by taking a photograph of an informational sign on the first frame of the roll. This sign would have the job and film roll number written on it so as to identify the pictures contained on the roll.

For example:

American Chemical Services
Roll Number 1
Frame Number 1 of 36
1 Nov 1988

All sampling documentation will be maintained in Warzyn files as outlined in the QAPP.

TABLE 1
SITE CHARACTERIZATION SAMPLING EFFORT

	INVESTIGATIVE	DUPLICATE	FIELD BLANKS
Groundwater (GW)			
Phase I	6	1	1
Phase II A (up to)	12	2	2
Phase II B (up to) full TCL	9	1	1
*Phase II B (up to) reduced parameter list	(9)	(1)	(1)
Surface Water (SW)	11	2	2
Sediment (SD)	11	2	0
Private Wells (PW)	10	1	1
Leachate (LE)	4	1	1
ACS Effluent (AE)	4	1	1
SUBTOTAL	67	11	9
Chemical Subtotal	87		
Geotechnical	90		
Geotechnical Subtotal	90		

TOTAL: 177

Note:

* Numbers not included in total

TABLE 2
SOURCE CHARACTERIZATION SAMPLING EFFORT

	INVESTIGATIVE	DUPLICATE	FIELD BLANKS
PHASE I			
Waste Pit (WP)	6	1	0
Natural Soil Pit (NP)	6	1	0
Waste Boring (WB)	8	1	0
Natural Soil Boring (NB)	8	1	0
Soil Area (SA)	8	1	0
Soil Boring (SB)	12	2	0
Chemical Subtotal	48	7	0
PHASE I TOTAL: 55			
PHASE II			
To Be Defined in Phase I	20	2	0
PHASE II TOTAL: 22			

Notes:

Blanks are not necessary for solid material samples.

TABLE 3
SAMPLE QUANTITIES, BOTTLES, PRESERVATIVES AND PACKAGING
FOR WATER, SEDIMENT AND LEACHATE SAMPLES

Analysis	Bottles and Jars	Preservation	Holding Time	Volume of Sample	Shipping	Normal Packaging
WATER AND LEACHATE						
Low Concentration (Organics)						
Semi-Volatiles	One 1-liter amber bottle (teflon-lined cap)	Iced to 4°C	5 days until extraction, 40 days after extraction	Fill bottle to neck	Shipped Daily by Overnight Carrier	No. 1 foam liner or vermiculite
Pesticides/PCBs	One 1-liter amber bottle (teflon-lined caps)	Iced to 4°C	5 days until extraction, 40 days after extraction	Fill bottle to neck	Shipped Daily by Overnight Carrier	No. 1 foam liner or vermiculite
Volatiles	Two 40-ml volatile organic analysis (VOA vials)	Iced to 4°C HCL to pH <2	7 days (48 hours for surface water)	Fill completely no headspace	Shipped Daily by Overnight Carrier	No. 1 foam liner or vermiculite
Low Concentration (Inorganics)						
Metals (groundwater)	One 1-liter high density polyethylene bottle	Filter through 0.45 um filter, HNO_3, to pH <2 Iced to 4°C Optional	6 months (Hg, 26 days)	Fill to shoulder of bottle	Shipped Daily by Overnight Carrier	No. 2 foam liner or vermiculite
Metals (leachate, surface water and private water supply wells)	One 1-liter high density polyethylene bottle	HNO_3 to pH <2 Iced to 4°C	28 days	Fill to shoulder of bottle	Shipped Daily by Overnight Carrier	No. 2 foam liner or vermiculite
Cyanide	One 1-liter high density polyethylene bottle	NaOH to pH >12 Iced to 4°C	14 days	Fill to shoulder of bottle	Shipped Daily by Overnight Carrier	No. 2 foam liner or vermiculite
Other Analysis						
Chlorides, Alkalinity Sulfate	One 1-liter high density polyethylene	Iced to 4°C	28 days (14 days for alkalinity)	Fill to shoulder of bottle	Shipped Daily by Overnight Carrier	No. 2 foam liner or vermiculite
Total Organic Carbon, Ammonia, Nitrate-Nitrite, Chemical Oxygen Demand	One 1-liter polyethylene high density bottle	Iced to 4°C H_4SO_4 to pH <2	28 days	Fill to shoulder	Shipped Daily by Overnight Carrier	No. 2 foam liner or vermiculite
Total Dissolved Solids Total Suspended Solids	One 1-liter polyethylene high density bottle	Iced to 4°C	7 days (filter upon receipt at lab)	Fill to shoulder	Shipped Daily by Overnight Carrier	No. 2 foam liner or vermiculite

TABLE 3 (Continued)

SOIL/SEDIMENT

Low or Med Concentration (Organics)						
Acid extractables, base/neutral extractables, pesticides/PCBs	One 8-oz wide mouth glass jar	Iced to 4°C	10 days until extraction, 40 days after extraction	Fill 3/4 full	Shipped Daily by Overnight Carrier	Foam liner No. 3 (Med in cans/ vermiculite)
Volatiles	Two 120-ml VOA vials	Iced to 4°C	10 days	Fill completely no headspace	Shipped Daily by Overnight Carrier	Vermiculite (Med in cans/ vermiculite)
Low or Med Concentration (Inorganics)						
Metals and Cyanide	One 8-oz wide mouth glass jar	Iced to 4°C	6 months (14 days for cyanide)	Fill 3/4 full	Shipped Daily by Overnight Carrier	Foam liner No. 3 (Med in cans/ vermiculite)
Physical Analyses						
Grain Size, moisture content	One 8-oz wide mouth glass jar	None	not established	Fill 3/4 full	Shipped Daily by Overnight Carrier	Vermiculite
Atterberg Limits	One 8-oz wide mouth glass jar	None	not established	Fill 3/4 full	Shipped Daily by Overnight Carrier	Vermiculite
Permeability	3-in Shelby Tubes	4°C	not established	Fill 3/4 full	Shipped Daily by Overnight Carrier	Vermiculite

TABLE 4
SUMMARY OF PHASE I SOURCE CHARACTERIZATION
SAMPLING AND ANALYSIS PROGRAM

Sample Matrix[1]	Laboratory	Laboratory Parameters[2]	No. of Investigative Samples	No. of Field Duplicates	No. of Matrix Spike/[3] Matrix Spike Duplicates	Total No. of Samples
Waste Pits	Hazleton	TCL Volatiles	6	1	1	8
	Hazleton	TCL Semi-Volatiles	6	1	1	8
	Hazleton	TCL PCB/Pesticides	6	1	1	8
	Warzyn	TCL Metals	6	1	0	7
	Warzyn	Cyanide	6	1	0	7
Natural Soils -Waste Pit	Hazleton	TCL Volatiles	6	1	0	7
	Hazleton	TCL Semi-Volatiles	6	1	0	7
	Hazleton	TCL PCB/Pesticides	6	1	0	7
	Warzyn	TCL metals	6	1	0	7
	Warzyn	Cyanide	6	1	0	7
	Warzyn	Volatile Residue	6	1	0	7
Waste Borings	Hazleton	TCL Volatiles	8	1	0	9
	Hazleton	TCL Semi-Volatiles	8	1	0	9
	Hazleton	TCL PCB/Pesticides	8	1	0	9
	Warzyn	TCL Metals	8	1	0	9
	Warzyn	Cyanide	8	1	0	9
Natural Soils -Waste Borings	Hazleton	TCL Volatiles	8	1	1	10
	Hazleton	TCL Semi-Volatiles	8	1	1	10
	Hazleton	TCL PCB/Pesticides	8	1	1	10
	Warzyn	TCL Metals	8	1	0	9
	Warzyn	Cyanide	8	1	0	9
	Warzyn	Volatile Residue	8	1	0	9
Soil Areas	Hazleton	TCL Volatiles	8	1	1	10
	Hazleton	TCL Semi-Volatiles	8	1	1	10
	Hazleton	TCL PCB/Pesticides	8	1	1	10
	Warzyn	TCL Metals	8	1	0	9
	Warzyn	Cyanide	8	1	0	9
Soil Borings	Hazleton	TCL Volatiles	12	2	0	14
	Hazleton	TCL Semi-Volatiles	12	2	0	14
	Hazleton	TCL PCB/Pesticides	12	2	0	14
	Warzyn	TCL metals	12	2	0	14
	Warzyn	Cyanide	12	2	0	14

Notes
1 Samples will be considered low or medium concentration.
2 See Appendix B for TCL Analyte lists - also up to 30 tentatively identified compounds.
3 Sample numbers do not reflect the additional volumes required for matrix spike/matrix spike duplicate analysis.
4 Field and trip blanks are not required for soil/waste samples.
5 Qualitative screening with HNu or OVA will be done for investigative and duplicate samples only.

TABLE 5
SUMMARY OF SITE CHARACTERIZATION SAMPLING AND ANALYSIS PROGRAM

Sample(1) Matrix	Laboratory	Laboratory Parameters(2,5)	Study(3) Phase	No. of Investigative Samples	No. of Field Duplicates	No. of Field Blanks	Matrix Spike/(4) Matrix Spike Duplicate	Total No. of Samples
Groundwater	Hazleton	TCL Volatiles	1	6	1	1	1	9
			2A	18	2	2	1	23
			2B	*				*
	Hazleton	TCL Semi-Volatiles	1	6	1	1	1	9
			2A	18	2	2	1	23
			2B	*				*
	Hazleton	TCL PCB/Pesticides	1	6	1	1	1	9
			2A	18	2	2	1	23
			2B	*				*
	Warzyn	TCL Metals (Dissolved)	1	6	1	1	0	8
			2A	18	2	2	0	22
			2B	*				*
	Warzyn	TCL Metals (Total), TSS	1	2	1	1	0	4
			2A	5	1	1	0	7
			2B	*				*
	Warzyn	Cyanide (Filtered)	1	6	1	1	0	8
			2A	18	2	2	0	22
			2B	*				*
	Warzyn	Chloride, Alkalinity, Sulfate	1	6	1	1	0	8
			2A	18	2	2	0	22
			2B	*				*
	Warzyn	Ammonia, Nitrate-Nitrite, TOC, COD	1	6	1	1	0	8
			2A	18	2	2	0	22
			2B	*				*
	Warzyn	Total Dissolved Solids	1	6	1	1	0	8
			2A	18	2	2	0	22
			2B	*				*
Surface Water	Hazleton	TCL Volatiles	1	11	2	2	1	16
	Hazleton	TCL Semi-Volatiles	1	11	2	2	1	16
	Hazleton	TCL PCB/Pesticides	1	11	2	2	1	16
	Warzyn	TCL Metals (Total)	1	11	2	2	0	15
	Warzyn	Cyanide (Unfiltered)	1	11	2	2	0	15
	Warzyn	Chloride, Alkalinity, Sulfate	1	11	2	2	0	15
	Warzyn	Ammonia, Nitrate-Nitrite, COD	1	11	2	2	0	15
Sediment	Hazleton	TCL Volatiles	1	11	2	2	1	16
	Hazleton	TCL Semi-Volatiles	1	11	2	2	1	16

TABLE 5 (Continued)
SUMMARY OF SITE CHARACTERIZATION SAMPLING AND ANALYSIS PROGRAM

Sample(1) Matrix	Laboratory	Laboratory Parameters(2,5)	Study(3) Phase	No. of Investigative Samples	No. of Field Duplicates	No. of Field Blanks	Matrix Spike/(4) Matrix Spike Duplicate	Total No. of Samples
	Hazleton	TCL PCB/Pesticides	1	11	2	2	1	16
	Warzyn	TCL Metals	1	11	2	2	0	15
	Warzyn	Cyanide	1	11	2	2	0	15
Private	Hazleton	TCL Volatiles	2	10	1	1	1	13
Wells	Hazleton	TCL Semi-Volatiles	2	10	1	1	1	13
(Low	Hazleton	TCL PCB/Pesticides	2	10	1	1	1	13
Detection	Warzyn	TCL Metals (Total)	2	10	1	1	0	12
Limits)	Warzyn	Cyanide (Unfiltered)	2	10	1	1	0	12
	Warzyn	Chloride, Alkalinity, Sulfate,	2	10	1	1	0	12
	Warzyn	Ammonia, Nitrate-Nitrite, COD	2	10	1	1	0	12
Leachate	Hazleton	TCL Volatiles	1	4	1	1	1	7
Wells	Hazleton	TCL Semi-Volatiles	1	4	1	1	1	7
	Hazleton	TCL PCB/Pesticides	1	4	1	1	1	7
	Warzyn	TCL Metals (Total)	1	4	1	1	0	6
	Warzyn	Cyanide (Unfiltered)	1	4	1	1	0	6
	Warzyn	Chloride, Alkalinity, Sulfate	1	4	1	1	0	6
	Warzyn	Ammonia, Nitrate-Nitrite, COD, TOC	1	4	1	1	0	6
	Warzyn	TDS, TSS	1	4	1	1	0	6
ACS Effluent	Hazleton	TCL Volatiles	1	4	1	1	1	7
	Hazleton	TCL Semi-Volatiles	1	4	1	1	1	7
	Hazleton	TCL PCB/Pesticides	1	4	1	1	1	7
	Warzyn	TCL Metals (Total)	1	4	1	1	0	6
	Warzyn	Cyanide (Unfiltered	1	4	1	1	0	6
	Warzyn	Chloride, Alkalinity, Sulfate	1	4	1	1	0	6
	Warzyn	Ammonia, Nitrate-Nitrite, COD, TOC	1	4	1	1	0	6
	Warzyn	TSS, TDS	1	4	1	1	0	6
Geotechnical	Warzyn	Atterberg limits	1	18	0	0	0	18
Samples-Wells	Warzyn	Particle Size	1	18	0	0	0	18
	Warzyn	Coefficient of Permeability	1	18	0	0	0	18
	Warzyn	Cation Exchange Capacity	1	18	0	0	0	18
	Warzyn	Moisture Content	1	18	0	0	0	18

TABLE 5 (Continued)
SUMMARY OF SITE CHARACTERIZATION SAMPLING AND ANALYSIS PROGRAM

Notes

1 Samples will be considered low or medium concentration.

2 See Appendix B for TCL analyte lists, also up to 30 tentatively identified compounds.

3 The star (*) indicates that the number of samples and specific parameters will be determined from Phase 1 and 2A results. Preliminary assessment indicates that up to 9 wells will be sampled for the complete TCL, and the remaining number will be sampled for a reduced parameter list. Also note that Phase 2A sample number is given as the expected maximum.

4 Sample numbers do not reflect the additional volume of samples required for matrix spikes and matrix spike duplicate analysis.

5 Temperature, pH and specific conductance measurements will be taken in the field for aqueous samples. Qualitative screening with the HNu or OVA will be performed on solid samples.

TABLE 6
ORGANIC PARAMETERS
CLP TARGET COMPOUND LIST AND
CONTRACT REQUIRED DETECTION LIMITS (CRDL)*

	Volatiles	CAS Number	Quantitation Limits** Water ug/l	Quantitation Limits** Low Soil/ Sediment[a] ug/kg
1.	Chloromethane	74-87-3	10	10
2.	Bromomethane	74-83-9	10	10
3.	Vinyl Chloride	75-01-4	10	10
4.	Chloroethane	75-00-3	10	10
5.	Methylene Chloride	75-09-2	5	5
6.	Acetone	67-64-1	10	10
7.	Carbon Disulfide	75-15-0	5	5
8.	1,1-Dichloroethene	75-35-4	5	5
9.	1,1-Dichloroethane	75-35-3	5	5
10.	1,2-Dichloroethene (Total)	540-59-0	5	5
11.	Chloroform	67-66-3	5	5
12.	1,2-Dichloroethane	107-06-2	5	5
13.	2-Butanone	78-93-3	10	10
14.	1,1,1-Trichloroethane	71-55-6	5	5
15.	Carbon Tetrachloride	56-23-5	5	5
16.	Vinyl Acetate	108-05-4	10	10
17.	Bromodichloromethane	75-27-4	5	5
18.	1,2-Dichloropropane	78-87-5	5	5
19.	cis-1,3-Dichloropropene	10061-01-5	5	5
20.	Trichloroethene	79-01-6	5	5
21.	Dibromochloromethane	124-48-1	5	5
22.	1,1,2-Trichloroethane	79-00-5	5	5
23.	Benzene	71-43-2	5	5
24.	trans-1,3-Dichloropropene	10061-02-6	5	5
25.	Bromoform	75-25-2	5	5
26.	4-Methyl-2-pentanone	108-10-1	10	10
27.	2-Hexanone	591-78-6	10	10
28.	Tetrachloroethene	127-18-4	5	5
29.	Toluene	108-88-3	5	5
30.	1,1,2,2-Tetrachloroethane	79-34-5	5	5
31.	Chlorobenzene	108-90-7	5	5
32.	Ethyl Benzene	100-41-4	5	5
33.	Styrene	100-42-5	5	5
34.	Total Xylenes	1330-20-7	5	5

	Semi-Volatiles	CAS Number	Quantitation Limits** Water ug/l	Low Soil Sediment[a] ug/kg
35.	Phenol	108-95-2	10	330
36.	bis(2-Chloroethyl)ether	111-44-4	10	330
37.	2-Chlorophenol	95-57-8	10	330
38.	1,3-Dichlorobenzene	541-73-1	10	330
39.	1,4-Dichlorobenzene	106-46-7	10	330
40.	Benzyl Alcohol	100-51-6	10	330
41.	1,2-Dichlorobenzene	95-50-1	10	330
42.	2-Methylphenol	95-48-7	10	330
43.	bis(2-Chloroisopropyl)ether	108-60-1	10	330
44.	4-Methylphenol	106-44-5	10	330
45.	N-Nitroso-Dinpropylamine	621-64-7	10	330
46.	Hexachloroethane	67-72-1	10	330
47.	Nitrobenzene	98-95-3	10	330
48.	Isophorone	78-59-1	10	330
49.	2-Nitrophenol	88-75-5	10	330
50.	2,4-Dimethylphenol	105-67-9	10	330
51.	Benzoic Acid	65-85-0	50	1600
52.	bis(2-Chloroethoxy)methane	111-91-1	10	330
53.	2,4-Dichlorophenol	120-83-2	10	330
54.	1,2,4-Trichlorobenzene	120-82-1	10	330
55.	Naphthalene	91-20-3	10	330
56.	4-Chloroaniline	106-47-8	10	330
57.	Hexachlorobutadiene	87-68-3	10	330
58.	4-Chloro-3-methylphenol (para-chloro-meta-cresol)	59-50-7	10	330
59.	2-Methylnaphthalene	91-57-6	10	330
60.	Hexachlorocyclopentadiene	77-47-4	10	330
61.	2,4,6-Trichlorophenol	88-06-2	10	330
62.	2,4,5-Trichlorophenol	95-95-4	50	1600
63.	2-Chloronaphthalene	91-58-7	10	330
64.	2-Nitroaniline	88-74-4	50	1600
65.	Dimethyl Phthalate	131-11-3	10	330
66.	Acenaphthylene	208-96-8	10	330
67.	2,6-Dinitrotoluene	606-20-2	10	330
68.	3-Nitroaniline	99-09-2	50	1600
69.	Acenaphthene	83-32-9	10	330
70.	2,4-Dinitrophenol	51-28-5	50	1600
71.	4-Nitrophenol	100-02-7	50	1600
72.	Dibenzofuran	132-64-9	10	330
73.	2,4-Dinitrotoluene	121-14-2	10	330
74.	Diethylphthalate	84-66-2	10	330
75.	4-Chlorophenyl phenyl ether	7005-72-3	10	330
76.	Fluorene	86-73-7	10	330

		CAS Number	Quantitation Limits** Water ug/l	Low Soil Sediment(c) ug/kg
77.	4-Nitroaniline	100-01-6	50	1600
78.	4,6-Dinitro-2-methylphenol	534-52-1	50	1600
79.	N-nitrosodiphenylamine	86-30-6	10	330
80.	4-Bromophenyl phenyl ether	101-55-3	10	330
81.	Hexachlorobenzene	118-74-1	10	330
82.	Pentachlorophenol	87-86-5	50	1600
83.	Phenanthrene	85-01-8	10	330
84.	Anthracene	120-12-7	10	330
85.	Di-n-butylphthalate	84-74-2	10	330
86.	Fluoranthene	206-44-0	10	330
87.	Pyrene	129-00-0	10	330
88.	Butylbenzylphthalate	85-68-7	10	330
89.	3,3'-Dichlorobenzidine	91-94-1	10	330
90.	Benzo(a)anthracene	56-55-3	20	660
91.	Chrysene	218-01-9	10	330
92.	bis(2-ethylhexyl)phthalate	117-81-7	10	330
93.	Di-n-octylphthalate	117-84-0	10	330
94.	Benzo(b)fluoranthene	205-99-2	10	330
95.	Benzo(k)fluoranthene	207-08-9	10	330
96.	Benzo(a)pyrene	50-32-8	10	330
97.	Indeno(1,2,3-cd)pyrene	193-39-5	10	330
98.	Dibenz(a,h)anthracene	53-70-3	19	330
99.	Benzo(g,h,i)perylene	191-24-2	10	330
	Pesticides/PCBs			
100.	alpha-BHC	319-84-6	0.05	8.0
101.	beta-BHC	319-85-7	0.05	8.0
102.	delta-BHC	319-86-8	0.05	8.0
103.	gamma-BHC (Lindane)	58-89-9	0.05	8.0
104.	Heptachlor	76-44-8	0.05	8.0
105.	Aldrin	309-00-2	0.05	8.0
106.	Heptachlor epoxide	1024-57-3	0.05	8.0
107.	Endosulfan I	959-98-8	0.05	8.0
108.	Dieldrin	60-57-1	0.10	16.0
109.	4,4'-DDE	75-55-9	0.10	16.0
110.	Endrin	72-20-8	0.10	16.0
111.	Endosulfan II	33213-65-9	0.10	16.0
112.	4,4-DDD	72-54-8	0.10	16.0
113.	Endosulfan Sulfate	1031-07-8	0.10	16.0
114.	4,4'-DDT	50-29-3	0.10	16.0

		CAS Number	Quantitation Limits** Water ug/l	Low Soil Sediment(c) ug/kg
115.	Endrin Ketone	53494-70-5	0.10	16.0
116.	Methoxychlor	72-43-5	0.5	80.0
117.	alpha-Chlorodane	5103-71-9	0.5	80.0
118.	gamma-Clordane	5103-74-2	0.5	80.0
119.	Toxaphene	8001-35-2	1.0	160.0
120.	AROCLOR-1016	12674-11-2	0.5	80.0
121.	AROCLOR-1221	11104-28-2	0.5	80.0
122.	AROCLOR-1232	11141-16-5	0.5	80.0
123.	AROCLOR-1242	53469-21-9	0.5	80.0
124.	AROCLOR-1248	12672-29-6	0.5	80.0
125.	AROCLOR-1254	11097-69-1	1.0	160.0
126.	AROCLOR-1260	11096-82-5	1.0	160.0

NOTES

a. Medium Soil/Sediment Contract Required Quantitation Limits (CRQL) for Volatile TCL Compounds are 125 times the individual Low Soil/Sediment CRQL.

b. Medium Soil/Sediment Contract Required Quantitation Limits (CRQL) for Semivolatile TCL Compounds are 60 times the individual Low Soil/Sediment CRQL.

c. Medium Soil/Sediment Contract Required Quantitation Limits (CRQL) for Pesticide/PCB TCL compounds are 15 times the individual low Soil/Sediment CRQL.

* Specific quantitation limits are highly matrix dependent. The quantitation limits listed herein are provided for guidance and may not always be achievable. For quantification limits for water samples from private wells, see SOP.

** Quantitation limits listed for soil/sediment are based on wet weight. The quantitation limits calculated by the laboratory for soil/sediment, calculated on dry weight basis as required by the contract, will be higher. Quantification limits for water samples from private wells are lower than tabled values, see SOP for details.

TABLE 7
TARGET COMPOUND LIST
INORGANIC PARAMETERS

ELEMENTS DETERMINED BY INDUCTIVELY COUPLED PLASMA EMISSION OR ATOMIC ABSORPTION SPECTROSCOPY

Metal	Required Detection Level(1) Water ug/l
Aluminum	200
Antimony	60
Arsenic	10
Barium	200
Beryllium	5
Cadmium	5
Calcium	5000
Chromium	10
Cobalt	50
Copper	25
Iron	100
Lead	5
Magnesium	5000
Manganese	15
Mercury	0.2
Nickel	40
Potassium	5000
Selenium	5
Silver	10
Sodium	5000
Thallium	10
Vanadium	50
Zinc	20
Other	
Cyanide	10

NOTES

(1) Subject to the restrictions specified in the first part of Part G, Section IV of Exhibit D (Alternative Methods - Catastrophic Failure) of SOW-7/87. Any analytical method specified in SOW 7/87, Exhibit D may be utilized as long as the documented instrument or method detection limits meet the Contract Required Detection Limit (CRDL) requirements. Higher detection limits may only be used in the following circumstance:

If the sample concentration exceeds five times the detection limit of the instrument or method in use, the value may be reported even though the instrument or method detection limit may not equal the Contract Required Detection Limit. This is illustrated in the example below:

For Lead:

Method in use - ICP
Instrument Detection Limit (IDL) - 40
Sample concentration - 220
Contract Required Detection Limit (CRCL) - 5

(2) The value of 200 may be reported even though instrument detection limits obtained in pure water that may be met during the procedure in Exhibit E of SOW 7/87. The detection limits for samples may be considerably higher depending on the sample matrix.

TABLE 8
NON-TCL
ADDITIONAL WATER QUALITY PARAMETERS

Parameter	Detection Limits (mg/l)
Total Organic Carbon.....	1.0
Total Suspended Solids.....	1
Total Dissolved Solids.....	10
Chemical Oxygen Demand.....	2.0
Alkalinity (as $CACO^3$).....	5.0
Ammonia.....	0.10
Nitrate-Nitrite.....	0.02
Chloride.....	1.0
Sulfate.....	5.0

TABLE 9
INORGANIC PARAMETERS
NON-TCL LOW DETECTION
LIMITS

Metal	Required Detection Level Water ug/l
Aluminum	100
Antimony	5
Arsenic	5
Barium	50
Beryllium	5
Cadmium	0.5
Calcium	1000
Chromium	10
Cobalt	10
Copper	10
Iron	100
Lead	2
Magnesium	1000
Manganese	10
Mercury	0.2
Nickel	20
Potassium	2000
Selenium	2
Silver	5
Sodium	1000
Thallium	2
Vanadium	10
Zinc	20
Other	
Cyanide	10

DRAINAGE DITCH

GRAND TRUNK RAILROAD

MW4D
MW4
MW3

CHESAPEAKE & OHIO RAILROAD

E
M
FIRE POND
G
F
P
K
R
J
I

AVENUE

T3

TOWN OF GRIFFITH SANITARY LANDFILL

T1

C

T2

COLFAX

D

L

O

REDER ROAD

CHICAGO & ERIE RAILROAD

MARSH

north

SCALE IN FEET

0 50 100 200

* SEE NOTE

EPA IDENTIFIER	NAME OF AREA
C	OFF-SITE CONTAINMENT AREA
D	GRIFFITH CITY LANDFILL
E	ON-SITE CONTAINMENT AREA
F	OLD STILL BOTTOMS POND
G	TREATMENT POND #1
K I J	OLD WASTE WATER TRENCHES
L	KAPICA DRUM DRAINING AREA
M	OLD DRUM STORAGE AREA
O	KAPICA DRUM PROPERTY
P	FUME INCINERATOR
R	PREVIOUS SPILL/FIRE

* NOTE: SURFACE WATER POINT FALLS BEYOND THE SOUTHEAST BORDER OF THIS MAP

LEGEND

- AMERICAN CHEMICAL SERVICE INC.
- KAPICA DRUM INC.
- GRIFFITH LANDFILL PROPERTY
- T1 EXISTING TEST WELL
- PROPOSED SHALLOW PIEZOMETERS
- PROPOSED LEACHATE PIEZOMETERS
- PROPOSED SURFACE WATER ELEVATION POINTS
- MONITORING WELLS PROPOSED PHASE I
- PROPOSED LEACHATE SAMPLING WELLS

FIGURE 1

HYDROGEOLOGIC STUDY WATER LEVEL CONTROL POINTS

REMEDIAL INVESTIGATION/
FEASIBILITY STUDY
AMERICAN CHEMICAL SERVICES SITE
GRIFFITH, INDIANA

WARZYN
WARZYN ENGINEERING INC.
Madison · Milwaukee
Minneapolis · Chicago
Detroit

Project Number 60251-B2

Designed By
Drawn By SR
Checked By MAH
Approved By RJV
Date 9/23/88
Scale AS SHOWN
Reference

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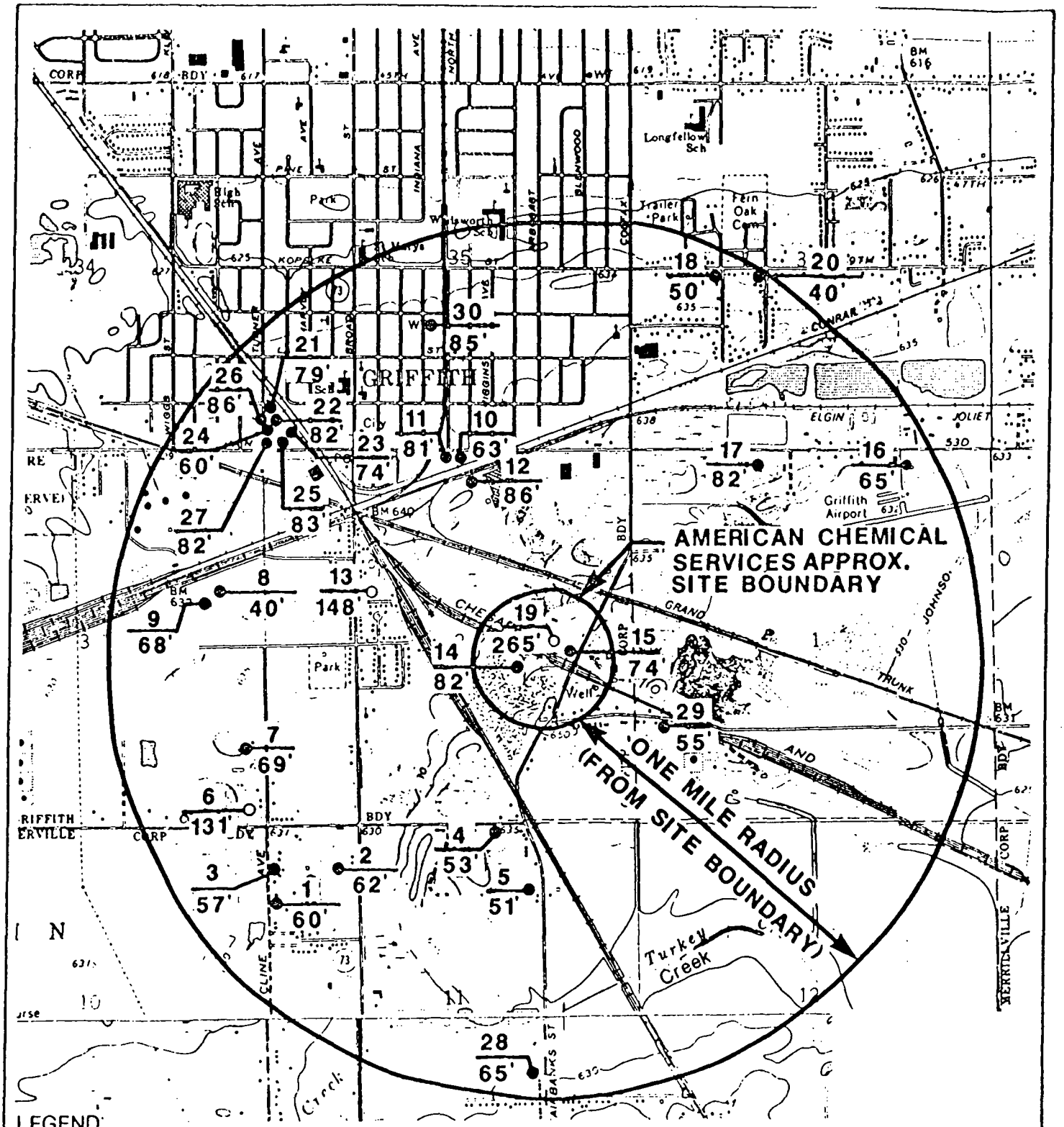

LEGEND

1 - WELL REFERENCE NUMBER
60 - DEPTH OF WELL (FEET)

● WELL SCREENED IN UNCONSOLIDATED AQUIFER

○ WELL SCREENED IN ROCK AQUIFER

north
SCALE: 1"=2000'

NOTE

1. BASE MAP DEVELOPED FROM THE HIGHLAND, INDIANA AND THE ST. JOHN, INDIANA 7 1/2 MINUTE USGS QUADRANGLE MAPS. DATED 1968 AND 1962 RESPECTIVELY PHOTOREVISED 1980.

2. WELL REFERENCE NUMBERS REFER TO ATEC REPORT, JANUARY 1985.

FIGURE 2

WARZYN

REMEDIAL INVESTIGATION/FEASIBILITY STUDY
WATER WELL LOCATIONS
AMERICAN CHEMICAL SERVICES SITE
GRIFFITH, INDIANA

DWN JC	APP'D PJV	DATE 9/23/88	60251-A3

ELEDYNE POST N67178

DRAINAGE DITCH

GRAND TRUNK RAILROAD

MW4D
MW4
MW3

CHESAPEAKE & OHIO RAILROAD

E
M
FIRE POND
G
F
K
P
R
J
I

AVENUE

T3

TOWN OF GRIFFITH SANITARY LANDFILL

CHICAGO & ERIE RAILROAD

T1
C
T2
COLFAX
D
L
O

REDER ROAD

MARSH

north

SCALE IN FEET

0 50 100 200

PA DENTIFIER	NAME OF AREA
C	OFF-SITE CONTAINMENT AREA
D	GRIFFITH CITY LANDFILL
E	ON-SITE CONTAINMENT AREA
F	OLD STILL BOTTOMS POND
G	TREATMENT POND #1
K I J	OLD WASTE WATER TRENCHES
L	KAPICA DRUM DRAINING AREA
M	OLD DRUM STORAGE AREA
O	KAPICA DRUM PROPERTY
P	FUME INCINERATOR
R	PREVIOUS SPILL/FIRE

LEGEND

- AMERICAN CHEMICAL SERVICE INC.
- KAPICA DRUM INC.
- GRIFFITH LANDFILL PROPERTY
- SOIL BORING
- SOIL AREA

FIGURE 3

WARZYN

Project Number 60251-86

SOIL BORING & SOIL AREA LOCATIONS
REMEDIAL INVESTIGATION/
FEASIBILITY STUDY
AMERICAN CHEMICAL SERVICES SITE
GRIFFITH, INDIANA

WARZYN
WARZYN ENGINEERING INC
Madison · Milwaukee
Minneapolis · Chicago
Detroit

Designed By
Drawn By S.R.
Checked By
Approved By PDV
Date 9/23/88
Scale AS SHOWN
Reference

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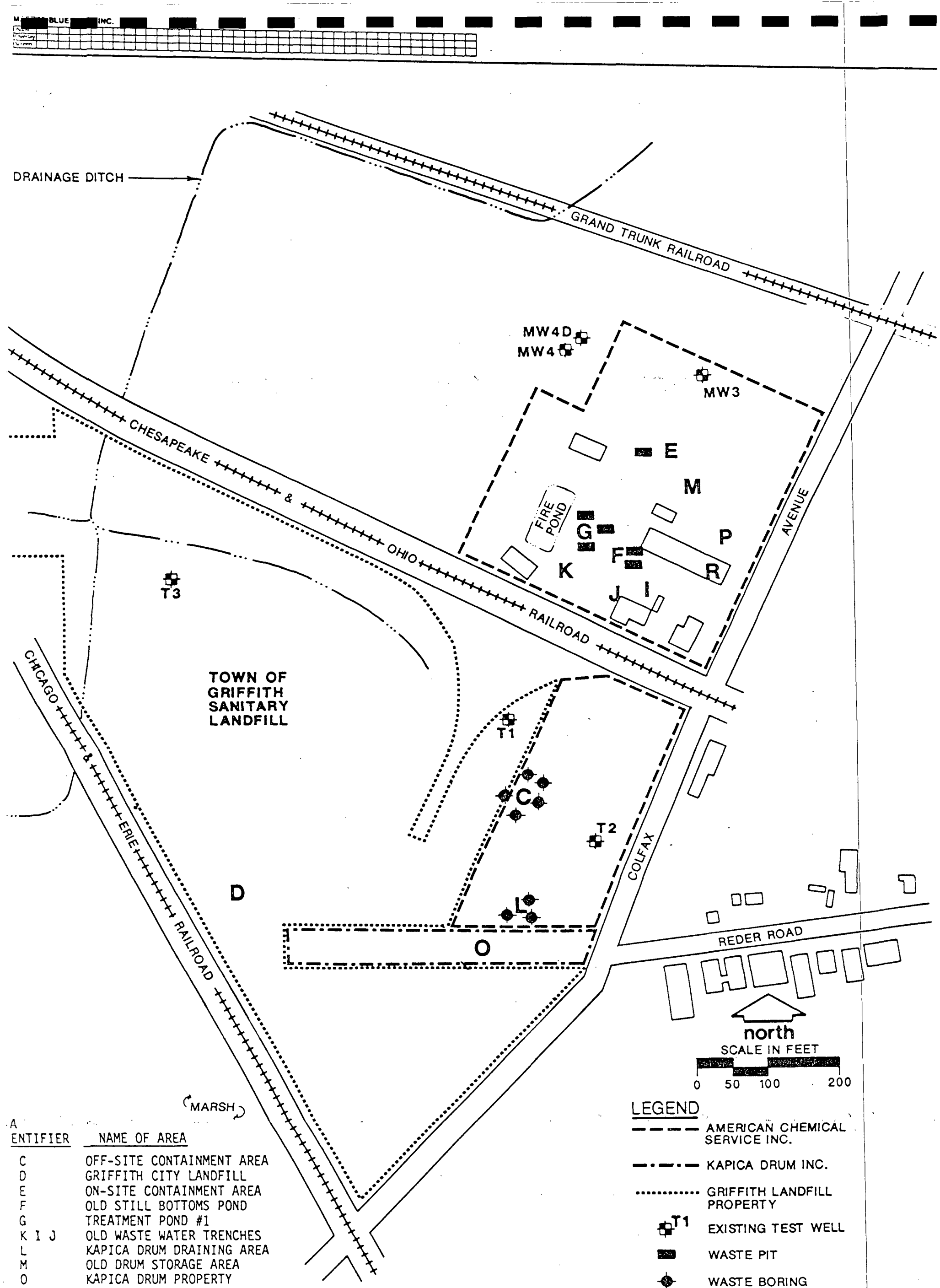

A ENTIFIER	NAME OF AREA
C	OFF-SITE CONTAINMENT AREA
D	GRIFFITH CITY LANDFILL
E	ON-SITE CONTAINMENT AREA
F	OLD STILL BOTTOMS POND
G	TREATMENT POND #1
K I J	OLD WASTE WATER TRENCHES
L	KAPICA DRUM DRAINING AREA
M	OLD DRUM STORAGE AREA
O	KAPICA DRUM PROPERTY
P	FUME INCINERATOR
R	PREVIOUS SPILL/FIRE

FIGURE 4

WARZYN

Project Number 60251-B5

WASTE PIT & WASTE BORING LOCATIONS
REMEDIAL INVESTIGATION/
FEASIBILITY STUDY
AMERICAN CHEMICAL SERVICES SITE
GRIFFITH, INDIANA

WARZYN
WARZYN ENGINEERING INC
Madison · Milwaukee
Minneapolis · Chicago
Detroit

Designed By
Drawn By
Checked By
Approved By
Date 9/28/88
Scale AS SHOWN
Reference

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WARREN

Warren Engineering Inc
One Science Court
University Research Park
P.O. Box 5385
Madison, Wisconsin 53705
(608) 273-0440

CHAIN OF CUSTODY RECORD

PROJ. NO.	PROJECT NAME
SAMPLERS: *(Signature)*	

LAB NO.	DATE	TIME	COMP.	GRAB	STATION LOCATION	NO. OF CONTAINERS							REMARKS

Relinquished by: *(Signature)*	Date / Time	Received by: *(Signature)*	Relinquished by: *(Signature)*	Date / Time	Received by: *(Signature)*
Relinquished by: *(Signature)*	Date / Time	Received by: *(Signature)*	Relinquished by: *(Signature)*	Date / Time	Received by: *(Signature)*
Relinquished by: *(Signature)*	Date / Time	Received for Laboratory by: *(Signature)*		Date / Time	

Remarks

Figure 5. Chain-of-Custody Record

Figure 6. Chain-of-Custody Seal

ANALYTICAL SERVICES

WARZYN
ENGINEERING INC

One Science Court
University Research Park
P.O. Box 5385
Madison, WI 53705
(608) 273-0440

Project # _____ Lab # _____

Sample Name _____

Date Collected _____ By _____

Parameter(s) _____

Preservative(s) _____

Figure 7. Sample label

SAMPLE IDENTIFICATION RECORD

CASE/JOB NUMBER	MATRIX	SAMPLE NUMBER	LAB	LAB NUMBER	CHAIN OF CUSTODY	DATE SAMPLED	DATE SHIPPED	AIRBILL NUMBER

Figure 8. Sample Identification Record.

APPENDIX B

ANALYTE LISTS

ORGANIC PARAMETERS
CLP TARGET COMPOUND LIST AND
CONTRACT REQUIRED DETECTION LIMITS (CRDL)*

	Volatiles	CAS Number	Quantitation Limits** Water ug/l	Quantitation Limits** Low Soil/ Sediment[a] ug/kg
1.	Chloromethane	74-87-3	10	10
2.	Bromomethane	74-83-9	10	10
3.	Vinyl Chloride	75-01-4	10	10
4.	Chloroethane	75-00-3	10	10
5.	Methylene Chloride	75-09-2	5	5
6.	Acetone	67-64-1	10	10
7.	Carbon Disulfide	75-15-0	5	5
8.	1,1-Dichloroethene	75-35-4	5	5
9.	1,1-Dichloroethane	75-35-3	5	5
10.	1,2-Dichloroethene (Total)	540-59-0	5	5
11.	Chloroform	67-66-3	5	5
12.	1,2-Dichloroethane	107-06-2	5	5
13.	2-Butanone	78-93-3	10	10
14.	1,1,1-Trichloroethane	71-55-6	5	5
15.	Carbon Tetrachloride	56-23-5	5	5
16.	Vinyl Acetate	108-05-4	10	10
17.	Bromodichloromethane	75-27-4	5	5
18.	1,2-Dichloropropane	78-87-5	5	5
19.	cis-1,3-Dichloropropene	10061-01-5	5	5
20.	Trichloroethene	79-01-6	5	5
21.	Dibromochloromethane	124-48-1	5	5
22.	1,1,2-Trichloroethane	79-00-5	5	5
23.	Benzene	71-43-2	5	5
24.	trans-1,3-Dichloropropene	10061-02-6	5	5
25.	Bromoform	75-25-2	5	5
26.	4-Methyl-2-pentanone	108-10-1	10	10
27.	2-Hexanone	591-78-6	10	10
28.	Tetrachloroethene	127-18-4	5	5
29.	Toluene	108-88-3	5	5
30.	1,1,2,2-Tetrachloroethane	79-34-5	5	5
31.	Chlorobenzene	108-90-7	5	5
32.	Ethyl Benzene	100-41-4	5	5
33.	Styrene	100-42-5	5	5
34.	Total Xylenes	1330-20-7	5	5

	Semi-Volatiles	CAS Number	Quantitation Limits** Water ug/l	Low Soil Sediment[a] ug/kg
35.	Phenol	108-95-2	10	330
36.	bis(2-Chloroethyl)ether	111-44-4	10	330
37.	2-Chlorophenol	95-57-8	10	330
38.	1,3-Dichlorobenzene	541-73-1	10	330
39.	1,4-Dichlorobenzene	106-46-7	10	330
40.	Benzyl Alcohol	100-51-6	10	330
41.	1,2-Dichlorobenzene	95-50-1	10	330
42.	2-Methylphenol	95-48-7	10	330
43.	bis(2-Chloroisopropyl)ether	108-60-1	10	330
44.	4-Methylphenol	106-44-5	10	330
45.	N-Nitroso-Dinpropylamine	621-64-7	10	330
46.	Hexachloroethane	67-72-1	10	330
47.	Nitrobenzene	98-95-3	10	330
48.	Isophorone	78-59-1	10	330
49.	2-Nitrophenol	88-75-5	10	330
50.	2,4-Dimethylphenol	105-67-9	10	330
51.	Benzoic Acid	65-85-0	50	1600
52.	bis(2-Chloroethoxy)methane	111-91-1	10	330
53.	2,4-Dichlorophenol	120-83-2	10	330
54.	1,2,4-Trichlorobenzene	120-82-1	10	330
55.	Naphthalene	91-20-3	10	330
56.	4-Chloroaniline	106-47-8	10	330
57.	Hexachlorobutadiene	87-68-3	10	330
58.	4-Chloro-3-methylphenol (para-chloro-meta-cresol)	59-50-7	10	330
59.	2-Methylnaphthalene	91-57-6	10	330
60.	Hexachlorocyclopentadiene	77-47-4	10	330
61.	2,4,6-Trichlorophenol	88-06-2	10	330
62.	2,4,5-Trichlorophenol	95-95-4	50	1600
63.	2-Chloronaphthalene	91-58-7	10	330
64.	2-Nitroaniline	88-74-4	50	1600
65.	Dimethyl Phthalate	131-11-3	10	330
66.	Acenaphthylene	208-96-8	10	330
67.	2,6-Dinitrotoluene	606-20-2	10	330
68.	3-Nitroaniline	99-09-2	50	1600
69.	Acenaphthene	83-32-9	10	330
70.	2,4-Dinitrophenol	51-28-5	50	1600
71.	4-Nitrophenol	100-02-7	50	1600
72.	Dibenzofuran	132-64-9	10	330
73.	2,4-Dinitrotoluene	121-14-2	10	330
74.	Diethylphthalate	84-66-2	10	330
75.	4-Chlorophenyl phenyl ether	7005-72-3	10	330
76.	Fluorene	86-73-7	10	330

		CAS Number	Quantitation Limits** Water ug/l	Low Soil Sediment[c] ug/kg
77.	4-Nitroaniline	100-01-6	50	1600
78.	4,6-Dinitro-2-methylphenol	534-52-1	50	1600
79.	N-nitrosodiphenylamine	86-30-6	10	330
80.	4-Bromophenyl phenyl ether	101-55-3	10	330
81.	Hexachlorobenzene	118-74-1	10	330
82.	Pentachlorophenol	87-86-5	50	1600
83.	Phenanthrene	85-01-8	10	330
84.	Anthracene	120-12-7	10	330
85.	Di-n-butylphthalate	84-74-2	10	330
86.	Fluoranthene	206-44-0	10	330
87.	Pyrene	129-00-0	10	330
88.	Butylbenzylphthalate	85-68-7	10	330
89.	3,3'-Dichlorobenzidine	91-94-1	10	330
90.	Benzo(a)anthracene	56-55-3	20	660
91.	Chrysene	218-01-9	10	330
92.	bis(2-ethylhexyl)phthalate	117-81-7	10	330
93.	Di-n-octylphthalate	117-84-0	10	330
94.	Benzo(b)fluoranthene	205-99-2	10	330
95.	Benzo(k)fluoranthene	207-08-9	10	330
96.	Benzo(a)pyrene	50-32-8	10	330
97.	Indeno(1,2,3-cd)pyrene	193-39-5	10	330
98.	Dibenz(a,h)anthracene	53-70-3	19	330
99.	Benzo(g,h,i)perylene	191-24-2	10	330
	Pesticides/PCBs			
100.	alpha-BHC	319-84-6	0.05	8.0
101.	beta-BHC	319-85-7	0.05	8.0
102.	delta-BHC	319-86-8	0.05	8.0
103.	gamma-BHC (Lindane)	58-89-9	0.05	8.0
104.	Heptachlor	76-44-8	0.05	8.0
105.	Aldrin	309-00-2	0.05	8.0
106.	Heptachlor epoxide	1024-57-3	0.05	8.0
107.	Endosulfan I	959-98-8	0.05	8.0
108.	Dieldrin	60-57-1	0.10	16.0
109.	4,4'-DDE	75-55-9	0.10	16.0
110.	Endrin	72-20-8	0.10	16.0
111.	Endosulfan II	33213-65-9	0.10	16.0
112.	4,4-DDD	72-54-8	0.10	16.0
113.	Endosulfan Sulfate	1031-07-8	0.10	16.0
114.	4,4'-DDT	50-29-3	0.10	16.0

		CAS Number	Quantitation Limits** Water ug/l	Low Soil Sediment(c) ug/kg
115.	Endrin Ketone	53494-70-5	0.10	16.0
116.	Methoxychlor	72-43-5	0.5	80.0
117.	alpha-Chlorodane	5103-71-9	0.5	80.0
118.	gamma-Clordane	5103-74-2	0.5	80.0
119.	Toxaphene	8001-35-2	1.0	160.0
120.	AROCLOR-1016	12674-11-2	0.5	80.0
121.	AROCLOR-1221	11104-28-2	0.5	80.0
122.	AROCLOR-1232	11141-16-5	0.5	80.0
123.	AROCLOR-1242	53469-21-9	0.5	80.0
124.	AROCLOR-1248	12672-29-6	0.5	80.0
125.	AROCLOR-1254	11097-69-1	1.0	160.0
126.	AROCLOR-1260	11096-82-5	1.0	160.0

NOTES

a. Medium Soil/Sediment Contract Required Quantitation Limits (CRQL) for Volatile TCL Compounds are 125 times the individual Low Soil/Sediment CRQL.

b. Medium Soil/Sediment Contract Required Quantitation Limits (CRQL) for Semivolatile TCL Compounds are 60 times the individual Low Soil/Sediment CRQL.

c. Medium Soil/Sediment Contract Required Quantitation Limits (CRQL) for Pesticide/PCB TCL compounds are 15 times the individual low Soil/Sediment CRQL.

* Specific quantitation limits are highly matrix dependent. The quantitation limits listed herein are provided for guidance and may not always be achievable. For quantification limits for water samples from private wells, see SOP.

** Quantitation limits listed for soil/sediment are based on wet weight. The quantitation limits calculated by the laboratory for soil/sediment, calculated on dry weight basis as required by the contract, will be higher. Quantification limits for water samples from private wells are lower than tabled values, see SOP for details.

TARGET COMPOUND LIST
INORGANIC PARAMETERS

ELEMENTS DETERMINED BY INDUCTIVELY COUPLED PLASMA EMISSION OR ATOMIC ABSORPTION SPECTROSCOPY

Metal	Required Detection Level(1) Water ug/l
Aluminum	200
Antimony	60
Arsenic	10
Barium	200
Beryllium	5
Cadmium	5
Calcium	5000
Chromium	10
Cobalt	50
Copper	25
Iron	100
Lead	5
Magnesium	5000
Manganese	15
Mercury	0.2
Nickel	40
Potassium	5000
Selenium	5
Silver	10
Sodium	5000
Thallium	10
Vanadium	50
Zinc	20
Other	
Cyanide	10

NOTES

(1) Subject to the restrictions specified in the first part of Part G, Section IV of Exhibit D (Alternative Methods - Catastrophic Failure) of SOW-7/87. Any analytical method specified in SOW 7/87, Exhibit D may be utilized as long as the documented instrument or method detection limits meet the Contract Required Detection Limit (CRDL) requirements. Higher detection limits may only be used in the following circumstance:

If the sample concentration exceeds five times the detection limit of the instrument or method in use, the value may be reported even though the instrument or method detection limit may not equal the Contract Required Detection Limit. This is illustrated in the example below:

For Lead:

Method in use - ICP
Instrument Detection Limit (IDL) - 40
Sample concentration - 220
Contract Required Detection Limit (CRCL) - 5

(2) The value of 200 may be reported even though instrument detection limits obtained in pure water that may be met during the procedure in Exhibit E of SOW 7/87. The detection limits for samples may be considerably higher depending on the sample matrix.

NON-TCL
ADDITIONAL WATER QUALITY PARAMETERS

Parameter	Detection Limits (mg/l)
Total Organic Carbon	1.0
Total Suspended Solids	1
Total Dissolved Solids	10
Chemical Oxygen Demand	2.0
Alkalinity (as $CACO^3$)	5.0
Ammonia	0.10
Nitrate-Nitrite	0.02
Chloride	1.0
Sulfate	5.0

INORGANIC PARAMETERS
NON-TCL LOW DETECTION LIMITS

Metal	Required Detection Level Water ug/l
Aluminum	100
Antimony	5
Arsenic	5
Barium	50
Beryllium	5
Cadmium	0.5
Calcium	1000
Chromium	10
Cobalt	10
Copper	10
Iron	100
Lead	2
Magnesium	1000
Manganese	10
Mercury	0.2
Nickel	20
Potassium	2000
Selenium	2
Silver	5
Sodium	1000
Thallium	2
Vanadium	10
Zinc	20
Other	
Cyanide	10

APPENDIX C

HAZLETON LABORATORIES AMERICA

STANDARD OPERATING PROCEDURES USING NON - CLP PROTOCOL

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ASSAY TITLE: Determination of Organochlorine Pesticides and Polychlorinated Biphenyls (PCBs) in Drinking Water

AREA OF APPLICABILITY: Hazleton Laboratories America, Inc. Environmental Analysis

SCOPE:

This method covers the determination of the priority pollutant and target compound list (TCL) organochlorine pesticides and PCBs in drinking water sources using gas chromatography with electron capture (GC-EC) detection. The compounds determined by this method are reported with detection limits lower than those generated by the standard pesticide/PCB screen. All positive results reported using this method are reported only following second column confirmation. The following compounds are calibrated and analyzed for under this method:

Aldrin	4,4'-DDT	Methoxychlor
alpha-BHC	Dieldrin	Toxaphene
beta-BHC	Endosulfan I	PCB-1016
gamma-BHC (Lindane)	Endosulfan II	PCB-1221
delta-BHC	Endosulfan sulfate	PCB-1232
alpha-chlordane	Endrin	PCB-1242
gamma-chlordane	Endrin aldehyde	PCB-1248
Technical chlordane	Endrin ketone	PCB-1254
4,4'-DDD	Heptachlor	PCB-1260
4,4'-DDE	Heptachlor epoxide	

PRINCIPLE:

A 1-L sample is extracted with methylene chloride using a separatory funnel. The methylene chloride extract is dried with anhydrous sodium sulfate and exchanged to hexane during the concentration step. The final extract volume is taken to 1.0 mL for analysis. The extract is separated by gas chromatography and the analytes of interest are measured with an electron capture detector. This method provides an alumina column cleanup procedure and an elemental sulfur removal procedure to aid in the elimination of interferences that may be encountered.

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SENSITIVITY, PRECISION AND ACCURACY:

The method detection limits presented in Table 1 represent the sensitivities that can be achieved in ground water in the absence of interferences. Precision and accuracy for this method, as generated from an in house validation study, is presented in Table 2.

REFERENCES:

Environmental Protection Agency (EPA) Method 608 (Federal Register, 49(209):43,321-43,336, October 16, 1984).

Environmental Protection Agency (EPA) Contract Laboratory Program, Statement of Work for "Organic Analysis Multi-Media Multi-Concentration, October 1986. Revisions: January 1987; February 1987; July 1987; August 1987. Exhibits: B, D, E.

APPROVED BY: Mark J. McNabb DATE: 3-9-88
Mark McNabb
Group Leader
Environmental Analysis

David C. Hills DATE: 3-9-88
David C. Hills
Manager
Environmental Analysis

REVIEWED BY: Debra Curley Arndt DATE: 3/15/88
Debra Curley Arndt
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(1076D)

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SAFETY PRECAUTIONS:

The toxicity or carcinogenicity of chemicals used in this method have not been precisely defined; each chemical should be treated as a potential health hazard, and exposure to these chemicals should be minimized. Each analyst is responsible for maintaining awareness of OSHA regulations regarding safe handling of chemicals used in this method. Additional references to laboratory safety are available for the information of the analyst.

The following method analytes have been tentatively classified as known or suspected human or mammalian carcinogens: 4,4'-DDT, 4,4'-DDD, the BHCs, and the PCBs. Primary standards of these toxic compounds should be prepared in a hood. A NIOSH/MESA-approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

INTERFERENCES:

Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample-processing hardware that lead to discrete artifacts and/or elevated baselines in gas chromatograms. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks. Interferences by phthalate esters can pose major problems in pesticide analysis when using the EC detector. These compounds generally appear in the chromatogram as broad eluting peaks. Common flexible plastics contain varying amounts of phthalates. These phthalates are easily extracted or leached from such materials during laboratory operations. Cross-contamination of clean glassware routinely occurs when plastics are handled. Interferences from phthalates can best be minimized by avoiding the use of plastics in the laboratory. Exhaustive cleanup of reagents and glassware may be required to eliminate background phthalate contamination.

Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending on the nature and diversity of the site being sampled. Cleanup procedures provided in this method may be used to minimize or overcome such interferences.

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QUALITY ASSURANCE:

The minimum quality assurance quality control (QA/QC) operations necessary to satisfy the analytical requirements associated with the determination of the pesticide/PCB compounds listed in this method are as follows:

- Method Blank Analysis
- Surrogate Spike Recovery and Retention Time Monitoring
- Matrix Spike/Matrix Spike Duplicate Analysis
- Specific QA/QC for Pesticide Analysis

1. Method Blank Analysis

A method blank is a volume of deionized, distilled laboratory water carried through the entire analytical scheme (extraction, concentration, and analysis). The method blank volume must be approximately equal to the sample volumes being processed.

A method blank is performed with every 20 samples processed and/or whenever samples are extracted, whichever is most frequent. It is the analyst's responsibility to ensure that method interferences caused by contaminants in solvents, reagents, and glassware are minimized. An acceptable laboratory method blank should contain less than or equal to the reported method detection limit of any single pesticide/PCB target compound.

If a laboratory method blank exceeds the above criteria, the analyst must consider the analytical system to be out of control. The source of the contamination must be investigated and appropriate corrective measures MUST be taken and documented before further sample analysis proceeds. All samples processed with a method blank that is out of control MUST be reextracted and reanalyzed.

2. Surrogate Spike Analysis

All samples, blanks, and matrix spikes are fortified with the surrogate compound dibutylchlorendate (DBC) before extraction to monitor the preparation and analysis of samples. The spiking level is 0.1 µg/L, based on an extraction volume of 1 L, which will produce an extract concentration (before any optional dilutions) of 0.1 µg/mL.

Surrogate spike recovery must be evaluated by determining whether the concentration (measured as percent recovery) falls inside the advisory recovery limits listed below.

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Advisory Surrogate Spike Recovery Limits

Fraction	Surrogate Compound	Water
Pest.	Dibutylchlorendate	(24-154)*

* These limits are for advisory purposes only. They are not used to determine if a sample should be reanalyzed.

3. Matrix Spike/Matrix Spike Duplicate (MS/MSD) Analysis

In order to evaluate the matrix effect of the sample on the analytical methodology and provide both precision and accuracy information, an MS/MSD analysis is performed with each set of 20 samples. Spiking is performed using a mixture of the following six individual pesticide compounds:

- Heptachlor
- Aldrin
- Dieldrin
- Lindane
- Endrin
- 4,4'-DDT

Individual component recoveries of the matrix spike are calculated using Equation 3.1.

$$\text{Matrix spike percent recovery} = \frac{SSR - SR}{SA} \times 100 \qquad \text{Eq. 3.1}$$

Where: SSR = Spike sample results
SR = Sample result
SA = Spike added from spiking mix

The analyst is required to calculate the relative percent difference (RPD) between the matrix spike and matrix spike duplicate. The RPD for each component is calculated using Equation 3.2.

$$RPD = \frac{D_1 - D_2}{(D_1 + D_2)/2} \times 100 \qquad \text{Eq. 3.2}$$

Where: D_1 = First sample value
D_2 = Second sample value (duplicate)

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Matrix Spike Recovery Limits

Fraction	Matrix Spike Compound	Water*
Pesticide	Lindane	46-118
Pesticide	Heptachlor	29-119
Pesticide	Aldrin	30-108
Pesticide	Dieldrin	39-133
Pesticide	Endrin	53-114
Pesticide	4,4'-DDT	38-130

* These limits are for advisory purposes only. They are not to be used to determine if a sample should be reanalyzed.

4. Pesticide Retention Time Windows

The external standard quantitation method must be used to quantitate all pesticides/PCBs. Before performing any sample analysis, the analyst is required to determine the retention time window for each pesticide/PCB target compound and the surrogate spike compound, DBC. These retention time windows are used to make tentative identification of pesticides/PCBs during sample analysis.

Before establishing retention time windows, the GC operating conditions (oven temperature and flow rate) must be adjusted such that 4,4'-DDT has a retention time of greater than or equal to 12 minutes on packed GC columns, except on OV-1 or OV-101 columns.

Establish retention time windows as follows:

- Before initiating analysis on a GC system and each time a new GC column is installed, make three injections of all single component pesticide mixtures, multi-response pesticides, and PCBs throughout the course of a 72-hour period. The concentration of each pesticide/PCB should be sufficient to provide a response that is approximately half scale. The three injections of each compound are made at approximately equal intervals during the 72-hour period, (i.e., each compound is injected near the beginning, middle, and end of the 72-hour period).

- Verify the retention time shift for DBC in each standard. The retention time shift between the initial and subsequent standards must be less than 2.0% difference for packed columns and less than 1.5% difference for wide-bore capillary columns. If this criterion is not met, continue injecting replicate standards until the criterion is satisfied.

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- Calculate the standard deviation of the three absolute retention times for each single component pesticide. For multiresponse pesticides or PCBs, choose one major peak from the envelope and calculate the standard deviation of the three retention times for that peak.

- The standard deviations determined are used to determine the retention time window for a particular 72-hour sequence. Apply plus or minus three times the standard deviations to the retention time of each pesticide/PCB determined for the first analysis of the pesticide/PCB standard in a given 72-hour analytical sequence. This range of retention times defines the retention time window for the compound of interest for that 72-hour sequence. Note that by definition, the retention time of a pesticide/PCB from the first analysis of that compound in the 72-hour sequence is the center of the retention time window (do not use the retention time measured during the initial determination of the retention time windows as the center of the retention time window). The experience of the analyst should weigh heavily in the interpretation of chromatograms. For multiresponse pesticide/PCBs, the analyst should use the retention time window, but should rely primarily on pattern recognition.

- In those cases where the retention time window for a particular pesticide/PCB is less than 0.01 minutes, the analyst may use whichever of the following formulas apply.

  - For packed columns, the retention time window of the particular pesticide/PCB is calculated as ±1% of the initial retention time of the compound in the 72-hour sequence.

  - For wide-bore capillary columns [inner diameter (i.d.) greater than 0.32 mm], the retention time window of the particular pesticide/PCB is calculated as ±0.75% of the initial retention time of the compound in the 72-hour sequence.

  - For narrow-bore capillary columns (i.d. less than 0.32 mm), the retention time window of the particular pesticide/PCB is calculated as ±0.15% of the initial retention time of the compound in the 72-hour sequence.

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5. Primary GC Column Analysis

Primary analysis determines whether or not pesticides/PCBs are present in the sample, and establishes a tentative identification of each compound. Quantitation may be performed on the primary analysis if the analysis meets all of the QC criteria specified for quantitation. NOTE: To determine that no pesticides/PCBs are present at or above the required quantitation limit is a form of quantitation.

Separation should be greater than or equal to 25% resolution between the peaks. This criteria must be considered when determining whether to quantitate on the primary analysis or the confirmation analysis. When this criterion cannot be met, quantitation is adversely affected because of the difficulty in determining where to establish the baseline.

Evaluation Standard Mixtures

- Prepare Evaluation Standard Mixes A, B, and C (aldrin, endrin, 4,4'-DDT and DBC) at the three concentration levels described in the method. Analyze the three evaluation standard mixes sequentially at the beginning of each 72-hour period (see Figure 1).

- Calculate the calibration factor (ratio of the total area to the mass injected) for each compound in Evaluation Standard Mixes A, B, and C using Equation 5.1.

$$\text{Calibration factor} = \frac{\text{Total area of peak}}{\text{Mass injected (in nanograms)}} \qquad \text{Eq. 5.1}$$

- Using the calibration factors from above, calculate the percent relative standard deviation (%RSD) for each compound at the three concentration levels using Equation 5.2. The %RSD for aldrin, endrin, 4,4'-DDT and DBC must be less than or equal to 10.0%. If the %RSD exceeds 10.0% for 4,4'-DDT, a three-point DDT series (DDT, DDD, DDE) may be run and used to establish a calibration curve for those three compounds; otherwise, corrective action must be taken to bring the DDT %RSD within 10%.

- NOTE: The 10.0% RSD linearity criteria pertains only to columns being used for pesticide/PCB quantitation. If a column is used only for surrogate quantitation, the 10.0% RSD is only required for DBC.

$$\%\ RSD = \frac{SD}{\bar{x}} \times 100 \qquad \text{Eq. 5.2}$$

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Where: Standard deviation (SD) = $\sqrt{\sum_{i=1}^{N} \frac{(x_1 - x)^2}{N-1}}$

$\bar{x}$ = Mean of initial three calibration factors (per compound).

Evaluate the chromatogram from the analysis of the Evaluation Standard Mix B. The appearance of peaks in addition to the four main pesticide peaks indicates a breakdown of endrin and/or 4,4'-DDT.

Calculate the percent breakdown for endrin and/or 4,4'-DDT on the mixed phase (1.5% OV-16/1.95% OV-210 or equivalent) GC column using Equations 5.3 and 5.4. The percent breakdown for endrin or 4,4'-DDT must not exceed 20.0%. Corrective action must be taken before analysis continues if this criterion is not met.

$$\text{\% breakdown for 4,4'-DDT} = \frac{\text{Total DDT degradation peak area (DDE, DDD)}}{\text{Total DDT peak area (DDT, DDE, DDD)}} \times 100 \qquad \text{Eq. 5.3}$$

$$\text{\% breakdown for Endrin} = \frac{\text{Total eldrin degradation peak areas (endrin aldehyde, endrin ketone)}}{\text{Total endrin peak area (endrin, endrin aldehyde, endrin ketone)}} \qquad \text{Eq. 5.4}$$

Calculate the percent breakdown for endrin and/or 4,4'-DDT on the OV-1 or equivalent GC column using Equations 5.3 and 5.4. The percent breakdown for Endrin or 4,4'-DDT must not exceed 20.0%. Corrective action must be taken before analysis continues if this criterion is not met.

If there is evidence of a peak at the retention time for endrin aldehyde/4,4'-DDD (which coelute on the OV-1 or equivalent GC column), calculate a combined percent breakdown for endrin/4,4'-DDT using Equation 5.5. The combined endrin/4,4'-DDT percent breakdown must not exceed 20.0%, or else corrective action must be taken before analysis continues. The term "peak height" may be substituted for the term "peak area."

$$\text{Combined \% breakdown} = \frac{\text{Total endrin/DDT degradation peak area (DDD, DDE, endrin aldehyde, endrin ketone)}}{\text{Total endrin/DDT peak area (endrin, endrin aldehyde, endrin ketone, DDT, DDD, DDE)}} \qquad \text{Eq. 5.5}$$

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Suggested Maintenance

Corrective measures may require any one or more of the following remedial actions:

- Packed columns. For instruments with off-column injection, replace the demister trap, and clean and deactivate the glass injection port insert, or replace it with a cleaned and deactivated insert. Inspect the injection end of the column and remove any foreign material (broken glass from the rim of the column or pieces of septa). Replace the glass wool with fresh deactivated glass wool. Also, it may be necessary to remove the first few millimeters of packing material if any discoloration is noted. Swab out the inside walls of the column if any residue is present. If these procedures fail to eliminate the degradation problem, it may be necessary to deactivate the metal injector body (described below) and/or repack/replace the column.

- Capillary columns. Clean and deactivate the glass injection port insert or replace it with a cleaned and deactivated insert. Break off the first few inches (up to 1 ft) of the injection-port side of the column. Remove the column and backflush with solvent according to the manufacturer's instructions. If these procedures fail to eliminate the degradation problem, it may be necessary to deactivate the metal injector body and/or replace the column.

- Metal Injector Body. Turn off the oven and remove the analytical column when the oven has cooled. Remove the glass injection port insert (instruments with off-column injection or Grob). Allow the injection port temperature to come to room temperature. Inspect the injection port and remove any noticeable foreign material.

Place a beaker beneath the injector port inside the GC oven. Using a wash bottle, serially rinse the entire inside of the injector port with acetone and then toluene, catching the rinsings in the beaker.

Prepare a solution of deactivating agent (Sylon-CT or equivalent) following manufacturer's directions. After all metal surfaces inside the injector body have been thoroughly coated with the deactivation solution, serially rinse the injector body with toluene, methanol, acetone, and hexane. Reassemble the injector and replace the GC column.

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Individual Standard Mixtures A and B

Prepare Individual Standard Mixtures A and B containing the single-component pesticides. One mixture of all of the single component pesticides is acceptable when using a capillary column if resolution of all compounds is achieved. Prepare separate solutions of all multi-response pesticides and PCBs. (Aroclor 1016 and Aroclor 1260 may be combined in a single mixture.)

Analyze Individual Standard Mixtures A and B and all multi-response pesticide/PCBs at the beginning of each 72-hour period (Figure 1) and analyze Individual Standard Mixtures A and B at the intervals specified in the analytical sequence in Figure 1 and whenever sample analysis is completed. The calibration factor for each standard quantitated (Individual Standard Mix A or B) (Equation 5.6), must not exceed a 15.0% difference for a quantitation run, nor exceed a 20.0% difference for a confirmation run during the 72-hour period. Calculate the percent difference using Equation 5.7. Deviations greater than 15.0% require the analyst to repeat the samples analyzed following the quantitation standard that exceeded the criterion.

$$\text{Calibration factor} = \frac{\text{Total area of peak*}}{\text{Mass injected (in nanograms)}} \qquad \text{Eq. 5.6}$$

*For multiresponse pesticide/PCBs, use the total area of all peaks used for quantitation. The term "peak height" may be substituted for the term "peak area."

$$\text{Percent difference} = \frac{R_1 - R_2}{R_1} \times 100 \qquad \text{Eq. 5.7}$$

Where: R_1 = Calibration factor from first analysis
R_2 = Calibration factor from second or subsequent analysis

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Sample Analysis (Primary GC Column)

Samples are analyzed according to the sequence described in Figure 1.

The retention time shift for DBC must be evaluated after the analysis of each sample. The retention time shift must be less than a 2.0% difference for packed GC columns between the initial standard analysis and any sample or standard analyzed during the 72-hour period. The percent difference for wide-bore capillary columns (i.d. greater than 0.32 mm) must be less than 1.5%. The percent difference for narrow-bore capillary columns (i.d. less than 0.32 mm) must be less than 0.3% (Equation 5.8).

$$\text{Percent Difference} = \frac{RT_1 - RT_S}{RT_1} \times 100 \qquad \text{Eq. 5.8}$$

Where: RT_1 = Absolute retention time of DBC in the initial standard (Evaluation Standard Mix A)

RT_S = Absolute retention time of DBC in the sample or subsequent standard

Evaluate the GC column throughout the analysis of samples by injecting Evaluation Standard Mix B at the frequency outlined in Figure 1.

Calculate the percent breakdown for 4,4'-DDT and endrin using Eq. 5.5. Take corrective action when the breakdown for 4,4'-DDT or endrin exceeds 20.0%.

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Figure 1

72-Hour Sequence for Pesticide/PCB Analysis

1. Evaluation Standard Mix A
2. Evaluation Standard Mix B
3. Evaluation Standard Mix C
4. Individual Standard Mix A*
5. Individual Standard Mix B*
6. Toxaphene
7. Technical Chlordane
8. Aroclors 1016/1260
9. Aroclor 1221
10. Aroclor 1232
11. Aroclor 1242
12. Aroclor 1248
13. Aroclor 1254
14. 5 Samples
15. Evaluation Standard Mix B
16. 5 Samples
17. Individual Standard Mix A or B
18. 5 Samples
19. Evaluation Standard Mix B
20. 5 Samples
21. Individual Standard Mix A or B (whichever was not run in Step 16)
22. 5 Samples
23. Repeat the above sequence starting with Step 14
24. Pesticide/PCB analysis sequence must end with Individual Standard Mixes A and B regardless of number of samples analyzed.

* These may be one mixture (provided adequate separation can be shown)

6. Confirmation Analysis (GC/EC)

Confirmation analysis confirms the presence of all compounds tentatively identified in the primary analysis. Therefore, the only standards required are the evaluation standard mixes (to check linearity and degradation criteria) and standards of all compounds to be confirmed. The linearity criterion on the confirmation column for pesticides is not required unless the column is used for quantitation. The 72-hour sequence described in Figure 1 is therefore modified to fit each case. Quantitation may be performed on the confirmation analysis. If toxaphene or DDT is to be quantitated, additional linearity requirements are necessary.

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Separation should be greater than or equal to 25% resolution between peaks. This criteria must be considered when determining whether to quantitate on the primary analysis or the confirmation analysis. When this criterion cannot be met, quantitation is adversely affected because of the difficulty in determining where to establish the baseline.

For a fused silica capillary confirmation (FSCC), there must be greater than or equal to 25% resolution (valley) between the following pesticide pairs:

- Beta-BHC and delta-BHC
- Dieldrin and 4,4'-DDT
- 4,4'-DDD and endrin aldehyde
- Endosulfan sulfate and 4,4'-DDT

All QC specified previously must be adhered to, i.e., the greater than or equal to 12 minutes retention time for 4,4'-DDT, and the specified criteria for 4,4'-DDT and endrin degradation, linearity, calibration factor for standards, and retention time shift for DBC. The retention time requirement for 4,4'-DDT does not have to be met if the confirmation column is OV-1 or OV-101.

Begin the confirmation analysis GC sequence with the three concentration levels of Evaluation Standard Mixes A, B, and C. The exception to this occurs when toxaphene and/or the DDT series are confirmed and quantitated. There are four combinations of pesticides that could occur, therefore, the following sequences must be followed depending on the situation.

<u>Toxaphene only</u>. Begin the sequence with Evaluation Mix B to check degradation, followed by three concentration levels of toxaphene. Check linearity by calculating %RSD. If less than or equal to 10.0% RSD, use the appropriate calibration factor for calculation. If greater than 10.0% RSD, plot a standard curve and determine the ng for each sample in that set from the curve.

<u>DDT, DDE, DDD only</u>. Begin the sequence with Evaluation Mix B. Then inject three concentration levels of a standard containing DDE, DDD, and DDT. Calculate linearity and follow the requirements specified earlier under the primary GC analysis for each compound to be quantitated.

<u>DDT series and toxaphene</u>. Begin the sequence with Evaluation Mix B. Then inject three concentration levels of toxaphene and another three levels of the DDT series. Calculate linearity and follow the requirements specified under the primary GC analysis for each compound to be quantitated.

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Other pesticides/PCBs plus DDT series and/or toxaphene. Begin the sequence with Evaluation Standard Mixes A, B, and C. Calculate linearity on the four compounds in the Evaluation Standards mixes. If DDT and/or one or more of the other compounds are greater than 10.0% RSD and/or degradation exceeds the criterion, corrective maintenance as outlined earlier should be performed before repeating the above chromatography evaluation. If only DDT exceeds the linearity criteria and one or more of the DDT series is to be quantitated, inject three concentration levels of the DDT series (DDT, DDE, DDD) as described in the earlier paragraph (do not repeat Evaluation Mix B). If none of the DDT series is to be quantitated and DDT exceeds the 10.0% RSD, simply record the %RSD on the proper form. Anytime toxaphene is to be quantitated follow the instructions as given in the paragraph describing toxaphene only.

After the linearity standards are injected, continue the confirmation analysis injection sequence with all compounds tentatively identified during primary analysis to establish the daily retention time windows for the confirmation analysis. Analyze all confirmation standards for a case at the beginning, at intervals specified in the following paragraph and at the end. Any pesticide outside of its established retention time window requires immediate investigation and correction before continuing the analysis. The analyst must reanalyze all samples between the standard that exceeds the criterion and a subsequent standard that meets the criterion.

Begin injection of samples at this point of the confirmation analysis sequence. Analyze groups of five samples with a standard pertaining to the samples after each group (Evaluation Mix B is required after the first five samples, and every 10 samples thereafter, e.g., after 5, 15, 25, etc.). The alternating standard's calibration factors must be within 15.0% of each other if quantitation is performed. Deviations larger than 15.0% require the laboratory to repeat the samples analyzed between the standard that exceeds the criterion and a subsequent standard that meets the criterion. The 15.0% criterion only pertains to compounds being quantitated.

If more than one standard is required to confirm all compounds tentatively identified in the primary analysis, include an alternate standard after each 10 samples.

Samples must also be repeated if the degradation of either DDT and/or Endrin exceed 20.0% on the intermittent Evaluation Standard Mix B.

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If the samples are split between two or more instruments, all standards and blanks pertaining to those samples must be analyzed on each instrument.

Inject the method blanks (extracted with each set of samples) on every GC and GC column on which the samples are analyzed.

APPARATUS:

- Separatory funnel - 2,000 mL with Teflon® stopcock.
- Drying column - Chromatographic column approximately 400 mm x 19 mm i.d., with coarse frit. (Substitution of a small pad of disposable Pyrex® glass wool for the frit will help prevent cross-contamination of sample extracts.)
- Concentrator tube - Kuderna-Danish, 10 mL, graduated (Kontes K-570050-025 or equivalent). Calibration must be checked at the volumes employed in the test. Ground glass stopper is used to prevent evaporation of extracts.
- Evaporative flask - Kuderna-Danish, 500 mL (Kontes K-57000010500 or equivalent). Attach to concentrator tube with springs.
- Snyder column - Kuderna-Danish, three-ball macro (Kontes D-503000-0121 or equivalent).
- Snyder column - Kuderna-Danish, two-ball micro (Kontes D-569001-0219 or equivalent).
- Chromatographic column for alumina - 8-mL (200 mm X 3 mm i.d.) polypropylene column (Kontes D-520160 or equivalent), or 6-mL (150 mm x 8-mm i.d.) glass column (Kontes K-420155 or equivalent), or 5-mL serological pipettes plugged with a small piece of Pyrex glass wool or polyethylene porous disk (Kontes K-420162).
- Pyrex glass wool - Pre-rinse glass wool with appropriate solvents to ensure its cleanliness.
- Silicon carbide boiling chips - Approximately 10/40 mesh. Heat to 400°C for 30 minutes or Soxhlet extract with methylene chloride.

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- Water bath - Heated, with concentric ring cover, capable of temperature control (± 2°C). The bath should be used in a hood.

- Balance - Analytical, capable of accurately weighing ±0.0001 g.

- Nitrogen evaporation device equipped with a water bath that can be maintained at 35- to 40°C. The N-Evap by Organomation Associates, Inc., South Berlin, Massachusetts (or equivalent) is suitable.

- Gas chromatograph - An analytical system complete with gas chromatograph and all required accessories including syringes, analytical columns, gases, electron capture detector, and strip-chart recorder with recording integrator. A data system is required for measuring peak areas or peak heights and recording retention times.

- Quantitation and/or confirmation columns:

  Column 1: 6-ft long, 4-mm i.d. glass packed column
  1.5% SP-2250/1.95% SP-2401 on 100/120 Suppelcoport

  Column 2: 6-ft long, 4-mm i.d. glass packed column
  3% SP-2100 on 100/120 Suppelcort

  Column 3: 30-m long, 0.53-mm i.d. fused silica megabore cap column DB-5

  Column 4: 30-m long, 0.53-mm i.d. fused silica megabore cap column DB-608

REAGENTS:

Reagent water - Reagent water is defined as a water in which an interferent is not observed at or above the method detection limit of each parameter of interest.

Acetone, hexane, isoctane (2,2,4-trimethylpentane), methylene chloride - Pesticide quality or equivalent.

Sodium sulfate - (ACS) granular, anhydrous. Purify by heating at 400°C for 4 hours in a shallow tray.

Alumina - Neutral, Super I Woelm or equivalent. (Universal Scientific, Incorporated, Atlanta, Georgia or equivalent.) Prepare Activity III by adding 7% (v/w) reagent water to the Super I neutral alumina. Tumble or shake in a

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wrist-action shaker for a minimum of 2 hours or preferably overnight. There should be no lumps present. Store in a tightly sealed glass container. A 25-cycle Soxhlet extraction of the alumina with methylene chloride is required if a solvent blank analyzed by the pesticide technique indicates any interferences for the compounds of interest.

Alumina Equivalency Check. Check recovery of all single component pesticides following the procedure as outlined under the procedure. The percent recovery for all single component pesticides must be greater than or equal to 80%, except for endosulfan sulfate, which must be greater than or equal to 60%, and endrin aldehyde, which is not recovered. The data must be retained by the laboratory and made available for inspection during on-site evaluations. If the alumina deactivated with 7% (v/w) reagent water does not prove adequate to remove the BNA surrogates and other interferences, the alumina may be deactivated with as much as 9% reagent water, so long as the criteria for tribromophenol and the recovery of all single component pesticides can be met.

Sodium hydroxide solution (10N)-(ACS). Dissolve 40 g NaOH in reagent water and dilute to 100 mL.

Tetrabutylammonium (TBA) - Sulfite reagent. Dissolve 3.39 g tetrabutylammonium hydrogen sulfate in 100 mL distilled water. To remove impurities, extract this solution three times with 20-mL portions of hexane. Discard the hexane extracts, and add 25 g sodium sulfite to the water solution. Store the resulting solution, which is saturated with sodium sulfite, in an amber bottle with a Teflon-lined screw cap. This solution can be stored at room temperature for at least 1 month.

Pesticide surrogate standard spiking solution.

The surrogate standard is added to all samples and calibration solutions; the compound specified for this purpose is DBC.

Prepare a surrogate standard spiking solution at a concentration of 1 µg/1.00 mL in acetone. Store the spiking solutions at 4°C (±2°C) in Teflon-sealed containers. The solutions should be checked frequently for stability. These solutions must be replaced after 12 months, or sooner, if comparison with quality control check samples indicates a problem.

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Sulfuric acid solution (1+1)-(ACS). Slowly add 50 mL H_2SO_4 (sp. gr. 1.84) to 50 mL of reagent water.

Stock standard solutions (1.00 µg/mL) - Stock standard solution can be prepared from pure standard materials or purchased as certified solutions.

Prepare stock standard solutions by accurately weighing about 0.0100 g of pure material. Dissolve the material in toluene, dilute to volume in a 10-mL volumetric flask with isoctane. Larger volumes can be used at the convenience of the analyst. If compound purity is certified at 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards can be used at any concentration if they are traceable to EMSL/LV supplied standards.

Transfer the stock standard solutions into a bottle/vial with Teflon-lined septa. Store at 4°C (±2°C) and protect from light. Stock standard solutions must be replaced after 12 months, or sooner, if comparison with check standards indicate a problem.

Pesticide matrix standard spiking solution. Prepare a spiking solution of acetone or methanol that contains the following pesticides in the concentrations specified.

Pesticide	µg/1.0 mL
Lindane	0.2
Heptachlor	0.2
Aldrin	0.2
Dieldrin	0.5
Endrin	0.5
4,4' DDT	0.5

Matrix spikes are also to serve as duplicates by spiking two 1-L portions from the one sample chosen for spiking.

Evaluation Standard Mixtures - Prepare working standard mixtures diluted with hexane containing aldrin, endrin, 4,4'-DDT, and DBC to evaluate the GC column. Prepare three concentration levels as follows:

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Standard I.D.	Aldrin (µg/ml)	Endrin (µg/ml)	4,4' DDT (µg/ml)	DBC µg/ml
EVAL A	0.005	0.010	0.010	0.010
EVAL B	0.025	0.050	0.050	0.050
EVAL C	0.05	0.100	0.100	0.100

Working Standard Solutions:

Individual Standard Mixtures - These include all single-component organochlorine pesticides as well as the surrogate compound DBC. Two mixtures of the individual component standards are prepared to prevent coelution of components when using packed columns. Prepare the two individual standard mixtures, diluted in hexane, containing the following pesticides in the concentrations specified.

Individual Mix A		Individual Mix B	
Pesticide	µg/ml	Pesticide	µg/ml
gamma-BHC	0.025	alpha-BHC	0.025
Heptachlor	0.025	beta-BHC	0.025
Aldrin	0.025	delta-BHC	0.025
Heptachlor epoxide	0.025	p,p^1-DDE	0.05
Endosulfan I	0.025	Endrin	0.05
Dieldrin	0.05	p,p^1-DDD	0.05
p,p^1 DDT	0.05	Endosulfan sulfate	0.05
Endrin aldehyde	0.05	Endrin ketone	0.05
Endosulfan II	0.05	alpha-chlordane	0.025
Methoxychlor	0.25	gamma-chlordane	0.025
Dibutylchlorendate	0.10	Dibutylchlorendate	0.10

Multicomponent Standards - All multicomponent standards, e.g., PCB aroclors, toxaphene, and technical chlordane, must be in separate solutions with the exception of aroclors 1016/1260. Dibutylchlorendate is also to be included in each multicomponent standard mixture. Prepare the following standards in hexane at the specified concentrations:

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Standard I.D.	µg/ml
Toxaphene	0.40
Technical Chlordane	0.20
PCB 1016/1260	0.10
PCB 1232	0.10
PCB 1242	0.10
PCB 1248	0.10
PCB 1254	0.10
PCB 1260	0.10

Procedure

1. Sample Storage and Holding Times

1.1 Procedures for Sample Storage

1.1.1 The samples must be protected from light and refrigerated at 4°C (±2°C) from the time of receipt until extraction and analysis.

1.1.2 After analysis, extracts and unused sample volume must be protected from light and refrigerated at 4°C ±2° for the periods specified in the contract schedule.

1.2 Holding Time

All samples should be extracted within 7 days of collection and completely analyzed within 40 days of extraction.

2. Sample Extraction - Separatory Funnel

2.1 Samples may be extracted using separatory funnel techniques. If emulsions prevent acceptable solvent recovery with separatory funnel extractions, continuous liquid-liquid extraction may be used. The separatory funnel extraction scheme described below assumes a sample volume of 1 L.

2.2 Using a 1-L graduated cylinder, measure out a 1-L sample aliquot and place it into a 2-L separatory funnel. Check the pH of the sample with wide-range pH paper and adjust to between 5 and 9 pH with 10N sodium hydroxide and/or 1:1 sulfuric acid solution. (Note: Recovery of DBC will be low if pH is outside this range. Alpha-BHC, gamma-BHC, Endosulfan I and II, and endrin are subject to

decomposition under alkaline conditions, and therefore may not be detected if the pH is above nine). Add 100 µL of surrogate standard spiking solution into the separatory funnel and mix well. Add 100 µL of pesticide matrix spiking solution to each of two 1-L portions from the sample selected for spiking. (If insufficient sample is available to perform matrix spikes, prepare duplicate control spikes, using laboratory reagent water and analyze in lieu of the matrix spikes.)

2.3 Add 60 mL methylene chloride to the separatory funnel and extract the sample by shaking the funnel for 2 minutes, with periodic venting to release excess pressure. Allow the organic layer to separate from the water phase for a minimum of 10 minutes. If the emulsion interface between layers is more than one-third of the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, and may include: stirring, filtration of the emulsion through glass wool, centrifugation, or other physical means. Drain methylene chloride into a 250-mL Erlenmeyer flask.

2.4 Add a second 60-mL volume of methylene chloride to the sample bottle and repeat the extraction procedure a second time, combining the extracts in the Erlenmeyer flask. Perform a third extraction in the same manner.

2.5 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporative flask. Other concentration devices or techniques may be used in place of the K-D if equivalency is demonstrated for all pesticides listed in this method.

2.6 Pour the combined extract through a drying column containing about 10 cm of anhydrous granular sodium sulfate, and collect the extract in the K-D concentrator. Rinse the Erlenmeyer flask and column with 20 to 30 mL of methylene chloride to complete the quantitative transfer.

2.7 Add one or two clean boiling chips to the evaporative flask and attach a three-ball Snyder column. Pre-wet the Snyder column by adding about 1 mL methylene chloride to the top. Place the K-D apparatus on a hot water bath (80° to 90°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 10 to 15 minutes. At the

proper rate of distillation, the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus. Allow it to drain and cool for at least 10 minutes.

2.8 Momentarily remove the Snyder column, add 50 mL of hexane and a new boiling chip, and re-attach the Snyder column. Pre-wet the column by adding about 1 mL of hexane to the top. Concentrate the solvent extract as before. The elapsed time of concentration should be 5 to 10 minutes. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus and allow it to drain and cool at least 10 minutes.

2.9 Remove the Snyder column, and rinse the flask and its lower joint into the concentrator tube with 1 to 2 mL of hexane.

3. Nitrogen Blowdown

3.1 Place the concentrator tube in a warm water bath (35°C) and evaporate the solvent volume to 0.5 mL using a gentle stream of clean, dry nitrogen (filtered through a column of activated carbon). Caution: New plastic tubing must not be used between the carbon trap and the sample, as it may introduce interferences. The internal wall of the tube must be rinsed down several times with hexane during the operation, and the final volume must be brought to 0.5 mL. During evaporation, the tube solvent level must be kept below the water level of the bath. The extract must never be allowed to become dry.

3.2 Dilute the extract to 1 mL with acetone and proceed to Step 5 Alumina Column Cleanup.

4. Sample Extraction - Continuous Liquid-Liquid Extractor

4.1 When experience with a sample from a given source indicates that a serious emulsion problem will result, or if an emulsion is encountered in Step 2.3 using a separatory funnel, a continuous extractor should be used.

4.2 Using a 1-L graduated cylinder, measure out a 1-L sample aliquot and place it into the continuous extractor. Add 100 µl of surrogate standard spiking solution into the continuous extractor and mix well. Check the pH of the sample with wide-range pH paper and adjust the pH to between 5 and 9 with 10N sodium hydroxide and/or 1:1 sulfuric acid solution.

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4.3 Add 500 mL of methylene chloride to the distilling flask. Add sufficient reagent water to ensure proper operation and extract for 18 hours. Allow to cool, then detach the boiling flask and dry. Concentrate the extract as in Steps 2.5 through 3.2.

5. Alumina Column Cleanup

5.1 Add 3 g of Activity III neutral alumina to the 10-mL chromatographic column. Tap the column to settle the alumina. Do not pre-wet the alumina.

5.2 Transfer the 1 mL of hexane/acetone extract from Step 3.2 to the top of the alumina using a disposable Pasteur pipet. Collect the eluate in a clean 10-mL concentrator tube.

5.3 Add 1 mL of hexane to the original extract concentrator tube to rinse it. Transfer these rinsings to the alumina column. Elute the column with an additional 9 mL of hexane. Do not allow the column to go dry during the addition and elution of the sample.

5.4 Concentrate the cleaned-up extract using the nitrogen blowdown technique as described in Step 3.0, adjusting the final volume to 1.0 mL with hexane. The pesticide/PCB fraction is ready for analysis. Store the extracts at 4°C (±2°C) in the dark in Teflon-sealed containers until analyses are performed.

6. Optional Sulfur Cleanup

6.1 Transfer the 1-mL extract from Step 5.4 to a 50-mL clear glass bottle or vial with a Teflon-lined screw cap. Rinse the concentrator tube with 1 mL of hexane, adding the rinsings to the 50-mL bottle.

6.2 Add 1 mL of TBA-sulfite reagent and 2 mL of 2-propanol, cap the bottle, and shake it for at least 1 minute. If the sample is colorless or if the initial color is unchanged, and if clear crystals (precipitated sodium sulfite) are observed, sufficient sodium sulfite is present. If the precipitated sodium sulfite disappears, add more crystalline sodium sulfite in approximately 100-mg portions until a solid residue remains after repeated shaking.

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6.3 Add 5 mL of distilled water and shake the sample for at least 1 minute. Allow the sample to stand 5 to 10 minutes. Transfer the hexane layer (top) to a concentrator ampule and go back to Step 5.4.

7. Calibration

7.1 The gas chromatographic system must be calibrated using the external standard technique for all columns used for quantitation.

7.2.1 Prepare calibration standards at a minimum of three concentration levels for each parameter of interest by adding volumes of one or more stock standards to a volumetric flask and diluting to volume with hexane. One of the external standards should be at a concentration near, but above, the MDL and the other concentrations found in real samples, or should define the working range of the detector. This should be done on each quantitation column and each instrument used for this analysis.

7.2.2 Using injections of 2 to 5 µL of each calibration standard, tabulate peak height or area responses against the mass injected. The results can be used to prepare a calibration curve for each compound.

8. GC-EC Primary Analysis (Quantitation may be performed on primary or confirmation analyses.)

8.1 Adjust oven temperature and carrier gas flow rates so that the retention time for 4,4'-DDT is equal to or greater than 12 minutes.

8.2 Table 3 provides examples of operating conditions for the gas chromatograph. Separation should be greater than or equal to 25% resolution between peaks. Percent resolution is calculated by dividing the height of the valley by the peak height of the smaller peak being resolved, multiplied by 100. This criterion must be considered when determining whether to quantitate on the primary analysis or the confirmation analysis. When this criterion can not be met, quantitation is adversely affected because of the difficulty in determining where to establish the baseline.

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8.2.1 Inject 2 to 5 µL of the sample or standard extract using the solvent-flush technique or auto sampler. Smaller (1.0 µL) volumes can be injected only if automatic devices are employed. Record the volume injected and the total extract volume.

8.2.2 Inject Individual Standard Mixes A and B and all multi-response pesticides/PCBs at the beginning of each 72-hour sequence. (See Paragraph 8.2.8.6). To establish the retention time window within each 72-hour sequence for the pesticide/PCB of interest, use the absolute retention time from the above chromatograms as the mid-point, and plus or minus three times the standard deviation as described earlier in Part 4 of the Quality Assurance Section. Individual Standard Mixes A and B are analyzed alternately and intermittently throughout the analysis. Any pesticide outside of its established retention time window requires immediate investigation and correction before continuing the analysis.

8.2.3 Sample analysis of extracts can begin when linearity and degradation QA/QC requirements specified in the Quality Assurance Section are met.

8.2.4 NOTE: The 10.0% RSD linearity criterion is <u>only</u> required on the column(s) being used for pesticide/PCB quantitation. If a column is used for surrogate quantitation only, the 10.0% RSD is required only for DBC.

8.2.5 Analyze samples in groups of no more than five samples. After the analysis of the first group of up to five samples, analyze Evaluation Mix B. Analyze another group of up to five samples, followed by the analysis of Individual Mix A or B. Subsequent groups of up to five samples may be analyzed by repeating this sequence, alternately analyzing Evaluation Mix B and Individual Mix A or B between the groups as shown in Paragraph 8.2.8.6. The Pesticide/PCB analytical sequence <u>must</u> end with Individual Mix A <u>and</u> B regardless of the number of samples analyzed.

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8.2.6 If a multiresponse pesticide/PCB is detected in either of the preceding groups of five samples, the appropriate multiresponse pesticide/PCB may be substituted for Individual Mix A or B. All standards listed in Paragraph 8.2.8.6 must be included for every sample set and must be analyzed within the same 72-hour period as those samples. If the samples are split between two or more instruments, the complete set of standards must be analyzed on each instrument with the same 72-hour requirement. All standards must be analyzed before the samples to avoid the effects of poor chromatography caused by the unsuspected injection of a highly concentrated sample.

8.2.7 Paragraphs 8.2.8.1 and 8.2.8.5 contain GC performance criteria. If it is determined during the course of a 72-hour sequence that one or more of the criteria have been violated, stop the run and take corrective action. After the corrective action has been taken, the 72-hour sequence may be restarted as follows: If a standard violated the criterion, restart the sequence with that standard, determine that the criteria have been met, and continue with sample analyses according to Paragraph 8.2.8.6. If a sample violated the criterion, restart the sequence with the standard that would have <u>followed</u> that group of samples (thereby preserving the sequence of standards in Paragraph 8.2.8.6), determine that the criteria have been met, and continue with sample analyses according to Paragraph 8.2.8.6.

8.2.8 If it is determined <u>after</u> the completion of a 72-hour sequence that one or more of the criteria have been violated, proceed as follows: If a standard violated the criterion, all samples analyzed after that standard must be reanalyzed as part of a new 72-hour sequence. If a subsequent standard in the original sequence met all the criteria, then only those samples analyzed between the standard that <u>did</u> <u>not</u> meet the criterion and the standard that <u>did</u> meet the criterion must be reanalyzed as part of a new 72-hour sequence. If only samples violated the criteria, then those samples must be reanalyzed as part of a new 72-hour sequence.

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8.2.8.1. Differences in the calibration factors for each standard in Individual Standard Mixes A and B must not exceed 20.0% (15.0% for any standard compound used for quantitation) during the 72-hour primary analysis. Calculate the difference using the initial individual standard mix versus all subsequent individual standard mixes analyzed during the 72-hour sequence.

8.2.8.2 The retention time shift of DBC in any standard or sample must be less than 2.0% difference for packed columns, less than 1.5% difference for wide-bore capillary columns (i.d. greater than 0.32 mm), and less than 0.3% difference for narrow-bore capillary columns (i.d. less than 0.32 mm).

8.2.8.3 Samples must also be repeated if the degradation of DDT and/or endrin exceeds 20.0% respectively on the intermittent analysis of Evaluation Standard Mix B.

8.2.8.4 All pesticide standards must fall within the established 72-hour retention time windows.

8.2.8.5 Highly colored extracts may require a dilution.

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8.2.8.6 The 72-hour sequence must be as follows.

72-Hour Sequence for Pesticide/PCB Analysis:

1. Evaluation Standard Mix A
2. Evaluation Standard Mix B
3. Evaluation Standard Mix C
4. Individual Standard Mix A
5. Individual Standard Mix B
6. Toxaphene
7. Technical Chlordane
8. Aroclors 1016/1260
9. Aroclor 1221
10. Aroclor 1232
11. Aroclor 1242
12. Aroclor 1248
13. Aroclor 1254
14. Five samples
15. Evaluation Standard Mix B
16. Five samples
17. Individual Standard Mix A or B
18. Five samples
19. Evaluation Standard Mix B
20. Five samples
21. Individual Standard Mix A or B (whichever not run in Step 16)
22. Five samples
23. Repeat the above sequence starting with Evaluation Standard Mix B (Step 14 above).
24. Pesticide/PCB analysis sequence must end with Individual Standard Mix A and B regardless of number of samples analyzed.

8.3 Evaluation of Chromatograms.

8.3.1 Consider the sample as negative when its peaks, depending on the pesticide's response factor, result in concentrations less than the required quantitation level. The sample is complete at this point. Confirmation is not required.

8.3.2 Tentative identification is made when the unknown's retention time matches the retention time of a corresponding standard that was chromatographed on the same instrument within a 72-hour period.

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8.3.3 Determine if any target pesticides/PCBs are present. Pattern recognition techniques, based on chromatograms of standards, are recommended for the identification of PCB compounds.

8.3.3.1 If the response for any of these compounds is 100% or less of full scale, the extract is ready for confirmation and quantitation.

8.3.3.2 If the response for any compound is greater than full scale, dilute the extract so that the peak will be between 50% and 100% full scale and reanalyze. Also use this dilution for confirmation and quantitation.

8.3.3.3 For dilution greater than 10 fold. Also inject an aliquot of a dilution 10-fold more concentrated to determine if other compounds of interest are present at lower concentrations.

8.3.3.4 Computer reproductions of chromatograms manipulated to ensure all peaks are on scale over a 100-fold range are an accepted substitute. However, this can be no greater than a 100-fold range. This is to prevent retention time shifts by column or detector overload. Linearity must be demonstrated over the 100-fold range using higher concentrations of the evaluation mixture.

8.3.4 Quantitation may be performed on the primary analysis, with the exception of toxaphene and possibly the DDT series. If DDT exceeds the 10.0% RSD linearity criterion, then quantitations for any DDE, DDD, and DDT in a sample must be on the confirmation analysis. Toxaphene must always be quantitated on the confirmation analysis. See Quality Assurance Section for special QC requirements for quantitations.

8.3.5 If identification of compounds of interest are prevented by the presence of interferences, further cleanup may be required.

8.3.6 When selecting a GC column for confirmation and/or quantitation, be sure that none of the compounds to be confirmed/quantitated overlap, e.g., do not select the 3% OV-1 column if DDE and dieldrin are to be confirmed and/or quantitated.

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9. GC/EC Confirmation Analysis

9.1 Confirmation analysis confirms the presence of all compounds tentatively identified in the primary analysis.

Therefore, the only standards that are required are the evaluation standard mixes (to check linearity and degradation criteria) and standards of all compounds to be confirmed. The linearity criterion on the confirmation column for pesticides is not required unless the column is used for quantitation. The 72-hour sequence in Paragraph 8.2.8.6 is therefore modified to fit each case. Quantitation may be performed on the confirmation analysis. If toxaphene or DDT is to be quantitated, additional linearity requirements are specified in Step 9.5.1.

9.2 Table 3 provides examples of operating conditions for the gas chromatograph. Separation should be greater than or equal to 25% resoluton between peaks. Percent resolution is calculated by dividing the height of the valley by the peak height of the smaller peak being resolved, multiplied by 100. This criterion must be considered when determining whether to quantitate on the primary analysis or the confirmation analysis. When this criterion cannot be met, quantitation is adversely affected because of the difficulty in determining where to establish the baseline.

9.3 For a fused silica capillary column confirmation, there must be greater than or equal to 25% resolution (valley) between the following pesticide pairs:

- Beta-BHC and delta-BHC
- Deildrin and 4,4'-DDT
- 4,4'-DDD and endrin aldehyde
- Endosulfan sulfate and 4,4'-DDT

9.4 All QC requirements specified earlier in the Quality Assurance Section must be adhered to, i.e., the greater than or equal to 12-minute retention time for 4,4'-DDT, the criteria for 4,4'-DDT and endrin degradation, linearity, calibration factor for standards, and retention time shift for DBC. The retention time criterion for 4,4'-DDT does <u>not</u> have to be met if the confirmation column is OV-1.

9.5 Inject 2 to 5 µL (1 to 2 µL for capillary columns) of the sample extract and standards using the solvent-flush technique or auto samples.

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One-microliter volumes can be injected only if automatic devices are employed. Record the volume injected and the total extract volume. The detector attenuation must provide peak response equivalent to the primary analysis response for each compound to be confirmed.

9.5.1 Begin the confirmation analysis GC sequence with the three concentration levels of Evaluation Standard Mixes A, B, and C. The exception to this occurs when toxaphene and/or the DDT series are to be confirmed and quantitated. There are four combinations of pesticides that could occur; therefore, the following sequences must be followed depending on the situation.

9.5.1.1 Toxaphene only - Begin the sequence with Evaluation Mix B to check degradation, followed by three concentration levels of toxaphene. Check linearity by calculating %RSD.

9.5.1.2 If less than or equal to 10.0% RSD, use the appropriate equation in Paragraph 8 for calculation. If greater than 10.0% RSD, plot a standard curve and determine the ng for each sample in that set from the curve.

9.5.1.3 DDT, DDE, DDD only - Begin the sequence with Evaluation Mix B. Then inject three concentration levels of a standard containing DDE, DDD, and DDT. Calculate linearity and follow the requirements specified in Paragraph 9.5.1.1 for each compound to be quantitated.

9.5.1.4 DDT series and toxaphene - Begin the sequence with Evaluation Mix B. Then inject three concentration levels of toxaphene and another three levels of the DDT series. Calculate linearity and follow the requirements specified in Paragraph 9.5.1.1 for each compound to be quantitated.

9.5.1.5 Other pesticides/PCBs plus DDT series and/or toxaphene - Begin the sequence with Evaluation Standard Mixes A, B, and C. Calculate linearity on the four compounds in the Evaluation Standard mixes. If DDT and/or one or more of the other compounds are greater than 10.0% RSD and/or degradation exceeds the criterion, corrective maintenance should be performed before repeating the above chromatography evaluations. If only DDT exceeds the linearity criterion and one or more of the DDT series is to be quantitated, follow Paragraph 9.5.1.3 (do not repeat Evaluation Mix B).

9.5.1.6 If none of the DDT series is to be quantitated and DDT exceeds the 10.0% RSD, simply record the %RSD on the proper form. Any time toxaphene is to be quantitated, follow Paragraph 9.5.1.1.

9.5.2 After the linearity standards are injected, continue the confirmation analysis sequence by injecting standards for all compounds tentatively identified in the primary analysis, to establish the 72-hour retention time windows. Analyze all confirmation standards for a case at the beginning, at intervals specified in Step 9.5.3., and at the end. Any pesticide outside of its established retention time window requires immediate investigation and correction before continuing the analysis. The analyst must reanalyze all samples which follow the standard that exceeds the criterion.

9.5.3 After injection of the appropriate standards as described in the proceeding paragraph, begin injection of samples. Analyze groups of five samples. Analyze Evaluation Mix B after the first group of five samples. After the second group of five samples, analyze a standard pertaining to the samples in the preceeding groups (i.e., standard mix containing those compounds requiring confirmation). Continue analyzing groups of five samples, alternately preceding samples between groups of five samples.

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The alternating standard's calibration factors must be within 15.0% of each other if quantitation is performed. Deviations larger than 15.0% require the analyst to repeat the analyses of samples which were analyzed after the standard that exceeds the criterion. The 15.0% criterion only pertains to compounds being quantitated.

9.5.4 If more than one standard is required to confirm all compounds tentatively identified in the primary analysis, alternate the standards with Evaluation Standard Mix B. Samples must also be repeated if the degradation of either DDT and/or endrin exceeds 20.0% on the intermittent Evaluation Standard Mix B.

If the samples are split between two or more instruments, all standards and blanks pertaining to those samples must be analyzed on each instrument.

9.5.5 Inject the method blank (extracted with each set of samples) on every GC and GC column on which the samples are analyzed.

9.6 Evaluation of Chromatograms

9.6.1 A compound tentatively identified in the primary analysis is confirmed in the retention time from the confirmation analysis falls within the retention time window of a corresponding standard that was chromatographed on the same instrument within a 72-hour period.

9.6.2 Quantitation should be performed on the column (primary or confirmation) that provides the best separation from interfering peaks. Note: To determine that no pesticides/PCBs are present at or above the contract required quantitation limit is a form of quantitation.

9.6.2.1 Quantitation of Chlordane. Because weathering and/or different formulations of chlordane usually modify the pattern exhibited by technical chlordane, this method is not appropriate for determining technical chlordane. Instead, standards for alpha chlordane and gamma chlordane are used for quantitation, and each isomer of chlordane is reported separately.

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9.6.3 Computer reproduction of chromatograms that are attenuated to ensure that all peaks are on scale over a 100-fold range are acceptable. However, this can be no greater than a 100-fold range. This is to prevent retention time shifts by column or detector overload. Also, peak response must be greater than 25% of full scale deflection to allow visual pattern recognition of multicomponent compounds, and individual compounds must be visible.

9.6.4 If identification of compounds of interest are prevented by the presence of interferences, further cleanup is required. If sulfur is evident, go to Step 6 (Optional Sulfur Cleanup).

9.6.5 If unknown interferences or poor chromatography are noted only in the sample chromatogram, it is recommended that gel permeation chromatography cleanup is applied.

9.6.6 Calculate surrogate standard recovery on all samples, blanks, and spikes unless the surrogate was diluted out. Determine if recovery is within limits and report.

9.6.7 If target pesticide/PCB compounds were identified in the unspiked sample from which the matrix spike and matrix spike duplicate were prepared, confirmation analysis is required for the matrix spike and matrix spike duplicate. If target pesticide/PCB compounds were not identified in the unspiked sample, confirmation of the matrix spike and matrix spike duplicate is not required.

10. Calculations

10.1 Calculate the concentration in the sample using the following equation for external standards. Response can be measured by the manual peak height technique or by automated peak height or peak area measurements from an integrator.

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10.1.1 Water

$$\text{Concentration} \quad (\mu g/L) = \frac{(A_x)\ (I_s)\ (V_t)}{(A_s)\ (V_i)\ (V_s)}$$

Where:

A_x = Response for the parameter to be measured
A_s = Response for the external standard
V_t = Volume of total extract (µL) (take into account any dilutions)
I_s = Amount of standard injected in nanograms (ng)
V_i = Volume of extract injected (µL)
V_s = Volume of water extracted (mL)

10.2 For multicomponent mixtures (chlordane, toxaphene, and PCB) match retention times of peaks in the standard with peaks in the sample. Quantitate every identifiable peak (greater than 50% of the total area must be used) unless interference with individual peaks persist after cleanup. Add peak height or peak area of each identified peak in the chromatogram. Calculate as total response in the sample versus total response in the standard.

10.3 Calculation of surrogate and matrix spike recoveries.

$$\text{Percent recovery} = \frac{Qd}{Qa} \times 100\%$$

Where:

Qd = Quantity determined by analysis
Qa = Quantity added to sample

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Table 1

Method Detection Limits

Compound	Method Detection Limit (µg/L)
Aldrin	0.005
alpha-BHC	0.002
beta-BHC	0.003
gamma-BCH (lindane)	0.005
delta-BHC	0.002
alpha-chlordane	0.003
gamma-chlordane	0.009
Technical chlordane	0.05*
4,4'-DDD	0.005
4,4'-DDE	0.005
4,4'-DDT	0.010
Dieldrin	0.011
Endosulfan I	0.004
Endosulfan II	0.012
Endosulfan sulfate	0.006
Endrin	0.007
Endrin aldehyde	0.012
Endrin ketone	0.005
Heptachlor	0.006
Heptachlor epoxide	0.005
Methoxychlor	0.060
Toxaphene	0.10*
PCB-1016	0.04
PCB-1221	0.05*
PCB-1232	0.05*
PCB-1242	0.05*
PCB-1248	0.05*
PCB-1254	0.05*
PCB-1260	0.03

* Detection limits estimated

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Table 2

Precision and Accuracy Data
Pesticide/PCB Screen

Compound	Spike Level (µg/L)	Average Recovery (µg/L)	Average Recovery (%)	Standard Deviation (µg/L)
Aldrin	0.0125	0.00858	69	0.00159
alpha-BHC	0.0125	0.0105	84	0.000706
beta-BHC	0.0125	0.0102	82	0.000837
gamma-BCH (lindane)	0.0125	0.00955	76	0.00152
delta-BHC	0.0125	0.0106	85	0.000561
alpha-chlordane	0.0125	0.0116	93	0.000866
gamma-chlordane	0.0125	0.0130	104	0.00298
Technical chlordane	ND	-	-	-
4,4'-DDD	0.025	0.0228	91	0.00157
4,4'-DDE	0.025	0.0220	88	0.00168
4,4'-DDT	0.025	0.0209	84	0.00350
Dieldrin	0.025	0.0187	75	0.00809
Endosulfan I	0.0125	0.0104	83	0.00129
Endosulfan II	0.025	0.0204	81	0.00382
Endosulfan sulfate	0.025	0.0212	85	0.00181
Endrin	0.025	0.0206	82	0.00245
Endrin aldehyde	0.025	0.0180	72	0.00370
Endrin ketone	0.025	0.0229	92	0.00143
Heptachlor	0.0125	0.00930	74	0.00188
Heptachlor epoxide	0.0125	0.0106	85	0.00164
Methoxychlor	0.125	0.118	94	0.0189
Toxaphene	ND	-	-	-
PCB-1016	0.050	0.0675	135	0.0101
PCB-1221	ND	-	-	-
PCB-1232	ND	-	-	-
PCB-1242	ND	-	-	-
PCB-1248	ND	-	-	-
PCB-1254	ND	-	-	-
PCB-1260	0.050	0.0626	125	0.0229

ND Not determined.

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Table 3.0

Recommended GC Operating Conditions

Column 1: COLUMN: 6 ft x 4 mm i.d., 1.5% SP-2250/1.95% SP-2401 on 100/120 Suplecoport
TEMP OF: INJ 200°C, COL 210°C, DET 300°C
Ar/CH_4: 95/5 FLOW RATE 60 mL/minute
RECORDER: 1 mV full scale; 0.5 cm/minute

Column 2: COLUMN: 6 ft x 4 mm i.d., 3% OV-1% on 80/100 GAS CHROM Q
TEMP OF: INJ 200°C, COL 210°C, DET 300°C
Ar/CH_4: 95/5 FLOW RATE 60 mL/minute
RECORDER: 1 mV full scale; 15 in/hour

Column 3: COLUMN: 30 m x 0.53 mm i.d., DB 608 FSOT Megabore
TEMP OF: INJ 150°C, DET 300°C
PROGRAM: INITIAL TEMP 150°C, Hold 0 minutes, RATE 8°C/minute; FINAL TEMP 250°C, HOLD 16 minutes
CARRIER GAS: Helium at 6 mL/minute
MAKE-UP GAS: Nitrogen at 30 mL/minute
RECORDER: 1mV full scale; 10 mm/minute

Column 4: COLUMN: 30 m x 0.53 mm i.d., DB 5 Megabore
TEMP OF: INJ 150°C, DET 300°C
PROGRAM: INITIAL TEMP 150°C
RATE 8°C/minute; FINAL TEMP 250°C, HOLD 16 minutes
CARRIER GAS: Helium at 6.5 mL/minute
MAKE-UP GAS: Nitrogen at 30 mL/minute
RECORDER: 1mV full scale; 10 mm/minute

DRAFT

ASSAY TITLE: Low Level Semivolatile Analysis of Water Samples by Gas Chromatography/Mass Spectroscopy

AREA OF APPLICABILITY: Hazleton Laboratories America, Inc. Environmental Analysis

SCOPE:

This method covers the determination of the priority pollutant and Target Compound List (TCL) semivolatile organics in drinking water sources using gas chromatography/mass spectrometry (GCMS). The compounds determined by this method are reported with detection limits lower than those generated by the standard GCMS semivolatile screen. The standard list of compounds calibrated and analyzed for are presented in Table 10 as an attachment.

PRINCIPLE:

A 1-L sample is serially extracted with methylene chloride at a pH greater than 11 and again at a pH less than 2, using a separatory funnel or continuous extraction technique. The methylene chloride extracts are dried and concentrated separately and stored at 4°C until instrumental analysis. Just prior to analysis the two extracts (>pH 11 and <pH 2) are combined and reduced to a final volume of 0.5 mL. The extract is separated by gas chromatography and the analytes of interest are measured by a mass spectrometer detector in the electron impact mode.

SENSITIVITY, PRECISION, ACCURACY:

The method detection limits presented in Table 10 represent the sensitivities that can be achieved in ground water in the absence of interferences.

Precision and accuracy for this method, as generated from an inhouse validation study, is presented in Table 10.

REFERENCES:

1. Environmental Protection Agency (EPA) Method 625 (Federal Register 49 (209): 43385-43406, October 16, 1984).

2. Environmental Protection Agency (EPA) Contract Laboratory Program, Statement of Work for "Organic Analysis Multi-Media Multi-Concentration", October 1986. Revisions: January 1987; February 1987; July 1987; August 1987. Exhibits: B, D, E.

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SAFETY PRECAUTIONS:

The toxicity or carcinogenicity of chemicals used in this method have not been precisely defined; each chemical should be treated as a potential health hazard and exposure to these chemicals should be minimized. Each analyst is responsible for maintaining awareness of OSHA regulations regarding safe handling of chemicals used in this method. Additional references to laboratory safety are available for the information of the analyst.

The following parameters covered by this method have been tentatively classified as known or suspected, human or mammalian carcinogens: benzo(a)anthracene, benzidine, 3,3'-dichlorobenzidine, benzo(a)pyrene, dibenzo(a,h)anthracene, and N-nitrosodimethylamine. Primary standards of these toxic compounds should be prepared in a hood. A NIOSH/MESA approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

INTERFERENCES:

Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware, that lead to discrete artifacts or elevated baselines in the total ion current profiles (TICPs). All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks. Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from source to source.

QUALITY ASSURANCE:

This section outlines the minimum quality control (QC) operations necessary to satisfy the analytical requirements associated with the determination of semivolatile organic TCL compounds in water. The QC operations are as follows:

1. Documentation of GC/MS mass calibration and abundance pattern
2. Documentation of GC/MS response factor stability
3. Internal standard response and retention time monitoring
4. Method blank analysis
5. Surrogate spike response monitoring
6. Matrix spike and matrix spike duplicate analysis

<u>Tuning and GC/MS Mass Calibration</u>

1. It is necessary to establish that a given GC/MS meets the standard mass spectral abundance criteria before initiating any on-going data collection. This is accomplished through the analysis of Decafluorotriphenylphosphine (DFTPP).

1.1 Decafluorotriphenylphosphine (DFTPP)

1.1.1 Each GC/MS system used for the analysis of semivolatile compounds must be hardware-tuned to meet the abundance criteria listed in Table 1 for a 50-ng injection of DFTPP. DFTPP may be analyzed separately or as part of the calibration standard. The criteria must be demonstrated daily or for each 12-hour period, whichever is more frequent, before samples can be analyzed. DFTPP must be injected to meet this criterion.

1.1.2 Whenever corrective action is taken that may change or affect the tuning criteria for DFTPP (e.g., ion source cleaning or repair, etc.), the tune must be verified irrespective of the 12-hour tuning requirements.

Table 1. DFTPP Key Ions and Ion Abundance Criteria

Mass	Ion Abundance Criteria
51	30.0 - 60.0% of mass 198
68	Less than 2.0% of mass 69
70	Less than 2.0% of mass 69
127	40.0 - 60.0% of mass 198
197	Less than 1.0% of mass 198
198	Base peak, 100% relative abundance
199	5.0 - 9.0% of mass 198
275	10.0 - 30.0% of mass 198
365	Greater than 1.00% of mass 198
441	Present but less than mass 443
442	Greater than 40.0% of mass 198
443	17.0 - 23.0% of mass 442

Calibration of the GC/MS System

2. Before the analysis of samples and required blanks, and after tuning criteria have been met, the GC/MS system must be initially calibrated at a minimum of three concentrations to determine the linearity of response utilizing TCL compound standards. Once the system has been calibrated, the calibration must be verified each 12-hour time period for each GC/MS system.

2.1 Prepare calibration standards to yield the following specific concentrations.

2.1.1 Semivolatile TCL Compounds

Initial calibration of semivolatile TCL compounds is required at 20, 50, and 100 total nanograms.

2.2 Analyze each calibration standard and tabulate the area of the primary characteristic ion (Tables 2 and 3) against concentration for each compound including all required surrogate compounds. The relative retention times of each compound in each calibration run should agree within 0.06 relative retention time units. Late eluting compounds usually will have much better agreement.

Using Table 4, calculate the RRF for each compound at each concentration level using Equation 1.

$$RRF = \frac{A_x}{A_{is}} \times \frac{C_{is}}{C_x} \qquad \text{Equation 1}$$

Where:

A_x = Area of the characteristic ion for the compound to be measured.

A_{is} = Area of the characteristic ion for the specific internal standards from Tables 2 or 3.

C_{is} = Concentration of the internal standard (ng/µL).

C^x = Concentration of the compound to be measured (ng/µL).

2.2.1 Using the relative response factors (RRF) from the initial calibration, calculate the %RSD for compounds labeled as Calibration Check Compounds and shown in Table 4 using Equation 2.

$$\%RSD = \frac{SD}{x} \times 100 \qquad \text{Equation 2}$$

Where:

RSD = Relative Standard Deviation

SD = Standard Deviation of initial response factors (per compound)

Where: $$SD = \sum_{i=1}^{N} \frac{(X_i - \bar{x})^2}{N-1}$$

$\bar{x}$ = Mean of initial relative response factors (per compound)

The %RSD for each individual Calibration Check Compound (see Table 5) must be less than or equal to 30.0%. This criteria must be met for the initial calibration to be valid.

2.3 A system performance check must be performed to ensure that minimum average RRF are met before the calibration curve is used.

2.3.1 For semivolatiles, the System Performance Check Compounds (SPCCs) are: N-Nitroso-Di-n-Propylamine, Hexachlorocyclopentadiene, 2,4-Dinitrophenol, and 4-Nitrophenol. The minimum acceptable average RRF for these compounds is 0.050. SPCCs typically have very low RRFs (0.1 - 0.2) and tend to decrease in response as the chromatographic system begins to deteriorate or the standard material begins to deteriorate. These compounds are usually the first to show poor performance. Therefore, they must meet the minimum requirement when the system is calibrated.

2.3.2 The initial calibration is valid only after both the %RSD for CCC compounds and the minimum RRF for SPCC have been met. Only after both these criteria are met can sample analysis begin.

Table 2

Characteristic Ions for Semivolatile TCL Compounds

Parameter	Primary Ion	Secondary Ion(s)
Phenol	94	65, 66
bis(-2-Chloroethyl)Ether	93	63, 95
2-Chlorophenol	128	64, 130
1,3-Dichlorobenzene	146	148, 113
1,4-Dichlorobenzene	146	148, 113
Benzyl alcohol	108	79, 77
1,2-Dichlorobenzene	146	148, 113
2-Methylphenol	108	107
bis(-2-Chloroisopropyl)Ether	45	77, 79
4-Methylphenol	108	107
N-Nitroso-di-propylamine	70	42, 101, 130
Hexachloroethane	117	201, 199
Nitrobenzene	77	123,65
Isophorone	82	95, 138
2-Nitrophenol	139	65, 109
2,4-Dimethylphenol	107	121, 122
Benzoic acid	122	105,77
bis(-2-Chloroethoxy)Methane	93	95, 123
2,4-Dichlorophenol	162	164, 98
1,2,4-Trichlorobenzene	180	182, 145
Naphthalene	128	129, 127
4-Chloroaniline	127	129
Hexachlorobutadiene	225	223, 227
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, 200
2-Chloronaphthalene	162	164, 127
2-Nitroaniline	65	92, 138
Dimethyl phthalate	163	194, 164
Acenaphthylene	152	151, 153
3-Nitroaniline	138	108, 92
Acenaphthene	153	152, 154
2,4-Dinitrophenol	184	63, 154
4-Nitrophenol	109	139, 65
Dibenzofuran	168	139
2,4-Dinitrotoluene	165	63, 182
2,6-Dinitrotoluene	165	89, 121
Diethylphthalate	149	177, 150
4-Chlorophenyl-phenylether	204	206, 141

Table 2 (Continued)

Characteristic Ions for Semivolatile TCL Compounds

Parameter	Primary Ion	Secondary Ion(s)
Fluorene	166	165, 167
4-Nitroaniline	138	92, 108
4,6-Dinitro-2-Methylphenol	198	182, 77
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	179, 176
Di-N-Butylphthalate	149	150, 104
Fluoranthene	202	101, 100
Pyrene	202	101, 100
Butylbenzylphthalate	149	91, 206
3,3'-Dichlorobenzidine	252	254, 126
Benzo(a)Anthracene	228	229, 226
bis(2-Ethylhexyl)Phthalate	149	167, 279
Chrysene	228	226, 229
Di-N-Octyl phthalate	149	-
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

Table 3

Characteristic Ions for Surrogates and
Internal Standards for Semivolatile Compounds

	Primary Ion	Secondary Ion(s)
Surrogates		
Phenol-d_5	99	42, 71
2-Fluorophenol	112	64
2,4,6-Tribromophenol	330	332, 141
d-5 Nitrobenzene	82	128, 54
2-Fluorobiphenyl	172	171
Terphenyl	244	122, 212
Internal Standards		
1,4-Dichlorobenzene-d_4	152	115
Naphthalene-d_8	136	68
Acenaphthene-d_{10}	164	162, 160
Phenanthrene-d_{10}	188	94, 80
Chrysene-d_{10}	240	120, 236
Perylene-d_{12}	264	260, 265

Table 4

Semivolatile Internal Standards with Corresponding TCL Analytes Assigned for Quantitation

1,4-Dichlorobenzene-d	Naphthalene-d	Acenaphthene-d	Phenanthrene-d	Chrysene-d	Perylene-d
Phenol	Nitrobenzene	Hexachlorocyclo-pentadiene	4,6-Dinitro-2-methylphenol	Pyrene	Di-n-octyl phthalate
bis(2-chloroethyl) ether	Isophorone	2,4,6-Trichloro-phenol	N-nitrosodi-phenylamine	Butylbenzyl phthalate	Benzo(b)fluor-anthene
2-Chlorophenol	2-Nitrophenol	2,4,5-Trichloro-phenol	1,2-Diphenylhy-drazine	3,3'Dichloro-benzidine	Benzo(k)fluor-anthene
1,3-Dichlorobenzene	2,4-Dimethyl-phenol	2-Chloronaphthalene	4-Bromophenyl phenyl ether	Benzo(a)-anthracene	Benzo(a)pyrene
1,4-Dichlorobenzene	Benzoic acid	2-Nitroaniline	Hexachloro-benzene	bis(2-ethyl-hexyl)phthalate	Indeno(1,2,3-c pyrene
Benzyl alcohol	bis(2-Chloro-ethoxy)methane	Dimethyl phthalate	Pentachloro-phenol	Chrysene	Dibenz(a, h) anthracene
1,2-Dichlorobenzene	2,4-Dichloro-phenol	Acenaphthylene	Phenanthrene	Terphenyl-d_{14} (surr)	Benzo(g,h,i) perylene
2-Methylphenol	1,2,4-Trichloro-benzene	3-Nitroaniline	Anthracene		
bis(2-Chloroiso-propyl)ether	Naphthalene	Acenaphthene	Di-n-butyl phthalate		
4-Methylphenol	4-Chloroaniline	2,4-Dinitrophenol	Fluoranthene		
N-nitroso-Di-n-propylamine	Hexachloro-butadiene	4-Nitrophenol			
Hexachloroethane	4-Chloro-3-methylphenol	Dibenzofuran			
2-Fluorophenol (surr)	2-Methylnaphth-alene	2,4-Dinitrotoluene			
Phenol-d_6 (surr)	Nitrobenzene-d_5 (surr)	2,6-Dinitrotoluene			
		Diethyl phthalate			
		4-Chlorophenyl-phenyl ether			
		Fluorene			
		4-Nitroaniline			
		2-Fluorobiphenyl (surr)			
		2,4,6-Tribromo phenol			

2.4 Continuing Calibration

A calibration standard(s) containing all semivolatile TCL compounds, including all required surrogates, must be analyzed each 12 hours during analysis. Compare the RRF data from the standards each 12 hours with the average RRF from the initial calibration for a specific instrument. A system performance check must be made each 12 hours. If the SPCC criteria are met, a comparison of relative response factors is made for all compounds. This is the same check that is applied during the initial calibration. If the minimum RRFs are not met, the system must be evaluated and corrective action must be taken before sample analysis begins.

2.4.1 Some possible problems are standard mixture degradation, injection port inlet contamination, contamination at the from end of the analytical column, and active sites in the column or chromatography system. This check must be met before analysis begins. The minimum RRF for semivolatile SPCC is 0.050.

2.4.2 Calibration Check Compounds (CCC)

After the system performance check is met, CCCs listed in Table 5 are used to check the validity of the initial calibration. Calculate the percent difference using Equation 2.3.

$$\% \text{ Difference} = \frac{RRF_I - RRF_C}{RRF_I} \qquad \text{Equation 3}$$

Where:

RRF_I = Average response factor from initial calibration

RRF_C = Response factor from current verification check standard.

2.4.2.1 If the percent difference for any compound is greater than 20%, the laboratory should consider this a warning limit. If the percent difference for each CCC is less than or equal to 30%, the initial calibration is assumed to be valid. If the criteria are not met (>30% difference), for any one calibration check compound, corrective action <u>MUST</u> be taken.

Table 5 Calibration Check Compounds

Base/Neutral Fraction	Acid Fraction
Acenaphthene	4-Chloro-3-Methylphenol
1,4-Dichlorobenzene	2,4-Dichlorophenol
Hexachlorobutadiene	2-Nitrophenol
N-Nitroso-di-n-phenylamine	Phenol
Di-n-octylphthalate	Pentachlorophenol
Fluoranthene	2,4,6-Trichlorophenol
Benzo(a)pyrene	

Continuing calibration: 20 ng except for the following: Benzoic acid, 2,4-Dinitrophenol, 2,4,5-trichlorophenol, all three nitroaniline isomers, 4-Nitrophenol, 4,6-Dinitro-2-methylphenol, and pentachlorophenol which are to be injected at 50 ng.

2.5 Documentation

Calculate and report the RRF and percent difference (%D) for all compounds. Ensure that the minimum RRF for semivolatile SPCCs is 0.050. The %D for each CCC compound must be less than or equal to 30.0%.

3. Internal Standard Evaluation

Internal standard responses and retention times in all samples must be evaluated during or immediately after data acquisition. If the retention time for any internal standard changes by more than 30 seconds from the latest daily (12 hour) calibration standard, the chromatographic system must be inspected for malfunctions, and corrections made as required. The EICP of the internal standards must be monitored and evaluated for each sample, blank, matrix spike, and matrix spike duplicate. If the EICP area for any internal standard changes by more than a factor of two (-50% to +100%), the mass spectrometric system must be inspected for malfunction and corrections made as appropriate. When corrections are made, re-analysis of samples analyzed while the system was malfunctioning is necessary.

Method Blank Analysis

4. A method blank is a volume of deionized, distilled laboratory water, carried through the entire analytical scheme (extraction, concentration, and analysis). The method blank volume must be approximately equal to the sample volumes or sample weights being processed.

4.1 A method blank is performed with every 20 samples processed and/or whenever samples are extracted, whichever is most frequent.

Surrogate Spike (SS) Analysis

5. Surrogate standard determinations are performed on all samples and blanks. All samples and blanks are fortified with surrogate spiking compounds before purging or extraction in order to monitor preparation and analysis of samples.

5.1 Each sample, matrix spike, matrix spike duplicate, and blank are spiked with surrogate compounds before extraction. The surrogate spiking compounds shown in Table 6 are used to fortify each sample, matrix spike, matrix spike duplicate, and blank with the proper concentrations. Performance based criteria are generated from laboratory results. Therefore, deviations from the spiking protocol will not be permitted.

Table 6 Surrogate Spiking Compounds

Compounds	Amount in Sample	
	Fraction	Water (ug)
Nitrobenzene-d_5	BNA	25
2-Fluorobiphenyl	BNA	25
p-Terphenyl-d_{14}	BNA	25
Phenol-d_5	BNA	50
2-Fluorophenol	BNA	50
2,4,6-Tribromophenol	BNA	50

5.2 Surrogate spike recovery must be evaluated by determining whether the concentration (measured as percent recovery) falls inside the recovery limits listed in Table 7.

Table 7 Required Surrogate Spike Recovery Limits

Fraction	Surrogate Compound	Water
BNA	Nitrobenzene-d_5	35-114
BNA	2-Fluorobiphenyl	43-116
BNA	p-Terphenyl-d_{14}	33-141
BNA	Phenol-d_5	10-94
BNA	2-Fluorophenol	21-100
BNA	2,4,6-Tribromophenol	10-123

5.3 The analyst must take the actions listed below if either of the following conditions exists:

- o Recovery of any one surrogate compound in <u>either</u> base neutral or acid fraction is below 10%.

- o Recoveries of two surrogate compounds in <u>either</u> base neutral or acid fractions are outside surrogate spike recovery limits.

5.3.1 The analyst shall document (in this instance, document means to write down and discuss the problem and corrective action taken in the Case Narrative) deviations outside of acceptable quality control limits and take the following actions:

5.3.1.1 Check calculations to ensure that there are no errors; check internal standard and surrogate spiking solutions for degradation, contamination, etc., also check instrument performance.

5.3.1.2 If the steps in 5.3.1.1 fail to reveal a problem, then reanalyze the extract. If reanalysis of the extract solves the problem, then the problem was within the analyst's control. Therefore, <u>only</u> <u>submit</u> data from the analysis with surrogate spike recoveries <u>within</u> the control windows. This shall be considered the <u>initial</u> analysis and shall be reported as such on all data deliverables.

5.3.1.3 If the steps in 5.3.1.2 fail to solve the problem, then reextract and reanalyze the sample. If the reextraction and reanalysis solves the problem, then the problem was in the analyst's control. Therefore, <u>only</u> <u>submit</u> data from the extraction and analysis with surrogate spike recoveries <u>within</u> the control windows. This shall be considered the <u>initial</u> analysis and shall be reported as such on all data deliverables.

5.3.1.4 If the reextraction and reanalysis of the sample does not solve the problem, i.e., surrogate recoveries are outside the control windows for both analyses, then submit the surrogate spike recovery data and the sample data from <u>both</u> analyses. Distinguish between the initial analysis and the reanalysis on all data deliverables.

5.4 Documentation

The laboratory shall report surrogate recovery data for the following:

- o Method blank analysis
- o Sample analysis
- o Matrix spike/matrix spike duplicate analysis
- o All sample reanalyses that substantiate a matrix effect

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

6.1 MS/MSD Frequency of Analysis

A matrix spike and matrix spike duplicate must be performed for each group of samples of a similar matrix, once:

- o Each case of field samples received, OR
- o Each 20 field samples in a case, OR

whichever is most frequent.

6.2 Use the compounds listed in Table 8 to prepare matrix spiking solutions. Optional dilution steps must be accounted for when calculating percent recovery of the matrix spike and matrix spike duplicate samples.

Table 8 Matrix Spiking Solutions

Base/Neutrals	Spike Amount (µg)	Acids	Spike Amount (µg)
1,2,4-Trichlorobenzene	25	Pentachlorophenol	50
Acenaphthene	25	Phenol	50
2,4-Dinitrotoluene	25	2-Chlorophenol	50
Pyrene	25	4-Chloro-3-Methyl-phenol	50
1,4-Dichlorobenzene	25	4-Nitrophenol	50

6.2.1 Samples requiring optional dilutions and chosen as the matrix spike/matrix spike duplicate samples, must be analyzed at the same dilution as the original unspiked sample.

6.3 Individual component recoveries of the matrix spike are calculated using Equation 4

$$\text{Matrix Spike Percent Recovery} = \frac{SSR - SR}{SA} \times 100 \qquad \text{Equation 4}$$

Where:

SSR = Spike sample results.
SR = Sample result.
SA = Spike added from spiking mix.

6.4 Relative Percent Difference (RPD)

The analyst is required to calculate the relative percent difference between the matrix spike and matrix spike duplicate. The relative percent differences (RPD) for each component are calculated using Equation 5.

$$RPD = \frac{D_1 - D_2}{(D_1 + D_2)/2} \times 100 \qquad \text{Equation 5}$$

Where:

RPD = Relative percent difference
D_1 = First sample value
D_2 = Second sample value (duplicate)

6.5 The matrix spike (MS) results (concentrations) for nonspiked semivolatile TCL compounds shall be reported and the matrix spike percent recoveries shall be summarized (Table 9).

Table 9 Matrix Spike Recovery Limits

Fraction	Matrix Spike Compound	Water
BN	1,2,4-Trichlorobenzene	39-98
BN	Acenaphthene	46-118
BN	2,4-Dinitrotoluene	24-96
BN	Pyrene	26-127
BN	N-Nitroso-Di-n-Propylamine	41-116
BN	1,4-Dichlorobenzene	36-97
Acid	Pentachlorophenol	9-103
Acid	Phenol	12-89
Acid	2-Chlorophenol	27-123
Acid	4-Chloro-3-Methylphenol	23-97
Acid	4-Nitrophenol	10-80

APPARATUS:

- Separatory funnel - 2,000 mL, with Teflon® stopcock.
- Drying column - 19 mm ID chromatographic column with coarse frit. (Substitution of a small pad of Pyrex glass wool for the frit will prevent cross contamination of sample extracts.)
- Concentrator tube - Kuderna-Danish, 10 mL, graduated (Kontes K-570050-1025 or equivalent). Calibration must be checked at the volumes employed in the test. Ground glass stopper is used to prevent evaporation of extracts.
- Evaporative flask - Kuderna-Danish, 500 mL (Kontes K-570001 0500 or equivalent). Attach to concentrator tube with springs.
- Snyder column - Kuderna-Danish, three-ball macro (Kontes K503000 0121 or equivalent).
- Snyder column - Kuderna-Danish, two-ball micro (Kontes K569001 0219 or equivalent).
- Vials - amber glass, 2 mL capacity with Teflon-lined screw-cap.
- Continuous liquid-liquid extractors - equipped with Teflon or glass connecting joints and stopcocks requiring no lubrication (Hershberg-Wolf Extractor-Ace Glass Company, Vineland, NJ, P/N 6841-10 or equivalent).
- Silicon carbide boiling chips - approximately 10/40 mesh. Heat to 400°C for 30 minutes or Soxhlet extract with methylene chloride.
- Water bath - heated, with concentric ring cover, capable of temperature control (±2°C). The bath should be used in a hood.
- 3.4 Balance - analytical, capable of accurately weighing ±0.0001 g.
- 3.5 Nitrogen evaporation device equipped with a water bath that can be maintained at 35-40°C. The N-Evap by Organomation Associates, Inc., South Berlin, Maryland (or equivalent) is suitable.
- Gas chromatograph/mass spectrometer system.
- Gas chromatograph - an analytical system complete with a temperature programmable gas chromatograph suitable for splitless injection and all required accessories including syringes, analytical columns, and gases.
- Column - 30 m x 0.25 mm ID (or 0.32 mm) bonded-phase silicone coated fused silica capillary column (J&W Scientific DB-5 or equivalent). A film thickness of 1.0 micron is recommended because of its larger capacity. A film thickness of 0.25 micron may be used.

- Mass spectrometer - capable of scanning from 35 to 500 amu every 1 second or less, utilizing 70 volts (nominal) electron energy in the electron impact ionization mode and producing a mass spectrum which meets all required criteria when 50 ng of decafluorotriphenylphosphine (DFTPP) is injected through the GC inlet.

- NOTE: DFTPP criteria must be met before any sample extracts are analyzed. Any samples analyzed when DFTPP criteria have not been met will require reanalysis.

- Data system - a computer system must be interfaced to the mass spectrometer that allows the continuous acquisition and storage on machine readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that allows searching any GC/MS data file for ions of a specific mass and plotting such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundance in any EICP between specified time or scan number limits.

REAGENTS:

- Reagent water - reagent water is defined as a water in which an interferent is not observed at or above the method detection limit of each parameter of interest.

- Sodium hydroxide solution (10N) - dissolve 40 g NaOH in reagent water and dilute to 100 mL.

- Sodium thiosulfate - (ACS) granular.

- Sulfuric acid solution (1+1) - slowly add 50 mL of H_2SO_4 (sp gr.1.84) to 50 mL of reagent water.

- Acetone, methanol, methylene chloride - pesticide quality or equivalent.

- Sodium sulfate - (ACS) powdered, anhydrous. Purify by heating at 400°C for four hours in a shallow tray, cool in a desiccator, and store in a glass bottle. Baker anhydrous powder, Catalog No. 73898 or equivalent.

- Surrogate standard spiking solution.

- Surrogate standards are added to all samples and calibration solutions; the compounds specified for this purpose are phenol-d_6, 2,4,6-tribromophenol, 2-fluorophenol, nitrobenzene-d_5, terphenyl-d_{14}, and 2-fluorobiphenyl.

- Prepare a surrogate standard spiking solution that contains the base/neutral compounds at a concentration of 100 µg/mL, and the acid compounds at 200 µg/mL. Store the spiking solutions at 4°C (±2°C) in Teflon-sealed containers. The solutions should be checked frequently for stability. These solutions must be replaced after twelve months, or sooner if comparison with quality control check samples indicates a problem.

- BNA Matrix standard spiking solution. The matrix spike solution consists of:

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	

- Prepare a spiking solution that contains each of the base/neutral compounds above at 100 µg/1.0 mL in methanol and the acid compounds at 200µg/1.0 mL in methanol.

- Internal standards - 1,4-dichlorobenzene-d_4, naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, perylene-d_{12}. An internal standard solution can be prepared by dissolving 200 mg of each compound in 50 mL of methylene chloride. It may be necessary to use 5 - 10% benzene or toluene in this solution and a few minutes of ultrasonic mixing in order to dissolve all the constituents. The resulting solution will contain each standard a concentration of 4,000 ng/µL. A 10-µL portion of this solution should be added to each 1 mL of sample extract (5 µl to 0.5 mL). This will give a concentration of 40 ng/µL of each constituent.

- Prepare calibration standards at three concentration levels. Each calibration standard should contain each compound of interest and each surrogate standard.

  NOTE: Great care must be taken to maintain the integrity of all standard solutions. Store all standard solutions at -10° to -20°C in screw-cap amber bottles with Teflon-liners. Fresh standards should be prepared every 12 months at a minimum. The continuing calibration standard should be prepared weekly and stored at 4°C (±2°C).

PROCEDURE:

1. Sample Storage and Holding Times

1.1 Procedures for Sample Storage

1.1.1 The samples must be protected from light and refrigerated at 4°C (±2°C) from the time of receipt until extraction and analysis.

1.2 Holding Times

2.1 The extraction of water samples shall be completed within 5 days of sample receipt or within 7 days of sample collection.

2. Sample Extraction - Separatory Funnel

2.1 Samples are extracted using separatory funnel techniques. The separatory funnel extraction scheme described below assumes a sample volume of 1-L.

2.2 Using a 1-L graduated cylinder, measure out a 1-L sample aliquot and place it into a 2-L separatory funnel. Add 250 µl of surrogate standard spiking solution into the separatory funnel and mix well. Add 250 µl of BNA matrix spiking solution to each of two 1-L portions from the sample selected for spiking. Check the pH of the sample with wide range pH paper and adjust to pH> 11 with 10N sodium hydroxide.

2.3 Add 60 mL of methylene chloride to the separatory funnel and extract the sample by shaking the funnel for 2 minutes, with periodic venting to release excess pressure. Allow the organic layer to separate from the water phase for a minimum of 10 minutes. If the emulsion interface between layers is more than one-third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, and may include: stirring, filtration of the emulsion through glass wool centrifugation, or other physical methods. Collect the methylene chloride extract in a 250-mL Erlenmeyer flask.

2.4 Add a second 60-mL volume of methylene chloride to the sample bottle and repeat the extraction procedure a second time, combining the extracts in the Erlenmeyer flask. Perform a third extraction in the same manner. Label the combined extract as the base/neutral fraction.

2.5 Adjust the pH of the aqueous phase to less than 2 using sulfuric acid (1 + 1). Serially extract three times with 60-mL aliquots of methylene chloride, as per Paragraph 5.3. Collect and combine the extracts in a 250 mL Erlenmeyer flask and label the combined extract as the acid fraction.

2.6 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporative flask.

2.7 Transfer the individual base/neutral and acid fractions by pouring extracts through separate drying columns containing about 10 cm of anhydrous granular sodium sulfate, and collect the extracts in the separate K-D concentrators. Rinse the Erlenmeyer flasks and columns with 20 to 30 mL of methylene chloride to complete the quantitative transfer.

2.8 Add one or two clean boiling chips and attach a three-ball Snyder column to the evaporative flask. Pre-wet the Snyder column by adding about 1 mL methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (80° to 90°C) so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 10 to 15 minutes. At the proper rate of distillation, the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1-2 mL of methylene chloride. A 5-mL syringe is recommended for this operation.

2.9 Micro Snyder column technique - add another one or two clean boiling chips to the concentrator tube and attach a two-ball micro Snyder column. Pre-wet the Snyder column by adding about 0.5 mL of methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (80° to 90°C) so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 5 to 10 minutes. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches about 0.5 mL, remove the K-D apparatus from the water bath and allow it to drain for at least 10 minutes while cooling. Remove the Snyder column and rinse its flask and its lower joint into the concentrator tube with 0.2 mL of methylene chloride. Adjust the final volume to 1.0 mL with methylene chloride. If GC/MS analysis will not be performed immediately, stopper the concentrator tube and store refrigerated. If the extracts will be stored longer than 2 days, they should be transferred to individual Teflon-sealed screw-cap bottles and labeled base/neutral or acid fraction, appropriate.

3. Calibration

3.1 Each GC/MS system must have the hardware tuned to meet the criteria listed in Table 1 for a 50-ng injection of decafluorotriphenyl phosphine (DFTPP). No sample analyses can begin until all these criteria are met. This criteria must be demonstrated each 12-hour shift. DFTPP has to be injected to meet this criterion. Post-acquisition manipulation of abundances is not acceptable.

3.2 The internal standards should permit most components of interest in a chromatogram to have retention times of 0.80 to 1.20 relative to the internal standards. Use the base peak ion from the specific internal standard as the primary ion for quantification (Table 2.2). If interferences are noted, use the next most intense ion as the secondary ion, i.e., for 1,4-dichlorobenzene-d_4 use m/z 152 for quantification.

3.2.1 The internal standards are added to all calibration standards and all sample extracts just prior to analysis by GC/MS. A 10-µL aliquot of the internal standard solution should be added to a 1-mL aliquot of calibration standards.

3.3 Analyze 1 µL of each calibration standard and tabulate the area of the primary characteristic ion against concentration for each compound including the surrogate compounds. Calculate relative response factors (RRF) for each compound using Equation 1.

$$RRF = \frac{A_x}{A_{is}} \times \frac{C_{is}}{C_x} \qquad \text{Equation 1}$$

Where:

A_x = Area of the characteristic ion for the compound to be measured.

A_{is} = Area of the characteristic ion for the specific internal standard from Table 3.

C_{is} = Concentration of the internal standard (ng/µL).

C^x = Concentration of the compound to be measured (ng/µL).

3.3.1 The average relative response factor (RRF) should be calculated for all compounds. A system performance check must be made before this calibration curve is used. Four compounds (the system performance check compounds) are checked for a minimum average relative response factor. These compounds (the SPCC) are N-nitroso-di-n-propylamine, hexachlorocyclopentadiene, 2,4-dinitrophenol, 4-nitrophenol.

3.3.2 A % relative standard deviation (%RSD) is calculated for 11 compounds labeled the calibration check compounds (CCC) on Form VI SV and in Table 2.3. a maximum %RSD is also specified for these compounds. These criteria must be met for the calibration curve to be valid.

3.4 A check of the calibration curve must be performed once every 12 hours during analysis. These criteria are described in detail under the Quaity Assurance section of this method. The minimum RRF for the system performance check compounds must be checked. If this criteria is met, the RRFs of all compounds are calculated. A percent difference of the daily (12 hour) RRF compared to the average RRF from the initial curve is calculated. A maximum percent difference of 30% is allowed for each compound flagged as 'CCC'. Only after both these criteria are met can sample analysis begin.

3.5 Internal standard responses and retention times in all standards must be evaluated during or immediately after data acquisition. If the retention time for any internal standard changes by more than 30 seconds from the latest daily (12 hour) calibration standard, the chromatographic system must be inspected for malfunctions, and corrections made as required. The EICP of the internal standards must be monitored and evaluated for each standard. If the EICP area for any internal standard changes by more than a factor of two (-50% to +100%), the mass spectrometric system must be inspected for malfunction and corrections made as appropriate. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is necessary.

4. <u>GCMS Analysis</u>

4.1 The following instrumental parameters are required for all performance tests and for all sample analyses:

Electron energy	- 70 volts (nominal)
Mass range	- 35 to 500 amu
Scan time	- not to exceed 1 second/scan

4.2 Combine the base/neutral extract and the acid extract and concentrate or adjust for a final volume of 0.5 mL.

4.3 Internal standard solution (5 µL) is added to each sample extract. Analyze the extract by GC/MS using a bonded-phase silicone-coated fused silica capillary column. The recommended GC operating conditions to be used are as follows:

Initial column temperature hold	- 40°C for 4 minutes
Column temperature program	- 40-270°C at 10°/minute
Final column temperature hold	- 270°C for 10 minutes
Injector temperature	- 250-300°C
Transfer line temperature	- 250-300°C
Source temperature	- according to manufacturer's specifications
Injector-Grob-type, splitless	
Sample volume	- 1 - 2 µL
Carrier gas	- Helium at 30 cm^3/second

5. Qualitative Analysis

5.1 The compounds listed in the Target Compound List (TCL), shall be identified by an analyst competent in the interpretation of mass spectra by comparison of the sample mass spectrum to the mass spectrum of a standard of the suspected compound. Two criteria must be satisfied to verify the identifications: (1) elution of the sample component at the GC relative retention time as the standard component, and (2) correspondence of the sample component and standard component mass spectra.

5.1.1 For establishing correspondence of the GC relative retention time (RRT), the sample component RRT must compare within ±0.06 RRT units of the RRT of the standard component. For reference, the standard must be run on the same shift as the sample. If coelution of interfering components prohibits accurate assignment of the sample component RRT from the total ion chromatogram, the RRT should be assigned by using extracted ion current profiles for ions unique to the component of interest.

5.1.2 For comparison of standard and sample component mass spectra, mass spectra obtained on the analyst's GC/MS are required. Once obtained, these standard spectra may be used for identification purposes, only if the GC/MS meets the DFTPP daily tuning requirements. These standard spectra may be obtained from the run used to obtain reference RRTs.

5.1.3 The requirements for qualitative verification by comparison of mass spectra are as follows:

5.1.3.1 All ions present in the standard mass spectra at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100%) must be present in the sample spectrum.

5.1.3.2 The relative intensities of ions specified in 5.1.3.1 must agree within plus or minus 20% between the standard and sample spectra. (Example: for an ion with an abundance of 50% in the standard spectra, the corresponding sample ion abundance must be between 30 and 70%.)

5.1.3.3 Ions greater than 10% in the sample spectrum but not present in the standard spectrum must be considered and accounted for by the analyst making the comparison. The verification process should favor false positives. All compounds meeting the identification criteria must be reported with their spectra. For all compounds below the MDL report the actual value followed by "J", e.g., "3J".

5.1.4 If a compound cannot be verified by all of the criteria in 5.1.3, but in the technical judgement of the mass spectral interpretation specialist the identification is correct, then the Contractor shall report that identifications and proceed with quantification.

5.2 A library search shall be executed for non-TCL sample components for the purpose of tentative identification. For this purpose, the 1985 release of the National Bureau of Standards Mass Spectral Library (or a more recent release), containing 42,261 spectra, shall be used.

5.2.1 Up to 20 nonsurrogate organic compounds of greatest apparent concentration not listed for the combined base/neutral/acid fraction shall be tentatively identified via a forward search of the NBS mass spectral library. (Substances with responses less than 10% of the nearest internal standard are not required to be searched in this fashion.) Only after visual comparison of sample spectra with the nearest library searches will the mass spectral interpretation specialist assign a tentative identification. NOTE: Computer generated library search routines must not use normalization routines that would misrepresent the library or unknown spectra when compared to each other.

5.2.2 Guidelines for making tentative identification:

5.2.2.1 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.

5.2.2.2 The relative intensities of the major ions should agree within ±20%. (Example: for an ion with an abundance of 50% in the standard spectra, the corresponding sample ion abundance must be between 30 and 70%.)

5.2.2.3 Molecular ions present in reference spectrum should be present in sample spectrum.

5.2.2.4 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.

5.2.2.5 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 compounds. NOTE: Data system library reduction programs can sometimes create these discrepancies.

5.2.3 If in the technical judgement of the mass spectral interpretation specialist no valid tentative identification can be made, the compound should be reported as unknown. The mass spectral specialist should give additional classification of the unknown compound, if possible (i.e., unknown phthalate, unknown hydrocarbon, unknown acid type, unknown chlorinated compound). If probable molecular weights can be distinguished, include them.

6. Quantitation

6.1 TCL components identified shall be quantified by the internal standard method. The internal standard used shall be the one nearest the retention time to that of a given analyte. The EICP area of characteristic ions of analytes listed in Tables 2 and 3 are used.

Internal standard responses and retention times in all samples must be evaluated during or immediately after data acquisition. If the retention time for any internal standard changes by more than 30 seconds from the latest daily (12 hour) calibration standard, the chromatographic system must be inspected for malfunctions, and corrections made as required. The EICP of the internal standards must be monitored and evaluated for each sample, blank, matrix spike, and matrix spike duplicate. If the EICP area for any internal standard changes by more than a factor of two (-50% to +100%), the mass spectrometric system must be inspected for malfunction and corrections made as appropriate. When corrections are made, re-analysis of samples analyzed while the system was malfunctioning is necessary.

6.2 The RRF from the daily standard analysis is used to calculate the concentration in the sample. Secondary ions may be used if interferences are present. The area of a secondary ion cannot be substituted for the area of a primary ion unless a RRF is calculated using the secondary ion. When TCL compounds are below quantitation limits but the spectra meets the identification criteria, report the concentration with a "J".

6.2.1 Calculate the concentration in the sample using the RRF as determined in Paragraph 4.3 and the following equation:

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

A_x = Area of the characteristic ion for the compound to e measured

A_{is} = Area of the characteristic ion for the internal standard

I_s = Amount of internal standard injected in nanograms (ng)

V_o = Volume of water extracted in milliliters (mL)

V_i = Volume of extract injected (µL)

V_t = Volume of total extract

6.3 An estimated concentration for Non-TCL components tentatively identified shall be quantified by the internal standard method. For quantification, the nearest internal standard <u>free of interferences</u> shall be used.

6.3.1 The formula for calculating concentrations is the same as in Paragraph 6.2.1. Total area counts (or peak heights) from the total ion chromatograms are to be used for both the compound to be measured and the internal standard. A RRF of one (1) is to be assumed. The value from this quantitation shall be qualified as estimated. This estimated concentration should be calculated for all tentatively identified compounds as well as those identified as unknowns.

6.4 Calculate surrogate standard recovery on all samples, blanks, and spikes. Determine if recovery is within limits and report.

6.4.1 If recovery is not within limits (i.e., if two surrogates from either base/neutral or acid fractions are out of limits or if recovery of any one surrogate in either fraction is below 10%), the following is required.

- o Check to be sure there are not errors in calculations, surrogate solutions, and internal standards. Also, check instrument performance.
- o Reanalyze the sample if none of the above reveal a problem.

6.4.2 If none of the steps above solve the problem, then reextract and reanalyze the sample. If the reextraction and reanalysis of the sample solves the problem, then the problem was within the laboratory's control. Therefore, only submit data from the analysis with surrogate spike recoveries within the control windows. This shall be considered the initial analysis and shall be reported as such.

6.4.3 If the reextraction and reanalysis of the sample does not solve the problem, i.e., the surrogate recoveries are outside the control limits for both analyses, then submit the surrogate spike recovery data and the sample analysis data from analysis of both sample extracts. Distinguish between the initial analysis and the reanalysis on all data deliverables.

6.4.4 If the sample with surrogate recoveries outside the limits is the sample used for the matrix spike and matrix spike duplicate and the surrogate recoveries of the matrix spike and matrix spike duplicate show the same pattern (i.e., outside the limits), then the sample, matrix spike, and matrix spike duplicate do not require reanalysis. Document in the narrative the similarity in surrogate recoveries.

DRAFT

ASSAY TITLE: The Analysis of Volatile Organics with Low Detection Limits by Purge and Trap Gas Chromatography/Mass Spectrometry Method

AREA OF APPLICABILITY: Hazleton Laboratories America, Inc.
Mass Spectrometry Section

SCOPE:

This purge and trap gas chromatography-mass spectrometry (GC-MS) method is applicable to the determination of volatile organic compounds in municipal (drinking) water and groundwater. The compounds listed in Table 1 (see attachments) represent the standard list of analytes determined by this method.

This method is restricted to use by, or under the supervision of, analysts who are experienced in the operation of a purge and trap system, by GC-MS, and in the interpretation of mass spectra.

PRINCIPLE:

An inert gas is bubbled through a 25-mL water sample contained in a specially designed purging chamber at ambient temperature. The purgeables are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent trap where the purgeables are trapped. After purging is completed, the trap is heated and back flushed with the inert gas to desorb the purgeables onto a gas chromatographic column. The gas chromatograph is temperature programmed to separate the purgeables, which are then detected with a mass spectrometer.

SENSITIVITY:

The method detection limits presented in Table 6 represent the sensitivities that can be achieved in ground water in the absence of interferences.

PRECISION, ACCURACY:

Precision and accuracy for this method, as generated from an inhouse validation study, is presented in Table 7.

REFERENCES:

1. Environmental Protection Agency (EPA) Method 624 (Federal Register, 49 (209): 43373-43384, October 16, 1984).

2. Environmental Protection Agency (EPA) Method 524.1, Revised 1985, "Methods for Determination of Organic Compounds in Finished Drinking Water and Raw Source Water", September 1986.

3. Environmental Protection Agency (EPA) Contract Laboratory Program, Statement of Work for "Organic Analysis Multi-Media Multi-Concentration", October 1986. Revisions: January 1987, February 1987, July 1987, August 1987. Exhibits: B, D, E.

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Debra Curley Arndt
Manager
Quality Assurance Unit

(1066D)

SAFETY PRECAUTIONS:

The toxicity or carcinogenicity of chemicals used in this method has not been precisely defined.

- Treat each chemical as a potential health hazard, and minimize exposure to these chemicals.

Maintain an awareness of Occupational Safety and Health Administration (OSHA) regulations regarding safe handling of chemicals used in this method.

- Make a reference file of material data handling sheets available to all personnel involved in the chemical analysis.

- Additional references to laboratory safety are available for the information of the analyst.

The following parameters covered by this method have been tentatively classified as known, or suspected, human or mammalian carcinogens: benzene, tetrachloroethene, trichloroethene, carbon tetrachloride, 1,2-dichloroethane, 1,1,2,2-tetrachloroethane, 1,1,2-trichloroethane, chloroform, 1,2-dibromomethane and vinyl chloride.

- Prepare primary standards of these compounds under a hood. Wear a toxic gas respirator, approved by the National Institute of Occupational Safety and Health/Mining Enforcement and Safety Administration (NIOSH/MESA) when handling high concentrations of these toxic compounds.

Observe all laboratory safety precautions as outlined in the Hazleton Laboratories America, Inc., Safety Training Manual.

INTERFERENCES:

Impurities in the purge gas, organic compounds outgassing from the plumbing ahead of the trap, and solvent vapors in the laboratory account for the majority of contamination problems. The analytical system is demonstrated to be free from contamination under the conditions of the analysis by running laboratory reagent blanks. Non-Teflon® plastic tubing, non-Teflon thread sealants, or flow controllers with rubber components in the purge and trap system are not used.

QUALITY ASSURANCE:

The minimum quality assurance/quality control (QA/QC) operations necessary to satisfy the analytical requirements associated with the determination of the volatile compounds listed in this method are as follows:

- Documentation of GC/MS Mass Calibration and Abundance Pattern

- Documentation of GC/MS Response Factor Stability

- Internal Standard Response and Retention Time Monitoring
- Method Blank Analysis
- Surrogate Spike Recovery Monitoring
- Matrix Spike and Matrix Spike Duplicate Analysis

1. GCMS Tuning and Mass Calibration

Establish that the GC-MS system meets the standard spectral abundance criteria before initiating any data collection. Tune the GC-MS system hardware to meet the abundance criteria listed in Table 1 for a maximum of a 50 ng injection of 4-bromofluorobenzene (BFB). Do not analyze the BFB simultaneously with any calibration standards or blanks. Demonstrate this criteria daily.

- Meet the BFB criteria before any standards, samples, or blanks are analyzed.
- Document the GC-MS tuning and mass calibration each time the system is tuned.
- Demonstrate that the GC-MS system can generate easily recognizable spectra using 1.5 µg/L for VOA's.

Table 1

BFB Key Ions and Abundance Criteria

Mass Criteria	Ion Abundance
50	15.0 - 40.0 percent of the base peak
75	30.0 - 60.0 percent of the base peak
95	base peak, 100 percent relative abundance
96	5.0 - 9.0 percent of base peak
173	less than 2.0 percent of mass 174
174	greater than 50.0 percent of the base peak
175	5.0 - 9.0 percent of mass 174
176	greater than 95.0 percent but less than 101.0 percent of mass 174
177	5.0 - 9.0 percent of mass 176

2. Calibration of GC-MS System

2.1 Initial Standard Calibration

Calibrate the GC-MS system at a minimum of three concentrations to determine the linearity of response using TCL compound standards before the analysis of samples and required blanks, and after the tuning criteria have been met.

Prepare calibration standards (using 50 µg/mL HSL mix and 50 µg/mL Purgeables ABC mix) to yield the following specific concentrations: 5, 10, and 20 µg/L. Include surrogates and internal standards at 10 µg/L with each of the calibration standards.

Analyze each calibration standard and tabulate the area of the primary characteristic ion against concentration for each compound including all required surrogate compounds. The relative retention time (RRT) of each compound in each calibration run must agree within 0.06 RRT units.

Use Table 2 and Equation 1 to calculate the relative response factors (RRF) for each compound at each concentration level.

Equation 1

$$RRF = \frac{A_x}{A_{is}} \times \frac{C_{is}}{C_x}$$

Where:

A_x = Area of the characteristic ion for the compound to be measured
A_{is} = Area of the characteristic ion for the specific internal standards from Table 2 (attachments)
C_{is} = Concentration of the internal standard (ng/µL)
C_x = Concentration of the compound to be measured (ng/µL)

Use Equation 2 and the relative response factors (RRF) from the initial calibration to calculate the percent relative standard deviation (% RSD) for the calibration compounds.

Equation 2

$$\%RSD = \frac{SD}{x} \times 100$$

Where:

RSD = Relative standard deviation.

SD = Standard deviation of initial relative response factors

Equation 3

$$\text{Where: } SD = \sum_{i=1}^{N} \frac{(x_i - x)^2}{N-1}$$

x = Mean of initial relative response factors (per compound)

All RF must be above 0.05 except 2-Butanone.

The initial calibration is valid only after the percent RSD for calibration compounds are <40%. Common laboratory solvents (methylene chloride and acetone) are known to bias the results to more than 40% RSD.

Table 2

Volatile Internal Standards with Corresponding TCL Analytes Assigned for Quantitation

Bromochloromethane	1,4-Difluorobenzene	Chlorobenzene-d_5
Chloroethane	2-Butanone	2-Hexanone
Bromomethane	1,1,1-Trichloroethane	4-Methyl-2-Pentanone
Vinyl chloride	Carbon tetrachloride	Tetrachloroethene
Chloroethane	Vinyl acetate	1,1,2,2-Tetrachloroethane
Methylene chloride	Bromodichloromethane	Toluene
Acetone	1,2-Dichloropropane	Chlorobenzene
Carbon disulfide	trans-1,3-Dichloropropene	Ethylbenzene
1,1-Dichloroethene	Trichloroethene	Styrene
1,1-Dichloroethane	Dibromochloromethane	Xylene (total)
1,2-Dichloroethene (total)	1,1,2-Trichloroethane	Bromofluorobenzene (surr)
Chloroform	Benzene	Toluene-d_8 (surr)
1,2-Dichloroethane	cis-1,3-Dichloropropene	
1,2-Dichloroethane-d4 (surr)	Bromoform	

(surr) = Surrogate compound

2.2 Continuing Calibration Check

A calibration standard(s) containing all volatile TCL compounds, including all required surrogates must be analyzed every 12 hours during analysis. (The concentration for each TCL compound is 10 µg/L). Compare the relative response factor data taken from the standards each twelve hours with the average relative response factor from the initial calibration for a specific instrument.

Use Equation 4 to calculate the percentage difference (% difference) for all compounds and check the validity of the initial calibration.

Equation 4

$$\% \text{ Difference} = \frac{RRF_i - RRF_c}{RRF_i} \times 100$$

Where:

RRF_i = Average relative response factor from initial calibration

RRF_c = Relative response factor from current calibration check standard

If the percentage difference is less than, or equal to, 25.0%, assume that the initial calibration is valid. If the criteria are not met, take corrective action. This may involve rerunning the initial three-point curve.

3. Evaluate the internal standard responses and retention times in all samples immediately after, or during, data acquisition. If the retention time for any internal standard changes by more than 30 seconds; inspect the chromatographic system for malfunctions and make corrections. Monitor the area of the extracted ion current profile (EICP) of the internal standards and evaluate the EICP for each sample, blank, matrix spike, and matrix spike duplicate. If the EICP for any of the internal standard changes from the latest calibration check standard by more than a factor of two (-50% to 100%), inspect the mass spectrometer for malfunction, and make corrections.

4. Method Blank Analysis

Analyze the method blank (consists of reagent water) once for each 12-hour period. Ensure that the method blank volume is approximately equal to the sample volume being processed. Demonstrate that the method blank is free of contamination.

5. Surrogate Spike Analysis

Perform surrogate recovery determinations on all samples and blanks. Add the surrogate compound to each sample, matrix spike, matrix-spiked duplicate, and blank. Use the amount of the surrogate standard and the acceptable percentage recovery limits that are listed in Table 3.

Acceptable surrogate recovery limits are in Table 3. In the case of highly concentrated or "dirty" samples, the recovery limits may not be applicable. Make a professional judgment as to whether the sample is to be reanalyzed to demonstrate a matrix problem. Check the GC-MS system by analyzing a method blank.

Table 3

Surrogate Spike Compounds,
Concentrations and Recovery Limits

Compounds	Concentration (ppb)	Percentage of Recovery
Toluene-d_8	10	80 - 120
4-Bromofluorobenzene	10	80 - 120
1,2-dichloroethane-d_4	10	76 - 120

6. Matrix Spike/Matrix Spike Duplicate Analysis

In order to evaluate the matrix effect of the sample on the analytical methodology and provide both precision and accuracy information, a matrix spike and matrix spike duplicate (MS/MSD) analysis is performed with each set of 20 samples. Spiking is performed at a level of 10 µg/L, using a mixture of the following compounds:

- Benzene
- Toluene
- Trichloroethene
- Chlorobenzene
- 1,1-Dichloroethene

Calculate the individual component recoveries of the matrix spikes using Equation 5.

Equation 5

$$\text{Matrix Spike Percent Recovery} = \frac{SSR - SR}{SA} \times 100$$

Where:

SSR = Spike sample results
SR = Sample results
SA = Spike added from spiking mix

Calculate the relative percentage difference (RPD) for each component using Equation 6.

Equation 6

$$RPD = \frac{D_1 - D_2}{(D_1 + D_2)/2} \times 100$$

Where:

RPD = Relative percentage difference
D_1 = First sample value
D_2 = Second sample value (duplicate)

Table 4
Matrix Spike Recovery Limits

Fraction	Matrix Spike Compound	Control Limit*
VOA	Benzene	66-142
VOA	Toluene	76-125
VOA	Trichloroethene	71-120
VOA	Chlorobenzene	75-130
VOA	1,1-Dichloroethene	61-145

* These limits are for advisory purposes only. They are not to be used to determine if a sample should be re-analyzed.

APPARATUS:

Sample Containers

- Vials, 40 mL, screw-cap vials with PTFE-faced silicone septum seals.

Purge and Trap System (Tekmar LSC-2 or equiavlane)

- Purging device, all-glass, capable of accepting 25-mL samples with a water column of at least 5 cm deep, and with a glass frit (3-cm diameter at origin). Wash vials and seals with detergent, rinse with tap water and then distilled water, dry at 105°C, and then allow to cool in an area free of organic vapors.

- Volatile trap, at least 25 cm long, with an inside diameter of at least 0.105 inches. The trap requires two phases: tenax and silica gel. Before daily use, condition the trap for 10 minutes at 220°C and back flood with an inert gas flow of at least 20 mL/minute Vent the trap effluent to the room through a charcoal trap.

- Desorber, capable of rapidly preheating the trap to 180°C, and then desorbing the trap to the GC column, and maintaining a trap temperature of 180°C.

GC-MS System

- Gas chromatograph, Hewlett-Packard 5993 or equivalent, must be capable of temperature programming and achieving an initial column temperature of 30° to 45°C. Use variable constant differential-flow controllers capable of maintaining constant flow rates throughout the desorbtion and temperature program.

- Gas chromatography column, 8 ft x 1/8 O.D. glass column, packed with 1% SP-1000 on Carbopack B (60/80 mesh), or equivalent.

- Mass spectrometer, Finnigan 5100 or equivalent, capable of scanning from 20 to 260 amu every 7 s or less, using 70 V (nominal) of electron energy in the electron impact ionization mode, and producing a mass spectrum that meets all the criteria in Table 3 (attachments) when 50 ng of 4-bromofluorobenzene (BFB) is injected through the GC inlet.

- GC-MS interface, constructed of all-glass or glass-lined materials. Glass is deactivated by silanizing with dichloro- dimethylsilane.

Data System

- Computer system, interfaced to the mass spectrometer, allows continuous acquisition and storage of on machine-readable media of all mass spectra obtained through the duration of the chromatographic program. Use a computer with software that can search for any GC-MS data file for specific m/z (masses) and plot such m/z abundance versus time or scan number. Software must also be able to integrate the abundance, between

Syringe and Syringe Valves

- Syringes, 5- and 25-mL glass hypodermic with luerlock tip (two each)
- Micro syringes, 25 and 100 µL
- Gas syringes, 1.0 and 5.0 mL gas tight, with shut off valve

Miscellaneous

- Standard storage containers, 3.7-mL screw-cap amber vials
- Mini-inert valves, screw cap.

REAGENTS:

- Reagent water, producing less than a 0.4-µg/L response for the compounds being monitored, except those compounds recognized as common laboratory solvents (methylene chloride, acetone, 2-butanone, toluene).

- Methanol, demonstrated to be free of analytes (Spike 100 µL into 25 mL of reagent water and analyze. This produces a response of less than 0.4 µg/L.)

Stock Standards

- Prepare the working standard for the HSL mix separately, or add to the purgeables (A, B, or C) working standards. It is convenient to prepare them separately because the purgeables working standards must be replaced more frequently than the HSL mix.

Preparation of a 50 µg/mL HSL Mix

The solution provided from Supelco has 2 mg/mL of each compound. Place approximately 9 mL of methanol in a 10-mL volumetric flask. Using a 500 µL gas tight syringe, add exactly 250 µL of Supelco HSL Standard Mix to the volumetric flask. Ensure that the drops fall directly into the alcohol without touching the side of the flask. Dilute the flask to volume with methanol, stopper and invert three times. This yields a solution with each compound at 500 µg/mL. Store at 0°C. This standard should be replaced monthly.

Preparation of a 50 µg/mL Purgeables A, B, and C

Mixtures A, B, and C contain a different group of compounds. All are at 200 µg/mL. Place Purgeables C (the gases) in dry ice for 10 minutes. Using a 500-µL gas-tight syringe, add 250 µL each of methanol, Purgeables A, Purgeables B and Purgeables C to a milliliter micro-reaction vessel equipped with a mini-inert valve closure. Store the vial at 0°C. Replace Purgeables A, B, and C standards weekly to maintain proper concentration of the gases.

Preparation of a 50 µg/mL Internal Standard Mix

Supelco Purgeables Internal Standard Mix-624 provides the desired compounds in methanol at 1,000 µg/mL. Place approximately 9 mL methanol in a 10-mL volumetric flask. Using a 500-µL gas-tight syringe, add exactly 500 µL of the internal standard mix to the methanol. Ensure that the drops fall directly into the alcohol without touching the sides of the flask. Dilute volume with methanol, stopper, and invert three times. Store at 0°C.

Preparation of a 25 µg/mL Surrogates Standard Mix

Supelco Purgeables Surrogate Standard Mix provides the desired compounds in methanol at 250 µg/mL. Place approximately 8 mL methanol in a 10-mL volumetric flask. Using a 500- or 1,000-µL gas-tight syringe, add exactly 1.0 mL of surrogate standard mix to the methanol using the technique described previously. Dilute to volume with methanol, stopper, and invert three times. Store at 0°C.

Sample Spiking or Matrix Spike Standard

- Matrix spike solution, containing the five compounds listed in Table 2 (Attachment B). No mix is commercially available that has only these compounds. Prepare the stock standard from neat.

Preparation of a Matrix Spike Stock Standard (2 mg/mL)

Place approximately 24 mL methanol in a 25-mL volumetric flask. Allow flask, allow to stand unstoppered for 10 minutes, or until all alcohol-wetted surfaces have dried and tare. Using a 100-µL syringe, add 50 mg of the first compound; ensure that all of the drops fall directly into the alcohol without touching the flask neck. Re-tare the flask, and add 50 mg of the next compound. Repeat the process until all of the compounds have been added. Dilute to volume with methanol, stopper, and invert three times. Transfer contents to appropriate storage containers with no headspace and store at 0°C.

Preparation of a Matrix Spike Working Standard (50 µg/mL)

Place approximately 9 mL of methanol in a 10-mL volumetric flask. Using a 500-µL gas-tight syringe, add 250 µL of the 2.0 mg/mL stock solution to the flask using the technique described previously. Dilute to volume with methanol, stopper, and invert three times. Store at 0°C.

SAMPLE COLLECTION, PRESERVATION, AND STORAGE:

<u>Sample Collection</u>

- Include trip blanks with each sample set (composed of the samples collected from the same general sampling site at approximately the same time). Fill at least of two sample bottles with reagent water and seal at the laboratory, and then ship these to the sampling site along with the empty sample bottles. Whenever a set of samples is shipped and stored, it is accompanied by trip blanks.

- Collect one field blank sample, which is composed of deionized laboratory water per group of 20 or fewer samples. Prepare this blank in the field as follows: Allow deionized laboratory water to contact the sampling equipment and then pour it into the sampling vial. Ensure that no air bubbles are trapped in the field blank sample when the vial is sealed.

- Collect all samples in duplicate (triplicate when high levels requiring screening and dilution are suspected). Fill sample bottles to overflowing. Ensure that no air bubbles pass through the sample as the bottle is filled, or become trapped in the sample when the bottle is sealed.

- When sampling from a water tap, open the tap and allow the system to flush until the water temperature has stabilized (usually about 10 minutes). Adjust the flow to above 500 mL/minute and collect duplicate samples from the stream.

- When sampling from an open body of water, fill a 1-qt wide-mouth bottle or 1-L breaker with sample from a representative area, and carefully fill duplicate sample bottles from the 1-qt container.

Sample Preservation

- Chill the samples to 4°C on the day of collection and maintain them at that temperature until analysis. Package the field samples that are not received at the laboratory on the day of collection for shipment with sufficient ice to ensure that they are at 4°C on arrival at the laboratory.

- Analyze all samples within 10 days of sample receipt or within 14 days of sample collection.

SAMPLE ANALYSIS:

1. Quality Control Requirements

Analyze the samples after the initial quality assurance activities are successfully completed. Twelve hours after the completion of the initial tuning, conduct an instrument tuning and calibration-check analysis. Any major system maintenance, such as a source cleaning or installation of a new column, requires re-tuning and recalibration, irrespective of the 12-hour requirement (see Initial Calibration). Only the calibration verification is done for minor maintenance (Continuing Calibration).

1.1 For highly concentrated or "dirty" samples, the EICP area for any internal standard may change by more than a factor of two. Make a professional judgment as to whether the sample is to be reanalyzed to demonstrate a matrix problem. Check the GC-MS system by analyzing a method blank.

1.2 Check each analytical run for saturation. The level at which an individual compound will saturate the detection system is a function of the overall system sensitivity and the mass spectral characteristics of that compound.

1.3 If any compound in any sample exceeds the initial calibration range, dilute that sample. Re-adjust the internal standard concentration and reanalyze the sample.

PROCEDURE:

1. Upon receipt, samples should be stored at 4°C.

2. Sample Analysis

All standards, blanks, and samples should be analyzed in the following fashion:

2.1 Purging

2.1.1 Set up the purge and trap system. Adjust the purge gas (helium) flow rate to 40 mL/minute.

2.1.2 Allow the sample to come to ambient temperature before injecting it into the syringe.

2.1.3 Remove the plunger from a 25-mL syringe and attach a closed syringe valve to it.

2.1.4 Open the sample bottle (or standard) and carefully pour the sample into the syringe barrel to just short of overflowing.

2.1.5 Replace the syringe plunge and compress the sample.

2.1.6 Hold the syringe in an upright position with the syringe valve set on top of the syringe. Open the syringe valve, vent any residual air and adjust the sample volume to 25 mL.

2.1.7 Because this process of taking an aliquot destroys the validity of the sample for future analysis, fill a second syringe at this time to protect against possible loss of data.

2.1.8 Add 10 µl of the surrogate spiking solution (25 ng/µl) and 5 µl of the internal standard spiking solution (50 ng/µl) through the valve bore and then close the valve.

2.1.9 Attach the syringe-syringe valve assembly to the syringe valve on the purging device.

2.1.10 Open the syringe valves and inject the sample into the purging chamber. Close both valves.

2.1.11 Purge the sample for 11.0 ±0.1 minutes at ambient temperature.

2.1.12 After the 11-minute purge, attach the trap to the chromatograph and adjust the purge and trap system to the desorb mode.

2.2. Gas Chromatography-Mass Spectrometry Analysis

2.2.1 Set up the GC-MS operating parameters.

Carrier gas flow rate: 40 mL/minute
Injector temperature: 220°C
Oven temperature: Hold at 45°C for 3 minutes and then heat to 220°C at 8°C/minute. Hold at 200°C until the programmed run time expires.
Transfer line temperature: 225°C
Ion source temperature: 200°C
Scan range: 35-250 amu
Electron energy: 70 V
Scan Time: To give at least 5 scans per peak but not to exceed 7 seconds per peak.

2.2.2 Introduce the trapped materials to the GC column by rapidly heating the trap to 180°C while back flooding the trap with an inert gas between 20 and 60 mL/minute for 4 minutes. If rapid heating of the trap cannot be achieved, use the GC column as a second trap by cooling it to 30°C, or subambient temperature (cryogenic trapping) if the problem persists, instead of the initial program temperature of 45°C.

2.2.3 As the trap is being desorbed into the gas chromatograph, empty the purging chamber using the sample introduction syringe. Wash the chamber with two 25-mL flushes of reagent water.

2.2.4 After desorbing the sample from the trap for 4 minutes, recondition the trap by returning the purge and trap system to the purge mode. Wait 15 seconds, and then close the syringe valve on the purging device to begin gas flow through the trap. Maintain the trap temperature at 180°C. After 7 minutes, turn off the trap heater and open the syringe valve to stop the gas flow through the trap. When the trap is cool, the next sample can be analyzed.

2.2.5 If the response for any m/z exceeds the working range of the system, prepare dilution of the sample with reagent water from the aliquot in the second syringe and reanalyze.

3. Daily Analysis Scheme

3.1 Achieve acceptable abundance criteria (see Table 4) for BFB at the beginning of each day that analyses are performed. This test must be passed prior to analysis of any standards, blanks, or samples.

3.2 Upon achieving the key abundance criteria for BFB, calibrate the instrument as described in the Quality Assurance section, paragraph 2.

3.3 After the instrumental calibration requirements are met, analyze a method blank (25 mL aliquot of reagent water plus 250 ng each internal standards mix and surrogate standards mix) to demonstrate that the instrument is free of contamination.

3.4 Proceed with sample analysis.

4. Qualitative Identification

4.1 Obtain EICPs for the primary m/z (Table 5, attachments) and at least two secondary masses for each parameter of interest. The following criteria must be met:

4.2 Ensure that the characteristic masses of each parameter of interest is maximized in the same, or within one, scan of each other.

4.3 Ensure that the relative retention time fall within ±.06 units of the relative retention time of the standard component.

4.4 Ensure that the relative peak heights of the three characteristic masses in the EICPs fall within ±20% of the relative intensity of these masses in a reference mass spectrum.

4.5 A library search shall be executed for non-TCL sample components for the purpose of tentative identification. For this purpose, the 1985 release of the National Bureau of Standards Mass Spectral Library (or a more recent release), containing 42,261 spectra, shall be used.

4.6 Up to 10 nonsurrogate organic compounds of greatest apparent concentration not listed as target volatile compounds shall be tentatively identified via a forward search of the NBS mass spectral library. (Substances with responses less than 10% of the nearest internal standard are not searched in this fashion.) Only after visual comparison of sample spectra with the nearest library searches will the mass spectral interpretation specialist assign a tentative identification. NOTE: Computer-generated library search routines must not use normalization routines that would misrepresent the library or unknown spectra when compared to each other.

4.7 Guidelines for making tentative identification:

4.7.1 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.

4.7.2 The relative intensities of the major ions should agree within ±20%. (Example: For an ion with an abundance of 50% in the standard spectra, the corresponding sample ion abundance must be between 30 and 70%.)

4.7.3 Molecular ions present in reference spectrum should be present in sample spectrum.

4.7.4 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.

4.7.5 Ions present in the reference spectum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or co-eluting compounds. NOTE: Data system library reduction programs can sometimes create these discrepancies.

4.8 If in the technical judgment of the mass spectral interpretation specialist no valid tentative identification can be made, the compound should be reported as unknown. The mass spectral specialist should give additional classification of the unknown compound, if possible (i.e., unknown phthalate, unknown hydrocarbon, unknown acid type, unknown chlorinated compound). If probable molecular weights can be distinguished, include them.

5. Quantitation

5.1 When a parameter has been identified, the quantitation of that parameter is based on the integrated abundance from the EICPs of the primary characteristic m/z given in Table 5.

5.2 Equation 7 is used to calculate the concentration in the sample using the response factor (RF) determined in Calibration of GC-MS System section.

Equation 7

$$\text{Concentration } (\mu g/L) = \frac{A_s \times C_{is}}{A_{is} \times RF}$$

Where:

A_s = Area of the characteristic m/z for the parameter or surrogate standard to be measured

A_{is} = Area of the characteristic m/z for the internal standard

C_{is} = Concentrations of the internal standard

Report result is given in µg/L without correction for recovery data.

5.3 An estimated concentration for Non-TCL components tentatively identified shall be quantified by the internal standard method. For quantification, the nearest internal standard free of interferences shall be used. The formula for calculating concentrations is the same as in Equation 7. Total area counts (or peak heights) from the total ion chromatograms are to be used for both the compound to be measured and the internal standard. A RRF of one (1) is to be assumed. The value from this quantitation shall be qualified as estimated. This estimated concentration should be calculated for all tentatively identified compounds as well as those identified as unknowns.

CALCULATIONS:

Description of calculations has been included in the previous section.

Table 5

Characteristic Ions for Volatile Compounds

Parameter	Primary Ion	Secondary Ion(s)
Chloromethane	50	52
Bromomethane	94	96
Vinyl chloride	62	64
Chloroethane	64	66
Methylene chloride	84	49, 51, 86
Acetone	43	58
Carbon disulfide	76	78
1,1-Dichloroethene	96	61, 98
1,1-Dichloroethane	63	65, 83, 85, 98, 100
1,2-Dichloroethene (total)	96	61, 98
Chloroform	83	85
1,2-Dichloroethane	62	64, 100, 98
2-Butanone	72	57
1,1,1-Trichloroethane	97	99, 117, 119
Carbon tetrachloride	117	119, 121
Vinyl acetate	43	86
Bromodichloromethane	83	85
1,1,2,2-Tetrachloroethane	83	85, 131, 133, 166
1,2-Dichloropropane	63	65, 114
trans-1,3-Dichloropropene	75	77
Trichloroethene	130	95, 97, 132
Dibromochloromethane	129	208, 206
1,1,2-Trichloroethane	97	83, 85, 99, 132, 134
Benzene	78	--
cis-1,3-Dichloropropene	75	77
Bromoform	173	171, 175, 250, 252, 254, 256
2-Hexanone	43	58, 57, 100
4-Methyl-2-pentanone	43	58, 100
Tetrachloroethene	164	129, 131, 166
Toluene	92	91
Chlorobenzene	112	114
Ethyl benzene	106	91
Styrene	104	78, 103
Total xylenes	106	91

a The primary ion should be used unless interferences are present, in which case, a secondary ion may be used.

Table 6

Analytes and Detection Limits
by GC-MS Method

Parameter	CAS Number	Detection Limits Water (µg/L)
Chloromethane	74-87-3	.712
Bromomethane	74-83-9	.223
Vinyl Chloride	75-01-4	.423
Chloroethane	75-00-3	.924
Methylene Chloride	75-09-2	.747
Acetone	67-64-1	.697
Carbon Disulfide	75-15-0	.255
1,1-Dichloroethene	75-35-4	.289
1,1-Dichloroethane	75-35-3	.238
t,2-Dichloroethene (total)	156-60-5	.217
Chloroform	67-66-3	.269
1,2-Dichloroethane	107-06-2	.660
2-Butanone[a]	78-93-3	5.0
1,1,1-Trichloroethane	71-55-6	.876
Carbon Tetrachloride	56-23-5	.303
Vinyl Acetate	108-05-4	1.100
Bromodichloromethane	75-27-4	.279
1,1,2,2-Tetrachloroethane	79-34-5	.392
1,2-Dichloropropane	78-87-5	.309
trans-1,3-Dichloropropene	10061-02-6	.240
Trichloroethene	79-01-6	.206
Dibromochloromethane	124-48-1	.268
1,1,2-Trichloroethane	79-00-5	.262
Benzene	71-43-2	.248
cis-1,3-Dichloropropene	10061-01-5	.385
2-Chloroethyl vinyl ether	110-75-8	.355
Bromoform	75-25-2	.684
2-Hexanone	591-78-6	.479
4-Methyl-2-Pentanone	108-10-1	.541
Tetrachloroethene	127-18-4	.336
Toluene	108-88-3	.244
Chlorobenzene	108-90-7	.182
Ethyl benzene	100-41-4	.876
Styrene	100-42-5	.266
Total xylenes		.741

a Based on laboratory experience.

Table 7

Precision and Accuracy Data Low Level GCMS Volatiles
(25 mL Sample Purge)

Compound	Spike Level (µg/L)	Average Recovery (µg/L)	(%)	Standard Deviation (µg/L)
Chloromethane	1.0	0.806	80.6	0.237
Bromomethane	1.0	0.904	90.4	0.0743
Vinyl Chloride	1.0	0.788	78.8	0.141
Chloroethane	1.0	1.14	114	0.308
Methylene Chloride	1.0	1.32	132	0.249
Acetone	1.0	1.48	148	0.232
Carbon Disulfide	1.0	1.05	105	0.0851
1,1-Dichloroethene	1.0	0.881	88.1	0.0963
1,1-Dichloroethane	1.0	0.917	91.7	0.0793
Total 1,2-Dichloroethene	1.0	0.930	93	0.0722
Chloroform	1.0	1.05	105	0.0897
1,2-Dichloroethane	1.0	0.89	89.4	0.220
2-Butanone	ND	ND	ND	ND
1,1,1-Trichloroethane	1.0	0.917	91.7	0.292
Carbon Tetrachloride	1.0	0.836	83.6	0.101
Vinyl Acetate	1.0	1.31	131	0.367
Bromodichloromethane	1.0	0.948	94.8	0.0958
1,2-Dichloropropane	1.0	0.952	95.2	0.103
Trans-1,3-Dichloropropene	0.78	0.746	95.7	0.0799
Trichloroethene	1.0	0.924	92.4	0.0686
Dibromochloromethane	1.0	0.997	99.7	0.0892
1,1,2-Trichloroethane	1.0	1.00	100	0.0875
Benzene	1.0	0.954	95.4	0.0828
Cis-1,3-Dichloropropene	1.22	1.09	89.3	0.128
2-Chloroethyl vinyl ether	1.0	0.925	92.5	0.108
Bromoform	1.0	0.958	95.8	0.228
4-Methyl-2-Pentanone	1.0	1.15	115	0.180
2-Hexanone	1.0	0.916	91.6	0.160
Tetrachloroethene	1.0	0.911	91.1	0.112
1,1,2,2-Tetrachloroethane	1.0	0.968	96.8	0.130
Toluene	1.0	0.952	95.2	0.0814
Chlorobenzene	1.0	0.986	98.6	0.0606
Ethyl benzene	1.0	0.854	85.4	0.292
Styrene	1.0	1.05	105	0.0888
Total xylenes	1.0	0.967	96.7	0.247

ND = Not Determined

APPENDIX D

WARZYN ENGINEERING INC
STANDARD OPERATING PROCEDURES
USING NON-CLP PROTOCOL

ATOMIC ABSORPTION SPECTROMETRY
FURNACE - DIRECT INJECTION

Scope and Application: Metals in solution can be readily analyzed by Atomic Absorption Spectrometry using either flame, furnace or hydride techniques. The furnace - direct injection technique allows for lower detection limits. The use of the graphite platform in furnace analysis can improve sensitivity and reduce some matrix interferences.

Method: Furnace; direct injection

Reference: EPA 1983, Section 200

"Analytical Methods for Furnace Atomic Absorption Spectroscopy", 1980, Perkin-Elmer Corporation

"Model 2380 Atomic Absorption Spectrophotometer", 1981, Perkin-Elmer Corporation

"Techniques in Graphite Atomic Absorption Spectroscopy", 1985, Perkin-Elmer Corporation

Sample Handling: Acidify with concentrated nitric acid to pH<2. Drinking waters and filtered groundwater samples free of particulate matters and organics may be analyzed directly, while wastewaters, leachates, solids, etc., must be digested prior to analysis (refer to appropriate digestion procedures). Samples must be analyzed within 6 months.

Reagents and Apparatus:

1. 2380 Perkin-Elmer spectrophotometer
2. Required metal lamp and power source
3. HGA 400 Perkin-Elmer furnace and programmer
4. AS40 Perkin-Elmer Autosampler
5. 024 Perkin-Elmer recorder
6. Stock and standard solutions for required metal
7. Class A volumetric glassware
8. Instra-analyzed nitric acid
9. Milli-Q water
10. Argon gas-prepurified
11. Graphite tubes (pyrolytically coated)
12. Graphite tubes and platforms (pyrolytically-coated)
13. Eppendorf 100-1000 microliter pipeter
14. Disposable 10 mL beakers

Procedure:

A. Installation of Furnace

1. Remove the sample compartment door and tray.

2. Disconnect the tiedown cable, drainhoses.

3. Remove the burner head unit by loosening the 2 side knurled knobs and the unit should pull out. Store below the A.A. Lower the platform to lowest possible stage.

4. Loosen the locking screw on the furnace stand.

5. Lift the furnace up, and position the furnace on the pegs in the sample compartment, and screw into place.

6. Turn on water.

7. Attach the drain hose to auto sampler.

8. Attach the D.I. water supply to auto sampler.

Note - See the furnace maintenance procedures. The maintenance must be done with each day of use of the furnace.

B. Furnace Alignment

1. Plug in the lamp.

2. Dial in the desired wavelength. Adjust the wavelength with the fine adjust knob to the highest energy reading on the GAIN control. Adjust the lamp using the knobs in the lamp compartment in the above manner.

3. Turn ON the programmer and auto sample unit.

4. Turn on the gas supply (Argon) with the pressure at 350kPa.

5. Remove the furnace windows.

6. Pull the furnace unit out of the light path. (Make sure all wires are out of light path.)

7. A.Z. the instrument.

8. Put the furnace unit back into position.

9. Adjust the furnace with the two gray knobs on the unit. Adjust the furnace to the nearest 0.000 Absorbance you can obtain.

10. Replace the windows. The absorbance should be about 0.100.

11. Switch the gas to open.

12. Pull the right hand furnace half to the side.

13. Insert the graphite tube.

14. Insert the tube alignment tool into the sampling opening; carefully turning the tube so the tip of the tool goes into the sample hole in the tube.

15. Close the furnace.

16. Switch the gas to ON.

17. Remove the alignment tool.

C. Conditioning a Graphite Tube

Conditioning of the graphite tube should be done when you begin the day, change to a new tube, or change to another element. The conditioning of a tube removes impurities on the tube's surface.

1. Push and hold for 5 seconds the MANUAL TEMP key at 100°C. Do this 4 times. Do the same at 2700°C repeatedly until smoking has stopped, and no absorbance signal is obtained when the tube is taken through the element's program.

D. Aligning the Auto-Sampler Arm

1. Connect the drain bottle and the distilled water reservoir to the auto sampler.

2. Turn ON the auto sampler. The sampler will go through a five step rinse cycle.

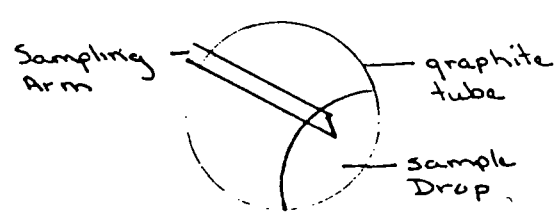
3. Manually move the arm towards the furnace.

4. Adjust the arm so that the tip goes smoothly into the graphite tube.

   a. Unlock the arm by turning the red knob clockwise.

   b. Adjust the arm vertically and horizontally using the gray knobs at the front end left of the sampler.

   c. The height is adjusted using the silver knurled knob. The tip of the arm will be close to the tube wall but not touching. This can be checked using the dental mirror. See figure below:



Notes:

1. See the separate procedures involved with programming elements for the furnace, and programming the auto sampler.

2. Use 1:1 nitric for all glassware cleaning and standard preparation.

E. Programming the Auto Sampler

1. Push STAND-BY to get into operating mode.

2. Enter Method 1.

3. Enter the number of standards used (if in concentration mode only!).

4. Enter the number of the last cup in the run.

5. Enter two replicates.

6. Enter sample volume-usually 20 unless otherwise stated by procedures.

7. Push RESET-this brings the tray back to the starting position.

8. Push START to begin the run.

9. Turn on the Perkin-Elmer 024 recorder.

10. Insert blanks, standards and samples in the autosampler tray. Start the auto sampler and analyze the blanks, standards and samples. Analyze an EPA reference standard to verify the curve. This standard must be within the 95% confidence limits before continuing with the analysis of the samples.

11. Analyze samples by methods described in the furnace section of this manual. Refer to specific metal operating procedures for notes on interferences, use of matrix modifiers, quality control and any other adjustments to this instrument operation procedure.

Terminology

ALT. VOLUME may be used to specify a volume of an alternate solution to be added to the sample (ex. Matrix Modifier).

MANUAL may be used as follows:

a. to move tray to a specific number. Push the number of the space then the manual button.

b. to inject one sample repeatedly. When the sampler is aligned with the number you want to repeat, push the manual button once to start the repeats.

c. to stop repeats -- push manual button again.

CHECK when pushed, the indicator light flashes. Push the operator button and the numbers entered will be displayed.

F. Auto-Concentration - Furnace

The machine is calibrated against one to three standards. The standard curve is drawn as a straight line between the zero and S_1. Again, a straight line is drawn between S_1 to S_2, and S_2 to S_3. (Refer to Figure 1 in the MetalFl SOP, page 7.)

If you should encounter an error code during calibration, the operator's manual has a listing of error codes and their meanings.

Signal - Conc.	t = see specific SOP's
Mode - pk Ht or pk area (see specific SOP's)	Ave - 2

Type the S_1 (first standard) value and push S_1 button
Type the S_2 (second standard) value and push the S_2 button

Procedure

1. Analyze the blank and auto-zero (AZ) Type in S_1 value, push the S_1 button. Repeat with desired standards.

2. Analyze S_1 standard, the A.A. will standardize S_1, after the 2 readings. Repeat until desired number of standards are standardized (usually have 2 standards for calibration).

3. Analyze samples, check standards periodically during the run, re-standardize if necessary.

Notes

You can AZ any time during a run.
If you re-standardize this S_1 value, you have to re-standardize the S_2 and S_3.

G. Method of Standard Addition - Furnace

The method of standard additions is a useful tool which enables us to achieve an accurate determination of an element in the presence of an interference. Standard additions are required for EP Toxicity metals.

For an accurate value of an element, the working curve must be linear throughout the range of concentration encountered by the samples plus the additions.

SIGNAL - ABS t = (see specific SOP's)
Ave - 2

MODE - pk Ht or pk area (see specific SOP's)

Procedure

1. Take four aliquots of the sample at a set volume.

2. Add the same volume of blank to the first beaker.

3. Add the same volume of successive standards to the remaining beakers.

4. Mix by swirling.

Example - Beaker 1	Beaker 2	Beaker 3	Beaker 4
1/2 ml sample	1/2 ml sample	1/2 ml sample	1/2 ml sample
1/2 ml blank	1/2 ml 1 PPM Std.	1/2 ml 2 PPM Std.	1/2 ml 4 PPM Std.

5. Aspirate the reagent blank and Auto-zero (A.Z.)

6. Aspirate the sample beakers from the blank to the highest spiked beaker.

7. Record all four absorbance readings for the sample.

Calculations

Plot the absorbance readings against the concentrations of the standards added. The intercept of the concentration axis equals the concentration of the element in the sample. (See figure 2 on MetalFL1-7). Linear Regression may be used.

H. Furnace Shut Down

At the end of furnace work, follow the shut down procedure:

1. Turn the B.G. corrector to the Atomic Absorption position.

2. Turn SIGNAL to the lamp position. TURN lamp current to zero, EDL Lamps - turn power pack off. Be careful to store hot EDL's in a horizontal position.

3. Turn off water system.

4. Turn off Argon gas.

5. Turn off hood.

6. Turn off programmer and auto sampler unit.

7. Disconnect drain hose, and unscrew D.I. water supply from the auto sampler.

8. Remove the furnace by loosening the 4 screws. Pull furnace straight out of the compartment. Position furnace on the stand. Tighten the locking screws into position.

9. Insert burner head unit.

10. Connect tiedown cable and drain hoses.

11. Replace compartment door and tray. The AA is now ready for flame analysis.

I. Furnace Maintenance

The following maintenance is to be done each day the furnace is operated.

1. Clean the furnace windows.

   a. Pop out furnace windows from furnace unit.

   b. Unscrew window casting - gently dislodge windows from casting.

   c. Put windows in alcohol.

   d. Clean with Kim-wipe.

   e. Rinse with D.I. water - dry

   f. Place windows in casting. Screw in finger tight.

2. Check machine windows and clean if needed (same as procedure in A.A. maintenance).

3. Check cones - change the cones if they appear pitted (see P.E. Furnace Manual).

4. Empty drain bottle.

5. Rinse D.I. water bottle and fill with new D.I. water.

6. Clean cones with alcohol on a Q-tip. Rinse with D.I. water. Be Careful! Cones are very fragile.

Quality Control:

1. Refer to specific metal standard operating procedures.

Notes:

1. Samples must be diluted to obtain concentrations within the optimum range.

2. Standards must be prepared in the same acid concentrations as the samples being analyzed.

3. Refer to the Perkin-Elmer Procedures Manual for further instructions and troubleshooting.

	Revision Date
Michael J. Linskens Laboratory Manager	11-14-86
Kim D. Finner Analytical Laboratory QA/QC Officer	4-13-87
QA Officer	

[ALM-3-4]

ATOMIC ABSORPTION SPECTROMETRY
FLAME - DIRECT ASPIRATION

Scope and Application: Metals in solution can be readily analyzed by Atomic Absorption Spectrometry using either flame or furnace techniques. The flame-direct aspiration can be used for most metals but is generally not as sensitive as the furnace method. Both the air-acetylene and nitrous oxide-acetylene flame techniques are described in this operating procedure as well as the use of emission spectroscopy.

Method: Flame; direct aspiration

Reference: EPA 1983, Section 200

"Analytical Methods for Atomic Absorption Spectrophotometry", 1982, Perkin-Elmer Corporation

"Model 2380 Atomic Absorption Spectrophotometry", 1981, Perkin-Elmer Corporation

Sample Handling: Acidify with concentrated nitric acid to pH<2. Drinking waters and filtered groundwater free of particulate matter and organics may be analyzed directly, while wastewaters, leachates, solids, etc. must be digested prior to analysis (refer to appropriate digestion procedures). Samples must be analyzed within 6 months from sampling date.

Reagents and Apparatus:

1. 2380 Perkin-Elmer Spectrophotometer
2. Stock and standard metal solutions
3. Class A volumetric glassware
4. Instra-analyzed nitric acid
5. Milli-Q water
6. Required lamp and power source
7. Disposable 10 mL beakers
8. Eppendorf 100-1000 uL pipeter
9. Acetylene gas
10. Air supply
11. Nitrous oxide gas
12. Air-acetylene burner head with impact bead or nitrous oxide-acetylene burner head with flow spoiler

Procedure:

A. Instrument Set-up Procedure for Flame Atomic Absorption

1. Turn power button to the ON position.

2. Plug in lamp.

   a. Hollow Cathode Lamp: Have the signal control in the lamp position. Turn the lamp knob until the desired mAmps is shown on the lamp/energy display. Warm lamp for 15 minutes.

   b. Electrodless Electrode Discharge Lamp (EDL) Turn on the EDL power supply unit. Adjust the power to the watts needed. Warm up one half hour. Make sure the watts are at or slightly higher than the recommended watts. Otherwise, this will shorten the life of the lamp and elements can appear noisy.

3. Turn Signal to Set-up.

   a. Turn the slit knob to the designated slit (see SOPs). Normal Slit settings are for flame and hydride work Alternate Slit setting are for furnace work.

   b. Adjust the Coarse Adjust knob to the desired wavelength.

   c. Using the Fine Adjust knob - turn to the highest energy level reading on the lamp/energy display. The Gain control may be used to decrease or increase the energy as needed.

   d. Adjust the lamp position; using the two knobs on the lamp holder. Again, adjust to the highest energy reading on the lamp/energy display. Alignment is critical for high quality results and ease of use.

4. Turn signal to Abs. (Absorbance).
   Turn Mode to Cont. (Continuous read).
   Insert .5 sec t.
   Push AZ (Auto-zero).

B. Burner Head Set-up and Alignment

Insert appropriate burner head (5cm burner head for the nitrous-oxide/acetylene flame, 10cm burner head for the air/acetylene flame) so the small peg on the burner chamber fits into the slot in the base of the burner head. Tighten the outer ring.

1. Snap the safety chains in place.

2. Insert the plug into the hole at the right rear of the burner platform.

3. Using the right-hand silver knob - raise the burner head until a reading above 0.000 appears on the read-out display.

4. Turn the knob back to a reading of 0.000. Lower the burner head 1/4 turn below this 0.000 reading. (This adjusts the burner head to a position below the light path.)

Turn ON the Background Corrector if running an element with a wavelength below 350 mm.

1. AAEN - shows the lamp energy.

2. BGEN - shows the background corrector's energy.

*These two readings should be approximately the same. (Usually close to 75/74).

If the BG CORR - (to the right of the read-out display) begins to flash, pull the lever (inside the lamp compartment) forward. This moves a filter into place.

C. Air-Acetylene Flame Ignition and Analysis

1. Set fuel flow to specifications (approximately 10-20 psi)

2. Set oxidant flow to specifications (approximately 40-50 psi)

3. Ignite the flame.

4. Let the flame stabilize a few minutes.

D. Alignment of Burner Head

Adjust the burner head to the best position as follows:

1. Auto-zero the machine while aspirating a blank.

   Enter in 0.5 sec t on the keyboard
   Put signal in Abs.
   MODE in CONT.

2. Aspirate a standard with an absorbance of about 0.200 and adjust the burner head towards the back of the instrument. Adjust to the highest Abs. reading on the display.

E. Nebulizer Adjustment

With the first element of the day, clean neubulizer with brass cleaning wire and adjust the neubulizer as follows:

1. Aspirate the standard and open the neubulizer with the silver ring until air bubbles begin to appear in the standard.

2. Adjust the silver ring to the highest Abs. reading that can be obtained.

3. Tighten locking nut.

Now the instrument is ready for the day. The following two methods can be used to determine the metals content.

1. Auto-concentration.

2. Standard-additions.

See the section on each procedure for further instructions.

F. Nitrous Oxide-Acetylene Flame Ignition and Analysis

1. Follow A, B and C (steps 1-3) of this instrument operating procedure through the ignition of the air-acetylene flame using the 5 cm burner head and flow spoiler for nitrous oxide-acetylene analysis.

2. Set the nitrous oxide tank output regulator to between 40 to 85 psig.

3. With the air-acetylene flame lit adjust fuel and oxidated rates until a white flame is achieved, then switch over to the nitrous oxide-acetylene flame.

4. Once the nitrous oxide-acetylene flame is ignited, adjust the oxidant and fuel rates to achieve a flame with a rose-red inner core approximately 1/2-3/4 in. high.

5. Aspirate a standard with an absorbance of about 0.200. Maximize this reading by adjusting the burner head (do not raise or lower the head) and aspiration rate.

6. While aspirating a blank, press the auto zero button. Aspirate standards and record the absorbances. Analyze an EPA reference standard to verify the curve. The reference standard must be within the 95% confidence limits before continuing.

7. Analyze samples. Refer to specific metal standard operating procedures for notes on interferences, use of matrix modifiers, quality control and any other adjustments to this instrument operating procedure.

8. Switch back to the air-acetylene flame when done.

G. Flame Emission Analysis

1. Follow parts A, B and C (steps 1-4) as if you were setting up to run copper. All conditions (burner head alignment, fuel and oxidant rates, aspiration rate, etc) must be maximized before switching to emission.

2. Unplug the copper lamp.

3. Set the required wavelength and slit width for the metal which is to be analyzed by emission spectroscopy.

4. Set the signal to EM, mode to CONT.
   While aspirating a blank, press the auto zero button.

5. While aspirating a standard of concentration at the high end of the optimum range, set the gain to about 75. Using the wavelength fine adjustment knob, maximize the gain reading. Turn the gain back to 75. This peaks out the wavelength.

6. Then aspirate standards and record the emission readings (The gain readings and emission readings will increase as the concentrations of standards aspirated increase.) Analyze an EPA reference standard to verify the curve. The reference standard must be within the 95% confidence limits before continuing. Refer to standard operating procedures for each metal for specific requirements.

7. Analyze samples. Refer to standard operating procedures for quality control and any other specific requirements and notes.

H. Auto-Concentration

The machine is calibrated against one to three standards. The standard curve is drawn as a straight line between the zero and S_1. Again, a straight line is drawn between S_1 to S_2, and S_2 to S_3.

(See Figure 1) MetalFl1-7

If you should encounter an error code during calibration, the operator's manual has a listing of error codes and their meanings.

Signal - Conc.	t = 2 sec.
Mode - Hold	Ave - 3

Type the S_1 value and push S_1 button
Type the S_2 value and push the S_2 button

Procedure

1. Aspirate the blank and auto-zero (AZ)

2. Aspirate S_1 standard, push the S_1 button. Repeat until desired number of standards are entered.

3. Aspirate samples, check standards during the run, re-standardize if necessary.

Notes

You can AZ any time during a run.
If you re-standarize this S_1 value, you have to re-standardize the S_2 and S_3.

I. Method of Standard Addition

The method of standard additions is a useful tool which enables us to achieve an accurate determination of an element in the presence of an interference. Standard additions are required for EP Toxicity metals.

For an accurate value of an element, the working curve must be linear throughout the range of concentration encountered by the samples plus the additions.

SIGNAL - ABS t - 2 sec.

MODE - HOLD Ave - 3

Procedure

1. Take four aliquots of the sample at a set volume.
2. Add the same volume of blank to the first beaker.
3. Add the same volume of successive standards to the remaining beakers.
4. Mix by swirling.

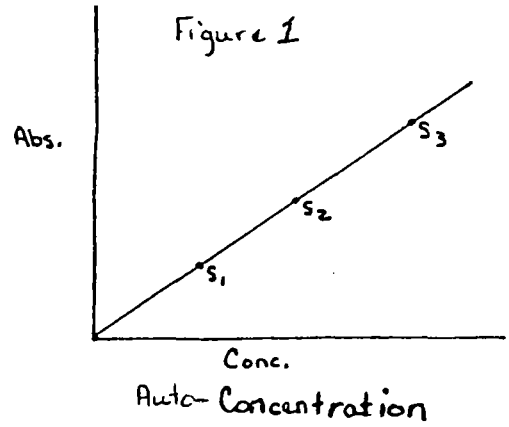
Example -	Beaker 1	Beaker 2	Beaker 3	Beaker 4
	3 ml sample	3 ml sample	3 ml sample	3 ml sample
	3 ml blank	3 ml 1 PPM Std.	3 ml 2 PPM Std.	3 ml 4 PPM Std.

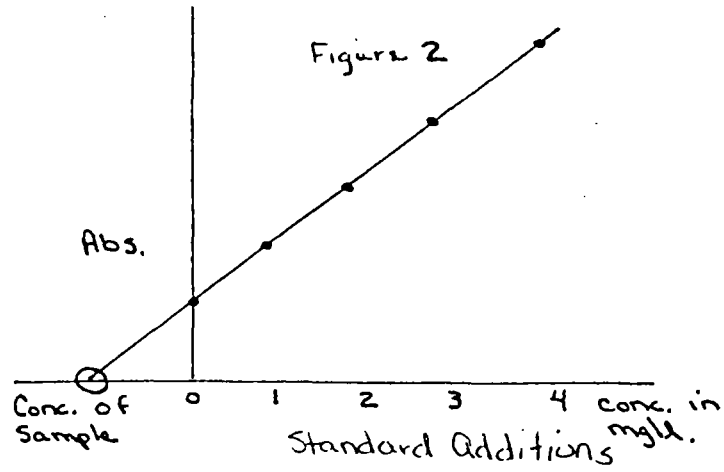
5. Aspirate the reagent blank and Auto-zero (A.Z.)
6. Aspirate the sample beakers from the blank to the highest spiked beaker.
7. Record all four absorbance readings for the sample.

Calculations

Plot the absorbance readings against the concentrations of the standards added. The intercept of the concentration axis equals the concentration of the element in the sample. (See figure 2 on following page). Linear regression may be used.

Note: When doing furnace Std. Additions, pipet 1/2 ml of sample and standard directly into the cups. Mix thoroughly.





J. General Instrument Shut-down

1. Turn off the air-acetylene flame by first turning off the fuel supply, then turning off the oxidant supply. (The order is important or a flashback may occur!) Turn B.G. corrector to the A.A. Position, Signal to Lamp.

2. Turn off the gas tanks and air supply. Bleed lines of all gases.

3. Turn off the lamp. Be careful to store hot EDL's in a horizontal position. Put lamps away.

4. Turn the gain counter clockwise as far as it will go.

5. Turn off the P.E. 2380 power switch.

6. Put burner head in D.I. water overnight.

7. Rinse the burner chamber with D.I. water.

K. Atomic Absorption - Maintenance

The daily and weekly and monthly maintenance procedures are discussed in this section.

Daily Cleaning Schedule

1. Burner Heads

Due to the nature of our samples (mainly high dissolved solids) clean the burner head daily. Proceed as follows:

a. Soak the burner heads in a weak detergent solution, overnight.

b. In the morning, rinse the burner head with D.I. water and wipe dry.

c. Replace the burner head in the burner chamber.

d. Using a name card or equivalent, clean the burner head slot.

e. Press the oxidant button on the A.A. (this forces air through the burner head) wipe off excess water expelled.

2. Burner Chamber

a. Rinse the chamber at the end of each day.

1. Remove burner head.

2. Pour D.I. water into burner chamber. This flushes the drain system as well as the burner chamber.

3. Windows

Check the windows of the A.A., if they are dirty, clean with isopropol alcohol; rinse with D.I. water.

4. Nebulizer

Each morning, push the brass wire through the capillary. This will dislodge any solid particles.

If you notice a low sensitivity reading or the capillary isn't aspirating as fast as before, repeat the above procedure.

Weekly Cleaning Schedule

1. Empty the drain jug

a. Empty jug into sink, being careful due to the acid content.

b. Rinse the jug with tap water.

c. Fill the jug with D.I. water to a few inches above the drain hose. Water must cover the hose or a flashback may occur.

2. Cleaning the neubilizer

a. Remove neubulizer from the burner.

b. Unscrew the neubilizer.

c. Carefully pull out the needle assembly (good picture in P.E. Model 2380 Atomic Absorption Manual page 12-6.)

d. Remove front end cap and O-ring.

e. Clean each section with soap and water. Rinse thoroughly.

f. Lightly grease the O-rings (may be found in top drawer by A.A.)

3. Cleaning the Neubilizer Assembly

a. Put the neublizer together, being careful the needle into the main component with the needle or face is facing the opening in the body.

b. Continue to reassemble the nebulizer.

c. Insert the nebulizer in the burner

d. Adjust the aspiration rate as described in the set-up procedure

Monthly Cleaning Schedule

1. Clean the entire A.A. burner and drain system.

a. Aspirate a ten percent detergent for 10-15 minutes.

b. Aspirate D.I. water for 30 minutes to flush system thoroughly.

2. Drain air compressor and change the air filter if necessary.

3. Nebulizer (Refer to figure 2)

a. Cleaning the nebulizer

1. Remove the black nebulizer oxidant tubing and loosen the clamp screw. Remove the nebulizer from the burner end cap.

2. Unscrew and remove the knurled knob (1) and washer (3)

3. Carefully pull out the needle assembly (4) and inspect the inner end for deposits. Clean if required and lay aside.

4. Remove O-ring from the other end (12), unscrew and remove the front end cap (11), and pull out the venturi (10).

5. Remove the insert (8) by pushing out with a wooden probe (pencil).

6. Clean all components with soap and water, gently using a scrub pad and without scratching metal (soaking may be used on difficult deposits.

7. Inspect O-rings (replace when necessary), clean with soap and water, dry and lightly grease (special grease is in top drawer by A.A.)

b. Assembling the nebulizer

1. Slide the needle assembly into the insert as far as it will go, and replace into the left end of the nebulizer body.

   Note Make sure the slanted needle opening is facing the opening of the body.

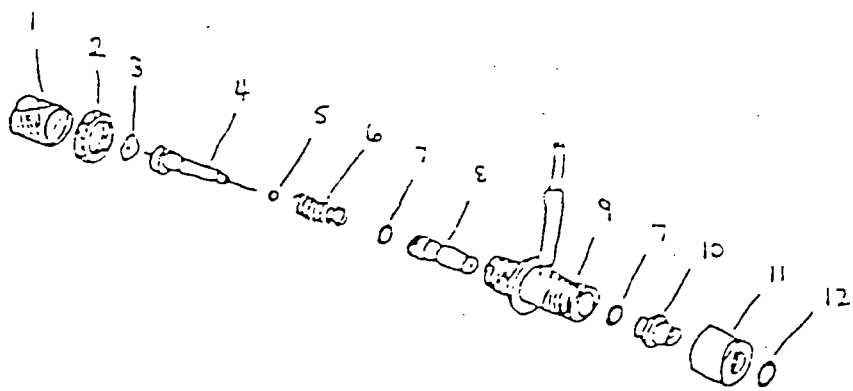
2. Replace the washer and knurled knob (the needle tip should protrude from the small aperture in the insert end).

3. Install the venturi over the needle tip; put on and tighten the front end cap and replace the o-ring on the end of the venturi.

4. Insert the nebulizer back in the burner, connect the oxidant tubing and tighten the clamp screw.

5. Adjust the aspiration rate and lock setting with the locking ring (2).

Nebulizer



1) Knurled Knob
2) Locking Ring
3) Washer
4) Needle Assembly
5) O-Ring
6) Spring
7) O-Ring (2)
8) Insert
9) Nebulizer Body
10) Venturi
11) Front End Cap
12) O-Ring

Quality Control:

1. Refer to specific metal standard operating procedures.

Notes:

1. Refer to Perkin-Elmer Operating Procedures manual for further instructions.

2. Intermediate standards must be prepared fresh from purchased stock solutions every 6 months. Working standards must be prepared fresh every 2 months.

3. Standards are to be prepared in the same acid concentration as the samples being analyzed.

	Revision Date
Michael Linskens Michael J. Linskens Laboratory Manager	11-14-86
Kim Finner Kim D. Finner Analytical Laboratory QA Officer	4-13-87
Thomas J. Lynch Thomas J. Lynch QA Officer	

ALUMINUM

Method: AA - Flame; Direct Aspiration

Reference: EPA 1983, Method 202.1

"Analytical Methods for Atomic Absorption Spectrophotometry", 1982, Perkin-Elmer Corporation

Detection Limit: 0.20 mg/L

Optimum Concentration Range: 0.20 - 50.0 mg/L

Sample Handling: Acidify with nitric acid to pH < 2. Drinking waters and filtered groundwater free of particulate matter and organics may be analyzed directly, while wastewaters, leachates, solids, etc. must be digested prior to analysis (refer to appropriate digestion procedures). Analyze within 6 months.

Instrument Conditions:

1. Aluminium hollow cathode lamp with lamp energy set at 25.
2. Wavelength: 309.3 nm
3. Slit Width: 0.7 Normal
4. Fuel: Acetylene
5. Oxidant: Nitrous oxide
6. Type of flame: Red
7. Standards to use for curve set-up: 5.00, 10.0, 20.0, 50.0 mg/L.

Reagent Preparation: (Prepare fresh every 6 months unless otherwise noted.)

1. Standard Aluminum Solution (100 mg/L Aluminum): Pipet 10 mL of the 1000 ppm stock aluminum solution into a 100 mL volumetric flask, add 1/2 mL HNO_3, and dilute to the mark with Milli-Q water.
2. Standards (Prepare fresh every month.):

Concentration of Standard	Volume of Aluminum Standard	Dilute to
5.00 mg/L	0.5 mL of 1000 mg/L Al	100 mL
10.0 mg/L	1 mL of 1000 mg/L Al	100 mL
20.0 mg/L	2 mL of 1000 mg/L Al	100 mL
50.0 mg/L	5 mL of 1000 mg/L Al	100 mL

3. Potassium Chloride Solution: In a 1 liter volumetric flask, dissolve 95g KCL in Milli-Q water and dilute to the mark.

Notes:

1. Samples must be diluted to obtain concentrations within the optimum concentration range.

2. Standards are to be prepared in the same acid concentration as the samples being analyzed.

3. The use of background correction is required.

4. Aluminum is partially ionized in the nitrous oxide-acetylene flame. This problem can be controlled by the addition of potassium. Add 2 mL of 1000 ppm potassium to 100 mL samples, blanks and standards.

Procedure: For the analysis procedure, refer to the Atomic Absorption Spectrometry, Flame - Direct Aspiration section of this manual.

If aluminum is to be run in concentration mode, use the 10.0 and 50.0 mg/L aluminum standards for standardization and follow the procedure for analyzing in concentration mode.

To 10 mL of samples, blanks and standards, add 0.2 mL KCL solution. Mix and analyze.

Quality Control:

1. Establish a standard curve with the standards listed above plus a blank. Record the absorbance check standard in the absorbance check book. The absorbances should remain consistent from run to run. If not, necessary troubleshooting must be performed before continuing (check wavelength, flame head alignment, lamp alignment, etc.).

2. A quality control calibration standard of 10.0 mg/L is to be analyzed, at a minimum, after every 10 samples. If less than 10 samples are analyzed, a calibration standard is still required. The last sample analyzed in the run is to be the calibration standard. These standards must be within the acceptable ranges or the samples run after the last acceptable check standard are to be reanalyzed. Record the calibration standards in the quality control book. The confidence limits are noted in the quality control book.

3. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Duplicates are to be averaged. Spike samples with a standard of twice the concentration of the sample in a 1:1 ratio of sample to standard. Spike recoveries and duplicates are to be within acceptable ranges or the use of dilution or method of standard additions is to be applied to reduce the interferences.

Calculations:

1. Plot concentration vs absorbance on graph. Determine unknowns using graph, or

2. Calculate using linear regression, or

3. Calculate using concentration mode.

ANTIMONY

Method: AA - Furnace; Direct Injection

Reference: EPA 1983, Method 204.2

"Analytical Methods for Furnace Atomic Absorption Spectrophotometry", 1982, Perkin-Elmer Corporation

"Techniques in Graphite Furnace Atomic Absorption Spectrophotometry", 1985, Perkin-Elmer Corporation

Contact Laboratory Program, "Statements of Work", July, 1985

Detection Limit: 0.005 mg/L

Optimum Concentration Range: 0.005 - 0.050 mg/L

Instrument Conditions:

1. Antimony electrodeless discharge lamp with lamp energy set at 7.
2. Wavelength: 217.6 nm
3. Slit Width: 0.2 Alternate
4. Mode: Peak Height
5. HGA Furance Programming:

   Step 1: 120 (dry temp) 10 (ramp time) 20 (hold time)
   Step 2: 900 (char temp) 5 (ramp time) 20 (hold time)
   Step 3: 2400 (atom temp) 0 (ramp time) 3 (hold time)

   * Also press the read, record and stop flow buttons; t = 3 sec.

   Step 4: 2400 (max temp) 0 (ramp time) 3 (hold time)

   Press the record button.

6. Sample Volume : 20 uL
7. Standards to use for curve set-up: 10.0, 20.0, 50.0 ug/L.
8. Platform is required.

Sample Handling: Acidify with nitric acid to pH <2. Analyze within 6 months.

[C-600-91a]

Reagent Preparation:

1. Standard Antimony Solution (1000 ug/L Antimony): Pipet 1.00 mL of the 1000 ppm stock antimony solution into a 1000 mL volumetric flask, add 1/2 mL HNO_3 and dilute to the mark with D.I. water. Prepare fresh every month.

2. Standards (Prepare fresh every week.):

Concentration of Standard	Volume of Antimony Standard	Dilute to
10.0 ug/L	1 mL of 1000 ug/L Sb	100 mL
20.0 ug/L	2 mL of 1000 ug/L Sb	100 mL
50.0 ug/L	5 mL of 1000 ug/L Sb	100 mL

3. Nickel Nitrate 5% Solution: Dissolve 25.0g of nickel nitrate in 100 mL of D.I. water.

Notes:

1. Samples must be diluted to obtain concentrations within the optimum concentration range.

2. Standards are to be prepared in the same acid concentrations as the samples being analyzed.

3. The use of background correction is required.

4. The use of halide acids should be avoided.

5. Nickel nitrate is added as a matrix modifier to control interferences.

6. Platform technique is required.

Procedure: For the analysis procedure, refer to the Atomic Absorption Spectrometry, Furnace - Direct Injection section of this manual.

To 5 mL of samples, blanks, and standards add 0.1 mL of Ni $(NO_3)_2$ solution.

For the use of concentration mode, use the 20.0 and 50.0 standards and follow the procedure for using the concentration mode.

Quality Control:

1. Establish a standard curve with the standards listed above plus a blank. Record the absorbance check standard in the absorbance check book. The absorbances should remain consistent from run to run. If

not, necessary troubleshooting must be performed before continuing (check wavelength, furnace alignment, lamp alignment, graphite tube, etc.).

2. A quality control calibration standard of 20.0 ug/L is to be analyzed, at a minimum, after every 10 samples. If less than 10 samples are analyzed, a calibration standard is still required. The last sample analyzed in the run is to be the calibration standard. These standards must be within acceptable ranges or the samples run after the last acceptable calibration standard are to be reanalyzed. Record the calibration standard in the quality control book. The confidence limits are noted in the quality control book.

3. Digest a duplicate and spike; a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a digested duplicate and spike are still required. Duplicates are to be averaged. Spike samples with standard of twice the concentration of the sample in a 1:1 ratio of sample to standards. Spike recoveries and duplicate results are to be within an acceptable ranges or the use of dilution, or method of standard additions is to be applied to reduce the interferences.

4. For every sample analyzed, an analytical spike (at the bench) must be run to verify that standard additions are not required. Criteria for standard additions are:

   a. If the spike recovery is within 85-115%, standard additions are not required.

   b. If the spike recovery is outside 85-115%, standard additions are required.

5. An EPA reference standard will be analyzed with each analysis.

Calculations:

1. Plot concentrations vs. absorbance (or peak height) on graph. Determine unknowns using graph, or

2. Calculate using linear regression, or

3. Calculate using the concentration mode.

[C-600-91a]

ANTIMONY

Method: AA - Flame; Direct Aspiration

Reference: EPA 1983, Method 204.1

"Analytical Methods for Atomic Absorption Spectrophotometry", 1982, Perkin-Elmer Corporation

Detection Limit: 0.50 mg/L

Optimum Concentration Range: 0.50 - 20.0 mg/L

Sample Handling: Acidify with nitric acid to pH < 2. Drinking waters and filtered groundwater free of particulate matter and organics may be analyzed directly, while wastewaters, leachates, solids, etc. must be digested prior to analysis (refer to appropriate digestion procedures). Analyze within 6 months.

Instrument Conditions:

1. Antimony electrodeless discharge lamp with lamp energy set at 7.
2. Wavelength: 217.6 nm
3. Slit Width: 0.2 Normal
4. Fuel: Acetylene
5. Oxidant: Air
6. Type of flame: Oxidizing, lean, blue
7. Standards to use for curve set-up: 2.00, 5.00, 10.0, 20.0 mg/L.

Reagent Preparation: (Prepare fresh every 6 months unless otherwise noted.)

1. Standard Antimony Solution (100 mg/L Antimony): Pipet 10 mL of the 1000 ppm stock antimony solution into a 100 mL volumetric flask, add 1/2 mL HNO_3, and dilute to the mark with Milli-Q water.
2. Standards (Prepare fresh every month.):

Concentration of Standard	Volume of Antimony Standard	Dilute to
2.00 mg/L	2 mL of 100 mg/L Sb	100 mL
5.00 mg/L	5 mL of 100 mg/L Sb	100 mL
10.0 mg/L	10 mL of 100 mg/L Sb	100 mL
20.0 mg/L	20 mL of 100 mg/L Sb	100 mL

Notes:

1. Samples must be diluted to obtain concentrations within the optimum concentration range.

2. Standards are to be prepared in the same acid concentrations as the samples being analyzed.

3. The use of background correction is required.

4. This flame procedure can be used for digested samples, EP Toxicity samples or any other samples where high concentrations of antimony are expected and low detection limits are not required.

5. Lead, in concentrations of >100 mg/L, may interfere. Use an alternate wavelength of 231.1 nm in this situation.

Procedure: For the analysis procedure, refer to the Atomic Absorption Spectrometry, Flame - Direct Aspiration section of this manual.

If antimony is to be analyzed in concentration mode, use the 10.0 and 20.0 standards for standardization and follow the procedure for analyzing in the concentration mode.

Quality Control:

1. Establish a standard curve with the standards listed above plus a blank. Record the absorbance check standard in the absorbance check book. The absorbances should remain consistent from run to run. If not, necessary troubleshooting must be performed before continuing (check wavelength, flame head alignment, lamp alignment, etc.).

2. A quality control calibration standard of 5.00 mg/L is to be analyzed, at a minimum, after every 10 samples. If less than 10 samples are analyzed, a calibration standard is still required. The last sample analyzed in the run is to be the calibration standard. These standards must be within acceptable ranges or the samples run after the last acceptable check standard are to be reanalyzed. Record the calibration standards in the quality control book. The confidence limits are noted in the quality control book.

3. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Duplicates are to be averaged. Spike samples with a standard of twice the concentration of the sample in a 1:1 ratio of sample to standard. Spike recoveries and duplicates are to be within acceptable ranges or the use of dilution or method of standard additions is to be applied to reduce the interferences.

Calculations:

1. Plot concentration vs absorbance on graph. Determine unknowns using graph, or

2. Calculate using linear regression, or

3. Calculate using concentration mode.

ARSENIC

Method: AA - Furnace; Direct Injection

Reference: EPA 1983, Method 206.2

"Analytical Methods for Furnace Atomic Absorption Spectrophotometry", 1982, Perkin-Elmer Corporation

"Techniques in Graphite Furnace Atomic Absorption Spectrophotometry", 1985, Perkin-Elmer Corporation

Contract Laboratory Program, "Statement of Work", July, 1985

Detection Limit: 0.002 mg/L

Optimum Concentration Range: 0.002 - 0.050 mg/L

Sample Handling: Acidify with nitric acid to pH < 2. Analyzed within 6 months. All samples must be digested prior to analysis.

Instrument Conditions:

1. Arsenic electrodeless discharge lamp with lamp energy set at 8.
2. Wavelength: 193.7 nm
3. Slit Width: 0.7 Alternate
4. Mode: Peak height
5. HGA Furnace Programming:

Step 1:	130	(dry temp)	10	(ramp time)	20	(hold time)
Step 2:	1300	(char temp)	10	(ramp time)	10	(hold time)
Step 3:	2500	(atom temp)	0	(ramp time)	3	(hold time)

* Also press the read, record and stop flow buttons; enter t = 3 sec.

Step 4:	2500	(max temp)	0	(ramp time)	3	(hold time)

Press record button.

6. Sample Volume: 20 uL
7. Standards to use for curve set-up: 5.0, 10.0, 20.0, 50.0 ug/L.
8. Pyrolytic tubes must be used.

Reagent Preparation:

1. Standard Arsenic Solution (1000 ug/L Arsenic): Pipet 1.00 mL of the 1000 ppm stock arsenic solution into a 1000 mL volumetric flask, add 1/2 mL HNO_3, and dilute to the mark with Milli-Q water. Prepare fresh every month.

2. Standards (Prepare fresh every week.):

Concentration of Standard	Volume of Arsenic Standard	Dilute to
0 ug/L	0 mL of 1000 ug/L As	100 mL
5 ug/L	1/2 mL of 1000 ug/L As	100 mL
10 ug/L	1 mL of 1000 ug/L As	100 mL
20 ug/L	2 mL of 1000 ug/L As	100 mL
50 ug/L	5 mL of 1000 ug/L As	100 mL

Notes:

1. Samples must be diluted to obtain concentrations within the optimum concentration range.

2. Standards are to be prepared in the same acid concentrations as the samples being analyzed.

3. Nickel nitrate is added as a matrix modifier to minimize volatilization losses during the drying and charring steps.

4. The use of the background correction is required.

5. High concentrations of phosphorus interfere with this procedure. The gaseous hydride method for arsenic should be used in these cases.

Procedure: For the analysis procedure, refer to the Atomic Absorption Spectrometry, Furnace - Direct Injection section of this manual.

Prior to Analysis: To 5 mL of digested sample or standard, add 0.1 mL of 5% nickel nitrate solution. Mix well.

If Arsenic is to be analyzed in concentration mode, use the 20 and 50 ug/L arsenic standards and the procedures for analyzing in the concentration mode.

Quality Control:

1. Establish a standard curve with the standards listed above plus a blank. Record the absorbance check standard in the absorbance check book. The absorbances should remain consistent from run to run. If not, necessary troubleshooting must be performed before continuing (check wavelength, furnace alignment, lamp alignment, graphite tube, etc.).

2. A quality control calibration standard of 20 ug/L is to be analyzed, at a minimum, after every 10 samples. If less than 10 samples are analyzed, a calibration standard is still required. The last sample analyzed in the run is to be the calibration standard. These standards must be within acceptable ranges or the samples run after the last acceptable calibration standard are to be reanalyzed. Record the calibration standard in the quality control book. The confidence limits are noted in the quality control book.

3. A digested duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a digested duplicate and spike are still required. Duplicates are to be averaged. Spike samples with a standard of twice the concentration of the sample in a 1:1 ratio of sample to standards. Spike recoveries and duplicate results are to be within acceptable ranges or the use of dilution, or method of standard additions is to be applied to reduce the interferences.

4. For every sample analyzed, an analytical spike (at the bench) must be run to verify that standard additions are not required. Criteria for standard additions are:

   a. If the spike recovery is within 85 - 115%, standard additions are not required.

   b. If the spike recovery is outside 85 - 115%, standard additions are required.

5. An EPA reference sample will be analyzed with each analysis.

Calculations:

1. Plot concentrations vs. absorbance on graph. Determine unknowns using graph, or

2. Calculate using linear regression, or

3. Calculate using the concentration mode.

BARIUM

Method: AA - Flame; Direct Aspiration

Reference: EPA 1983, Method 208.1

"Analytical Methods for Atomic Absorption Spectrophotometry", 1982, Perkin-Elmer Corporation

Contract Laboratory Program, "Statement of Work", July, 1985

Detection Limit: 0.20 mg/L

Optimum Concentration Range: 0.20 - 10.0 mg/L

Sample Handling: Acidify with nitric acid to pH < 2. Drinking waters and filtered groundwater free of particulate matter and organics may be analyzed directly, while wastewaters, leachates, solids, etc. must be digested prior to analysis (refer to appropriate digestion procedures). Analyze within 6 months.

Instrument Conditions:

1. Barium hollow cathode lamp with lamp energy set at 25.
2. Wavelength: 553.6 nm
3. Slit Width: 0.2
4. Fuel: Acetylene
5. Oxidant: Nitrous oxide
6. Type of flame: Red
7. Standards to use for curve set-up: 1.00, 2.00, 5.00, 10.0 mg/L.

Reagent Preparation: (Prepare fresh every 6 months unless otherwise noted.)

1. Standard Barium Solution (100 mg/L Barium): Pipet 10 mL of the 1000 ppm stock barium solution into a 100 mL volumetric flask, add 1/2 mL HNO_3 and dilute to the mark with Milli-Q water.

2. Standards (Prepare fresh every 1 month.):

Concentration of Standard	Volume of Barium Standard	Dilute to
1.00 mg/L	1 mL of 100 mg/L Ba	100 mL
2.00 mg/L	2 mL of 100 mg/L Ba	100 mL
5.00 mg/L	5 mL of 100 mg/L Ba	100 mL
10.0 mg/L	10 mL of 100 mg/L Ba	100 mL

3. Potassium chloride solution: In a 1 liter volumetric flask, dissolve 95g KCl in Milli-Q water and dilute to the mark.

Notes:

1. Samples must be diluted to obtain concentrations within the optimum concentration range.

2. Standards are to be prepared in the same acid concentrations as the samples being analyzed.

3. Barium is easily ionized in the nitrous oxide-acetylene flame. This can be controlled by the addition of potassium. Add 2 mL of 1000 ppm potassium to 100 mL sample and standards.

4. High calcium can cause an extremely noisy signal and high false positive values.

5. This flame procedure can be used for digested samples, EP Toxicity samples or any other samples where low detection limits are not required. EP Toxicity samples must be spiked to verify that standard additions are not required.

Procedure: For the analysis procedure, refer to the Atomic Absorption Spectrometry, Flame - Direct Aspiration section of this manual.

Potassium chloride solution is added as a matrix modifier to the samples and standards at a ratio of 0.2 mL KCL to 10 mL of sample or standard.

If barium is to be run in concentration mode, use the 5.00 and 10.0 standards and follow the procedure for analyzing in the concentration mode.

Quality Control:

1. Establish a standard curve with the standards listed above plus a blank. Record the absorbance check standard in the absorbance check book. The absorbances should remain consistent from run to run. If not, necessary troubleshooting must be performed before continuing (check wavelength, flame head alignment, lamp alignment, etc.).

2. A quality control calibration standard of 5.00 mg/L is to be analyzed, at a minimum, after every 10 samples. If less than 10 samples are analyzed, a calibration standard is still required. The last sample analyzed in the run is to be the calibration standard. These standards must be within acceptable ranges or the samples run after the last acceptable check standard are to be reanalyzed. Record the calibration standards in the quality control book. The confidence limits are noted in the quality control book.

3. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Duplicates are to be averaged. Spike samples with a standard of twice the concentration of the sample in a 1:1 ratio of sample to standard. Spike recoveries and duplicates are to be within acceptable ranges or the use of dilution or method of standard additions is to be applied to reduce the interferences.

Calculations:

1. Plot concentration vs absorbance on graph. Determine unknowns using graph, or

2. Calculate using linear regression, or

3. Calculate using concentration mode.

BERYLLIUM

Method: AA - Flame; Direct Aspiration

Reference: EPA 1983, Method 210.1

"Analytical Methods for Atomic Absorption Spectrophotometry", 1982, Perkin-Elmer Corporation

Detection Limit: 0.02 mg/L

Optimum Concentration Range: 0.02 - 2.00 mg/L

Sample Handling: Acidify with nitric acid to pH < 2. Drinking waters and filtered groundwater free of particulate matter and organics may be analyzed directly, while wastewaters, leachates, solids, etc. must be digested prior to analysis (refer to appropriate digestion procedures). Analyze within 6 months.

Instrument Conditions:

1. Beryllium hollow cathode lamp with lamp energy set at 30.
2. Wavelength: 234.9 nm
3. Slit Width: 0.7 Normal
4. Fuel: Acetylene
5. Oxidant: Nitrous oxide
6. Type of flame: Red
7. Standards to use for curve set-up: 0.20, 0.50, 1.00, 2.00 mg/L.

Reagent Preparation: (Prepare fresh every 6 months unless otherwise noted.)

1. Standard Beryllium Solution (10.0 mg/L Beryllium): Pipet 10 mL of the 1000 ppm stock beryllium solution into a 1000 mL volumetric flask, add 1/2 mL HNO_3, and dilute to the mark with Milli-Q water.
2. Standards (Prepare fresh every month.):

Concentration of Standard	Volume of Beryllium Standard	Dilute to
0.20 mg/L	2 mL of 10.0 mg/L Be	100 mL
0.50 mg/L	5 mL of 10.0 mg/L Be	100 mL
1.00 mg/L	10 mL of 10.0 mg/L Be	100 mL
2.00 mg/L	20 mL of 10.0 mg/L Be	100 mL

Notes:

1. Samples must be diluted to obtain concentrations within the optimum concentration range.

2. Standards are to be prepared in the same acid concentrations as the samples being analyzed.

3. The use of background correction is required.

4. Sodium and silicon in excess of 1000 mg/L severely depress the absorbance for beryllium. The addition of oxine (8-hydroxyquinoline) as a matrix modifier will control these interferences.

5. Aluminum of concentrations of 500 ug/L will depress the sensitivity.

Procedure: For the analysis procedure, refer to the Atomic Absorption Spectrometry, Flame - Direct Aspiration section of this manual.

If beryllium is to be run in concentration mode, use the 1.00 and 2.00 standards and follow the procedure for analyzing in the concentration mode.

Quality Control:

1. Establish a standard curve with the standards listed above plus a blank. Record the absorbance check standard in the absorbance check book. The absorbances should remain consistent from run to run. If not, necessary troubleshooting must be performed before continuing (check wavelength, flame head alignment, lamp alignment, etc.).

2. A quality control calibration standard of 0.50 mg/L is to be analyzed, at a minimum, after every 10 samples. If less than 10 samples are analyzed, a calibration standard is still required. The last sample analyzed in the run is to be the calibration standard. These standards must be within the acceptable ranges or the samples run after the last acceptable check standard are to be reanalyzed. Record the calibration standards in the quality control book. The confidence limits are noted in the quality control book.

3. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Duplicates are to be averaged. Spike samples with a standard of twice the concentration of the sample in a 1:1 ratio of sample to standard. Spike recoveries and duplicates are to be within acceptable ranges or the use of dilution or method of standard additions is to be applied to reduce the interferences.

Calculations:

1. Plot concentration vs absorbance on graph. Determine unknowns using graph, or

2. Calculate using linear regression.

3. Calculate using the concentration mode.

[ALM-10-2]

CADMIUM

Method: AA - Flame; Direct Aspiration

Reference: EPA 1983, Method 213.1

"Analytical Methods for Atomic Absorption Spectrophotometry", 1982, Perkin-Elmer Corporation

Detection Limit: 0.01 mg/L

Optimum Concentration Range: 0.01 - 1.00 mg/L

Sample Handling: Acidify with nitric acid to pH < 2. Drinking waters and filtered groundwater free of particulate matter and organics may be analyzed directly, while wastewaters, leachates, solids, etc. must be digested prior to analysis (refer to appropriate digestion procedures). Analyze within 6 months.

Instrument Conditions:

1. Cadmium hollow cathode lamp with lamp energy set at 4.
2. Wavelength: 228.8 nm
3. Slit Width: 0.7 Normal
4. Fuel: Acetylene
5. Oxidant: Air
6. Type of flame: Oxidizing, lean, blue
7. Standards to use for curve set-up: 0.10, 0.20, 0.50, 1.00 mg/L.

Reagent Preparation: (Prepare fresh every 6 months unless otherwise noted.)

1. Standard Cadmium Solution (10.0 mg/L Cadmium): Pipet 1 mL of the 1000 ppm stock cadmium solution into a 100 mL volumetric flask, add 1/2 mL HNO_3 and dilute to the mark with Milli-Q water.
2. Standards (Prepare fresh every month.):

Concentration of Standard	Volume of Cadmium Standard	Dilute to
0.10 mg/L	1 mL of 10.0 mg/L Cd	100 mL
0.20 mg/L	2 mL of 10.0 mg/L Cd	100 mL
0.50 mg/L	5 mL of 10.0 mg/L Cd	100 mL
1.00 mg/L	10 mL of 10.0 mg/L Cd	100 mL

Notes:

1. Samples must be diluted to obtain concentrations within the optimum concentration range.

2. Standards are to be prepared in the same acid concentrations as the samples being analyzed.

3. The use of background correction is required.

4. This flame procedure can be used for digested samples, EP Toxicity samples, or any other samples where low detection limits are not required. EP Toxicity samples must be spiked to verify that standard additions are not required.

Procedure: For the analysis procedure, refer to the Atomic Absorption Spectrometry, Flame - Direct Aspiration section of this manual.

If cadmium is to be run in the concentration mode, use the 0.50 and 1.00 standards and follow the procedure for analyzing in concentration mode.

Quality Control:

1. Establish a standard curve with the standards listed above plus a blank. Record the absorbance check standard in the absorbance check book. The absorbances should remain consistent from run to run. If not, necessary troubleshooting must be performed before continuing (check wavelength, flame head alignment, lamp alignment, etc.).

2. A quality control calibration standard of 0.10 mg/L is to be analyzed, at a minimum, after every 10 samples. If less than 10 samples are analyzed, a calibration standard is still required. The last sample analyzed in the run is to be the calibration standard. These standards must be within the acceptable ranges or the samples run after the last acceptable check standard are to be reanalyzed. Record the calibration standards in the quality control book. The confidence limits are noted in the quality control book.

3. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Duplicates are to be averaged. Spike samples with a standard of twice the concentration of the sample in a 1:1 ratio of sample to standard. Spike recoveries and duplicates are to be within acceptable ranges or the use of dilution or method of standard additions is to be applied to reduce the interferences.

Calculations:

1. Plot concentration vs absorbance on graph. Determine unknowns using graph or

2. Calculate using linear regression or

3. Calculate using the concentration mode.

[ALM8-10]

CADMIUM

Method: AA - Furnace; Direct Injection

Reference: EPA 1983, Method 213.2

"Analytical Methods for Furnace Atomic Absorption Spectrophotometry", 1982, Perkin-Elmer Corporation

"Techniques in Graphite Furnace Atomic Absorption Spectrophotometry", 1985, Perkin-Elmer Corporation

Contract Laboratory Program, "Statement of Work", July, 1985

Detection Limit: 0.0002 mg/L

Optimum Concentration Range: 0.0002 - 0.0020 mg/L

Sample Handling: Acidify with nitric acid to pH < 2. All samples must be digested prior to analysis (refer to appropriate digestion procedures). Analyze within 6 months.

Instrument Conditions:

1. Cadmium hollow cathode lamp with lamp energy set at 4.

2. Wavelength: 228.8 nm

3. Slit Width: 0.7 Alternate

4. Mode: Peak area

5. HGA Furnace Programming:

Step 1:	120	(dry temp)	10	(ramp time)	20	(hold time)
Step 2:	250	(char temp)	10	(ramp time)	20	(hold time)
Step 3:	2100	(atom temp)	2	(ramp time)	3	(hold time)

* Also press the read, record and stop flow buttons; enter t = 5 sec

Step 4:	2700	(max temp)	1	(ramp time)	5	(hold time)

Press record button.

6. Sample Volume: 20 uL

7. Standards to use for curve set-up: 0.50, 1.00, 2.00, ug/L

8. Pyrolytic tubes must be used.

Reagent Preparation:

1. Standard Cadmium Solution (1000 ug/L Cadmium): Pipet 1.00 mL of the 1000 ppm stock cadmium solution into a 1000 mL volumetric flask, add 1/2 mL HNO_3, and dilute to the mark with Milli-Q water. Prepare fresh every month.

2. Working Cadmium Solution (100 ug/l Cadmium): Pipet 10 mL of the 1000 ug/l cadmium into a 100 mL volumetric flask and dilute to the mark with Milli-Q water. Prepare fresh every month.

3. Standards (Prepare fresh every week.):

Concentration of Standard	Volume of Cadmium Standard	Dilute to
0.00 ug/L	0 mL of 100 ug/L Cd	100 mL
0.50 ug/L	0.5 mL of 100 ug/L Cd	100 mL
1.00 ug/L	1 mL of 100 ug/L Cd	100 mL
2.00 ug/L	2 mL of 100 ug/L Cd	100 mL

Notes:

1. Samples must be diluted to obtain concentrations within the optimum concentration range.

2. Standards are to be prepared in the same acid concentrations as the samples being analyzed.

3. The use of background correction is required.

4. The cadmium flame procedure is recommended where concentrations of greater than 0.10 mg/L are expected.

Procedure: For the analysis procedure, refer to the Atomic Absorption Spectrometry, Furnace - Direct Injection section of this manual.

Use of peak area is required.

If cadmium is to be analyzed in concentration mode, use the 1.00 and 2.00 ug/L cadmium standards and follow the procedures for analyzing in the concentration mode.

Quality Control:

1. Establish a standard curve with the standards listed above plus a blank. Record the absorbance check standard in the absorbance check book. The absorbances should remain consistent from run to run. If not, necessary troubleshooting must be performed before continuing (check wavelength, furnace alignment, lamp alignment, graphite tube, etc.).

2. A quality control calibration standard of 1.00 ug/L is to be analyzed, at a minimum, after every 10 samples. If less than 10 samples are analyzed, a calibration standard is still required. The last sample analyzed in the run is to be the calibration standard. These standards must be within the acceptable ranges or the samples run after the last acceptable calibration standard are to be reanalyzed. Record the calibration standard in the quality control book. The confidence limits are noted in the quality control book.

3. A digested duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a digested duplicate and spike are still required. Duplicates are to be averaged. Spike samples with a standard of twice the concentration of the sample in a 1:1 ratio of sample to standards. Spike recoveries and duplicates are to be within acceptable ranges or the use of dilution, or method of standard additions is to be applied to reduce the interferences.

4. For every sample analyzed, an analytical spike (at the bench) must be run to verify that standard additions are not required. Criteria for standard additions is:

   a. If the spike recovery is within 85 - 115%, standard additions are not required.

   b. If the spike recovery is outside 85 - 115%, standard additions are required.

5. An EPA reference sample will be analyzed with each analysis.

Calculations:

1. Plot concentrations vs. peak area on graph. Determine unknowns using graph, or

2. Calculate using linear regression, or

3. Calculate using concentration mode.

Revision Dates

9/25/87

Michael Linskens 9/25/87
Michael J. Linskens
Laboratory Manager

Kim Finner
Kim D. Finner
Analytical Laboratory QA Officer

Lawrence D. Andersen
Lawrence D. Andersen
Vice President, Technical Services

CALCIUM

Method: AA - Flame; Direct Aspiration

Reference: EPA 1983, Method 215.1

"Analytical Methods for Atomic Absorption Spectrophotometry", 1982, Perkin-Elmer Corporation

Detection Limit: 0.05 mg/L

Optimum Concentration Range: 0.05 - 25.0 mg/L

Sampling Handling: Acidify with nitric acid to pH < 2. Drinking waters and filtered groundwater free of particulate matter and organics may be analyzed directly, while wastewaters, leachates, solids, etc. must be digested prior to analysis (refer to appropriate digestion procedures). Analyze within 6 months.

Instrument Conditions:

1. The Ca-Mg combination hollow cathode lamp is used. Set lamp energy to 25.
2. Wavelength: 422.7 nm
3. Slit Width: 0.7 Normal
4. Fuel: Acetylene
5. Oxidant: Air
6. Type of flame: Oxidizing, lean, blue
7. Standards to use for curve set-up: 2.00, 5.00, 10.00, 25.0 mg/L.

Reagent Preparation: (Prepare fresh every 6 months unless otherwise noted.)

1. Standard Calcium Solution (100 mg/L Calcium): Pipet 10 mL of the 1000 ppm stock calcium solution into a 100 mL volumetric flask, add 1/2 mL HNO_3, and dilute to the mark with Milli-Q water.
2. Standards (Prepare fresh every 2 months.):

Concentration of Standard	Volume of Calcium Standard	Dilute to
2.00 mg/L	2 mL of 100 mg/L Ca	100 mL
5.00 mg/L	5 mL of 100 mg/L Ca	100 mL
10.0 mg/L	10 mL of 100 mg/L Ca	100 mL
25.0 mg/L	25 mL of 100 mg/L Ca	100 mL

3. Lanthanum Chloride Solution: In a 500 mL volumetric flask, dissolve 29g of La_2O_3 slowly and in small portions, in 250 mL conc. HCL (CAUTION: Reaction is violent!) and dilute to 500 mL with Milli-Q water.

Notes:

1. Samples must be diluted to obtain concentrations within the optimum concentration range.

2. Standards are to be prepared in the same acid concentrations as the samples being analyzed.

3. Silicon, aluminum, phosphate and sulfate depress the signal for calcium. Lanthanum chloride is added as a matrix modifier to control these interferences.

Procedure: For the analysis procedure, refer to the Atomic Absorption Spectrometry, Flame - Direct Aspiration section of this manual but make the following changes:

1. Turn the burner head counter clockwise as far as it will go (approximately a 45° angle).

2. Lanthanum chloride solution is added as a matrix modifier to the samples and standards in a ratio of 1.0 mL lanthanum chloride solution to 10 mL samples, blanks and standards.

3. If calcium is to be run in the concentration mode, use the 5.00 and 25.0 standards and follow the procedure for analyzing in concentration mode.

Quality Control:

1. Establish a standard curve with the standards listed above plus a blank. Record the absorbance check standard in the absorbance check book. The absorbances should remain consistent from run to run. If not, necessary troubleshooting must be performed before continuing (check wavelength, flame head alignment, lamp alignment, etc.).

2. A quality control calibration standard of 10.0 mg/L is to be analyzed, at a minimum, after every 10 samples. If less than 10 samples are analyzed, a calibration standard is still required. The last sample analyzed in the run is to be the calibration standard. These standards must be within acceptable ranges or the samples run after the last acceptable check standard are to be reanalyzed. Record the calibration standards in the quality control book. The confidence limits are noted in the quality control book.

3. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Duplicates are to be averaged. Spike samples with a standard of twice the concentration of the sample in a 1:1 ratio of sample to standard. Spike recoveries and duplicates are to be within acceptable ranges or the use of dilution or method of standard additions is to be applied to reduce the interferences.

Calculations:

1. Plot concentration vs absorbance on graph. Determine unknowns using graph, or

2. Calculate using linear regression.

3. Calculate using the concentration mode.

	Revision Date
Michael Linskens 1/4/88	11-14-86
Michael J. Linskens Laboratory Manager	4-13-87
Kim Finner 1/6/88	1-6-88
Kim D. Finner Analytical Laboratory QA/QC Officer	
Lawrence D. Andersen 1/6/88	
Lawrence D. Andersen Vice President, Technical Services	

[ALM-8-7]

CHROMIUM

Method: AA - Flame; Direct Aspiration

Reference: EPA 1983, Method 218.1

"Analytical Methods for Atomic Absorption Spectrophotometry", 1982, Perkin-Elmer Corporation

Detection Limit: 0.05 mg/L

Optimum Concentration Range: 0.05 - 5.00 mg/L

Sample Handling: Acidify with nitric acid to pH < 2. Drinking waters and filtered groundwater free of particulate matter and organics may be analyzed directly, while wastewaters, leachates, solids, etc. must be digested prior to analysis (refer to appropriate digestion procedures). Analyze within 6 months.

Instrument Conditions:

1. Chromium hollow cathode lamp with lamp energy set at 25.
2. Wavelength: 357.9 nm
3. Slit Width: 0.7 Normal
4. Fuel: Acetylene
5. Oxidant: Air
6. Type of flame: Reducing, rich, yellow
7. Standards to use for curve set-up: 0.50, 1.00, 2.00, 5.00 mg/L.

Reagent Preparation: (Prepare fresh every 6 months unless otherwise noted.

1. Standard chromium solution (100 mg/L Chromiumn): Pipet 10 mL of the 1000 ppm stock chromium solution into a 100 mL volumetric flask, add 1/2 mL HNO^3, and dilute to the mark with DI water.

[V-600-99A]

2. Standards (Prepare fresh every 2 months.):

Concentration of Standard	Volume of Chromium Standard	Dilute to
0.50 mg/L	0.5 mL of 100 mg/L Cr	100 mL
1.00 mg/L	1 mL of 100 mg/L Cr	100 mL
2.00 mg/L	2 mL of 100 mg/L Cr	100 mL
5.00 mg/L	5 mL of 100 mg/L Cr	100 mL

3. Ammonium bifluoride (10%): Dissolve 10g of ammonium bifluoride and 2g of sodium sulfate in DI water. Dilute to 100 mL.

Notes:

1. Samples must be diluted to obtain concentrations within the optimum concentration range.

2. Standards are to be prepared in the same acid concentrations as the samples being analyzed.

3. A solution of ammonium bifluoride and sodium sulfate is added as a matrix modifier to control interferences from iron, nickel and other metals.

4. This flame procedure can be used for digested samples, EP Toxicity samples or any other samples where low detection limits are not required. EP Toxicity samples must be spiked to verify that standard additions are not requi$d.

Procedure: For the analysis procedure, refer to the Atomic Absorption Spectrometry, Flame - Direct Aspiration section of this manual.

Add 1 ml of ammonium bifluoride solution to 10 ml of samples, blanks, and standards.

If chromium is to be run in the concentration mode, use the 2.00 and 5.00 standards and follow the procedure for analyzing in the concentration mode.

Quality Control:

1. Establish a standard curve with the standards listed above plus a blank. Record the absorbance check standard in the absorbance check book. The absorbances should remain consistent from run to run. If not, necessary troubleshooting must be performed before continuing (check wavelength, flame head alignment, lamp alignment, etc.).

[V-600-99A]

2. A quality control calibration standard of 2.00 mg/L is to be analyzed, at a minimum, after every 10 samples. If less than 10 samples are analyzed, a calibration standard is still required. The last sample analyzed in the run is to be the calibration standard. These standards must be within the acceptable ranges or the samples run after the last acceptable check standard are to be reanalyzed. Record the calibration standards in the quality control book. The confidence limits are noted in the quality control book.

3. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Duplicates are to be averaged. Spike samples with a standard of twice the concentration of the sample in a 1:1 ratio of sample to standard. Spike recoveries and duplicates are to be within acceptable ranges or the use of dilution or method of standard additions is to be applied to reduce the interferences.

Calculations:

1. Plot concentration vs absorbance on graph. Determine unknowns using graph or

2. Calculate using linear regression or

3. Calculate using the concentration mode.

[V-600-99A]

CHROMIUM

Method: AA - Furnace; Direct Injection

Reference: EPA 1983, Method 218.2

"Analytical Methods for Furnace Atomic Absorption Spectrophotometry", 1982, Perkin-Elmer Corporation

"Techniques in Graphite Furnace Atomic Absorption Spectrophotometry", 1985, Perkin-Elmer Corporation

Contract Laboratory Program, "Statement of Work", July, 1985

Detection Limit: 0.0002 mg/L

Optimum Concentration Range: 0.0002 - 0.010 mg/L

Sample Handling: Acidify with nitric acid to pH < 2. Drinking waters and filtered groundwater free of particulate matter and organics may be analyzed directly, while wastewaters, leachates, solids, etc. must be digested prior to analysis (refer to appropriate digestion procedures). Analyze within 6 months.

Instrument Conditions:

1. Chromium hollow cathode lamp with lamp energy set at 25.

2. Wavelength: 357.9 nm

3. Slit Width: 0.7 Alternate

4. Mode: Peak height

5. HGA Furnace Programming:

Step 1:	130	(dry temp)	15	(ramp time)	15	(hold time)
Step 2:	1000	(char temp)	10	(ramp time)	15	(hold time)
Step 3:	2300	(atom temp)	0	(ramp time)	3	(hold time)

* Also press the read, record and stop flow buttons; enter t = 3 sec

Step 4:	2300	(max temp)	0	(ramp time)	3	(hold time)

Press the record button.

6. Sample Volume: 20 uL

7. Standards to use for curve set-up: 1.00, 5.00, 10.0 ug/L.

Reagent Preparation:

1. Standard Chromium Solution (1000 ug/L Chromium): Pipet 1.00 mL of the 1000 ppm stock Chromium solution into a 1000 mL volumetric flask, add 1/2 mL HNO_3, and dilute to the mark with Milli-Q water. Prepare fresh every month.

2. Working Chromium Standard (100 ug/L Chromium): Pipet 10 mL of the 1000 ug/L chromium into a 100 mL volumetrick flask and dilute to the mark with Milli-Q water. Prepare fresh every month.

3. Standards (Prepare fresh every week.):

Concentration of Standard	Volume of Chromium Standard	Dilute to
1.00 ug/L	1.0 mL of 100 ug/L Cr	100 mL
5.00 ug/L	5.0 mL of 100 ug/L Cr	100 mL
10.0 ug/L	10.0 mL of 100 ug/L Cr	100 mL

4. Calcium Nitrate: 11.8g $Ca(NO_3)_2$, dilute to 100 mL a volumetric flask.

5. Hydrogen Peroxide: 30% H_2O_2, purchased.

6. Mixed $Ca(NO_3)$ + H_2O_2 Solution: 10 mL $Ca(NO_3)_2$ mL in a volumetric flask solution + 10 mL H_2O_2, dilute to 100 mL.

Notes:

1. Samples must be diluted to obtain concentrations within the optimum concentration range.

2. Standards are to be prepared in the same acid concentrations as the samples being analyzed.

3. Low concentrations of calcium may cause interferences, yet at concentrations above 200 mg/L calcium, the effect is constant. To ensure a constant effect, calcium is added as a matrix modifier.

4. 30% hydrogen peroxide is added (1 mL of 30% H_2O_2 to 100 mL sample and standards) to convert all chromium to the trivalent state.

5. Be careful when reporting units!

Procedure: For the analysis procedure, refer to the Atomic Absorption Spectrometry, Furnace - Direct Injection section of this manual.

To 10 mL of samples, standards, and blanks add 1 mL of the $Ca(NO_3)$ + H_2O_2 solution.

If chromium is to be analyzed in concentration mode, use the 5.00 and 10.0 ug/L chromium standards and follows the procedure for analyzing in the concentration mode.

Quality Control:

1. Establish a standard curve with the standards listed above plus a blank. Record the absorbance check standard in the absorbance check book. The absorbances should remain consistent from run to run. If not, necessary troubleshooting must be performed before continuing (check wavelength, furnace alignment, lamp alignment, graphite tube, etc.).

2. A quality control calibration standard of 5.0 ug/l is to be analyzed, at a minimum, after every 10 samples. If less than 10 samples are analyzed, a calibration standard is still required. The last sample analyzed in the run is to be the calibration standard. These standards must be within acceptable ranges or the samples run after the last acceptable calibration standard are to be reanalyzed. Record the calibration standard in the quality control book. The confidence limits are noted in the quality control book.

3. Digest a duplicate and spike; a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a digested duplicate and spike are still required. Duplicates are to be averaged. Spike samples with a standard of twice the concentration of the sample in a 1:1 ratio of sample to standards. Spike recoveries and duplicate results are to be within acceptable ranges or the use of dilution, or method of standard additions is to be applied to reduce the interferences.

4. For every sample analyzed, an analytical spike (at the bench) must be run to verify that standard additions are not required. Criteria for standard additions are:

   a. If the spike recovery is within 85-115%, standard additions are not required.

   b. If the spike recovery is outside 85 - 115%, standard additions are required.

5. An EPA reference sample will be analyzed with each analysis.

Calculations:

1. Plot concentrations vs. absorbance (or peak height) on graph. Determine unknowns using graph, or

2. Calculate using linear regression, or

3. Calculate using the concentration mode.

	Revision Date
Michael Linskens 1/4/88 Michael J. Linskens Laboratory Manager	11-14-86 4-13-87
Kim Finner 1/6/88 Kim D. Finner Analytical Laboratory QA/QC Officer	1-6-88
Lawrence D. Andersen 1/6/88 Lawrence D. Andersen Vice President, Technical Services	

COBALT

Method: AA - Flame; Direct Aspiration

Reference: EPA 1983, Method 219.1

"Analytical Methods for Atomic Absorption Spectrophotometry", 1982, Perkin-Elmer Corporation

Detection Limit: 0.05 mg/L

Optimum Concentration Range: 0.05 - 5.00 mg/L

Sample Handling: Acidify with nitric acid to pH < 2. Drinking waters and filtered groundwater free of particulate matter and organics may be analyzed directly, while wastewaters, leachates, solids, etc. must be digested prior to analysis (refer to appropriate digestion procedures). Analyze within 6 months.

Instrument Conditions:

1. Cobalt hollow cathode lamp with lamp energy set at 7.
2. Wavelength: 240.7 nm
3. Slit Width: 0.2 Normal
4. Fuel: Acetylene
5. Oxidant: Air
6. Type of flame: Oxidizing, lean, blue
7. Standards to use for curve set-up: 0.50, 1.00, 2.00, 5.00 mg/L.

Reagent Preparation: Prepare fresh every 6 months unless otherwise noted.

1. Standard Cobalt Solution (10.0 mg/L Cobalt): Pipet 1.0 mL of the 1000 ppm stock cobalt solution into a 100 mL volumetric flask, add 1/2 ml HNO_3 and dilute to the mark with Milli-Q water.
2. Standards (Prepare fresh every month.):

Concentration of Standard	Volume of Cobalt Standard	Dilute to
0.50 mg/L	5 mL of 10.0 mg/L Co	100 mL
1.00 mg/L	10 mL of 10.0 mg/L Co	100 mL
2.00 mg/L	20 mL of 10.0 mg/L Co	100 mL
5.00 mg/L	50 mL of 10.0 mg/L Co	100 mL

Notes:

1. Samples must be diluted to obtain concentrations within the optimum concentration range.

2. Standards are to be prepared in the same acid concentrations as the samples being analyzed.

3. The use of background correction is required.

4. This flame procedure can be used for digested samples, EP Toxicity samples or any other samples where high concentrations of cobalt (concentrations greater than 0.50 mg/L) are expected and low detection limits are not required.

Procedure: For the analysis procedure, refer to the Atomic Absorption Spectrometry, Flame - Direct Aspiration section of this manual.

If cobalt is to be analyzed in concentration mode, use the 2.00 and 5.00 standards and follow the procedure for analyzing in the concentration mode.

Quality Control:

1. Establish a standard curve with the standards listed above plus a blank. Record the absorbance check standard in the absorbance check book. The absorbances should remain consistent from run to run. If not, necessary troubleshooting must be performed before continuing (check wavelength, flame head alignment, lamp alignment, etc.).

2. A quality control calibration standard of 1.00 mg/L is to be analyzed, at a minimum, after every 10 samples. If less than 10 samples are analyzed, a calibration standard is still required. The last sample analyzed in the run is to be the calibration standard. These standards must be within acceptable ranges or the samples run after the last acceptable check standard are to be reanalyzed. Record the calibration standards in the quality control book. The confidence limits are noted in the quality control book.

3. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Duplicates are to be averaged. Spike samples with a standard of twice the concentration of the sample in a 1:1 ratio of sample to standard. Spike recoveries and duplicates are to be within acceptable ranges or the use of dilution or method of standard additions is to be applied to reduce the interferences.

Calculations:

1. Plot concentration vs absorbance on graph. Determine unknowns using graph, or

2. Calculate using linear regression, or

3. Calculate using concentration mode.

[ALM-8-14]

COPPER

Method: AA - Flame; Direct Aspiration

Reference: EPA 1983, Method 220.1

"Analytical Methods for Atomic Absorption Spectrophotometry", 1982, Perkin-Elmer Corporation

Detection Limit: 0.02 mg/L

Optimum Concentration Range: 0.02 - 5.00 mg/L

Sample Handling: Acidify with nitric acid to pH < 2. Drinking waters and filtered groundwater free of particulate matter and organics may be analyzed directly, while wastewaters, leachates, solids, etc. must be digested prior to analysis (refer to appropriate digestions procedures). Analyze within 6 months.

Instrument Conditions:

1. The Copper hollow cathode lamp is used. Set lamp energy to 18.
2. Wavelength: 324.7 nm
3. Slit Width: 0.7 Normal
4. Fuel: Acetylene
5. Oxidant: Air
6. Type of flame: Oxidizing, lean, blue
7. Standards to use for curve set-up: 0.50, 1.00, 2.00, 5.00 mg/L.

Reagent Preparation: (Prepare fresh every 6 months unless otherwise noted.)

1. Standard Copper Solution (100 mg/L Copper): Pipet 10 mL of the 1000 ppm stock copper solution into a 100 mL volumetric flask, add 1/2 mL HNO_3, and dilute to the mark with Milli-Q water.
2. Standards (Prepare fresh every month.):

Concentration of Standard	Volume of Copper Standard	Dilute to
0.50 mg/L	0.5 mL of 100 mg/L Cu	100 mL
1.00 mg/L	1 mL of 100 mg/L Cu	100 mL
2.00 mg/L	2 mL of 100 mg/L Cu	100 mL
5.00 mg/L	5 mL of 100 mg/L Cu	100 mL

Notes:

1. Samples must be diluted to obtain concentrations within the optimum concentration range.

2. Standards are to be prepared in the same acid concentrations as the samples being analyzed.

3. The use of background correction is required.

Procedure: For the analysis procedure, refer to the Atomic Absorption Spectrometry, Flame - Direct Aspiration section of this manual.

If copper is to be run in the concentration mode, use the 2.00, and 5.00 mg/L copper standards and follow the procedure for analyzing in the concentration mode.

Quality Control:

1. Establish a standard curve with the standards listed above plus a blank. Record the absorbance check standard in the absorbance check book. The absorbances should remain consistent from run to run. If not, necessary troubleshooting must be performed before continuing (check wavelength, flame head alignment, lamp alignment, etc.).

2. A quality control calibration standard of 1.00 mg/L is to be analyzed, at a minimum, after every 10 samples. If less than 10 samples are analyzed, a calibration standard is still required. The last sample analyzed in the run is to be the calibration standard. These standards must be within acceptable ranges or the samples run after the last acceptable check standard are to be reanalyzed. Record the calibration standards in the quality control book. The confidence limits are noted in the quality control book.

3. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Duplicates are to be averaged. Spike samples with a standard of twice the concentration of the sample in a 1:1 ratio of sample to standard. Spike recoveries and duplicates are to be within acceptable ranges or the use of dilution or method of standard additions is to be applied to reduce the interferences.

Calculations:

1. Plot concentration vs absorbance on graph. Determine unknowns using graph, or

2. Calculate using linear regression, or

3. Calculate using the concentration mode.

IRON

Method: AA - Flame; Direct Aspiration

Reference: EPA 1983, Method 236.1

"Analytical Methods for Atomic Absorption Spectrophotometry", 1982, Perkin-Elmer Corporation

Detection Limit: 0.05 mg/L

Optimum Concentration Range: 0.05 - 5.00 mg/L

Sample Handling: Acidify with nitric acid to pH < 2. Drinking waters and filtered groundwater free of particulate matter and organics may be analyzed directly, while wastewaters, leachates, solids, etc. must be digested prior to analysis (refer to appropriate digestion procedures). Analyze within 6 months.

Instrument Conditions:

1. The Iron hollow cathode lamp is used. Set lamp energy to 18.
2. Wavelength: 248.3 nm
3. Slit Width: 0.2 Normal
4. Fuel: Acetylene
5. Oxidant: Air
6. Type of flame: Oxidizing, lean, blue
7. Standards to use for curve set-up: 0.50, 1.00, 2.00, 5.00 mg/L.

Reagent Preparation: (Prepare fresh every 6 months unless otherwise noted.)

1. Standard Iron Solution (100 mg/L Iron): Pipet 10 mLs of the 1000 ppm stock iron solution into a 100 mL volumetric flask, add 1/2mL HNO_3, and dilute to the mark with Milli-Q water.
2. Standards (Prepare fresh every month.):

Concentration of Standard	Volume of Iron Standard	Dilute to
0.50 mg/L	1/2 mL of 100 mg/L Fe	100 mL
1.00 mg/L	1 mL of 100 mg/L Fe	100 mL
2.00 mg/L	2 mL of 100 mg/L Fe	100 mL
5.00 mg/L	5 mL of 100 mg/L Fe	100 mL
10.0 mg/L	10 mL of 100 mg/L Fe	100 mL
25.0 mg/L	25 mL of 100 mg/L Fe	100 mL
50.0 mg/L	50 mL of 100 mg/L Fe	100 mL
75.0 mg/L	75 mL of 100 mg/L Fe	100 mL

Notes:

1. Be very careful when scaling in wavelength, a nearby one exists.

2. Samples must be diluted to obtain concentrations within the optimum concentration range.

3. Standards are to be prepared in the same acid concentrations as the samples being analyzed.

4. The use of background correction is required.

5. An alternate wavelength of 373.7 nm can be used for high iron concentrations (concentrations greater than 5.00 mg/L). The optimum concentration range at this wavelength is 1.00 - 100 mg/L iron. Standards to use are: 1.00, 10.0, 25.0, 50.0 mg/L. The quality control calibration standard is the 10.0 mg/L iron standard. All other instrument conditions remain the same as those at the 248.3 nm wavelength.

Procedure: For the analysis procedure, refer to the Atomic Absorption Spectrometry, Flame - Direct Aspiration section of this manual.

If iron is to be run in the concentration mode, use the 2.00 and 5.00 mg/L iron standards (use the 25.0 and 75.0 mg/L iron standards if using the 373.7 nm wavelength) and follow the procedure for analyzing in the concentration mode.

Quality Control:

1. Establish a standard curve with the standards listed above plus a blank. Record the absorbance check standard in the absorbance check book. The absorbances should remain consistent from run to run. If not, necessary troubleshooting must be performed before continuing (check wavelength, flame head alignment, lamp alignment, etc.).

2. A quality control calibration standard of 0.50 mg/L is to be analyzed, at a minimum, after every 10 samples. If less than 10 samples are analyzed, a calibration standard is still required. The last sample analyzed in the run is to be the calibration standard. These standards must be within acceptable ranges or the samples run after the last acceptable check standard are to be reanalyzed. Record the calibration standards in the quality control book. The confidence limits are noted in the quality control book.

3. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Duplicates are to be averaged. Spike samples with a standard of twice the concentration of the sample in a 1:1 ratio of sample to standard. Spike recoveries and duplicates are to be within acceptable ranges or the use of dilution or method of standard additions is to be applied to reduce the interferences.

Calculations:

1. Plot concentration vs absorbance on graph. Determine unknowns using graph, or

2. Calculate using linear regression, or

3. Calculate using the concentration mode.

[ALM-8-3]

LEAD

Method: AA - Flame; Direct Aspiration

Reference: EPA 1983, Method 239.1

"Analytical Methods for Atomic Absorption Spectrophotometry", 1982, Perkin-Elmer Corporation

Detection Limit: 0.10 mg/L

Optimum Concentration Range: 0.10 - 10.0 mg/L

Sample Handling: Acidify with nitric acid to pH < 2. Drinking waters and filtered groundwater free of particulate matter and organics may be analyzed directly, while wastewaters, leachates, solids, etc. must be digested prior to analysis (refer to appropriate digestion procedure). Analyze within 6 months.

Instrument Conditions:

1. Lead electrodeless dishcarge lamp with lamp energy set at 10.
2. Wavelength: 283.3 nm
3. Slit Width: 0.7 Normal
4. Fuel: Acetylene
5. Oxidant: Air
6. Type of flame: Oxidizing, lean, blue
7. Standards to use for curve set-up: 1.00, 2.00, 5.00, 10.0 mg/L.

Reagent Preparation: Prepare fresh every 6 months unless otherwise noted.

1. Standard Lead Solution (100 mg/L Lead): Pipet 10 mL of the 1000 ppm stock lead solution into a 100 mL volumetric flask, add 1/2 mL HNO_3, and dilute to the mark with Milli-Q water.
2. Standards (Prepare fresh every month.):

Concentration of Standard	Volume of Lead Standard	Dilute to
1.00 mg/L	1 mL of 100 mg/L Pb	100 mL
2.00 mg/L	2 mL of 100 mg/L Pb	100 mL
5.00 mg/L	5 mL of 100 mg/L Pb	100 mL
10.0 mg/L	10 mL of 100 mg/L Pb	100 mL

Notes:

1. Samples must be diluted to obtain concentrations within the optimum concentration range.

2. Standards are to be prepared in the same acid concentrations as the samples being analyzed.

3. The use of background correction is required.

4. This flame procedure can be used for digested samples, EP Toxicity samples or any other samples where low detection limits are not required. EP Toxicity samples must be spiked to verify that standard additions are not required.

Procedure: For the analysis procedure, refer to the Atomic Absorption Spectrometry, Flame - Direct Aspiration section of this manual.

If lead is to be analyzed by the concentration mode, use the 5.00 and 10.00 mg/L lead standards and follow the procedure for analyzing in the concentration mode.

Quality Control:

1. Establish a standard curve with the standards listed above plus a blank. Record the absorbance check standard in the absorbance check book. The absorbances should remain consistent from run to run. If not, necessary troubleshooting must be performed before continuing (check wavelength, flame head alignment, lamp alignment, etc.).

2. A quality control calibration standard of 5.00 mg/L is to be analyzed, at a minimum, after every 10 samples. If less than 10 samples are analyzed, a calibration standard is still required. The last sample analyzed in the run is to be the calibration standard. These standards must be within acceptable ranges or the samples run after the last acceptable check standard are to be reanalyzed. Record the calibration standards in the quality control book. The confidence limits are noted in the quality control book.

3. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Duplicates are to be averaged. Spike samples with a standard of twice the concentration of the sample in a 1:1 ratio of sample to standard. Spike recoveries and duplicates must be within acceptable ranges or the use of dilution or method of standard additions is to be applied to reduce the interferences.

Calculations:

1. Plot concentration vs absorbance on graph. Determine unknowns using graph or

2. Calculate using linear regression or

3. Calculate using the concentration mode.

LEAD

Method: AA - Furnace; Direct Injection

Reference: EPA 1983, Method 239.2

"Analytical Methods for Furnace Atomic Absorption Spectrophotometry", 1982, Perkin-Elmer Corporation

"Techniques in Graphite Furnace Atomic Absorption Spectrophotometry", 1985, Perkin-Elmer Corporation

Contract Laboratory Program, "Statement of Work", July 1985

Detection Limit: 0.003 mg/L

Optimum Concentration Range: 0.003 - 0.050 mg/L

Sample Handling: Acidify with nitric acid to pH < 2. Drinking waters and filtered groundwater free of particulate matter and organics may be analyzed directly, while wastewaters, leachates, solids, etc. must be digested prior to analysis (refer to appropriate digestion procedures). Analyze within 6 months.

Instrument Conditions:

1. Lead electrodeless discharge lamp with lamp energy set at 10.

2. Wavelength: 283.3 nm

3. Slit Width 0.7 Alternate

4. Mode: Peak height

5. HGA Furnace Programming:

Step 1:	130	(dry temp)	10	(ramp time)	20	(hold time)
Step 2:	500	(char temp)	15	(ramp time)	10	(hold time)
Step 3:	2400	(atom temp)	2	(ramp time)	2	(hold time)

* Also press the read, record and stop flow buttons; enter t = 4 sec.

Step 4:	2400	(max temp)	2	(ramp time)	2	(hold time)

Press record button.

6. Sample Volume: 20 uL

7. Standards to use for curve set-up: 5.0, 10.0, 20.0, 50.0 ug/L.

Reagent Preparation:

1. Standard Lead Solution (1000 ug/L Lead): Pipet 1.00 mL of the 1000 ppm stock lead solution into a 1000 mL volumetric flask, add 1/2 mL HNO_3, and dilute to the mark with Milli-Q water. Prepare fresh every month.

2. Standards (Prepare fresh every week.):

Concentration of Standard	Volume of Lead Standard	Dilute to
5.0 ug/L	1/2 mL of 1000 ug/L Pb	100 mL
10.0 ug/L	1 mL of 1000 ug/L Pb	100 mL
20.0 ug/L	2 mL of 1000 ug/L Pb	100 mL
50.0 ug/L	5 mL of 1000 ug/L Pb	100 mL

3. Lanthanum Nitrate Solution: Dissolve 58.64g of La_2O_3 in 100 mL concentrated nitric acid and dilute to 1000 mL with Milli-Q water.

Notes:

1. Samples must be diluted to obtain concentrations within the optimum concentration range.

2. Standards are to be prepared in the same acid concentrations as the samples being analyzed.

3. The use of background correction is required.

4. Sulfate is a negative interference for lead. Lanthanum nitrate solution is added as a matrix modifier in a 1:10 ratio of lanthanum nitrate to sample and standards prior to analysis.

5. Be careful when reporting units!

Procedure: For the analysis procedure, refer to the Atomic Absorption Spectrometry, Furnace - Direct Injection section of this manual.

To 10 mL samples, blanks and standards, add 1 mL of $La(NO_3)_2$ solution.

If lead is to be analyzed in concentration mode, use the 20.0 and 50.0 ug/L lead standard and follow the procedure for analyzing in the concentration mode.

Quality Control:

1. Establish a standard curve with the standards listed above plus a blank. Record the absorbance check standard in the absorbance check book. The absorbances should remain consistent from run to run. If not, necessary troubleshooting must be performed before continuing (check wavelength, furnace alignment, lamp alignment, graphite tube, etc.).

2. A quality control calibration standard of 20.0 ug/l is to be analyzed, at a minimum, after every 10 samples. If less than 10 samples are analyzed, a calibration standard is still required. The last sample analyzed in the run is to be the calibration standard. These standards must be within acceptable ranges or the samples run after the last acceptable calibration standard are to be reanalyzed. Record the calibration standard in the quality control book. The confidence limits are noted in the quality control book.

3. Digest a duplicate and spike; a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a digested duplicate and spike are still required. Duplicates are to be averaged. Spike samples with a standard of twice the concentration of the sample in a 1:1 ratio of sample to standards. Spike recoveries and duplicate results are to be within acceptable ranges or the use of dilution, or method of standard additions is to be applied to reduce the interferences.

4. For every sample analyzed, an analytical spike (at the bench) must be run to verify that standard additions are not required. Criteria for standard additions are:

   a. If the spike recovery is within 85-115%, standard additions are not required.

   b. If the spike recovery is outside 85 - 115%, standard additions are required.

5. An EPA reference sample will be analyzed with each analysis.

Calculations:

1. Plot concentrations vs. absorbance (or peak height) on graph. Determine unknowns using graph, or

2. Calculate using linear regression, or

3. Calculate using the concentration mode.

	Revision Date
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Kim Finner 1/6/88 Kim D. Finner Analytical Laboratory QA/QC Officer	1-6-88
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[ALM-8a-22]

MAGNESIUM

Method: AA - Flame; Direct Aspiration

Reference: EPA 1983, Method 242.1

"Analytical Methods for Atomic Absorption Spectrophotometry", 1982, Perkin-Elmer Corporation

Detection Limit: 0.05 mg/L

Optimum Concentration Range: 0.05 - 10.0 mg/L

Sample Handling: Acidify with nitric acid to pH < 2. Drinking waters and filtered groundwater free of particulate matter and organics may be analyzed directly, while wastewaters, leachates, solids, etc. must be digested prior to analysis (refer to appropriate digestion procedure). Analyze within 6 months.

Instrument Conditions:

1. The Ca-Mg combination hollow cathode lamp is used. Set lamp energy to 25.
2. Wavelength: 285.2 nm
3. Slit Width: 0.7 Normal
4. Fuel: Acetylene
5. Oxidant: Air
6. Type of flame: Oxidizing, lean, blue
7. Standards to use for curve set-up: 1.00, 2.00, 5.00, 10.0 mg/L.

Reagent Preparation: Prepare fresh every 6 months unless otherwise noted.

1. Standard Magnesium Solution (100 mg/L Magnesium): Pipet 10 mL of the 1000 ppm stock magnesium solution into a 100 mL volumetric flask, add 1/2 mL HNO_3, and dilute to the mark with Milli-Q water.
2. Standards (Prepare fresh every month.):

Concentration of Standard	Volume of Magnesium Standard	Dilute to
1.0 mg/L	1 mL of 100 mg/L Mg	100 mL
2.0 mg/L	2 mL of 100 mg/L Mg	100 mL
5.0 mg/L	5 mL of 100 mg/L Mg	100 mL
10.0 mg/L	10 mL of 100 mg/L Mg	100 mL

3. Lanthanum Chloride Solution: In a 500 mL volumetric flask, dissolve 29 g La_2O_3, in small portions, in 250 mL of concentrated HCL (CAUTION-Reaction is violent!), and dilute to mark with Milli-Q water.

Notes:

1. Samples must be diluted to obtain concentrations within the optimum concentration range.

2. Standards are to be prepared in the same acid concentrations as the samples being analyzed.

3. The use of background correction is required.

4. Silicon and aluminium depress the signal for magnesium. Lanthanum chloride is added as a matrix modifier to control these interferences.

5. Sodium, POtassium and Calcium can interfere if above concentrations of 400 mg/L.

Procedure: For the analysis procedure, refer to the Atomic Absorption Spectrometry, Flame - Direct Aspiration section of this manual but make the following changes:

1. Turn the burner head counter clockwise as far as it will go (approximately a 45° angle).

2. Lanthanum chloride solution is added as a matrix modifier to the samples, standards, and blanks, in a ratio of 1 mL Lanthanum chloride solution to 10 mL sample or standard.

3. If magnesium is to be analyzed in concentration mode, use the 5.0 and 10.0 standards and follow the procedure for analyzing in the concentration mode.

Quality Control:

1. Establish a standard curve with the standards listed above plus a blank. Record the absorbance check standard in the absorbance check book. The absorbances should remain consistent from run to run. If not, necessary troubleshooting must be performed before continuing (check wavelength, flame head alignment, lamp alignment, etc.).

2. A quality control calibration standard of 5.0 mg/L is to be analyzed, at a minimum, after every 10 samples. If less than 10 samples are analyzed, a calibration standard is still required. The last sample analyzed in the run is to be the calibration standard. These standards must be within acceptable ranges or the samples run after the last acceptable check standard are to be reanalyzed. Record the calibration standard in the quality control book. The confidence limits are noted in the quality control book.

3. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Duplicates are to be averaged. Spike samples with a standard of twice the concentration of the sample in a 1:1 ratio of sample to standard. Spike recoveries and duplicates are to be within acceptable ranges or the use of dilution or method of standard additions is to be applied to reduce the interferences.

Calculations:

1. Plot concentration vs absorbance on graph. Determine unknowns using graph, or

2. Calculate using linear regression.

3. Calculate using concentration mode.

[ALM-8-6]

MANGANESE

Method: AA - Flame; Direct Aspiration

Reference: EPA 1983, Method 243.1

"Analytical Methods for Atomic Absorption Spectrophotometry", 1982, Perkin-Elmer Corporation

Detection Limit: 0.02 mg/L

Optimum Concentration Range: 0.02 - 2.50 mg/L

Sample Handling: Acidify with nitric acid to pH < 2. Drinking waters and filtered groundwater free of particulate matter and organics may be analyzed directly, while wastewaters, leachates, solids, etc. must be digested prior to analysis (refer to appropriate digestion procedures). Analyze within 6 months.

Instrument Conditions:

1. The Manganese hollow cathode lamp is used. Set lamp energy to 18.
2. Wavelength: 279.5 nm
3. Slit Width: 0.2 Normal
4. Fuel: Acetylene
5. Oxidant: Air
6. Type of flame: Oxidizing, lean, blue
7. Standards to use for curve set-up: 0.25, 0.50, 1.00, 2.50 mg/L.

Reagent Preparation: Prepare fresh every 6 months unless otherwise noted.

1. Standard Manganese Solution (100 mg/L Manganese): Pipet 10 mL of the 1000 ppm stock manganese solution into a 100 mL volumetric flask, add 1/2 mL HNO_3 and dilute to the mark with Milli-Q water.
2. Standards (Prepare fresh every month.):

Concentration of Standard	Volume of Manganese Standard	Dilute to
0.25 mg/L	1/2 mL of 1.00 mg/L Mn	100 mL
0.50 mg/L	1 mL of 50 mg/L Mn	100 mL
1.00 mg/L	2 mL of 50 mg/L Mn	100 mL
2.50 mg/L	5 mL of 50 mg/L Mn	100 mL

Notes:

1. Samples must be diluted to obtain concentrations within the optimum concentration range.

2. Standards are to be prepared in the same acid concentrations as the samples being analyzed.

3. The use of background correction is required.

Procedure: For the analysis procedure, refer to the Atomic Absorption Spectrometry, Flame - Direct Aspiration section of this manual.

If manganese is to be run in the concentration mode, use the 1.00, and 2.50 mg/L manganese standards and follow the procedure for analyzing in the concentration mode.

Quality Control:

1. Establish a standard curve with the standards listed above plus a blank. Record the absorbance check standard in the absorbance check book. The absorbances should remain consistent from run to run. If not, necessary troubleshooting must be performed before continuing (check wavelength, flame head alignment, lamp alignment, etc.).

2. A quality control calibration standard of 0.50 mg/L is to be analyzed, at a minimum, after every 10 samples. If less than 10 samples are analyzed, a calibration standard is still required. The last sample analyzed in a run is to be the calibration standard. These standards must be within acceptable ranges or the samples run after the last acceptable check standard are to be reanalyzed. Record the calibration standards in the quality control book. The confidence limits are noted in the quality control book.

3. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Duplicates are to be averaged. Spike samples with a standard of twice the concentration of the sample in a 1:1 ratio of sample to standard. Spike recoveries and duplicate results are to be within acceptable ranges or the use of dilution or method of standard additions is to be applied to reduce the interferences.

Calculations:

1. Plot concentration vs absorbance on graph. Determine unknowns using graph, or

2. Calculate using linear regression, or

3. Calculate using the concentration mode.

[ALM-8-5]

TOTAL MERCURY
Liquid Samples

Scope and Application: This method is applicable to drinking, surface, groundwater, domestic, and industrial wastewaters.

Method: Manual Cold Vapor

Reference: EPA 1983, Method 245.1

Detection Limits: 0.0002 mg/L (in 100 mL sample)

Optimum Range: 0.0002-0.010 mg/L

Sample Handling: Preserve with concentrated HNO_3 to pH <2. Analyze within 28 days of sampling.

Reagents and Apparatus:

1. Mercury cold-vapor Analyzer System
2. Water bath set @ 95*C
3. BOD bottles; 300 mL
4. Class A volumetric glassware
5. Instra-Analyzed sulfuric acid
6. Instra-analyzed nitric acid
7. Potassium persulfate
8. Potassium permanganate
9. Sodium chloride
10. Hydroxylamine hydrochloride solution
11. Stannous chloride
12. Various Class A volumetric pipettes
13. Mercury lamp
14. Mercury stock and standard solutions
15. Drierite
16. Activated charcoal
17. Glass wool
18. Tygon tubing

Reagent Preparation: (Prepare fresh every 6 months, unless otherwise noted.)

1. Sulfuric acid (0.5 N): Pipet 14.0 mL of conc. H_2SO_3 to 500 mL D.I. water in a 1 liter volumetric flask, dilute to the mark. PREPARE IN THE HOOD!

2. Stannous chloride (10% w/v): Add 100.0 g stannous chloride to 1 liter of 0.5 N sulfuric acid.

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3. Sodium chloride-hydrdoxylamine hydrochloride solution: Dissolve 120.0 g of sodium chloride and 120.0 g of hydroxylamine hydrochloride in D.I. water, dilute to 1 liter.

4. Potassium permanganate (5% solution, w/v): Dissolve 50.0 g of potassium permanganate in D.I. water, dilute to 1 liter.

5. Potassium persulfate (5% solution, w/v): Dissolve 50.0 g of potassium persulfate in D.I. water, dilute to 1 liter.

6. Intermediate mercury standard (10.0 mg/L): Transfer 1.0 mL stock mercury (1000 mg/L) solution, plus 1/2 mL nitric acid, into a 100 mL volumetric flask and dilute to the mark with D.I. water. Prepare fresh daily!

7. Working mercury standard (0.100 mg/L): Transfer 1.0 mL of the 10.0 mg/L intermediate standard, plus 1/2 mL nitric acid, into a 100 mL volumetric flask and dilute to the mark with D.I. water. Prepare fresh daily!

Notes:

1. The mercury standards are volatile and unstable. Standards must be prepared daily.

2. Because of the toxic nature of mercury vapor, precaution must be taken to avoid inhalation. Vent the mercury vapor into an exhaust hood or pass the vapor through an absorbing media.

3. A 10% solution of stannous sulfate may be substituted for stannous chloride.

4. Hydroxylamine sulfate may be used rather than hydroxylamine hydrochloride.

5. Standard additions must be used for all EP extracts and delisting petitions.

6. The calibration check standard is a 0.005 mg/L standard.

7. Interferences:

   a. Potassium permanganate is added to eliminate interferences from sulfide. Concentrations as high as 20 mg/L sulfide as sodium sulfide do not interfere.

   b. Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/L have no effect on recovery of mercury from spiked samples.

[C-600-82]

c. Seawaters, brines, and industrial effluents, high in chlorides, will require additional potassium permanganate. During the oxidation step, chlorides are converted to free chlorine which also absorbs at the same wavelength as mercury. Care must 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 chloride reagent. In addition, the dead air space in the BOD bottle must be purged before adding the stannous sulfate.

d. Certain volatile organic materials that absorb at this wavelength may also cause an interference. A preliminary run without reagents should determine if this type of interference is present.

Instrument Conditions:

1. Mercury electrodeless discharge lamp with lamp energy set at 6.
2. Wavelength: 253.6 nm. Background is required.
3. Slit Width: 0.7
4. Mode: Peak height
5. Time = 25 seconds
6. Standards to use for curve set-up: 2.0, 5.0, 10.0 ug/L.

Cold Vapor System Set-up:

Cell Alignment:

1. Insert quart cell in burner chamber. (Replace the burner head in the burner chamber.)
2. Align cell in light path (use 0.5 sec t, adjust to the lowest abs. reading).
3. Check drying tube and charcoal tube - replace if necessary (see attached page).
4. Insert aerator into a BOD bottle filled with 100 mLs D.I. water.
5. Turn on pump. Turn on strip recorder.
6. Let warm-up a few minutes.
7. Zero machine.

Procedure:

All glassware is to be washed with soap and water, rinsed with tap water, acid rinsed with 10% HNO_3, and final rinsed with D.I. water.

A. Standard Preparation

1. The standard curve is to consist of the following standards:

Standard Concentration
0.00 ug/L
2.00 ug/L
5.00 ug/L
10.0 ug/L

2. Pipet 0, 2.0, 5.0, and 10.0 mL aliquots of 0.10 ug/mL working stock mercury solution to 300 mL BOD bottles.

3. Add D.I. water to bring volume to 100 mL and continue with the digestion procedure.

B. Sample Preparation:

1. Transfer 100 mL, or an aliquot diluted to 100 mL, to a 300 mL BOD bottle.

   To Spike: Pipette 5.0 mL of 0.10 mg/L standard into the sample bottle. Proceed as written.

C. Digestion:

1. Add 5 mL conc. sulfuric acid and 2.5 mL conc. nitric acid to each bottle. Mix by swirling.

2. Add 15 mL potassium permanganate solution to each bottle, mix by swirling. Allow to stand for at least 15 minutes. If the bottle does not remain purple in color, additional potassium permanganate is required.

3. Add 8 mL of potassium persulfate solution to each bottle and heat for 2 hours in a water bath maintained at 95°C. Check the bottles periodically throughout the 2 hours to insure the samples remain purple. Add potassium permanganate if needed.

4. Cool to room temperature.

[C-600-82]

D. Sample Analysis:

1. Add 6 mL of sodium chloride-hydroxylamine hydrochloride solution to reduce excess permanganate. If necessary, additional amounts of sodium chloride hydroxylamine hydrochloride may be required to discharge the purple color. Swirl.

2. Add 5 mL of stannous chloride solution and immediately insert the aerator, making sure that the stopper provides a good seal.

3. Press the read button.

4. Record the absorbance value on the bench sheet.

5. Remove the aerator, rinse aerator, and place it in the D.I. blank bottle.

6. Allow strip recorder to return to baseline.

7. Repeat for additional samples.

Quality Control:

1. Establish a standard curve with the standards listed above plus a blank. Record the absorbance check standard in the absorbance check book. The absorbances should remain consistent from run to run. If not, necessary troubleshooting must be performed before continuing (check wavelength, tubing, lamp alignment, pump, etc.)

2. A quality control calibration standard of 0.005 mg/L is to be analyzed initially, and after every 10 samples. This standard is to be carried through the digestion procedure. If less than 10 samples are analyzed, a calibration standard is still required. The last sample must be within acceptable ranges or the samples run after the last acceptable calibration standard are to be reanalyzed. Record the calibration standard in the quality control book. The confidence limits are noted in the quality control book.

3. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Duplicates are to be averaged. Spike recoveries and duplicate results are to be within acceptable ranges or the use of matrix modifiers, dilution, or method of standard additions is to be applied to reduce the interferences.

Calculation:

1. Average the standard readings, subtract the absorbance of the blank standard from all readings.

2. Calculate using linear regression.

   Calculate the spike recovery as follows:

$$\% \text{ Recovery} = \frac{\text{ug (spike)} - \text{ug (sample)}}{0.5 \text{ ug}}$$

NICKEL

Method: AA - Flame; Direct Aspiration

Reference: EPA 1983, Method 249.1

"Analytical Methods for Atomic Absorption Spectrophotometry", 1982, Perkin-Elmer Corporation

Detection Limit: 0.04 mg/L

Optimum Concentration Range: 0.04 - 5.00 mg/L

Sample Handling: Acidify with nitric acid to pH < 2. Drinking waters and filtered groundwater free of particulate matter and organics may be analyzed directly, while wastewaters, leachates, solids, etc. must be digested prior to analysis (refer to appropriate digestion procedure). Analyze within 6 months.

Instrument Conditions:

1. Nickel hollow cathode lamp with lamp energy set at 25.
2. Wavelength: 232.0 nm
3. Slit Width: 0.2 Normal
4. Fuel: Acetylene
5. Oxidant: Air
6. Type of flame: Oxidizing, lean, blue
7. Standards to use for curve set-up: 0.50, 1.00, 2.00, 5.00 mg/L.

Reagent Preparation: Prepare fresh every 6 months unless otherwise noted.

1. Standard Nickel Solution (100 mg/L Nickel): Pipet 10 mL of the 1000 ppm stock nickel solution into a 100 mL volumetric flask, add 1/2 mL HNO_3, and dilute to the mark with Milli-Q water.
2. Standards (Prepared fresh every month.):

Concentration of Standard	Volume of Nickel Standard	Dilute to
0.50 mg/L	1/2 mL of 100 mg/L Ni	100 mL
1.00 mg/L	1 mL of 100 mg/L Ni	100 mL
2.00 mg/L	2 mL of 100 mg/L Ni	100 mL
5.00 mg/L	5 mL of 100 mg/L Ni	100 mL

Notes:

1. Samples must be diluted to obtain concentrations within the optimum concentration range.

2. Standards are to be prepared in the same acid concentrations as the samples being analyzed.

3. The use of background correction is required.

4. A nearby wavelength is present. Take care in selection of this wavelength.

Procedure: For the analysis procedure, refer to the Atomic Absorption Spectrometry, Flame - Direct Aspiration section of this manual.

If nickel is to be run in the concentration mode, use the 2.00, 5.00 mg/L nickel standards and follow the procedure for analyzing in the concentration mode.

Quality Control:

1. Establish a standard curve with the standards listed above plus a blank. Record the absorbance check standard in the absorbance check book. The absorbances should remain consistent from run to run. If not, necessary troubleshooting must be performed before continuing (check wavelength, flame head alignment, lamp alignment, etc.).

2. A quality control calibration standard of 0.50 mg/L is to be analyzed, at a minimum, after every 10 samples. If less than 10 samples are analyzed, a calibration standard is still required. The last sample analyzed in the run is to be the calibration standard. These standards must be within acceptable ranges or the samples run after the last acceptable check standard are to be reanalyzed. Record the calibration standards in the quality control book. The confidence limits are noted in the quality control book.

3. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Duplicates are to be averaged. Spike samples with a standard of twice the concentration of the sample in a 1:1 ratio of sample to standard. Spike recoveries and duplicate results are to be within acceptable ranges or the use of dilution or method of standard additions is to be applied to reduce the interferences.

Calculations:

1. Plot concentration vs absorbance on graph. Determine unknowns using graph, or

2. Calculate using linear regression, or

3. Calculate using the concentration mode.

POTASSIUM

Method: Flame Emission; Direct Aspiration

Reference: "Analytical Methods for Atomic Absorption Spectrophotometry", 1982, Perkin-Elmer Corporation

Detection Limit: 0.10 mg/L

Optimum Concentration Range: 0.10 - 5.00 mg/L

Sample Handling: Acidify with nitric acid to pH < 2. Drinking waters and filtered groundwater free of particulate matter and organics may be analyzed directly, while wastewaters, leachates, solids, etc. must be digested prior to analysis (refer to appropriate digestion procedures). Analyze within 6 months.

Instrument Conditions:

1. Set signal to emission. (No lamp is required.)
2. Wavelength: 766.5 nm
3. Slit Width: 0.2 Normal
4. Fuel: Acetylene
5. Oxidant: Air
6. Type of flame: Oxidizing, lean, blue
7. Standards to use for curve set-up: 0.50, 1.00, 2.00, 5.00 mg/L.

Reagent Preparation: (Prepare fresh every 6 months unless otherwise noted.)

1. Standard Potassium Solution (100 mg/L Potassium): Pipet 10 mL of the 1000 ppm stock potassium solution into a 100 mL volumetric flask, add 1/2 mL HNO_3, and dilute to the mark with Milli-Q water.
2. Standards (Prepare fresh every month.):

Concentration of Standard	Volume of Potassium Standard	Dilute to
0.50 mg/L	0.5 mL of 100 mg/L	100 mL
1.00 mg/L	1 mL of 100 mg/L	100 mL
2.00 mg/L	2 mL of 100 mg/L	100 mL
5.00 mg/L	5 mL of 100 mg/L	100 mL

Notes:

1. Samples must be diluted to obtain concentrations within the optimum concentration range.

2. Standards are to be prepared in the same acid concentrations as the samples being analyzed.

Procedure: For the analysis procedure, refer to the Atomic Absorption Spectrometry, Flame - Direct Aspiration section of this manual.

If potassium is to be analyzed in concentration mode, use the 2.00 and 5.00 standards and follow the procedure for analyzing in the concentration mode.

Quality Control:

1. Establish a standard curve with the standards listed above plus a blank. Record the check standard in the absorbance check book. The emission readings should remain consistent from run to run. If not, necessary troubleshooting must be performed before continuing (check wavelength, flame head alignment, etc.).

2. A quality control calibration standard of 1.00 mg/L is to be analyzed, at a minimum, after every 10 samples. If less than 10 samples are analyzed, a calibration standard is still required. The last sample analyzed in the run is to be the calibration standard. These standards must be within acceptable ranges or the samples run after the last acceptable check standard are to be reanalyzed. Record the calibration standards in the quality control book. The confidence limits are noted in the quality control book.

3. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Duplicates are to be averaged. Spike samples with a standard of twice the concentration of the sample in a 1:1 ratio of sample to standard. Spike recoveries and duplicate to be within acceptable ranges or the use of dilution or method of standard additions is to be applied to reduce the interferences.

Calculations:

1. Plot concentration vs absorbance on graph. Determine unknowns using graph, or

2. Calculate using linear regression, or

3. Calculate using the concentration mode.

SELENIUM

Method: AA - Furnace; Direct Injection

Reference: EPA 1983, Method 270.2

"Analytical Methods for Furnace Atomic Absorption Spectrophotometry", 1982, Perkin-Elmer Corporation

"Techniques in Graphite Furnace Atomic Absorption Spectrophotometry", 1985, Perkin-Elmer Corporation

Detection Limit: 0.002 mg/L

Optimum Concentration Range: 0.002 - 0.050 mg/L

Instrument Conditions:

1. Selenium electrodeless discharge lamp with lamp energy set at 6.
2. Wavelength: 196.0 nm
3. Slit Width: 0.7 Alternate
4. Mode: Peak height
5. HGA Furnace Programming:

Step 1:	130	(dry temp)	10	(ramp time)	20	(hold time)
Step 2:	850	(char temp)	10	(ramp time)	20	(hold time)
Step 3:	2200	(atom temp)	0	(ramp time)	3	(hold time)

* Also press the read, record and stop flow buttons

Step 4:	2500	(max temp)	2	(ramp time)	3	(hold time)

Press record button.

6. Sample Volume: 20 uL
7. Standards to use for curve set-up: 5.0, 10.0, 20.0, 50.0 ug/L.
8. Platform is required.

Sample Handling: Acidify with nitric acid to pH < 2. Analyze within 6 months.

Reagent Preparation:

1. Standard Selenium Solution (1000 ug/L Selenium): Pipet 1.00 mL of the 1000 ppm stock selenium solution into a 1000 mL volumetric flask, add 1/2 HNO_3, and dilute to the mark with Milli-Q water. Prepare fresh every month.

2. Standards (Prepare fresh every week.):

Concentration of Standard	Volume of Selenium Standard	Dilute to
0 ug/L	0 mL of 1000 ug/L Se	100 mL
5 ug/L	1/2 mL of 1000 ug/L Se	100 mL
10.0 ug/L	1 mL of 1000 ug/L Se	100 mL
20.0 ug/L	2 mL of 1000 ug/L Se	100 mL
50.0 ug/L	5 mL of 1000 ug/L Se	100 mL

3. Nickel Nitrate 5% Solution: Dissolve 25.0 grms of Nickel nitrate to 100 mLs of D.I. water

Notes:

1. Samples must be diluted to obtain concentrations within the optimum concentration range.

2. Standards and samples are to be digested prior to analysis. (See AsSedig for aqueous samples and SoilDig for non-aqueous samples.)

3. Chloride (> 800 mg/L) and sulfate (> 200 mg/L) interfere with this selenium procedure. Nickel nitrate is added as a matrix modifier to minimize these interferences.

4. Background correction is required.

5. Selenium may also be analyzed by the gaseous hydride technique.

6. Platform technique is required.

Procedure: For the analysis procedure, refer to the Atomic Absorption Spectrometry, Furnace - Direct Injection section of this manual.

For concentration mode, use the 20.0 and 50.0 standards and follow the procedure for analyzing using the concentration mode.

Quality Control:

1. Establish a standard curve with the standards listed above plus a blank. Record the absorbance check standard in the absorbance check book. The absorbances should remain consistent from run to run. If not, necessary troubleshooting must be performed before continuing (check wavelength, furnace alignment, lamp alignment, graphite tube, etc.).

2. ~~A quality control calibration standard of 20.0 ug/L is to be analyzed,~~ at a minimum, after every 10 samples. If less than 10 samples are analyzed, a calibration standard is still required. The last sample analyzed in the run is to be the calibration standard. These standards must be within acceptable ranges or the samples run after the last acceptable calibration standard are to be reanalyzed. Record the calibration standard in the quality control book. The confidence limits are noted in the quality control book.

3. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Duplicates are to be averaged. Spike samples with a standard of twice the concentration of the sample in a 1:1 ratio of sample to standards. Spike recoveries and duplicates are to be within acceptable ranges or the use of matrix modifiers, dilution, or method of standard additions is to be applied to reduce the interferences.

4. An EPA reference standard will be analyzed with each analysis.

Calculations:

1. Plot concentrations vs. absorbance (or peak height) on graph. Determine unknowns using graph, or

2. Calculate using linear regression, or

3. Calculate using concentration mode.

SILVER

Method: AA - Flame; Direct Aspiration

Reference: EPA 1983, Method 272.1

"Analytical Methods for Atomic Absorption Spectrophotometry", 1982, Perkin-Elmer Corporation

Detection Limit: 0.01 mg/L

Optimum Concentration Range: 0.01 - 2.00 mg/L

Sample Handling: Acidify with nitric acid to pH < 2. Drinking waters and filtered groundwater free of particulate matter and organics may be analyzed directly, while wastewaters, leachates, solids, etc. must be digested prior to analysis (refer to appropriate digestion procedure). Analyze within 6 months.

Instrument Conditions:

1. Silver hollow cathode lamp with lamp energy set at 12.
2. Wavelength: 328.1 nm
3. Slit Width: 0.7 Normal
4. Fuel: Acetylene
5. Oxidant: Air
6. Type of flame: Oxidizing, lean, blue
7. Standards to use for curve set-up: 0.50, 1.00, 2.00 mg/L.

Reagent Preparation: (Prepare fresh every 6 months unless otherwise noted.)

1. Standard Silver Solution (100 mg/L Silver): Pipet 10 mL of the 1000 ppm stock silver solution into a 100 mL volumetric flask, add 1/2 mL HNO_3, and dilute to the mark with Milli-Q water.
2. Standards (Prepare fresh every month.):

Concentration of Standard	Volume of Silver Standard	Dilute to
0.50 mg/L	0.5 mL of 100 mg/L Ag	100 mL
1.00 mg/L	1 mL of 100 mg/L Ag	100 mL
2.00 mg/L	2 mL of 100 mg/L Ag	100 mL

Notes:

1. Samples must be diluted to obtain concentrations within the optimum concentration range.

2. Standards are to be prepared in the same acid concentrations as the samples being analyzed.

3. The use of background correction is required.

4. This flame procedure can be used for digested samples, EP Toxicity samples or any other samples where low detection limits are not required. EP Toxicity samples must be spiked to verify that standard additions are not required.

5. Any groundwater samples which silver is detected, must be verified by furnace. (Detection limit is at the WI PAL limit.)

Procedure: For the analysis procedure, refer to the Atomic Absorption Spectrometry, Flame - Direct Aspiration section of this manual.

If silver is to be run in the concentation mode, use the 1.00 and 2.00 mg/L silver standards and follow the procedure for analyzing in the concentration mode.

Quality Control:

1. Establish a standard curve with the standards listed above plus a blank. Record the absorbance check standard in the absorbance check book. The absorbances should remain consistent from run to run. If not, necessary troubleshooting must be performed before continuing (check wavelength, flame head alignment, lamp alignment, etc.).

2. A quality control calibration standard of 0.50 mg/L is to be analyzed, at a minimum, after every 10 samples. If less than 10 samples are analyzed, a calibration standard is still required. The last sample analyzed in the run is to be the calibration standard. These standards must be within acceptable ranges or the samples run after the last acceptable check standard are to be reanalyzed. Record the calibration standards in the quality control book. The confidence limits are noted in the quality control book.

3. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Duplicates are to be averaged. Spike samples with a standard of twice the concentration of the sample in a 1:1 ratio of sample to standard. Spike recoveries and duplicates are to be within acceptable ranges or the use of dilution or method of standard additions is to be applied to reduce the interferences.

Calculations:

1. Plot concentration vs absorbance on graph. Determine unknowns using graph or

2. Calculate using linear regression or

3. Calculate using the concentration mode.

THALLIUM

Method: AA - Flame; Direct Aspiration

Reference: EPA 1983, Method 279.1

"Analytical Methods for Atomic Absorption Spectrophotometry", 1982, Perkin-Elmer Corporation

Detection Limit: 0.50 mg/L

Optimum Concentration Range: 0.50 - 10.0 mg/L

Sample Handling: Acidify with nitric acid to pH < 2. Drinking waters and filtered groundwater free of particulate matter and organics may be analyzed directly, while wastewaters, leachates, solids, etc. must be digested prior to analysis (refer to appropriate digestion procedures). Analyze within 6 months.

Instrument Conditions:

1. Thallium electrodeless discharge lamp with lamp energy set at 9.
2. Wavelength: 276.8 nm
3. Slit Width: 0.7 Normal
4. Fuel: Acetylene
5. Oxidant: Air
6. Type of flame: Oxidizing, lean, blue
7. Standards to use for curve set-up: 1.00, 2.00, 5.00, 10.0 mg/L.

Reagent Preparation: Prepare fresh every 6 months unless otherwise noted.

1. Standard Thallium Solution (10.0 mg/L Thallium): Pipet 1.0 mL of the 1000 ppm stock thallium solution into a 100 mL volumetric flask, add 1/2 mL HNO_3, and dilute to the mark with Milli-Q water.
2. Standards (Prepare fresh every month.):

Concentration of Standard	Volume of Thallium Standard	Dilute to
1.00 mg/L	1 mL of 100 mg/L Tl	100 mL
2.00 mg/L	2 mL of 100 mg/L Tl	100 mL
5.00 mg/L	5 mL of 100 mg/L Tl	100 mL
10.00 mg/L	10 mL of 100 mg/L Tl	100 mL

Notes:

1. Samples must be diluted to obtain concentrations within the optimum concentration range.

2. Standards are to be prepared in the same acid concentrations as the samples being analyzed.

3. The use of background correction is required.

4. This flame procedure can be used for digested samples, EP Toxicity samples or any other samples where low detection limits are not required. EP Toxicity samples must be spiked to verify that standard additions are not required.

5. The use of halide acids is to be avoided.

Procedure: For the analysis procedure, refer to the Atomic Absorption Spectrometry, Flame - Direct Aspiration section of this manual.

If thallium is to be run in concentration mode, use the 5.00 and 10.0 standards and follow the procedure for analyzing in concentration mode.

Quality Control:

1. Establish a standard curve with the standards listed above plus a blank. Record the absorbance check standard in the absorbance check book. The absorbances should remain consistent from run to run. If not, necessary troubleshooting must be performed before continuing (check wavelength, flame head alignment, lamp alignment, etc.).

2. A quality control calibration standard of 5.00 mg/L is to be analyzed, at a minimum, after every 10 samples. If less than 10 samples are analyzed, a calibration standard is still required. The last sample analyzed in the run is to be the calibration standard. These standards must be within the acceptable ranges or the samples run after the last acceptable check standard are to be reanalyzed. Record the calibration standards in the quality control book. The confidence limits are noted in the quality control book.

3. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Duplicates are to be averaged. Spike samples with a standard of twice the concentration of the sample in a 1:1 ratio of sample to standard. Spike recoveries and duplicate are to be within acceptable ranges or the use of dilution or method of standard additions is to be applied to reduce the interferences.

Calculations:

1. Plot concentration vs absorbance on graph. Determine unknowns using graph, or

2. Calculate using linear regression, or

3. Calculate using concentration mode.

[ALM-8-13]

THALLIUM

Method: AA - Furnace; Direct Injection

Reference: EPA 1983, Method 279.2

"Analytical Methods for Furnace Atomic Absorption Spectrophotometry", 1982, Perkin-Elmer Corporation.

"Techniques in Graphite Furnace Atomic Absorption Spectrophotometry", 1985, Perkin-Elmer Corporation.

Detection Limit: 0.005 mg/L

Optimum Concentration Range: 0.005 - 0.050 mg/L

Instrument Conditions:

1. Thallium electrodeless discharge lamp with lamp energy set at 9.
2. Wavelength: 276.8 nm
3. Slit Width: 0.7 Alternate
4. HGA Furnace Programming:

   Step 1: 130 (dry temp) 10 (ramp time) 20 (hold time)
   Step 2: 500 (char temp) 10 (ramp time) 20 (hold time)
   Step 3: 1400 (atom temp) 0 (ramp time) 3 (hold time)

   * Also press the read, record and stop flow buttons; t = 3 sec.

   Step 4: 2500 (max temp) 0 (ramp time) 3 (hold time)

   Press the record button.

5. Sample Volume: 20 uL
6. Standards to use for curve set-up: 10.0, 20.0, 50.0 ug/L.
7. Platform is required.

Sample Handling: Acidify with nitric acid to pH <2. Analyze within 6 months.

[C-600-97a]

Reagent Preparation:

1. Standard Thallium Solution (1000 ug/L Thallium): Pipet 1.00 mL of the 1000 ppm stock thallium solution into a 1000 mL volumetric flask, add 1/2 mL HNO_3 and dilute to the mark with D.I. water. Prepare fresh every month.

2. Standards (Prepare fresh every week.):

Concentration of Standard	Volume of Thallium Standard	Dilute to
10.0 ug/L	1 mL of 1000 ug/L Tl	100 mL
20.0 ug/L	2 mL of 1000 ug/L Tl	100 mL
50.0 ug/L	5 mL of 1000 ug/L Tl	100 mL

Notes:

1. Samples must be diluted to obtain concentrations within the optimum concentration range.

2. Standards are to be prepared in the same acid concentrations as the samples being analyzed.

3. The use of background correction is required.

4. Be careful when reporting the units.

Procedure: For the analysis procedure, refer to the Atomic Absorption Spectrometry, Furnace - Direct Injection section of this manual.

For the use of the concentration mode, use the 20.0 and 50.0 standards and follow the procedure for analyzing in the concentration mode.

Quality Control:

1. Establish a standard curve with the standards listed above plus a blank. Record the absorbance check standard in the absorbance check book. The absorbances should remain consistent from run to run. If not, necessary troubleshooting must be performed before continuing (check wavelength, furnace alignment, lamp alignment, graphite tube, etc.).

2. A quality control calibration standard of 20.0 ug/L is to be analyzed, at a minimum, after every 10 samples. If less than 10 samples are analyzed, a calibration standard is still required. The last sample analyzed in the run is to be the calibration standard. These

standards must be within acceptable ranges or the samples run after the last acceptable calibration standard are to be reanalyzed. Record the calibration standard in the quality control book. The confidence limits are noted in the quality control book.

3. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Duplicates are to be averaged. Spike samples with a standard of twice the concentration of the sample in a 1:1 ration of sample to standards. Spike recoveries and duplicates are to be within an acceptable range or the use of matrix modifiers, dilution, or method of standard additions is to be applied to reduce the interferences.

4. An EPA reference standard will be analyzed with each analysis.

Calculations:

1. Plot concentrations vs. absorbance (or peak height) on graph. Determine unknowns using graph, or

2. Calculate using linear regression, or

3. Calculate using concentration mode.

VANADIUM

Method: AA - Flame; Direct Aspiration

Reference: EPA 1983, Method 286.1

"Analytical Methods for Atomic Absorption Spectrophotometry", 1982, Perkin-Elmer Corporation

Detection Limit: 1.00 mg/L

Optimum Concentration Range: 1.00 - 50.0 mg/L

Sample Handling: Acidify with nitric acid to pH < 2. Drinking waters and filtered groundwater free of particulate matter and organics may be analyzed directly, while wastewaters, leachates, solids, etc. must be digested prior to analysis (refer to appropriate digestion procedures). Analyzed within 6 months.

Instrument Conditions:

1. Vanadium hollow cathode lamp.
2. Wavelength: 318.4 nm
3. Slit Width: 0.7 Normal
4. Fuel: Acetylene
5. Oxidant: Nitrous oxide
6. Type of flame: Red
7. Standards to use for curve set-up: 5.00, 10.0, 20.0, 50.0 mg/L.

Reagent Preparation: Prepare fresh every 6 months unless otherwise noted.

1. Standards (Prepare fresh every month.):

Concentration of Standard	Volume of Vanadium Standard	Dilute to
5.00 mg/L	0.5 of 1000 mg/L V	100 mL
10.0 mg/L	1 of 1000 mg/L V	100 mL
20.0 mg/L	2 of 1000 mg/L V	100 mL
50.0 mg/L	5 of 1000 mg/L V	100 mL

2. Aluminum nitrate solution: In a 200 mL volumetric flask, dissolve 139g $Al(NO_3)_3$ in 150 mL of Milli-Q water. Heat to dissolve into solution. Allow to cool. Dilute to 200 mL with Milli-Q water.

Notes:

1. Samples must be diluted to obtain concentrations within the optimum concentration range.

2. Standards are to be prepared in the same acid concentrations as the samples being analyzed.

3. The use of background correction is required.

4. High concentrations of aluminum and titanium increase the sensitivity of vanadium. This interference can be controlled by adding excess aluminum to both samples and standards (2 mL of aluminum nitrate solution to 100 mL samples and standards).

Procedure: For the analysis procedure, refer to the Atomic Absorption Spectrometry, Flame - Direct Aspiration section of this manual.

Add 0.2 mL of $AlNO_3$ to 10 mL of samples, blanks and standards.

If vanadium is to be run in the concentration mode, use the 20.0 and 50.0 standards and follow the procedure for analyzing in the concentration mode.

Quality Control:

1. Establish a standard curve with the standards listed above plus a blank. Record the absorbance check standard in the absorbance check book. The absorbances should remain consistent from run to run. If not, necessary troubleshooting must be performed before continuing (check wavelength, flame head alignment, lamp alignment, etc.).

2. A quality control calibration standard of 20.0 mg/L is to be analyzed, at a minimum, after every 10 samples. If less than 10 samples are analyzed, a calibration standard is still required. The last sample analyzed in the run is to be the calibration standard. These standards must be within the acceptable ranges or the samples run after the last acceptable check standard are to be reanalyzed. Record the calibration standards in the quality control book. The confidence limits are noted in the quality control book.

3. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Duplicates are to be averaged. Spike samples with a standard of twice the concentration of the sample in a 1:1 ratio of sample to standard. Spike recoveries and duplicate to be within an acceptable ranges or the use of dilution or method of standard additions is to be applied to reduce the interferences.

Calculations:

1. Plot concentration vs absorbance on graph. Determine unknowns using graph, or

2. Calculate using linear regression, or

3. Calculate using the concentration mode.

ZINC

Method: AA - Flame; Direct Aspiration

Reference: EPA 1983, Method 289.1

"Analytical Methods for Atomic Absorption Spectrophotometry", 1982, Perkin-Elmer Corporation

Detection Limit: 0.01 mg/L

Optimum Concentration Range: 0.01 - 1.00 mg/L

Sample Handling: Acidify with nitric acid to pH < 2. Drinking waters and filtered groundwater free of particulate matter and organics may be analyzed directly, while wastewaters, leachates, solids, etc. must be digested prior to analysis (refer to appropriate digestion procedures). Analyze within 6 months.

Instrument Conditions:

1. The Zinc hollow cathode lamp with lamp energy set at 27.
2. Wavelength: 213.9 nm
3. Slit Width: 0.7 Normal
4. Fuel: Acetylene
5. Oxidant: Air
6. Type of flame: Oxidizing, lean, blue
7. Standards to use for curve set-up: 0.10, 0.20, 0.40, 1.00 mg/L.

Reagent Preparation: (Prepare fresh every 6 months unless otherwise noted.)

1. Standard Zinc Solution (20.0 mg/L Zinc): Pipet 2 mLs of the 1000 ppm stock zinc solution into a 100 mL volumetric flask, add 1/2 mL HNO_3, and dilute to the mark with Milli-Q water.
2. Standards (Prepare fresh every month.):

Concentration of Standard	Volume of Zinc Standard	Dilute to
0.10 mg/L	0.5 mL of 20.0 mg/L Zn	100 mL
0.20 mg/L	1 mL of 20.0 mg/L Zn	100 mL
0.40 mg/L	2 mL of 20.0 mg/L Zn	100 mL
1.00 mg/L	5 mL of 20.0 mg/L Zn	100 mL

Notes:

1. Samples must be diluted to obtain concentrations within the optimum concentration range.

2. Standards are to be prepared in the same acid concentrations as the samples being analyzed.

3. The use of background correction is required.

4. Zinc's may be run at a 30° angle for high level samples. High standards are made accordingly.

Procedure: For the analysis procedure, refer to the Atomic Absorption Spectrometry, Flame - Direct Aspiration section of this manual.

If zinc is to be run in the concentration mode, use the 0.40 and 1.00 mg/L zinc standards and follow the procedure for analyzing in the concentration mode.

Quality Control:

1. Establish a standard curve with the standards listed above plus a blank. Record the absorbance check standard in the absorbance check book. The absorbances should remain consistent from run to run. If not, necessary troubleshooting must be performed before continuing (check wavelength, flame head alignment, lamp alignment, etc.).

2. A quality control calibration standard of 0.20 mg/L is to be analyzed, at a minimum, after every 10 samples. If less than 10 samples are analyzed, a calibration standard is still required. The last sample analyzed in the run is to be the calibration standard. These standards must be within the acceptable ranges or the samples run after the last acceptable check standard are to be reanalyzed. Record the calibration standards in the quality control book. The confidence limits are noted in the quality control book.

3. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Duplicates are to be averaged. Spike samples with a standard of twice the concentration of the sample in a 1:1 ratio of sample to standard. Spike recoveries and duplicates results are to be within acceptable ranges or the use of dilution or method of standard additions is to be applied to reduce the interferences.

Calculations:

1. Plot concentration vs absorbance on graph. Determine unknowns using graph, or

2. Calculate using linear regression, or

3. Calculate using the concentration mode.

TOTAL VOLATILE SOLIDS

Scope and Application: This method determines the weight of solid material combustible at 550°C, and is applicable to sewage, sludge, industrial wastes, soils and sediments.

Method: Gravimetric, ignition at 550°C

Reference: EPA 1983, Method 160.4
Standard Methods, 16th Edition, 1985, Method 209F. (Pages 99-100)

Sample Handling: Refrigerate at 4°C and analyze within 7 days of collection.

Reagents and Apparatus:

1. Porcelain evaporating dishes
2. Muffle furnace, set at 550°C
3. Dessicator
4. Analytical balance

Notes:

1. This is not an accurate measure of organic carbon.

2. The most common error is failure to obtain a representative sample. Make sure the sample is thoroughly mixed or composited prior to analysis.

3. The muffle furnace is slow to heat to 550°C. Turn muffle furnace on early in the day.

4. When opening and closing the muffle, remember to stay to the side of the compartment.

5. Use tongs when placing dishes in/out of the muffle furnace. The temperature is very high!

6. Take weighings quickly - wet samples tend to lose weight by evaporation. Dried samples can be hygroscopic and rapidly absorb atmospheric moisture.

Procedure:

Preparation of Evaporation Dish

1. All glassware is to be soap and water washed, tap rinsed, and deionized water rinsed prior to analysis.

2. Ash a clean evaporating dish at 550 ±50°C for one hour in muffle furnace.

3. Cool in dessicator for at least one hour and weigh. Dishes may be prepared and stored in desiccator until ready for use.

Sample Analysis

4. Fluid samples - Stir to mix.

   - Place 25 to 50g of sample in the prepared evaporating dish and weigh.

   - Evaporate to dryness on a water bath.

   - Dry at 103 - 105°C overnight.

   - Place in desiccator and cool to room temperature.

   - Weigh.

   Solid Samples - If sample contains pieces of solid material, pulverize the sample coarsely.

   - Place 25 to 50g of sample into prepared evaporating dish and weigh.

   - Place in oven at 103 - 105°C overnight.

   - Place in desiccator and cool to room temperature.

   - Weigh.

5. After the total solids have been determined, ignite the residue left in the evaporating dish at 550°C in the muffle furnace.

   Note: If residue for step 4 contains large amounts of organic matter, first ignite the residue over a gas burner in an exhaust hood; then proceed with step 5.

6. Let dish cool partially by the air. Then, cool in a dessicator for at least one hour and weigh. Repeat the ashing cycle (igniting, cooling, dessicating, and weighing) until a weight loss of <0.4% is obtained.

Quality Control:

1. Duplicate 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate is still required. Duplicates should be within acceptable ranges. The duplicate results are to be averaged.

2. A blank dish is carried throughout the entire procedure, as a check on contamination (glassware, oven, muffle furnace, etc.)

Calculations:

$$\text{TVS, mg/kg} = \frac{\text{wt. dried residue (g)} - \text{wt. residue after ignition (g)}}{\text{wt. dried residue (g)}} \times 1000000$$

$$\text{TVS, \%} = \frac{\text{wt. dried residue (g)} - \text{wt. residue after ignition (g)}}{\text{wt. dried residue (g)}} \times 100$$

	Revision Date
Michael Linskens 10/19/87 Michael J. Linskens Laboratory Manger	7-23-86
Kim Finner Kim D. Finner Analytical Laboratory QA/QC Officer	5-21-87
Lawrence D. Andersen Lawrence D. Andersen Vice President, Technical Services	

ACID DIGESTIONS FOR SEDIMENTS, SLUDGES AND SOILS -

Scope and Application: This method is an acid digestion procedure used to prepare sediments, sludges, and soil samples for analysis by flame or furnace atomic absorption spectropscopy (AAS) or by inductively coupled argon plasma spectroscopy (ICP). Samples prepared by this method may be analyzed by AAS or ICP for the following metals:

Aluminum	Chromium	Nickel
Antimony	Cobalt	Potassium
Arsenic	Copper	Silver
Barium	Iron	Selenium
Beryllium	Lead	Thallium
Cadmium	Magnesium	Vanadium
Calcium	Manganese	Zinc

Method: Nitric acid, hydrogen peroxide and hydrochloric acid digestion for flame work and antimony by furnace; nitric acid/hydrogen peroxide digestion for furnace work.

Reference: EPA SW-846, "Test Methods for Evaluating Solid Waste", July, 1982. Methods 3020 and 3050.

Contract Laboratory Program - "Statement of Work", July, 1985.

Sample Handling: Set up digestion as soon as possible; digested sample must be analyzed within 6 months.

Reagents and Apparatus:

1. Hot plate
2. Mortar and Pestle
3. 250 mL beakers
4. Class A volumetric glassware
5. Milli-Q water
6. 30% hydrogen peroxide
7. Instra-analyzed nitric acid
8. Instra-analyzed HCL acid
9. Stock and standard metal solutions
10. Whatman #42 filter paper
11. Glass or plastic funnels
12. Watch glasses

Reagent Preparation:

1. Intermediate and Working Metal Solutions: Refer to the specific metal SOP for instructions on preparation.

2. 1:1 Nitric Acid: Using a 250 mL volumetric cylinder, add 250 mL Milli-Q water. Cautiously add 250 mL concentrated nitric acid. Mix.

3. 1:1 HCL: Using a 250 mL volumetric cylinder, add 250 mL Milli-Q water. Cautiously add, 250 mL concentrated hydrochloric acid. Mix.

Notes:

1. Arsenic and selenium by the AA-furnace techniques follow this digestion procedure and nickel nitrate is added prior to analysis.

2. Mercury by the AA-Cold Vapor technique has a separate digestion procedure.

3. All blanks, duplicates and spikes must be carried through the digestion procedure along with a digestion check standard.

4. If elevated levels are expected, increase the spike concentration accordingly.

Procedure:

A. Digestion for Flame Work and Furnace Analysis of Antimony:

1. All glassware used must be acid rinsed with 1:1 nitric prior to use.

2. Pulverize and thoroughly mix the sample.

3. Weigh out approximately 1.000 g - 1.500 g of the sample into a 250 mL beaker on analytical balance. Record the weight of the sample used on the digestion sheet.

4. Add 10 mL of 1:1 HNO_3. Mix and cover with a watchglass. Place samples on the hot plate and heat at medium heat (95° C). Reflux for 10 minutes.

5. Take sample off hot plate and allow to cool. Add 5 mL concentrated HNO_3. Return to hot plate and reflux for 30 minutes.

6. Cool. Add 2 mL Milli-Q water and 3 mL 30% H_2O_2.

7. Heat until effervesence subsides. Cool.

8. Continue the addition of 30% H_2O_2 in 1 mL aliquots with warming until the effervesence is minimal or appearance of sample is unchanged. DO NOT add more than a total of 10 mL 30% H_2O_2.

9. Cool. Add 5 mL 1:1 HCL and 10 mL Milli-Q water.

10. Cover and heat for 10 minutes.

11. Cool. Quantitatively transfer to 100 mL volumetric flasks while filtering through a Whatman #42 filter to remove sediment. Rinse beaker and filter paper 3 times and dilute to 100 mL with Milli-Q water. The final acid concentration is approximately 2.5% HCL and 5.0% HNO_3. Dilute the digestate 1:1 with deionized water. (200 mL final volume.)

B. Digestion for Furnace Work, except for Antimony:

1. Follow the digestion procedure above for flame work through Step 8.

2. Continue to heat until the volume is reduced to approximately 2 mL. (Watch closely; bumping and spattering may occur.)

3. Cool. Add 10 mL Milli-Q water and warm on hot plate.

4. Cool. Quantitatively transfer to 100 mL volumetric flasks while filtering through a Whatman #42 filter to remove sediment. Rinse the beakers and filter paper 3 times and dilute to 100 mL with Milli-Q water. The final acid concentration is approximately 2.0% HNO_3. Dilute the digestate 1:1 with deionized water (200 mL final volume).

Quality Control:

1. Refer to each specific metal SOP for quality control requirements.

2. If a digested spike is diluted out of the working concentration (too low to detect) run a manual spike. The data is acceptable if the manual spike is within acceptable ranges. If the manual spike is outside the QC ranges, the sample and spike must be re-digested.

Revision Date

9/25/87

Michael Linskens 9/25/87
Michael J. Linskens
Laboratory Manager

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ACID DIGESTION FOR WASTEWATER, GROUNDWATER AND EP TOXICITY SAMPLES

Scope and Application: This acid digestion is applicable to all aqueous sample matrices. A nitric/hydrochloric acid digestion is used for all metals which are to be analyzed by the AA-flame technique and for the furnace analysis of antimony. Metals which are to be analyzed by the AA-furnace technique will follow the nitric acid/ hydrogen peroxide digestion.

Method: Nitric and nitric/hydrochloric acid digestions.

Reference: EPA SW-846, "Test Methods for Evaluating Solid Wastes", July, 1982. Methods 3010 and 3020.

Contract Laboratory Program, "Statement of Work", July, 1985.

Sample Handling: Aqueous samples must be acidified with concentrated nitric acid to pH < 2. Set up digestion as soon as possible; digested sample must be analyzed within 6 months.

Reagents and Apparatus:

1. Hot Plate
2. 250 mL beakers
3. 100 mL graduated cylinders
4. Class A volumetric glassware
5. Milli-Q water
6. Instra-analyzed nitric acid
7. Instra-analyzed HCL acid
8. Stock and standard metal solutions
9. Whatman #42 filter paper
10. Glass funnels
11. Watch glasses
12. 30% hydrogen peroxide

Reagent Preparation:

1. Intermediate and Working Metal Solutions: Refer to the specific metal SOP for instructions on preparation.

Notes:

1. All blanks, duplicates, and spikes, as well as a digested check standard must be carried through this digestion procedure.

Procedure:

A. Digestion For AA-Flame and Antimony by Furnace:

1. All glassware must be acid-washed with 1:1 nitric acid and thoroughly rinsed with Milli-Q water prior to use.

2. Measure out 100 mL aliquots of samples, blanks, and standards into 250 mL beakers using a graduated cylinder.

3. Add 2 mL of 1:1 HNO_3 and 10 mL of 1:1 HCL.

4. Cover with a watch glass and heat on the hot plate until the volume has been reduced to between 25 and 50 mL. Make certain that the sample does not boil.

5. Quantitatively transfer digested samples, blanks, and standards into 100 mL volumetric flasks. Filter samples through Whatman #42 filters, rinse beakers and filters with Milli-Q water and dilute to 100 mL. Alternatively, samples can be transfered to 100 mL volumetric flasks, without filtering. Dilute to volume and let any insoluble material settle overnight.

6. Samples are now ready for analysis using the AA-flame procedure.

B. Digestion For AA-Furnace (except Antimony):

1. All glassware must be acid-washed with 1:1 nitric acid and thoroughly rinsed with Milli-Q water prior to use.

2. Measure 100 mL aliquots of samples, blanks, and standards into 250 mL beakers using a graduated cylinder.

3. Add 1.0 mL of 1:1 HNO_3 and 2 mL of 30% H_2O_2.

4. Cover with a watch glass and heat on the hot plate at 95°C for 2 hours or until the volume is reduced to between 25 and 50 mL. Make certain that the sample does not boil.

5. Quantitatively transfer digested samples, blanks, and standards into 100 mL volumetric flasks. Filter samples through Whatman #42 filters, rinse beakers and filters with Milli-Q water and dilute to 100 mL. Alternatively, samples can be transfered to 100 mL volumetric flask without filtering. Dilute to volume and let any insoluble material settle overnight.

6. Samples are now ready for analysis using the AA furnace procedures.

Quality Control

1. Refer to each specific metal SOP for quality control requirements.

2. If a digested spike is diluted out of the working concentration range (too low to detect) run a manual spike. The data is acceptable if the manual spike is within acceptable ranges. If the manual spike is outside the QC ranges, the sample and spike must be re-digested at a dilution.

Revision Date

Michael Linskens 9/25/87
Michael J. Linskens
Laboratory Manager

9/25/87

Kim Finner
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Analytical Laboratory QA/QC Officer

Lawrence D. Andersen
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AUTOANALYZER

Scope and Application: Ions can be readily analyzed by a flow-injection autoanalyzer. The flow injection design gives the system excellent washout characteristics, to prevent carry over and cross contamination. The autoanalzyer is generally more sensitive and accurate than the manual wet-chemistry techniques.

Method: Flow injection

References: Lachat Instruments, 1986.

Sample Handling: See separate SOP's for requirements.

Reagents and Appartus:

1. Lachat 3-channel autoanalyzer
2. Stock and standard ion solutions
3. Class A volumetric flasks
4. Class A volumetric pipets
5. Milli-Q water
6. Required interference filters
7. Disposable 4 mL cups
8. Automatic sampler
9. Proportioning pump
10. Injection module
11. Colorimeters
12. Manifolds
13. Columns - if needed
14. Helium gas
15. Computer
16. Printer

Procedure:

A. Instrument Set-up

1. Depress red power switch on power strip located behind the computer terminal. This will turn on the computer, the screen, and the printer.

2. Depress red power switch on rear power strip on Lachat system.

4. Select manifold and make appropriate hydraulic connections.

Hydraulic connections:

a. Use correct sample loop length to connect. Lines 1, 4.

b. Line 2 is carrier line.

c. Line 3 goes to manifold.

d. Line 5 goes to waste container.

e. Line 6 comes from sample probe.

f. Connect manifold to flow through cell.

Tension levers should be up when pump tubing is inserted. Snap pump tubing cartridges into place.

5. Insert correct filter.

6. Pump Milli-Q water through lines for 5 minutes by depressing the pump ON button. Check for leaks.

7. Computer - At the C> type in "quikcalc". This calls up the Lachat software and puts you at the master menu. Press <enter>.

8. Put lines into reagents and/or degassed Milli-Q water.

9. Computer - Select "Load/Stop Background Method" on the master menu. Press <enter>.

10. Select appropriate method. Press <enter>.

11. Printer should be set at FONT 0.

12. Pump reagents until a steady baseline is achieved.

13. When using a method with a column (SO_4 or NO_3), the column may be inserted at this point. See method SOP's for more details.

14. For each analytical channel, adjust zero knob so that the baseline is near the bottom of the screen (between .000 - .030).

15. Adjust gain while injecting top standard.

    a. Place autosampler probe into the highest standard bottle.

    b. After 20-30 seconds, press cycle button on front panel so that LED light is red. This is the load position.

    c. After 25 seconds (or less depending on sample loop size), press cycle button so that LED light is green. This is the inject position.

    d. Adjust gain knob on detector so that peak reading on the colorimeter is 1.700-1.950.

    e. Repeat until gain is properly adjusted.

    f. Wipe probe and replace the autosampler probe into the sampler.

16. Select menu item by going into foreground. (Press and hold Alt key, then press Esc key).

    a. Select "Sample Tray Information and Start Analysis" on master menu. Press <Enter>.

    b. Press <Enter> or type in sample tray reference number if it is a tray which has already been typed in.

    c. Enter tray ID and operator. Check "Display Standards Position in Tray" to insure the tray is set-up properly.

    d. Select "Enter Sample ID's". Press <enter>.

    e. Type in sample information. Check standards will automatically be placed in the tray information portion.

    f. Press Esc once to return to menu.

17. Put tray with samples in appropriate cup locations on autosampler. Position tray to the cup containing standard A (usually #35 or so). Select "Start Analysis." Press <enter>.

18. The second screen will ask if the tray has standards or not. If you standardized the first tray of the run and all the check standards are within QC ranges, recalibration for the next tray is <u>not</u> necessary. Select appropriate option. Press <enter>.

19. Press Alt, Esc keys together, to get back to background to view the calibration peaks.

After calibration is complete:

- go into the foreground (Press Alt, Esc keys)
- select "display calibration graph" (Press <enter>)
- review the data
- return to the background (Press Alt, Esc keys)
  - press "G" for good calibration. Analysis will continue.
  - press "R" for re-calibration. Remember to refill standard cups and reposition sample tray <u>before</u> pressing "R"!

B. <u>Instrument Shut-Down</u>

1. Press Alt/Esc keys to get to the foreground. Select "Load/Stop Background Method". Press <enter>. To question-"Stop background (Y/N)?" Press "Yes". Press Esc key to main menu.
2. If column is used, stop the pump and disconnect from manifold.
3. Pull lines from reagents into a wash beaker of D.I..
4. Pump D.I. through lines for 2-5 minutes.
5. Pump air through lines until manifold is dry.
6. Turn off pump.
7. Release tubing cartridges and lower tension levers. Release tubing.
8. Turn off main switch on rear power strip.
9. Empty and rinse waste containers, if necessary.
10. Perform back-up on current data files, once a week. (see section C)
11. Turn off the computer and printer.

C. Backing-up the Data Files

1. Exit to DOS

2. At C> Type: cd\fialab\data Press <enter>

3. At C> Type: copy *.rpt a: Press <enter>
   After everything is copied - remove disc.

4. At C> Type: del *.* Press <enter>

5. Are you sure (Y/N)? Type: Y Press <enter>

6. At C> Type: cd\ Press <enter>

7. Turn off the red switch on the computer power strip to turn off the computer, printer and screen.

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Revision Date

8-18-87

9-25-87

ALKALINITY--AUTOANALYZER

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

Reference: EPA 1983, Method 310.2
Lachat Instruments 1986, Method 10-303-31-1-C

Sample Handling: Refrigerate at 4°C and analyze within 14 days of collection.

Detection Limit: 5.0 mg/L as $CaCO_3$

Optimum Concentration Range: 5.0 - 500 mg/L

Instrument Conditions:

1. Pump speed: 35
2. Cycle period: 60 seconds
3. Load period: 30 seconds
4. Inject period: 15 seconds
5. Inject to start of peak period: 10 seconds
6. Inject to end of peak period: 56 seconds
7. Gain: 150 x 10
8. Zero: 180
9. Interference filter: 410 nm
10. Sample loop: 90 cm
11. Standards for curve set-up: 0, 20.0, 50.0, 100, 250, 500 mg/L.

Reagent Preparation: (Prepare fresh every 6 months, unless otherwise stated.)

1. Degassed Milli-Q water - 2 options:

   a. Boil Milli-Q water vigorously for 5 minutes. Cool and store in cubitainer.

   b. Bubble helium, using the fritted gas dispersion tube, through the Milli-Q water (15 min/20 L.) Store in cubitainer.

2. Stock alkalinity standard (1000 mg/L as Na_2CO_3): In a 1 liter volumetric flask, dissolve 1.060 g of anhydrous primary standard grade sodium carbonate (Na_2CO_3-dried at 140°C for 4 hours) in approximately 900 mL of helium purged Milli-Q water, and dilute to mark.

3. Standards: (Prepare fresh every 2 months.)

Concentration of Standard	Letter Identifier	Volume of Alk. Standard	Dilute to
0 mg/L	A	0	200 mL
20.0 mg/L	B	4.0	200 mL
50.0 mg/L	C	10.0	200 mL
100 mg/L	D	50.0	500 mL
250 mg/L	E	125.0	500 mL
500 mg/L	F	100.0	200 mL

NOTE: Final volumes are not the same!
Computer refers to standards by letter.

4. Sodium hydroxide (0.1M): In a 1 liter flask, dissolve 4.0 g sodium hydroxide (NaOH) and dilute to the mark with Milli-Q water.

5. Hydrochloric acid (0.1M): In a 1 liter flask, dilute 8.3 mL of concentrated HCL in Milli-Q water and dilute to the mark.

6. KHP buffer (25.0 mM, pH 3.1): In a 1 liter flask, dissolve 5.10 g of potassium acid phthalate (KHP) ($KHC_3H_4O_4$) in approximately 500 mL of helium purged Milli-Q water. Add 87.6 mL of 0.1M HCL and dilute to the mark. Adjust the pH of the buffer to 3.1 with 0.1M HCL or 0.1M NaOH. STORE IN GLASS AND PREPARE MONTHLY!

7. Methyl orange reagent: In a 1 liter volumetric flask, dissolve 0.125 g of methyl orange indicator in about 700 mL of helium-purged Milli-Q water and dilute to the mark. Store in glass!

Notes:

1. Samples must be diluted to obtain concentrations within the optimum working range.

2. The gain and zero settings are guidelines and must be adjusted each day to optimize.

3. The alkalinity standards can be combined with chloride and sulfate standards for use with the 3 channel method.

4. Turbidity will interfere. Samples must be filtered prior to analysis. (Use Whatman #1 or #4.)

5. Color will interfere, dilute the sample and also spike this sample to confirm the quality of the result.

System Operation:

A. Refer to "Auto Analyzer Operation start-up procedure." (IOP# LAA-section A)

B. Analyze a blank and an EPA check standard at the beginning of each run.

C. Use 125 mg/L for the spike level.

D. The calibration check standard is 100 mg/L (D).

E. Refer to "Auto Analyzer shut-down procedure". (IOP# LAA-section B)

Quality Control:

1. Establish a standard curve with the standards listed above. Record the check standard in the check standard book. The concentration should remain consistent from run to run. If not, necessary troubleshooting must be performed before continuing (check reagents, pump tubing, valves, etc.).

2. A quality control calibration standard of 100 mg/L is to be analyzed, at a minimum, after every 10 samples. If less than 10 samples are analyzed, a calibration standard is still required. The last sample analyzed in the run is to be the calibration standard. These standards must be within the acceptable ranges or the samples run after the last acceptable check standard are to be reanalyzed. Record the calibration standards in the quality control book. The acceptable limits are noted in the quality control book.

3. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Duplicates are to be averaged. Spike samples with a standard in a 1:1 ratio of sample to standard. Spike recoveries and duplicates are to be within acceptable ranges or troubleshooting must be performed.

Calculation:

1. Calculate with Lachat QuikChem software, in the concentration mode, using the IBM XT computer.

Revision Dates

8-18-87

9-25-87

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CHLORIDE - AUTOANALYZER

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

References: EPA 1983, Method 325.2
Lachat Instruments 1986, Method 10-117-07-1-B

Sample Handling: Refrigerate at 4°C and analyze within 28 days of collection.

Detection Limit: 1.0 mg/L.

Optimum Concentration Range: 1.0 - 100 mg/L

Instrument Conditions:

1. Pump speed: 35
2. Cycle speed: 30 seconds
3. Load period: 15 seconds
4. Inject period: 15 seconds
5. Inject to start of peak period: 8 seconds
6. Inject to end of peak period: 35 seconds
7. Gain: 200
8. Zero: 250
9. Interference filter; 480 nm
10. Sample loop: 20 cm
11. Standards for curve set-up: 0, 10.0, 20.0, 50.0, 80.0, 100.

Reagent Preparation: (Prepare fresh every 6 months, unless otherwise noted.)

1. Degassed Milli-Q water - 2 options:

   a. Boil Milli-Q water vigorously for 5 minutes. Cool and store in cubitainer.

   b. Bubble helium, using the fritted gas dispersion tube, through the Milli-Q water. (15 min/20 L.) Store in cubitainer.

2. Stock chloride standard (1000 mg/L Cl): In a 1 liter volumetric flask, dissolve 1.648 g of primary grade sodium chloride (NaCl), previously dried at 103°C, in 500 mL Milli-Q water. Dilute to the mark and invert to mix.

3. Standards: (Prepare fresh every 2 months.)

Concentration of Standard	Letter Identifier	Volume of Cl Standard	Dilute to
0 mg/L	A	0	200
10.0 mg/L	B	2.0	200
20.0 mg/L	C	4.0	200
50.0 mg/L	D	25.0	500
80.0 mg/L	E	40.0	500
100 mg/L	F	20.0	200

Note: Final volumes are not the same!
Computer refers to standards by letter.

4. Stock mercuric thiocyanate reagent: In a 1 liter volumetric flask, dissolve 4.17g of mercuric thiocyanate ($Hg(SCN)_2$) in one liter of methanol. Invert to mix. Store in amber glass.

CAUTION: Mercury is a very toxic metal. WEAR GLOVES!

5. Stock ferric nitrate reagent (0.5M): In a 1 liter volumetric flask, dissolve 202.0g of ferric nitrate ($Fe(NO_3)_3 \cdot 9H_2O$) in approximately 800 mL of deionized water. Add 25 mL of concentrated nitric acid and dilute to one liter. Invert to mix.

6. Combined color reagent: Mix 150 mL of stock mercuric thiocyanate solution with 150 mL of stock ferric nitrate reagent and dilute to 1000 mL with deionized water. Vacuum filter through a 0.45 micron membrane filter.

Notes:

1. Samples must be diluted to obtain concentrations within the optimum working range.

2. The gain and zero settings are guidelines and must be adjusted each day to optimize.

3. The chloride standards may be combined with alkalinity and sulfate standards for use with the 3 channel method.

4. Any sample with turbidity must be filtered prior to analysis. (Use Whatman #1 or #4.)

5. Color is an interference, dilute the sample and also spike this sample to confirm the quality of the result.

System Operation:

A. Refer to "Auto Analyzer Operation Start-up procedure". (IOP# LAA-section A)

B. Analyze a blank and an EPA check standard at the beginning of each run.

C. Use a 40 ppm Cl for the spike level.

D. The calibration check standard is 50 mg/L (D).

E. Refer to "Auto Analyzer Shut-down procedure". (IOP# LAA-section B)

Quality Control:

1. Establish a standard curve with the standards listed above. Record the check standard in the check standard book. The concentration should remain consistent from run to run. If not, necessary troubleshooting must be performed before continuing (check reagent, pump tubing, valves, etc.).

2. A quality control calibration standard of 50.0 mg/L is to be analyzed, at a minimum, after every 10 samples. If less than 10 samples are analyzed, a calibration standard is still required. The last sample analyzed in the run is to be the calibration standard. These standards must be within the acceptable ranges or the samples run after the last acceptable check standard are to be reanalyzed. Record the calibration standards in the quality control book. The acceptable limits are noted in the quality control book.

3. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Duplicates are to be averaged. Spike samples with a standard in a 1:1 ratio of sample to standard. Spike recoveries and duplicates are to be within acceptable ranges or troubleshooting must be performed.

Calculations:

1. Calculate with Lachat QuikChem software, in the concentration mode, using the IBM XT computer.

	Revision Date
Michael Linskens 9/25/87 Michael J. Linskens Laboratory Manager	8-18-87
Kim Finner Kim D. Finner Analytical Laboratory QA/QC Officer	9-25-87
Lawrence D. Andersen Lawrence D. Andersen Vice President, Technical Services	

NITRATE - AUTOANALYZER

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

Reference: EPA 1983, Method 353.2
Lachat Instruments, 1986

Detection Limit: 0.02 mg/L

Optimum Range: 0.02 - 2.00 mg/L NO_3.

Sample Handling: Analyze within 48 hours of collection. If this is not possible, preserve the sample with 2 mL concentrated H_2SO_4/1 liter and analyze within 14 days.

Instrument Conditions:

1. Pump speed: 35
2. Cycle period: 50 seconds
3. Load period: 20 seconds
4. Inject period: 20 seconds
5. Inject to start of peak period: 22 seconds
6. Inject to end of peak period: 68 seconds
7. Gain: 450
8. Zero: 400
9. Interference filter: 520 nm
10. Sample loop: 17 cm
11. Standards for curve set-up: 0, 0.20, 0.50, 1.00, 2.00
12. Column: (see reagents 7-10)

Reagent Preparation: (Prepare fresh every 6 months, unless otherwise stated.)

1. Degassed Milli-Q water (2 options):

   a. Boil Milli-Q water vigorously for 5 minutes. Cool and store in a cubitainer, or

   b. Bubble helium, using the fritted gas dispersion tube, through the Milli-Q water. Store in a cubitainer. (15 min/20 L)

2. Stock nitrate standard (100 mg/L NO_3): In a 1 liter volumetric flask, dissolve 0.7218 potassium nitrate (KNO_3) in about 600 mL of Milli-Q water. Add 2 mL of chloroform, as a preservative. Dilute to the mark. Store in a dark glass bottle.

3. Working stock nitrate standard (10 mg/L NO_3): In a 100 mL volumetric flask, pipet 10.0 mL of the stock nitrate standard and dilute to the mark with Milli-Q water. Standard is good for 2 weeks if H_2SO_4 preserved.

4. Standards: (Prepare fresh every 2 weeks.) Preserve with 0.2 mL H_2SO_4.

Concentration of Standard	Letter Identifier	Volume of NO_3 Standard	Dilute to
0 mg/L	A	0	100 mLs
0.20 mg/L	B	2.0	100 mLs
0.50 mg/L	C	5.0	100 mLs
1.00 mg/L	D	10.0	100 mLs
2.00 mg/L	E	20.0	100 mLs

Note: Computer refers to standards by letter.

5. Sodium hydroxide (15M): To 250 mL of Milli-Q water, add 150.0g NaOH. SLOWLY! This solution will get very HOT! Swirl to dissolve. Store in a plastic bottle.

6. Ammonium chloride buffer solution: In a 1 liter volumetric flask, dissolve 85.0g of ammonium chloride (NH_4Cl) and 1.0g of disodium ethylenediamine tetracetate dihydrate (EDTA) in approximately 800 mL Milli-Q water. Adjust the pH to 8.5 with the 15M NaOH. Dilute to the mark.

7. Sulfanilamide color reagent: In a 1 liter volumetric flask, add approximately 800 mL of Milli-Q water. Then add 100 mL concentrated phosphoric acid (H_3PO_4). Add 40.0g sulfanilamide and dissolve completely. Dissolve 1.0g N-1-naphthlethylenediamine dihydrochloride (NED) and dilute to one liter. Store in dark bottle at 4°C. Stable for 2 months when refrigerated.

8. Column Preparation:

   a. Cadmium preparation: Place 10-20g of coarse cadmium powder (granules) in a 250 mL beaker and wash with 50 mL of acetone, then distilled water, then two 50 mL portions of 1 M hydrochloric acid (8 mL concentrated hydrochloric acid plus 92 mL deionized water). Then rinse thoroughly with deionized water. If using cadmium for second time, rinse with 1 M hydrochloric acid before beginning process. CAUTION: Collect and store all waste cadmium. Wear gloves!

   b. Copperization: Prepare a 2% copper sulfate solution (20g $CuSO_4 \cdot 5H_2O$) per liter of deionized water) and add a 100 mL portion to the cadmium prepared in "a" above. Swirl gently for about 5 minutes, then decant the liquid and repeat with a fresh 100 mL portion of 2% copper sulfate. Continue this process until colloidal copper is visible in the supernatant (a red-brown precipitate) and solution remains blue in color. Decant and wash with at least 5 portions of ammonium chloride solution (Reagent #6) to remove the colloidal copper. The cadmium should be black or dark gray. The cadmium granules may be stored in a stoppered bottle in ammonium chloride solution (Reagent 6).

c. Packing the column (wear gloves!): Place a small piece of polyurethane foam (or glass wool) loosely in the end of the glass tube. Insert the plugged end of the glass tube into the column end fitting. Cut a length of 0.032" id teflon tubing 3 to 4 inches longer than the column.

Insert the teflon tube in the end fitting and fill the whole tube with water, holding the flexible tube in a U-shape so that the ends are level. Place the second end fitting on the other end of the teflon tubing. (Placing a small funnel onto the end fitting may aid filling.) Taking care that no air bubbles are introduced, place the copperized cadmium granules in the column. Tap the column gently, every 1-2 cm, to pack the granules. When the column is packed to within about 5 mm of the end of the glass column, insert another foam plug, then the column end fitting. Store the column with the ends connected with a length of teflon tubing, as air pockets or having the column dry out will necessitate repacking. If air remains in the column, connect the column to the manifold and turn the pump on maximum. Tap column firmly until all air is removed.

d. Column activation: The column must be activated before use or it will not reduce nitrate. This may be accomplished by pumping the 10 mg/L nitrate standard through the sampler line. When the solution is injected, a brilliant pink color will be visible in the coil. The cadmium column effeciency should be above 80%, if less, the column must be repacked.

Notes:

1. Interferences:

- Build up of suspended matter in the reduction column will restrict sample flow. Since nitrate-nitrogen is found in a soluble state, the sample must be pre-filtered.

- Low results might be obtained for samples that contain high concentrations of iron, copper or other metals. EDTA is added to the samples to eliminate these interferences.

- Samples that contain large concentrations of oil and grease will coat the surface of the column. This interference is eliminated by pre-extracting the sample with an organic solvent.

2. Samples must be diluted to obtain concentrations within the optimum working range.

3. The gain and zero settings are guidelines and must be adjusted each day to optimize.

4. Color will intefere; dilute the sample and also spike this sample to confirm the quality of the result.

5. ACS grade ammonium chloride has been found occasionally to contain significant nitrate contamination, so an alternative preparation for the ammonium chloride buffer (Reagent 6) is as follows:

   In the hood, add 126 mL concentrated HCl to a 1 liter volumetric flask containing 500 mL degassed Milli-Q water. Mix. Add 95 mL ammonium hydroxide and 1.0 gm disodium EDTA. Dissolve and dilute to the mark. The pH should be 8.5 $\pm$ .1, adjust pH if necessary.

System Operation:

1. Refer to Auto Analyzer Operation - Start-up Procedure (IOP# LAA-section A).

2. After pumping reagents through the lines, turn off the pump and insert column, making sure that air bubbles are not introduced into the column.

3. Activate column. (See #8d. above.)

4. Analyze a blank and EPA check standard at the beginning of each run.

5. Use 0.5 ppm spike levels. The calibration check standard is 1.00 mg/L NO_3 (D).

6. If only nitrate is requested, nitrites must be analyzed and subtracted from the nitrate + nitrite value.

7. However, since this method analyzes both forms of nitrogen, if the nitrate + nitrite result is <0.02, nitrite does not need to be run for that sample.

8. After use, turn off the pump and remove the column from the manifold.

9. Refer to Auto Analyzer Shut-down Procedure. (IOP# LAA-section B.)

Quality Control:

1. Establish a standard curve with the standards listed above. Record the check standard in the check standard book. The concentration should remain consistent from run to run. If not, necessary troubleshooting must be performed before continuing (check reagents, pump tubing, valves, etc.).

2. A quality control calibration standard of 1.00 mg/L is to be analyzed, at a minimum, after every 10 samples. If less than 10 samples are analyzed, a calibration standard is still required. The last sample analyzed in the run is to be the calibration standard. These standards must be within the acceptable ranges or the samples run after the last acceptable check standard are to be reanalzyed. Record the calibration standards in the quality control book. The acceptable limits are noted in the quality control book.

3. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Duplicates are to be averaged. Spike samples with a standard in a 1:1 ratio of sample to standard. Spike recoveries and duplicates are to be within acceptable ranges or troubleshooting must be performed.

Calculation:

1. Calculate with Lachat QuikChem software, in the concentration mode, using the IBM XT computer.

Revision Dates

8-18-87

Michael Linskens 8/20/87
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Lawrence Andersen 8/20/87
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SULFATE - AUTOANALYZER

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

Reference: EPA, 1983, Method 375.2
Lachat Instruments, 1986, QuikChem Method 10-116-10-2-B

Detection Limit: 5.0 mg/L

Optimum Concentration Range: 5.0 - 200 mg/L

Sample Handling: Refrigerate at 4°C and analyze within 28 days of collection.

Instrument Condition:

1. Load time: 20 seconds
2. Inject Period: 30 seconds
3. Inject to peak start period: 9 seconds
4. Inject to peak end period: 54 seconds
5. Cycle time: 50 seconds
6. Gain: 200
7. Zero: 700
8. Interference filter: 460 nm
9. Sample loop: 10 cm
10. Standards to use for curve set-up: 0, 25.0, 50.0, 100, 150, 200 mg/L.

Reagent Preparation: (Prepare fresh every 6 months, unless otherwise noted.)

1. Degassing with helium - 2 options:

   a. Boil Milli-Q water vigorously for 5 minutes. Cool and store in cubitainer.

   b. Bubble helium, using the fritted gas dispersion tube, through the Milli-Q water. (15 min/20 L.) Store in cubitainer.

2. Carrier (0.3 ppm $SO_4^=$): In a 1 liter volumetric flask, add 0.3 mL of 1000 ppm stock sulfate solution and dilute to mark with degassed Milli-Q water.

3. Barium chloride solution (6.24M): In a 1 liter volumetric flask, dissolve 1.526 g of barium chloride dihydrate ($BaCl_2 \cdot 2H_2O$) in 500 mL of degassed Milli-Q water and dilute to 1 liter.

4. Hydrochloric acid (1.0N): In a 100 mL volumetric flask, containing approximately 80 mL of Milli-Q water, add 8.3 mL of concentrated hydrochloric acid and dilute to the mark with Milli-Q water.

5. Barium - MTB color reagent: (The purity of the methylthymol blue and the alcohol can be critical. USE THE SOURCES STATED BELOW.)

   In a dry 1000 mL volumetric flask, place 0.2364 g of methylthymol blue (3', 3"bis-N,N-bis carboxymethyl)-amino methylthymolsulfonephthalein pentasodium salt (Kodak No. 8068). Add 50 mL of barium chloride solution ("3" above). The solution may be used to aid in the transfer of the dye. Swirl to dissolve. Add 8.0 mL of the 1.0 N HCl solution ("4" above) and mix - solution should turn orange. Add 142 mL deionized water and dilute to 1000 mL with ethanol (Aldrich 24.511.9) Mix. The pH of this solution should be 2.5. Prepare this solution the day before use and store it refrigerated in an amber bottle.

6. Sodium hydroxide (50% stock solution): Cautiously dissolve 500 g of sodium hydroxide (NaOH) in 600 mL of Milli-Q water. Cool and dilute to 1 liter. Store in plastic bottle. CAUTION: The solution will become very hot!

7. Sodium hydroxide (0.18 N): In a 1 liter volumetric flask, add 14.4 mL of 50% sodium hydroxide ("6" above) to degassed Milli-Q water, and dilute to the mark.

8. Buffered EDTA (for cleaning manifold): In a 1 liter volumetric flask, dissolve 6.75 g ammonium chloride (NH_4Cl) in 500 mL Milli-Q water. Add 57 mL concentrated ammonium hydroxide and 40.0 g tetrasodium EDTA dihydrate. Dissolve by swirling; dilute to the mark with Milli-Q water.

9. Sulfate stock (1000 mg/L): Dry approximately 2 g of sodium sulfate (Na_2SO_4) at 105°C for 2 hours. Cool in a desiccator. In a 1 liter volumetric flask, dissolve 1.479 g of the dried sodium sulfate in Milli-Q water and dilute to 1 liter. (1.0 mL = 1.0 mg $SO_4^{=}$).

10. Working standard: (Prepare fresh every 2 months)

Concentration of Standard	Letter Identifier	Volume of Stock Sulfate Standard	Dilute to
0 mg/L	A	0	200 mL
25.0 mg/L	B	5.0	200 mL
50.0 mg/L	C	10.0	200 mL
100 mg/L	D	50.0	500 mL
150 mg/L	E	75.0	500 mL
200 mg/L	F	40.0	200 mL

Note: Final volumes are not the same.
Computer refers to standards by letter.

Preparation of Ion Exchange Column:

1. Make a slurry of approximately 0.5 g of BioRex 70, 50-100 mesh ion exchange resin in Milli-Q water.

2. Remove one column end from the glass column. Fill the column with water, then aspirate the slurry or allow it to settle by gravity to pack the column. Take care to avoid trapping air bubbles in the column and its fittings at this point and all subsequent operations.

3. After the resin has settled, replace the end fitting. To ensure a good seal, remove any resin particles from the threads of the glass, the column end and the end fittings. To store the column, the ends of the Teflon tubing may be joined with a union.

4. To test the effectiveness of the column, make up a standard of pure sodium sulfate and compare its peak height to an identical standard with hardness typical of the samples added. If the column is being depleted, the standard with hardness will read lower because the divalent cations are complexing the free MTB. The concentration of the standard should be mid-range. If depletion has occured, repack the column with fresh resin.

5. Regenerating Resin: Batch regeneration is recommended because the hydrogen form of BioRex 70 can swell considerably more than the sodium form. Collect the used resin in a small beaker or flask. Wash with dilute HCl until the wash tests free of calcium and/or magnesium. This procedure removes the divalent cations by converting the carboxylate exchange group to the protonated form - COOH. Convert the resin back to the sodium form by neutralizing with washes of 0.5M NaOH until the wash has a pH of 9 or greater. Rinse with deionized water for storage or repacking. A column may be used for 3-4 trays (approximately 150 samples) before it needs to be replaced.

Notes:

1. Samples must be diluted to obtain concentrations within the optimum working range.

2. Sulfate standards may be combined with alkalinity and chloride standards for use with the 3-channel method.

3. The gain and zero settings are guidelines and must be adjusted each day to optimize.

4. Inteferences:

- The cation exchange column removes multivalent cations. Run a mid-range sulfate standard containing a typical concentration of $CaCO_3$ periodically to check performance. Any decrease in peak height should indicate the need to regenerate or replace the resin. (At 600 ppm $CaCO_3$, the column is good for 80 + injections.)

- Samples with pH less <2 should be neutralized. High acid concentrations can displace multivalent cations from the column.

- *Color will interfere. Dilute the sample and also spike this sample* to confirm the quality of the result.

- Turbidity - turbid samples may be filtered (use Whatman #1 or #4) prior to analysis on Lachat.

- Orthophosphate also forms a precipitate with barium at high pH. Check the response of pure orthophosphate standards, if samples are known to be high in PO_4=.

5. Troubleshooting:

A. Baseline noise with reagents pumping.

1. Noise with column in line but good baseline without column.

   a. Repack column, air bubbles may be causing pulsing.

   b. Check flow fit connectors and end fittings on column for blockage or leaks.

2. Noise with and without column in line.

   a. Degas carrier and/or reagents. Fine bubbles cause sharp spikes on baseline.

   b. Place a longer piece of manifold tubing on the outlet of the flow cell leading to the waste container. This method requires the use of the screw type flow cell.

   c. Replace the pump tubes. The silicone tube, used for the color reagent, wears faster than the PVC pump tubes.

   d. With water pumping in the lines, check all hydraulic connections for blockages, leaks, etc.

B. Baseline drift.

1. Clean the manifold with the buffered EDTA.

2. Turn the gain high and use the shortest sample loop possible. This improves the linearity of the calibration curve, prolongs the useful life of the column, and minimizes the build up of $BaSO_4$ on the manifold tubing.

System Operation:

1. Refer to "Auto Analyzer Operation Start-up procedure" (SOP# LAA-section A).

2. Pump reagents through lines until baseline is stable. Then turn off pump and insert column.

3. Pump reagents through the lines before inserting the column. Use a short piece of manifold tubing in place of the column. When all air has passed and the baseline is steady, turn off the pump and insert the column. The column should be placed in a vertical position with flow in the top and out the bottom. In this configuration, the column will operate effectively even if the resin packs down more to leave a gap at the top. Resume pumping.

4. Analyze a blank and an EPA check standard at the beginning of each run.

5. Use a 75 ppm spike level. The calibration check standard is 100 mg/L (D).

6. To shut down, turn off pump and remove the column.

   To remove the column:

   a. Turn off the pump.
   b. Remove the column.
   c. Join ends of the column with a union.
   d. Replace the column on the manifold with the short teflon tubing piece.
   e. Rinse manifold with Milli-Q water.
   f. Rinse manifold with EDTA cleaning solution.
   g. Rinse manifold again with Milli-Q water.
   h. Pump dry.
   Follow "Auto Analyzer Shut-down procedures" (SOP# LAA-Section B).

Quality Control:

2. A quality control calibration standard of 100 mg/L is to be analyzed, at a minimum, after every 10 samples. If less than 10 samples are analyzed, a calibration standard is still required. The last sample analyzed in the run is to be the calibration standard. These standards must be within the acceptable ranges or the samples run after the last acceptable check standard are to be reanalyzed. Record the calibration standards in the quality control book. The confidence limits are noted in the quality control book.

3. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Duplicates are to be averaged. Spike samples with a standard of a 1:1 ratio of sample to standard. Spike recoveries and duplicates are to be within acceptable ranges or troubleshooting must be performed.

Calculations:

1. Calculate with the Lachat QuikChem software, in the concentration mode, using the IBM-XT computer.

	Revision Date
Michael Linskens 9/25/87	8-18-87
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AMMONIA NITROGEN

Scope and Application: This method is applicable to the determination of ammonia-nitrogen in drinking water, surface water, groundwater, sludges, soils, and industrial wastes.

Method: Micro-distillation, Colorimetric

Reference: EPA, 1983, Method 350.2

Detection Limit: 0.10 mg/L for aqueous samples
5.00 mg/kg for soils and sludges

Optimum Range: 0.10 - 2.00 mg/L for aqueous samples
5.00 - 100 mg/kg for soils and sludges

Sample Handling: Acidify aqueous samples with concentrated sulfuric acid to pH <2 and refrigerate at 4°C. Refrigerate soils ans sludges at 4°C. Analyze within 28 days of sampling.

Reagents and Apparatus:

1. Kjeldahl flasks, 100 mL
2. Keeney distillation apparatus
3. Spectrophotometer, set at 425nm with sipper cell
4. Erlenmeyer flasks, 50 mL
5. Sulfuric acid, concentrated
6. Milli-Q water
7. pH meter, 0.1 pH unit sensitivity
8. Volumetric glassware, Class A (pipets and flasks)
9. Top loading balance, 0.01g sensitivity
10. Graduated cylinders, 50 mL
11. Mixing cylinders, 50 mL
12. Ammonium chloride (NH_4Cl)
13. Boric acid (H_3BO_3)
14. Mercuric iodide (HgI_2)
15. Potassium iodide (KI)
16. Sodium hydroxide (NaOH)
17. Sodium tetraborate ($Na_2B_4O_7 \cdot 10H_2O$)
18. Sodium thiosulfate ($Na_2S_2O_3 \cdot 5H_2O$)
19. Analytical balance, 0.0001g sensitivity
20. 150 mL beaker
21. Stir bars and stir plate

Reagent Preparation: (Prepare fresh every 6 months, unless otherwise stated).

1. Ammonium chloride stock solution(1000 mg/L): In a 1 liter volumetric flask, dissolve 3.819g NH_4Cl in approximately 300 mL Milli-Q water and bring to volume.

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2. Ammonium chloride standard solution (10 mg/L): Dilute 10.0 mL of the ammonium chloride stock solution to 1 liter with Milli-Q water in a volumetric flask.

3. Boric acid solution: Dissolve 20.0g H_3BO_3 in Milli-Q water and dilute to 1 liter in a volumetric flask.

4. Nessler reagent: Dissolve 100g of mercuric iodide and 70g of potassium iodide in about 200 mL of Mill-Q water. Add this mixture slowly, while stirring to a COOLED solution of 160g NaOH in 500 mL Milli-Q water. Dilute the mixture to 1 liter. Store in a Pyrex bottle and keep out of direct sunlight.

5. Sodium hydroxide (1N): Dissolve 40g of NaOH in Milli-Q water and dilute to 1 liter.

6. Sodium hydroxide (0.1N): Dilute 100 mL of 1N NaOH to 1 liter with Milli-Q water.

7. Sodium tetraborate solution (0.025M): Dissolve 9.5g of $Na_2B_4O_7 \cdot 10H_2O$ or 5.0g anhydrous $Na_2B_4O_7$ in Milli-Q water and dilute to 1 liter.

8. Borate buffer: Add 88 mL of 0.1N NaOH solution to 500 mL of 0.025M sodium tetraborate solution. Dilute to 1 liter.

9. Sodium thiosulfate (1/70N): Dissolve 3.5g $Na_2S_2O_3 \cdot 5H_2O$ in Milli-Q water and dilute to 1 liter. (1 mL of this solution will remove 1 mg/L of residual chlorine in 500 mL of sample).

NOTES:

1. Residual chlorine must be removed prior to distillation by pretreating the sample with sodium thiosulfate solution.

2. Pre-steam the distillation apparatus with 10% NaOH before use for each batch analyzed.

3. Cyanate and some volatile alkaline compounds may cause an offcolor nesslerization. This off-color can be eliminated by boiling the sample at a low pH (pH 2-3) to drive off the compound. This should be done prior to the distillation step.

Procedure: Sample must be homogenized prior to analysis to ensure a representative sample aliquot.

Distillation:

1. All glassware is to be soap and wate washed, tap water rinsed, and Milli-Q water rinsed prior to use.

2. The reservoir should be 2/3 full with Milli-Q water. Add a few boiling chips. Add sulfuric acid to reservoir to bring to a pH <2. Turn on the heater. Set heater control to about 6. Allow the steam reservoir to heat up. This unit will take about 45 minutes to heat-up. Turn the heater control to about a setting of 9 and bring to boiling. Analysis can begin once boiling begins.

3. Prepare the distillation apparatus as follows: Steam out the distillation apparatus with a 10% NaOH solution. Analyze a blank to confirm no trace of ammonia exists (no color change with the addition of the Nessler reagent to the distillate).

4. Aqueous samples:

   Place 40 mL or an aliquot of sample diluted to 50 mL in a 150 mL beaker. Record the volume used. Add 1N NaOH while stirring very slowly until the pH is 9.5 using pH paper.

   To spike: Place 45 mL sample and 5 mL of the 10 mg/L ammonia standard to the Kjeldahl flask and continue with procedure.

   Non-aqueous samples:

   Place approximately 1.0g in a 150 mL beaker. Record weight used. Add 50 mL Milli-Q water and adjust the pH with 1N NaOH, while stirring slowly, to pH 9.5 using pH paper.

   To spike: Place 1.0g sample, 1 mL of the 1000 mg/L ammonia standard in the Kjeldahl flask. Add 50 mL Milli-Q water and continue with procedure.

5. Transfer the pH-adjusted sample to a 100 mL Kjeldahl flask. Add 2.5 mL of borate buffer.

6. Add 5 mL of boric acid to a 50 mL Erlenmeyer flask and place flask at the condenser outlet with the tip of the condenser immersed in the boric acid.

7. Connect the Kjeldahl flask to the distillation apparatus and secure with springs.

8. Open the stopcock to the still on the condensation chamber. Close the drain stopcock. The steam will now pass through the Kjeldahl flask.

9. Steam distill 30-40 mL at a rate of 4-5 mL/min.

10. Remove the Erlenmeyer flask.

11. Rinse the tip of the condenser and steam outlet into a waste beaker.

12. Continue distilling remaining samples, blanks and standards. When all samples, blanks and standards are distilled, the colorimetric determination can be performed.

Colorimetric Determination:

1. Prepare the following series of blanks and standards in 50 mL mixing cylinders (These do not need to be taken through the distillation step).

mL of 10 mg/L ammonium chloride solution	Dilute to	Concentration (mg/L
0	50 mL	BLANK
0.5	50 mL	0.10
1.0	50 mL	0.20
2.0	50 mL	0.40
5.0	50 mL	1.00
10.0	50 mL	2.00

2. Add 2.0 mL of Nessler reagent to the blank and standards. Stopper and mix by inverting several times.

3. After 20 minutes, read the absorbances on the spectrophotometer set at 425nm using the sipper cell. Zero the spectrophotometer to the distilled reagent blank.

4. Transfer distilled samples to 50 mL volumetric flasks and dilute to 50 mL with Milli-Q water. Mix.

5. Determine the ammonia in the distillate as follows:

   - Transfer 25 mL of distillate, or an aliquot diluted to 25 mL, to a mixing cylinder.
   - Add 1 mL of Nessler reagent and mix by inverting several times.
   - After 20 minutes, read the absorbance as described in Step 3.

Calculations:

1. Aqueous Samples:

   a. Calculate using linear regression.

   b. Multiply in any dilution factors performed in the distillation and colorimetric steps to obtain the final result in mg/L.

2. Non-Aqueous Samples:

a. Calculate using regression to obtain a mg/L value.

b. Multiply in any dilution factor performed in the colorimetric step (mg/L).

c. Multiply result obtained from "Step b" by 50 and divide by grams of sample used to obtain the final result in mg/kg.

3. Spike calculation:

$$\% \text{ Recovery} = \frac{\begin{bmatrix}\text{Total mL}\\ \text{SA + STD}\end{bmatrix}\begin{bmatrix}\text{Conc. of}\\ \text{spike}\end{bmatrix} - \begin{bmatrix}\text{mL}\\ \text{SA used}\end{bmatrix}\begin{bmatrix}\text{Conc. of}\\ \text{SA}\end{bmatrix}}{(\text{mL STD used})\ (\text{Conc. STD})}$$

Where SA = sample
STD = standard

Quality Control:

1. Establish a standard curve with the standards listed above plus a blank. The standard curve must be carried through the distillation process. Record the absorbance check standards (1.00 mg/L) in the absorbance check book. The absorbances should remain consistent from run to run. If not, necessary troubleshooting must be performed before continuing (check wavelength, spectrometer bulb, solutions, etc.).

2. A distilled blank and standard (1.00 mg/L) is to be analyzed initially and at the end of the analytical run. The standard must be within acceptable ranges (± 10% of true value), or troubleshooting must be performed.

3. A quality control calibration standard of 1.00 mg/L is to be analyzed, initially and after every 10 samples. This standard does not need be carried through the distillation procedure. The last sample analyzed in the run is to be the calibration standard. These standards must be within the acceptable ranges (± 10% of the true value) or the samples run after the last acceptable check standard are to be reanalyzed.

4. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Duplicates are to be averaged. Spike recoveries and duplicate results are to be within acceptable ranges.

CHEMICAL OXYGEN DEMAND

Scope and Application: This method is applicable to surfacewater, sewages, wastewater, and groundwater.

Method: Dichromate reflux, Colorimetric

Reference: EPA 1983, Method 410.4.

Detection Limit: 20 mg/L

Optimum Range: 20-700 mg/L

Sample Handling: Preserve with sulfuric acid to a pH <2 and refrigerate at 4°C. Analyze within 28 days.

Reagents and Apparatus:

1. Dichromate - mercuric sulfate-sulfuric acid digestion solution
2. Silver sulfate - sulfuric acid catalyst solution
3. COD standard solutions
4. Block digestor, set at 150°C
5. 16 x 100 mm culture tubes with teflon lined screw caps
6. Eppendorf macropipeter, 0-5 mL
7. Spectrophotometer, set at 600 nm wavelength with sipper cell
8. Eppendorf microliter pipeter, 10-100 ul
9. 2 Repipette Dispensers, 1000 mL
10. Milli-Q water

Reagent Preparation: (Prepare fresh every 6 months, unless otherwise noted.)

1. Digestion Solution: Add 10.2 g of dried potassium dichromate ($K_2Cr_2O_7$), 33.3 g of mercuric sulfate ($HgSO_4$) and 167 mL of concentrated H_2SO_4 to about 500 mL of Milli-Q water; dilute to 1000 mL in a volumetric flask and stir until dissolved. Store in a dark place.

2. Silver Sulfate-Sulfuric Acid Catalyst Solution: Add 22.0 g of silver sulfate (Ag_2SO_4) to a 2.5L bottle of conc. H_2SO_4. Stir to dissolve.

3. COD Stock Standard, 1000 mg/L: Carefully weigh 0.8500g of dried potassium acid phthalate (KHP), dissolve in Mill-Q water and dilute to 1 liter in a volumetric flask. Refrigerate.

4. Working COD Standards: (Prepare fresh monthly and refrigerate.)

   A. 700 mg/L COD Standard: To a 100 mL volumetric flask, add 70 mL of 1000 mg/L COD Stock Standard and dilute to the mark with Milli-Q water.

B. 300 mg/L COD Standard: To a 100 mL volumetric flask, add 30 mL of 1000 mg/L stock standard and dilute to the mark with Milli-Q water.

C. 100 mg/L COD Standard: To a 100 mL volumetric flask, add 10 mL of 1000 mg/L COD Stock Standard and dilute to the mark with Milli-Q water.

D. 50 mg/L COD Standard: To a 100 mL volumetric flask, add 5 mL of 1000 mg/L COD Stock Standard and dilute to the mark with Milli-Q water.

E. 20 mg/L COD Standard: To a 100 mL volumetric flask, add 2 mL of 1000 mg/L COD Intermediate Standard and dilute to the mark with Milli-Q water.

Notes:

1. If a dark green or turquoise color occurs when sample is added or when the tube is being heated; it is over the upper limit of the curve and must be diluted.

2. Interference: Chlorides represent a positive interference. Mercuric sulfate is added to the digestion tubes to complex the chloride. Mercuric sulfate can complex up to 2,000 mg/L chloride before reacting with dichromate in the sample. If chloride exceeds 2,000 mg/L, dilute the sample.

3. Reagents are corrosive and toxic. Avoid skin contact.

4. Store standards in the refrigerator.

5. Store the dichromate solution and prepared tubes in the dark.

6. To clean the tubes, rinse several times in Milli-Q water.

Procedure:

1. All glassware is to be soap and water washed, tap rinsed and Milli-Q water rinsed prior to analysis. Rinse digestion tubes and caps with Milli-Q water prior to use. Caps deterioriate over time. Discard caps after 3 uses.

2. Into each tube, pipet exactly 1.5 mL of COD digestion solution, using repipetter dispenser.

3. Into each tube, pipet exactly 3.5 mL of the silver sulfate-sulfuric acid solution, using the repipetter dispenser, down the side of the tube. These tubes may be stored, with caps having teflon liners, indefinitely. Store in the dark!

4. The standard curve consists of the following standards:

   3 Milli-Q water blanks
   2-20 mg/L
   2-50 mg/L
   1-100 mg/L
   1-300 mg/L
   1-700 mg/L

   The standards are carried through the digestion step.

5. To Spike: In a disposable cup, place 2.5 mL sample, add 2.5 mL of the 300 mg/L standard. Mix well. Take 2.5 mL of this mixture, proceed as follows.

   Using the Oxford 0-5 mL pipet, add 2.5 mL of sample, standard, blank or spike to the tube. Be careful to avoid air bubbles in the pipet tip and to eject all of the sample. Cap tubes tightly and mix by inverting 10-12 times.

6. Place tubes in a block heater at 150°C for 2 hours. Block heater should be preheated at least 1 hour prior to use.

7. Remove tubes from block heater. Cool to room temperature. Read the absorbance on spectrophotometer, set at 600 nm, using the sipper cell. Samples can be stored in refrigerator overnight and read the next day. Do not shake tubes. Be very careful not to aspirate any of the precipitate in the bottom of the tube. Initially zero with the blank standard, and after 20 samples rezero.

Quality Control:

1. Establish a standard curve with the standards listed above plus a blank. Record the absorbance check standard in the absorbance check book. The absorbances should remain consistant from run to run. If not, necessary troubleshooting must be performed before continuing (check wavelength, spectrophotometer bulb, solution, etc.)

2. A quality control calibration standard of 100 mg/L COD is to be analyzed, initially and after every 10 samples. If less than 10 samples are analyzed, a calibration standard is still required. The last sample analyzed in the run is to be the calibration standard. These standards must be within the acceptable ranges or the samples run after the last acceptable check standard are to be reanalyzed. Record the calibration standards in the quality control book. The confidence limits are noted in the quality control book.

3. Duplicate and spike a miniumum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Duplicates are to be averaged. Spike recoveries and duplicate results are to be within acceptable ranges.

Calculation:

1. Calculate using linear regression.

To Calculate Spike:

$$\% \text{ Recovery} = \frac{(\text{spike value}) - (0.5)(\text{sample value})}{150} \times 100$$

	Revision Date
Michael Linskens Michael J. Linskens Laboratory Manager	7-23-86
Kim Finner Kim D. Finner Analytical Laboratory QA/QC Officer	4-27-87
Thomas J. Lynch Thomas J. Lynch QA Officer	

[AL-1-13]

TOTAL ORGANIC CARBON

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

Method: Wet oxidation, non-dispersive infra-red detection

Reference: EPA 1983, Method 415.1 and OI Model 524C Total Carbon System Manual

Detection Limit: 1.0 mg/L

Optimum Range: 1.0-25 mg/L

Sample Handling: Acidify with concentrated sulfuric acid to pH <2 and refrigerate at 4°C. Analyze within 28 days.

Reagents and Apparatus:

1. OI Model 524C Total Carbon System
2. 10 mL sealed ampules
3. Commercial grade O_2 gas
4. Disposable propane gas cylinder
5. Commercial-grade N_2 gas
6. Eppendorf microliter pipet, 100-1000 uL
7. Eppendorf macropipet, 0-5 mL
8. Silicone grease
9. Saturated potassium persulfate solution
10. Organic carbon standard solutions
11. Phosphoric acid solution, 10%
12. Milli-Q water

Reagent Preparation:

1. Total Organic Carbon (TOC) Stock Solution, 1000 mg/L: Dry potassium biphthalate (KHP) at 105°C for 2 hours. Cool in a dessicator. Weigh exactly 2.1254 g KHP and dilute with Milli-Q water to 1000 mL in a volumetric flask.

2. Standard Carbon Solutions:

   25 mg/L TOC Standard: To a 1000 mL volumetric flask, pipet 25.0 mL stock carbon solution, and dilute to the mark with Milli-Q water.

   10 mg/L TOC Standard: To a 1000 mL volumetric flask, pipet 10.0 mL stock cabron solution, and dilute to the mark with Milli-Q water.

   5 mg/L TOC Standard: To a 1000 mL volumetric flask, pipet 5.0 mL stock carbon solution, and dilute to the mark with Milli-Q water.

   3 mg/L TOC Standard: To a 1000 mL volumetric flask, pipet 3.0 mL stock carbon solution, and dilute to the mark with Milli-Q water.

1 mg/L TOC Standard: To a 100 mL volumetric flask, pipet 10.0 mL of a 10.0 mg/L work carbon solution, and dilute to the mark with Milli-Q water.

3. Potassium Persulfate Solution, Saturated: Fill a 1 liter glass stoppered bottle 3/4 full with Milli-Q water. Add potassium persulfate until no more crystals will dissolve.

4. Phosphoric acid solution, 10% (v/v): Add 100 mL of phosphoric acid to 900 mL Milli-Q water.

Notes:

1. Contamination can be a problem. Keep ampules covered with aluminum foil after opening.

2. Purge and seal the ampules believed to contain the lowest carbon content first.

3. Always use clean purge tubes and purge cones. Clean with Milli-Q water, or a 10% HCL solution followed by Milli-Q water rinse.

4. The flow rate of N_2 must remain constant.

5. Changes in flow rate may be due to:

   a. Exhausted primary drying tube
   b. Leaky ampule seal
   c. Glass lodged in purge tube

6. Check zero and span settings monthly.

7. Change secondary drying tube daily.

8. Leave IR power on.

9. High suspended solids can give variable results. It is important that the sample is well mixed prior to measuring out the sample.

Procedure:

1. All glassware is to be soap and water washed, tap rinsed and Milli-Q rinsed prior to analysis.

2. Snap open an ampule along scoring.

3. Using Eppendorf 1000 microliter pipet, pipet 1000 uL of saturated potassium persulfate solution into ampule.

4. Using calibrated Oxford macropipet, carefully pipet 5.0 mL of sample into ampule.

5. Using Eppendorf 1000 microliter pipet, pipet 200 uL of 10% phosphoric acid solution into ampule.

6. Place ampule on purging rack and place a purge tube into ampule to the bottom of the ampule. (There is room to purge 10 samples at a time.)

7. Purge each sample for at least 6 minutes with nitrogen (N_2) gas.

8. Light microburner. Place ampule into clamping assembly, leaving purge tube in-place in ampule. Base of ampule should be snug with base of clamping assembly.

9. Swing microburner into place and seal ampule.

10. Continue purging while sealing the tube being careful not to fuse the purging tube while sealing. Do this by raising the purge tube just above the sealing point of the ampule.

11. Swing microburner back as soon as ampule is sealed.

12. Remove sealed ampule from holder. Open clamping assembly and drop hot ampule tip into a beaker partially filled with water.

13. Continue with steps 8-11 for the remaining samples.

14. Place ampules in an oven set at 95°C for 2 hours. Cool.

15. Place plastic stress adaptor and gum rubber seal on neck of ampule. (Silicon grease may be necessary.)

16. Place ampule in breaking assembly and turn clamping screw until ampule is firmly in-place. Check seals to make sure these are no air leaks.

17. Lower purge tube until it is level with the tip of the ampule.

18. Open zero gas valve (N_2). Adjust flow to 13 (200 mL/min.) on flowmeter. Purge air from top of ampule until integrator stops. Clear integrator.

19. Close zero gas valve (N_2). Wait for flow to drop to zero.

20. Raise purge tube clear of plunger cutters.

21. Break ampule with a downward, twisting motion.

22. Check ampule for cracks or leaks.

23. Put purge tube down into solution in ampule, about 1/8" from bottom.

24. Open zero gas valve (N_2). Flow rate should be 13 (200 mL/min.).

25. Allow ampule to purge until integrator stops.

26. Record the reading and clear the integrator.

27. Remove ampule from assembly and discard.

Daily Instrument Set-Up:

1. Check to make sure the IR detector is on (red light should be on). If not left on, allow warm-up time of at least one hour.

2. Place standardization vial with plastic adapter and gum rubber seal in ampule-breaking assembly.

3. Turn valves on front panel to "Ampule Mode" and "I.R. Flow".

4. Open N_2 valve on top of tank (pressure regulator set at 20 PSI).

5. Open zero gas (N_2) valve by lifting handle straight out.

6. Adjust flow rate to a flow meter reading of 13 (200 mL/min).

7. Turn integrator unit on clear and zero.

8. Check purging and sealing unit to ensure that a disposable propane gas cylinder is connected to adapter.

9. Open O_2 valve on top of tank (pressure regulator set at 20 PSI).

10. Turn on catalyst heater on front panel of purge and seal unit. Allow unit to purge at 500°C for one hour.

11. Check the ascarite in the tubes in the sides of the units. It should be brown to light tan in color. If white, it is CO_2 saturated and must be replaced.

12. Check drying tubes on front of ampule panel. If they appear wet or "clumpy", replace with fresh dessicant (magnesium perchlorate).

13. Change secondary drying tube.

Daily Instrument Shut-Down:

1. Turn integrator power switch off.

2. Close O_2, propane, and N_2 cylinder valves.

3. Close O_2 and N_2 toggle valves.

4. Remove and clean cutter plunger and barrel with Milli-Q water. Wipe dry.

5. Lubricate O-rings with silicone grease and re-install cutter plunger and barrel.

6. Re-install standardization vial.

7. Turn catalyst heater switch off.

8. Leave I.R. power on.

Quality Control:

1. Standard curve is to consist of the following standards; set in duplicate:

   Milli-Q water blank
   1.0 mg/L
   3.0 mg/L
   5.0 mg/L
   10.0 mg/L
   20.0 mg/L

2. The quality control check standard is to be analyzed before and after every 10 samples. The 10 mg/L check standard must be within the critical levels or the samples analyzed prior to the last check standard are to be reanalyzed. Before the samples are reanalyzed, the analyst must diagnose the problem and consult with the laboratory supervisor until the problem has been resolved and approved. Record the result of the check standard in the quality control check standard book.

3. Duplicate 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate is still required. Average the results.

4. Spike 1 out of 10 samples. If less than 10 samples are analyzed, a spike is still required. For spikes, pipet 4 mL of sample and 1 mL of 20 mg/L organic carbon standard. Spike recoveries and duplicate results are to be within acceptable calculated ranges.

Calculation:

1. Plot a standard curve from a series of standards. Calculate directly from graph.

2. Calculate using linear regression.

Revision Date

7-23-86

9-25-87

Michael Linskens 9/25/87
Michael J. Linskens
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Vice President, Technical Services

[ALM-1A-1]

TOTAL SUSPENDED SOLIDS

Scope and Application: This method is applicable to drinking water, surface water, groundwater, domestic and industrial wastewaters.

Method: Gravimetric, dried at 103-105°C

Reference: EPA 1983, Method 160.2

Detection Limit: 2 mg/L (using a 500 mL sample volume)

Sample Handling: Refrigerate at 4°C and analyze within 7 days of sampling.

Reagents and Apparatus:

1. Glass fiber filters, Whatman GF/C
2. Gelman filtration funnel and support
3. Suction flask, 1000 mL.
4. Aluminum foil weighing dishes
5. Graduated cylinder, 100 mL
6. Drying oven set at 103-105°C
7. Dessicator
8. Analytical balance
9. Deionized water

Notes:

1. Interferences: Samples with high dissolved solids may have a positive interference, and the filter should therefore be rinsed well with deionized water under suction after the sample has gone through the filter.

2. Select a sample volume that will filter without overloading the filter. The amount of vacuum applied to filter the sample should not be excessive. Excessive vacuum will cause the filter to breakdown and lose weight.

Procedure:

1. All glassware is to be soap and water washed, tap rinsed, and deionized rinsed prior to analysis.

2. Prepare the glass fiber filter by placing it on the filter support, applying vacuum, and rinsing with three-20 mL portions of deionized water through it.

3. Place the filter in an aluminum weighing dish and dry at 103-105°C for one hour.

4. Place in a dessicator, and cool before weighing (at least one hour). Repeat this cycle until a constant weight ($\pm$ 0.5 mg) is obtained. Filters may be prepared ahead of time and stored in the dessicator until ready to use.

5. Weigh the aluminum dish containing the prepared filter on the analytical balance and record the weight.

6. Assemble the filtering apparatus. Begin applying vacuum. Wet the filter with a little D.I. water.

7. Shake the sample well and pour an appropriate volume using a graduated cylinder. The use of pipets is required for volumes of 25 mL and less. Record the volume.

8. With the vacuum still on, rinse the apparatus with 3-10 mL portions of D.I. water. Continue the vacuum until filtration is complete.

9. With forceps, carefully remove the filter from the support and place in the same aluminum dish.

10. Place in the drying oven and dry at 103-105°C for one hour.

11. Cool in a dessicator for one hour and weigh. Record the weight.

12. Repeat drying cycle until weight change is $\leq$0.5 mg. Record the final weight.

Quality Control:

1. Duplicate 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate is still required. Duplicates should be within acceptable ranges. Duplicates are to be averaged.

2. A blank dish and filter are carried through the entire procedure, as a check on contamination (cleanliness of dishes, oven, pipettes, etc.)

Calculations:

$$\text{TSS, mg/L} = \frac{(A-B)}{C} \times 1000000$$

Where A = weight of filter, aluminum pan and residue (g)
B = weight of filter and aluminum pan (g)
C = sample volume (mL)

	Revision Date
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Kim Finner Kim D. Finner Analytical Laboratory QA/QC Officer	5-21-87
Thomas J. Lynch Thomas J. Lynch QA Officer	

TOTAL DISSOLVED SOLIDS

Scope and Application: This method is applicable to drinking water, surface water, groundwater, and domestic and industrial wastewaters.

Method: Gravimetric, dried at 180°C

Reference: EPA 1983, Method 160.1

Detection Limit: 10 mg/L (using a 100 mL sample volume)

Sample Handling: Refrigerate at 4°C and analyze sample within 7 days of sampling.

Reagents and Apparatus:

1. Glass fiber filters, Whatman GF/C
2. Gelman filtration funnel and support
3. Suction flask, 1000 mL
4. Porcelain evaporating dishes
5. Graduated cylinder, 100 mL
6. Drying oven at 180°C ± 2°C
7. Dessicator
8. Analytical balance
9. Deionized water

Notes:

1. Interferences: Samples with high concentrations of bicarbonate, Ca, Mg, Cl, and SO_4 will require prolonged drying, dessication, and rapid weighing.

2. Total residue should be < 200 mg. Excessive residue (>200 mg) is difficult to dry thoroughly. Use a smaller volume if TDS is suspected to be high; likewise use a larger volume if TDS is suspected to low.

3. Groundwater samples which have already been filtered through a 0.45 micron membrane filter do not need to be carried through the filtration step of the procedure.

Procedure:

1. All glassware is to be soap and water washed, tap rinsed and deionized rinsed prior to analysis.

2. Evaporating Dish Preparation: If volatile dissolved solids is also to be analyzed, prepare the evaporating dishes by ashing at 550 ±50°C for one hour in a muffle furnace.

   Otherwise, heat the dishes at 180 ± 2°C for one hour. Cool in dessicator. Weigh. Record the weight. The dishes must be cool before being weighed (about one hour). Repeat this cycle until a constant weight is obtained (± 0.5 mg). Weigh just before use.

3. Filter Preparation: Place the glass fiber filter on the filtration support, place the funnel on top, and wash the filter with three-20 mL portions of deionized water while vacuum is applied. Discard the washings. The filters may be prepared ahead of time. If this is the case, dry them for 1 hour at 103 - 105°C and store in the dessicator until needed.

4. Assemble the filtering apparatus, place a prepared filter on the support and begin suction. Shake the sample and measure out 100 mL in graduated cylinder.

5. Filter the sample, then rinse the cylinder and funnel with a small amount of deionized water. Apply vacuum until all the sample has been filtered. Rinse with 3 - 10 mL portions of D.I. water and continue the vacuum until filtration is complete.

6. Pipet 50 mL of the filtrate (less, if the sample is expected to have a high dissolved solids content) into a prepared evaporating dish.

7. Evaporate the sample to dryness in the oven at 180 ±2°C. Cool in a dessicator for at least one hour and weigh. Repeat the drying cycle until the weight loss is ≤0.5 mg.

Quality Control:

1. Duplicate 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate is still required. Duplicates should be within acceptable ranges. Duplicate results are to be averaged.

2. A blank must be analyzed with each run. (This is a check on contamination, cleanliness of dishes, oven, pipettes, etc.).

Calculation:

$$\text{TDS, mg/L} = \frac{(A-B)}{C} \times 1000000$$

Where A = weight of dish plus residue (g)
B = weight of dish (g)
C = volume of filtered sample used (mL)

	Revision Date
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CATION EXCHANGE CAPACITY OF SOILS

Scope of Application: This method is applicable to soil samples collected as part of the American Chemical Services RI/FS. A total of 20 soil samples are anticipated.

Method: Cation exchange capacity of soils.

Reference: ASA-SSSA, 1982. Methods of Soil Analysis, Part 2. Chemical and Microbiological Properties. Agronomy Monograph No. 9 (2nd Edition).

Sample Handling: Samples will be air dried at 60°C upon receipt. A separate sample aliquot will be oven dried to determine moisture content. Samples will be stored until analysis.

Interference - Corrective Action: If the soil is initially high in salts (EC ≥ 4 mmho/cm) wash the soil with one 33-ml increment of water before beginning saturation (avoid excessive washing to prevent loss of particles during decantation).

Quality Control

1. Laboratory duplicates should be run at a frequency of one per ten investigative samples and at least one per sample set. Duplicates should agree within 20 percent.

Apparatus:

1. Atomic absorption spectrometer
2. Centrifuge
3. Round-bottom, narrow-neck centrifuge tubes, 50 ml
4. Ultrasonic disperser with microtip focusing horn
5. Reciprocating shaker
6. Balance (.01 g sensitivity)
7. Automatic coulometric/amperometric Cl^-titrator

Reagents:

1. Saturating solution, 0.4N NaOAc-0.1N, NaCl, 60% ethanol, pH 8.2 solution: Combine 544.32 g of sodium acetate (NaOAc), 58.44 g of sodium chloride (NACl), and 6 liters of ethanol, and dilute to 10 liters with distilled water. Adjust the pH by stirring and dropwise addition of 6N sodium hydroxide (NaOH). Determine the Na/Cl ratio of this solution.

2. Extracting solution, 0.5N magnesium nitrate [$Mg(NO_3)$]: Weigh out 641.1 g of $Mg(NO_3)_2 \cdot 6H_2O$, and dilute to 10 liters.

3. Suppresant solution for Na+: Add 6.358 g of lithium chloride (LiCl) and make to 1 liter in distilled water (0.15N).

4. Nitric acid-acetic acid/polyvinyl alcohol (PVA): Dissolve 1.8 g of powdered PVA in 100 ml of demineralized water with heating and stirring, cool to room temperature. Add 6.4 ml of conc nitric acid (HNO_3) and 100 ml of glacial acetic acid to a 1-liter volumetric flask containing 600 ml of demineralized water, and mix thoroughly. Add the cooled PVA solution to the nitric acid-acetic acid solution, mix, cool, and make to volume with demineralized water. Store this nitric acid-acetic acid/PVA reagent in a tightly stoppered container at room temperature. This reagent is stable for at least 12 months.

Procedure:

Sample Preparation

1. Weigh out samples of 4 to 5 g of air-dry soil (correct to oven-dry moisture content as determined using a separate subsample), and place in centrifuge tube.

2. Add 33 ml of saturating solution, stopper the tube, and shake for 5 min. Unstopper, and centrifuge at relative centrigual force of 1,000 until the supernatant liquid is clear (about 5 min). Decan the supernatant liquid and discard. Add fresh saturating, solution, insert sonifier tip, and "sonify" for 10 to 30 sec to disperse sediment, then continue as above. Make four successive "equilibrations," discarding the supernatant liquid each time.

3. Add 33 ml of extracting solution, shake for 5 min, centrifuge until the supernatant liquid is clear, and decant the extracted solution into a 100-ml volumetric flask. Repeat the extraction steps two more times with fresh extracting solution, and make to volume.

4. Determine Na^+ (Na_t) and Cl^-(Cl_t) in dilutions of this extracted solution using standards made up in the same batch of extracting solution. Chloride is determined so that the soluble Na^+ (Na_{sol}) carried over from the saturation step to the extraction step can be deducted from the total Na to obtain exchangeable Na^+ (Na_{exch}):

$$CEC = (Na_t - Na_{sol}) = Na_t - (Cl_t)\ (Na/Cl)sat\ sol$$

Chloride Determination:

5. Add 4 ml of nitric acid-acetic acid/PVA reagent together with a sample aliquot (<3 ml) to a titration vial.

6. Position vial in the coulometric/amperometric titrator, immersing the electrode assembly into the solution.

7. Zero the timer, and initiate automatic titration at low, medium, or high current setting. Note the titration times of blank, standards, and samples.

Sodium Determination

8. Add enough lithium chloride suppressant solution to sample, blank and standard aliquots to give 10% (by volume) in the final solution.

9. Adjust the atomic absorption spectrometer controls and settings for sodium as recommended by the manufacturer.

10. Calibrate the instrument with at least 4 Na standard solutions ranging from 0 to 1 meq/liter.

11. Any dilutions should be made in such a way that the standards and unknowns have the same final $Mg(NO_3)_2$ concentration.

12. Record results in meq Na^+/liter of aspirated solution.

Calculations:

Cloride

Cl^- in meq/liter
= (K) (Titration time of sample minus titration time of blank)/aliquot

where K is a standardization factor and aliquot is sample size in ml.

K = (Volume of Cl^- standard in ml) (Conc of Cl^- standard in meq/liter/(titration time of standard minus blank).

Sodium:

Na^+ meq/liter original sample

= (meq Na^+/liter in aspirated sample) x (analytical dilution factor)

Cation Exchange Capacity:

CEC in meq/100 g = (10/weight soil sample in g)

[(Na concentration in meq/liter) (DF_{Na}) - (Cl concentration in meq/liter)

(DF_{Cl}) $(NaCl)_{sat\ sol}$]

where DF represents the dilution factor, i.e., (final analytical volume in milliliters)/(aliquot volume in milliliters).

[jpl-602-47]

GRAIN SIZE ANALYSIS OF SOIL

Scope and Application: This method is applicable to soil samples collected as part of the Muskego Sanitary Landfill RI/FS. The Muskego site RI/FS is a PRP lead investigation.

Method: Particle size analysis of soil.

Reference: ASTM Methods D421, and D422 and D2217 (see attached).

Detection Limit: 2 percent by weight.

Sample Handling: Samples will be air dried at 60°C upon receipt. After drying, the sample, or a representative portion of the sample, will be separated into fractions passing and retained on a 2mm sieve per ASTM Method D421 or D2217. The fractions will then be stored until analysis.

Reagents and Apparatus:

1. Balance (0.01 g sensitivity)
2. Dispersion cup
3. Hydrometer
4. Sedimentation cylinder
5. Thermometer (0.5°C sensitivity)
6. Sieves (see ASTM D422 Section 3.6)
7. Temperature controlled room (±1°C)
8. 4% Sodium hexametaphosphate solution

Reagent Preparation:

The sodium hexametaphosphate solution is to have been prepared within 30 days of use.

Procedures:

1. The sample fraction greater than 2mm is fractioned by sieving using sieves and procedures as outlined in Section 6 of ASTM D422. The sum of the masses of the sieved fractions should be within ± 2 g of the original fraction mass.

2. Determine the hygroscopic moisture content of the less than 2mm fraction by drying a minimum 10 to 15 g subsample to constant weight at 110 plus or minus 5 degree C.

3. Disperse a 50 g sample if the sample is primarily silt and clay or a 100 g sample is primarily sand for one minute using a dispersion cup as outlined in Section 9 of ASTM D422.

4. Transfer the dispersed sample to a sedimentation cylinder, suspend the sample by successive inversions and record hydrometer readings after sedimentation times of 1, 2, 3, 6, 15, 60, 120, 300, 420 and 1440 minutes.

5. After hydrometer readings are complete, the hydrometer and hygroscopic moisture specimens are combined with the remaining P10 and R10 material for sieving.

Reportables:

1. Submit all raw data including container tare weights, hydrometer readings (along with any correction factor associated with the hydrometer used) and temperatures.

2. A data summary will be provided as described in Sections 17 and 18 of ASTM Method D422.

Quality Control:

1. Laboratory Duplicates will be run at a frequency of one per ten investigative samples and at least one per sample set. Duplicates should agree within 10 percent.

2. If performance criteria for duplicates is exceeded, the Warzyn project manager (Mike Radcliffe, 608-273-0440) should be notified as soon as possible so a determination regarding reanalysis can be made.

NOTE 9—Other in situ test procedures are being prepared by ASTM Committee D-18.

9.2 The soil and rock investigation should consist of the following steps.

9.2.1 A review of all available information on the geologic history and formation of rock, or soil, or both, and ground-water conditions occurring at the proposed location and in the immediate vicinity.

9.2.2 On-site investigation of the surface and subsurface materials by either wash borings, hand- or power-auger borings, test pits, rotary or cable-tool (churn) drilling, and geophysical methods.

9.2.2.1 A determination of the depths to water table and firm foundation material, either bedrock or satisfactory load-bearing soils.

9.2.2.2 Field identification of soil and rock types with depth records of their occurrence, and location of their structural discontinuities.

9.2.2.3 The recovery of representative disturbed samples for laboratory classification tests of soil, rock, and local construction material. These should be supplemented by undisturbed specimens suitable for the determination of those engineering properties pertinent to the investigation.

9.2.3 An evaluation of performance of existing installations in the immediate vicinity of the proposed site, relative to their foundation material and environment.

10. Classification of Material

10.1 Treat samples of soils and rock submitted to the laboratory for identification and classification tests in accordance with one of the following:

10.1.1 Test Method D 2487.

10.1.2 Practice D 3282.

10.1.3 Descriptive Nomenclature C 294. This is a brief, useful description of the more common minerals and rocks as they occur in nature.

11. Interpretation of Results

11.1 Interpret the results of an investigation only in terms of actual findings and make every effort to collect and include all field and laboratory data from previous investigations in the same area. Extrapolation of data into local areas not surveyed and tested can be done only where geologically uniform subsurface disposition of soil and rock are known to exist. Engineering properties of the soils and rocks encountered on important projects should not be predicted wholly on field identifications or classification but should be checked by laboratory and field tests made on samples collected in accordance with 8.1 and 9.1.

11.2 The recommendations for design parameters can be made only by professional engineers or geologists who have specialized in the field of soils and foundations or highway engineering, and who are familiar with the problems for which the study is being made. Soil mechanics, rock mechanics, and geomorphological concepts must be combined with a knowledge of structural or pavement engineering in order to make a complete application of the results of the soil and rock survey. A more detailed study than that envisioned by this recommended practice may be necessary before design recommendations can be made.

12. Report

12.1 A subsurface investigation report should:

12.1.1 Locate the area investigated in terms pertinent to the project. This may include sketch maps or aerial photos on which the test holes, pits, and sample areas are located, as well as topographic items relevant to the determination of the various soil and rock types such as contours, streambeds, pot holes, cliffs, etc. Where feasible, include a geologic map of the area investigated in the report.

12.1.2 Include copies of all borings and test-hole logs and of all laboratory test results.

12.1.3 Describe and relate the findings obtained under Sections 3, 4, 5, and 6, using the subhead titles for the respective sections.

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This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, 1916 Race St., Philadelphia, Pa. 19103.

Standard Practice for DRY PREPARATION OF SOIL SAMPLES FOR PARTICLE-SIZE ANALYSIS AND DETERMINATION OF SOIL CONSTANTS[1]

This standard is issued under the fixed designation D 421; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This practice covers the dry preparation of soil samples as received from the field for particle-size analysis and the determination of the soil constants.

1.2 *This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of whoever uses this standard to consult and establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Applicable Documents

2.1 *ASTM Standards:*

D 2217 Practice for Wet Preparation of Soil Samples for Particle-Size Analysis and Determination of Soil Constants[2]

E 11 Specification for Wire-Cloth Sieves for Testing Purposes[3]

3. Significance and Use

3.1 This practice can be used to prepare samples for particle-size and plasticity tests where it is desired to determine test values on air-dried samples, or where it is known that air drying does not have an effect on test results relative to samples prepared in accordance with Practice D 2217.

4. Apparatus

4.1 *Balance*, sensitive to 0.1 g.

4.2 *Mortar and Rubber-Covered Pestle*, suitable for breaking up the aggregations of soil particles.

4.3 *Sieves*—A series of sieves, of square mesh woven wire cloth, conforming to Specification E 11. The sieves required are as follows:

No. 4 (4.75-mm)
No. 10 (2.00-mm)
No. 40 (425-μm)

4.4 *Sampler*—A riffle sampler or sample splitter, for quartering the samples.

5. Sampling

5.1 Expose the soil sample as received from the field to the air at room temperature until dried thoroughly. Break up the aggregations thoroughly in the mortar with a rubber-covered pestle. Select a representative sample of the amount required to perform the desired tests by the method of quartering or by the use of a sampler. The amounts of material required to perform the individual tests are as follows:

5.1.1 *Particle-Size Analysis*—For the particle-size analysis, material passing a No. 10 (2.00-mm) sieve is required in amounts equal to 115 g of sandy soils and 65 g of either silt or clay soils.

5.1.2 *Tests for Soil Constants*—For the tests for soil constants, material passing the No. 40

[1] This practice is under the jurisdiction of ASTM Committee D-18 on Soil and Rock and is the direct responsibility of Subcommittee D18.03 on Texture, Plasticity, and Density Characteristics of Soils.

Current edition approved July 26, 1985. Published September 1985. Originally published as D 421 – 35 T. Last previous edition D 421 – 58 (1978)[ε1].

[2] *Annual Book of ASTM Standards*, Vol 04.08.

[3] *Annual Book of ASTM Standards*, Vol 14.02.

(425-μm) sieve is required in total amount of 220 g, allocated as follows:

Test	Grams
Liquid limit	100
Plastic limit	15
Centrifuge moisture equivalent	10
Volumetric shrinkage	30
Check tests	65

6. Preparation of Test Sample

6.1 Select that portion of the air-dried sample selected for purpose of tests and record the mass as the mass of the total test sample uncorrected for hygroscopic moisture. Separate the test sample by sieving with a No. 10 (2.00-mm) sieve. Grind that fraction retained on the No. 10 sieve in a mortar with a rubber-covered pestle until the aggregations of soil particles are broken up into the separate grains. Then separate the ground soil into two fractions by sieving with a No. 10 sieve.

6.2 Wash that fraction retained after the second sieving free of all fine material, dry, and weigh. Record this mass as the mass of coarse material. Sieve the coarse material, after being washed and dried, on the No. 4 (4.75-mm) sieve and record the mass retained on the No. 4 sieve.

7. Test Sample for Particle-Size Analysis

7.1 Thoroughly mix together the fractions passing the No. 10 (2.00-mm) sieve in both sieving operations, and by the method of quartering or the use of a sampler, select a portion weighing approximately 115 g for sandy soils and approximately 65 g for silt and clay soil for particle-size analysis.

8. Test Sample for Soil Constants

8.1 Separate the remaining portion of the material passing the No. 10 (2.00-mm) sieve into two parts by means of a No. 40 (425-μm) sieve. Discard the fraction retained on the No. 40 sieve. Use the fraction passing the No. 40 sieve for the determination of the soil constants.

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This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, 1916 Race St., Philadelphia, PA 19103.

Designation: D 422 – 63 (Reapproved 1972)[ε1]

Standard Method for PARTICLE-SIZE ANALYSIS OF SOILS[1]

This standard is issued under the fixed designation D 422; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

NOTE—Section 2 was added editorially and subsequent sections renumbered in July 1984.

1. Scope

1.1 This method covers the quantitative determination of the distribution of particle sizes in soils. The distribution of particle sizes larger than 75 μm (retained on the No. 200 sieve) is determined by sieving, while the distribution of particle sizes smaller than 75 μm is determined by a sedimentation process, using a hydrometer to secure the necessary data (Notes 1 and 2).

NOTE 1—Separation may be made on the No. 4 (4.75-mm), No. 40 (425-μm), or No. 200 (75-μm) sieve instead of the No. 10. For whatever sieve used, the size shall be indicated in the report.

NOTE 2—Two types of dispersion devices are provided: (1) a high-speed mechanical stirrer, and (2) air dispersion. Extensive investigations indicate that air-dispersion devices produce a more positive dispersion of plastic soils below the 20-μm size and appreciably less degradation on all sizes when used with sandy soils. Because of the definite advantages favoring air dispersion, its use is recommended. The results from the two types of devices differ in magnitude, depending upon soil type, leading to marked differences in particle size distribution, especially for sizes finer than 20 μm.

2. Applicable Documents

2.1 *ASTM Standards:*

D421 Practice for Dry Preparation of Soil Samples for Particle-Size Analysis and Determination of Soil Constants[2]

E 11 Specification for Wire-Cloth Sieves for Testing Purposes[3]

E 100 Specification for ASTM Hydrometers[4]

3. Apparatus

3.1 *Balances*—A balance sensitive to 0.01 g for weighing the material passing a No. 10 (2.00-mm) sieve, and a balance sensitive to 0.1 % of the mass of the sample to be weighed for weighing the material retained on a No. 10 sieve.

3.2 *Stirring Apparatus*—Either apparatus A or B may be used.

3.2.1 Apparatus A shall consist of a mechanically operated stirring device in which a suitably mounted electric motor turns a vertical shaft at a speed of not less than 10 000 rpm without load. The shaft shall be equipped with a replaceable stirring paddle made of metal, plastic, or hard rubber, as shown in Fig. 1. The shaft shall be of such length that the stirring paddle will operate not less than ¾ in. (19.0 mm) nor more than 1½ in. (38.1 mm) above the bottom of the dispersion cup. A special dispersion cup conforming to either of the designs shown in Fig. 2 shall be provided to hold the sample while it is being dispersed.

3.2.2 Apparatus B shall consist of an air-jet dispersion cup[5] (Note 3) conforming to the general details shown in Fig. 3 (Notes 4 and 5).

NOTE 3—The amount of air required by an air-jet dispersion cup is of the order of 2 ft^3/min; some small air compressors are not capable of supplying sufficient air to operate a cup.

NOTE 4—Another air-type dispersion device, known as a dispersion tube, developed by Chu and Davidson at Iowa State College, has been shown to give

[1] This method is under the jurisdiction of ASTM Committee D-18 on Soil and Rock and is the direct responsibility of Subcommittee D18.03 on Texture, Plasticity, and Density Characteristics of Soils.

Current edition approved Nov. 21, 1963. Originally published 1935. Replaces D 422 – 62.

[2] *Annual Book of ASTM Standards*, Vol 04.08.

[3] *Annual Book of ASTM Standards*, Vol 14.02.

[4] *Annual Book of ASTM Standards*, Vol 14.01.

[5] Detailed working drawings for this cup are available at a nominal cost from the American Society for Testing and Materials, 1916 Race St., Philadelphia, PA 19103. Order Adjunct No. 12-404220-00.

drometer 152H it is the difference between the reading and zero. Bring the liquid and the hydrometer to the other temperature to be used, and secure the composite correction as before.

8. Hygroscopic Moisture

8.1 When the sample is weighed for the hydrometer test, weigh out an auxiliary portion of from 10 to 15 g in a small metal or glass container, dry the sample to a constant mass in an oven at 230 ± 9°F (110 ± 5°C), and weigh again. Record the masses.

9. Dispersion of Soil Sample

9.1 When the soil is mostly of the clay and silt sizes, weigh out a sample of air-dry soil of approximately 50 g. When the soil is mostly sand the sample should be approximately 100 g.

9.2 Place the sample in the 250-mL beaker and cover with 125 mL of sodium hexametaphosphate solution (40 g/L). Stir until the soil is thoroughly wetted. Allow to soak for at least 16 h.

9.3 At the end of the soaking period, disperse the sample further, using either stirring apparatus A or B. If stirring apparatus A is used, transfer the soil - water slurry from the beaker into the special dispersion cup shown in Fig. 2, washing any residue from the beaker into the cup with distilled or demineralized water (Note 9). Add distilled or demineralized water, if necessary, so that the cup is more than half full. Stir for a period of 1 min.

NOTE 9—A large size syringe is a convenient device for handling the water in the washing operation. Other devices include the wash-water bottle and a hose with nozzle connected to a pressurized distilled water tank.

9.4 If stirring apparatus B (Fig. 3) is used, remove the cover cap and connect the cup to a compressed air supply by means of a rubber hose. A air gage must be on the line between the cup and the control valve. Open the control valve so that the gage indicates 1 psi (7 kPa) pressure (Note 10). Transfer the soil - water slurry from the beaker to the air-jet dispersion cup by washing with distilled or demineralized water. Add distilled or demineralized water, if necessary, so that the total volume in the cup is 250 mL, but no more.

NOTE 10—The initial air pressure of 1 psi is required to prevent the soil - water mixture from entering the air-jet chamber when the mixture is transferred to the dispersion cup.

9.5 Place the cover cap on the cup and open the air control valve until the gage pressure is 20 psi (140 kPa). Disperse the soil according to the following schedule:

Plasticity Index	Dispersion Period, min
Under 5	5
6 to 20	10
Over 20	15

Soils containing large percentages of mica need be dispersed for only 1 min. After the dispersion period, reduce the gage pressure to 1 psi preparatory to transfer of soil - water slurry to the sedimentation cylinder.

10. Hydrometer Test

10.1 Immediately after dispersion, transfer the soil - water slurry to the glass sedimentation cylinder, and add distilled or demineralized water until the total volume is 1000 mL.

10.2 Using the palm of the hand over the open end of the cylinder (or a rubber stopper in the open end), turn the cylinder upside down and back for a period of 1 min to complete the agitation of the slurry (Note 11). At the end of 1 min set the cylinder in a convenient location and take hydrometer readings at the following intervals of time (measured from the beginning of sedimentation), or as many as may be needed, depending on the sample or the specification for the material under test: 2, 5, 15, 30, 60, 250, and 1440 min. If the controlled water bath is used, the sedimentation cylinder should be placed in the bath between the 2- and 5-min readings.

NOTE 11—The number of turns during this minute should be approximately 60, counting the turn upside down and back as two turns. Any soil remaining in the bottom of the cylinder during the first few turns should be loosened by vigorous shaking of the cylinder while it is in the inverted position.

10.3 When it is desired to take a hydrometer reading, carefully insert the hydrometer about 20 to 25 s before the reading is due to approximately the depth it will have when the reading is taken. As soon as the reading is taken, carefully remove the hydrometer and place it with a spinning motion in a graduate of clean distilled or demineralized water.

NOTE 12—It is important to remove the hydrometer immediately after each reading. Readings shall be taken at the top of the meniscus formed by the suspension around the stem, since it is not possible to secure readings at the bottom of the meniscus.

10.4 After each reading, take the temperature of the suspension by inserting the thermometer into the suspension.

11. Sieve Analysis

11.1 After taking the final hydrometer reading, transfer the suspension to a No. 200 (75-μm) sieve and wash with tap water until the wash water is clear. Transfer the material on the No. 200 sieve to a suitable container, dry in an oven at 230 ± 9°F (110 ± 5°C) and make a sieve analysis of the portion retained, using as many sieves as desired, or required for the material, or upon the specification of the material under test.

CALCULATIONS AND REPORT

12. Sieve Analysis Values for the Portion Coarser than the No. 10 (2.00-mm) Sieve

12.1 Calculate the percentage passing the No. 10 sieve by dividing the mass passing the No. 10 sieve by the mass of soil originally split on the No. 10 sieve, and multiplying the result by 100. To obtain the mass passing the No. 10 sieve, subtract the mass retained on the No. 10 sieve from the original mass.

12.2 To secure the total mass of soil passing the No. 4 (4.75-mm) sieve, add to the mass of the material passing the No. 10 sieve the mass of the fraction passing the No. 4 sieve and retained on the No. 10 sieve. To secure the total mass of soil passing the ⅜-in. (9.5-mm) sieve, add to the total mass of soil passing the No. 4 sieve, the mass of the fraction passing the ⅜-in. sieve and retained on the No. 4 sieve. For the remaining sieves, continue the calculations in the same manner.

12.3 To determine the total percentage passing for each sieve, divide the total mass passing (see 12.2) by the total mass of sample and multiply the result by 100.

13. Hygroscopic Moisture Correction Factor

13.1 The hydroscopic moisture correction factor is the ratio between the mass of the oven-dried sample and the air-dry mass before drying. It is a number less than one, except when there is no hygroscopic moisture.

14. Percentages of Soil In Suspension

14.1 Calculate the oven-dry mass of soil used in the hydrometer analysis by multiplying the air-dry mass by the hygroscopic moisture correction factor.

14.2 Calculate the mass of a total sample represented by the mass of soil used in the hydrometer test, by dividing the oven-dry mass used by the percentage passing the No. 10 (2.00-mm) sieve, and multiplying the result by 100. This value is the weight W in the equation for percentage remaining in suspension.

14.3 The percentage of soil remaining in suspension at the level at which the hydrometer is measuring the density of the suspension may be calculated as follows (Note 13): For hydrometer 151H:

$$P = [(100\,000/W) \times G/(G - G_1)](R - G_1)$$

NOTE 13—The bracketed portion of the equation for hydrometer 151H is constant for a series of readings and may be calculated first and then multiplied by the portion in the parentheses.

For hydrometer 152H:

$$P = (Ra/W) \times 100$$

where:

a = correction faction to be applied to the reading of hydrometer 152H. (Values shown on the scale are computed using a specific gravity of 2.65. Correction factors are given in Table 1),

P = percentage of soil remaining in suspension at the level at which the hydrometer measures the density of the suspension,

R = hydrometer reading with composite correction applied (Section 7),

W = oven-dry mass of soil in a total test sample represented by mass of soil dispersed (see 14.2), g,

G = specific gravity of the soil particles, and

G_1 = specific gravity of the liquid in which soil particles are suspended. Use numerical value of one in both instances in the equation. In the first instance any possible variation produces no significant effect, and in the second instance, the composite correction for R is based on a value of one for G_1.

15. Diameter of Soil Particles

15.1 The diameter of a particle corresponding to the percentage indicated by a given hydrometer reading shall be calculated according to Stokes' law (Note 14), on the basis that a particle of this diameter was at the surface of the suspension at the beginning of sedimentation and had settled to the level at which the hydrometer is measuring the density of the suspension. Accord-

results equivalent to those secured by the air-jet dispersion cups. When it is used, soaking of the sample can be done in the sedimentation cylinder, thus eliminating the need for transferring the slurry. When the air-dispersion tube is used, it shall be so indicated in the report.

NOTE 5—Water may condense in air lines when not in use. This water must be removed, either by using a water trap on the air line, or by blowing the water out of the line before using any of the air for dispersion purposes.

3.3 *Hydrometer*—An ASTM hydrometer, graduated to read in either specific gravity of the suspension or grams per litre of suspension, and conforming to the requirements for hydrometers 151H or 152H in Specifications E 100. Dimensions of both hydrometers are the same, the scale being the only item of difference.

3.4 *Sedimentation Cylinder*—A glass cylinder essentially 18 in. (457 mm) in height and 2½ in. (63.5 mm) in diameter, and marked for a volume of 1000 mL. The inside diameter shall be such that the 1000-mL mark is 36 ± 2 cm from the bottom on the inside.

3.5 *Thermometer*—A thermometer accurate to 1°F (0.5°C).

3.6 *Sieves*—A series of sieves, of square-mesh woven-wire cloth, conforming to the requirements of Specification E 11. A full set of sieves includes the following (Note 6):

3-in. (75-mm)	No. 10 (2.00-mm)
2-in. (50-mm)	No. 20 (850-µm)
1½-in. (37.5-mm)	No. 40 (425-µm)
1-in. (25.0-mm)	No. 60 (250-µm)
¾-in. (19.0-mm)	No. 140 (106-µm)
⅜-in. (9.5-mm)	No. 200 (75-µm)
No. 4 (4.75-mm)	

NOTE 6—A set of sieves giving uniform spacing of points for the graph, as required in Section 17, may be used if desired. This set consists of the following sieves:

3-in. (75-mm)	No. 16 (1.18-mm)
1½-in. (37.5-mm)	No. 30 (600-µm)
¾-in. (19.0-mm)	No. 50 (300-µm)
⅜-in. (9.5-mm)	No. 100 (150-µm)
No. 4 (4.75-mm)	No. 200 (75-µm)
No. 8 (2.36-mm)	

3.7 *Water Bath or Constant-Temperature Room*—A water bath or constant-temperature room for maintaining the soil suspension at a constant temperature during the hydrometer analysis. A satisfactory water tank is an insulated tank that maintains the temperature of the suspension at a convenient constant temperature at or near 68°F (20°C). Such a device is illustrated in Fig. 4. In cases where the work is performed in a room at an automatically controlled constant temperature, the water bath is not necessary.

3.8 *Beaker*—A beaker of 250-mL capacity.

3.9 *Timing Device*—A watch or clock with a second hand.

4. Dispersing Agent

4.1 A solution of sodium hexametaphosphate (sometimes called sodium metaphosphate) shall be used in distilled or demineralized water, at the rate of 40 g of sodium hexametaphosphate/litre of solution (Note 7).

NOTE 7—Solutions of this salt, if acidic, slowly revert or hydrolyze back to the orthophosphate form with a resultant decrease in dispersive action. Solutions should be prepared frequently (at least once a month) or adjusted to pH of 8 or 9 by means of sodium carbonate. Bottles containing solutions should have the date of preparation marked on them.

4.2 All water used shall be either distilled or demineralized water. The water for a hydrometer test shall be brought to the temperature that is expected to prevail during the hydrometer test. For example, if the sedimentation cylinder is to be placed in the water bath, the distilled or demineralized water to be used shall be brought to the temperature of the controlled water bath; or, if the sedimentation cylinder is used in a room with controlled temperature, the water for the test shall be at the temperature of the room. The basic temperature for the hydrometer test is 68°F (20°C). Small variations of temperature do not introduce differences that are of practical significance and do not prevent the use of corrections derived as prescribed.

5. Test Sample

5.1 Prepare the test sample for mechanical analysis as outlined in Practice D 421. During the preparation procedure the sample is divided into two portions. One portion contains only particles retained on the No. 10 (2.00-mm) sieve while the other portion contains only particles passing the No. 10 sieve. The mass of air-dried soil selected for purpose of tests, as prescribed in Practice D 421, shall be sufficient to yield quantities for mechanical analysis as follows:

5.1.1 The size of the portion retained on the No. 10 sieve shall depend on the maximum size of particle, according to the following schedule:

Nominal Diameter of Largest Particles, in. (mm)	Approximate Minimum Mass of Portion, g
⅜ (9.5)	500
¾ (19.0)	1000
1 (25.4)	2000
1½ (38.1)	3000
2 (50.8)	4000
3 (76.2)	5000

5.1.2 The size of the portion passing the No. 10 sieve shall be approximately 115 g for sandy soils and approximately 65 g for silt and clay soils.

5.2 Provision is made in Section 5 of Practice D 421 for weighing of the air-dry soil selected for purpose of tests, the separation of the soil on the No. 10 sieve by dry-sieving and washing, and the weighing of the washed and dried fraction retained on the No. 10 sieve. From these two masses the percentages retained and passing the No. 10 sieve can be calculated in accordance with 12.1.

NOTE 8—A check on the mass values and the thoroughness of pulverization of the clods may be secured by weighing the portion passing the No. 10 sieve and adding this value to the mass of the washed and oven-dried portion retained on the No. 10 sieve.

SIEVE ANALYSIS OF PORTION RETAINED ON NO. 10 (2.00-mm) SIEVE

6. Procedure

6.1 Separate the portion retained on the No. 10 (2.00-mm) sieve into a series of fractions using the 3-in. (75-mm), 2-in. (50-mm), 1½-in. (37.5-mm), 1-in. (25.0-mm), ¾-in. (19.0-mm), ⅜-in. (9.5-mm), No. 4 (4.75-mm), and No. 10 sieves, or as many as may be needed depending on the sample, or upon the specifications for the material under test.

6.2 Conduct the sieving operation by means of a lateral and vertical motion of the sieve, accompanied by a jarring action in order to keep the sample moving continuously over the surface of the sieve. In no case turn or manipulate fragments in the sample through the sieve by hand. Continue sieving until not more than 1 mass % of the residue on a sieve passes that sieve during 1 min of sieving. When mechanical sieving is used, test the thoroughness of sieving by using the hand method of sieving as described above.

6.3 Determine the mass of each fraction on a balance conforming to the requirements of 3.1. At the end of weighing, the sum of the masses retained on all the sieves used should equal closely the original mass of the quantity sieved.

HYDROMETER AND SIEVE ANALYSIS OF PORTION PASSING THE NO. 10 (2.00-mm) SIEVE

7. Determination of Composite Correction for Hydrometer Reading

7.1 Equations for percentages of soil remaining in suspension, as given in 14.3, are based on the use of distilled or demineralized water. A dispersing agent is used in the water, however, and the specific gravity of the resulting liquid is appreciably greater than that of distilled or demineralized water.

7.1.1 Both soil hydrometers are calibrated at 68°F (20°C), and variations in temperature from this standard temperature produce inaccuracies in the actual hydrometer readings. The amount of the inaccuracy increases as the variation from the standard temperature increases.

7.1.2 Hydrometers are graduated by the manufacturer to be read at the bottom of the meniscus formed by the liquid on the stem. Since it is not possible to secure readings of soil suspensions at the bottom of the meniscus, readings must be taken at the top and a correction applied.

7.1.3 The net amount of the corrections for the three items enumerated is designated as the composite correction, and may be determined experimentally.

7.2 For convenience, a graph or table of composite corrections for a series of 1° temperature differences for the range of expected test temperatures may be prepared and used as needed. Measurement of the composite corrections may be made at two temperatures spanning the range of expected test temperatures, and corrections for the intermediate temperatures calculated assuming a straight-line relationship between the two observed values.

7.3 Prepare 1000 mL of liquid composed of distilled or demineralized water and dispersing agent in the same proportion as will prevail in the sedimentation (hydrometer) test. Place the liquid in a sedimentation cylinder and the cylinder in the constant-temperature water bath, set for one of the two temperatures to be used. When the temperature of the liquid becomes constant, insert the hydrometer, and, after a short interval to permit the hydrometer to come to the temperature of the liquid, read the hydrometer at the top of the meniscus formed on the stem. For hydrometer 151H the composite correction is the difference between this reading and one; for hy-

ing to Stokes' law:

$$D = \sqrt{[30n/980(G - G_1)]} \times L/T$$

where:

D = diameter of particle, mm,

n = coefficient of viscosity of the suspending medium (in this case water) in poises (varies with changes in temperature of the suspending medium),

L = distance from the surface of the suspension to the level at which the density of the suspension is being measured, cm. (For a given hydrometer and sedimentation cylinder, values vary according to the hydrometer readings. This distance is known as effective depth (Table 2)),

T = interval of time from beginning of sedimentation to the taking of the reading, min,

G = specific gravity of soil particles, and

G_1 = specific gravity (relative density) of suspending medium (value may be used as 1.000 for all practical purposes).

NOTE 14—Since Stokes' law considers the terminal velocity of a single sphere falling in an infinity of liquid, the sizes calculated represent the diameter of spheres that would fall at the same rate as the soil particles.

15.2 For convenience in calculations the above equation may be written as follows:

$$D = K\sqrt{L/T}$$

where:

K = constant depending on the temperature of the suspension and the specific gravity of the soil particles. Values of K for a range of temperatures and specific gravities are given in Table 3. The value of K does not change for a series of readings constituting a test, while values of L and T do vary.

15.3 Values of D may be computed with sufficient accuracy, using an ordinary 10-in. slide rule.

NOTE 15—The value of L is divided by T using the C- and D-scales, the square root being indicated on the A-scale. Without ascertaining the value of the square root it may be multiplied by K, using either the C- or D-scale.

16. Sieve Analysis Values for Portion Finer than No. 10 (2.00-mm) Sieve

16.1 Calculation of percentages passing the various sieves used in sieving the portion of the sample from the hydrometer test involves several steps. The first step is to calculate the mass of the fraction that would have been retained on the No. 10 sieve had it not been removed. This mass is equal to the total percentage retained on the No. 10 sieve (100 minus total percentage passing) times the mass of the total sample represented by the mass of soil used (as calculated in 14.2) and the result divided by 100.

16.2 Calculate next the total mass passing the No. 200 sieve. Add together the fractional masses retained on all the sieves, including the No. 10 sieve, and subtract this sum from the mass of the total sample (as calculated in 14.2).

16.3 Calculate next the total masses passing each of the other sieves, in a manner similar to that given in 12.2.

16.4 Calculate last the total percentages passing by dividing the total mass passing (as calculated in 16.3) by the total mass of sample (as calculated in 14.2), and multiply the result by 100.

17. Graph

17.1 When the hydrometer analysis is performed, a graph of the test results shall be made, plotting the diameters of the particles on a logarithmic scale as the abscissa and the percentages smaller than the corresponding diameters to an arithmetic scale as the ordinate. When the hydrometer analysis is not made on a portion of the soil, the preparation of the graph is optional, since values may be secured directly from tabulated data.

18. Report

18.1 The report shall include the following:

18.1.1 Maximum size of particles,

18.1.2 Percentage passing (or retained on) each sieve, which may be tabulated or presented by plotting on a graph (Note 16),

18.1.3 Description of sand and gravel particles:

18.1.3.1 Shape—rounded or angular,

18.1.3.2 Hardness—hard and durable, soft, or weathered and friable,

18.1.4 Specific gravity, if unusually high or low,

18.1.5 Any difficulty in dispersing the fraction passing the No. 10 (2.00-mm) sieve, indicating any change in type and amount of dispersing agent, and

18.1.6 The dispersion device used and the length of the dispersion period.

NOTE 16—This tabulation of graph represents the gradation of the sample tested. If particles larger than those contained in the sample were removed before testing, the report shall so state giving the amount and maximum size.

18.2 For materials tested for compliance with definite specifications, the fractions called for in such specifications shall be reported. The fractions smaller than the No. 10 sieve shall be read from the graph.

18.3 For materials for which compliance with definite specifications is not indicated and when the soil is composed almost entirely of particles passing the No. 4 (4.75-mm) sieve, the results read from the graph may be reported as follows:

(I) Gravel, passing 3-in. and retained on No. 4 sieve ..... %

(II) Sand, passing No. 4 sieve and retained on No. 200 sieve ..... %

(a) Coarse sand, passing No. 4 sieve and retained on No. 10 sieve ..... %

(b) Medium sand, passing No. 10 sieve and retained on No. 40 sieve ..... %

(c) Fine sand, passing No. 40 sieve and retained on No. 200 sieve ..... %

(III) Silt size, 0.074 to 0.005 mm ..... %

(IV) Clay size, smaller than 0.005 mm ..... %

Colloids, smaller than 0.001 mm ..... %

18.4 For materials for which compliance with definite specifications is not indicated and when the soil contains material retained on the No. 4 sieve sufficient to require a sieve analysis on that portion, the results may be reported as follows (Note 17):

SIEVE ANALYSIS

Sieve Size	Percentage Passing
3-in.	.....
2-in.	.....
1½-in.	.....
1-in.	.....
½-in.	.....
⅜-in.	.....
No. 4 (4.75-mm)	.....
No. 10 (2.00-mm)	.....
No. 40 (425-μm)	.....
No. 200 (75-μm)	.....
HYDROMETER ANALYSIS	
0.074 mm	.....
0.005 mm	.....
0.001 mm	.....

NOTE 17—No. 8 (2.36-mm) and No. 50 (300-μm) sieves may be substituted for No. 10 and No. 40 sieves.

TABLE 1 Values of Correction Factor, a, for Different Specific Gravities of Soil Particles[A]

Specific Gravity	Correction Factor[A]
2.95	0.94
2.90	0.95
2.85	0.96
2.80	0.97
2.75	0.98
2.70	0.99
2.65	1.00
2.60	1.01
2.55	1.02
2.50	1.03
2.45	1.05

[A] For use in equation for percentage of soil remaining in suspension when using Hydrometer 152H.

TABLE 2 Values of Effective Depth Based on Hydrometer and Sedimentation Cylinder of Specified Sizes[A]

Hydrometer 151H		Hydrometer 152H			
Actual Hydrometer Reading	Effective Depth, L, cm	Actual Hydrometer Reading	Effective Depth, L, cm	Actual Hydrometer Reading	Effective Depth, L, cm
1.000	16.3	0	16.3	31	11.2
1.001	16.0	1	16.1	32	11.1
1.002	15.8	2	16.0	33	10.9
1.003	15.5	3	15.8	34	10.7
1.004	15.2	4	15.6	35	10.6
1.005	15.0	5	15.5		
1.006	14.7	6	15.3	36	10.4
1.007	14.4	7	15.2	37	10.2
1.008	14.2	8	15.0	38	10.1
1.009	13.9	9	14.8	39	9.9
1.010	13.7	10	14.7	40	9.7
1.011	13.4	11	14.5	41	9.6
1.012	13.1	12	14.3	42	9.4
1.013	12.9	13	14.2	43	9.2
1.014	12.6	14	14.0	44	9.1
1.015	12.3	15	13.8	45	8.9
1.016	12.1	16	13.7	46	8.8
1.017	11.8	17	13.5	47	8.6
1.018	11.5	18	13.3	48	8.4
1.019	11.3	19	13.2	49	8.3
1.020	11.0	20	13.0	50	8.1
1.021	10.7	21	12.9	51	7.9
1.022	10.5	22	12.7	52	7.8
1.023	10.2	23	12.5	53	7.6
1.024	10.0	24	12.4	54	7.4
1.025	9.7	25	12.2	55	7.3
1.026	9.4	26	12.0	56	7.1
1.027	9.2	27	11.9	57	7.0
1.028	8.9	28	11.7	58	6.8
1.029	8.6	29	11.5	59	6.6
1.030	8.4	30	11.4	60	6.5

TABLE 2 Continued

Hydrometer 151H		Hydrometer 152 H			
Actual Hydrometer Reading	Effective Depth, L, cm	Actual Hydrometer Reading	Effective Depth, L, cm	Actual Hydrometer Reading	Effective Depth, L, cm
1.031	8.1				
1.032	7.8				
1.033	7.6				
1.034	7.3				
1.035	7.0				
1.036	6.8				
1.037	6.5				
1.038	6.2				

[A] Values of effective depth are calculated from the equation

$$L = L_1 + \tfrac{1}{2}\,[L_2 - (V_b/A)]$$

where:

L = effective depth, cm,
L_1 = distance along the stem of the hydrometer from the top of the bulb to the mark for a hydrometer reading, cm,
L_2 = overall length of the hydrometer bulb, cm,
V_b = volume of hydrometer bulb, cm³, and
A = cross-sectional area of sedimentation cylinder, cm².

Values used in calculating the values in Table 2 are as follows:

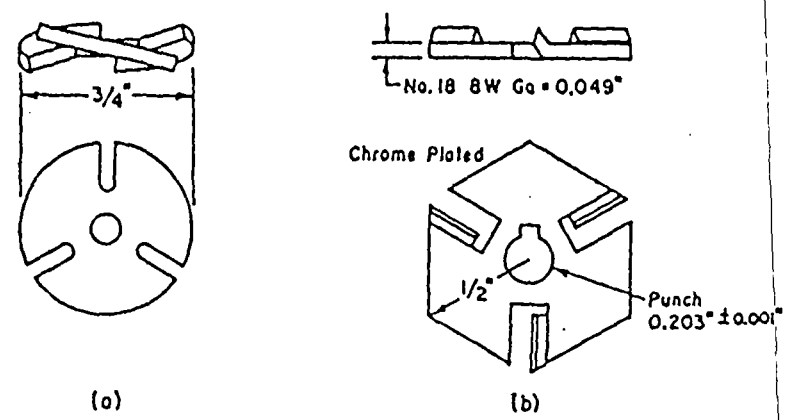
For both hydrometers, 151H and 152H:
L_2 = 14.0 cm
V_b = 67.0 cm³
A = 27.8 cm²

For hydrometer 151H:
L_1 = 10.5 cm for a reading of 1.000
= 2.3 cm for a reading of 1.031

For hydrometer 152H:
L_1 = 10.5 cm for a reading of 0 g/litre
= 2.3 cm for a reading of 50 g/litre

TABLE 3 Values of K for Use in Equation for Computing Diameter of Particle in Hydrometer Analysis

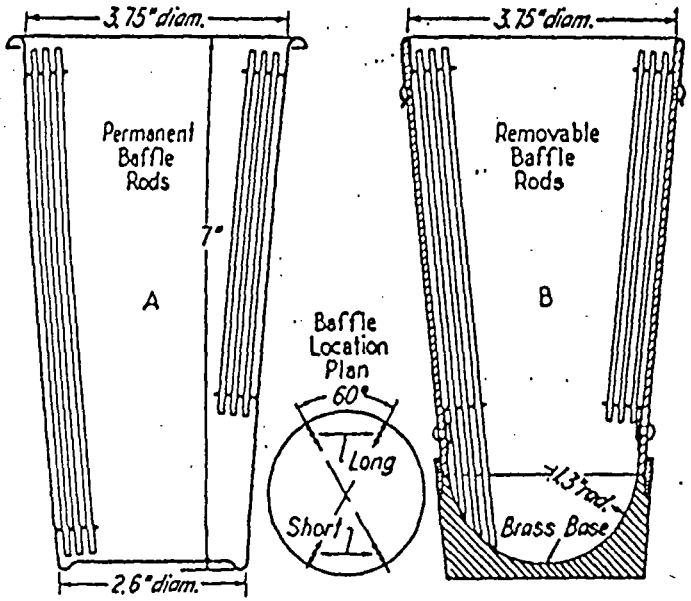
Temperature, °C	Specific Gravity of Soil Particles								
	2.45	2.50	2.55	2.60	2.65	2.70	2.75	2.80	2.85
16	0.01510	0.01505	0.01481	0.01457	0.01435	0.01414	0.01394	0.01374	0.01356
17	0.01511	0.01486	0.01462	0.01439	0.01417	0.01396	0.01376	0.01356	0.01338
18	0.01492	0.01467	0.01443	0.01421	0.01399	0.01378	0.01359	0.01339	0.01321
19	0.01474	0.01449	0.01425	0.01403	0.01382	0.01361	0.01342	0.1323	0.01305
20	0.01456	0.01431	0.01408	0.01386	0.01365	0.01344	0.01325	0.01307	0.01289
21	0.01438	0.01414	0.01391	0.01369	0.01348	0.01328	0.01309	0.01291	0.01273
22	0.01421	0.01397	0.01374	0.01353	0.01332	0.01312	0.01294	0.01276	0.01258
23	0.01404	0.01381	0.01358	0.01337	0.01317	0.01297	0.01279	0.01261	0.01243
24	0.01388	0.01365	0.01342	0.01321	0.01301	0.01282	0.01264	0.01246	0.01229
25	0.01372	0.01349	0.01327	0.01306	0.01286	0.01267	0.01249	0.01232	0.01215
26	0.01357	0.01334	0.01312	0.01291	0.01272	0.01253	0.01235	0.01218	0.01201
27	0.01342	0.01319	0.01297	0.01277	0.01258	0.01239	0.01221	0.01204	0.01188
28	0.01327	0.01304	0.01283	0.01264	0.01244	0.01255	0.01208	0.01191	0.01175
29	0.01312	0.01290	0.01269	0.01249	0.01230	0.01212	0.01195	0.01178	0.01162
30	0.01298	0.01276	0.01256	0.01236	0.01217	0.01199	0.01182	0.01165	0.01149



Metric Equivalents

in.	0.001	0.049	0.203	½	¾
mm	0.03	1.24	5.16	12.7	19.0

FIG. 1 Detail of Stirring Paddles



Metric Equivalents

in.	1.3	2.6	3.75
mm	33	66	95.2

FIG. 2 Dispersion Cups of Apparatus

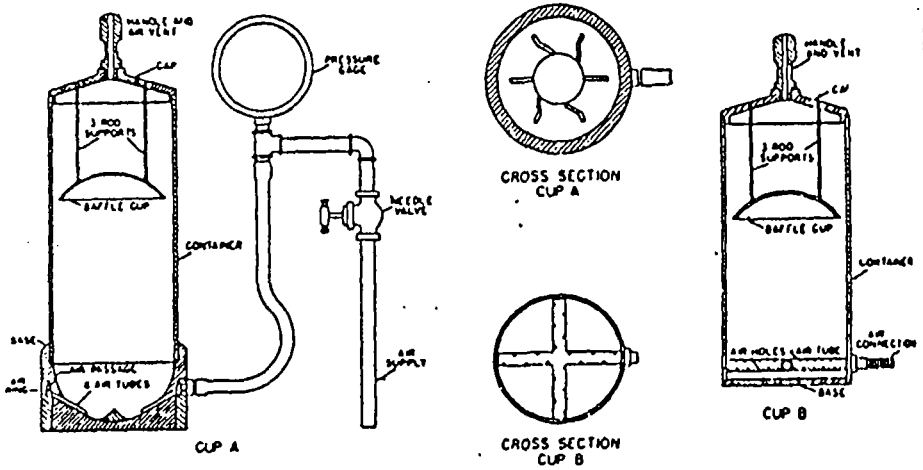
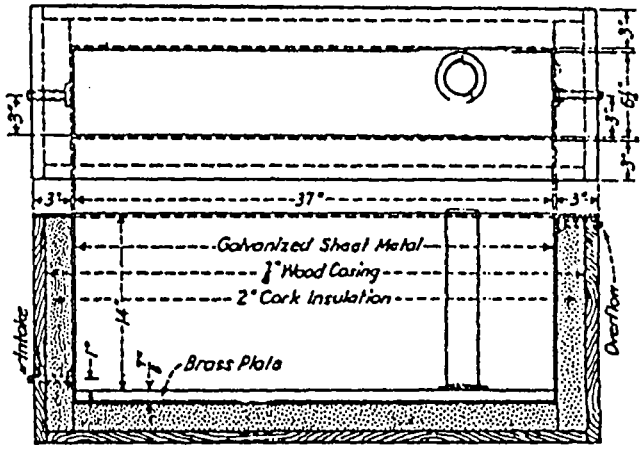


FIG. 3 Air-Jet Dispersion Cups of Apparatus B



Metric Equivalents

in.	⅞	1	3	6¼	14	37
mm	22.2	25.4	76.2	158.2	356	940

FIG. 4 Insulated Water Bath

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This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, 1916 Race St., Philadelphia, Pa. 19103.

content. Reduction of moisture content may be accomplished as follows: by exposure to air at ordinary room temperature, by heating in an oven at a temperature not exceeding 230°F (110°C), by boiling, by filtering on a Büchner funnel, or by use of filter candles. During evaporation and cooling, stir the sample often enough to prevent overdrying of the fringes and soil pinnacles on the surface. Cool the heated sample to normal room temperature before testing. For soil samples containing soluble salts, use a method of water reduction that will not eliminate the soluble salts from the test sample. Protect the prepared sample in a suitable container from further drying until all required tests have been performed.

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Designation: D 2325 – 68 (Reapproved 1981)[ε1]

Standard Test Method for CAPILLARY-MOISTURE RELATIONSHIPS FOR COARSE- AND MEDIUM-TEXTURED SOILS BY POROUS-PLATE APPARATUS[1]

This standard is issued under the fixed designation D 2325; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

[ε1] NOTE—Section 2 was added editorially and editorial changes were made throughout in October 1984.

1. Scope

1.1 This test method covers the determination of capillary-moisture relationships for coarse- and medium-textured soils as indicated by the soil-moisture tension relations for tensions between 10 and 101 kPa (0.1 and 1 atm). Under equilibrium conditions, moisture tension is defined as the equivalent negative gage pressure, or suction, corresponding to a soil moisture content. This test method determines the equilibrium moisture content retained in a soil subjected to a given soil-water tension. This test method is not suitable for very fine-textured soils.

NOTE 1—For determination of capillary-moisture relationships for fine-textured soils, refer to Test Method D 3152.

2. Applicable Documents

2.1 *ASTM Standards:*

D421 Practice for Dry Preparation of Soil Samples for Particle-Size Analysis and Determination of Soil Constants[2]

D698 Test Methods for Moisture-Density Relations of Soils and Soil-Aggregate Mixtures Using 5.5-lb (2.49-kg) Rammer and 12-in. (305-mm) Drop[2]

D3152 Test Method for Capillary Moisture Relationships for Fine-Textured Soils by Pressure-Membrane Apparatus[2]

3. Summary of Method

3.1 Saturated soil samples are placed in contact with a saturated porous plate installed within a pressure chamber. The bottom of each plate is covered by a rubber membrane, or otherwise sealed to be airtight. The bottom of each plate is maintained at atmospheric pressure by means of a small drain tube or opening through the side of the pressure chamber. A desired air pressure admitted to the pressure chamber, and consequently to the top of the porous plate, creates a pressure drop across the porous plate. The saturated soil samples on the plates establish equilibrium with the water in the plate. The water, held at a tension less than the pressure drop across the porous plate, will then move out of the soil, through the plate, and out through the drain tube. When water has ceased to flow from the sample and porous plate, (indicating equilibrium for that particular tension), the moisture content of each sample is determined. A series of these tests at various tensions is required to prepare a complete curve of the capillary-moisture relationship for any particular soil.

4. Apparatus

4.1 An assembly of the apparatus is shown in Fig. 1.

4.1.1 *Porous Plate Apparatus*, consisting of the following:

4.1.1.1 *Pressure Container*, (such as a pressure cooker), of approximately 15-L (16-qt) capacity.

[1] This test method is under the jurisdiction of ASTM Committee D-18 on Soil and Rock and is the direct responsibility of Subcommittee D18.04 on Hydrologic Properties of Soils and Rocks.

Current edition approved Sept. 13, 1968. Originally issued as D 2325 – 64 T. Last previous edition D 2325 – 64 T.

[2] *Annual Book of ASTM Standards*, Vol 04.08.

4. *Apparatus*

4.1 *Balance*, sensitive to 0.1 g.

4.2 *Mortar and Rubber-Covered Pestle*, suitable for breaking up the aggregations of soil particles.

4.3 *Sieves*, No. 10 (2.00-mm) and No. 40 (425-µm), of square mesh woven-wire cloth, conforming to Specification E 11.

4.4 *Sampler*—A riffle sampler or sample splitter for quartering the samples.

4.5 *Drying Apparatus*—Thermostatically controlled drying oven for use at 140°F (60°C) or below and at 230°F (110°C), infrared lamps; air drier; or other suitable device for drying samples.

4.6 *Filter Funnels or Candles*—Büchner funnels 10 in. (254 mm) in diameter and filter paper or filter candles.

4.7 *Miscellaneous Equipment*—Pans 12 in. (304.8 mm) in diameter and 3 in. (76.2 mm) in depth; a suitable container that will prevent loss of moisture during storage of the moist test sample prepared in Procedure B.

PROCEDURE A

5. Sampling

5.1 Dry the soil sample as received from the field, using one of the following methods: (*1*) in air at room temperature, (*2*) in a drying oven at a temperature not exceeding 140°F (60°C), or (*3*) using any warming device that will not raise the temperature of the sample above 140°F. Break up thoroughly any aggregations of particles using the mortar and rubber-covered pestle or other suitable device (Note 1). Select a representative portion by the method of quartering or by use of the sampler. This portion must be sufficient to provide samples for particle-size analyses of material retained on and passing the No. 10 (2.00-mm) sieve, and to provide an adequate amount of material passing the No. 40 (425-µm) sieve for the tests to determine soil constants. The amounts of material required to perform the individual tests are as follows:

Particle-Size Analysis of Material Retained on No. 10 (2.00-mm) Sieve:	
Gravelly soils, g	4 000 to 10 000
Sandy soils, g	1 500
Silty or clayey soils, g	400
Particle-Size Analysis of Material Passing No. 10 (2.00-mm) Sieve:	
Sandy soils, g	115
Silty or clayey soils, g	65
Tests for Determination of Soil Constants:	
Liquid limit, g	100
Plastic limit, g	15
Centrifuge moisture equivalent, g	10
Shrinkage factors, g	30
Check tests, g	65

NOTE 1—When the sample contains particles of shale or sandstone or similar weak material, proper care must be exercised to avoid excessive reduction in the size of the particles.

6. Preparation of Test Samples

6.1 *For Particle-Size Analysis:*

6.1.1 Weigh the portion of the test sample selected for particle-size analysis and record the weight of test sample uncorrected for hygroscopic moisture. Separate this material into two portions using the No. 10 (2.00-mm) sieve. Set aside the portion passing for later recombination with additional material washed from the portion retained on the No. 10 (2.00-mm) sieve.

6.1.2 Place the material retained on the No. 10 (2.00-mm) sieve in a pan, cover with water and allow to soak until the particle aggregations become soft. After soaking, wash the material on a No. 10 (2.00-mm) sieve in the following manner: Place an empty No. 10 (2.00-mm) sieve on the bottom of a clean pan and pour the water from the soaked sample into the sieve. Add sufficient water to bring the level approximately ½ in. (12.7 mm) above the mesh of the sieve. Transfer the soaked material to the sieve in increments not exceeding 1 lb (0.45 kg), stirring each increment with the fingers while agitating the sieve up and down. Crumble or mash any lumps that have not slaked, using the thumb and fingers. Raise the sieve above the water in the pan and complete the washing operation using a small amount of clean water. Transfer the washed material on the sieve to a clean pan before placing another increment of soaked material on the sieve.

6.1.3 Dry the material retained on the No. 10 (2.00-mm) sieve at a temperature of 230 ± 9°F (110 ± 5°C), sieve on the No. 10 (2.00-mm) sieve, and add the material passing the sieve to similar material obtained in 6.1.1. Set aside the material retained on the sieve for use in the particle-size analysis.

6.1.4 Set aside the pan containing the washings for a period of several hours or until the water above the particles is clear. Decant, pipet, or siphon off as much of the clear water as possible (Note 2). Dry the soil remaining in the pan at a temperature not exceeding 140°F (60°C). Grind the dried soil in the mortar with the rubber-covered pestle or other suitable device, and combine with similar material obtained in 6.1.1.

6.1.5 Alternatively, after all the soaked material has been washed, remove most of the water by filtering the wash water on one or more Büchner funnels fitted with filter paper or by using filter candles. Remove the moist soil from the filter paper or filter candles, combine with any sediment remaining in the pan, and dry at a temperature not exceeding 140°F (60°C). Grind the dried soil in the mortar with a rubber-covered pestle or other suitable device and combine with similar material obtained in 6.1.1.

NOTE 2—In some instances, the wash water will not become clear in a reasonable length of time; in this case the entire volume must be evaporated.

6.2 *For Determination of Soil Constants*—Proceed in accordance with 6.1, substituting a No. 40 (425-µm) sieve for the No. 10 (2.00-mm) sieve.

NOTE 3—In some areas it is possible that the cations of salts present in the tap water may exchange with the natural cations in the soil and alter significantly the values of the soil constants should tap water be used in the soaking and washing operations. Unless it is known that such cations are not present in the tap water, distilled or demineralized water should be used. The soaking and washing operation will remove soluble salts contained in the soil. When soluble salts are present in the soil, the wash water should be saved and evaporated, and the salts returned to the soil sample.

7. Test Samples

7.1 Keeping each portion separate from the other portion, mix thoroughly the portions of the soil sample passing the No. 10 (2.00-mm) sieve and the No. 40 (425-µm) sieve. By the method of quartering or by the use of the sampler, select and weigh out test samples of the weights indicated in Section 5, as may be needed to make the required tests.

PROCEDURE B

8. Samples

8.1 Samples prepared in accordance with this procedure must be shipped from the field to the laboratory in sealed containers and must contain all their natural moisture. Samples obviously containing only particles passing the No. 10 (2.00-mm) sieve may be tested in the particle-size analysis without first washing on the No. 10 (2.00-mm) sieve. Samples obviously containing only particles passing the No. 40 (425-µm) sieve may be used in the tests to determine soil constants without first washing on the No. 40 (425-µm) sieve.

9. Preparation of Test Samples

9.1 *For Particle-Size Analysis:*

9.1.1 Select and weigh a representative portion of the moist sample estimated to contain 50 g of particles passing the No. 10 (2.00-mm) sieve for silty and clayey soil, or 100 g for sandy soil. For samples containing particles not passing the No. 10 (2.00-mm) sieve for which a particle-size analysis is required, select and weigh a representative sample estimated to contain the required amounts of particles both passing and not passing the No. 10 (2.00-mm) sieve. Determine the moisture content at 230 ± 9°F (110 ± 5°C) using an auxiliary sample, for use in Method D 422.

9.1.2 Soak the moist sample and wash on a No. 10 (2.00-mm) sieve as described in 6.1.2. After washing, dry the material retained on the No. 10 (2.00-mm) sieve in an oven at a temperature of 230 ± 9°F (110 ± 5°C), weigh, and retain for the particle-size analysis. If the volume of the wash water and soil is too large for use in the sedimentation procedure of the test for particle-size analysis, evaporate excess water by exposure to air at room temperature, by heating in an oven at a temperature not exceeding 230°F (110°C), or by boiling. Regardless of the method of evaporation used, the following precautions must be taken: (*1*) stir the slurry from time to time to prevent a dry soil ring from forming on the walls of the evaporation vessel, and (*2*) return the temperature of the sample to room temperature before testing.

9.2 *For Determination of Soil Constants*—Select a representative portion of the moist sample estimated to contain sufficient particles passing the No. 40 (425-µm) sieve to make the required tests for determination of soil constants. Soak this selected portion of the moist sample and wash on the No. 40 (425-µm) sieve as described in 6.2 (Note 2). Reduce the moisture content of the material passing the No. 40 (425-µm) sieve until the mass reaches a putty-like consistency (such as 30 to 35 drops of the cup in the liquid limit test) but never below the natural moisture

10. Pr[redacted]n and [redacted]racy

10.1 Requirements for the precision and accuracy of this test method have not yet been developed.

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Standard Practice for WET PREPARATION OF SOIL SAMPLES FOR PARTICLE-SIZE ANALYSIS AND DETERMINATION OF SOIL CONSTANTS[1]

This standard is issued under the fixed designation D 2217; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

This practice has been approved for use by agencies of the Department of Defense and for listing in the DoD Index of Specifications and Standards.

1. Scope

1.1 This practice covers the wet preparation of soil samples as received from the field for particle-size analysis and determination of soil constants.

1.2 Procedure A provides for drying the field sample at a temperature not exceeding 140°F (60°C), making a wet separation on the No. 10 (2.00-mm) sieve, or No. 40 (425-μm) sieve, or both, as needed, and finally drying at a temperature not exceeding 140°F. Procedure B provides that the sample shall be kept at a moisture content equal to or greater than the natural water content. The procedure to be used should be indicated in the specification for the material being tested. If no procedure is specified, the provisions of Procedure B shall govern.

1.3 *This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of whoever uses this standard to consult and establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Applicable Documents

2.1 *ASTM Standards:*

D421 Practice for Dry Preparation of Soil Samples for Particle-Size Analysis and Determination of Soil Constants[2]

D422 Method for Particle-Size Analysis of Soils[2]

E 11 Specification for Wire Cloth Sieves for Testing Purposes[3]

3. Significance and Use

3.1 Procedure A is used to prepare soil samples for plasticity tests and particle-size analysis when the coarse-grained particles of a sample are soft and pulverize readily, as in Practice D 421, or when the fine particles are very cohesive and tend to resist removal from the coarse particles.

3.2 Some soils never dry out in nature and may change their characteristics greatly when dried. If the true natural gradation and plasticity characteristics of such soils are desired, these soils should be shipped to the laboratory in sealed containers and processed in accordance with Procedure B of this practice.

3.3 Liquid limit and plasticity index values derived from samples containing their natural moisture are usually, but not always, equal to or higher than values derived from similar samples of the dried soil. In the case of fine-grained organic soil, there is a radical drop in plasticity due to oven drying.

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[1] This practice is under the jurisdiction of ASTM Committee D-18 on Soil and Rock and is the direct responsibility of Subcommittee D18.03 on Texture, Plasticity, and Density Characteristics of Soils.

Current edition approved July 26, 1985. Published September 1985. Originally published as D 2217 – 63 T. Last previous edition D 2217 – 66 (1978)ε[1].

[2] *Annual Book of ASTM Standards*, Vol 04.08.

[3] *Annual Book of ASTM Standards*, Vol 14.02.

PERMEABILITY OF SOIL

Scope and Application: This method is applicable to soil samples collected as part of the Muskego Sanitary Landfill RI/FS.

Method: Permeability Test with Back Pressure (Flexible Wall permeability).

Reference: Appendix VII, Section 7, Engineer Manual EM 1110-2-1906 (30 November 1970), Headquarters, Department of the Army, Office of the Chief of Engineers (see Attachment One).

Precision: The method is applicable to soil having a saturated permeability of less than 1 x 10-3 cm/sec. Overall precision is expected to be less than 50 relative percent difference (RPD).

Sample Handling: Samples will be collected in 3 inch diameter Shelby tubes, capped and store at 4 degrees centigrade until analyzed.

Reagents and Equipment:

1. 0.005N CaSO4 in dearied, deionized water (boiled).
2. Pressure chamber for permeability testing.
3. Scale capable of weighing to the nearest 0.01 gram.
4. Sample extruder capable of extruding the soil core from the Shelby tube in the same direction of travel that it entered.
5. Specimen trimming equipment, which may include soil lathe, wire saw, spatulas, knives, steel rasp or steel straight edge.
6. Flexible membrane which shall encase the lateral boundaries of the specimen and prevent leakage.
7. Drying oven (105° C).

Procedure:

1. Extrude sample from the Shelby tube in the same direction the sample entered the tube.
2. Select and trim a minimum 6 inch length of undistrubed core for use. Avoid smearing of the sample ends while trimming samples.
3. Retain a separate section of core for determination of specific gravity (ASTM D854-83, see Attachment Two).

4. Measure and record the length and diameter of the trimmed specimen to the nearest 0.01 inch and the wet weight to the nearest 0.1%.

5. Performance of the test shall follow that described under paragraph 7a, page VII-17 of EM 1110-2-1906 (attached).

6. After permeability testing is completed, determine the dry weight of the sample by drying at 105 degree centigrade.

Results:

1. Conductivity will be calculated using the falling head method (See Attachment three).
2. Results will be presented in the format shown on Attachment Three.

Quality Control:

1. Samples analysed for quality control purposes will be limited to field duplicates. As samples for permeability testing are taken from intact cores (ie. not measured on homogenized, repacked samples), it is not possible to obtain what could be considered a laboratory duplicate. Results of field duplicates are expected to agree within 50 relative percent difference (RPD).

KDF/CAW/DLN
[KAW-7-28]

ATTACHMENT THREE

WARZYN ENGINEERING INC

FLEXIBLE WALL
FALLING HEAD/RISING HEAD
PERMEABILITY TEST RESULTS

PROJECT:

LOCATION:

Test No. _____
Job No. _____
Date _____
Sheet _____ of _____

1409 EMIL STREET • P.O. BOX 9538, MADISON, WIS. 53715 • TEL. (608) 257-4848

SAMPLE						
DEPTH						
SOIL DESCRIPTION						
	INITIAL	FINAL	INITIAL	FINAL	INITIAL	FINAL
SAMPLE DIAMETER (cm)						
SAMPLE AREA, A (cm^2)						
SAMPLE LENGTH, L (cm)						
MOISTURE CONTENT, %						
DRY DENSITY (PCF)						
MAXIMUM GRADIENT						
NET CONFINING PRESSURE (PSI)						

COEFFICIENT OF PERMEABILITY, k (cm/sec)

RUN NO. 1			
2			
3			
4			
5			
6			
7			
8			
9			
10			
AVERAGE k, (cm/sec)			

FORMULA: $k = \frac{2.3\ a\ L}{2At} \log_{10} \frac{h_0}{h_1}$ Where a = cross-sectional area of standpipe,
t = time for water level to fall from initial height, h_0, to final height, h_1
(All other terms are defined above)

REMARKS:

ATTERBERG LIMITS

Scope and Application: This method determines the liquid limit, plastic limit and plasticity index of soil samples from Shelby tubes after permeability testing.

Method: Standard Test Method for Liquid Limit, Plastic Limit and Plasticity Index of Soils ASTM D-4318 (Liquid Limit by One-Point Test) with minor modifications.

Sample Handling: Samples will remain in Shelby tubes and be shipped daily by overnight carrier.

Reference: Annual Book of ASTM Standards, 1987, Soil and Rock; Building Stones; Geotextiles, Vol. 04.08, Section 4, Construction.

Apparatus:

1. Brass cup
2. Grooving tools
3. Liquid limit drop device
4. Soil sieves
5. Height Gage
6. Balance
7. Drying oven & moisture containers
8. Hard rubber base

Notes:

1. The liquid and plastic limits of many soils that have been allowed to dry before testing may be considerably different from values obtained on undried samples. If the liquid and plastic limits of soils are used to correlate or estimate the engineering behavior of soils in their moist state, samples should not be permitted to dry before testing unless data on dried samples are specifically desired.

2. The composition and concentration of soluble salts in a soil affect the values of the liquid and plastic limits, as well as the water content values of the soil (see Method D 2216). Special consideration should therefore be given to soils from a marine environment or other sources where high soluble salt concentrations may be present. The degree to which the salts present in these soils are diluted or concentrated must be given consideration if meaningful results are to be obtained.

3. Since the tests described herein are performed only on that portion of a soil which passes the 425-um (No. 40) sieve, the relative contribution of this portion of the soil to the properties of the sample as a whole must be considered when using these tests to evaluate the properties of a soil.

Procedure:

Sample Preparation: One-point Liquid Limit

1. Samples for One-point Liquid Limit analysis will be prepared according to ASTM D4318 procedure, Section 10.1 (wet preparation) or 10.2 (dry preparation).

2. Samples for Plastic Limit analysis will be prepared according to ASTM D4318 procedure, Section 16.1.

Sample Analysis:

1. The sample will be processed to remove any material retained on a 425-um (No. 40) sieve. The liquid limit will be determined by performing trials in which a portion of the sample is spread in a brass cup, divided in two by a grooving tool, and then allowed to flow together from the blows caused by repeatedly dropping the cup in a standard mechanical device. ASTM D4318, Sections 13 and 14. indicate the one-point liquid limit test can be used when the number of blows is between 20 and 30. A minimum of two trials are performed. If the number of blows differ by no more than 1 blow, then the moisture content is determined. If the number of blows differs by more than 1 blow, then the test is repeated until two consecutive trails agree within 1 blow.

2. The plastic limit will be determined by alternately pressing together and rolling into a 3.2 mm (1/8 in.) diameter thread a small portion of plastic soil until its water content is reduced to a point at which the thread crumbles and is no longer able to be pressed together and rerolled. The water content of the soil at this stage is reported as the plastic limit.

3. The plasticity index is calculated as the difference between the liquid limit and the plastic limit.

Calculations:

1. The "K" factor for liguid limit in Table 1 of ASTM D4318 is applied to the moisture content from the liquid limt trials to determine the liquid limit value.

2. Threads of soil will be rolled to the targeted diameter until a total specimen weight of 50 grams or more is obtained. The moisture content of the specimen is the plastic limit value.

3. The plasticity index is equal to the liquid limit minus the plastic limit.

Quality Control:

1. Duplicate 2 out of 10 for sets of less than or equal to 10 samples and 1 out of 10 for sets greater than 10. Duplicates should be less than or equal to 10%.

Standard Test Method for LIQUID LIMIT, PLASTIC LIMIT, AND PLASTICITY INDEX OF SOILS[1]

This standard is issued under the fixed designation D 4318; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

This test method has been approved for use by agencies of the Department of Defense and for listing in the DoD Index of Specifications and Standards

1. Scope

1.1 This test method covers the determination of the liquid limit, plastic limit, and the plasticity index of soils as defined in Section 3.

1.1.1 Two procedures for preparing test specimens and two procedures for performing the liquid limit are provided as follows:

A Multipoint test using a wet preparation procedure, described in Sections 10.1, 11, and 12.

B Multipoint test using a dry preparation procedure, described in Sections 10.2, 11, and 12.

C One-point test using a wet preparation procedure, described in Sections 13, 14, and 15.

D One-point test using a dry preparation procedure, described in Sections 13, 14, and 15.

The procedure to be used shall be specified by the requesting authority. If no procedure is specified, Procedure A shall be used.

NOTE 1—Prior to the adoption of this test method, a curved grooving tool was specified as part of the apparatus for performing the liquid limit test. The curved tool is not considered to be as accurate as the flat tool described in 6.2 since it does not control the depth of the soil in the liquid limit cup. However, there are some data which indicate that typically the liquid limit is slightly increased when the flat tool is used instead of the curved tool.

1.1.2 The plastic limit test procedure is described in Sections 16, 17, and 18. The plastic limit test is performed on material prepared for the liquid limit test. In effect, there are two procedures for preparing test specimens for the plastic limit test.

1.1.3 The procedure for calculating the plasticity index is given in Section 19.

1.2 The liquid limit and plastic limit of soils (along with the shrinkage limit) are often collectively referred to as the Atterberg limits in recognition of their formation by Swedish soil scientist, A. Atterberg. These limits distinguish the boundaries of the several consistency states of plastic soils.

1.3 As used in this test method, soil is any natural aggregation of mineral or organic materials, mixtures of such materials, or artificial mixtures of aggregates and natural mineral and organic particles.

1.4 The multipoint liquid limit procedure is somewhat more time consuming than the one-point procedure when both are performed by experienced operators. However, the one-point procedure requires the operator to judge when the test specimen is approximately at its liquid limit. In cases where this is not done reliably, the multipoint procedure is as fast as the one-point procedure and provides additional precision due to the information obtained from additional trials. It is particularly recommended that the multipoint procedure be used by inexperienced operators.

1.5 The correlations on which the calculations of the one-point procedure are based may not be valid for certain soils, such as organic soils or

[1] This test method is under the jurisdiction of ASTM Committee D-18 on Soil and Rock and is the direct responsibility of Subcommittee D18.03 on Texture, Plasticity and Density Characteristics of Soils.

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soils from a marine environment. The liquid limit of these soils should therefore be determined by the multipoint procedure (Procedure A).

1.6 The liquid and plastic limits of many soils that have been allowed to dry before testing may be considerably different from values obtained on undried samples. If the liquid and plastic limits of soils are used to correlate or estimate the engineering behavior of soils in their natural moist state, samples should not be permitted to dry before testing unless data on dried samples are specifically desired.

1.7 The composition and concentration of soluble salts in a soil affect the values of the liquid and plastic limits as well as the water content values of soils (see Method D 2216). Special consideration should therefore be given to soils from a marine environment or other sources where high soluble salt concentrations may be present. The degree to which the salts present in these soils are diluted or concentrated must be given consideration if meaningful results are to be obtained.

1.8 Since the tests described herein are performed only on that portion of a soil which passes the 425-µm (No. 40) sieve, the relative contribution of this portion of the soil to the properties of the sample as a whole must be considered when using these tests to evaluate the properties of a soil.

1.9 The values stated in acceptable metric units are to be regarded as the standard. The values given in parentheses are for information only.

1.10 *This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of whoever uses this standard to consult and establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Applicable Documents

2.1 *ASTM Standards:*

C 702 Methods for Reducing Field Samples of Aggregate to Testing Size[2]

D 75 Practice for Sampling Aggregates[3]

D 420 Recommended Practice for Investigating and Sampling Soil and Rock for Engineering Purposes[4]

D 653 Terms and Symbols Relating to Soil and Rock[4]

D 1241 Specification for Materials for Soil-Aggregate Subbase, Base, and Surface Courses[4]

D 2216 Method for Laboratory Determination of Water (Moisture) Content of Soil, Rock, and Soil-Aggregate Mixtures[4]

D 2240 Test Method for Rubber Property—Durometer Hardness[5]

D 2487 Test Method for Classification of Soils for Engineering Purposes[4]

D 2488 Practice for Description and Identification of Soils (Visual-Manual Procedure)[4]

D 3282 Practice for Classification of Soils and Soil-Aggregate Mixtures for Highway Construction Purposes[4]

E 11 Specification for Wire-Cloth Sieves for Testing Purposes[6]

E 319 Methods of Testing Single-Arm Balances[6]

E 898 Method of Testing Top-Loading, Direct-Reading Laboratory Scales and Balances[6]

3. Definitions

3.1 *Atterberg limits*—originally, seven "limits of consistency" of fine-grained soils were defined by Albert Atterberg. In current engineering usage, the term usually refers only to the liquid limit, plastic limit, and in some references, the shrinkage limit.

3.2 *consistency*—the relative ease with which a soil can be deformed.

3.3 *liquid limit (LL)*—the water content, in percent, of a soil at the arbitrarily defined boundary between the liquid and plastic states. This water content is defined as the water content at which a pat of soil placed in a standard cup and cut by a groove of standard dimensions will flow together at the base of the groove for a distance of 13 mm (½ in.) when subjected to 25 shocks from the cup being dropped 10 mm in a standard liquid limit apparatus operated at a rate of 2 shocks per second.

[2] *Annual Book of ASTM Standards*, Vol 04.02.

[3] *Annual Book of ASTM Standards*, Vols 04.02, 04.03, and 04.08.

[4] *Annual Book of ASTM Standards*, Vol 04.08.

[5] *Annual Book of ASTM Standards*, Vol 09.01.

[6] *Annual Book of ASTM Standards*, Vol 14.02.

NOTE 2—The undrained shear stre
liquid limit is considered to be 2 ±0.2

3.4 *plastic limit (PL)*—the wa
percent, of a soil at the boundar
plastic and brittle states. The w
this boundary is the water content
can no longer be deformed by r
mm (⅛ in.) in diameter threads
bling.

3.5 *plastic soil*—a soil which l
water content over which it exh
and which will retain its shape on

3.6 *plasticity index (PI)*—the r
content over which a soil behav
Numerically, it is the difference be
uid limit and the plastic limit.

3.7 *liquidity index*—the ratio, e
percentage, of (1) the natural wate
soil minus its plastic limit, to (2
index.

3.8 *activity number (A)*—the ra
plasticity index of a soil to (2) th
weight of particles having an equiv
smaller than 0.002 mm.

4. Summary of Method

4.1 The sample is processed to
material retained on a 425-µm (N
The liquid limit is determined b
trials in which a portion of the san
in a brass cup, divided in two by a g
and then allowed to flow togeth
shocks caused by repeatedly droppi
a standard mechanical device. Th
liquid limit, Procedures A and B, r
or more trials over a range of wate
be performed and the data from the
or calculated to make a relationship
the liquid limit is determined. Th
liquid limit, Procedures C and D, e
from two trials at one water conte
by a correction factor to determir
limit.

4.2 The plastic limit is determir
nately pressing together and rollin
mm (⅛ in.) diameter thread a sma
plastic soil until its water content is
point at which the thread crumble
longer able to be pressed together a
The water content of the soil at
reported as the plastic limit.

NOTE 2—The undrained shear strength of soil at the liquid limit is considered to be 2 ±0.2 kPa (0.28 psi).

3.4 *plastic limit (PL)*—the water content, in percent, of a soil at the boundary between the plastic and brittle states. The water content at this boundary is the water content at which a soil can no longer be deformed by rolling into 3.2 mm (⅛ in.) in diameter threads without crumbling.

3.5 *plastic soil*—a soil which has a range of water content over which it exhibits plasticity and which will retain its shape on drying.

3.6 *plasticity index (PI)*—the range of water content over which a soil behaves plastically. Numerically, it is the difference between the liquid limit and the plastic limit.

3.7 *liquidity index*—the ratio, expressed as a percentage, of (*1*) the natural water content of a soil minus its plastic limit, to (*2*) its plasticity index.

3.8 *activity number (A)*—the ratio of (*1*) the plasticity index of a soil to (*2*) the percent by weight of particles having an equivalent diameter smaller than 0.002 mm.

4. Summary of Method

4.1 The sample is processed to remove any material retained on a 425-µm (No. 40) sieve. The liquid limit is determined by performing trials in which a portion of the sample is spread in a brass cup, divided in two by a grooving tool, and then allowed to flow together from the shocks caused by repeatedly dropping the cup in a standard mechanical device. The multipoint liquid limit, Procedures A and B, requires three or more trials over a range of water contents to be performed and the data from the trials plotted or calculated to make a relationship from which the liquid limit is determined. The one-point liquid limit, Procedures C and D, uses the data from two trials at one water content multiplied by a correction factor to determine the liquid limit.

4.2 The plastic limit is determined by alternately pressing together and rolling into a 3.2 mm (⅛ in.) diameter thread a small portion of plastic soil until its water content is reduced to a point at which the thread crumbles and is no longer able to be pressed together and rerolled. The water content of the soil at this stage is reported as the plastic limit.

4.3 The plasticity index is calculated as the difference between the liquid limit and the plastic limit.

5. Significance and Use

5.1 This test method is used as an integral part of several engineering classification systems to characterize the fine-grained fractions of soils (see Test Method D 2487 and Practice D 3282) and to specify the fine-grained fraction of construction materials (see Specification D 1241). The liquid limit, plastic limit, and plasticity index of soils are also used extensively, either individually or together with other soil properties to correlate with engineering behavior such as compressibility, permeability, compactibility, shrink-swell, and shear strength.

5.2 The liquid and plastic limits of a soil can be used with the natural water content of the soil to express its relative consistency or liquidity index and can be used with the percentage finer than 2-µm size to determine its activity number.

5.3 The one-point liquid limit procedure is frequently used for routine classification purposes. When greater precision is required, as when used for the acceptance of a material or for correlation with other test data, the multipoint procedure should be used.

5.4 These methods are sometimes used to evaluate the weathering characteristics of clay-shale materials. When subjected to repeated wetting and drying cycles, the liquid limits of these materials tend to increase. The amount of increase is considered to be a measure of a shale's susceptibility to weathering.

5.5 The liquid limit of a soil containing substantial amounts of organic matter decreases dramatically when the soil is oven-dried before testing. Comparison of the liquid limit of a sample before and after oven-drying can therefore be used as a qualitative measure of organic matter content of a soil.

6. Apparatus

6.1 *Liquid Limit Device*—A mechanical device consisting of a brass cup suspended from a carriage designed to control its drop onto a hard rubber base. A drawing showing the essential features of the device and the critical dimensions is given in Fig. 1. The design of the device may vary provided that the essential functions are

preserved. The device may be operated either by a hand crank or by an electric motor.

6.1.1 *Base*—The base shall be hard rubber having a D Durometer hardness of 80 to 90, and a resilience such that an 8-mm (5/16-in.) diameter polished steel ball, when dropped from a height of 25 cm (9.84 in.) will have an average rebound of at least 80 % but no more than 90 %. The tests shall be conducted on the finished base with feet attached.

6.1.2 *Feet*—The base shall be supported by rubber feet designed to provide isolation of the base from the work surface and having an A Durometer hardness no greater than 60 as measured on the finished feet attached to the base.

6.1.3 *Cup*—The cup shall be brass and have a weight, including cup hanger, of 185 to 215 g.

6.1.4 *Cam*—The cam shall raise the cup smoothly and continuously to its maximum height, over a distance of at least 180° of cam rotation. The preferred cam motion is a uniformly accelerated lift curve. The design of the cam and follower combination shall be such that there is no upward or downward velocity of the cup when the cam follower leaves the cam.

NOTE 3—The cam and follower design in Fig. 1 is for uniformly accelerated (parabolic) motion after contact and assures that the cup has no velocity at drop off. Other cam designs also provide this feature and may be used. However, if the cam-follower lift pattern is not known, zero velocity at drop off can be assured by carefully filing or machining the cam and follower so that the cup height remains constant over the last 20 to 45° of cam rotation.

6.1.5 *Carriage*—The cup carriage shall be constructed in a way that allows convenient but secure adjustment of the height of drop of the cup to 10 mm (0.394 in.). The cup hanger shall be attached to the carriage by means of a pin which allows removal of the cup and cup hanger for cleaning and inspection.

6.1.6 *Optional Motor Drive*—As an alternative to the hand crank shown in Fig. 1, the device may be equipped with a motor to turn the cam. Such a motor must turn the cam at 2 ±0.1 revolutions per second, and must be isolated from the rest of the device by rubber mounts or in some other way that prevents vibration from the motor being transmitted to the rest of the apparatus. It must be equipped with an ON-OFF switch and a means of conveniently positioning the cam for height of drop adjustments. The results obtained using a motor-driven device must not differ from those obtained using a manually operated device.

6.2 *Flat Grooving Tool*—A grooving tool having dimensions shown in Fig. 2. The tool shall be made of plastic or noncorroding metal. The design of the tool may vary as long as the essential dimensions are maintained. The tool may, but need not, incorporate the gage for adjusting the height of drop of the liquid limit device.

6.3 *Gage*—A metal gage block for adjusting the height of drop of the cup, having the dimensions shown in Fig. 3. The design of the tool may vary provided the gage will rest securely on the base without being susceptible to rocking, and the edge which contacts the cup during adjustment is straight, at least 10 mm (3/8 in.) wide, and without bevel or radius.

6.4 *Containers*—Small corrosion-resistant containers with snug-fitting lids for water content specimens. Aluminum or stainless steel cans 2.5 cm (1 in.) high by 5 cm (2 in.) in diameter are appropriate.

6.5 *Balance*—A balance readable to at least 0.01 g and having an accuracy of 0.03 g within three standard deviations within the range of use. Within any 15-g range, a difference between readings shall be accurate within 0.01 g (Notes 4 and 5).

NOTE 4—See Methods E 898 and E 319 for an explanation of terms relating to balance performance.

NOTE 5—For frequent use, a top-loading type balance with automatic load indication, readable to 0.01 g, and having an index of precision (standard deviation) of 0.003 or better is most suitable for this method. However, nonautomatic indicating equal-arm analytical balances and some small equal arm top pan balances having readabilities and sensitivities of 0.002 g or better provide the required accuracy when used with a weight set of ASTM Class 4 (National Bureau of Standards Class P) or better. Ordinary commercial and classroom type balances such as beam balances are not suitable for this method.

6.6 *Storage Container*—A container in which to store the prepared soil specimen that will not contaminate the specimen in any way, and which prevents moisture loss. A porcelain, glass, or plastic dish about 11.4 cm (4½ in.) in diameter and a plastic bag large enough to enclose the dish and be folded over is adequate.

6.7 *Ground Glass Plate*—A ground glass plate at least 30 cm (12 in.) square by 1 cm (3/8 in.) thick for mixing soil and rolling plastic limit threads.

6.8 *Spatula*—A spatula or pill knife having a blade about 2 cm (3/4 in.) wide by abo (4 in.) long. In addition, a spatula havi about 2.5 cm (1 in.) wide and 15 cm (6 has been found useful for initial mixi ples.

6.9 *Sieve*—A 20.3 cm (8 in.) diam µm (No. 40) sieve conforming to the ments of Specification E 11 and havin least 5 cm (2 in.) above the mesh. A 2- 10) sieve meeting the same requirem also be needed.

6.10 *Wash Bottle*, or similar cont adding controlled amounts of water to washing fines from coarse particles.

6.11 *Drying Oven*—A thermostatic trolled oven, preferably of the forced-d capable of continuously maintaining a ture of 110 ±5°C throughout the drying The oven shall be equipped with a ther of suitable range and accuracy for m oven temperature.

6.12 *Washing Pan*—A round, flat-b pan at least 7.6 cm (3 in.) deep, slightly the bottom than a 20.3-cm (8-in.) diame

6.13 *Rod* (optional)—A metal or pl or tube 3.2 mm (1/8 in.) in diameter and cm (4 in.) long for judging the size of pla threads.

7. Materials

7.1 A supply of distilled or demineral ter.

8. Sampling

8.1 Samples may be taken from any that satisfies testing needs. However, C 702, and Practice D 75, and Recom Practice D 420 should be used as guide lecting and preserving samples from types of sampling operations. Samples w be prepared using the wet preparation pr 10.1, must be kept at their natural water prior to preparation.

8.2 Where sampling operations ha served the natural stratification of a sam various strata must be kept separated a performed on the particular stratum of with as little contamination as possibl other strata. Where a mixture of mater be used in construction, combine the components in such proportions that the ant sample represents the actual const case.

blade about 2 cm (¾ in.) wide by about 10 cm (4 in.) long. In addition, a spatula having a blade about 2.5 cm (1 in.) wide and 15 cm (6 in.) long has been found useful for initial mixing of samples.

6.9 *Sieve*—A 20.3 cm (8 in.) diameter, 425-µm (No. 40) sieve conforming to the requirements of Specification E 11 and having a rim at least 5 cm (2 in.) above the mesh. A 2-mm (No. 10) sieve meeting the same requirements may also be needed.

6.10 *Wash Bottle*, or similar container for adding controlled amounts of water to soil and washing fines from coarse particles.

6.11 *Drying Oven*—A thermostatically controlled oven, preferably of the forced-draft type, capable of continuously maintaining a temperature of 110 ±5°C throughout the drying chamber. The oven shall be equipped with a thermometer of suitable range and accuracy for monitoring oven temperature.

6.12 *Washing Pan*—A round, flat-bottomed pan at least 7.6 cm (3 in.) deep, slightly larger at the bottom than a 20.3-cm (8-in.) diameter sieve.

6.13 *Rod* (optional)—A metal or plastic rod or tube 3.2 mm (⅛ in.) in diameter and about 10 cm (4 in.) long for judging the size of plastic limit threads.

7. Materials

7.1 A supply of distilled or demineralized water.

8. Sampling

8.1 Samples may be taken from any location that satisfies testing needs. However, Methods C 702, and Practice D 75, and Recommended Practice D 420 should be used as guides for selecting and preserving samples from various types of sampling operations. Samples which will be prepared using the wet preparation procedure, 10.1, must be kept at their natural water content prior to preparation.

8.2 Where sampling operations have preserved the natural stratification of a sample, the various strata must be kept separated and tests performed on the particular stratum of interest with as little contamination as possible from other strata. Where a mixture of materials will be used in construction, combine the various components in such proportions that the resultant sample represents the actual construction case.

8.3 Where data from this test method are to be used for correlation with other laboratory or field test data, use the same material as used for these tests where possible.

8.4 Obtain a representative portion from the total sample sufficient to provide 150 to 200 g of material passing the 425-µm (No. 40) sieve. Free flowing samples may be reduced by the methods of quartering or splitting. Cohesive samples shall be mixed thoroughly in a pan with a spatula, or scoop and a representative portion scooped from the total mass by making one or more sweeps with a scoop through the mixed mass.

9. Calibration of Apparatus

9.1 *Inspection of Wear:*

9.1.1 *Liquid Limit Device*—Determine that the liquid limit device is clean and in good working order. The following specific points should be checked:

9.1.1.1 *Wear of Base*—The spot on the base where the cup makes contact should be worn no greater than 10 mm (⅜ in.) in diameter. If the wear spot is greater than this, the base can be machined to remove the worn spot provided the resurfacing does not make the base thinner than specified in 6.1 and the other dimensional relationships are maintained.

9.1.1.2 *Wear of Cup*—The cup must be replaced when the grooving tool has worn a depression in the cup 0.1 mm (0.004 in.) deep or when the edge of the cup has been reduced to half its original thickness. Verify that the cup is firmly attached to the cup hanger.

9.1.1.3 *Wear of Cup Hanger*—Verify that the cup hanger pivot does not bind and is not worn to an extent that allows more than 3-mm (⅛-in.) side-to-side movement of the lowest point on the rim.

9.1.1.4 *Wear of Cam*—The cam shall not be worn to an extent that the cup drops before the cup hanger (cam follower) loses contact with the cam.

9.1.2 *Grooving Tools*—Inspect grooving tools for wear on a frequent and regular basis. The rapidity of wear depends on the material from which the tool is made and the types of soils being tested. Sandy soils cause rapid wear of grooving tools; therefore, when testing these materials, tools should be inspected more frequently than for other soils. Any tool with a tip width greater than 2.1 mm must not be used. The depth

of the tip of the grooving tool must be 7.9 to 8.1 mm.

NOTE 6—The width of the tip of grooving tools is conveniently checked using a pocket-sized measuring magnifier equipped with a millimetre scale. Magnifiers of this type are available from most laboratory supply companies. The depth of the tip of grooving tools can be checked using the depth measuring feature of vernier calipers.

9.2 *Adjustment of Height of Drop*—Adjust the height of drop of the cup so that the point on the cup that comes in contact with the base rises to a height of 10 ±0.2 mm. See Fig. 4 for proper location of the gage relative to the cup during adjustment.

NOTE 7—A convenient procedure for adjusting the height of drop is as follows: place a piece of masking tape across the outside bottom of the cup parallel with the axis of the cup hanger pivot. The edge of the tape away from the cup hanger should bisect the spot on the cup that contacts the base. For new cups, placing a piece of carbon paper on the base and allowing the cup to drop several times will mark the contact spot. Attach the cup to the device and turn the crank until the cup is raised to its maximum height. Slide the height gage under the cup from the front, and observe whether the gage contacts the cup or the tape. See Fig. 4. If the tape and cup are both contacted, the height of drop is approximately correct. If not, adjust the cup until simultaneous contact is made. Check adjustment by turning the crank at 2 revolutions per second while holding the gage in position against the tape and cup. If a ringing or clicking sound is heard without the cup rising from the gage, the adjustment is correct. If no ringing is heard or if the cup rises from the gage, readjust the height of drop. If the cup rocks on the gage during this checking operation, the cam follower pivot is excessively worn and the worn parts should be replaced. Always remove tape after completion of adjustment operation.

MULTIPOINT LIQUID LIMIT—PROCEDURES A AND B

10. Preparation of Test Specimens

10.1 *Wet Preparation*—Except where the dry method of specimen preparation is specified (10.2), prepare specimens for test as described in the following sections.

10.1.1 *Samples Passing the 425-µm (No. 40) Sieve*—When by visual and manual procedures it is determined that the sample has little or no material retained on a 425-µm (No. 40) sieve, prepare a specimen of 150 to 200 g by mixing thoroughly with distilled or demineralized water on the glass plate using the spatula. If desired, soak soil in a storage dish with small amount of water to soften the soil before the start of mixing. Adjust the water content of the soil to bring it to a consistency that would require 25 to 35 blows of the liquid limit device to close the groove (Note 8). If, during mixing, a small percentage of material is encountered that would be retained on a 425-µm (No. 40) sieve, remove these particles by hand, if possible. If it is impractical to remove the coarser material by hand, remove small percentages (less than about 15 %) of coarser material by working the specimen through a 425-µm (No. 40) sieve using a piece of rubber sheeting, rubber stopper, or other convenient device provided the operation does not distort the sieve or degrade material that would be retained if the washing method described in 10.1.2 were used. If larger percentages of coarse material are encountered during mixing, or it is considered impractical to remove the coarser material by the methods just described, wash the sample as described in 10.1.2. When the coarse particles found during mixing are concretions, shells, or other fragile particles, do not crush these particles to make them pass a 425-µm (No. 40) sieve, but remove by hand or by washing. Place the mixed soil in the storage dish, cover to prevent loss of moisture, and allow to stand for at least 16 h (overnight). After the standing period and immediately before starting the test, thoroughly remix the soil.

NOTE 8—The time taken to adequately mix a soil will vary greatly, depending on the plasticity and initial water content. Initial mixing times of more than 30 — in may be needed for stiff, fat clays.

10.1.2 *Samples Containing Material Retained on a 425-µm (No. 40) Sieve:*

10.1.2.1 Select a sufficient quantity of soil at natural water content to provide 150 to 200 g of material passing the 425-µm (No. 40) sieve. Place in a pan or dish and add sufficient water to cover the soil. Allow to soak until all lumps have softened and the fines no longer adhere to the surfaces of the corase particles (Note 9).

NOTE 9—In some cases, the cations of salts present in tap water will exchange with the natural cations in the soil and significantly alter the test results should tap water be used in the soaking and washing operations. Unless it is known that such cations are not present in the tap water, distilled or demineralized water should be used. As a general rule, water containing more than 100 mg/L of dissolved solids should not be used for washing operations.

10.1.2.2 When the sample contains a large percentage of material retained on the 425-µm (No. 40) sieve, perform the following operation in increments, washing no m 0.5 kg (1 lb) of material at one time P 425-µm (No. 40) sieve in the bottom of t pan. Pour the soil water mixture onto tl If gravel or coarse sand particles are prese as many of these as possible with small qu of water from a wash bottle, and discard natively, pour the soil water mixture ov mm (No. 10) sieve nested atop the 425-µ 40) sieve, rinse the fine material throu remove the 2-mm (No. 10) sieve. After v and removing as much of the coarser mat possible, add sufficient water to the pan t the level to about 13 mm (½ in.) above the of the 425-µm (No. 40) sieve. Agitate the by stirring with the fingers while raisi lowering the sieve in the pan and swirl suspension so that fine material is washe the coarser particles. Disaggregate fine soil that have not slaked by gently rubbing the the sieve with the fingertips. Complete the ing operation by raising the sieve above th surface and rinsing the material retained small amount of clean water. Discard m retained on the 425-µm (No. 40) sieve.

10.1.2.3 Reduce the water content of tl terial passing the 425-µm (No. 40) sieve t approaches the liquid limit. Reduction of content may be accomplished by one or a bination of the following methods: (*a*) ex the air currents at ordinary room tempe (*b*) exposing to warm air currents from a such as an electric hair dryer, (*c*) filterin Buckner funnel or using filter candles, (*d* canting clear water from surface of suspe or (*e*) draining in a colander or plaster of dish lined with high retentivity, high wet-str filter paper.[7] If a plaster of paris dish is usec care that the dish never becomes suffic saturated that it fails to actively absorb wate its surface. Thoroughly dry dishes between During evaporation and cooling, stir the s often enough to prevent overdrying of the fi and soil pinnacles on the surface of the mi For soil samples containing soluble salts, method of water reduction such as *a* or *c* will not eliminate the soluble salts from th specimen.

10.1.2.4 Thoroughly mix the material pa the 425-µm (No. 40) sieve on the glass plate the spatula. Adjust the water content of the ture, if necessary, by adding small incremer

(No. 40) sieve, perform the following washing operation in increments, washing no more than 0.5 kg (1 lb) of material at one time. Place the 425-µm (No. 40) sieve in the bottom of the clean pan. Pour the soil water mixture onto the sieve. If gravel or coarse sand particles are present, rinse as many of these as possible with small quantities of water from a wash bottle, and discard. Alternatively, pour the soil water mixture over a 2-mm (No. 10) sieve nested atop the 425-µm (No. 40) sieve, rinse the fine material through and remove the 2-mm (No. 10) sieve. After washing and removing as much of the coarser material as possible, add sufficient water to the pan to bring the level to about 13 mm (½ in.) above the surface of the 425-µm (No. 40) sieve. Agitate the slurry by stirring with the fingers while raising and lowering the sieve in the pan and swirling the suspension so that fine material is washed from the coarser particles. Disaggregate fine soil lumps that have not slaked by gently rubbing them over the sieve with the fingertips. Complete the washing operation by raising the sieve above the water surface and rinsing the material retained with a small amount of clean water. Discard material retained on the 425-µm (No. 40) sieve.

10.1.2.3 Reduce the water content of the material passing the 425-µm (No. 40) sieve until it approaches the liquid limit. Reduction of water content may be accomplished by one or a combination of the following methods: (*a*) exposing the air currents at ordinary room temperature, (*b*) exposing to warm air currents from a source such as an electric hair dryer, (*c*) filtering in a Buckner funnel or using filter candles, (*d*) decanting clear water from surface of suspension, or (*e*) draining in a colander or plaster of paris dish lined with high retentivity, high wet-strength filter paper.[7] If a plaster of paris dish is used, take care that the dish never becomes sufficiently saturated that it fails to actively absorb water into its surface. Thoroughly dry dishes between uses. During evaporation and cooling, stir the sample often enough to prevent overdrying of the fringes and soil pinnacles on the surface of the mixture. For soil samples containing soluble salts, use a method of water reduction such as *a* or *b* that will not eliminate the soluble salts from the test specimen.

10.1.2.4 Thoroughly mix the material passing the 425-µm (No. 40) sieve on the glass plate using the spatula. Adjust the water content of the mixture, if necessary, by adding small increments of distilled or demineralized water or by allowing the mixture to dry at room temperature while mixing on the glass plate. The soil should be at a water content that will result in closure of the groove in 25 to 35 blows. Return the mixed soil to the mixing dish, cover to prevent loss of moisture, and allow to stand for at least 16 h. After the standing period, and immediately before starting the test, remix the soil thoroughly.

10.2 *Dry Preparation:*

10.2.1 Select sufficient soil to provide 150 to 200 g of material passing the 425-µm (No. 40) sieve after processing. Dry the sample at room temperature or in an oven at a temperature not exceeding 60°C until the soil clods will pulverize readily. Disaggregation is expedited if the sample is not allowed to completely dry. However, the soil should have a dry appearance when pulverized. Pulverize the sample in a mortar with a rubber tipped pestal or in some other way that does not cause breakdown of individual grains. When the coarse particles found during pulverization are concretions, shells, or other fragile particles, do not crush these particles to make them pass a 425-µm (No. 40) sieve, but remove by hand or other suitable means, such as washing.

10.2.2 Separate the sample on a 425-µm (No. 40) sieve, shaking the sieve by hand to assure thorough separation of the finer fraction. Return the material retained on the 425-µm (No. 40) sieve to the pulverizing apparatus and repeat the pulverizing and sieving operations as many times as necessary to assure that all finer material has been disaggregated and material retained on the 425-µm (No. 40) sieve consists only of individual sand or gravel grains.

10.2.3 Place material remaining on the 425-µm (No. 40) sieve after the final pulverizing operations in a dish and soak in a small amount of water. Stir the soil water mixture and pour over the 425-µm (No. 40) sieve, catching the water and any suspended fines in the washing pan. Pour this suspension into a dish containing the dry soil previously sieved through the 425-µm (No. 40) sieve. Discard material retained on the 425-µm (No. 40) sieve.

10.2.4 Adjust the water content as necessary by drying as described in 10.1.2.3 or by mixing on the glass plate, using the spatula while adding increments of distilled or demineralized water,

[7] S and S 595 filter paper, available in 32-cm circles, has proven satisfactory.

until the soil is at a water content that will result in closure of the groove in 25 to 35 blows.

10.2.5 Put soil in the storage dish, cover to prevent loss of moisture and allow to stand for at least 16 h. After the standing period, and immediately before starting the test, thoroughly remix the soil (Note 8).

11. Procedure

11.1 Place a portion of the prepared soil in the cup of the liquid limit device at the point where the cup rests on the base, squeeze it down, and spread it into the cup to a depth of about 10 mm at its deepest point, tapering to form an approximately horizontal surface. Take care to eliminate air bubbles from the soil pat but form the pat with as few strokes as possible. Heap the unused soil on the glass plate and cover with the inverted storage dish or a wet towel.

11.2 Form a groove in the soil pat by drawing the tool, beveled edge forward, through the soil on a line joining the highest point to the lowest point on the rim of the cup. When cutting the groove, hold the grooving tool against the surface of the cup and draw in an arc, maintaining the tool perpendicular to the surface of the cup throughout its movement. See Fig. 5. In soils where a groove cannot be made in one stroke without tearing the soil, cut the groove with several strokes of the grooving tool. Alternatively, cut the groove to slightly less than required dimensions with a spatula and use the grooving tool to bring the groove to final dimensions. Exercise extreme care to prevent sliding the soil pat relative to the surface of the cup.

11.3 Verify that no crumbs of soil are present on the base or the underside of the cup. Lift and drop the cup by turning the crank at a rate of 1.9 to 2.1 drops per second until the two halves of the soil pat come in contact at the bottom of the groove along a distance of 13 mm (½ in.). See Fig. 6.

NOTE 10—Use the end of the grooving tool, Fig. 2, or a scale to verify that the groove has closed 13 mm (½ in.).

11.4 Verify that an air bubble has not caused premature closing of the groove by observing that both sides of the groove have flowed together with approximately the same shape. If a bubble has caused premature closing of the groove, reform the soil in the cup, adding a small amount of soil to make up for that lost in the grooving operation and repeat 11.1 to 11.3. If the soil slides on the surface of the cup, repeat 11.1 through 11.3 at a higher water content. If, after several trials at successively higher water contents, the soil pat continues to slide in the cup or if the number of blows required to close the groove is always less than 25, record that the liquid limit could not be determined, and report the soil as nonplastic without performing the plastic limit test.

11.5 Record the number of drops, N, required to close the groove. Remove a slice of soil approximately the width of the spatula, extending from edge to edge of the soil cake at right angles to the groove and including that portion of the groove in which the soil flowed together, place in a weighed container, and cover.

11.6 Return the soil remaining in the cup to the glass plate. Wash and dry the cup and grooving tool and reattach the cup to the carriage in preparation for the next trial.

11.7 Remix the entire soil specimen on the glass plate adding distilled water to increase the water content of the soil and decrease the number of blows required to close the groove. Repeat 11.1 through 11.6 for at least two additional trials producing successively lower numbers of blows to close the groove. One of the trials shall be for a closure requiring 25 to 35 blows, one for closure between 20 and 30 blows, and one trial for a closure requiring 15 to 25 blows.

11.8 Determine the water content, W_N, of the soil specimen from each trial in accordance with Method D 2216. Make all weighings on the same balance. Initial weighings should be performed immediately after completion of the test. If the test is to be interrupted for more than about 15 min, the specimens already obtained should be weighed at the time of the interruption.

12. Calculations

12.1 Plot the relationship between the water content, W_N, and the corresponding number of drops, N, of the cup on a semilogarithmic graph with the water content as ordinates on the arithmetical scale, and the number of drops as abscissas on the logarithmic scale. Draw the best straight line through the three or more plotted points.

12.2 Take the water content corresponding to the intersection of the line with the 25-drop abscissa as the liquid limit of the soil. Computational methods may be substituted for th ical method for fitting a straight line to and determining the liquid limit.

ONE-POINT LIQUID LIMIT—PROCEDURES C AND D

13. Preparation of Test Specimens

13.1 Prepare the specimen in the sam ner as described in Section 10, except mixing, adjust the water content to a con requiring 20 to 30 drops of the liquid lir to close the groove.

14. Procedure

14.1 Proceed as described in 11.1 th 11.5 except that the number of blows requ close the groove shall be 20 to 30. If less th or more than 30 blows are required, adju water content of the soil and repeat the dure.

14.2 Immediately after removing a content specimen as described in 11.5, r the soil in the cup, adding a small amou soil to make up for that lost in the groovin water content sampling operations. Repea through 11.5, and, if the second closing groove requires the same number of drops more than two drops difference, secure an water content specimen. Otherwise, remi entire specimen and repeat.

NOTE 11—Excessive drying or inadequate n will cause the number of blows to vary.

14.3 Determine water contents of specir as described in 11.8.

15. Calculations

15.1 Determine the liquid limit for each w content specimen using one of the follo equations:

$$LL = W_N\left(\frac{N}{25}\right)^{0.121} \quad \text{or}$$

$$LL = K(W_N)$$

where:

N = the number of blows causing closure of groove at water content,

W_N = water content, and

K = a factor given in Table 1.

The liquid limit is the average of the two t liquid limit values.

15.2 If the difference between the two ti

tional methods may be substituted for the graphical method for fitting a straight line to the data and determining the liquid limit.

ONE-POINT LIQUID LIMIT—PROCEDURES C AND D

13. Preparation of Test Specimens

13.1 Prepare the specimen in the same manner as described in Section 10, except that at mixing, adjust the water content to a consistency requiring 20 to 30 drops of the liquid limit cup to close the groove.

14. Procedure

14.1 Proceed as described in 11.1 through 11.5 except that the number of blows required to close the groove shall be 20 to 30. If less than 20 or more than 30 blows are required, adjust the water content of the soil and repeat the procedure.

14.2 Immediately after removing a water content specimen as described in 11.5, reform the soil in the cup, adding a small amount of soil to make up for that lost in the grooving and water content sampling operations. Repeat 11.2 through 11.5, and, if the second closing of the groove requires the same number of drops or no more than two drops difference, secure another water content specimen. Otherwise, remix the entire specimen and repeat.

NOTE 11—Excessive drying or inadequate mixing will cause the number of blows to vary.

14.3 Determine water contents of specimens as described in 11.8.

15. Calculations

15.1 Determine the liquid limit for each water content specimen using one of the following equations:

$$LL = W_N\left(\frac{N}{25}\right)^{0.121} \quad \text{or}$$

$$LL = K(W_N)$$

where:

N = the number of blows causing closure of the groove at water content,

W_N = water content, and

K = a factor given in Table 1.

The liquid limit is the average of the two trial liquid limit values.

15.2 If the difference between the two trial liquid limit values is greater than one percentage point, repeat the test.

PLASTIC LIMIT

16. Preparation of Test Specimen

16.1 Select a 20-g portion of soil from the material prepared for the liquid limit test, either after the second mixing before the test, or from the soil remaining after completion of the test. Reduce the water content of the soil to a consistency at which it can be rolled without sticking to the hands by spreading and mixing continuously on the glass plate. The drying process may be accelerated by exposing the soil to the air current from an electric fan, or by blotting with paper that does not add any fiber to the soil, such as hard surface paper toweling or high wet strength filter paper.

17. Procedure

17.1 From the 20-g mass, select a portion of 1.5 to 2.0 g. Form the test specimen into an ellipsoidal mass. Roll this mass between the palm or fingers and the ground-glass plate with just sufficient pressure to roll the mass into a thread of uniform diameter throughout its length (Note 12). The thread shall be further deformed on each stroke so that its diameter is continuously reduced and its length extended until the diameter reaches 3.2 ±0.5 mm (0.125 ±.020 in.), taking no more than 2 min (Note 13). The amount of hand or finger pressure required will vary greatly, according to the soil. Fragile soils of low plasticity are best rolled under the outer edge of the palm or at the base of the thumb.

NOTE 12—A normal rate of rolling for most soils should be 80 to 90 strokes per minute, counting a stroke as one complete motion of the hand forward and back to the starting position. This rate of rolling may have to be decreased for very fragile soils.

NOTE 13—A 3.2-mm (⅛-in.) diameter rod or tube is useful for frequent comparison with the soil thread to ascertain when the thread has reached the proper diameter, especially for inexperienced operators.

17.1.1 When the diameter of the thread becomes 3.2 mm, break the thread into several pieces. Squeeze the pieces together, knead between the thumb and first finger of each hand, reform into an ellipsoidal mass, and reroll. Continue this alternate rolling to a thread 3.2 mm in diameter, gathering together, kneading and rerolling, until the thread crumbles under the pres-

sure required for rolling and the soil can no longer be rolled into a 3.2-mm diameter thread (See Fig. 7). It has no significance if the thread breaks into threads of shorter length. Roll each of these shorter threads to 3.2 mm in diameter. The only requirement for continuing the test is that they are able to be reformed into an ellipsoidal mass and rolled out again. The operator shall at no time attempt to produce failure at exactly 3.2 mm diameter by allowing the thread to reach 3.2 mm, then reducing the rate of rolling or the hand pressure, or both, while continuing the rolling without further deformation until the thread falls apart. It is permissible, however, to reduce the total amount of deformation for feebly plastic soils by making the initial diameter of the ellipsoidal mass nearer to the required 3.2-mm final diameter. If crumbling occurs when the thread has a diameter greater than 3.2 mm, this shall be considered a satisfactory end point, provided the soil has been previously rolled into a thread 3.2 mm in diameter. Crumbling of the thread will manifest itself differently with the various types of soil. Some soils fall apart in numerous small aggregations of particles, others may form an outside tubular layer that starts splitting at both ends. The splitting progresses toward the middle, and finally, the thread falls apart in many small platy particles. Fat clay soils require much pressure to deform the thread, particularly as they approach the plastic limit. With these soils, the thread breaks into a series of barrel-shaped segments about 3.2 to 9.5 mm (⅛ to ⅜ in.) in length.

17.2 Gather the portions of the crumbled thread together and place in a weighed container. Immediately cover the container.

17.3 Select another 1.5 to 2.0 g portion of soil from the original 20-g specimen and repeat the operations described in 17.1 and 17.2 until the container has at least 6 g of soil.

17.4 Repeat 17.1 through 17.3 to make another container holding at least 6 g of soil. Determine the water content, in percent, of the soil contained in the containers in accordance with Method D 2216. Make all weighings on the same balance.

NOTE 14—The intent of performing two plastic limit trials is to verify the consistency of the test results. It is acceptable practice to perform only one plastic limit trial when the consistency in the test results can be confirmed by other means.

18. Calculations

18.1 Compute the average of the two water contents. If the difference between the two water contents is greater than two percentage points repeat the test. The plastic limit is the average of the two water contents.

PLASTICITY INDEX

19. Calculations

19.1 Calculate the plasticity index as follows:

$$PI = LL - PL$$

where:

LL = the liquid limit,

PL = the plastic limit.

Both LL and PL are whole numbers. If either the liquid limit or plastic limit could not be determined, or if the plastic limit is equal to or greater than the liquid limit, report the soil as nonplastic, NP.

20. Report

20.1 Report the following information:

20.1.1 Sample identifying information,

20.1.2 Any special specimen selection process used, such as removal of sand lenses from undisturbed sample,

20.1.3 Report sample as airdried if the sample was airdried before or during preparation,

20.1.4 Liquid limit, plastic limit, and plasticity index to the nearest whole number and omitting the percent designation. If the liquid limit or plastic limit tests could not be performed, or if the plastic limit is equal to or greater than the liquid limit, report the soil as nonplastic, NP,

20.1.5 An estimate of the percentage of sample retained on the 425-μm (No. 40) sieve, and

20.1.6 Procedure by which liquid limit was performed, if it differs from the multipoint method.

21. Precision and Bias

21.1 No interlaboratory testing program has as yet been conducted using this test method to determine multilaboratory precision.

21.2 The within laboratory precision of the results of tests performed by different operators at one laboratory on two soils using Procedure A for the liquid limit is shown in Table 2.

TABLE 1 Factors for Obtaining Liquid Limit Content and Number of Drops Causing Closure

N (Number of Drops)	K (Factor for Liquid
20	0.974
21	0.979
22	0.985
23	0.990
24	0.995
25	1.000
26	1.005
27	1.009
28	1.014
29	1.018
30	1.022

TABLE 1 Factors for Obtaining Liquid Limit from Water Content and Number of Drops Causing Closure of Groove

N (Number of Drops)	K (Factor for Liquid Limit)
20	0.974
21	0.979
22	0.985
23	0.990
24	0.995
25	1.000
26	1.005
27	1.009
28	1.014
29	1.018
30	1.022

TABLE 2 Within Laboratory Precision for Liquid Limit

	Average Value, $\bar{x}$	Standard Deviation, s
Soil A		
PL	21.9	1.07
LL	27.9	1.07
Soil B		
PL	20.1	1.21
LL	32.6	0.98

DIMENSIONS

LETTER	A Δ	B Δ	C Δ	E Δ	F	G	H	J Δ	K Δ	L Δ	M Δ
MM	54 ± 0.5	2 ± 0.1	27 ± 0.5	56 ± 2.0	32	10	16	60 ± 1.0	50 ± 2.0	150 ± 2.0	125 ± 2.0
LETTER	N	P	R	T	U Δ	V	W	Z			
MM	24	28	24	45	47 ± 1.0	3.8	13	6.5			

Δ ESSENTIAL DIMENSIONS

CAM ANGLE DEGREES	CAM RADIUS
0	0.742 R
30	0.753 R
60	0.764 R
90	0.773 R
120	0.784 R
150	0.796 R
180	0.818 R
210	0.854 R
240	0.901 R
270	0.945R
300	0.974R
330	0.995R
360	1.000 R

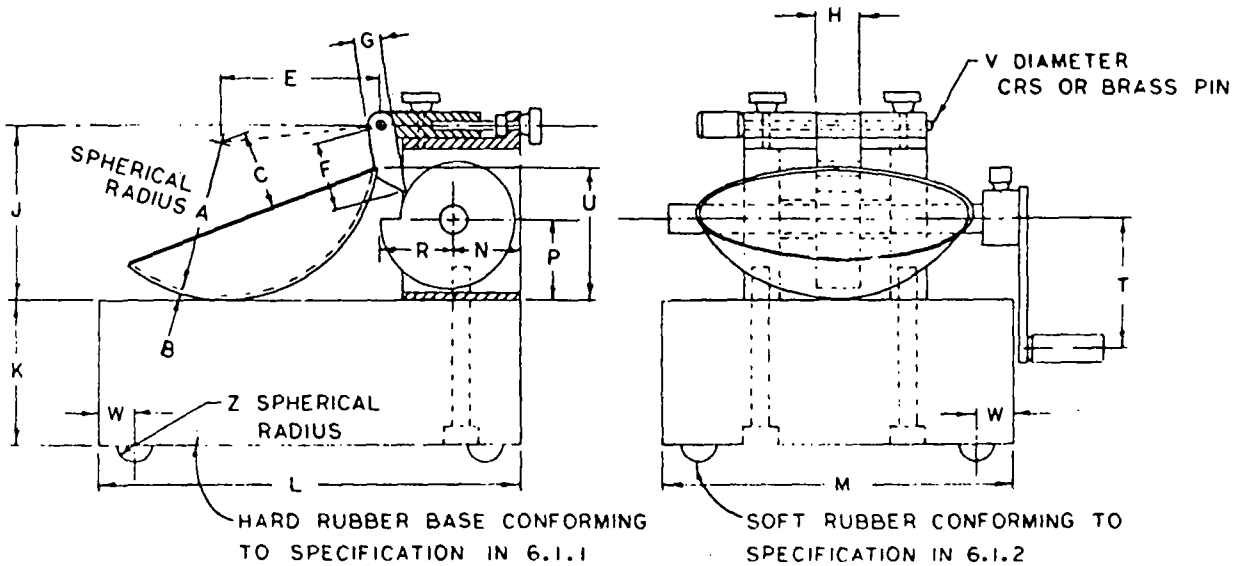


FIG. 1 Hand-Operated Liquid Limit Device

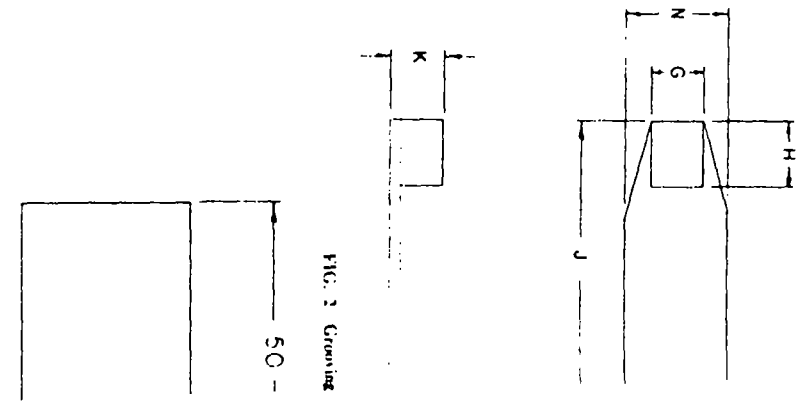


FIG. 2 Grooving

DIMENSIONS

LETTER	A Δ	B Δ
MM	2 ± 0.1	11 ± 0.2
LETTER	G	H
MM	10 MINIMUM	13

Δ ESSENTIAL DIMENSION

□ BACK AT LEAST 15 MM F

NOTE: DIMENSION A SHOULD BE 8.0–8.1 ADEQUATE SERVICE

DIMENSIONS

LETTER	A△	B△	C△	D△	E△	F△
MM	2 ± 0.1	11 ± 0.2	40 ± 0.5	8 ± 0.1	50 ± 0.5	2 ± 0.1
LETTER	G	H	J	K△	L△	N
MM	10 MINIMUM	13	60	10 ±0.05	60 DEG ± 1 DEG	20

△ ESSENTIAL DIMENSIONS

□ BACK AT LEAST 15 MM FROM TIP

NOTE : DIMENSION A SHOULD BE 1.9–2.0 AND DIMENSION D SHOULD BE 8.0–8.1 WHEN NEW TO ALLOW FOR ADEQUATE SERVICE LIFE

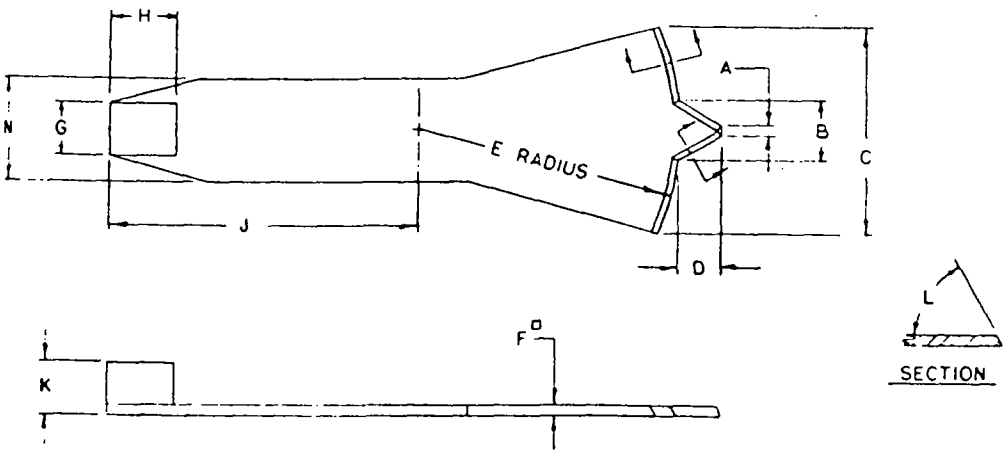
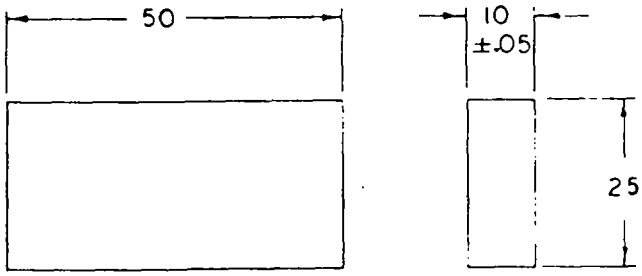


FIG. 2 Grooving Tool (Optional Height-of-Drop Gage Attached)



DIMENSIONS IN MILLIMETRES

FIG. 3 Height of Drop Gage

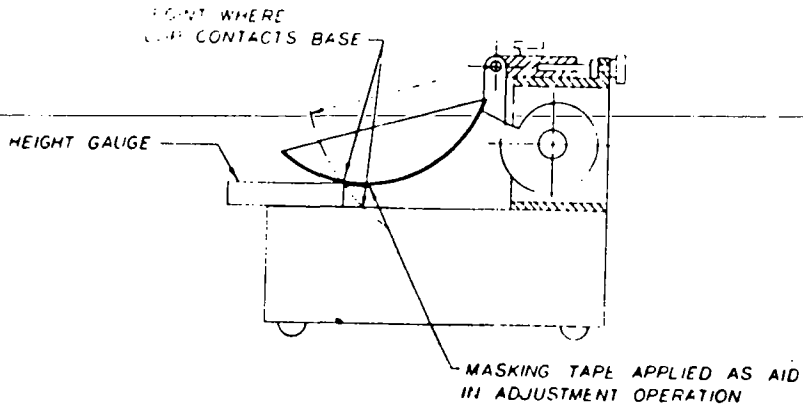


FIG. 4 Calibration for Height of Drop

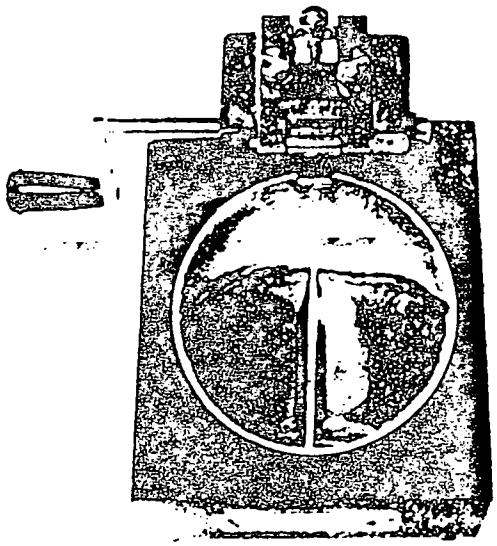


FIG. 5 Grooved Soil Pat in Liquid Limit Device

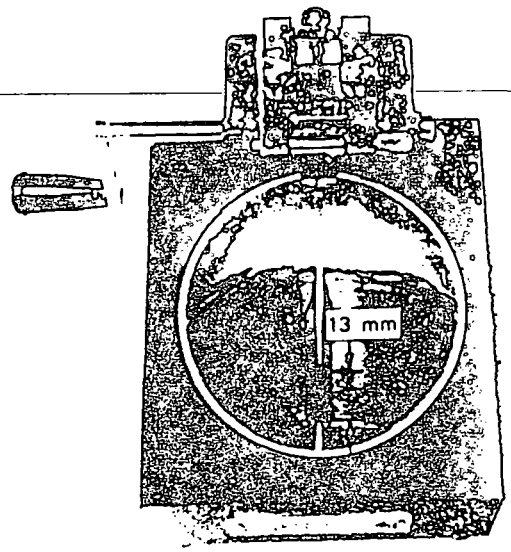


FIG. 6 Soil Pat After Groove Has Closed

FIG. 7 Lean Clay Soil at the Plastic Limit

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Standard Test Method f DISTRIBUTION RATIC METHOD[1]

This standard is issued under the fixed designation D original adoption or, in the case of revision, the year A superscript epsilon (ε) indicates an editorial change

As an aqueous fluid migrates dependent upon the chemistry c of other fluids and solid phas interactions determine the relat (such as ions) travel with respe importance in retarding the flow species at velocities less than the complex formation, precipitatic precipitating as the sulfate), oxic test method applies to situation exchange) are operable for the s porous media.

It is difficult to derive generaliz in the geological environment. I (K_d) has been used to quantify modeling (usually, but not solely used to assess the degree to whic fluid migrates through the geolog indication of how rapidly an ion under the geochemical conditions

This test method is for the labo may be used by qualified experts given underground geochemical important site-specific factors. It is qualifications required, or to just predictive purposes. Rather, this technique for determining the dis and solid, under a certain set of la

Justification for the distributio based on expediency in modeling to partitioning in soils, equilibriur

[1] This method is under the jurisdiction of ASTM Subcommittee D18.14 on Geotechnics of Waste Manage Current edition approved Nov. 28, 1983. Published J

WARZYN

Plan
Project No. 60251

Quality Assurance Project Plan
Remedial Investigation/ Feasibility Study
Volume 2 of 2 Laboratory Methods
American Chemical Services, Inc.
Griffith, Indiana

Prepared for:

American Chemical Services
Steering Committee
Chicago, Illinois

Prepared by:

Warzyn Engineering Inc.
Chicago, Illinois

September, 1988

APPENDIX E

FIELD MEASUREMENT OF pH AND OPERATION INSTRUCTIONS

3. Rinse electrode with deionized water between samples. Recheck calibration with pH7 buffer solution after every 5 samples.

4. Immerse electrode in solution allowing several minutes for meter to stabilize. Make sure the white KCl junction on side of electrode is in the solution. The level of electrode solution should be one inch above sample to be measured.

Notes:

1. When calibrating the meter, use pH buffers 7 and 4 for samples with pH $\leq$ 8, and buffers 7 and 10 for samples with pH $\geq$ 8. If meter will not read pH4 or 10, something may be wrong with the electrode. Return it to the lab with a note.

2. pH is a temperature dependent analysis. Therefore, temperatures of buffers and samples should be within about 2°C. For refrigerated or cool samples, use refrigerated buffers to calibrate meter.

3. Weak organic and inorganic salts and oil and grease are interferences in pH measurements. If oil and grease are visible, note on data sheet. Clean electrode with soap and water, followed by 10% HCl. Then recalibrate meter.

4. When not in use, the electrode should be stored in pH4 buffer.

5. Before going into the field:

   a) Check batteries;
   b) Do a quick calibration at pH7 and 4 to check electrode;
   c) Obtain fresh solutions.

6. Following field measurements:

   a) Report any problems;
   b) Compare with previous data;
   c) Clean all dirt off of meter and inside case;
   d) Make sure electrode is stored in pH4 buffer.

INSTRUCTION MANUAL
model 211
digital pH meter

ORION RESEARCH

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repair/service

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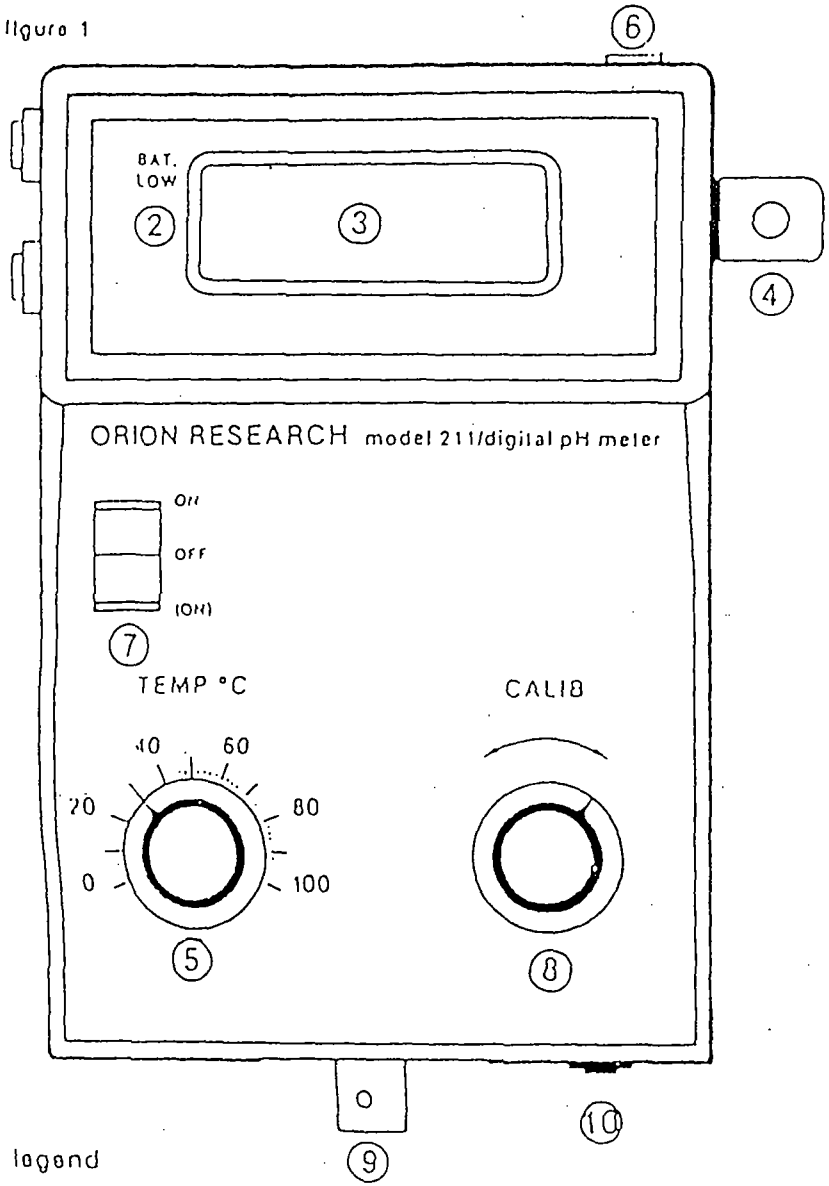
figure 1



legend

1. strip chart recorder binding posts
2. BAT LOW
3. LC display
4. support rod clip
5. temperature indicator control
6. AC line adapter input
7. function control
8. calibration control
9. electrode connector
10. slope control

introduction

The Model 211 is a battery- or line-operated (110/220 V AC adapter) digital pH meter for field or laboratory use. The meter is complete with strip chart recorder binding posts and is supplied with an unbreakable, gel-filled combination pH electrode, one packet of pH 7 buffer powder, one bottle for pH 7 buffer, one bottle for distilled water, support rod, electrode holder, AC adapter, six 1.5 V batteries, shorting plug, and carrying case.

instrument description

See figure 1.

1. strip chart recorder binding posts: black post is low (ground) and red post is high input side of recorder. See page 8.
2. BAT LOW: an arrow pointing towards BAT LOW appears on the display when battery requires replacement.
3. LC display: pH display over the range of 0 – 14 with ± .01 pH units resolution
4. support rod clip: holds steel rod used to mount electrode holder.
5. temperature indicator control (TEMP °C): compensates for variation in electrode slope or temperature changes. Used in two-buffer calibration
6. AC line adapter input: jack used to insert AC line adapter. With AC line adapter operational, the internal battery is bypassed.
7. function control: rocker switch with three positions - ON, OFF and (ON). Depress (ON) for a momentary reading. The switch will return to OFF when released.
8. calibration control (CALIB): used to calibrate the meter with buffers of known pH.
9. electrode connector: accepts BNC connector from pH electrode.
10. slope control: screwdriver adjustment used to set second buffer in two-buffer calibration.

instrument set-up

support rod

1. Insert steel support rod into the hole in the support rod clip on side of the meter.
2. Mount electrode holder on the rod by pinching to compress the spring. Release to hold in place.

power source

The Model 211 operates on six nonrechargeable 1.5 volt batteries or on 110 or 220 ± 20% V with an approved AC adapter (specify voltage when ordering). Low battery is indicated by the BAT LOW indicator on the display.

NOTE: Batteries are not rechargeable - use of line adapter whenever possible will prevent the unit's batteries from being discharged. If battery operation is desired, follow installation instructions under battery replacement.

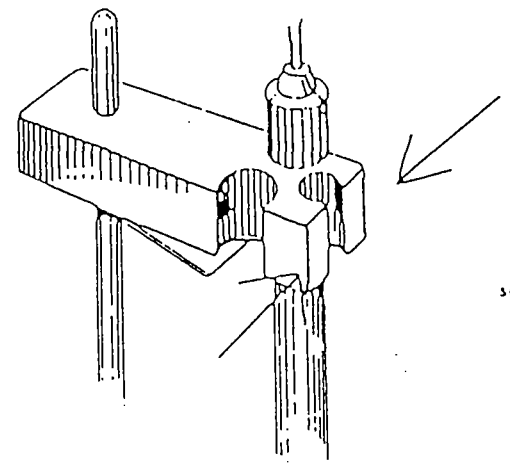
meter check-out

1. Install six AA batteries in the meter. Orient the (+) and (-) battery terminals to match the orientation shown in the battery compartment.
2. Depress ON button on the front panel. If the BAT. LOW indicator on the front display lights up, the batteries must be replaced.
3. If battery mode is not to be used, disregard steps 1 and 2. Insert pin end of appropriate AC line adapter into the meter, and the other end into the appropriate grounded AC line receptacle.
4. Attach BNC shorting plug to BNC input on the bottom side of the meter. Depress ON button on the front panel. Turn CALIB knob so display reads a steady 7.00. If this cannot be done consult ORION Technical Service.
5. Remove the shorting plug. Successful completion of steps 1-4 show the [illegible] is ready for use.

connecting electrode

1. Insert the BNC connector into the electrode jack on the bottom panel of the meter. Turn connector clockwise until it seats firmly.
2. Mount electrode in the electrode holder by spreading the electrode clip open and sliding the electrode into the holder so that the clip closes on electrode cap. See figure 2.
3. Follow measurement procedures to use the meter to measure pH.
4. Disconnnect electrode by turning connector counterclockwise until released from pin.

figure 2



squeeze as shown to insert electrode

neasurement procedures

eneral measurement technique

mperature: All samples and buffers should be at the same temperature, as mall variations in temperature can cause errors in measurement. The slope of e pH electrode, the potential of the reference electrode, and the pH of the buf- r are temperature-dependent.

eaning electrodes: Electrode should be rinsed and shaken between measure- ents to remove drops and to prevent solution carryover.

irring: Stir measured solutions moderately to obtain good contact between e glass bulb and the solution. Insert electrode to a depth of about 3 cm.

H measurements

ngle-buffer standardization
here maximum precision is not required)

OTE: For maximum accuracy it is recommended that a two-buffer calibration e performed once at the beginning of each day (see page 7). This procedure en- res the correct setting of the slope control. Subsequent measurements during e day may be made using a single point calibration.

1. Place the electrode in a buffer solution whose pH is near the expected pH of the sample. Insert electrode to a depth of about 3 cm and stir moderately.
2. Set the temperature indicator control to the temperature of the buffer.
3. Set the function control to ON and allow the buffer reading to stabilize. Adjust the CALIB so that the display indicates the pH of the buffer at the solution temperature. See Table 1.
4. Remove the electrode from the buffer solution and rinse by stirring moderately in distilled water. Shake off excess drops of water.
5. Place electrode in the sample to a depth of about 3 cm and stir moderately. Set the function control to ON and allow the reading to stabilize. Record the steady pH reading.

two-buffer standardization
(where maximum precision is required)

1. Select two buffers to bracket the expected pH of the sample, with one buffer having a pH of 7.
2. Place the electrode in the pH 7 buffer to a depth of about 3 cm and stir moderately. Set the temperature indicator control to the temperature of the buffer. Set the function control to ON and allow the reading to stabilize. Turn CALIB until the display indicates the pH of the buffer at the solution temperature. See table 1.
3. Remove electrode from the first buffer and rinse by stirring moderately in distilled water. Shake off excess drops of water.
4. Place the electrode in the second buffer to a depth of about 3 cm and stir moderately. Set the function control to ON and adjust the slope control until the pH at the solution temperature is displayed. See Table 1.
5. Remove the electrode and rinse by stirring moderately in distilled water. Shake off excess drops of water.
6. Place the electrode in the sample to a depth of about 3 cm and stir moderately. Set the function control to ON and allow the reading to stabilize. Record the steady pH reading.

TABLE 1

TEMP (°C)	pH 7.00 Buffer	pH 4.01 Buffer	pH 10.01 Buffer
5	7.08	4.00	10.25
10	7.06	4.00	10.18
15	7.03	4.00	10.12
20	7.01	4.00	10.06
25	7.00	4.01	10.01
30	6.98	4.02	9.97
35	6.98	4.02	9.93
40	6.97	4.03	9.89
50	6.97	4.06	9.83
60	6.98	4.09	--

battery replacement

o replace the batteries, remove the panel on the back of the meter. Be sure to bserve the polarity marking when inserting new batteries.

ecorder output

he red and black binding posts at the side of the meter provide an output for trip chart recording of absolute mV independent of function mode. For corders with input impedance of 100 Kilohms or greater, the output is fixed to bout 100 mV/pH. pH 14.00 output is 1.40 V. Lower impedance recorders may be sed but full-scale output is reduced.

1. Connect the lead from the high (input side of the recorder) to the red binding post and the lead from the low (ground) side to the black binding post.
2. Proceed according to directions in the strip chart recorder instruction manual

epair and service

RION warranty covers failures due to manufacturer's workmanship or material elect from the date of purchase by the user. User should return the warranty ard to ORION and retain proof of purchase. Warranty is void if product has been buised, misused, or repairs attempted by unauthorized persons.

Varranties herein are for products sold/installed for use only in the United States nd Canada. For ORION products purchased for use in all other countries consult ocal in-country, authorized ORION sales agent/distributor for product warranty formation

Return Authorization Number must be obtained from ORION Laboratory Products Customer Service before returning any product for in-warranty repair, eplacement or credit.

"No Lemon" Instrument Warranty

The instrument is covered by the ORION "No Lemon" warranty. If the instrument fails within twelve months from date of purchase for any reason other than abuse, the purchaser may elect to have it repaired or replaced at no charge. This warranty covers the original or replacement/repaired meter from date of original meter purchase; the warranty is not extended beyond the buyer's original warranty date.

accessories

815600	Ross™ epoxy body, bulb guard combination pH electrode
9104BN	Laboratory grade combination pH electrode (BNC connector)
910600	GX-series epoxy body, gel-filled combination electrode (BNC connector)
912600	GX-series epoxy body, gel-filled flask combination electrode (BNC connector)
913600	GX-series epoxy body, gel-filled flat surface combination pH electrode (BNC connector)
915600	RX-series refillable, epoxy body combination pH electrode (BNC connector)
9162BN	Combination pH electrode with rugged bulb (BNC connector)
9163BN	Combination pH electrode with needle shape (BNC connector)
910004	pH 4 buffer packets, box of 25 packets, each packet making 200 ml of buffer
910007	pH 7 buffer packets, box of 25 packets, each packet making 200 ml of buffer
910009	pH 9 buffer packets, box of 25 packets, each packet making 200 ml of buffer
910104	pH 4.01 buffer, 475 ml bottle
910107	pH 7.00 buffer, 475 ml bottle
910110	pH 10.01 buffer, 475 ml bottle
970899	Dissolved oxygen electrode
910002	Electrode holder
020030	Shorting plug
020120	110V AC line adapter
020121	220V AC line adapter

specifications

package contents	model 211 digital pH meter, with model 910600 gel-filled unbreakable combination pH electrode, support rod, electrode holder, bottles for pH 7 buffer and distilled water, one packet pH 7 buffer powder, AC adapter, six 1.5 V batteries, and carrying case
range	0 to 14 pH
resolution	± .01 pH
temperature compensation	manual (0 to 100°C)
isopotential point	pH 7 (fixed)
power requirement	six 1.5 V batteries; battery life: 3000 ten second intermittent measurements when line adapter is not used. line adapter: 110 or 220 V ± 20%, 50/60 Hz
dimensions	14 cm high x 9 cm wide x 4.5 cm deep
weight	0.4 kg

specifications subject to change without notice

notice of compliance

The Model 211 may generate radio frequency energy and if not installed and used properly, that is, in strict accordance with the manufacturer's instructions, may cause interference to radio and television reception. It has been type tested and found to comply with the limits for a Class B computing device in accordance with specifications in Subpart J of Part 15 of FCC Rules, which are designed to provide reasonable protection against such interference in a residential installation. However, there is no guarantee that interference will not occur in a particular installation. If the Model 211 does cause interference to radio or television reception, which can be determined by turning the unit off and on, the user is encouraged to try to correct the interference by one or more of the following measures:

- reorient the receiving antenna
- relocate the Model 211 with respect to the receiver
- move the Model 211 away from the receiver
- plug the Model 211 into a different outlet so that the meter and receiver are on different branch circuits

If necessary, the user should consult the dealer or an experienced radio/television technician for additional suggestions. The user may find the following booklet prepared by the Federal Communications Commission helpful:

"How to Identify and Resolve Radio-TV Interference Problems"

This booklet is available from the U.S. Government Printing Office, Washington, DC 20402, Stock No. 004-000-00345-4.

APPENDIX F

FIELD MEASUREMENTS OF SPECIFIC CONDUCTANCE AND TEMPERATURE

FIELD MEASUREMENT OF SPECIFIC CONDUCTANCE AND TEMPERATURE

Method: Specific Conductance, umhos @ 25°C

Reference: EPA 1979, Page 120.1, Standard Methods, 15th edition, pp 70-73

Detection Limit: 1 umho/cm @ 25°C

Optimum Range: 0.1 - 100,000 umhos/cm

Sample Handling: Determine on-site or within 24 hours

Reagents and Apparatus:

1. Conductivity meter (YSI) and electrodes.
2. Deionized water in squirt bottle.
3. Standard potassium chloride solution, 0.0100 N.

Procedure:

YSI Conductivity Meter

1. With mode switch at off position, check meter zero. If not zeroed, use meter screw and adjust to zero.
2. Plug probe into jack on side of meter.
3. Turn mode switch to red line, and turn red line knob until needle aligns with red line on dial. Change batteries if cannot be aligned.
4. Totally immerse probe in sample. Do not allow the probe to touch the sample container.
5. Turn mode switch to appropriate conductivity scale, X100, X10, or X1. Use a scale that will give a mid-range output on the meter.
6. Wait for needle to stabilize (about 15 sec.) and record conductivity multiplying by scale setting.
7. While gently agitating the probe, take sample temperature (°C) and record.
8. Rinse probe with deionized water.
9. Record specific conductivity (1st column) and temperature on F.O.S. sheet.

Notes:

1. Calculate conductivity using following formula:

$$G_{25} = \frac{G_T}{[1 + 0.02\ (T-25)]}$$

G_{25} = Conductivity at 25°C, umhos/cm

T = Temperature of sample, °C

G_T = Conductivity of sample at temperature T, umhos/cm

2. Report results for the standard solution with each data set.

3. Record on field sheet which meter and probe were used. Meter should be wiped clean as necessary.

4. After returning to lab, compare results with previous data. Report problems to lab personnel.

Reagent Preparation:

1. Stock Potassium Chloride Solution, 1.00 N: Dissolve 74.555 g. K Cl in Milli-Q water and dilute to 1,000 ml. in a volumetric flask.

2. Standard Potassium Chloride Solution, 0.0100N: Dilute to 10.0 mls. of stock solution to 1,000 mls. with Milli-Q water using a volumetric pipet and flask.

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GENERAL DESCRIPTION

The YSI Model 33 and 33M S-C-T Meters are portable, battery powered, transistorized instruments designed to accurately measure salinity, conductivity and temperature. They use a probe consisting of a rugged, plastic conductivity cell and a precision YSI thermistor temperature sensor combined in a single unit.

Conductivity with the Model 33 is expressed as micromhos/centimeter (μmhos/cm); with the 33M, it's millisiemens/meter (mS/m). These are measurements of the electrical conductance the sample would show if measured between opposite faces of a 1cm cube. (Conversion information: 1 μmho/cm = 0.1 mS/m.) Salinity is the number of grams of salt/kilogram of sample (‰ = parts per thousand). This measurement assumes the sample contains a "standard" sea water salt mixture. The sample temperature is measured in degrees Celsius.

Salinity measurements are manually temperature compensated by direct dial. Conductivity measurements are not temperature compensated, however, a temperature function is provided on the instrument to aid with calculation of corrections. Also, when just temperature and conductivity are known it is possible to calculate salinity and when only temperature and salinity are known it is possible to calculate conductivity.

SPECIFICATIONS

Model 33 Conductivity

Ranges	0-500, 0-5,000, 0-50,000 μmhos/cm with YSI 3300 Series Probes (Note: The "μmho" designations on the meter are a shorthand form for "μmho/cm".)
Accuracy	±2.5% max. error at 500, 5,000 and 50,000 plus probe ±3.0% max. error at 250, 2,500 and 25,000 plus probe See Error Section

Readability	2.5 μmhos/cm on 500 μmho/cm range 25 μmhos/cm on 5,000 μmho/cm range 250 μmhos/cm on 50,000 μmho/cm range
Temperature Compensation	None

Model 33M Conductivity

Ranges	0-50, 0-500, 0-5,000 mS/m with YSI 3300 Series Probes
Accuracy	±2.5% max. error at 50, 500 and 5,000 plus probe ±3.0% max. error at 25, 250 and 2,500 plus probe See Error Section
Readability	0.25 mS/m on 50 mS/m range 2.5 mS/m on 500 mS/m range 25.0 mS/m on 5,000 mS/m range
Temperature Compensation	None

Salinity

Range	0-40 ‰ in temperature range of -2 to +45°C
Accuracy	Above 4°C: ±0.9 ‰ at 40 ‰ and ±0.7 ‰ at 20 ‰ plus conductivity probe Below 4°C: ±1.1 ‰ at 40 ‰ and ±0.9 ‰ at 20 ‰ plus conductivity probe See Error Section
Readability	0.2 ‰ on 0-40 ‰ range
Temperature Compensation	Manual by direct dial from -2 to +45°C

Temperature	
Range	-2 to +50°C
Accuracy	±0.1°C at -2°C, ±0.6°C at 45°C plus probe See Error Section
Readability	±0.15°C at -2°C to ±0.37°C at 45°C
Power Supply	Two D-size alkaline batteries. Eveready E95 or equivalent provide approximately 200 hrs. of operation
Probe	YSI 3300 Series Conductivity/Temperature Probe Nominal Probe Constant K = 5/cm
Accuracy	±2% of reading for conductivity and salinity Error of ±0.1°C at 0°C and ±0.3°C at 40°C
Instrument	
Ambient Range	Satisfactory operation -5 to +45°C A maximum error of ±0.1% of the reading per °C change in instrument temperature can occur. This error is negligible if the instrument is readjusted to redline for each reading

OPERATION PROCEDURE

1. Setup
   (a) Adjust meter zero (if necessary) by turning the bakelite screw on the meter face so that the meter needle coincides with the zero on the conductivity scale
   (b) Calibrate the meter by turning the MODE control to REDLINE and adjusting the REDLINE control so the meter needle lines up with the redline on the meter face. If this cannot be accomplished, replace the batteries
   (c) Plug the probe into the probe jack on the side of the instrument
   (d) Put the probe in the solution to be measured (See Probe Use)
2. Temperature
   Set the MODE control to TEMPERATURE. Read the temperature on the bottom scale of the meter in degrees Celsius. Allow time for the probe temperature to come to equilibrium with that of the water before reading
3. Salinity
   (a) Transfer the temperature reading from Step 2 to the °C scale on the instrument
   (b) Switch the MODE control to the SALINITY position and read salinity on the red 0-40 ‰ meter range
   (c) Depress the CELL TEST button. The meter reading should fall less than 2‰. If greater, the probe is fouled and the measurement is in error. Clean the probe and re-measure
4. Conductivity on Model 33 (Model 33M data are in parentheses.)
   (a) Switch the MODE control to the X100 scale. If the reading is below 50 on the 0-500 range (5.0 on the 0-50 range) switch to the X10 scale. If the reading is still below 50 (5.0), switch to the X1 scale. Read the meter scale and multiply the reading appropriately. The answer is expressed in µmhos/cm (mS/m). Measurements are not temperature compensated

Example:	Meter Reading	24.7 (24.7)
	Scale	X10
	Answer	247.0 µmhos/cm (24.7 mS/m)

(b) When measuring on the X100 and X10 scales, depress the CELL TEST button. The meter reading should fall less than 2%, if greater, the probe is fouled and the measurement is in error. Clean the probe and re-measure.

NOTE: The CELL TEST does not function on the X1 scale.

5. Error

The maximum error in a reading can be calculated by using the graphs in the following sections.

(1) Temperature

The temperature scale is designed to give the minimum salinity error when the temperature readings are used to compensate salinity measurements.

Figure 1 shows total error for probe and instrument versus °C meter reading.

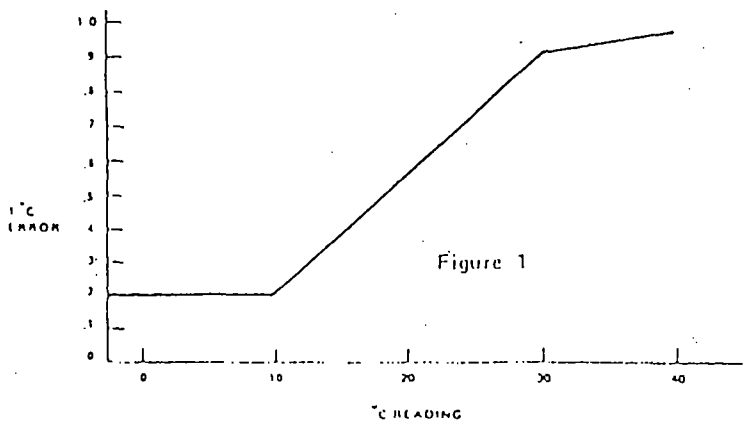


Figure 1

Example: Meter Reading 15°C
Total Error 0.4°C
Accuracy 15°C ± 0.4°C for probe and instrument combined

(2) Conductivity on Model 33 (Model 33M data are in parentheses.)

Figure 2 shows the worst-case conductivity error as a function of the conductivity reading for the probe and instrument combined.

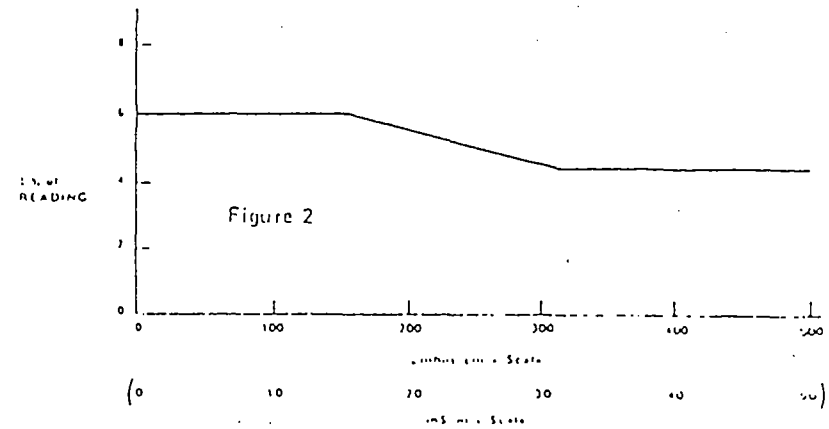


Figure 2

Example: Meter Reading 360 μmhos/cm (36 mS/m)
Scale X10
% Reading Error ± 4.5%
Accuracy 3600 ± 162 μmhos/cm (360 ± 16.2 mS/m) for probe and instrument

(3) Salinity

The salinity readings are a function of temperature and conductivity, therefore the accuracy is a function of both. The temperature scale and temperature control have been designed to minimize the temperature error contribution to the salinity error. The error shown in Figure 3 is the total of the temperature and conductivity probe, the temperature scale and the salinity scale error.

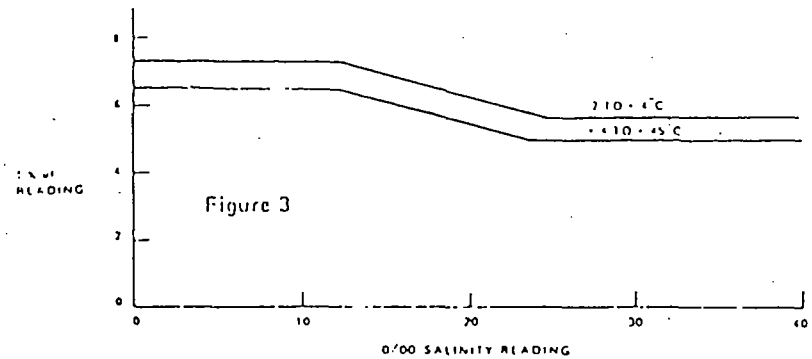
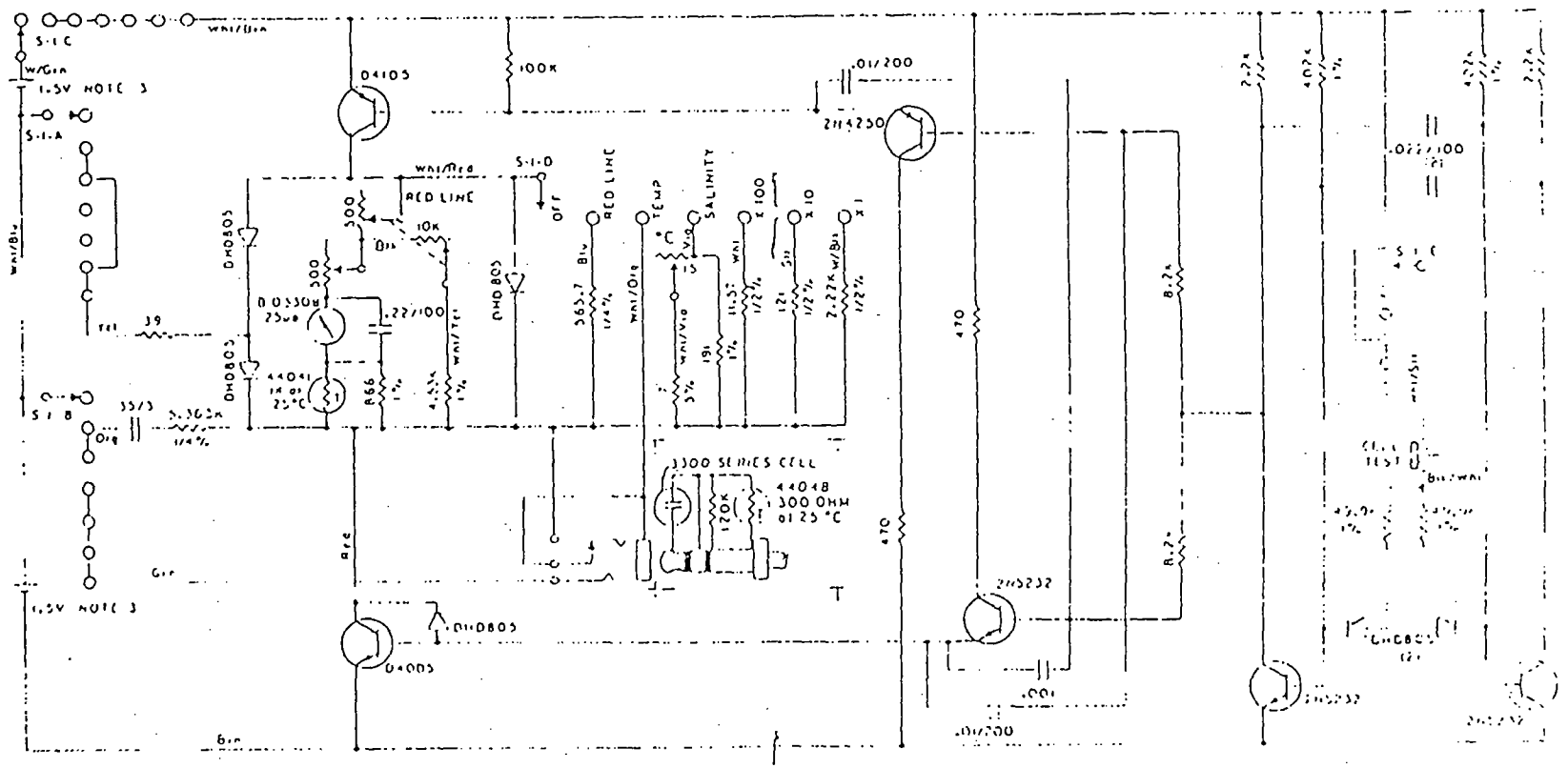


Figure 3

Example:	Meter Reading:	10 0/00, @ 10°C
	% of Reading Error.	6 5%
	Accuracy.	10 ‰ ± 0 65 ‰ for all errors, combined worst case.


1.5V NOTE 3
100K
.01/200
2N4250
2N5232
470
8.2k
2.2k
4.02k
.022/100
RED LINE
TEMP
SALINITY
X 100
X 10
X 1
3300 SERIES CELL
44048
1 300 OHM
01 25 °C
120K
.001
.01/200
.01/D805
D4005
D4105
D4005
D4005
D4005

CIRCUIT DESCRIPTION, MAINTENANCE AND CALIBRATION

1. Description

The circuit is composed of two parts, a multivibrator and switching transistors. The multivibrator produces a square waveform voltage. The square wave is applied to two switching transistors. They alternately apply two batteries of opposite polarity to the probe thus providing AC power which minimizes polarization effects. The meter is in series with one battery and measures the current from it. The current from the battery is proportional to the conductance of the cell. Salinity is measured in a special range conductivity circuit which includes a user-adjusted temperature compensator. In the temperature, redline and X1 positions the multivibrator operates at 100 Hz. In the salinity, X100 and X10 positions the multivibrator operates at 600 Hz and in these ranges pushing the CELL TEST button drops the frequency to 100 Hz allowing the operator to judge the degree of probe polarization.

2. Maintenance

The only maintenance required is battery replacement. Two "D" size alkaline flashlight cells, such as Eveready E95 or equivalent, will provide 200 hrs. of operation. Accuracy will not be maintained if zinc-carbon "D" cells are used. Battery replacement is indicated when the redline adjustment cannot be accomplished.

Replace batteries every six months to reduce the danger of corrosion due to leaky batteries. To replace batteries, remove the six screws from the rear plate. The battery holders are color coded. The Positive (+ button) end must go on red.

3. Calibration of Model 33 (Model 33M data are in parentheses.)

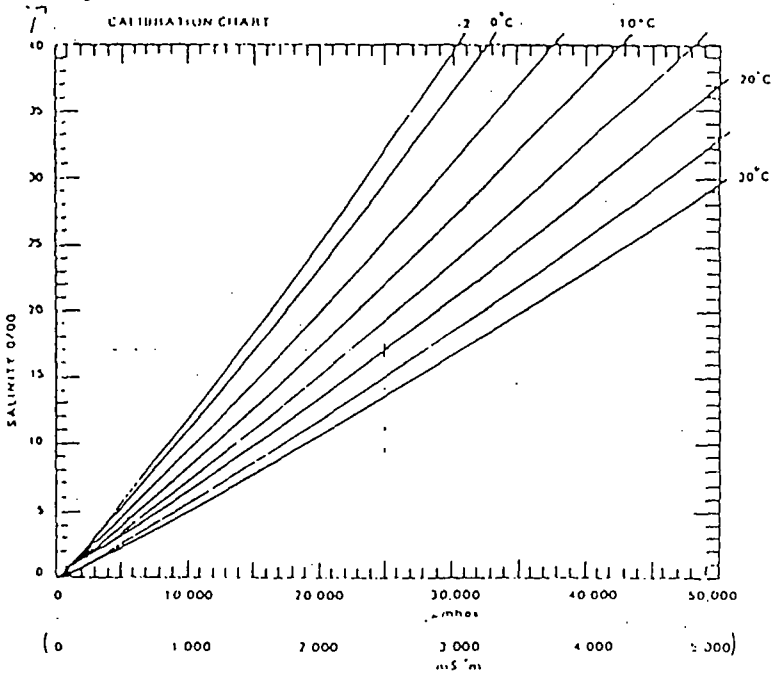
It is possible for the temperature knob to become loose or slip from its normal position. In an emergency the dial can be re-positioned. It must be emphasized that this is an emergency procedure only, and that the instrument should be returned to the factory for proper recalibration at the earliest opportunity.

(a) Read the temperature and conductivity of the solution. Determine the salinity of the solution by running a line vertically on the graph from this conductance value until it intersects the appropriate °C line (interpolate as required for temperature between the given °C lines). From this intersection extend a line horizontally to the edge of the graph. This determines the salinity for this sample.

Example: 25,000 μmhos/cm and 20°C gives a salinity of 17
(Example: 2.500 mS/m and 20°C gives a salinity of 17.)

(b) Remove the °C knob, switch to SALINITY, and turn the control shaft until the meter needle indicates the salinity value determined in Step (a). In the example given, the value is 17.

(c) Switch to TEMPERATURE. (Note: This temperature reading must be the same as Step (a), if not, begin again at Step (a).) Place the knob on the control shaft (without turning the control shaft) with the knob pointer at the same temperature as the meter reading and tighten both set screws securely.

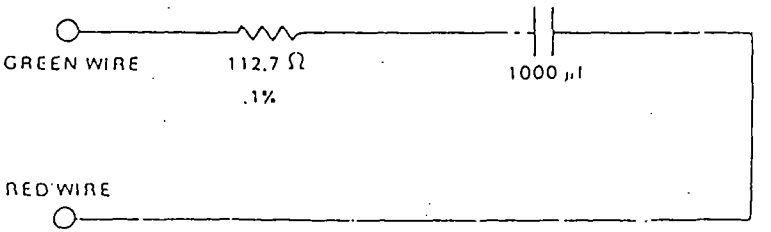


At earliest opportunity recalibrate using the following procedure or return the instrument to factory for service.

(a) Set the instrument for a salinity measurement as normal.

(b) Substitute a 1000 μf capacitor and 112.7 ohm 0.1% tolerance resistor for the probe.

Connect the resistor and capacitor between the green wire and red wire on the jack connections inside the instrument.



(c) Turn the temperature dial until the meter reads redline

Now install the temperature knob with the arrow at 25°C This is a temporary calibration only Return the instrument to the factory for proper recalibration

PROBE

1 Description of YSI 3300 Series Conductivity/Temperature Probe

The YSI 3300 Series Conductivity Probes are designed for field use, embodying construction and design for rugged, accurate service

Each probe features a built-in cell constant of 5 0 (500 0/M) ±2%, a precision YSI thermistor temperature sensor of ±0 1°C accuracy at 0°C and ±0 3°C at 40°C and a low capacitance cable assembly terminating in a three therminal 0 25" dia phone type connector.

The 3310 has a 10 ft cable and the 3311 is a 50 ft version Other lengths are available on special order

The probe has a rigid P V C body platinized pure nickel electrodes, and a durable cable providing resistance to a wide range of water-borne substances

2 Maintenance

(a) Cleaning

When the cell test indicates low readings the probable cause is dirty electrodes Hard water deposits oils and organic matter are the most likely contaminants

For convenient normal cleaning soak the electrodes for 5 minutes with a locally available bathroom tile cleaning preparation such as Dow Chemical Bathroom Cleaner Horizon Industries Rally Tile, Porcelain and Chrome Cleaner Johnson Wax Envy Instant Cleaner or Lysol Brand Basin Tub Tile Cleaner

For stronger cleaning a 5 minute soak in a solution made of 10 parts distilled water, 10 parts isopropyl alcohol and 1 part HCl can be used

Always rinse the probe after cleaning and before storage

CAUTION: Do not touch the electrodes inside the probe Platinum black is soft and can be scraped off

If cleaning does not restore the probe performance, re platinizing is required.

(b) Re Platinizing

Equipment Required —

(1) YSI #3140 Platinizing Solution, 2 fl oz (3% platinum chloride dissolved in 0 025% lead acetate solution)
(2) YSI Model 33 or 33M S-C-T Meter
(3) 50 ml glass breaker or equivalent bottle
(4) Distilled water

Procedure —

(1) Clean the probe as in Section (a) either method
(2) Place the cell in the beaker and add sufficient YSI #3140 solution to cover the electrodes Do not cover the top of the probe
(3) Plug the probe into the Model 33 or 33M, switch to the X100 scale to platinize the electrode Move the probe slightly to obtain the highest meter reading and continue platinizing for the approximate time shown below

Meter Reading		Time
µmhos/cm	mS/m	(minutes)
30,000	3,000	5
25,000	2,500	6
20,000	2,000	8
15,000	1,500	11
10,000	1,000	16

(4) After the elapsed time remove the probe and rinse in fresh water.

(5) Return the solution to its container. 2 oz. of solution should be sufficient for 50 treatments.

3. Probe Use

(a) Obstructions near the probe can disturb readings. At least two inches of clearance must be allowed from non-metallic underwater objects. Metallic objects such as piers or weights should be kept at least 6 inches from the probe.

(b) Weights are attached to the cable of the YSI 3310 and 3311 Probes. The YSI 3327 Weights are supplied in pairs with a total weight of 4 ounces per pair. Should it become necessary to add more weight to overcome water currents, we suggest limiting the total weight to two pounds (8 pairs). For weights in excess of two pounds use an independent suspension cable. In either case, weights must be kept at least 6 inches away from the probe.

(c) Gentle agitation by raising and lowering the probe several times during a measurement insures flow of specimen solution through the probe and improves the time response of the temperature sensor.

4 Cell Calibration & Standard Solutions

The YSI #3300 Series Cells are calibrated to absolute accuracy of ±1.5% based on a standard solution. Since the literature on conductivity does not indicate a consistently accepted standardization method we have chosen the 0.01 demal KCl solution method as determined by Jones and Bradshaw in 1937 as our standard. Recent textbooks, as well as the ASTM standards, concur with this choice.

The solution is prepared by diluting 0.745 grams of pure dry KCl with distilled water until the solution is 1 kilogram. The table below shows the values of conductivity this solution would have if the distilled water were non-conductive. However, since even high purity distilled water is slightly conductive, the measured conductivity will be higher by an amount equal to the water's conductivity.

Temperature °C	Conductivity µmhos/cm	Conductivity mS/m
15	1141.5	114.2
16	1167.5	116.8
17	1193.6	119.4
18	1219.9	122.0
19	1246.4	124.6
20	1273.0	127.3
21	1299.7	130.0
22	1326.6	132.7
23	1353.6	135.4
24	1380.8	138.1
25	1408.1	140.8
26	1436.5	143.7
27	1463.2	146.3
28	1490.9	149.1
29	1518.7	151.9
30	1546.7	154.7

The operator may use the standard solution and the table to check accuracy of a cell's constant or to determine an unknown constant. The formula is shown below

$$K = \frac{R(C_1 + C_2)}{10^6} \quad \text{or} \quad \frac{R(S_1 + S_2)}{10^3}$$

where. K = Cell constant

R = Measured resistance in Ω

C_1 = Conductivity in µmhos/cm

C_2 = Conductivity in µmhos/cm of the distilled water used to make solution

S_1 = Conductivity in mS/m
S_2 = Conductivity in mS/m of the distilled water used to make the solution.

R, C_1 and C_2, or S_1 and S_2, must either be determined at the same temperature or corrected to the same temperature to make the equation valid

Note: For further information on conductivity and the above standard information, refer to ASTM Standards Part 23 — Standard Methods of Test for Electrical Conductivity, or Water and Industrial Waste Water — ASTM Designation D1125 64

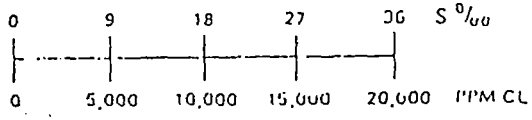
YSI MODEL 33 AND 33M USED WITH YSI 51A, 54 and 57 OXYGEN METERS

If the salinity measurement is to be used for salinity correction on the 51A, the reading should be converted to Chlorosity The formula is

$$\text{PPM Chlorosity} = \frac{\text{Salinity } ‰ - 0.03}{1.8} \times 10^3$$

For these instruments the 0.03 can be neglected so the equation simplifies to

$$\text{PPM Cl} = \frac{\text{SS } ‰ \times 10^3}{1.8}$$



For salinity correction when using the Model 57 use the salinity reading direct from the Model 33 or 33M No conversion is necessary.

Model 33 and 33M salinity readings taken in conjunction with Model 54 dissolved oxygen readings can be used to correct the Model 54 for salinity and to make post-measurement salinity corrections to dissolved oxygen data Correction tables are available from the factory

WARRANTY

All YSI products carry a one-year unconditional warranty on workmanship and parts, exclusive of batteries Damage through accident, misuse, or tampering will be repaired at a nominal charge

If you are experiencing difficulty with any YSI product, it may be returned to an authorized YSI dealer for repair, even if the warranty has expired If you need factory assistance for any reason contact

Service Department
Yellow Springs Instrument Co., Inc
P O Box 279
Yellow Springs, Ohio U S A
Phone (513) 767-7241

APPENDIX G

OPERATIONAL PROCEDURE FOR MODEL PI 101

PHOTOIONIZATION ANALYZER

EXTRACTED FROM PROTOTYPE PROCEDURE
BY
CHEN-WEN TSAI, U.S.EPA QAO

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OPERATION PROCEDURE FOR
HNu MODEL PI 101
PHOTOIONIZATION ANALYZER

I. INTRODUCTION

1.0 Operation Principle

The HNu Model 101 photoionization detector has been designed to measure the concentration of trace gases in many industrial or plant atmospheres. The instrument has similar capabilities outdoors. The analyzer employs the principle of photoionization for detection. This process is termed photoionization because the absorption of ultraviolet light (a photon) by a molecule leads to ionization via:

$$RH + h\nu \text{ ---------- } RH^{+} + e$$

where RH = trace gas
hv = a photon with an energy greater than or equal to an ionization potential of RH.

The sensor consists of a sealed ultraviolet light source that emits photons which are energetic enough to ionize many trace species (particularly organics), but do not ionize the major components of air such as O_2, N_2, CO, CO_2 or H_2O. A chamber adjacent to the ultraviolet light source contains a pair of electrodes. When a positive potential is applied to one electrode, the field created drives any ions, formed by absorption of UV light, to the collector electrode where the current (proportional to concentration) is measured. The useful range of the instrument is from a fraction of a ppm to about 2,000 ppm.

2.0 Instrument Sensitivity and Calibration

The instrument responds to atmospheric compounds with ionization potentials equal to or less than the ionization energy of the UV light source. If a compound in air has an ionization potential greater than the energy source of the lamp, it will not be detected. Table 1 presents organic and inorganic compounds and the light sources that should be used to detect each compound. The instrument is capable of using 1 of the 3 light sources - 9.5, 10.2, and 11.7 ev lamps. In addition, not all compounds respond equally to each light sources and thus they vary in their sensitivity to ionization. As a result of varying sensitivities to photoionization, the response given by the instrument may or may not reflect the actual atmospheric concentration of the compound being

detected. Table 2 represents the relative sensitivities for various gases relative to a 10.2 ev light source. Use this table to determine the approximate response of the instrument to a compound of interest, and to select the appropriate light (lamp) source.

There are two types of operations that are used for calibration. For Type 1 Operation, a non-regulatory (or non-target) compound such as isobutylene is used for calibration. In this case, the instrument reading is reported in terms relative to the calibration compound used for calibration. For the type 2 operation, the target compound or compounds are used for calibration. As a result, the instrument is calibrated to respond directly in ppm by volume of the target compound(s).

3.0 Instrument Specifications

3.1 Performance

- o Range: 0.1 to 2000 ppm
- o Detection Limit: 0.1 ppm
- o Sensitivity (max.): 0 to 2 ppm FSD over 100 division meter scale
- o Repeatability: ± 1% of FSD
- o Linear Range: 0.1 to 600 ppm
- o Useful Range: 0.1 to 2000 ppm
- o Response Time: less than 3 seconds to reach 90% full scale
- o Ambient humidity: up to 95% relative humidity
- o Operating Temperature: Ambient to 40°C (instrument is temperature compensated so that a 20°C change in temperature corresponds to a change in reading of ± 2% full scale at maximum sensitivity.

3.2 Power Requirements and Operating Times

- o Continuous use on battery: approximately 10 hours
- o Continuous use with HNu recorder reduces instrument battery operating time to approximately 5 hours

- o Recharge time: less than 14 hours; a 3 hours charge will charge up to 90% full charge

- o Recharge Current: maximum 0.4 amps at 15 VDC

II. OPERATIONAL PROCEDURE

1.0 Instrument Check-Out

1.1 Remove instrument box cover by pulling up on fasteners.

1.2 On the instrument panel, there will be a label containing information on light source, calibration date, calibration gas, and span setting.

1.2.1 If the instrument has not been calibrated in the last 14 days or since its last field use, it should be recalibrated. Check the instrument log, which should be maintained with the instrument, for the instrument status and its calibration history. For general use, the instrument should be calibrated to isobutylene at a span setting of 9.8.

1.2.2 Check the label for light source and refer to Table 1 for ionization potentials of various compounds. If the compound you wish to detect is not listed for the light sources provided with instrument, then the light source will have to be changed. Use the probe with the proper light source for the compounds to be detected.

1.2.3 Once it has been determined that the instrument has the correct lamp, the instrument may need to be recalibrated for the specific compound of interest. Use Procedure under 2.1.3 of this Section to calibrate the instrument.

1.2.4 Check the battery supply by connecting the probe to the instrument box, and turning the function switch to the battery check position (Figure 1). (Note: The battery check indicator will not function unless the probe is attached.) The meter needle should deflect to the far right or above the green zone. If the needle is below or just within the green zone or the red LED indicator is on, the battery should be recharged. Follow

the procedure described in Section III (Maintenance and Trouble shooting) to recharge the battery.

1.2.5 Repack the instrument for shipment to the field.

2.0 Field Operation

2.1 Calibration

2.1.1 Equipment and Materials

- o Calibration Gas (2 ranges)

  Low range 0-20 ppm and mid-range 20-200 ppm of isobutylene gas are used for standard field operation when contaminants are unknown or a mixture of gases is present. The isobutylene gas is used for general calibration because of the instrument's relatively high sensitivity to it and the non-toxic nature of the gas. Note: A specialty gas may be required if a single atmospheric contaminant is present and the contaminant has a sensitivity different from that of the calibration gas (isobutylene).

- o Tubing and fittings (see Figure 1).

- o Rotometer or bubble flow meter.

- o Field Log, calibration form, and data reporting form.

- o Table 1 for ionization potentials for compounds of interest.

2.1.2 Calibration Frequency

This instrument should be calibrated after each field use and prior to each field use. Continuous calibration check should be performed frequently during field operation (for example, check the instrument zero and calibration after every 10 measurements) and document the results properly. Caution: Do Not Change the Settings.

2.1.3 Calibration Procedure

2.1.3.1 Use a three-points procedure to facilitate the proper instrument calibration over appropriate operating ranges. Distinct mixtures of calibration gas with known concentration for selective operating range should be used for calibration. Each mixture should give a 3/4 scale deflection in its respective operating range.

2.1.3.2 Instrument Setup.

Step 1: Remove Instrument cover by pulling up on the side straps.

Step 2: Prior to calibration, check the function switch (Figure 2) on the control panel to make sure it is in the OFF position. The probe nozzle is stored inside the instrument cover. Remove cover plate by pulling up on the pins that fasten the cover plate.

Step 3: Remove the nozzle from the cover. Assemble probe by screwing nozzle into casing.

Step 4: Attach probe cable to instrument box inserting 12 pin interface connector of the probe cable into the connector on the instrument panel. Match the alignment keys and insert connector. Turn connector in clockwise direction until a distinct snap and lock is felt.

Step 5: Turn the function switch to the Battery Check position. When the battery is charged, the needle should read within or above the green battery arc on the scale plate. If the needle is below the green arc or the red LED light comes on, the instrument should be recharged prior to making any measurements. Implement steps in Section III to recharge battery.

Step 6: Turn the function switch to the ON position. In this position, the UV

light source should be on. To verify, gaze at the end of the probe for a purple glow. Do Not Look Directly at the Lamp Itself. If the lamp does not come on refer to Maintenance Step in 2.2 (Section III).

Step 7: To zero the instrument, turn the function switch to the standby position and rotate the zero potentiometer until the meter reads zero. Clockwise rotation of the zero potentiometer produces an upscale deflection while counter clockwise rotation yields a downscale deflection. (Note: No zero gas is needed since this is an electronic zero adjustment.) If the span adjustment is changed during instrument calibration, the zero should be rechecked and adjusted. If necessary, wait 15 to 20 seconds to ensure that the zero reading is stable. Readjust as necessary.

2.1.3.3 Calibration Steps

Step 1: Insert one end of T tube (Figure 1) into probe. Insert second end of probe into calibration gas in the 20-200 ppm range. The third end of probe should have the rotometer (bubble meter) attached.

Step 2: Set the function switch in the 0-200 ppm range. Crack the valve on the pressured calibration gas container until a slight flow is indicated on the rotometer. The instrument will draw in the volume required for detection with the rotometer indicating excess flow.

Step 3: Adjust the span potentiometer so that the instrument is reading the exact value of the calibration gas. (Calibration gas value is labeled on the cylinder).

Step 4: Turn instrument switch to the standby position and check the electronic zero. Reset zero

potentiometer as necessary following step 7 of 2.1.3.2.

Step 5: Record on form and field log all original and readjusted settings as specified in the form.

Step 6: Next, set the function switch to the 0-20 ppm. Remove the mid-range (20-200 ppm) calibration gas cylinder and attach the low range (0-20 ppm) calibration gas cylinder as described above.

Step 7: Do not adjust the span potentiometer. The observed reading should be ±3 ppm of the concentration specified for the low range calibration gas. If this is not the case, recalibrate the mid range scale repeating Step 1 thru 6 above. If the low range reading consistently falls outside the recommended tolerance range, the probe light source window likely needs cleaning. Clean window following Step 2 under 2.3 (Section III). When the observed reading is within the required tolerances, the instrument is fully calibrated.

2.2 Sample Measurement

Step 1: Place function switch in 0-20 ppm range for field monitoring. This will allow for the most sensitive, quick response in detecting airborne contaminants.

Step 2: Before entering a contaminated area, determine background concentration. This concentration should be used as a reference to readings made in the contaminated area. <u>Under no circumstance should one attempt to adjust the zero or span adjustments while the instrument is being operated in the field.</u>

Step 3: Take measurements in contaminated area, recording readings and locations. Should readings exceed the 0-20 scale, switch the function

switch to the 0-200 or 0-2,000 range as appropriate to receive a direct reading. Return the instrument switch to the 0-20 range when readings are reduced to that level. Record measurements in notebook or on an appropriate form.

Step 4: Keep in mind health and safety action guidelines for the level of protection you are wearing. Sustained readings above a certain level may force you to vacate an area or upgrade your level of protection.

Note: The instrument will not function properly in high humidity or when the window to the light housing is dirty. If the instrument response is erratic or lower than expected.

Step 5: When finished, use the reverse Steps 1 thru 5 of Section 2.1.3.2 (Instrument Setup) to shut down the instrument.

III. MAINTENANCE AND TROUBLE-SHOOTING

1.0 Battery Recharging

1.1 The instrument should be recharged 1 hour for each hour of use or overnight for a full day's use. (The battery will last 10 hours on a full charge.)

1.2 To recharge the battery (or instrument):

1.2.1 Turn the function switch to the off position.

1.2.2 Remove the charger from the instrument top compartment.

1.2.3 Place the charger plug into the jack on the left side of the instrument box.

1.2.4 Connect the charger unit to a 120 V AC supply.

1.2.5 Check charger function by turning the instrument switch to the battery check position. The meter should go upscale if

the charger is working and is correctly inserted into the jack.

1.2.6 Place instrument in instrument mode and charge for the appropriate time period.

1.2.7 Turn the instrument off following the recharge cycle. When disconnecting charger, remove from 120 V AC supply before removing the mini phone plug.

2.0 General Fault Determination and Correction

2.1 Battery level is low. Recharge if necessary implementing steps described under 1.0 (Section III). If the battery will not recharge, it will have to be replaced.

2.2 UV Lamp function - Gaze at sample inlet when mode switch is on an instrument function position and observe for purple glow of lamp. If the lamp does not glow in any of the three instrument function positions, it may be burned out and will have to be replaced. To replace the lamp:

1. Turn the function switch to the off position and disconnect the probe connector from the readout unit.

2. Remove the exhaust screw found near the base of the probe (Figure 3).

3. Grasp the end cap in one hand and the probe shell in the other and gently pull to separate the end cap and lamp housing from the shell.

4. Loosen the screws on the top of the end cap and separate the end cap and ion chamber from the lamp and lamp housing. Care must be taken so that the ion chamber does not fall out of the end cap and the lamp does not slide out of the lamp housing.

5. Turn the end cap over in your hand and tap on the top of it; the ion chamber should fall out of it.

6. Place one hand over the top of the lamp housing and tilt slightly. The light source will slide out of the housing.

7. Replace lamp with one of same energy source as the one removed by sliding it into the

housing. Note: The amplifier board and instrument circuitry are calibrated for one light energy.

8. Place the ion chamber on top of the lamp housing, checking to ensure that the contacts are aligned.

9. Place the end cap on top of the ion chamber and replace the two screws. The screws should be tightened only enough to seal the "O" ring. Do not overtighten.

10. Line up the pins on the base of the lamp housing with the pins inside the probe shell. Gently slide the housing assembly into the probe shell. Do not force the assembly as it only fits one way.

11. Replace and tighten the exhaust screw.

12. Reconnect the 12 pin connector and turn instrument mode switch to a function position. Check for glow of lamp. If lamp still does not function, the instrument has an electrical short or other problem that will have to be corrected at the factory.

2.3 Instrument appears to be functional, but responses are lower than expected or erratic. The window of the light source may be dirty and need to be cleaned. To clean the light source window:

1. Disassemble the probe assembly by repeating Steps 1 thru 6 under 2.2 above.

2. Clean the window of the light source using compound provided with instrument and soft clean cloth. Important: Use cleaning compound on the window of the 10.2 eV lamp only. The cleaning compound may damage the windows of the 9.5 and 11.7 eV lamps.

3. Reassemble the probe assembly repeating Step 7 through 12 above.

3.0 Specific Faults

3.1 No meter response in any switch position (including BATT CHK)

1. Broken meter movement: Tip instrument rapidly from side to side. Meter needle should move freely, and return to zero.

2. Electrical connection to meter is broken: Check all wires leading to meter and clean the contacts of quick-disconnects.

3. Battery is completely dead: Disconnect battery and check voltage with a volt-ohm meter.

4. Check 2 amp fuse.

5. If none of the above solves the problem, consult the factory.

3.2 Meter responds in BATT CHK position, but reads zero or near zero for all others.

1. Power supply defective: Check power supply voltages per Figure 4. If any voltage is out of specification, consult the factory.

2. Input transistor or amplifier has failed: Rotate zero control; meter should deflect up/down as control is turned. Open probe; both transistors should be fully seated in sockets.

3. Input signal connection broken in probe or readout: Check input connector on printed circuit board. Should be firmly pressed down. Check components on back side of printed circuit board. All connections should be solid, and no wires should touch any other object. Check all wires in readout for solid connections.

3.3 Instrument responds correctly in BATT CHK, and STBY, but not in measuring mode.

1. Check to see the light source is on (See Section 2.2).

2. Check high voltage power supply (See Figure 4).

3. Open end of probe, remove lamp and check high voltage on lamp contact ring.

4. If high voltage is present at all above points, light source has most likely failed. Consult the factory.

3.4 Instrument responds correctly in all positions, but signal is lower than expected.

1. Check span setting for correct value.

2. Clean window of light source (See 2.3).

3. Double check preparation of standards.

4. Check power supply 180 V output. See Figure 4.

5. Check for proper fan operation. Check fan voltage. See Figure 4.

6. Rotate span setting. Response should change if span pot is working properly.

3.5 Instrument responds in all switch positions, but is noisy (erratic meter movement).

1. Open circuit in feedback circuit. Consult the factory.

2. Open circuit in cable shield or probe shield. Consult the factory.

3.6 Instrument response is slow and/or irreproducible.

1. Fan operating improperly. Check fan voltage. See Figure 4.

2. Check calibration and operation.

3.7 Low battery indicator.

1. Indicator comes on if battery charge is low.

2. Indicator also comes on if ionization voltage is too high.

H

APPENDIX H

CALIBRATION AND MAINTENANCE OF ORGANIC VAPOR ANALYZER (OVA)

damaging the batteries. When finished, move the battery charger switch to OFF and disconnect from the Side Pack Assembly.

The following are special instructions relative to batteries which have been allowed to completely discharge.

It has been established that the above battery recharging procedures may not be sufficient when the operator of the instrument has inadvertently left the INSTR Switch ON for a period of time without recharging and allowed the battery to completely discharge.

When this happens and the above procedures fail to recharge the battery, the following should be accomplished:

1) Remove the battery from the instrument case.
2) Connect to any variable DC power supply.
3) Apply 40 volts at 1/2 amp maximum.
4) Observe the meter on the power supply frequently and as soon as the battery begins to draw current, reduce the voltage on the power supply at a slow rate until the meter reads approximately 15 volts. NOTE: The time required to reach the 15 volt reading will depend on degree of discharge.
5) Repeat steps a), b), c), and d) above to continue charging.

2.7.2 DC CHARGER

a) The optional DC charger is designed to both charge the battery and to provide power for operating the instrument from a 12 volt DC source, such as vehicle power.
b) Connect the DC charger cord to the connector on the battery cover of the Side Pack Assembly. Plug the line cord into the vehicle cigarette lighter or other power source connection.
c) In mobile applications, the DC charger is used to supply vehicle power to the instrument. Therefore, it may be left connected at all times.

2.8 CHARCOAL FILTERING

When it is desired to preferentially remove the heavier hydrocarbons, such as those associated with automobile exhaust, gasoline, etc., simply remove the pickup fixture from the end of the probe and install the optional charcoal filter assembly.

This same charcoal filter assembly can be installed directly into the Readout Assembly by using the adapter provided.

2.9 MOISTURE FILTERING

Filtering of moisture in the sample is not normally required. However, when moving in and out of buildings in cold weather, excessive condensation can form in the lines and detector chamber. In this case, the charcoal filter adapter can be filled with a desiccant such as "Drierite" which will filter out the moisture contained in the sample.

SECTION 3

SUMMARIZED OPERATING PROCEDURES

3.1 GENERAL

The procedures presented in this section are intended for use by personnel generally familiar with the operation of the instrument. Section 2 presents the comprehensive detailed operating procedures.

It is assumed that, prior to start up the positions of all switches and valves are in shut down configuration as described in paragraph 3.3.

3.2 START UP

a) Move PUMP Switch to ON and check battery condition by moving the INSTR Switch to the BATT position.
b) Move INSTR Switch to ON and allow five (5) minutes for warm-up.
c) Set Alarm Level Adjust Knob on back of Readout Assembly to desired level.
d) Set CALIBRATE Switch to X10 position, use CALIBRATE Knob and set meter to read 0.
e) Move PUMP Switch to ON position then place instrument panel in vertical position and check SAMPLE FLOW RATE indication.
f) Open the H2 TANK VALVE and the H2 SUPPLY VALVE.
g) Depress Igniter Button until burner lights. Do not depress Igniter Button for more than six (6) seconds. (If burner does not ignite, let instrument run for several minutes and again attempt ignition.)
h) Use CALIBRATE Knob to "zero" out ambient background. For maximum sensitivity below 10 ppm, set CALIBRATE Switch to X1 and readjust zero on meter. To avoid false flame-out alarm indication, set meter to 1 ppm with CALIBRATE Knob and make differential readings from there.

3.3 SHUT DOWN

a) Close the H2 SUPPLY VALVE and the H2 TANK VALVE.
b) Move the INSTR Switch and PUMP Switch to OFF.
c) Instrument is now in shut down configuration.

SECTION 4

CALIBRATION

4.1 GENERAL

The OVA is capable of responding to nearly all organic compounds. For precise analyses it will be necessary to calibrate the instrument with the specific compound of interest. This is especially true for materials containing elements other than carbon and hydrogen.

The instrument is factory calibrated to a methane in air standard. However, it can be easily and rapidly calibrated to a variety of organic compounds. A GAS SELECT control is incorporated on the instrument panel which is used to set the electronic gain to a particular organic compound.

Internal electronic adjustments are provided to calibrate and align the electronic circuits. There are four (4) such adjustments all located on the electronics board. One adjustment potentiometer, R-38, is used to set the power supply voltage and is a one-time factory adjustment. The remaining three adjustments, R-31, R-32 and R-33 are used for setting the electronic amplifier gain for each of the three (3) calibrate ranges. Access to the adjustments is accomplished by removing the instrument from its case. Figure 4-1 indicates the location of the adjustments.

4.2 ELECTRONIC ADJUSTMENTS

Primary calibration of this instrument is accomplished at the factory using methane in air sample gases.

4.2.1 GAIN ADJUSTMENT

a) Place instrument in normal operation with CALIBRATE Switch set to X10 and GAS SELECT control set to 300.
b) Use the CALIBRATE ADJUST (zero) Knob and adjust the meter reading to zero.
c) Introduce a methane sample of a known concentration (near 100 ppm) and adjust trimpot R-32 on circuit board (see Figure 4-1 for location) so that meter reads equivalent to the known sample.
d) This sets the instrument gain for methane with the panel mounted gain adjustment (GAS SELECT) set at a reference number of 300.
e) Turn off H2 SUPPLY VALVE to put out flame.

4.2.2 BIAS ADJUSTMENT

a) Leave CALIBRATE Switch on X10 position and use CALIBRATE ADJUST (zero) Knob to adjust meter reading to 4 ppm.
b) Place CALIBRATE Switch in X1 position and, using trimpot R-31 on circuit board, adjust meter reading to 4 ppm. (See Figure 4-1)
c) Move CALIBRATE Switch to X10 position again. Use CALIBRATE ADJUST (zero) Knob to adjust meter to a reading of 40 ppm.
d) Move CALIBRATE Switch to X100 position and use trimpot R-33 on circuit board to adjust meter reading to 40 ppm.
e) Move CALIBRATE Switch to X10 position and use CALIBRATE ADJUST (zero) Knob to adjust meter reading to zero.
f) Unit is now balanced from range to range, calibrated to methane, and ready to be placed in normal service.

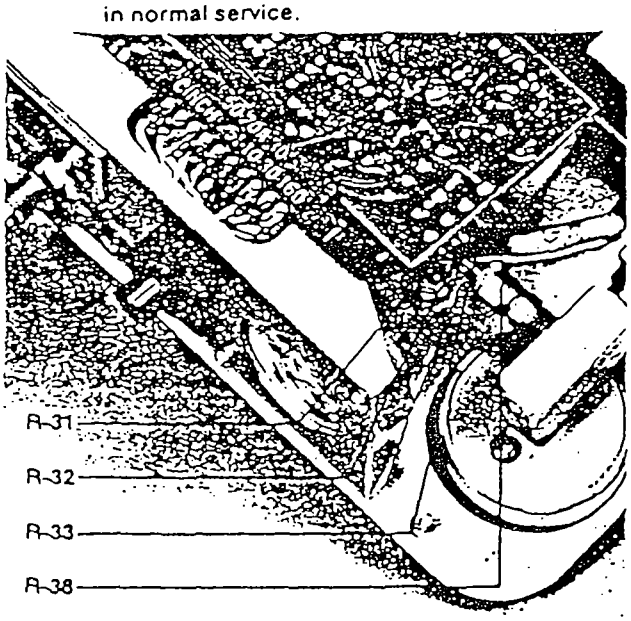


FIGURE 4-1. LOCATION OF ELECTRONIC ADJUSTMENTS
(Model OVA-118 shown; location typical to OVA-128)

4.3 CALIBRATION TO OTHER ORGANIC VAPORS

4.3.1 SETTING GAS SELECT CONTROL (Span)

Primary calibration of the instrument is accomplished using a known mixture of a specific organic vapor compound. After the instrument is in operation and the "normal background" is "zeroed out", draw a sample of the calibration gas into the instrument. The GAS SELECT Knob on the panel is then used to shift the readout meter indication to correspond to the concentration of the calibration gas mixture.

The instrument is then calibrated for the vapor mixture being used. After this adjustment, the setting on the "digidial" is read and recorded for that particular organic vapor compound. This exercise can be performed for a large variety of compounds and when desiring to read a particular compound the GAS SELECT control is turned to the predetermined setting for the compound. Calibration on any one range automatically calibrates the other two ranges.

4.3.2 USING EMPIRICAL DATA

Relative response data may be obtained, which can then be used to estimate concentrations of various vapors. With the instrument calibrated to methane, obtain the concentration reading for a calibration sample of the test vapor. The relative response, in percent, for that test vapor would then be the concentration read/concentration of the calibrated sample X 100.

4.3.3 PREPARATION OF CALIBRATION STANDARDS

4.3.3.1 COMMERCIAL SAMPLES

Commercially available standard samples offer the most convenient and reliable calibration standards and are recommended for the most precise analyses. Always remember to obtain the cylinder with the desired sample and the "balance as air". Sample should be drawn from the cylinder into a collapsed sample bag, then drawn from the bag by the instrument to prevent a pressure or vacuum at the sample inlet.

4.3.3.2 PURE GASEOUS SAMPLES

Obtain a large collapsible sample bag, preferably polyethylene such as a 40 gallon trash can liner. Insert a tube into the bag opening and tie shut around the tube. The tubing should have a shut-off valve or plug and be suitable for connecting the OVA input tube. Determine the volume of the bag by appropriate means (i.e., wet-test meter, dimensions of the bag, etc.). Forty gallon polyethylene bags provide a volume of approximately 140-160 liters. For gas samples, flush a 10 cc hypodermic syringe with the compound to be tested and then inject a 10 cc sample through the wall of the air-filled bag. Immediately after withdrawing the needle, cover the hole with a piece of plastic tape. Allow a few minutes for the sample to completely diffuse throughout the bag. Agitation will ensure complete diffusion. Connect the outlet tube to the OVA and take a reading. To verify repeatability of sampling technique, disconnect the bag and inject a second sample of the gas into the bag without emptying. Since only 2 or 3 liters will have been removed, the overall volume change will be small and the instrument reading should now be twice that of the

ginal. The concentration in ppm (V/V) will be equal to e sample size in cc divided by the volume of the bag in rs times 1000. For example, a 10 cc gas sample when ced in a 160 liter bag will provide a sample of 63 ppm, i., 10 X 1000/160 equals 63 ppm.

3.3.3 GASEOUS AND LIQUID SAMPLES (Alternate Method)

Obtain a five (5) gallon glass bottle and determine its volume by measuring the volume of water needed to fill (use of a 1000 ml graduated cylinder, obtainable from ientific supply houses, is convenient). Another approach is to weigh the empty bottle, fill it with water and weigh again. The difference between the two values is he weight of water. By multiplying the weight of water pounds by 0.455, you obtain the volume of the bottle liters. Empty the water out and allow the bottle to dry. Place a one-foot piece of plastic tubing in the flask to aid n mixing the vapors uniformly with the air. The volume such a bottle should be about 20 liters, which is 20,000 l. If the volume were 20,000 ml, then a 2 ml sample of a as placed in the bottle would be equivalent to 200 ml per 2 million ml or 100 ppm (V/V). Use of a gas tight syrge, readable in 0.01 ml, allows the preparation of mixres in the 1 - 2 ppm range, which are sufficient for the uantitative estimation of concentrations. A rubber stopper is loosely fitted to the top of the bottle and the eedle of the syringe placed inside the jug neck and the opper squeezed against the needle to decrease akage during sample introduction. Inject the sample into the bottle and withdraw the needle without removing the stopper. Put the stopper in tight and shake the ottle for a few minutes with sufficient vigor that the lastic tubing in the bottle moves around to ensure good mixture of the vapors with the air.

For liquid samples, use of the following equation will llow the calculation of the number of microliters of rganic liquid needed to be placed into the bottle to make 100 ppm (V/V) of vapor.

V1 equals V2 X Mw/244D

V1 - Volume of liquid in microliters needed to make an air mixture of 100 ppm (V/V)
V2 - Volume of bottle in liters
Mw - Molecular weight of substance
D - Density of substance

This procedure has the advantage that you can see when all of the organic liquid has vaporized and the volume can be determined readily.

For liquid samples, an alternate procedure involves the use of a diffusion dilution device such as that described by Desty, Geach and Goldup in "Gas Chromatography", R.P.W. Scott, ed., Academic Press, New York, 1961.

4.4 THEORY

Theoretical background and empirical data related to the Century Organic Vapor Analyzer is presented in 4.4.1 and 4.4.2.

4.4.1 HYDROCARBONS

In general, a hydrogen flame ionization detector is more sensitive for hydrocarbons than any other class of organic compounds. The response of the OVA varies from compound to compound, but gives excellent repeatable results with all types of hydrocarbons; i.e., saturated hydrocarbons (alkanes), unsaturated hydrocarbons (alkenes and alkynes) and aromatic hydrocarbons.

The typical relative response of various hydrocarbons to methane is as follows:

Compound	Relative Response (percent)
Methane	100 (reference)
Propane	64
N-butane	61
N-pentane	100
Ethylene	85
Acetylene	200
Benzene	150
Toluene	120
Ethane	90

4.4.2 OTHER ORGANIC COMPOUNDS

Compounds containing oxygen, such as alcohols, ethers, aldehydes, carbolic acid and esters give a somewhat lower response than that observed for hydrocarbons. This is particularly noticeable with those compounds having a high ratio of oxygen to carbon such as found in the lower members of each series which have only one, two or three carbons. With compounds containing higher numbers of carbons, the effect of the oxygen is diminished to such an extent that the response is similar to that of the corresponding hydrocarbons.

Nitrogen-containing compounds (i.e., amines, amides and nitriles) respond in a manner similar to that observed for oxygenated materials. Halogenated compounds also show a lower relative response as compared with hydrocarbons. Materials containing no hydrogen, such as carbon tetrachloride, give the lowest response; the presence of hydrogen in the compounds results in higher relative responses. Thus, $CHCl_3$ gives a much higher response than does CCl_4. As in the other cases, when the carbon to halogen ratio is 5:1 or greater, the response will be similar to that observed for simple hydrocarbons.

The typical relative response of various compounds to methane is as follows:

Methane	100 (calibration sample)
Ketones	
Acetone	60
Methyl ethyl ketone	80
Methyl isobutyl ketone	100
Alcohols	
Methyl alcohol	15
Ethyl	25
Isopropyl	65

Halogen compounds

Carbon tetrachloride	10
Chloroform	65
Trichloroethylene	70
Vinyl chloride	35

The OVA has negligible response to carbon monoxide and carbon dioxide which evidently, due to their structure, do not product appreciable ions in the detector flame. Thus, other organic materials may be analyzed in the presence of CO and CO_2.

SECTION 5

SAFETY CONSIDERATIONS

5.1 GENERAL

The Models OVA-108, OVA-128 and OVA-138 have been tested and certified by Factory Mutual Research Corporation (FM) as intrinsically safe for use in Class I, Division 1, Groups A, B, C & D hazardous atmospheres. Similar foreign certifications have been obtained, including BASEEFA and Cerchar approval for Group IIC, Temperature Class T4 on the Models OVA-108, OVA-128 and OVA-138, and equivalent approval from the Japanese Ministry of Labor for the Model OVA-128. Special restrictions must be strictly adhered to, to ensure the certification is not invalidated by actions of operating or service personnel.

All flame ionization hydrocarbon detectors are potentially hazardous since they burn hydrogen (H2) or H2 mixtures in the detector cell. Mixtures of H2 and air are flammable over a wide range of concentrations whether an inert gas such as nitrogen (N2) is present or not. Therefore, the recommended precautions and procedures should be followed for maximum safety. Safety considerations was a major factor in the design of the Organic Vapor Analyzer (OVA).

All connectors are of the permanent type as opposed to quick disconnect. To protect against external ignition of flammable gas mixtures, the flame detection chamber has porous metal flame arrestors on the sample input and the exhaust ports as well as on the H2 inlet connector. The standard battery pack and other circuits are internally current limited to an intrinsically safe level.

5.2 OPERATING, SERVICING AND MODIFYING

It is imperative that operation and service procedures described in this manual be carefully followed in order to maintain the intrinsic safety which is built into the OVA. No modification to the instrument is permissible. Therefore, component replacement must be accomplished with the same type parts.

5.3 ELECTRICAL PROTECTION

The 12V battery power supply circuit is current limited to an intrinsically safe level. Fuses are not utilized and all current limiting resistors and other components which are critical to the safety certification are encapsulated to prevent inadvertent replacement with components of the wrong value or specification. Under no circumstances should the encapsulation be removed.

5.4 FUEL SUPPLY & TANK

The OVA fuel tank has a volume of 75 to 85 cc which, when filled to the maximum rated pressure of 2300 PSIG, holds approximately 5/8 cubic foot of gas. The fuel used in the OVA is pure hydrogen which can be readily purchased in a highly pure form at nominal cost. The H2 tanks used in the instrument are made from stainless steel, proof-tested to 6,000 PSIG and 100% production tested to 4,000 PSIG.

5.5 H2 FLOW RESTRICTORS

Hydrogen gas gains heat when expanding and, therefore, should not be rapidly released from a high pressure tank to a low pressure environment. Flow restrictors are incorporated in the H2 refill fitting and H2 is restricted on the output side of the tank by the low flow rate control system. In addition, a special flow restrictor is incorporated in the FILL/BLEED valve of the hydrogen filling hose assembly. These precautions limit the flow rate of the H2 to prevent ignition due to self-heat from expansion.

5.6 DETECTOR CHAMBER

The OVA has a small flame ionization chamber cavity with sintered metal flame arrestors on both the input and output ports. The chamber is ruggedly constructed of teflon such that even if highly explosive mixtures of H2 and air are inadvertently created in the chamber and ignited, the chamber would NOT rupture.

5.7 H2 FILLING AND EMPTYING OPERATIONS

Precautions should be taken during H2 filling or H2 tank emptying operations to ensure that there are no sources of ignition in the immediate area. Since the instrument tank at 2300 PSIG holds only 5/8 cu. ft. of H2, the total quantity, if released to the atmosphere, would be quickly diluted to a non-flammable level. There is, however, the possibility of generating flammable mixtures in the immediate vicinity of the instrument during the filling or emptying operations if normal care is not exercised.

5.8 VENTING

The OVA case is vented to eliminate the possibility of trapping an explosive mixture of H2 and air inside the case.

SECTION 6

MAINTENANCE

GENERAL

This section describes the routine maintenance schedule recommended and provides procedures for trouble shooting malfunctions or failures in the instrument.

Appendix "A" to this manual contains the assembly drawings and associated parts list for the Side Pack Assembly and two major subassemblies; the Electronic Component Assembly and the Cylinder Assembly. These drawings and parts lists may be used for locating and identifying components. Also included in Appendix "A" is a schematic wiring diagram showing interconnecting wiring between major electronic assemblies and typical signal levels at selected points on the certified instruments. The enclosed drawings and parts lists are subject to change without notice and part replacement on any certified instrument should be verified to comply with the "no modifications permitted" requirement.

CAUTION

Maintenance personnel should be thoroughly familiar with instrument operation before performing maintenance. It is essential that all portions of this manual relating to safety of operation, servicing and maintenance, including Section 5, be thoroughly understood. There should be no potential igniters or flame in the area when filling, emptying or purging the hydrogen system and the instrument should be turned off.

Extreme care should be exercised to ensure that required parts replacement is accomplished with the same parts specified by Century. This is especially necessary on the Models OVA-108, OVA-128 and OVA-138 in order that their certification for use in hazardous atmospheres be maintained. No modifications are permitted. Disassemble instrument only in a non-hazardous atmosphere.

6.2 ROUTINE MAINTENANCE

Note that Figure 6-1 is a flow diagram of the basic gas handling system.

6.2.1 FILTERS

6.2.1.1 PRIMARY FILTER

This filter is located behind the sample inlet connector (Fitting Assembly) on the Side Pack Assembly and is removed for cleaning by using a thin wall socket to unscrew the Fitting Assembly. The filter cup, "O" ring and loading spring will then come out as shown in the Side Pack Assembly drawing in Appendix "A". The porous stainless filter cup can then be cleaned by blowing out or washing in a solvent. If a solvent is used, care should be taken to ensure that all solvent is removed by blowing out or heating the filter. Reassemble in reverse order ensuring that the "O" ring seal on the Fitting Assembly is intact.

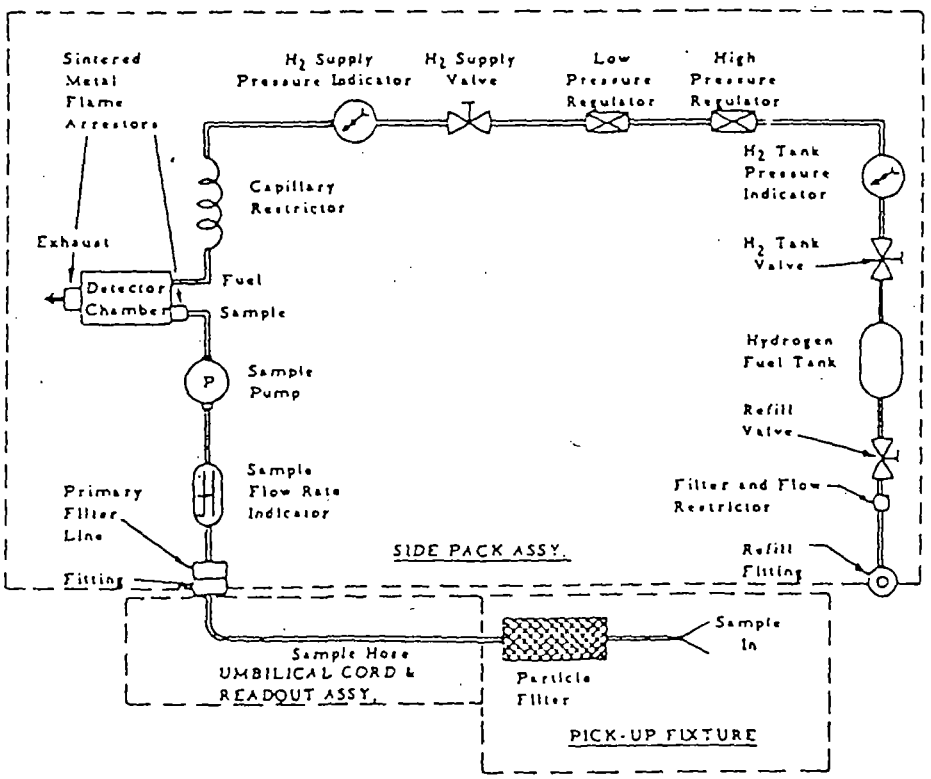


FIGURE 6-1. Flow Diagram - Gas Handling System

6.2.1.2 PARTICLE FILTERS

A particle filter is located in each pickup fixture. One of these filters must be in the sample line whenever the instrument is in use. The Models OVA-88 and OVA-138 use a disposable cellulose filter which should be changed as often as required. The Models OVA-98, OVA-108, OVA-118 and OVA-128 use a porous metal filter which can be replaced or cleaned using the cleaning procedure in paragraph 6.2.1.1.

6.2.1.3 MIXER/BURNER ASSEMBLY FILTER

Another porous metal particle filter is incorporated in the Mixer/Burner Assembly which screws into the Preamp Assembly. See Side Pack Assembly drawing. This filter is used as the sample mixer and inlet flame arrestor in the chamber. This filter should not become contaminated under normal conditions but can be cleaned or the assembly replaced if necessary.

Access to this filter for output surface cleaning is gained by simply unscrewing the exhaust port from the Preamp Assembly without removing the instrument from the case. The OVA-108, OVA-128 and OVA-138 instruments require removal of the safety cover prior to unscrewing the exhaust port. The Filter Assembly can now be seen on the side of the chamber (Preamp Assembly) and can be scrapped or cleaned with a small wire brush.

If filter replacement is required, install a new or factory rebuilt Mixer/Burner Assembly. In several OVA models, this requires removal of the Preamp Assembly.

6.2.1.4 EXHAUST FLAME ARRESTOR

A porous metal flame arrestor is located in the exhaust port of the detector chamber (Preamp Assembly). See Side Pack Assembly drawing. It acts as a particle filter on the chamber output and restricts foreign matter from entering the chamber. This filter may be cleaned, if required, by removing the exhaust port from the Preamp Assembly. The exhaust port is removed from the bottom of the case without case removal. Note that the filter is captive to the exhaust port on the Models OVA-108, OVA-128 and OVA-138. Clean the filter with a solvent or detergent but ensure that it is dry and any solvent completely baked out at 120°F before reinstalling.

6.2.2 PICKUP FIXTURES

The pickup fixtures should be periodically cleaned with an air hose and/or detergent water to eliminate foreign particle matter. If a solvent is used, the fixture should be subsequently cleaned with detergent and baked out at 120°F to eliminate any residual hydrocarbons from the solvent.

6.2.3 SEAL MAINTENANCE - CYLINDER ASSEMBLY

6.2.3.1 H2 TANK, H2 SUPPLY AND REFILL VALVES

After some time, the teflon washers under each valve packing nut can "cold flow" (move with pressure) and allow hydrogen to leak. Leakage can be determined by using Leak-Tec, Snoop or a soap solution around the valve stems. This leakage can usually be stopped by tightening the compression nut (adapter) as outlined below. See Side Pack Assembly and Cylinder Assembly drawings.

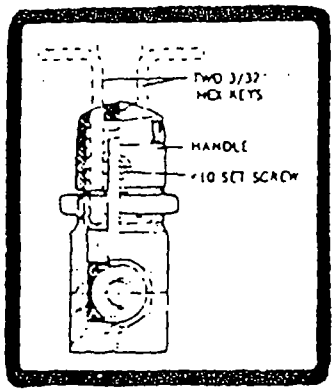
1) Remove instrument from the case by unlocking the four (4) 1/4 turn fasteners on the panel and removing the exhaust safety cover (if included), exhaust port and refill cap nut. Be sure refill valve is closed before removing refill cap nut.
2) Remove the valve knob screw and knob.
3) Loosen the panel nut with a 3/4" wrench.
4) The valve compression nut is located just under the panel. Tighten the compression nut—usually not more than 1/4 turn.

This compression is against soft material and only a small amount of force is necessary to sufficiently compress the teflon washers. If, after tightening, leakage still occurs, it would be advisable to replace the two teflon washers, as follows:

1) Drain hydrogen system slowly and to the extent necessary to work on the leaking valve(s). Observe safety precautions (see Section 5). There should be no potential igniters in the area.
2) Disconnect the capillary tube from the manifold at low pressure gauge (H2 Supply Pressure).
3) Remove all three (3) knob screws and knobs.
4) Remove the three (3) panel nuts and washers.
5) Carefully remove the tank assembly from the panel. NOTE: If OVA has GC Option installed, the GC valve assembly must be loosened or removed in order to remove the tank assembly from the panel.
6) Remove the compression nut on the valve that is not sealing properly. Remove the stem by unscrewing it from the valve body. Observe the sandwich of metal and teflon washers and note their order.
7) Visually check the Kel-F seat on the stem for cracks or foreign material. Wipe clean, if necessary, with a lint free cloth (no solvents or oils) and replace if damaged.
8) Remove the washers and replace the teflon washers (the factory procedure is a light wipe of hydrocarbon free silicone grease).
9) Replace the stem assembly in the valve body and tighten lightly.
10) Push the washers down into the compression area in the same order as noted upon removal. Replace the compression nut and tighten snugly.
11) Close the low pressure valve and fill the tank assembly. Check valves for leaks. Tighten again, if necessary, and reassemble the unit.

6.2.3.2 REFILLER VALVE PACKING ADJUSTMENT

Adjustment for the valve on the refiller can be made by loosening the set screw with a 3/32" hex key, so that the handle turns freely on the stem. Insert two (2) 3/32" hex keys through the holes provided in the handle and turn until they engage the holes in the packing adjuster. Then tighten the packing by turning the handle.



6.2.4 AIR SAMPLING SYSTEM MAINTENANCE

6.2.4.1 GENERAL

A potential problem associated with the OVA instrument is that leaks can develop in the air sample pumping system. These leaks can result in either dilution or loss of sample, causing low reading of vapor concentration and slow response time.

6.2.4.2 TESTING FOR LEAKS

The OVA's a re equipped with a flow gauge, which provides a method to check for air leaks. Assemble the pickup probe selected for use to the readout assembly and then position the sidepack vertically so the flow gauge may be observed. Cover the end of the pickup probe with your finger and observe that the ball in the flow gauge goes to the bottom, indicating no air flow (if ball has slight chatter while on bottom, this is acceptable). Cover the center of the chamber exhaust port with your thumb and again observe the ball going to the bottom. Another simple check is to expose the pickup probe to cigarette smoke or a light vapor (butane) and observe that the meter responds in approximately 1.5 - 2.0 seconds. It should be noted that slow meter response may also indicate a restriction in the air sampling system.

6.2.4.3 LEAK ISOLATION

Failure of the ball to go to the bottom when the inlet is blocked indicates a leak in the system between the probe and the pump inlet or the inlet check valve. To isolate the problem, remove parts, one at a time, and again block off the air inlet. Remove the pickup probe(s) and cover the air inlet at the Readout Assembly. If the ball goes to the bottom, check that the "readout to probe" seal washer is in place and replace the probes, holding them back against this seal while tightening the nut. Recheck, and if leakage is still present, it is probably in the probe (pickup fixture), which should be repaired or replaced.

If leakage is indicated as being past the readout handle when the connection to the sidepack is tight, disconnect the sample line at the fitting on the sidepack and cover this inlet with your finger. If the flow gauge ball goes to the bottom, the problem should be a leak in the umbilical cord/Readout Assembly, which should be investigated and repaired. There is also the possibility of a leaking check valve in the pump which would not show up on this test. If the leakage is not found in the umbilical cord, it is most likely in the pump check valve which should be repaired or replaced.

If the ball does not go to the bottom, the leak will be either in the flow gauge or it's connecting tubing. Visually check that the tubing is connected and if so, the flow gauge should be repaired or replaced. Check the "O" ring installation in the sample inlet connector (Fitting Assembly).

As an alternate approach, leaks on the inlet side of the pump can be detected by using alcohol on a "Q" Tip and lightly swabbing the connections one at a time or by directing organic vapor or smoke at the potential leakage points and observing the meter response or audible alarm.

Leaks (beyond the pump) are easier to locate, as any of the commercially available leak detection solutions can be used. Cover the exhaust port, which will place the exhaust system under pressure, and check each connection, one at a time. Replace the teflon tubing or retape the threaded connections with teflon joint tape. Check the igniter and Mixer/Burner Assembly where they screw into the detector, the high voltage terminal screw on the side of the Mixer/Burner and exhaust port itself. If after these checks, the flow gauge ball still will not go to the bottom with the exhaust blocked, the problem is likely a leaking exhaust check valve in the pump, which should be repaired or replaced.

6.2.5 CONTAMINATION CONTROL AND MAINTENANCE

6.2.5.1 GENERAL

On occasion, the background reading of the OVA may be relatively high under normal ambient conditions. Ambient background readings will vary somewhat depending on the geographical location where the instrument is being used. However, the background reading normally should be in the range of 3 to 5 ppm as methane. The acceptable background reading consists of 1 to 1-1/2 ppm of methane which is present in the normal air environment. In addition to the measurement of a normal methane background, there will normally be 2 to 4 ppm of equivalent methane background caused by acceptable levels of contamination in the hydrogen fuel and/or hydrogen fuel handling system resulting in a total equivalent methane reading of 3 to 5 ppm in clean air.

If the background reading goes above 5 ppm to 6 or 7 ppm, this is normally still acceptable since any measurement is additive to that background reading, i.e., 2 ppm on top of 5 or 2 ppm on top of 7 provides the same differential reading, however, the lower background is obviously desirable.

The background reading on the linear OVA's is zeroed out or nulled out—even though in reality the background still exists. The background reading on the

linear OVA's is measured by zeroing the meter with the flame out and noting the meter indication after the flame is on. However, on the logarithmic scaled OVA's the background reading is observed on the meter at all times. This is considered desirable since it assures the operator that the instrument is, in fact, operating properly. The background reading on the OVA's serves as a low level calibration point since it does represent the measurement of ambient levels of methane in the air, which are extremely stable and predictable any place in the world.

The cause for a high background reading is usually associated with contamination in the hydrogen fuel system. This will, of course, cause a background reading since this is the function of the basic detector "to measure contamination entering the detector chamber". In addition, contamination present in the hydrogen will many times leave a small unobservable deposit on the burner face which can continue to generate a background reading when the detector is in operation and the burner assembly is heated.

Another possible cause of contamination is the mixer/burner assembly when the contamination is trapped in the porous bronze sample filter. This is not a common problem and usually only happens when an unusually high level of contaminant is drawn into the assembly. Another possible cause of high background reading is contamination someplace in the air sample line to the detector. This is also uncommon but can be the source of the problem.

NOTE

OVA's that include the Chromatograph Option installed can also have an indication of high background related to saturation or contamination of the activated charcoal filter, which is in the line during chromatograph analysis, or of the column which is in the hydrogen line at all times.

6.2.5.2 ANALYSIS AND CORRECTION

Prior to analyzing the problem, the OVA should be checked for proper electronic operation. Check logarithmic instruments for proper high and low calibration points and for proper gas selector operation (see Section 4). On logarithmic OVA's, check Gas Selector by turning to 500 and observing the flame-out alarm comes on as the needle goes below 1 ppm. It should be ensured that the instrument is calibrated to methane as referenced.

If, after checking that the OVA is properly calibrated, the background is still higher than normal for ambient conditions, the following procedure should be followed to isolate the cause of the problem.

1) Let the OVA run for a period of time (15 to 30 minutes) and see if the background level decreases as a function of time. The background could go down and stay down as a result of clearing line contamination which is removable simply by the normal flow of air through the sample line.
2) Take a reading in a known, relatively clean air environment. Normally, outside air environment is clean enough to assess by comparison whether the background reading is internal to the instrument or is present in the laboratory, office or location where the instrument is being used.
3) If the OVA includes the Gas Chromatograph Option, depress the sample inject valve so that the activated charcoal is in the line and observe whether the background reading goes down and stays steady after the elution of the air peak. The reading should always go down or stay the same but never be a higher background reading with the sample valve depressed, since the charcoal filter will take out any trace elements of organic vapors in the air heavier than a C_2. If another activated charcoal filter is available, this may be attached to the end of the probe to scrub the air so that a clean air sample would be going to the detector. The external activated charcoal can be used on any instrument, with or without chromatograph, for providing a clean air sample to assess background level.
4) If background still stays up and cannot be reduced by any of the previous steps, the safety cover (if included) and the exhaust port on the detector chamber (Preamp Assembly) on the bottom of the case should be removed and the Mixer/Burner Assembly scraped or brushed with a small wire brush. (Reference paragraph 6.2.1.3.) This will remove any small quantities of contamination that are on the Mixer/Burner Assembly which could be the source of the background vapor. After cleaning the face of the burner and tube, replace the exhaust port and safety cover (if included) and reignite the OVA. If contamination on the burner face was the cause, the problem should be immediately resolved and the ambient background will drop to an acceptable level.
5) If the background is still present, place your finger over the inlet of the probe so as to reduce the flow of air to the detector chamber. Reduced flow rate may be observed either on the sample flow gauge or can normally be observed by the sound of the pump motor.
6) If the background drops immediately in response to the reduced flow of air to the chamber, this is an indication that the contamination is in the air sample line. Therefore, the various parts of the sample flow line such as pickup probes, umbilical cord to the instrument, etc., should be investigated by the process of elimination to see if the contamination can be isolated.
7) Serious contamination in the air sample line is very uncommon. However, if very large doses of very heavy compounds are sampled, there is a possibility of a residual contamination which would eventually clear itself out but may take a considerable period of time. A typical cause for the high background from the sample line is a

contaminated Mixer/Burner Assembly. See paragraph (4) above for cleaning procedure. If heavy contamination of the Mixer/Burner is still indicated by a high background, replace the Mixer/Burner Assembly. In several OVA models, this will require removal of the Preamp Assembly. The old Mixer/Burner Assembly should be either discarded or returned to the factory for cleaning and rebuilding.

8) In the event there is contamination in the pump or other internal parts of the sample flow lines which cannot be removed, the sample flow components would have to be disassembled and cleaned. This is normally a factory type operation. However, the components such as the pump can be replaced in the field along with any contaminated tubing in the sample lines.

9) High background readings on OVA's which include the Gas Chromatograph Option can be caused by other sources of contamination. If the charcoal in the charcoal filter mounted on the panel of the instrument is contaminated or saturated, contaminated air would be supplied to the detector and raise the ambient level background. To check for this, the charcoal filter cartridge can be removed from the panel and either a bypass tube put between the two connectors or the charcoal can be removed from the charcoal cartridge and the cartridge refilled with clean activated charcoal. This would determine if the charcoal was the source of the background reading. It is possible that an apparent high background reading could be due to contamination in the column that is on the instrument. This background could be caused by compounds that are slowly eluting from a column which has become contaminated. The easiest way to check for column contamination is to replace the column with a known clean column or a short empty piece of column tubing and see if the high background reading drops.

10) If all the above steps do not correct the high background problem, the cause will normally be contamination in the hydrogen fuel system.

Contamination in the hydrogen fuel system is usually the direct result of contamination in the hydrogen gas used or contamination introduced during the filling operation. Filling hose contamination can be caused by storing the hose in a contaminated area.

To remove contamination from the hydrogen fuel system, it should be purged with hydrogen. Effective purging of the hydrogen system is accomplished by disconnecting the capillary tube fitting which attaches on to the manifold block which has the low pressure gauge (H2 Supply Pressure Gauge and H2 Supply Valve). This disconnects the capillary tubing from the hydrogen line so that hydrogen may be purged at a reasonable rate from the tank assembly through the regulators, gauges and valves. After disconnecting the capillary, the hydrogen tank can be filled in the normal manner. The tank valve and H2 supply valve can then be opened which will bleed the hydrogen from the tank through the H2 fuel system purging out the contamination which is in vapor form. There is the possibility that contamination has been introduced into the hydrogen fuel system which is not readily purged out by the hydrogen gas but this is unlikely. After purging with clean hydrogen, approximately two or three times, the capillary tube should be reconnected and the background again checked. Five or ten minutes should be allowed before assessing the background reading, since contaminated hydrogen may still have been trapped in the capillary tube.

If another tank assembly in a clean instrument is available, the fuel system from the clean instrument can be connected to the contaminated instrument to absolutely verify that it is or is not in the hydrogen fuel supply system. The interconnection should be made to the capillary tube of the contaminated instrument.

6.2.6 FUSE REPLACEMENT

This paragraph applies only to the standard (non-certified) OVA's. There are two (2) overload fuses incorporated in the Battery Pack Assembly, one is a 3AG-1 AMP Slo-Blo in the power line to the pump and igniter and the other a 3AG-1/4 AMP in the power line to the electronics. Both fuses follow the current limiting resistors which provide primary short circuit protection. However, in the event of an excessive overload, the fuses will open and prevent overheating of the current limiting resistors. It should be pointed out that the 1 AMP Slo-Blo fuse will blow in approximately 8 to 12 seconds if the igniter switch is kept depressed. Normal ignition should take place in not more than 6 seconds. Therefore, do not depress igniter button for more than 6 seconds. If ignition does not occur, wait 1 to 2 minutes and try again. If the required 1 AMP Slo-Blo fuse cannot be readily obtained, replace temporarily with a 3 AMP-3 AG standard fuse.

6.3 TROUBLE SHOOTING

Table 6-1 presents a summary of recommended field trouble shooting procedures. If necessary, the instrument can be easily removed from the case by unlocking the four (4) 1/4 turn fasteners on the panel face and removing the refill cap and exhaust port. The battery pack is removed by taking out the four (4) screws on the panel and disconnecting the power connector at the battery pack.

6.4 FACTORY MAINTENANCE

To ensure continuous trouble-free operation, Century recommends a periodic factory maintenance, overhaul and recalibration. The recommended schedule is every six (6) to nine (9) months. This maintenance program includes replacement of plastic seals and parts as required, pump overhaul, motor check, new batteries, sample line cleaning, H2 leak check, recalibration, replacement of plastic hose as required, and detailed examination of the unit for any other required maintenance and repair.

The recommended procedure for maintenance and repair beyond the scope of this manual is to send the complete instrument or subassembly to the Century factory for repairs. The assemblies will be handled expeditiously for rapid turn-around.

8.5 FIELD MAINTENANCE

Although not recommended, where field maintenance beyond that described herein is considered essential, the assembly drawings, parts lists and schematics in Appendix "A" will be of assistance.

8.6 RECOMMENDED SPARES

Century does not recommend that spares be maintained for its instruments. However, if the instrument is to be used in a remote area or spares are desired for other reasons, the following list should be used as a guide.

RECOMMENDED SPARES

Item	Description	Part No.	Recommended Quantity					
			Standard			Approved		
			88	98	118	108	128	138
1	Igniter	510027-1	2	2	2			
2	Igniter	510461-1				2	2	2
3	Pump Valve	510067-3 (10/pkg.)	1	1	1	1	1	1
4	Pump Diaphragm (Buna-N)	510091-1	1					1
5	Pump Diaphragm (Teflon)	510063-1		1	1	1	1	
6	Cup, Filter (3/8 OD, SS)	510318-1 (5/pkg.)	1	1	1	1	1	1
7	Mixer/Burner Assy	510557-2	1					
8	Mixer/Burner Assy	510557-1		1	1			
9	Mixer/Burner Assy	510513-1				1	1	1
10	Wafer, Teflon, H_2 Valve	510160-1 (10/pkg.)	1	1	1	1	1	1
11	Washer, Brass, H_2 Valve	510160-2 (10/pkg.)	1	1	1	1	1	1
12	Exhaust Port Assy	510425-1	1	1	1			
13	Exhaust Port Assy	510530-1				1	1	1
14	Battery Pack Assy	510070-1	1	1	1			
15	Battery Pack Assy	510542-1				1	1	1
16	Sample Line Assy	510316-1		1	1	1	1	1
17	Particle Filters	510114-1	1					1
18	Particle Filters	510116-1		1	1	1	1	

NOTE: Unit quantity is each unless otherwise noted.

TABLE 6-1

TROUBLE	TROUBLE SHOOTING PROCEDURE	REMEDY
1) Low sample flow rate on flow indicator. Nominally 2 units on flow gauge. (See also 6 below and refer to paragraph 6.2.4)	a) Check primary filter in sidepack and particle filters in the pickup assembly.	Replace or clean filter if clogged. (See paragraph 6.2.1)
	b) Determine assembly containing restriction by process of elimination, i.e., remove probe, remove Readout Assembly, remove primary filter, etc.	Investigate the assembly containing this restriction to determine cause of blockage. Clean or replace as required.
	c) If the restriction is in the Side Pack Assembly, further isolate by disconnecting the sample flow tubing at various points, i.e., pump output, chamber input, etc. Note: The inherent restrictions due to length of sample line, flame arrestors, etc., must be taken into account when trouble shooting.	If in the detector chamber, remove and clean or replace porous metal flame arrestors. If pump is found to be the problem, remove and clean or replace.
2) H2 flame will not light. (See also 6 below)	a) Check sample flow rate (see 1 above).	If sample flow rate is low, follow procedure 1 above.
	b) Check igniter by removing the chamber exhaust port and observing the glow when the IGNITE Button is depressed.	If igniter does not light up, replace the plug. If igniter still does not light, check the battery and wiring
	c) Check for rated H2 Supply Pressure. (Listed on calibration plate on pump bracket.)	If low, remove battery pack and adjust to proper level by turning the allen wrench adjustment on the low pressure regulator cap.
	d) Check H2 flow rate by observing the PSI decrease in pressure on the H2 Tank Pressure gauge. The flow rate should be about 130 PSI decrease in pressure per hour. (Approximately 12 cc/min. at detector.) On instruments with GC Option, disconnect column and measure H2 flow rate with a bubble meter.	The normal cause for H2 flow restriction would be a blocked or partially blocked capillary tube. If flow rate is marginally low, attempt to compensate by increasing the H2 Supply Pressure by one-half or one PSI. If flow rate cannot be compensated for, replace capillary tubing.
	e) Check all H2 plumbing joints for leaks using soap bubble solution. Also, shut off all valves and note pressure decay on H2 tank gauge. It should be less than 350 PSIG per hour.	Repair leaking joint.
	f) Check to see if H2 supply system is frozen up by taking unit into a warm area.	If there is moisture in the H2 supply system and the unit must be operated in subfreezing temperatures, purge the H2 system with dry N2 and ensure the H2 gas used is dry.
	check battery level by connecting to charger	If in lead zone, battery may not have enough power to light flame (used with clean battery, mOVA)

	g) Remove exhaust port and check for contamination. (See Figure 6-2.)	If the chamber is dirty, clean with ethyl alcohol and dry by running pump for approximately 15 minutes. If H2 fuel jet is misaligned, ensure the porous metal flame arrestor is properly seated.
	h) Check spacing between collecting electrode and burner tip. Spacing should be 0.1 to 0.15 inches.	Adjust by screwing Mixer/Burner Assembly in or out. This spacing problem should only occur after reassembling a Mixer/Burner Assembly to a Preamp Assembly.
3) H2 flame lights but will not stay lighted	a) Follow procedures 2 (a), (c), (d), (e), (g) and (h) above. Also refer to 5 below.	
4) Flame-out alarm will not go on when H2 flame is out	a) Check instrument calibration setting and GAS SELECT control setting. Refer to paragraphs 2.3.1.2 and 2.3.2.	Readjust as required to proper setting. Note that on linear OVA's the flame-out alarm is actuated when the meter reading goes below zero. On logarithmic OVA's, the alarm is actuated when the signal level goes below 1 ppm methane or equivalent.
	b) Remove exhaust port and check for leakage current path in chamber (probably moisture or dirt in chamber).	Clean contamination and/or moisture from the chamber using a swab and alcohol, dry chamber by running pump for approximately 15 minutes.
	c) If above procedures do not resolve the problem, the probable cause is a malfunction in the preamp or power board assemblies.	Return preamp chamber or power board assembly to the factory for repair.
	d) Check volume control knob is turned up.	Adjust for desired volume.
5) False flame-out alarm. (Applies to linear OVA's)	a) Flame-out alarm is actuated on linear instruments when signal goes below electronic zero (eventhough flame is still on). This can be due to inaccurate initial setting, drift or a decrease in ambient concentration. Verify if this is the problem by zeroing meter with flame out and reigniting. (See paragraph 2.3.2)	When using the X1 range, adjust meter to 1 ppm rather than zero. See paragraph 2.3.2. Be sure instrument has been zeroed to "lowest expected ambient background level".
6) Slow response time, i.e., time to obtain response after sample is applied to input. (Refer to paragraph 6.2.4)	a) Check to ensure that probe is firmly seated on the rubber seal in the readout assembly.	Reseat by holding the probe firmly against the rubber seal and then lock in position with the knurled locking nut.
	b) Check sample flow rate per procedure 1 above.	See 1 above.

7) Slow recovery time, i.e., too long a time for the reading to get back to ambient after exposure to a high concentration of organic vapor.	a) This problem is normally caused by contamination in the sample input line, requiring pumping for a long period to get the system clean of vapors again. Charcoal in the lines would be the worst type of contamination. Isolate through the process of elimination. (See 1 (b)).	Clean or replace contaminated sample line or assembly as required.
	b) Check flame chamber for contamination.	Clean as required.
8) Ambient background reading in clean environment is too high. (Refer to paragraph 6.2.5)	a) An ambient background reading can be caused by hydrocarbons in the H2 fuel supply system. Place finger over sample probe tube restricting sample flow and if meter indication does not go down significantly the contamination is probably in the H2 fuel.	Use a higher grade of hydrocarbon free hydrogen. Check for contaminated fittings on filling hose assembly.
	b) An ambient background reading can be caused by a residue of sample, building up on the face of the sample inlet filter. If the test in 8 (a) above produces a large drop in reading, this is usually the cause.	Remove the exhaust port (it is not necessary to remove instrument from case), use small wire brush from the tool kit or a knife blade and lightly scrub surface of sample inlet filter.
	c) An ambient background reading can also be caused by hydrocarbon contamination in the sample input system. The most likely cause would be a contaminant absorbed or condensed in the sample line. Note: It should be emphasized that running the instrument tends to keep down the buildup of background vapors. Therefore, run the unit whenever possible and store it with the carrying case open in clean air.	Clean and/or replace the sample input lines. Normally the lines will clear up with sufficient running.
9) Pump will not run	a) Check 1 AMP Slo-Blo fuse on the battery pack cover. NOTE: Certified OVA's do not have fuses.	Replace fuse. IMPORTANT: Note that fuse is a Slo-Blo type. If fuse continues to blow when igniter switch is closed, check igniter for short circuit. If igniter is not the problem, there is a short in the wiring or pump motor. Return OVA to factory or authorized repair facility.
10) No power to electronics but pump runs	a) Check 1/4 AMP fuse on the battery pack cover. NOTE: Certified OVA's do not have fuses.	Replace fuse. If fuse continues to blow, there is a short in the electronics assembly. Return OVA to factory or authorized repair facility.
11) No power to pump or electronics.	a) Place battery on charger and see if power is then available. Recharge in a non-hazardous area only.	If power is available, battery pack is dead or open. Recharge battery pack. If still defective, replace battery pack. Reference paragraph 2.7.

APPENDIX I

DOCUMENT CONTROL AND THE EVIDENTIARY FILE SYSTEM

TABLE 1

DOCUMENT CLASSES AND STRUCTURE
FOR SUPERFUND EVIDENTIARY FILES

Document	File	Contents
File Index		Check out logs and list of active files
Contracts/ Proposals/Bids	A	Proposals, contracts, purchase orders, specifications - COPIES ONLY
Financial	B	Summary of invoice status; invoices correspondence re: accounts receivable; copy of budget and project task setup; COPIES ONLY
Correspondence	C	Various incoming and outgoing letters, memorandums, diary notes
		C1-In-house correspondence; diary notes and memos
		C2-Outgoing lettes/memos
		C3-Incoming correspondence
		C4-Correspondence logged
Work Plan Documents	D	Documents other than proposals; including Health and Safety plans, Sampling plans, QAPPs, permit plans; special instructions/outlines for conducting the project; Work Plans; WEI plans and specifications

QA File	E	QA Work Plan and budget; project history file; sample documentation records, etc. E1 Sample tags E2-Chain-of Custody Records E3-Receipt of Samples forms E4-Transfer of Samples forms
Field Data	F	Original field data/notebooks F1-Field boring logs F2-Well construction details F3-Geotechnical testing F4-Geophysical testing F5-Water Quality testing F6-Daily field logs F7-Baildown testing F8-Structural testing F9-Miscellaneous/Other
Laboratory Data	G	Laboratory test data, including original analytical logbooks, lab data, calculations, bench records, graphs, etc. for original data and quality control data G1-Analytical laboratory data G2-Geotechnical laboratory data G3-Materials testing laboratory data

		G4-Subcontracted laboratory data
Calculations	H	Calculations, quantity estimates, computer printouts of tabularized data
Photographs	I	Photographs, stereo pairs, site maps (published zoning, topography, geology, groundwater, bedrock, negatives)
Originals	J	Warzyn original reports or drafts
Warzyn Reports	K	Copies of the project report or previous pertinent WEI reports
Warzyn Drawings	L	Reference list of report drawings; copies or reduced copies of original drawings. Note: original or reduced mylars will be stored separately
Other Reports/Drawings	M	Non-Warzyn reports and drawings including literature, reference, etc.
Miscellaneous	N	Other file information which does not fit into other categories; file must be named
Checkprint	O	TEMPORARY FILE of checkprints, draft reports or other work in progress. File must be removed upon job completion.

DOCUMENT AUDIT CHECKLIST*

PROJECT NO. _____ DATE OF AUDIT _____

PROJECT LOCATION _____ SIGNATURE OF AUDITOR _____

FILE LOCATION _____

Yes__ No__ 1. Have individual files been assembled (field investigation, laboratory, other)?

Comments: _____

_____

_____

Yes__ No__ 2. Is each file inventoried?

Comments: _____

_____

_____

Yes__ No__ 3. Is there a list of accountable documents?

Comments: _____

_____

_____

Yes__ No__ 4. Are all accountable documents present or accounted for?

Comments: _____

_____

_____

* From NEIC Procedure Manual for the Evidence Audit of Enforcement Investigations by Contractor Evidence Audit Teams, EPA-300/9-81-003-R, April, 1984.

Yes__ No__ 5. Is a document numbering system used?

Comments:_____

_____

_____

Yes__ No__ 6. Has each document been assigned a document control number?

Comments:_____

_____

_____

Yes__ No__ 7. Are all documents listed on the inventory accounted for?

Comments:_____

_____

_____

Yes__ No__ 8. Are there any documents in the file which are not on the inventory?

Comments:_____

_____

_____

Yes__ No__ 9. Is the file stored in a secure area?

Comments:_____

_____

_____

Yes__ No__ 10. Are there any project documents which have been declared confidential?

Comments:_____

_____

_____

Yes__ No__ 11. Are confidential documents stored in a secure area separate from other project documents?

Comments: _____

_____

_____

Yes__ No__ 12. Is access to confidential files restricted?

Comments: _____

_____

_____

Yes__ No__ 13. Have confidential documents been marked or stamped "Confidential"?

Comments: _____

_____

_____

Yes__ No__ 14. Is confidential information inventoried?

Comments: _____

_____

_____

Yes__ No__ 15. Is confidential information numbered for document control?

Comments: _____

_____

_____

Yes__ No__ 16. Have any documents been claimed confidential under TSCA?

Comments: _____

_____

_____

[jap-800-64a]

APPENDIX J

INTERNAL CHAIN OF CUSTODY PROCEDURES FOR HAZELTON LABORATORIES AMERICA

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DEPARTMENT OPERATING PROCEDURE

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DATE: 2/11/87
REPLACES: 4/21/86

PROCEDURE IDENTIFICATION: EPA WA-82-A155 Hazardous Waste Analysis

PROCEDURE TITLE: Chain of Custody Procedures

AREA OF APPLICABILITY: Hazleton Laboratories America, Inc.
Environmental Analysis

PURPOSE:

Future legal proceedings may necessitate Hazleton Laboratories America, Inc. (HLA) to produce documentation that traces the custody of samples from receipt through completion of analysis. In lieu of this, it is necessary for HLA to guarantee the continuous custody of samples by either the sample custodian or the lab analyst.

PROCEDURE:

The following procedures for documentation of chain of custody for samples received under Contract WA-82-A155 will be followed in addition to or as an addendum to those previously stated under OP-DIV 7 and OP-PROJ 2.

1. All samples will be stored locked in refrigerators located on the third and fourth floors. A list of sample numbers, arranged by EPA case number, will be maintained by the sample custodian.

   1.1 All bottles received for extractable compounds (semivolatiles or pesticides) will be stored at 4°C in one of two double-door refrigerators located on 3 South in Room 301.

   1.2 All bottles received for volatile analysis will be stored at 4°C on 4 South in the Mass Spectrometry area, in the refrigerator designated for volatile samples only.

2. Only the designated sample custodian and supervisory personnel will have keys to the double-door refrigerators.

3. Samples will remain in the designated refrigerators until removed for sample preparation and/or analysis.

4. All transfers of samples into or out of the double door refrigerators will be documented on an internal chain of custody record (see attached). These records are maintained by the sample custodian.

5. Once a sample is removed from a refrigerator by the analyst, he/she is responsible for the custody of the sample. Each analyst must return samples to the double door refrigerator before the end of the working day. Samples are not allowed to sit on the bench over the evening.

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DATE: 2/11/87
REPLACES: 4/21/86

APPROVED BY: Mark A. Wirtz — DATE 2-11-87
Mark Wirtz
Environmental Analysis

David C. Hills — DATE 2-11-87
David Hills
Project Leader

REVIEWED BY: Debra Curley Arndt — DATE 2/11/87
Debra Curley Arndt
Manager, Quality Assurance Unit

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OP-PROJ. 1
ATTACHMENT

EPA WA-82-A155 HAZARDOUS WASTE ANALYSIS

Chain of Custody

Case No. _____

Storage Location _____
Storage Date _____

Laboratory Sample No.	Removed by	Date/Time Removed	Reason	Date/Time Returned

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PROJECT SPECIFIC DOCUMENTATION
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OP-PROJ. 1
ATTACHMENT

PROJECT IDENTIFICATION: EPA WA-82-A155 Hazardous Waste Analysis

PROCEDURE TITLE: Chain of Custody Procedures

DISTRIBUTION:

Name	Title	Department/Cost Center No.
David C. Hills	Section Supervisor	Environmental Analysis/6004
Mark Wirtz	Documentation Custodian/ Sample Custodian	Environmental Analysis/6004

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DATE: 2/11/87
REPLACES: 4/21/86

PROCEDURE IDENTIFICATION: EPA WA-82-A155 Hazardous Waste Analysis

PROCEDURE TITLE: Sample Receipt and Sample Logging Procedures

AREA OF APPLICABILITY: Hazleton Laboratories America, Inc.
Environmental Analysis

DISTRIBUTION:

See attached list.

PURPOSE:

These procedures are to be used in conjunction with the aforementioned project because of the nature of the samples and the special chain of custody procedures required.

SAFETY PRECAUTIONS:

All samples received under this contract should be considered hazardous and appropriate precautions should be taken when handling these samples. Upon initial receipt at Hazleton Laboratories America, Inc. (HLA) facilities, sample coolers should be inspected for any damage or leakage. Under no circumstances should any personnel other than the sample custodian or project leader open coolers. If damage or leakage is noted, stay clear of the coolers and notify the sample custodian or project leader immediately.

PROCEDURE:

1. The project leader will notify the sample custodian in writing of incoming samples.

2. When samples arrive at HLA, the shipping and receiving clerk or the receptionist will notify the sample custodian. The custodian will collect the samples and deliver them to a hood located on 3 South. The following procedures will be done by the sample custodian.

3. Examine the shipping container and record the following information in the project log book (one container per form).

   3.1 The presence/absence of custody seal on the shipping container.

   3.2 The condition of the custody seal (i.e., intact, broken).

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4. Open the shipping container in a well ventilated hood, remove the enclosed sample documents, and record the following information in the log book.

   4.1 The presence/absence of the chain of custody record(s).

   4.2 The presence/absence of Sample Management Office (SMO) forms (Traffic Reports, Chronicles).

   4.3 The presence/absence of airbills and/or bills of lading documenting shipment of the samples.

5. Remove the samples from the container and record the following information in the log book.

   5.1 Condition of samples (intact, broken, leaking, etc). Any broken and/or leaking samples should be carefully repacked, labeled as a Biohazard, and returned to the sponsor. The project leader should be notified and will contact the EPA project officer that the sample was received broken and returned.

   5.2 The presence/absence of sample tags.

   5.3 Sample tag numbers.

6. Compare the following documents to verify agreement of the information contained on them.

   6.1 Chain of custody records.

   6.2 Sample tags.

   6.3 SMO forms.

   6.4 Airbills or bills of lading.

   Document agreement and/or any discrepancies found. If discrepancies are found, contact the SMO for clarification and notify the appropriate laboratory personnel.

7. If there are no problems with the sample shipment, sign the chain of custody record in the "Received for lababoratory by:" box on the document. If problems are noted, sign for shipment and note problems in the "Remarks" box or reference other forms detailing the problems.

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8. Log-In the Samples.

   8.1 Figure 1 is an example of a type of form the sample custodian could use in order to log-in samples and to record the information previously described.

9. Send preprocessing request form to Sample Entry requesting that HLA numbers be assigned to the samples, and that they be logged onto the LIMS under the appropriate mnemonic for tracking and billing.

   9.1 The following LIMS mnemonics will be used for this contract:

   HGMS Hazardous Waste GCMS Analysis
   EPAP - Priority Pool Pesticides

   9.2 Upon receipt of sample HLA numbers, log these HLA numbers into the book.

10. Sample Storage.

   10.1 All bottles received for extractable compounds (semivolatiles or pesticides) will be stored at 4°C in one of two double-door refrigerators located on 3 South in Room 301.

   10.2 All bottles received for volatile analysis will be stored at 4°C on 4 South in the Mass Spectrometry area, in the refrigerator designated for volatile samples only. At the time of storage a storage blank will be prepared identified with the case number and date prepared. This blank will be analyzed with those samples stored on the designated date to monitor the potential for cross-contamination of samples during storage.

APPROVED BY: Mark A. Wirtz — DATE 2-11-87
Mark Wirtz
Environmental Analysis

David C. Hills — DATE 2-11-87
David Hills
Project Leader

REVIEWED BY: Debra Curley Arndt — DATE 2/11/87
Debra Curley Arndt
Manager, Quality Assurance Unit

(1459E)

DATE: _____

OP-PROJ. 2
ATTACHMENT

'MPLE CUSTODIAN SIGNATURE: _____

DOCUMENT CONTROL

'ECK THE APPROPRIATE RESPONSE

Custody Seal	present/absent intact/not intact
Chain-of-Custody	present/absent
Sample Tags	present/absent
Sample Tag Numbers	listed/not listed on chain-of-custody
SMO Forms	present/absent

CASE NUMBER _____

AIRBILL NUMBER _____

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ATE ECEIVED	TIME RECEIVED	CHAIN-OF-CUSTODY RECORD NUMBER	SMO SAMPLE NUMBERS	CORRESPONDING SAMPLE TAG NUMBERS	CORRESPONDING ASSIGNED LAB NUMBERS	DOES INFORMATION ON CUSTODY RECORDS, TRAFFIC REPORTS, AND SAMPLE TAGS AGREE?	REMARKS CONDITION OF SAMPLE

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OP-PROJ. 2
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PROJECT SPECIFIC SOP DISTRIBUTION

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PROJECT IDENTIFICATION: EPA WA-82-A155 Hazardous Waste Analysis

PROCEDURE TITLE: Sample Receipt and Sample Logging Procedures

DISTRIBUTION:

Name	Title	Department/Cost Center No.
David C. Hills	Project Leader	Environmental Analysis/6004
William Hamilton	Manager	Facility Services/6080
Paul Jacoby	Section Supervisor	Shipping and Receiving/6075
Judy Santos	Section Supervisor	Sample Entry/6099
Diane Loram	Manager	General Services/6072 (Building Receptionist)
Mark Wirtz	Documentation Custodian/ Sample Custodian	Environmental Analysis/6004

DEPARTMENT OPERATING PROCEDURE

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PROJECT IDENTIFICATION: EPA WA-82-A155 Hazardous Waste Analysis

PROCEDURE TITLE: Duties and Responsibilities of the Documentation Custodian and Procedures for Data Assembly and Filing

AREA OF APPLICABILITY: Hazleton Laboratories America, Inc. Environmental Analysis

DISTRIBUTION:

See attached list.

PURPOSE:

To specify the duties and procedures of the documentation custodian for the above-mentioned contract.

PROCEDURE:

1. The documentation custodian will organize and assemble all documents relating to each EPA case.

2. This procedure will ensure that all documents to be submitted to EPA are compiled in one location, preferably in single case files arranged by SMO sample number.

   2.1 Prepare case file folders as follows:.

      2.1.1 Assign one folder to each case according to SMO case number.

      2.1.2 Place all documents, sample tags, SMO forms, and laboratory-generated data, pertaining to one case in the assigned folder.

      2.1.3 Arrange all documents by type within the case folders, i.e., all sample tags together, all Traffic Reports together, all hardcopy Mass Spectra together, etc.

      2.1.4 File these document case files in one location in a secure area.

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3. Document Numbering and Inventory Procedure.

3.1 Assignment of Accountable Numbers to laboratory-generated data.

3.1.1 Inventory each document of a case and assign it a serialized number (an identifier) associating it with a particular case. For example:

SMO case #	-	serialized document folder
5081		01

3.1.2 Inventory and number all documents pertaining to each case including the following:

3.1.2.1 Sample traffic records, weekly reports.

3.1.2.2 Custody records, sample tags, airbills, internal custody records.

3.1.2.3 Laboratory log books, personal log books, instrument log books, benchsheets.

3.1.2.4 Laboratory data (sorted by sample), calibration and quality control results.

3.1.2.5 Data summaries and reports.

3.1.2.6 All other documents, forms, or records referencing the samples.

3.2 Preparation of a Document Inventory.

3.2.1 Prepare a document inventory list to provide a record of all documents and their corresponding document numbers that are included in the completed case file.

3.2.2 If documents for a case are sent to an EPA Region for enforcement action or other action, the laboratory will retain a copy of the document inventory list for that case.

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DATE: 4/21/86
REPLACES: 1/3/83

APPROVED BY: Mark A. Wirtz
Mark Wirtz
Environmental Analysis
DATE 4-17-86

David C. Hills
David Hills
Project Leader
DATE 4-17-86

REVIEWED BY: Debra Curley Arndt
Debra Curley Arndt
Manager, Quality Assurance Unit
DATE 4/21/86

(0725E)

OP-PROJ. 3
ATTACHMENT

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DOCUMENT INVENTORY LIST

Document Control Number		Number of Pages
	File Inventory	
	Sample Tags	
	Sample Tracking Documents	
	EPA Chain of Custody	
	Airbills	
	Organic Traffic Reports	
	Extraction Worksheets/Screens	
	Copies of Analyst's Notebook Pages	
	Identification/Quantitation Worksheets	
	Copies of GC and GC-MS Operation Logs	
	Copies of Standard Preparation Log	
	Other Correspondence/Memos	
	QC Summary Package	
	Data Summary Package	
	Sample Data Package	
	Raw QC Data Package	
	Standard Package	
	Pesticide Raw Data	

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PROJECT IDENTIFICATION: EPA WA-82-A155 Hazardous Waste Analysis

PROCEDURE TITLE: Duties and Responsibilities of the Documentation Custodian and Procedures for Data Assembly and Filing

DISTRIBUTION:

Name	Title	Department/Cost Center No.
David Hills	Section Supervisor	Environmental Analysis/6004
Mark Wirtz	Documentation Custodian/ Sample Custodian	Environmental Analysis/6004

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DEPARTMENT OPERATING PROCEDURE

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PROJECT IDENTIFICATION: EPA WA-82-A155 Hazardous Waste Analysis

PROCEDURE TITLE: Duties and Responsibilities of the Sample Custodian

AREA OF APPLICABILITY: Hazleton Laboratories America, Inc.
Environmental Analysis

DISTRIBUTION:

See attached list.

PURPOSE:

To specify the duties of the sample custodian for the above-mentioned contract.

PROCEDURE:

Duties and responsibilities include:

1. Receiving samples (OP-PROJ 2).

2. Inspecting sample shipping containers for presence/absence and condition of:

   2.1 Custody seals, locks, "evidence tape", etc.

   2.2 Container breakage and/or container integrity.

3. Recording condition of both shipping containers and sample containers (bottles, jars, cans, etc.) in log books or on appropriate forms.

4. Signing appropriate documents shipped with samples (i.e., chain of custody record(s), SMO Traffic Reports, etc).

5. Verifying and recording agreement or non-agreement of information on sample documents (i.e., sample tags, chain of custody records, Traffic Reports, airbills, etc.) in log books or on appropriate forms. If there is non-agreement, record the problems, contact the SMO for direction, and notify appropriate laboratory personnel.

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6. Initiating sample analysis procedures on appropriate laboratory documents or according to laboratory standard operating procedures including establishing case and sample files and inventory sheets.

7. Labeling samples with HLA sample numbers.

8. Securely storing samples, sample extracts, and spent samples.

9. Controlling access to stored samples and assuring that HLA standard operating procedures are followed when samples are removed from and returned to storage (see OP-PROJ 1).

10. Assuring that sample tags are removed from sample containers and are given to the laboratory personnel for inclusion in the sample case file. Missing tags are to be accounted for by putting a written memo into the sample case file. Information from the tags should be included in the memo, if available.

11. Monitoring storage conditions for proper sample preservation such as, refrigeration temperature and prevention of cross-contamination.

12. Returning shipping containers to the proper sampling teams.

APPROVED BY: Mark S Wirtz — DATE 4/17/86
Mark Wirtz
Environmental Analysis

David C. Hills — DATE 4-17-86
David Hills
Project Leader

REVIEWED BY: Debra Curley Arndt — DATE 4/21/86
Debra Curley Arndt
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(0726E)

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PROJECT SPECIFIC SOP DISTRIBUTION

PROJECT IDENTIFICATION: EPA WA-82-A155 Hazardous Waste Analysis

PROCEDURE TITLE: Duties and Responsibilities of the Sample Custodian

DISTRIBUTION:

Name	Title	Department/Cost Center No.
David Hills	Section Supervisor	Environmental Analysis/6004
Mark Wirtz	Documentation Custodian/ Sample Custodian	Environmental Analysis/6004

APPENDIX K

CALIBRATION AND MAINTENANCE OF GPK GAS METER

OPERATING INSTRUCTIONS
Model GPK or GK
COMBINED OXYGEN/COMBUSTIBLES INDICATOR

INSTRUCTIONS 23-9081
OPERATION AND MAINTENANCE
J-W MODEL GPK AND GK OXYGEN/
COMBUSTIBLE GAS INDICATOR

7.0 CALIBRATION (COMBUSTIBLES SECTION)

The standard calibration using methane has been selected so that most commonly encountered gases and vapors as listed below and the more volatile lacquer and paint thinners, all indicate quite accurately or within reasonable error on the side of safety.

Gases	Vapors	
Natural Gas	Pentane	Benzene
Methane	Hexane	Ethyl Ether
Ethane	Heptane	Acetone
Propane	Methyl Alcohol	Ethyl Acetate
Butane	Ethyl Alcohol	
Carbon Monoxide		
Acetylene		

7.1 Checking Combustibles Calibration Using Known Gas Sample (See Figure 12)

It is often necessary, and even mandatory, to periodically check the instrument against a known, standard blend of calibration gas.

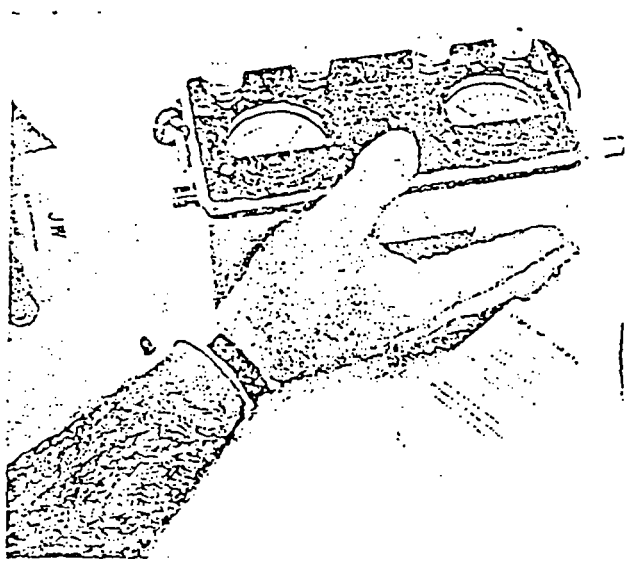


Figure 12 [illegible]

The J-W 550-075 Gas Indicator Test Kit provides a convenient method for testing the instrument's response to a known gas concentration. Methane is used as a calibration gas because indicator response to methane is more critical than response to most other gases. If the indicator has normal response to methane it will respond normally to most other combustible gases and vapors. Contained in the Kit are gas-filled ampoules and a plastic squeeze bottle which will produce a known 1.1% by volume methane/air mixture, when one ampoule (brown color coded end) is shattered in the bottle. Use the following procedure to calibrate the instrument.

(a) Remove the screw spout and squeeze plastic bottle several times to purge residual gas from previous test.

(b) Drop one glass ampoule into the plastic squeeze bottle and replace the screw spout. Make certain that red end cap is firmly in place.

(c) Shake the bottle until the ampoule is shattered by the breakers in the bottle. With the instrument in normal operation but without sample probe and hose attached, remove the red end cap, grasp the bottle firmly in the left hand and force the nozzle into the sample inlet fitting on the left side of the instrument. Inject gas sample while keeping pressure on the bottle.

Do not depend upon the pump or use of the aspirator bulb to draw sample through the instrument as this will result in leakage and unintentional dilution.

(d) Observe that the combustible meter pointer deflects upscale. Record the maximum meter reading indicated. An acceptable reading is approximately .25 L.E.L. on the combustible meter scale. .20 L.E.L. or less is unacceptable and is cause for recalibration.

NOTE: If low reading is obtained the first time, repeat the test to insure that no dilution occurred.

(e) Refer to Figure 13a for location of the calibration adjustment potentiometer, which is accessible through the small hole in back of the case. Use a small screwdriver to turn the slotted shaft *clockwise* to *increase* reading. This is a 25 turn potentiometer, so several turns may be required to bring the meter reading to .25 L.E.L. while simultaneously squeezing the plastic bottle. After readjusting the calibration potentiometer, repeat 7.1 (c) again as a final check.

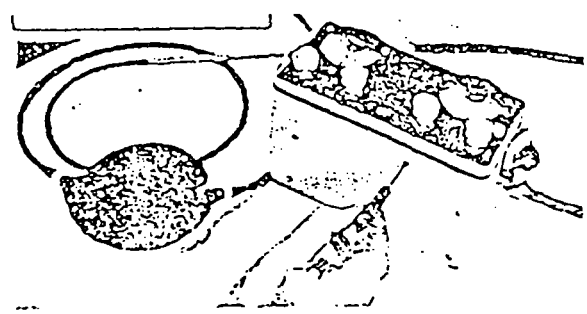


Figure 13a Adjusting Calibration Potentiometer

7.3 Testing Oxygen Cell for Calibration and Sensitivity

Operation of the instrument is normal if the meter can be set to read 21% on atmospheric air. A convenient test to prove response is to set the calibration to 21% and then blow slowly into the indicator inlet. As the lungs become exhausted the readings will go lower, a reduction to 15% being normal. With effort, the reading can be reduced as low as 10%.

To check performance near 0% oxygen, admit a small steady stream of oxygen free gas to inlet, such as nitrogen or natural gas. A cell in good condition will give a zero reading. A reading of 1% or more indicates need for reactivation.

8.0 MAINTENANCE SCHEDULE FOR MODELS GK AND GPK

DAILY:

The instrument should be checked for response before each day's operation as follows:

1. Check battery voltage reserve by observing whether voltage can be adjusted to at least 0.7 on the combustibles scale; then reset to green index arrow.
2. Check oxygen cell on fresh air and observe whether meter can be set to 21% O_2.
3. Check combustibles response by placing a few drops of gasoline or lighter fluid on a cloth, and proceeding as in Section 5.1 Step (e). Observe that combustibles pointer deflects upscale (if a slight explosion is heard, no harm will be done). Avoid excessive use of fluid as it will be difficult to clear the instrument.
4. Test leak tightness of sample inlet system by closing off the inlet fitting with finger and listen for pump slowdown to occur (GPK). With Model GK, check for internal leaks by squeezing the aspirator bulb, placing the finger over the inlet fitting, and releasing the bulb. If the bulb springs back quickly, an internal leak is present that should be corrected before using the instrument.
5. Replace cotton filter in probe chamber if working in an extremely dirty environment.

WEEKLY: Test instrument response to a known concentration of methane in air as outlined in Section 7.1.

MONTHLY (or as required):
Check combustibles reaction chamber for accumulations of dirt or foreign material that may restrict free movement of gas sample.

EVERY SIX MONTHS (or as required):
Maintain Oxygen Cell as outlined in Section 8.1.1 Step (a) through (e).

8.1 Oxygen Cell-Maintenance (Refer to Figures 14 and 15)

The 514-010 Oxygen Cell requires periodic maintenance and reactivation.

The 514-011 Reactivation Kit is supplied for this purpose. There are two levels of cell maintenance, which are described below.

Both operations can be carried out with one kit, as an adequate supply of electrolyte solution (KCl) is provided to fill the cell at least twice.

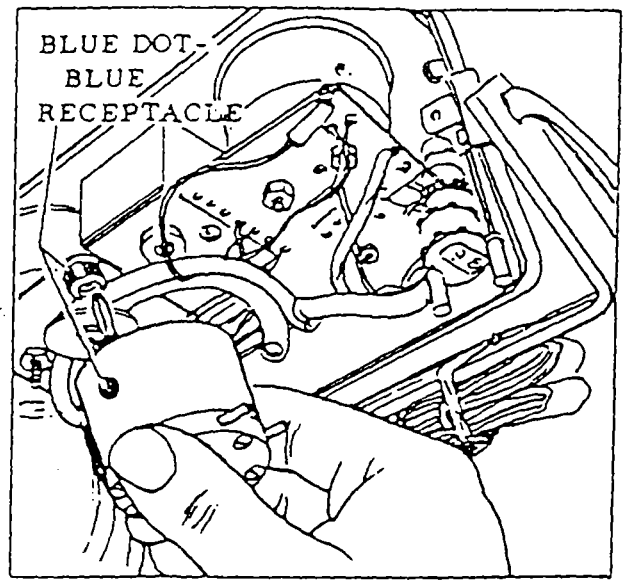


Figure 14: Correct method of connecting Oxygen Cell (note position of blue dot).

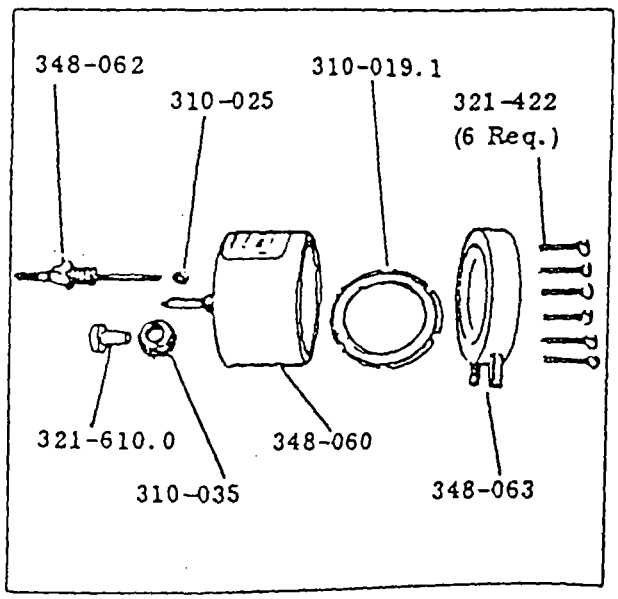


Figure 15. Parts identification for 514-010 Oxygen Cell.

8.1.1 Maintenance

The Oxygen Cell will usually operate up to 6 months without attention, but occasionally within this period, cell output may drop appreciably or change suddenly with sampling or sudden shock. To correct this condition, proceed with the following:

(a) Remove top panel from instrument case by loosening the two captive hold-down screws.

Unplug Oxygen Cell from the printed Circuit Board and disconnect the plastic tubing from the cell inlet and outlet nipples.

(b) Remove the nylon screw and seal ring on the electrical plug side of the cell. Refer to Figure 15 and unscrew the zinc electrode (banana plug nearest the blue dot on the side of cell) and remove it together with its O-Ring seal.

(c) Drain all the solution from the cell and completely fill with fresh KCl solution through either opening.

(d) Replace O-Ring on the zinc electrode, screw the electrode into the cell and tighten, using a small wrench. Install and retighten nylon screw with seal.

(e) Allow a few minutes for the cell to stabilize before attempting to make a reading.

NOTE: DO NOT WASH OR WIPE ELECTRODE AT ANY TIME.

8.1.2 Reactivation of Oxygen Cell (Refer to Figures 15, 16, 17)

In the event oxygen cell fails to function properly after changing solution as outlined in Section 8.1.1 or if it has been six months since solution was last changed, the cell may require reactivation. Reactivation Kit 514-011 is all that is required to completely reactivate the oxygen cell. The Kit contains a cap gasket with Teflon membrane, zinc electrode with O-ring, nylon screw with seal, KCl solution, nylon pad and brush.

To reactivate the cell, proceed as follows:

1. Remove nylon screw and seal and unscrew and remove zinc electrode and O-ring. Discard the zinc electrode, the screw, the O-ring and the seal.
2. Drain solution from cell.
3. Remove cap and gasket with membrane by removing the six screws which hold the cap in place. Discard the gasket with membrane.
4. Wash the cell thoroughly with cold, clean water. Use the brush to remove any white substance that may remain on the gold electrode. DO NOT USE ANY SOAP OR DETERGENT. If the white substance cannot be removed from sive nylon pad can be used to remove it, but the gold electrode should be handled very carefully and only slight pressure applied in cleaning with the nylon pad. Wash again with brush and water.
5. Put one drop of KCl solution on top of the gold electrode and put new gasket with membrane in place. The side of the gasket with the Teflon membrane should face the gold electrode.
6. Replace the cap, observing the direction of the sampling nipples. Nipples should point away from the label on the cell body. Tighten all screws until the cap shoulder is flush with the cell body.

The cell is now dry charged and can be stored as long as desirable.

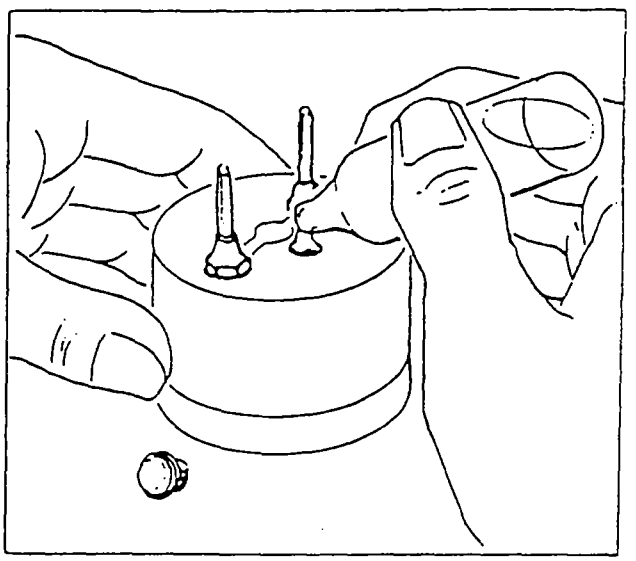
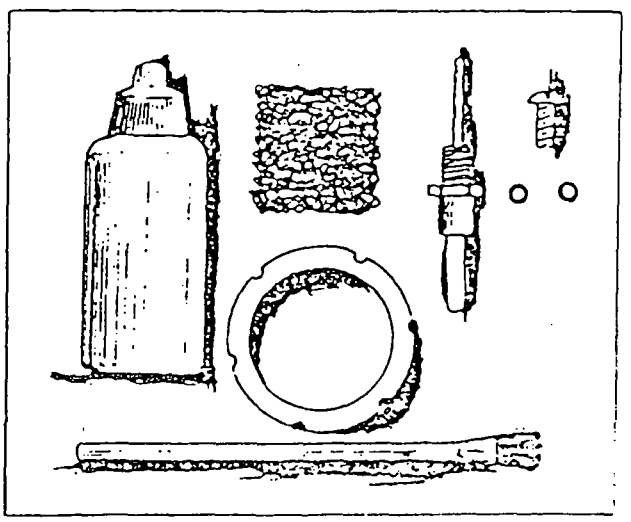


Figure 16: Activating cell with electrolyte (KCl solution)



To activate the cell:

1. Fill the cell with KCl solution, through either of the openings for the nylon screw or for the zinc electrode.
2. Check to see if the O-ring is still in the zinc electrode opening; if it is, remove it.
3. Be sure the new O-ring is in place on the zinc electrode, screw zinc electrode into cell and tighten with a small wrench.
4. Plug fill hole with nylon screw and new seal ring (310-035). The cell is now fully activated.

8.2 Oxygen Cell Contamination by Foreign Liquids

If any liquid has been accidently introduced into the sampling line and thus into the sampling chamber of the cell, it will be necessary to flush the system out with distilled water as soon as possible. To do this, use the following procedure:

(a) Disconnect the cell completely, remove, and pour distilled water into one sampling nipple until it comes out of the other. Drain water out and repeat this procedure several times.

(b) Insert the cell into the P.C. Board, observing plug color coding. Reconnect sample tubing, one to the inlet and the other directly to sample pump or aspirator bulb (bypass the combustibles reaction chamber).

(c) Turn "ON" the pump (Model GPK) and allow 5 minutes drying time for samoling chamber. For Model GK, stroke aspirator oulb about 50 times to insure cell chamber is .hroughly dried. The cell should now register normal output and is ready for use.

(d) Reconnect sample tubing so that outlet of O_2 cell goes to reaction chamber, and outlet of reaction chamber goes to pump inlet (or aspirator bulb).

8.3 Maintenance of the Combustibles Section

Filaments and Flame Arrestor (Refer to Figure 18)

There are two separate filament units: (1) the active filament, which is installed in the flame arrestor, and is the unit that actually comes in contact with the gas being tested; and (2) the reference filament that helps balance the electrical circuit.

The reference filament should rarely require replacement inasmuch as it operates at a very low voltage and never comes in contact with the gas. Replacement may be necessary if the indicator has been dropped or severly damaged, or if the instrument has been in frequent use over many years.

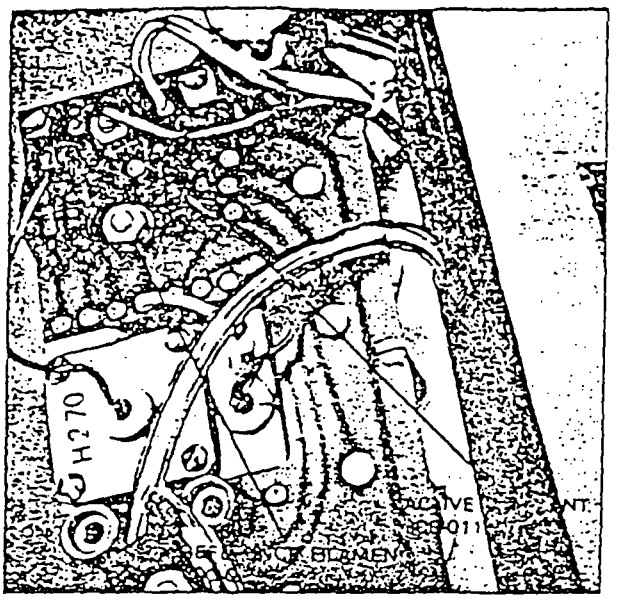


Figure 18: Active and reference filament locations.

The active filament should experience long life in ordinary service, probably on the order of a year or more, depending on frequency of use. The end of the useful life of the active filament is reached when it is no longer possible to bring the hand of the meter to "zero" with the zero adjustment. Another sign of trouble in the filament unit is when the meter pointer flies violently upscale with the instrument "ON," and zero adjustment is impossible. This usually means the active filament is burned out and must be replaced.

If the GK or GPK has been in use for a considerable period of time, or in moist or dusty conditions, it is frequently desirable to replace the filament flame arrestor assembly in combination. This is done by unplugging the O_2 cell, removing the four screws holding the brass plate to the underneath of the panel, and removing the filament lead from the subpanel terminal. When putting in a new filament flame arrestor assembly, make certain that the gasket is in place and compressed evenly by four screws.

When replacing the filament only, and reusing the flame arrestor, first remove and inspect the flame arrestor, checking for dust, corrosion or other damage. Replace gasket if it has deteriorated. Install new filament in place of old one, screwing it into the flame arrestor plate to compress the O-ring gasket as tightly as possible using the thumb and finger. When inserting filament be very careful not to touch or distort the platinum coil.

To replace the reference filament, first unsolder the black wire at subpanel, and unplug the O_2 cell. Then unscrew the knurled reference filament base from its cavity, using a pair of pliers. Install the new filament in the same position, tightening with pliers, and solder wire to subpanel.

NOTE: After replacement of either the active or reference filaments, perform the OPERATIONAL CHECK as outlined in Section 5.1, Steps (a) through (e).

Part numbers for filaments are:

800-007—Active Filament Flame Arrestor Assembly
800-011—Active Filament only (red wire)
800-022—Reference Filament only (black wire)
310-017—Flame Arrestor Gasket only

8.4 Battery Replacement and Charger Check (Refer to Figures 19, 20)

The most frequent form of maintenance will involve recharging the batteries as outlined in Section 5.3 and occasional burnishing of the silver contact buttons on the Printed Circuit Board with fine sandpaper (No. 400 or equivalent). The batteries can be recharged hundreds of times to render many years of useful service. Usually, the most probable cause of "apparent" battery failure can be traced to charger malfunction or contact problems. The batteries can only be charged with the instrument panel firmly in place. With the panel removed, the batteries can be inspected for deterioration by removing them from the storage compartment. When replacing batteries, be certain to reinstall them in the positions indicated on the side of the battery compartment.

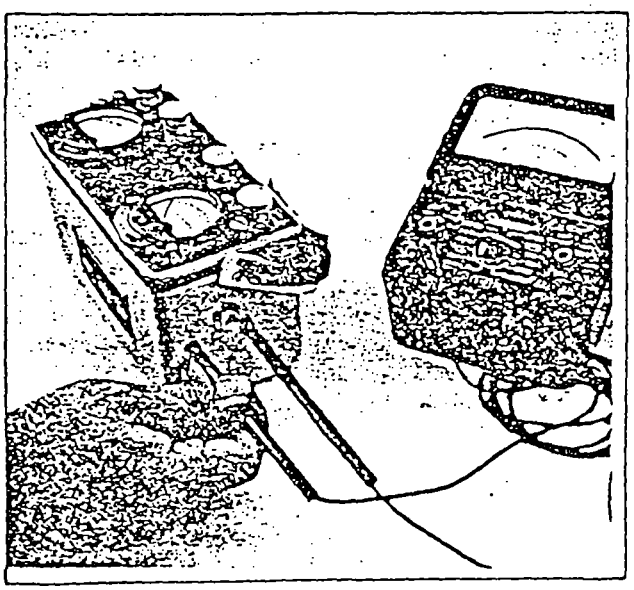


Figure 19: Checking power circuit for proper voltage (Section 8.4, Steps a and b)

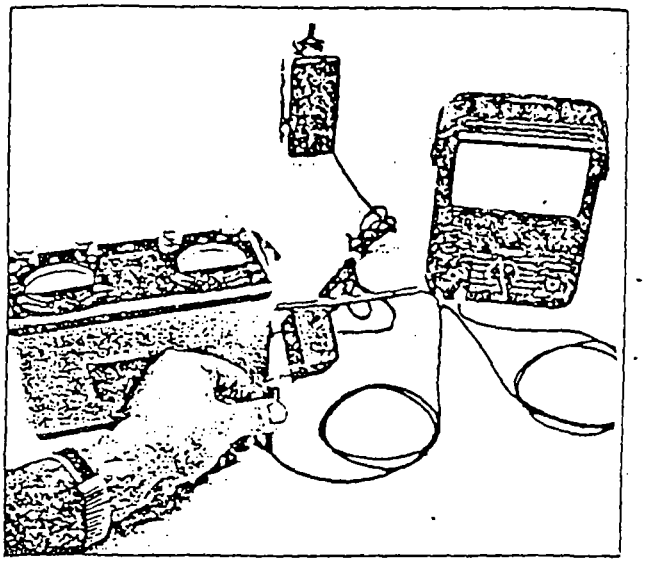


Figure 20: Measuring charge rate (Section 8.4, Step d).

NOTE: OBSERVE CORRECT POLARITY—INCORRECT BATTERY INSTALLATION CAN RESULT IN DAMAGE TO THE BATTERIES OR TO THE INSTRUMENT ITSELF. To insure that batteries are being recharged and that the Charger is functioning properly, perform the following check:

(a) Obtain a Multimeter and place the range selector on the 10 volt scale. Connect the meter test probes across the instrument charging jacks as illustrated in Figure 19. With the instrument FUNCTION CONTROL in the "OFF" position, the Multimeter should indicate 5 volts.

(b) Turn the FUNCTION CONTROL switch to the "ON" position and observe that battery voltage drops to 2.5 to 2.6 volts, then remove the meter probes. NOTE: Failure to obtain 2.5 volts indicates depleted batteries, open contact with subpanel buttons or open electrical connection. Correct malfunction before proceeding with the next step.

(c) Plug Charger line cord into 115 VAC outlet. Connect meter probes across charger pins and check output for approximately 5.5 volts (normal unloaded voltage).

(d) Now refer to Figure 20 and connect the Charger as shown with only the negative pin (—) connected to the black (—) charging jack. Place the Multimeter range selector to the 500 ma scale.

Connect the (+ red) positive meter probe to the remaining exposed pin on the Charger and the black (—) Multimeter probe to the red (+) charging jack of the GPK (GK). With Charger

connected to 115 VAC. Multimeter should indicate a charge rate of 120 to 150 ma (depending on battery state, line voltage, etc.) with the FUNCTION SWITCH in the "OFF" position. If Multimeter indicates "zero" ma, refer to Troubleshooting Section 8.9, Step 6.

(e) Now turn on the FUNCTION SWITCH to the "ON" position. Multimeter should indicate approximately 250 ma. (Never attempt to charge the batteries with the switch "ON," because the power consumption is greater than the Charger delivery rate.) If Multimeter indicates 300 ma or more, refer to Troubleshooting Section 8.9, Step 6.

NOTE: Failure to attain the above readings indicates a faulty Charger or Pump motor, open contact with subpanel buttons, or open electrical connection. If the correct indications are obtained, the circuit is normal and the batteries simply require recharging.

8.5 Testing Sample Flow Lines (Refer to Figure 17)

When installing the instrument panel in the bottom housing, take care not to pinch or obstruct the sample tubing. Always make certain that the sample tubing is placed in the cavity beside the battery compartment and arranged to prevent sharp bends or pinching when the panel is secured. For both Models GK and GPK, normal flow rate is approximately 2.5 liters per min. and response time to a combustible gas is approximately 5 seconds when short probe and 30" hose is used. Leaks or restrictions in the flow system will of course increase the response time.

A quick and simple check to determine the tightness of the sample system is to obstruct the flow at the probe tip or inlet fitting of the indicator. In the Model GPK the pump should slow or stop. If it does not, a leak in the pump or sample system is indicated. In the Model GK the aspirator bulb should be squeezed, released, and remain compressed for about 20 to 30 seconds. If the pump continues to operate normally or the bulb immediately springs back to its original form a leak exists which must be corrected before attempting to use the instrument.

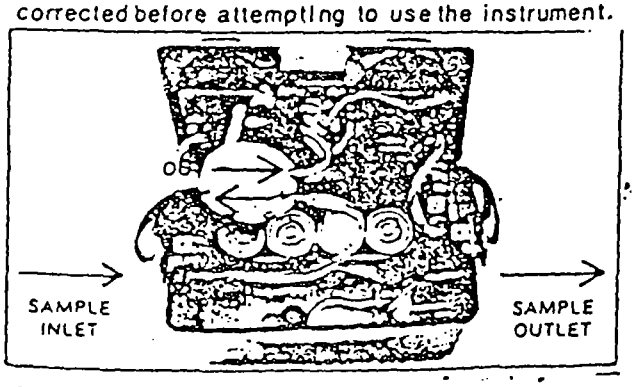


Figure 21: Sample tubing connections for all major components

8.6 GPK Sample Pump/Motor Replacement (Refer to Figure 18)

The GPK Sample Pump Assembly Code 342-626 is located adjacent to the outlet fitting in the Bottom housing.

To replace the Sample Pump Assembly, first remove the two screws from the outside of the lower case housing and release the pump assembly with mounting bracket. Mark the bracket "TOP" and "BOTTOM" for reference, then disconnect sample tubing. At the printed circuit board, unsolder the red and black leads to the pump motor and note the location for future reference.

With a 3/64" Allen wrench, loosen the set screw in the cam to free motor shaft, then remove the two screws from the motor mount.

Check valve action by sucking gently on the inlet tubing connection and blowing gently into the outlet tubing connection. The valves should resist either test and stay firmly closed. If the valves pass the above test, only the pump motor will require replacement. If not, the complete Sample Pump Assembly Code 342-626 must be overhauled or replaced.

Install new motor Code 04-4053 and secure to pump mounting bracket. Reinstall pump assembly and bracket, solder pump connections to printed circuit board and connect tubing as illustrated in Figure 22A

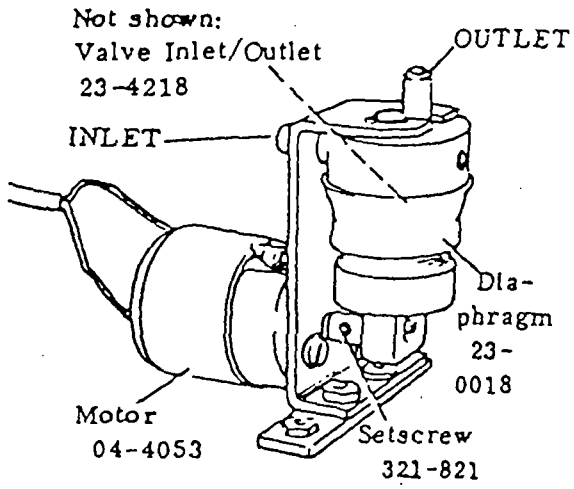


Figure 22: 342-626 Sample Pump with motor and mounting bracket. Inlet and Outlet tubing connections shown.

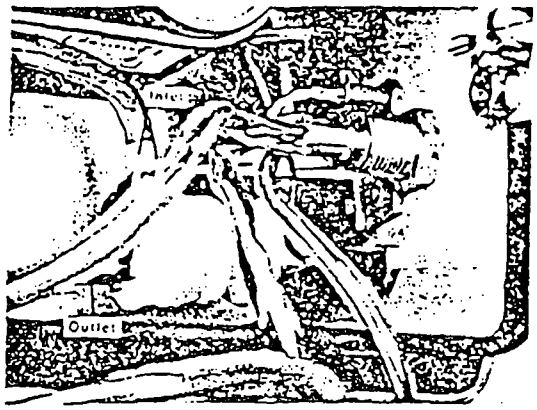


Figure 22A: Sample Pump Assy. properly Installed

8.7 Meter Replacement

Meter trouble is usually indicated by erratic action, for instance, the indicator meter pointer will start to go up smoothly, pause momentarily at a reading, and then jump quickly over the the next few divisions of the scale. Another sign of trouble is for a meter to be almost or entirely inactive, and to "stick" or show a permanent displacement of the pointer.

If the meter is giving trouble it may be removed by taking off the meter nuts and the meter hold down screws. Field repair of meters is generally inadvisable unless a qualified instrument repair facility is available.

PLEASE NOTE FOLLOWING BEFORE REPLACING METER:

The zero, calibrate and voltage adjuster knobs all turn an arm which runs back and forth over a resistance coil. To keep the sliding contact of the coil clean, it is good practice to turn the knobs back and forth three or four swings of the meter pointer each day as the instrument is first put into service.

8.8 Trouble Shooting Guide

SEE CHART ON OPPOSITE PAGE.

9.0 ACCESSORIES FOR MODELS GK, GPK

9.1 Probes and Sampling Hoses

When Models GK and GPK are purchased complete with carrying case and accessories, a short aluminum probe with filter and 30" of Nylon lined hose are supplied as standard (Stock No. 550-015).

For special applications as noted below, longer probes in aluminum and fiberglass (nonconducting) and longer hose assemblies can be supplied. Various styles are available, and extension hoses can be provided for coupling between the hose and the instrument. The aluminum probe is generally used except where the non-conducting properties of fiberglass are required for the application. Nylon lined hose is particularly resistant to organic vapors, such as the aromatics like xylene.

The following hose and probe combinations with standard union fittings are available.

1. Fiberglass probe with dust filter chamber and 42" nylon lined hose (Stock No. 550-013). Used primarily by utility companies where an electrically non-conducting probe is desired and gases such as natural and manufactured gas are sampled.

2. Aluminum probe (long) with dust filter chamber and 42" nylon lined hose (Stock No. 550-014). Used in nearly all other applications. Probe of 3/8" diameter is very rugged and is perforated a few inches from the tip to prevent liquid from getting into the sampling hose should the probe be accidentally placed in liquid. The hose is unaffected by petroleum vapors.

3. Five foot hose. Stock No. 550-060 (nylon lined). Used as an extension hose. Can be used with either (1) or (2) above. Longer lengths of hose, complete with unions, are available in 5, 10, 15, 20, 25 and 50 foot lengths.

4. Dust filter chamber with fittings (Stock No. 550-025). Useful where just a filter chamber is required at the instrument inlet. Standard hose (550-060, or longer extensions) can be attached for remote sampling.

9.2 Sample Line Moisture Trap (See Figure 23)

#550-081 Sample Line Chamber. Although the cotton filter in the filter chamber of the probe tends to trap water or other liquids before they reach the instrument, it is normally a wise procedure to use a water trap if there is a continual problem with excessive moisture.

The 550-081 Sample Line Chamber is designed to act as a moisture trap when there is danger of drawing liquid or water into the instrument, or to help dry a sample when it is filled with calcium chloride or other drying agent. It can also be used as an additional dust filter trap where extremely dusty atmospheres are encountered.

The Sample Line Chamber comes complete with fittings, one end attaching to the GK or GPK sample inlet, and the other end to the sampling hose. The Chamber itself is a clear lucite tube. The capacity of the chamber is about 3 oz.

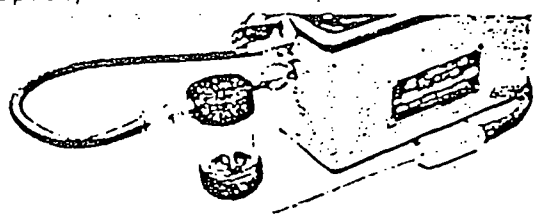


Figure 23: 550-081 Sample Line Chamber

APPENDIX L

FIELD MEASUREMENT OF PERMEABILITY USING THE BAIL DOWN TEST

FIELD MEASUREMENT OF PERMEABILITY
BAIL-DOWN TEST

INTRODUCTION

The objective is to determine hydraulic parameters (transmissivity, storativity, hydraulic conductivity) of the water-bearing strata. Single well aquifer tests are used because they may be conducted using a minimum of equipment, personnel, and time. They may also be done at many points within an aquifer and may be used to better plan a full-scale pumping test.

PROCEDURES

Each bail-down test is conducted by measuring the static water level with an electric water level indicator or cloth tape with attached sounding device, placing a pressure transducer (connected to a Hermit data logger[1]), below the water level, and removing one bailer volume from the well. The recovery of the water level back to the static level is recorded over the necessary period of time, using a logarithmic sampling mode on the data logger.

The electric water level tape and transducer are wiped, first with methanol and then with deionized water as they are placed in the wells, to prevent cross-contamination between wells. The bailer is lowered with an attached 1/8-inch stainless steel cable. The bailer and cable are decontaminated between uses by washing and rinsing with Liquinox soap and water, rinsing three times with methanol, and rinsing three times with deionized water. The bailer and cable are then allowed to air-dry on steel supports and are covered with new sheet plastic.

DATA REDUCTION

The data accumulated during the bail-down tests are used to calculate hydraulic parameters using several published methods. Hydraulic conductivity is calculated for shallow, unconfined wells using the Bouwer and Rice method (1976). The NAVFAC method (1971) is used for comparison. Transmissivities and storativities for the deeper, confined wells are determined using the curve matching method described by Cooper, et al. (1967). For comparison, hydraulic conductivities are also calculated using the Hvorslev method (1951). All methods assume an infinite, homogenous, isotropic aquifer and an instantaneous change in head in the well.

The method described by Bouwer and Rice (1976) is based upon modifications to the Thiem equation, with the use of an analog model. A straight line is drawn through a semi-log plot of relative head versus time, and the hydraulic conductivity is calculated using the slope of that line and the geometry of the well and aquifer. The formulation assumes that draw-down of the water table around the well is negligible, that flow in the

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1 Hermit Environmental Data Logger, Model SE1000B, In-Situ, Inc., Laramie, Wyoming 82070.

capillary fringe may be ignored, and that well losses are negligible. It is applicable to completely or partially penetrating wells in unconfined aquifers, but may be used for confined aquifers that receive water from the upper confining layer.

In the NAVFAC method (1971), a straight line is also drawn through a semi-log plot of recovery data for unconfined aquifers. The method is based on the Hvorslev method. It assumes that the well is cased below the water table, and the ratio of the screen length to the well radius (L/R) is greater than eight.

The Cooper, et al. (1967) formulation calculates the transmissivity of an aquifer by matching a plot of relative head (linear sclae) versus time (logarithmic scale) to one of a set of type curves. The method assumes that the change in head after a known volume of water is injected or removed is instantaneous and that the (non-flowing) well is screened over the entire thickness of an artesian aquifer. It is directly applicable to fully penetrating screened wells in confined aquifers, but may be used to determine the transmissivity of the portion of an aquifer over which a partially penetrating well is screened, assuming no vertical flow occurs.

The Hvorslev method (1951) is based on a solution of the LaPlace equation and does not account for aquifer storage. A straight line is drawn through a semi-log plot of relative head versus time. The time that would be required for complete equalization of head difference if the original rate of inflow were maintained (defined as the basic time lag, T_0, and equal to the time when H-h/H-Ho = 0.37) is used to calculate the hydraulic conductivity. The value of T_0 is measured graphically, and the ratio of the piezometer length to radius is assumed to be greater than eight (L/R>8).

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[jam-13-6]

APPENDIX M

CALIBRATION AND MAINTENANCE OF THE MONITOX HCN

Bedienungsanleitung
Operating Instructions

COMPUR 4100 SD

Monitox HCN

MDA Scientific, Inc.
405 Barclay Blvd.
Lincolnshire, Illinois 60069
Phone: 800-323-2000 (in IL 312/634-2800)
Telex: 72-6399 MDA-USA • Fax: 312-634-1371

9.85 - 1'

Compur-Electronic GmbH

5.6.

Hinweise zur Fehlersuche

Fehler	Hinweis
Batterietest Detektor geht nicht	Batterien wechseln (5.1.)
Funktionstest mit Generator geht nicht	a) Evtl. mit 2. Detektor nachprüfen, ob Generator o. k., sonst b) b) Filterkappe wechseln (5.2.), wenn nicht verschmutzt, c) c) neue Sensorzelle einbauen (5.3.).
Generator liefert nicht genug Gas	Zelle befeuchten, d. h. mit Feuchthaltekappe mehrere *Tage stehen lassen*, sonst Generatorzelle wechseln (5.4.).
Am Generator leuchtet rote LED beim Test auf	Generatorbatterie ersetzen (5.5.).

6.

Zubehör und Verbrauchsmaterial

Bestellnummern für Verkaufseinheiten

1. Gasdetektor HCN Digitalanzeige, 2 Alarmschwellen mit Dosimeter-Anschluß	U 5306 203
2. Zelle HCN mit Filterkappe	U 5800 103
3. Filterkappe HCN (10 Stück)	U 5810 341
4. Batterie PX 23 (1 Stück)	U 4990 001
5. Gasgenerator HCN	U 5390 300
6. Generatorzelle HCN	U 5820 300
7. Kalibriergasadapter	U 5900 106
8. Meßleitung: Eichen	U 5900 112
9. Digitalvoltmeter	U 5900 018
10. Stromgenerator	U 5900 023
11. Kalibrierkabelsatz für Stromgenerator	U 5900 125
12. Protokollheft	U 5900 004
13. Ohrhörer	U 5900 002

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Gas Detection and Warning System COMPUR 4100 SD Monitox HCN

The COMPUR 4100 SD Monitox Gas Detection and Warning System comprises

1 gas detector (alarm unit with digital display)
2 gas generator (test unit)
3 console (recommended accessory)
4 detectolog (recommended accessory)

The system is especially designed to monitor the TLV of HCN.

CAUTION!
Although the 4100 SD Monitox for HCN has been highly simplified for ease of operation by the user, it is nevertheless a complex measuring instrument which will operate reliably only if these operating instructions are carefully observed and if the instrument is checked regularly by the safety officer.

This applies in particular to the regular replacement of the cells and daily functional tests. The responsibility for any changes made in the alarm threshold settings must be borne entirely by the operator; COMPUR recommends the strict observance of the TLV. Since the unit is designed to be intrinsically safe, all repairs must be made by the manufacturer or other approved personnel.

COMPUR offers the instrument with the following factory settings:
first alarm threshold = at TLV = 10 ppm
second alarm threshold = at 2 TLV = 20 ppm

The detector cell will be destroyed if the detector is permanently exposed to a HCN-concentration exceeding 1000 ppm. In this case the cell has to be replaced.

1. Technical Description of the COMPUR 4100 SD Monitox Detector for HCN

1.1. Applications

The COMPUR 4100 SD Monitox is a personal monitor for HCN.

It is designed to be worn attached to the clothing near the breathing zone of the person to be protected. The detector produces an audible first alarm when the HCN-concentration exceeds the TLV (factory setting: 10 ppm) and a second alarm, when it exceeds 2 x TLV.

Independent of the alarm setting, the digital display shows the actual HCN-concentration in ppm (parts per million) in the nominal range of 0 – 100 ppm HCN.

In conjunction with the COMPUR 4102 Dosimeter, the unit can be employed to register HCN-concentrations at canfined spaces ranging from 0 to 10 x TLV.

The COMPUR 4100 SD Monitox cannot be used to measure process gas streams or in presence of continuous high HCN-concentrations.

1.2. Mode of Operation

Ambient air diffuses through the filter insert (a dust filter) (5) to the measuring cell. The measuring cell, a dual-electrode electrochemical cell with an organic electrolyte gel, generates an output current proportional to the partial pressure of HCN in the air.

A series of electronic amplifiers supply a voltage signal which is fed to the comparator for the alarm threshold. If the first alarm threshold is exceeded, an intermittent tone is produced; if the second alarm threshold has been exceeded a dual-tone signal is produced by the tone generator and loudspeaker (or earphone in very loud areas). The standardised analog signal corresponding to the actual HCN-concentrations (the TLV corresponds to 80 mV) can be fed to the Dosimeter.

The same signal is fed to the AD-converter driving the digital display. The display is adjusted to give a reading of 10 ppm at 80 mV input.

The 4100 SD Monitox consists of two separate power circuits (via two miniature batteries); the circuit for the analogue part is separated from that for the alarm-generation.

When the „on-off" switch is moved to the „Batt." position, the batteries will be tested before the instrument is turned on. In this switch position, the batteries are electronically tested under the high load of the final tone stages. If one of the batteries fails to reach the predetermined lower theoretical limit, no alarm will be heard.

1.3.

Technical Data for the COMPUR 4100 SD Monitox for HCN

Conformity certificate		BVS 82.013
Safety class		EEx ib II C T 6
Dimensions		104,4 x 62 x 24 mm
Weight (with batteries)		approx. 150 g
Power supply		2 x PX 23 (5,6 V)
Battery service life		approx. 1000 h.
Display range		0 – 100 ppm
Alarm volume		min. 80 dBA / 30 cm
Alarm levels		2 alarms, adjustable
Response time		T_{20} < 10 s T_{90} < 3 min.
Time to alarm	20 ppm 50 ppm	< 15 s < 3 s
Connection possibilities		earphone, dosimeter
Temperature range		0 – 50 °C
Relative humidity		10% – 95%
Zero point drift		< 1 ppm / 6 months
Sensitivity drift		< 15% / 6 months
Service life of the cell		min. 6 months (dependant on dose)

1.4.

Cross-sensitivities

Test components	Test concentration	Indication in ppm HCN
SO_2	5000 ppm / 40% rH	10
NO_2	10 ppm	– 6
NH_3	1000 ppm	10
CO	1000 ppm	—
CO_2	1000 ppm	—
H_2	1000 ppm	—
CH_2:CHCN	10 ppm	—
CH_3CN	200 ppm	—
$(CH_3)N$	500 ppm	17
CH_3OH	200 ppm	—
$COCl_2$	5 ppm	10
Cl_2	10 ppm	5
HCl	10 ppm	7
H_2S	2 ppm	10
Hydrocarbons, saturated	2% vol.	—
Hydrocarbons, unsaturated	1% vol.	—
Aromatic compounds (also alcylated)	200 ppm	—

2.

Technical Description of the COMPUR 4100 SD Monitox Gas Generator for HCN

2.1.

Applications

The HCN gas generator serves to enhance the reliability of the Monitox gas detection and warning system. The Monitox detecto must undergo a functional test by placing i on the generator before each use. The generation of a gas concentration exceeding the TLV ensures that the detect will respond reliably during use (picture 2).

The gas generator, however, is not designe to generate a calibration gas of known concentration. Daily testing of the Monito detector does not mean that the user is no recommended to change cell sequentially

The COMPUR 4100 Gas Generator must not be exposed to or used in explosive atmospheres.

N.B.: The generator cell may dry out at very low relative humidity in the air. I this case, it is necessary to put the moisture cap delivered with the generator on top of the generator always when it is not in use.

This ensures a correct gas concentration for the detector test.

2.2.

Mode of Operation

The switch on the generator is activated by placing the detector in the matching recess on the generator head.

A small fan feeds a flow of air past the generator cell directly to the detector cell. At the same time, gas is generated electrolytically in the generator cell in such an amount that the gas concentration is high enough to cause the detector to respond within 10 seconds (alarm threshold 10 ppm). The period of gas generation is indicated by the green LED.

The red LED indicates when the battery must be replaced.

After a 10 seconds interval, gas production is terminated and the fan conveys pure air until the detector is removed.

This functional test of the detector checks any of the following defects:

- clogging of the dust filter
- a malfunctioning cell
- a malfunctioning electronics system
- a malfunctioning generator.

2.3.

Technical Data of the COMPUR 4100 SD Monitox Gas Generator for HCN

Dimensions	133 x 65 x 40 mm
Weight (incl. batteries)	approx. 250 g
Temperature range	0 °C – 50 °C
Power supply	9 volt alkali battery, leakproof, e.g. Mallory 1604
Generator cell service life	approx. 3000 tests or for 1 year
Battery service life	approx. 3000 tests

3.

Use of the detector and generator

3.1.

Detector actuation and functional test

Battery Test

Turn the switch on the COMPUR 4100 SD Monitox to "Batt.". If the battery has sufficient power to operate the detector for eight hours, an audible (intermittent) tone will be heard. The LCD-display is switched off at the "Batt." test position. If no tone is emitted, this indicates that at least one of the batteries is exhausted. For safety reasons both batteries should be replaced (refer to section 5.1.).

When the audible tone has been heard (to preserve batteries, the test should be as short as possible), the switch is moved to "ON". The tone will cease. The LCD-display is operating now. It must show "0" ppm after some seconds.

Functional Test (picture 2)

Place the detector on top of the generator as illustrated.

As soon as the detector sounds its alarm, it must be removed from the generator. The detector is ready for operation once the alarm has ceased.

If the detector alarm does not sound within ten seconds the detector has to be checked and serviced. If necessary, the filter cap has to be replaced (see point 5.2.).

It is advisable to record the test and assignment of the gas detector in the detectolog.

The battery test and functional test must be performed prior to each use to thus ensure maximum safety.

During the gas test the LCD-display must show the response of the cell to HCN-concentration as well. As the alarm threshold is factoryset at 10 ppm the alarm should sound at 10 ppm. As the display reads a new value every second, the time for alarm and display of 10 ppm may be different.

3.2.
Use of the Gas Detector

The gas detector must be worn in the breathing zone of the person to be protected and the filter cap (5) should not be covered in any way.

The rubber lip on the carrying clip makes it possible to securely attach the Monitox to articles of clothing (e.g. the breast pocket).

If this is not deemed adequately secure, the chain supplied with the Monitox can be secured in the holes of the carrying clip. This enables the Monitox to be worn around the neck.

Wherever possible, the filter cap should be protected from water, dust-laden air or dirt. Both, the battery and functional tests (refer to point 3.1.) should be performed before the detector is put into operation.

If HCN gas concentration in the vicinity of the sensor exceeds the set alarm value, the alarm will sound after a delay dependent on the gas concentration (The higher the concentration, the more quickly the COMPUR 4100 SD Monitox will respond).

The alarm sounds at a level of at least 80 dB at a distance of about 30 centimeters (12 inches).

3.3.
Connecting the Earphone

When the detector is being utilised in an area with high background noise, the optional earphone should be used to be sure that the alarm will not go unnoticed. The earphone is connected to the earphone socket (9) on the detector. This socket disconnects the internal loudspeaker. If the earphone is being used, it is important that the tests also be conducted with the earphone plugged into the detector (refer to point 3.1.). When the earphone is not being used, the socket should be closed with the plastic plug.

3.4.
Connecting the Dosimeter

The COMPUR 4102 Mini-Dosimeter can be connected to the 4100 SD (refer to operating instructions for the 4102).

The generator test can also be carried out with the Dosimeter connected to the COMPUR 4100 SD if the detector is turned 180° about its longitudinal axis relative to the position shown in point 3.1. and then placed on the generator in that way, that the cell fits into the recess on the generator. The functional test is then started by pushing the generator button with one's finger.

The plug should be replaced in the Dosimeter socket whenever the Dosimeter is not being used.

3.5.
Digital Display

Additional to the warning-function of the COMPUR 4100 SD Monitox its digital display (6) gives a direct reading of the actual HCN concentration.

Thus it is possible to determine HCN-concentrations below and above the TLV-level, giving the skilled worker and industrial hygienist the means to detect unusual conditions of HCN-concentrations with high accuracy and resolution.

The COMPUR 4100 SD Monitox is, however, even with its digital display, primary a measuring and warning device for personal protection.

It has not been designed for measurement in process-control; moreover exposures to high HCN-concentrations for any length of time must be avoided, as the accuracy of the reading will suffer.

3.6.
Detector Deactivation and Storage

a) brief period of inactivity (up to a month)

the detector is deactivated (switch to "OFF")

b) Prolonged inactivity and storage

It is advisable to open the Monitox and remove both the cell and batteries, to provide them from leaking and corroding the interior of the Monitox (refer to the sections on cell and battery replacement 5.3.).

Before reutilizing the Monitox a new cell has to be installed.

4.

Calibration Instruction for the detector COMPUR 4100 SD Monitox

To enhance the intrinsic accuracy of the detector for HCN it is necessary to calibrate the detector either with a HCN nitrogen mixture with definite concentration of HCN or make an electronic adjustment by means of the COMPUR current generator U 5900 023.

4.1.

Accessories required

4.1.1.
Calibration with gas

a) calibration cap to place onto Monitox

b) flow meter

c) millivoltmeter 0 – 2000 mV; input resistance ≥ 1 M Ω

d) tubing, set of test cables, screw-driver

e) calibration gas, known concentration, about 10 ppm HCN in pure N_2

Remark: The generation and above all the stability time of HCN calibration gas is not without problems. So if only a small number of detectors are to be calibrated, the electronic method should be prefered.

4.1.2.
Calibration – Electronical Method (picture 6 and 7)

a) calibration unit (current generator)

b) millivoltmeter 0 – 2000 mV, input resistance ≥ 1 M Ω

c) set of test cables, screw-driver

4.2.

Zero calibration and gain adjustment with calibration gas

4.2.1.
Preparation

The Monitox is opened and positioned with the electronic components upward on a non-slip surface. The cover with the digital display is carefully put aside with the display upward.

Then the unit is switched on via "Batt." position to "ON". The LCD-display should read 00 ppm after several seconds.

The excellent zero-point stability of the cells will normally make unnecessary to adjust the zero-point. Deviations from zero are caused mostly by fault sensor cells.

For zero-checking remove sensor cell.

4.2.2.
Zero-Adjustment

Connect Millivoltmeter to tie down point (MP 2) and GND (MP 1) (picture 6). If the reading is not zero in clean air, and also is not zero without sensor cell, potentiometer (R 9) (offset voltage) has to be varied until the reading is zero.

Note: If reading is zero without cell and not zero with the cell, it may need up to one hour to stabilize the cell. If a cell has been removed for a longer period without short-circuiting the two connectors, the time to stabilize may be up to one day. A new cell therefore has short-circuit on the small pcb, that must be broken away before inserting the cell.

4.2.3.
Gain Adjustment with gas

The special calibration adapter is tightly put onto the dust filter on top of the detector cell.

Adjust a calibration-gas flow through the calibration cap; flow rate should be approx. 100 ccm per minute and the inlet must be the smaller pipe; to avoid pressure variations the outlet should be free of obstacles. After 5 minutes the display of the Monitox has reached its final value.

Connect millivoltmeter to tie down point (MP 2) and GND (MP 1). Depending on the concentration of the calibration gas the following voltage should be displayed: (adjust by means of pot R 7)

$$U = \frac{[c] \text{ in ppm}}{10 \text{ ppm}} \times 80 \text{ mV}$$

The display of the Monitox must show the gas concentration. In the opposite, adjust pot (R 15) until correct reading is shown.

4.2.4.
Gain-Adjustment with the current calibrator

Each detector cell produced by COMPUR is supplied with an indication of the output current at 10 ppm HCN. (Never throw away packings of replacement cells before having noted this indication!!!)

Remove detector cell. Insert calibration cable with the plug board into plug connector for detector cell. The gold contacts must touch the spring contacts. Connect other side of the cable to the current generator.

Make sure of correct polarity of plugs. Switch on generator, turn button till generator display shows output current of detector cell.

Remark: Display always shows actual value of current. If it is zero, check the contacts!

Connect voltmeter to tie down point (MP 2) and GND. Adjust sensibility by means of pot (R 7) until 80 mV is displayed. Monitox must now display 10 ppm. In opposite, adjust pot (R 15).

4.3.

Setting the Alarm thresholds

The alarms of the standard version are to be set on 10 ppm (first alarm 1 TLV) and 20 ppm (second alarm 2 x TLV).

To set the alarm levels, push the 2 mini-switches (S 1) to the right. The display of the Monitox shows now the level of the 1st alarm threshold. This can be adjusted by means of the potentiometer (R 30).

To adjust the 2nd alarm level, push the upper switch to the left. The display shows now the 2nd alarm threshold. This can be adjusted by means of the potentiometer (R 29).

After having adjusted the alarm levels, push both mini switches to the left. The Monitox display shows now the actual concentration of HCN.

4.4.

Concluding the adjustment operations

After the settings have been made, turn the switch on the pcb to "OFF"-position. Make sure that the switch-handle on the cover is also in the "OFF"-position. Then carefully replace the cover and fold the connecting cable between pcb and display so that it is neither squeezed in nor cracked. Tighten the screws. The Monitox is now ready for operation.

5.
Maintenance and Servicing Instructions

5.1.
Battery Replacement

1. Turn switch (7) to "OFF".
2. Remove three screws (12).
3. Turn detector over and remove front cover.
   Attention: Do not attempt to remove the cable between front panel and pbcl
4. Lift out battery housing, disconnect plug.
5. Unscrew and remove battery lids.
   Replace batteries with +pole towards lid.
   Replace lids.
6. Plug-in battery plug. Ensure cable and cable socket in right position.
7. Replace battery housing and front cover, carefully adjust the cable of the front panel, so that it is not damaged by fixing the front panel; then tighten the screws.
8. Repeat battery test.

5.2.
Filter Cap Replacement

1. Remove screws (7) (picture 4) and open detector.
2. Carefully remove sensor cell together with filter cap (5). Pull cap off cell (4).
3. Attach new filter cap (with identical gas label HCN) and return sensor cell to original position.
   Filter cap order number appears on plate attached to inside of front panel and is listed in section 6.
4. Replace front cover and tighten screws
5. Repeat performance test.

5.3.
Sensor Cell Replacement

1. Open detector (see 5.1.).
2. Remove cell together with filter cap.
3. Remove new cell and filter cap from storage container, pull transparent cap off the cell and replace this by the new filter cap. Correct position of filter cap is shown in illustration.
   Remove short-circuit protection attached to pcb by breaking it away.
4. Proceed current calibration (4.2.4.).
5. Replace sensor cell with filter cap in proper position.
6. Close Monitox.

5.4.
Generator Cell Replacement
(picture 5)

1. Open housing
   (as when replacing battery)
2. Unsolder fan leads (10).
3. Loosen four screws (11) and three screws (12).
4. Remove outlet, gas cell and fan through the front.
5. Carefully insert replacement unit U 5820 300 consisting of outlet, cell and fan and tighten screws (12).
6. Tighten screws (11). Align circuit board so that pin (13) reliably actuates switch (14) when gas detector attached.
7. Resolder fan leads (10).
8. Reassemble generator and tighten screws.
9. Testing: Use properly functioning gas detector for same gas. Switch to "ON", attach. Alarm must sound after about eight seconds.

5.5.
Generator Battery Replacement

Loosen four screws on rear housing panel. Carefully remove front cover. For correct positioning of battery, refer to illustration 5.

5.6.
Troubleshooting

Malfunction	Remedy
Battery test: no response	Replace batteries (5.1.)
Generator test: no response	a) Repeat test using 2nd detector, if no response, b) b) Replace filter cap (5.2.), if not dirty, c) c) Insert new sensor cell (5.3.)
Generator does not supply enough gas	Use moisturizing cap for several days, otherwise replace generator cell (5.4.).
Red LED lights up during test	Replace generator batteries (5.5.).

6.
Accessories and consumables

Part Numbers

1. Gas detector digital display, 2 alarm thresholds with Dosimeter output	U 5306 203
2. HCN cell with filter cap	U 5800 103
3. HCN filter cap (10 pcs.)	U 5810 341
4. Battery PX 23 (1 pc.)	U 4990 001
5. HCN gas generator	U 5390 300
6. HCN generator cell	U 5820 300
7. Calibration gas adapter	U 5900 106
8. Measuring cable: calibration	U 5900 112
9. Digital Voltmeter	U 5900 018
10. Current calibrator	U 5900 023
11. Calibration cable used in connection with current calibrator	U 5900 125
12. Detectolog	U 5900 004
13. Earphone	U 5900 002