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METAMORA LANDFILL SITE
QUALITY ASSURANCE PROJECT PLAN

REMEDIAL INVESTIGATION/ FEASIBILITY STUDY

CONTRACT NO. 1525

E.C. JORDAN PROJECT NO. 4465.93

PREPARED FOR

MICHIGAN DEPARTMENT OF NATURAL RESOURCES

JANUARY 1987

E.C. JORDAN CO.

1.0

QUALITY ASSURANCE PROJECT PLAN FOR THE REMEDIAL INVESTIGATION/FEASIBILITY STUDY OF THE

METAMORA LANDFILL SITE
METAMORA TOWNSHIP, LAPEER COUNTY, MICHIGAN

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3.0 PROJECT DESCRIPTION

3.1 PURPOSE

The purpose of the Quality Assurance Project Plan (QAPP) for the Remedial Investigation/Feasibility Study (RI/FS) of the Metamora Landfill Site is to indicate prime responsibilities and prescribe requirements for assuring that the project (as defined in the Remedial Investigation/Feasibility Study Work Plan for the Metamora Landfill Site (March, 1986, revised)) is planned and executed in a manner consistent with quality assurance objectives.

This QAPP provides guidance and specifications to assure that:

1. field determinations and analytical results are valid through preventive maintenance, calibration and analytical protocols;
2. samples are identified and controlled through sample tracking systems and chain-of-custody protocols;
3. records are retained as documentary evidence of the quality of samples, applied processes, equipment, and results;
4. generated data are validated and their use in calculations may be documented;
5. calculations and evaluations are accurate, appropriate and consistent throughout the projects; and
6. safety is maintained by requiring inclusion of the Health and Safety staff function in the project organization.

3.2 SCOPE

The requirements of this QAPP apply to E.C. Jordan Co. (Jordan) and subcontractor activities as appropriate for the Metamora Landfill Site RI/FS.

The prime responsibilities indicated in Section 4.0 extend to all quality-related controls and activities. The project specific QA/QC requirements noted in Sections 3, 5, 6 and 9 are aimed at preventing isolated sub-standard or erroneous actions from occurring in these essential areas. Where possible, Jordan's accompanying document "Standard Sampling and Sample Handling Procedures" is referenced to reduce the possibility of error.

The content and format of the QAPP is based on "Interim Guidelines and Specifications for Preparing Quality Assurance Project Plans - QAMS-005/80" prepared by U.S. EPA's Office of Research and Development. To make the QAPP easier to review, four appendices (A, B, C and D) are appended. These appendices address certain tasks or instruments (geophysical surveys; compatibility

testing; air sample testing for health and safety purposes, and waste testing for disposal purposes; and use of a Photovac 10S50 portable gas chromatograph) which are difficult to incorporate into the main body of the QAPP.

3.3 PROJECT SUMMARY

The following information summarizes the specific tasks required for the RI/FS of the Metamora Landfill Site as well as other pertinent information.

3.3.1 Project Background

The Metamora Landfill covers approximately 50 acres of a former gravel quarry located in Section 10, T6N, R10E (Metamora Township), Lapeer County, Michigan. The project site is an 80-acre area encompassing the 50-acre landfill. Waste disposal activities at the landfill have ceased, but gravel mining continues within the study area south of the landfill. The project site occupies a topographic high in the area with numerous steep excavation faces and borrow pits. The surrounding land uses are primarily residential and agricultural. The property immediately north of the landfill, and in scattered areas on the west and east, is heavily wooded and access is difficult. The village of Metamora is located approximately one-half mile west-southwest of the landfill.

The landfill began operation in 1966 as an unregulated open dump. In 1969, it was upgraded to meet prevailing standards and was licensed to receive general refuse. In addition to general refuse, the landfill received industrial and chemical wastes until its closure in 1980. A licensed solid waste transfer station is currently operated at the site.

Previous investigations by the Michigan Department of Natural Resources (MDNR) suggest that as many as 35,00 drums, some containing liquid wastes, may be present within the main landfill and in nearby shallow disposal areas. A magnetometer study conducted by MDNR in 1982 identified five discrete areas of anomalous magnetic readings. The source of three of the five anomalies are thought to be buried deep within the waste contained in the landfill proper. Because of their inaccessibility, however, they have never been excavated to determine the nature of the ferrous metals buried within. These three areas are estimated to represent the equivalent of about 10,000 drums.

The remaining two areas exhibiting anomalous magnetic readings are thought to contain as many as 25,000 drums buried at relatively shallow depths outside the limits of the landfill proper. A limited excavation program in each of these shallow-burial areas conducted in September, 1982, confirmed the presence of buried drums, as well as industrial solvents including toluene, ethyl benzene, and perchloroethylene. Toluene, benzene, xylene, pyrene, and concentrations of total metals have been found in groundwater from monitoring wells installed at the site during previous investigations. Table 3-1 summarizes concentrations of metals detected in groundwater at the site to date.

TABLE 3-1

SUMMARY OF METAL CONCENTRATIONS IN GROUNDWATER
AT THE METAMORA LANDFILL SITE

Metal	Concentration
Arsenic	less than .005 - .14 mg/l
Chromium	less than .005 - .005 mg/l (0.23 mg/l, total)
Copper	less than .005 - .044 mg/l
Lead	less than .020 - .063 mg/l (1.95 mg/l, total)
Nickel	less than .020 - .20 mg/l
Zinc	less than .005 - 22 mg/l (44 mg/l, total)

Concentrations represent dissolved metals unless otherwise noted.
This summary includes all samples collected by MDNR and Jordan to date.

3.3.2 Project Objectives

Jordan was contracted by the MDNR to conduct a Remedial Investigation/ Feasibility Study (RI/FS) at the Metamora Landfill Site.

The objective of the RI/FS at the Metamora Landfill Site is to undertake studies that will determine the nature and extent of environmental contamination at the site, determine the public health and environmental hazard posed by the site, and identify a cost-effective, environmentally sound and socially acceptable remedial program for the site.

Following is a summary of several of the specific objectives that will be addressed by the RI/FS:

- Determine the nature and extent of contamination at the project site.
- Determine if the site poses a hazard to public health and/or to the environment.
- Define pathways of contaminant migration from the site to assess the potential impact of contaminants on potential receptors such as local water wells, surface water, biota, etc.
- Identify on-site and off-site features that could affect contaminant migration, containment, or cleanup.
- Assess the potential for possible direct contact with contaminated soil by the public and define steps to reduce that potential.
- Identify and develop viable remedial action alternatives.
- Evaluate remedial action alternatives.
- Recommend an appropriate remedial program for the site including:
    1) no action (assessment of no action is required by the National Contingency Plan and forms the basis for the comparison of the effectiveness of other alternatives),
    2) measures to control the contaminant source by in-place containment or excavation and off-site disposal, and
    3) measures to control wastes that have migrated from the site.
- Prepare a conceptual design for the selected alternative.
- Assist the MDNR with its community relations efforts for the site.

3.3.3 Major Task Summary

The tasks will be divided into two phases - Initial Activities and Remedial Investigation Activities. Phase I, Initial Activities, include the following tasks:

Task 1 Prepare Work Plan
Task 2 Prepare a Quality Assurance Project Plan (QAPP)
Task 3 Describe the Current Situation
Task 4 Prepare a Health and Safety Plan
Task 5 Preinvestigation Evaluation
Task 6 Site Preparation
Task 7 Community Relations

Phase II is the Remedial Investigation. Phase II tasks include:

Task 8 Site Inventory
Task 9 Air Investigation
Task 10 Geophysical Investigation
Task 11 Soil/Soil Gas Sampling
Task 12 Soil Gas Survey
Task 13 Pollutant Characterization
Task 14 Monitoring Well Installation
Task 15 Groundwater Sampling
Task 16 Surface Water/Sediment Sampling
Task 17 Aquifer Testing
Task 18 Analytical Program
Task 19 Data Interpretation
Task 20 Remedial Investigation Report

3.3.4 Sampling Plan

Sampling and data collection activities associated with the Metamora Landfill Site RI are planned to begin in September, 1986. Sampling activities are summarized below.

- Air Investigation (Task 9) using a photoionization meter and an explosimeter. The main purpose of this task is to provide real-time air quality data during all field activities to ensure worker health and safety. If necessary, an expanded air quality monitoring program using charcoal tubes will be initiated. The number of charcoal tube samples to be collected during an expanded program is unknown. For Task 13, Pollutant Characterization, a separate air monitoring plan has been developed which includes 120 air samples collected on charcoal tubes.

- Geophysical Investigations (Task 10) including magnetic, electrical resistivity and seismic methods (see Appendix A). These surveys will

entail collecting data from numerous pre-determined locations around the site.

- The magnetometer survey will cover an approximate 2-acre area with readings taken within a 100-foot grid system. Individual magnetic stations will be established with reference to the survey grid with a cloth measuring tape.

- The pilot resistivity survey will include up to 10 vertical electric soundings. The full-scale program (if appropriate) will include up to 46 additional soundings.

- The pilot seismic survey will include up to 3,200 linear feet of seismic refraction profiling. The expanded seismic survey (if appropriate) will include up to 19,200 linear feet of addition profiling.

o Groundwater sampling (Task 15) will involve the collection of 79 samples. The groundwater sampling program includes three sampling events:

- Event 1: 19 samples from existing monitoring wells (prior to the installation of any new wells).

- Event 2: 30 samples from the 19 existing wells and 11 proposed wells (two weeks after the wells have been installed).

- Event 3: 30 samples from the 19 existing wells and 11 proposed wells (two weeks after sampling Event 2).

o Surface Water/Sediment Sampling (Task 16) will involve collecting 6 surface water samples, 6 sediment samples, and 6 leachate samples.

o Subsurface soil sampling (Tasks 11 and 14) includes the collection of 160 soil samples. The number of samples to be collected during each task are as follows:

- Task 11: 50 samples (30 for chemical analysis)
- Task 14: approximately 110 samples (20 for chemical analysis)

o Soil gas sampling (Tasks 11 and 12) includes the collection of 142 samples. The number of samples to be collected are as follows:

- Task 11: 50 samples
- Task 12 (pilot): 10 samples
- Task 12 (full scale): 82 samples

o Waste sampling (Task 13) during the Pollutant Characterization Task involves collecting approximately 1,200 samples (150 samples for chemical analysis).

The analytical program for the Metamora Landfill site is summarized in Table 3-2.

3.3.5 Outputs

Interim reports will be submitted to MDNR at the completion of each task. Major outputs, reports or plans will be submitted at the completion of the following tasks:

Task 1 - Work Plan
Task 2 - Quality Assurance Project Plan
Task 3 - Description of Current Situation
Task 4 - Health and Safety Plan
Task 5 - Preinvestigative Evaluation
Task 20 - RI Report
Task 22 - Response Objectives
Remedial Alternatives
Task 26 - Draft FS Report
Task 28 - Conceptual Design
Task 29 - FS Report

3.3.6 Schedule

Initial activities are expected to begin in August 1986. It is estimated that 13 months will be required to complete all of the tasks described in the Work Plan. This schedule commences following approval of the Work Plan.

Completion of the RI/FS on schedule is contingent upon a 45-day turnaround of analytical results from the U.S. EPA Contract Lab(s). In addition, MDNR and U.S. EPA must complete their reviews and provide their input in a timely manner to allow for completion of the final report within the designated time period.

TABLE 3-2
ANALYTICAL PROGRAM

	Field Measurements						Laboratory Measurements						
Media	pH	SC	Temp	PI	10350	Comp. Tests	CLP Inorganics	CLP Organics	Tenax tubes	Charcoal tubes	Dioxin/ Furans	RCRA EP Tox	PCBS
Air				A									
(Task 9)										A,B			
(Task 13)										120			
Groundwater													
(Task 14)	79	79	79		79		79	79					
Surface water													
(Task 16)	6	6	6				6	6					
Sediment													
(Task 16)							6	6					
Leachate													
(Task 16)	B	B	B				6	6					
Subsurface soil													
(Task 11)				50	50		30	30			15		
(Task 14)				110	110		20	20					
Soil Gas													
(Task 11)					50				B				
(Task 12)					92				B				
Waste													
(Task 13)						1200	150	150			150	150	

A - Number of samples unknown.
B - Analysis of these samples contingent upon field conditions.
SC - Specific conductance
Temp - Temperature
PI - Photoionization meter reading
10350 - Analysis or organic chemicals with a portable GC
Comp Tests - Compatibility tests
RCRA EP Tox - EP Toxicity tests for heavy metals and pesticides/herbicides

4.0 PROJECT ORGANIZATION AND RESPONSIBILITIES

4.1 ORGANIZATION

Jordan operates under a matrix system in which personnel belong to functional departments and, at the same time, are assigned to projects. Functional departments are responsible for developing and maintaining Jordan's engineering and scientific disciplines. They provide for personnel training and the establishment of engineering and scientific standards. Project organizations are responsible for achieving project objectives.

This portion of the QAPP addresses the project organization. Those who are assigned to a project organization are responsible for properly utilizing functional organization resources. In this way, the resources of the entire E.C. Jordan Co. are made available to each project, but responsibility for initiating services and for ensuring acceptable results remains within the project organization. This responsibility carries with it the authority to initiate, modify, and if necessary, stop activities as appropriate for the assurance of project quality. It is the Quality Assurance Coordinator's role to assist the Project Manager in meeting project goals while providing an independent evaluation of product quality.

4.2 SPECIFIC RESPONSIBILITIES

Figure 4-1 shows the project organization and its principal lines of communication. The Michigan Department of Natural Resources (MDNR) has overall responsibility for this project. The Officer-in-Charge (D. R. Cote) has overall responsibility for the project for the E. C. Jordan Co. and the Technical Project Director (TPD) (K. Kesler-Arnold) has responsibility for the day-to-day progress of the project. For non-CLP laboratory analyses (i.e., analyses to be performed by Clayton Environmental Consultants), responsibility for quality assurance will be taken by Jordan's TPD in conjunction with John Spurr, Clayton's Quality Assurance Coordinator. Jordan's Quality Review Team (D.B. Ertz and J.D. Tewhey) has overall quality assurance responsibility and the TPD is responsible for quality control on a daily basis. The TPD is responsible for final data review and assessment. Dr. Bruce Wallin, E.C. Jordan Co., is responsible for QA/QC reviews of CLP data. MDNR is responsible for the SAS preparation.

The responsibilities of the Jordan project staff positions and support organizations are summarized below.

- The Project Manager (PM) is responsible for maintaining a clear definition of, and adherence to, the project scope, schedule and budget. As part of this responsibility, the PM will:

  1. Serve as the communication link with the MDNR on all matters.

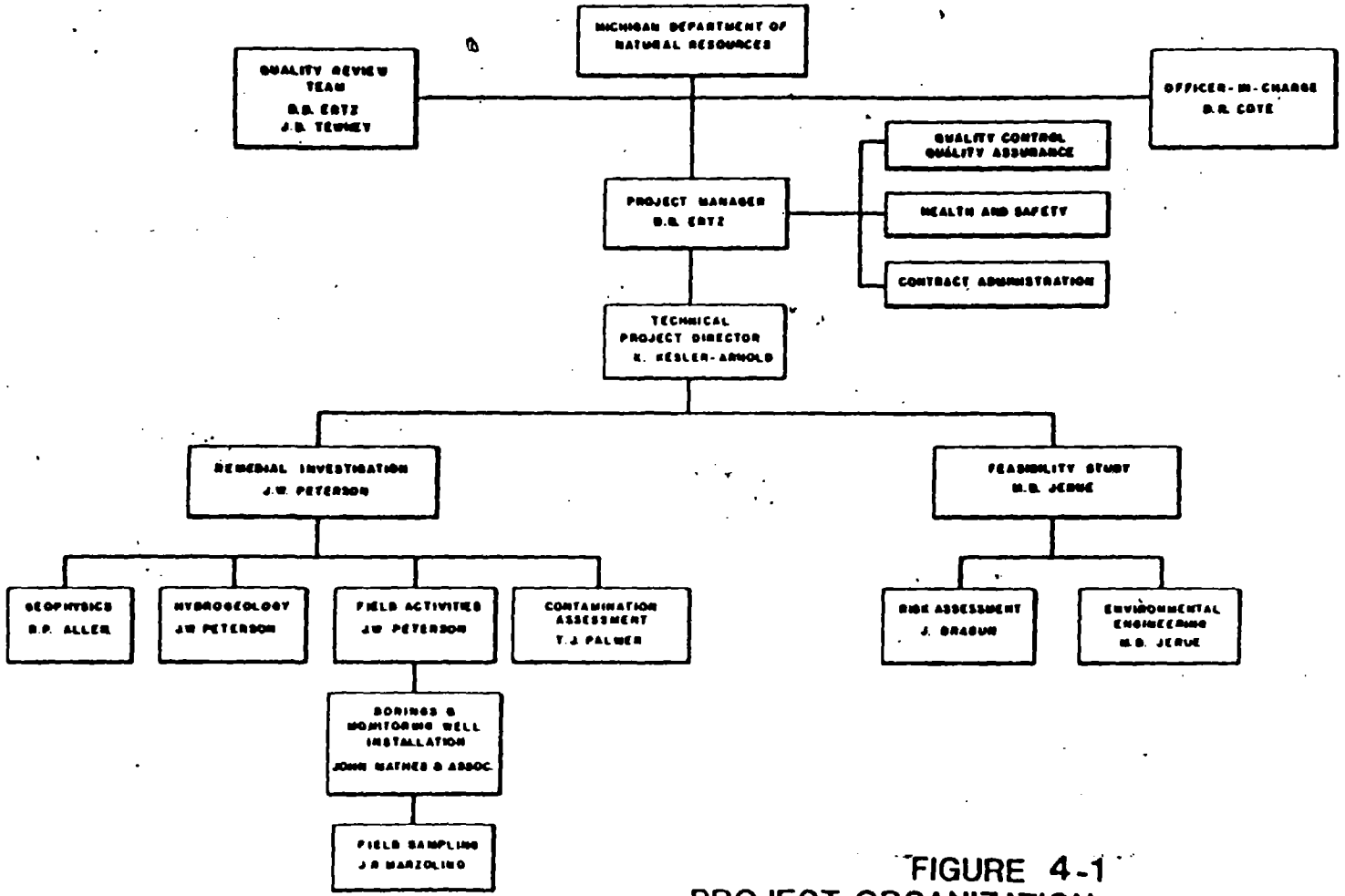

FIGURE 4-1
PROJECT ORGANIZATION
METAMORA LANDFILL

2. Administer all contracts with the MDNR and Jordan subcontractors.

3. Maintain budgetary and schedule surveillance and regularly inform the Technical Project Director of budgetary and scheduling status.

- The Technical Project Director (TPD) is responsible for staffing and conducting the project. The TPD will:

  1. Provide overall technical direction for preparation of work plans and the conduct of tasks performed under this contract.

  2. Maintain this QAPP.

  3. Indicate the types of QA records to be retained for the project.

  4. Provide for QA audits by Jordan personnel.

  5. Approve reports and material for release to the MDNR and other external organizations.

  6. Approve task plans and operating systems.

- Task Leaders are responsible for specific engineering, scientific and analytical operations. As part of this responsibility they will:

  1. Initiate, develop and check subtask plans including initiating, monitoring and accepting support services and products.

  2. Identify safety hazards and ensure that the associated risks are reduced to acceptable levels.

  3. Supervise and participate in operations, analyses, data collection, and data reduction.

  4. Maintain samples and their identification.

  5. Generate required QA records.

  6. Maintain compliance with site and corporate safety requirements.

  7. Implement quality corrective actions.

- The Quality Review Team (QRT) reports directly to the Corporate Project Officer. The team is responsible for on-going surveillance of project activities to ensure conformance to this Plan and to evaluate the effectiveness of its requirements. The team has access to the TPD, Project Director and Task Leaders, and any other Jordan personnel or Jordan subcontractors, as necessary, to resolve quality problems. The team has the authority to recommend that work be stopped when it appears that continuation of the work could jeopardize the quality of the project. As

part of this responsibility the team will:

1. Monitor the correction of quality problems, and alert other task leaders where similar problems might occur.

2. Provide for retention of QA records.

3. Participate in QA audits.

4. Recommend changes, as appropriate, to improve the effectiveness of this QAPP.

5. Review proposed additions and changes to this QAPP.

The QRT includes the Quality Assurance Coordinator (QAC) for this project. The QAC is responsible for:

1. Evaluating and recommending approval of this QAPP to the Quality Assurance Officer;

2. Scheduling and conducting systems and performance audits;

3. Providing QA reports to the PM and QRT on the results of audits and the need for preventive or corrective actions; and

4. Developing and initiating preventative and corrective actions as needed in conjunction with the PM and TPD.

o Project Support

John Mathes and Associates, Inc. (Mathes) will provide support services to Jordan in the areas of drilling, monitoring well installation, and soil sample collection during the soil gas surveys (Tasks 11 and 12) and the well installation task (Task 14).

Great Lakes Environmental, Inc. (GLE) will provide services during Task 13, Pollutant Characterization. These services will include all earthwork and drum handling, plus compatibility testing of waste samples (see Appendix B).

Clayton Environmental Consultants, Inc. (CEC) will provide laboratory services for the analysis of charcoal tubes, Tenax tubes and waste samples for EP Toxicity (metals and organics) and PCBs (see Appendix C).

5.0 QUALITY ASSURANCE OBJECTIVES

5.1 GENERAL

The quality of measurements made during this study may be determined by the characteristics of: a) accuracy, b) precision, c) representativeness, d) completeness, and e) comparability. Optimal objectives for each characteristic are established to select sampling protocols, and to identify applicable documentation, sample handling procedures and measurement system procedures. These objectives are established based on site conditions, objectives of the project, and knowledge of available measurement systems. The subsequent use of these measurements in calculations and evaluations is also subjected to aspects of this QAPP as described in following sections.

All data will be collected by Jordan, and all samples will be collected by Jordan for analysis by an U.S. EPA Contract laboratory or CEC (as appropriate), except for those measurements made in the field such as pH, temperature, etc. Data collection, sample collection, and handling of samples in the field, will be in accordance with the protocols established in this QAPP. Because most of the samples collected during this project will be analyzed by a Contract Lab, the analytical quality assurance objectives for this project have been established by the U.S. EPA Contract Laboratory Program (CLP).

5.2 REPRESENTATIVENESS

Measurements will be made so that results are as representative as practicable of the media (e.g., air, soil, water) and the conditions being measured. Sampling protocols have been developed to ensure that samples collected are representative of the media as practicable. Sample handling protocols (e.g., storage, preservation and transportation) developed through the CLP will be followed to protect the integrity of the collected samples. Proper documentation, in accordance with CLP requirements, will establish that protocols have been followed and sample identification and integrity assured.

5.3 PRECISION AND ACCURACY

Precision, the ability to replicate a value, and accuracy, the ability to obtain a true value, are addressed and analytical data quality objectives established for each major parameter to be measured at the site. These objectives are based on prior knowledge of the capabilities of the measurement system to be employed and may not be construed as including sampling variability. The precision and accuracy requirements vary, dependent on their intended use. For example, a screening tool to identify the general extent of chemical distribution will not require the same precision and accuracy required to define the exact nature and amount of chemicals present at specific locations.

Calculations performed with the data generated are also checked for accuracy by the Task Leader or his designee, and precision, i.e., comparability of calculation techniques between tasks, is assured by the TPD.

5.4 COMPLETENESS

The characteristic of completeness is a measure of the amount of valid data obtained compared to the amount that was specified to be obtained under normal conditions. The amount of valid data specified is established based on the measurements required to accomplish project objectives. The number of samples or measurements to be obtained was defined in Section 3.3.4, although the number of charcoal tube samples to be collected during an expanded air survey has not been determined. This is because the need for the expanded program will not be apparent until field work begins. The extent of completeness must be reviewed on a relative basis for sample collection activities.

5.5 COMPARABILITY

The characteristic of comparability reflects both internal consistency of measurements made at the site and expression of results in units consistent with other organizations reporting similar data. Each value reported for a given measurement should be similar to other values within the same data set and within other related data sets. Comparability of data and measuring procedures must also be addressed. This characteristic implies operating within the calibrated range of an instrument and utilizing analytical methodologies which produce comparable results (e.g., data obtained for phenol (wet chemistry) is not comparable to data obtained for phenol (GC)). Measurements compared to similar measurements which appear as "outliers" will be reassessed. Units of measurement will be externally comparable by utilizing the appropriate standard units for each measurement system.

5.6 QUALITY ASSURANCE OBJECTIVES

For the Metamora Landfill Site Project, the overall quality assurance objectives are:

- to produce documented, traceable, and consistent field and analytical data;
- to collect sufficient field, sampler and trip blank samples and field duplicates to allow an assessment of sample representativeness and sample collection protocol precision;
- to analyze sufficient internal blanks, reference standards and matrix spike samples to allow an assessment of analytical precision and accuracy. Sufficiency of analytical QC procedures is specified by the referenced methods (see Section 9.2); and
- to produce a documented, consistent and technically defensible site investigation report.

6.0 SAMPLING PROCEDURES

6.1 GENERAL

The quality of sample collection techniques is assured by keying the technique used to both the media/matrix to be sampled and the analytes of interest. For example, samples intended for semi-volatile organic analyses are collected in glass bottles; samples for volatile organic analyses are collected in glass vials capped with Teflon septums with "zero" headspace to minimize diffusive and evaporative losses; and samples for inorganic analyses are collected in linear polyethylene bottles. Sample containers will be provided through the U.S. EPA CLP.

Sources of environmental samples also require specialized collection techniques to preserve their integrity and ensure that a representative portion of the source is collected. Media-specific sample collection techniques are specified in the following section in those instances where standard operating procedures are inappropriate.

The quality of data collection techniques used during geophysical investigations is assured by using the appropriate techniques for the project objectives and the site conditions. It is also important to understand the limitations of the technique, and to use quality control techniques (such as reverse shooting during seismic surveys) or supplemental geophysical methods (such as magnetometer in conjunction with metal detector). Because the methodologies and quality control procedures used during a geophysical survey are difficult to address in a QAPP, the geophysical surveys to be used during the Metamora project are discussed in Appendix A.

6.2 PREPARATION OF SAMPLE CONTAINERS

Air Samples. Air samples may be collected and analyzed during Task 9, Air Investigation, if it is deemed necessary during the RI. Air samples will also be collected during Task 13, the Pollutant Characterization Study. Samples will be collected on standard 50/100 mg activated charcoal sorbent tubes. These tubes are received from the manufacturer in pre-prepared, sealed, glass tubes.

Deep Soil, Surface Soil, and Sediment Samples. Deep soil samples will be collected during Task 11 (Soil/Soil Gas Sampling) and Task 14 (Monitoring Well Installation), and sediment samples and leachate-saturated surface soil samples will be collected during Task 16 (Surface Water and Sediment Sampling). These samples will be analyzed through the CLP, and they will also be analyzed onsite using a Photovac 10S50 portable gas chromatograph (see Appendix D). Sample containers for samples sent to a contract laboratory will be provided and prepared by the U.S. EPA CLP. The proposed containers are listed below:

1 x 8-oz. wide-mouth glass jar for extractable organics
2 x 120-ml. wide-mouth glass vials for volatile organics
1 x 8-oz. wide-mouth glass jar for metals analysis

All samples are expected to be low hazard samples, but if medium hazard samples are encountered, they will be sealed in metal paint cans.

Samples collected for onsite analysis with the 10S50 will be collected in 40-ml. VOA vials. These vials will be supplied by I-Chem. I-Chem prepares bottles in accordance with CLP protocol.

Soil Gas Samples. Soil gas samples will be collected during Task 11 (Soil/Soil Gas Sampling) and Task 12 (Soil Gas Sampling). These samples will be obtained through a stainless steel probe with tygon tubing, and then contained in a 500 ml., glass, gas sample bulb with Teflon stopcocks at both ends. If determined to be necessary, soil gas samples may be collected on Tenax tubes, which are prepared and sealed by the manufacturer.

Prior to sampling, and between samples, the gas sample bulbs will be prepared by flushing them with hydrocarbon-free air. Air samples from the flushed bulbs will be extracted and analyzed with the 10S50 prior to use to assure that no chemical residue exists. The stainless steel probe will be decontaminated with TSP and water, followed by a distilled water rinse. New tygon tubing will be used for each sample.

Soil gas samples will be extracted from the gas sampling bulbs with a syringe. Prior to use, and between samples, the syringes will be filled with hydrocarbon-free air which will be analyzed by using the 10S50 to assure that no chemical residue exists.

Waste Samples. Task 13, Pollutant Characterization, involves the collection of waste samples for analysis through the CLP for organics, inorganics and dioxin (i.e., 2,3,7,8-TCDD/TCDF and total PCDD/PCDF). Samples will also be analyzed for EP Toxicity (metals and organics) and PCBs by CEC (see Appendix B). GLE will be involved in the compatibility testing portion of the project (see Appendix C).

Samples to be sent to a contract laboratory will be placed in containers prepared by, and supplied through, the CLP. It is anticipated that all of these samples will be classified as high hazard samples. Each sample will be collected in two 8-oz. glass vials filled half full (one for extractable and volatile organics, and one for inorganics). For dioxin analysis, each sample will be collected in one 4-oz. wide-mouth glass jar. These procedures apply to both liquid and solid samples.

The samples to be analyzed for EP Toxicity metals, pesticides and herbicides and PCBs will be collected in containers prepared by I-Chem. Containers from I-Chem are prepared in accordance with CLP procedures. One 8-oz. wide-mouth glass jar will be used to contain each sample.

The samples to be compatibility tested will be collected in containers prepared by I-Chem. One 8-oz. wide-mouth glass jar will be used to contain each sample.

Groundwater and Surface Water Samples. Groundwater samples will be collected during Task 15 (Groundwater Sampling) and surface water samples will be collected during Task 16 (Surface Water and Sediment Sampling). Samples will be analyzed through the CLP and also onsite using the 10S50 portable gas chromatograph. Samples to be sent to a contract laboratory will be placed in containers prepared by, and supplied through, the CLP. All samples are expected to be low hazard.

Sample containers for surface water and groundwater are listed below:

2 x 80-oz. Amber glass bottles for extractable organics
2 x 40-ml. glass vials for volatile organics
1 x 1-Liter polyethylene bottle for metals

Samples to be analyzed onsite with the 10S50 will be collected in 40 ml. glass vials supplied by I-Chem.

6.3 SAMPLE SITE LOCATION

Sample site locations are normally planned before the sampling crew is mobilized. The rationale and purpose of each portion of the sampling plan is identified in the site Work Plan. To permit proper evaluation of the sample analysis results it is important that the actual location of the samples be properly documented.

The proposed sampling locations for groundwater, surface water, sediment, subsurface soils, soil gas and wastes are included in the Metamora Landfill Site Work Plan. Air sampling locations will be selected in the field as necessary.

A topographic map with a 200-foot grid system has been established at the Metamora Landfill site. Each stake within the grid system has been labeled with x, y and z (elevation) coordinates. All samples will be located in the field with stakes and/or flagging, and then located on the site base map by measuring from the nearest grid stake or other landmark shown on the base map.

6.4 AIR SAMPLING

The objectives and approach to air sampling are described in Jordan's "Standard Sampling and Sample Handling Procedures", Section 2.1 (p. 2-1).

At Metamora, short term air monitoring is expected to be used predominantly during RI activities. An explosimeter and a photoionization (PI) meter are anticipated to be the instruments used most frequently. However, if workers are advised to upgrade their level of protection to level B (modified level C is anticipated), ambient air samples will be collected and analyzed.

To do this, air sampling pumps (such as MSA Monitaire Samplers) will be equipped with standard 50/100 mg activated charcoal sorbent tubes, and placed at various locations at or near the apparent source of contamination. A pump will also be placed at a location within 15 feet of the source of release by taping or fastening it to a stake, tree or other stationary object. The pumps will run for a minimum of four hours before the tubes are removed from the samplers and transported to CEC for GC/MS analysis (see Appendix C).

A more extensive air quality survey will be initiated during Task 13, the Pollutant Characterization Study, because of the potential release of volatile organic chemicals during excavation. The purpose of this air quality survey will be to determine the impact of the excavation activities on onsite and offsite ambient air quality.

Four ambient air monitoring stations will be established at each of the areas to be investigated. A fifth station will be established downwind of the excavation at the site fenceline. Each station will consist of a calibrated MSA Samplair Air Pump (or equivalent) equipped with 50/100 mg MSA charcoal tubes. One station will be chosen to have two pumps in order to collected duplicate samples. Sampling will be conducted prior to commencement of the excavation activities to establish background air quality, and throughout each day during excavation activities. Samples will be packaged and transported to CEC at the end of each day for GC/MS analysis.

6.5 SOIL SAMPLING

Relatively deep, subsurface soil samples will be collected in split-spoons during Task 11 (Soil/Soil Gas sampling) and Task 15 (Monitoring Well Installation). The procedure for collecting soil samples in split-spoons is detailed in Section 4.2 (p. 4-2) of Jordan's "Standard Sampling and Sample Handling Procedures".

Surface soil samples (leachate-saturated soil samples) will be collected during Task 16 (Surface Water and Sediment Sampling). Procedures are described in Section 4.4 (p. 4-15) of Jordan's "Standard Sampling and Sample Handling Procedures".

Soil samples collected for analysis by a Contract Laboratory will be preserved and handled in accordance with CLP procedures documented in Table 5-1 of Jordan's "Standard Sampling and Sample Handling Procedures", p. 5-4.

6.6 SEDIMENT SAMPLING

Sediment samples will be collected during Task 16, Surface Water and Sediment Sampling. The procedure for collecting sediment samples is detailed in Section 4.5 (p. 4-16) of Jordan's "Standard Sampling and Sample Handling Procedures".

Sediment samples collected for analysis by a Contract Laboratory will be preserved and handled in accordance with CLP procedures documented in Table 5-1 of Jordan's "Standard Sampling and Sample Handling Procedures", p. 5-4.

6.7 SOIL GAS SAMPLING

Soil gas sampling procedures are not discussed in Jordan's "Standard Sampling and Sample Handling Procedures"; therefore, the methodology is discussed below.

Objective

To obtain samples of soil gas suitable for onsite chemical analysis. The analytical results are expected to indicate areas of groundwater contamination.

Approach

Soil gas samples will be collected during Task 11 (Soil/Soil Gas Sampling) to provide information on soil chemistry (i.e., type and degree of contamination) around two areas at the site where drums containing wastes are believed to be buried. Collecting these samples around areas where contamination is expected to be the most severe will indicate whether or not soil gas sampling will be useful at this site. If it is successful during Task 11, a Pilot Soil Gas Survey will be initiated. Sampling locations will be near existing groundwater monitoring wells where the severity of contamination has been documented during previous sampling events. If the pilot survey is successful, a full-scale Soil Gas Survey will be conducted over most of the site.

6.7.1 Sampling Procedure

Shallow soil gas samples will be collected by pounding a 1 to 1 1/2 inch I.D., stainless steel probe into the soil with a small sledge hammer. For deeper samples (at depths greater than 5 to 10 feet), a drilling rig with hollow stem augers will be used to drill boreholes. The probe will be lowered through the hollow stem augers, and then pushed into undisturbed soil (about 5 feet) with the drilling rig's hydraulic system.

The probe will consist of ten (or more) 5-foot sections and one 3-foot section, all of which thread together. The down-hole end of the probe will be tappered to a point to enable the probe to more easily penetrate the soil. Several small diameter openings (approximately 1/16 inch in diameter) will provide inlets for soil gas to enter the lower 1-foot section of the probe. Once the probe is in place, a reducer will be threaded onto the upper section, and small diameter (approximately 1/8 inch) tygon tubing will be connected to the reducer (see Figure 6-1). The other end of the tubing will connect to a 500 ml, glass, gas sample bulb with Teflon stopcocks at both eneds and a septum in the center. Tygon tubing, attached to a battery-powered vacuum pump, will be attached to the other end of the bulb, making the gas sample

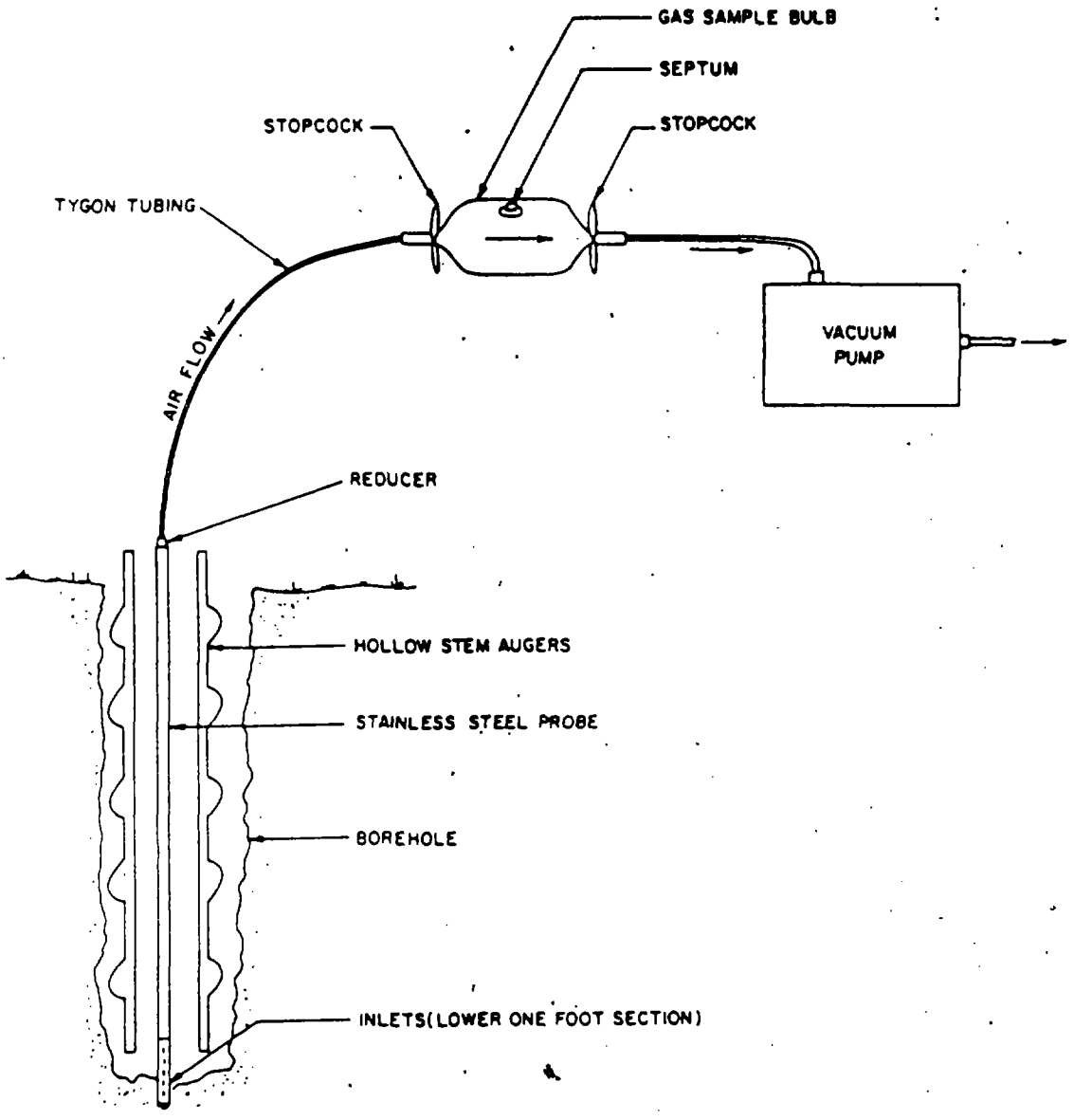

FIGURE 6-1
SCHEMATIC OF SOIL GAS SAMPLING SYSTEM
METAMORA LANDFILL

bulb "in-line" between the probe and the vacuum. A vacuum will be applied for 10 to 12 minutes to purge the probe, gas sample bulb, and tubing of ambient air. This represents approximately three air volumes, based on a vacuum rate of 1 liter/minute. After purging, the stopcocks will be shut to seal in the gas sample. The bulb will be disconnected from the tubing and trasnported to the field lab where the GC will be located. The sample will be extracted from the bulb through the septum with a syringe.

It is possible that soil gas samples may be collected on Tenax tubes as opposed to gas sampling bulbs. If Tenax tubes are used, they will simply be attached to the tygon tubing in place of the gas sample bulb after purging. Approximately 10 liters of air will be drawn through the tube. After the sample has been collected, the tube will be capped, labeled, and placed on ice for shipment to CEC's laboratory.

After obtaining a gas sample, the probe will be removed and the entire probe will be decontaminated with TSP and water, followed by a distilled water rinse. New tygon tubing will be used for each sample. The gas sample bulbs will be flushed with hydrocarbon-free air between samples by connecting them to a vacuum pump for about 2 minutes.

When measurable amounts of contamination are detected in a sample, the GC operator will extract and then analyze blank air samples from the air-flushed gas bulbs. This will also be done with the syringes. In this case, the syringe will simply be filled with hydrocarbon-free air and injected into the GC to assure that no residuals are present in the syringe. During the course of the survey, several blanks will also be run on the probe assembly to ensure that the decontamination procedures are effective and that cross-contamination is not occurring. This will be accomplished by pumping hydrocarbon-free air through the probe assembly after decon, using the same procedures followed for actual samples.

6.8 WASTE SAMPLING

The procedures used during test pitting operations are described in section 4.3 (p. 4-9) of Jordan's "Standard Sampling and Sample Handling Procedures". Section 4.3 provides information on general procedures and documentation during the development of a test pit. However, because sampling of unopened buried drums is excluded from the above-mentioned test pitting protocol, procedures for opening and sampling buried drums are described below.

Six test pits will be excavated in each of two areas at the Metamora Landfill. Magnetometer surveys have indicated that metallic objects are buried at these locations. As outlined in section 4.3, a backhoe will be used to excavate the test pits, and the backhoe's work will be directed by means of hand signals established prior to beginning work. When the backhoe is operating, only the individual directing the work will be allowed to approach the excavation. This individual will be stationed at a location where he and the operator are in visual contact and both can observe the excavation. Test pitting will be

initiated in an area free of buried metal, and will extend gradually inwards to the areas believed to contain metallic objects.
During the excavation process, if either the backhoe operator or the director observe possible buried drums, work will pause and a second backhoe, equipped with drum grappling equipment, will be moved into position. The director will then coordinate the efforts of the two operators in order to remove the drum from the excavation, and move it to an area where it can be placed in a recovery drum (if necessary) and sampled.

Each intact drum will be remotely opened by the operator of the second backhoe, which will be equipped with a drum puncturing devise (in addition to the drum grappling equipment). The efforts of the drum-puncturing operator will be directed by the senior member of a two person, drum staging/sampling crew. This crew will assist in the overpacking drums, obtaining samples, labeling the drums, and installing tops on the overpack drums.

After the drums have been punctured (due to incompatibilities, only one liquid-containing drum will be opened at a time), samples will be obtained with a glass dip-tube (for liquids), or a stainless steel dip-tube (for solids or sludges). Dip-tubes will be abandoned in their respective drums. Samples will be collected for onsite compatibility testing, and laboratory analysis (both CLP and CEC). Samples will be placed directly into the appropriate containers and labeled with the drum identification number. The outside of the sample containers will be decontaminated with TSP and water, and rinsed with distilled water before being transported to the compatibility testing lab or to the sample packaging area for shipment to a contract laboratory or CEC.

Waste samples collected for analysis by a Contract Laboratory will be preserved and handled according to CLP procedures for high hazard soil or water. These procedures are documented in Table 5-1 of Jordan's "Standard Sampling and Sample Handling Procedures", p. 5-4.

6.9 GROUNDWATER SAMPLING

Groundwater samples will be collected in accordance with Jordan's "Standard Sampling and Sample Handling Procedures", Section 3.2 (p. 3-4). Groundwater samples will be preserved and handled in accordance with CLP procedures (documented in Table 5-1 of Jordan's "Standard Sampling and Sample Handling Procedures", p. 5-4.

6.10 SURFACE WATER SAMPLING

Surface water samples will be collected in accordance with Jordan's "Standard Sampling and Sample Handling Procedures", Section 3.3 (p. 3-7). Surface water samples will be preserved and handled in accordance with CLP procedures (documented in Table 5-1 of Jordan's "Standard Sampling and Sample Handling Procedures", p. 5-4.

6.11 GEOPHYSICAL DATA COLLECTION

Three different geophysical techniques will be used at the Metamora Landfill Site: 1) seismic refraction; 2) electrical earth resistivity; and 3) magnetics. Seismic refraction will be used to determine the depth to the water table surface, the depth to the underlying clay layer, and the depth to bedrock. Electrical earth resistivity will be used to confirm the findings of the seismic refraction survey, and also to possibly define areas of inorganic groundwater contamination. The magnetometer survey will be used to define the location of buried metallic objects (presumably drums) at two onsite locations.

Geophysical techniques, instrumentation, data interpretation, and quality control procedures are discussed in Appendix A.

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Date September 29, 1986
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7.0 SAMPLE CUSTODY

Sample custody procedures established by EPA's CLP will be followed for all samples sent to an U.S. EPA Contract Lab. These procedures are described in Chapter III, sections C. and D. of "User's Guide to the Contract Laboratory Program". Traffic report forms, chain-of-custody forms, tags, and seals will be provided through the CLP.

For those samples being sent to CEC, chain-of-custody procedures specified in section 6 (p. 6-1) of Jordan's "Standard Sampling and Sample Handling Procedures" will be followed.

8.0 CALIBRATION PROCEDURES AND FREQUENCY

Instruments intended for field use during the Metamora Landfill Site RI include:

Tripar analyzer. See Jordan's "Standard Sampling and Sample Handling Procedures", section 8.2.3 (p. 8-9).

Photoionization meter. See Jordan's "Standard Sampling and Sample Handling Procedures", section 8.2.4 (p. 8-11).

National Mine Service Company MX241 Combustible/Oxygen Monitor. The procedures for calibration (which should be done everyday when the instrument is in use) are as follows:

1.) Switch the instrument on and allow the sensor to warm up for 15 minutes. In clean air, switch the instrument display to combustibles. Adjust the zero potentiometer (through the hole labeled "z") and obtain a readout of 000. (The instrument calibration potentiometers are accessed through holes in the end of the case top. To reveal these holes, loosen the knurled collar on the strap mounting post and swing aside the potentiometer access cover).

2.) Use the calibration cup (NMS P/N 1700-6933) to apply combustible gas of a known concentration to the instrument. The rate of gas flow should be 0.5 (± .05) liters per minute. Switch the instrument display to combustibles. Use the span potentiometer (through the hole labeled "s") to set the readout to the percent LEL corresponding to the known gas concentration. Variation in the flow rate will cause inaccurate calibration of the instrument.

3.) If the instrument cannot be calibrated, the span potentiometer may be at such a low setting that the instrument cannot respond properly. Turn the span potentiometer approximately 15 turns counterclockwise and then repeat the calibration procedure described above. Note that the calibration procedure calls for the adjustment of the zero potentiometer first. The span potentiometer should not be readjusted until the zero potentiometer is properly set.

4.) Remove the test gas and wait for approximately one minute for the gas to disperse. Check that the instrument readout returns to 000.

Radiation Alert Monitor 4. The procedures for instrument operation are as follows:

The radiation meter is factory-calibrated by a pulse generator and is typically ± 10% of full scale relative to Cesium 137. The monitor 4 is calibrated to ANSI standards by a certified laboratory.

The Monitor 4 detected the four main types of ionizing radiation: alpha, beta, gamma, and x-ray. It is calibrated for Cesium 137, but it also serves as an excellent indicator of relative intensities for other sources of ionizing radiation. The level of radiation for gamma and x-rays is measured in milli Roentgens per hour (mR/hr). Alpha and beta radiation are measured in counts per minute (CPM).

When using the Monitor 4, always keep the range switch in the xl position unless high levels of radiation are expected. If, while making a measurement, the meter goes off scale to the right, move the range switch to the next higher setting (x10 or x100). Note that the flashes from the count light and the audible beeps are progressively shorter in the x10 and x100 positions.

Battery life is up to 2,000 hours at background radiation levels. Frequently check the battery charge by moving the range switch to battery position and check the green-shaded scale. Should the battery need replacing, use one 9 volt alkaline battery and turn the monitor off before installing the battery.

ES-2415F Signal Enhancement Seismograph. See Appendix A.

Phillip R. Burger Model 1000D Vibration Seismograph. See Appendix A.

Keck Model No. IC-69 Earth Resistivity Instrument. See Appendix A.

Geometrics G-856 Proton Precession Magnetometer. See Appendix A.

EDA Omni IV Tie-line Magnetometer. See Appendix A.

Photovac 10S50 Portable Gas Chromatograph. See Appendix D.

9.0 ANALYTICAL PROCEDURES

9.1 SELECTION OF PARAMETERS

Laboratory analyses are scheduled for air, water, soil, waste and soil gas samples. The parameters to be analyzed are selected based on current information on contaminant wastes received at the site and previous environmental measurements. The selection rationale procedure illustrated in Table 9-1 is intended to simplify and streamline analytical programs by eliminating unnecessary analyses and assuring appropriate analysis for all required project data. Tables 9-2 and 9-3 indicate those parameters included in the CLP organics and inorganics analysis package. Contract required detection limits are also indicated.

A wide range of waste types are suspected of being disposed of at the Metamora site. Also, there is evidence that certain disposal areas had been burned in the past. Because of the potential of dioxin/furan wastes having been dumped at this site, and the potential of dioxins/furans having been formed during the burning episodes, selected soil and waste samples will be submitted to the CLP for dioxin/furan analysis (i.e., 2,3,7,8-TCDD/TCDF and total PCDD/PCDF).

9.2 SELECTION OF PROCEDURES

Procedures for sample analysis by the Contract Labs will be in accordance with the NCLP/Consensus Organics Protocol and the NCLP/Consensus Inorganics Protocol (IFB WA-85-J680 and IFB WA85-J838 respectively).

CEC will provide analytical assistance during this project by analyzing 1) air samples collected on charcoal tubes for organics; 2) soil gas samples collected on Tenax tubes for organics; 3) leachate (EP Toxicity) from waste samples for metals and organics; and 4) waste samples for PCBs. A summary of the analytical work to be provided by CEC is as follows:

Matrix	Analyte	Method	Reference
Air (charcoal)	Total hydrocarbons	GC/FID	NIOSH 127
Soil gas (Tenax)	Qualitative	GC/MS	TO-1 EPA-600/4-84-041
Leachate (EP Toxicity)	Metals	AA	EPA SW-846
	Pesticides	GC/ECD	EPA SW-846
	Herbicides	GC/ECD	EPA SW-846
Waste	PCBs	GC/ECD	EPA SW-846

GLE will provide on onsite laboratory and chemist to conduct compatibility tests during Task 13, Pollutant Characterization Study. Test procedures are included in Appendix B.

TABLE 9-2

HAZARDOUS SUBSTANCE LIST (HSL) ORGANICS AND
CONTRACT REQUIRED DETECTION LIMITS (CRDL)**
(ref. IFB WA-85-J680)

Volatiles	CAS Number	Detection Limits* Low Water ug/L	Low Soil/Sediment 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. trans-1,2-Dichloroethene	156-60-5	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. 1,1,2,2-Tetrachloroethane	79-34-5	5	5
19. 1,2-Dichloropropane	78-87-5	5	5
20. trans-1,3-Dichloropropene	10061-02-6	5	5
21. Trichloroethene	79-01-6	5	5
22. Dibromochloromethane	124-48-1	5	5
23. 1,1,2-Trichloroethane	79-00-5	5	5
24. Benzene	71-43-2	5	5
25. cis-1,3-Dichloropropene	10061-01-5	5	5

Volatiles	CAS Number	Detection Limits* Low Water[a] ug/L	Low Soil/Sediment[b] ug/Kg
26. 2-Chloroethyl Vinyl Ether	110-75-8	10	10
27. Bromoform	75-25-2	5	5
28. 2-Hexanone	591-78-6	10	10
29. 4-Methyl-2-pentanone	108-10-1	10	10
30. Tetrachloroethene	127-18-4	5	5
31. Toluene	108-88-3	5	5
32. Chlorobenzene	108-90-7	5	5
33. Ethyl Benzene	100-41-4	5	5
34. Styrene	100-42-5	5	5
35. Total Xylenes		5	5

[a] Medium Water Contract Required Detection Limits (CRDL) for Volatile HSL Compounds are 100 times the individual Low Water CRDL.

[b] Medium Soil/Sediment Contract Required Detection Limits (CRDL) for Volatile HSL Compounds are 100 times the individual Low Soil/Sediment CRDL.

Semi-Volatiles	CAS Number	Detection Limits* Low Water** ug/L	Low Soil Sediment** ug/kg
36. Phenol	108-95-2	10	330
37. bis(2-Chloroethyl) ether	111-44-4	10	330
38. 2-Chlorophenol	95-57-8	10	330
39. 1,3-Dichlorobenzene	541-73-1	10	330
40. 1,4-Dichlorobenzene	106-46-7	10	330
41. Benzyl Alcohol	100-51-6	10	330
42. 1,2-Dichlorobenzene	95-50-1	10	330
43. 2-Methylphenol	95-48-7	10	330
44. bis(2-Chloroisopropyl) ether	39638-32-9	10	330
45. 4-Methylphenol	106-44-5	10	330
46. N-Nitroso-Dipropylamine	621-64-7	10	330
47. Hexachloroethane	67-72-1	10	330
48. Nitrobenzene	98-95-3	10	330
49. Isophorone	78-59-1	10	330
50. 2-Nitrophenol	88-75-5	10	330
51. 2,4-Dimethylphenol	105-67-9	10	330
52. Benzoic Acid	65-85-0	50	1600
53. bis(2-Chloroethoxy) methane	111-91-1	10	330
54. 2,4-Dichloropnenol	120-83-2	10	330
55. 1,2,4-Trichlorobenzene	120-82-1	10	330
56. Naphthalene	91-20-3	10	330
57. 4-Chloroaniline	106-47-8	10	330
58. Hexachlorobutadiene	87-68-3	10	330
59. 4-Chloro-3-methylphenol (para-chloro-meta-cresol)	59-50-7	10	330
60. 2-Methylnaphthalene	91-57-6	10	330
61. Hexachlorocyclopentadiene	77-47-4	10	330
62. 2,4,6-Trichlorophenol	88-06-2	10	330
63. 2,4,5-Trichlorophenol	95-95-4	50	1600

Semi-Volatiles	CAS Number	Detection Limits[a] Low Water[b] ug/L	Low Soil/Sediment[c] ug/kg
64. 2-Chloronaphthalene	91-58-7	10	330
65. 2-Nitroaniline	88-74-4	50	1600
66. Dimethyl Phthalate	131-11-3	10	330
67. Acenaphthylene	208-96-8	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. 2,6-Dinitrotoluene	606-20-2	10	330
75. Diethylphthalate	84-66-2	10	330
76. 4-Chlorophenyl Phenyl ether	7005-72-3	10	330
77. Fluorene	86-73-7	10	330
78. 4-Nitroaniline	100-01-6	50	1600
79. 4,6-Dinitro-2-methylphenol	534-52-1	50	1600
80. N-nitrosodiphenylamine	86-30-6	10	330
81. 4-Bromophenyl Phenyl ether	101-55-3	10	330
82. Hexachlorobenzene	118-74-1	10	330
83. Pentachlorophenol	87-86-5	50	1600
84. Phenanthrene	85-01-8	10	330
85. Anthracene	120-12-7	10	330
86. Di-n-butylphthalate	84-74-2	10	330
87. Fluoranthene	206-44-0	10	330
88. Pyrene	129-00-0	10	330
89. Butyl Benzyl Phthalate	85-68-7	10	330
90. 3,3'-Dichlorobenzidine	91-94-1	20	660
91. Benzo(a)anthracene	56-55-3	10	330
92. bis(2-ethylhexyl)phthalate	117-81-7	10	330
93. Chrysene	218-01-9	10	330
94. Di-n-octyl Phthalate	117-84-0	10	330
95. Benzo(b)fluoranthene	205-99-2	10	330
96. Benzo(k)fluoranthene	207-08-9	10	330
97. Benzo(a)pyrene	50-32-8	10	330

Semi-Volatiles	CAS Number	Detection Limits* Low Water[c] ug/L	Low Soil/Sediment[d] ug/Kg
98. Indeno(1,2,3-cd)pyrene	193-39-5	10	330
99. Dibenz(a,h)anthracene	53-70-3	10	330
100. Benzo(g,h,i)perylene	191-24-2	10	330

[c]Medium Water Contract Required Detection Limits (CRDL) for Semi-Volatile HSL Compounds are 100 times the individual Low Water CRDL.

[d]Medium Soil Sediment Contract Required Detection Limits (CRDL) for Semi-Volatile HSL Compounds are 60 times the individual Low Soil/Sediment CRDL.

Pesticides	CAS Number	Detection Limits* Low Water[e] ug/L	Low Soil/Sediment[f] ug/Kg
101. alpha-BHC	319-84-6	0.05	8.0
102. beta-BHC	319-85-7	0.05	8.0
103. delta-BHC	319-86-8	0.05	8.0
104. gamma-BHC (Lindane)	58-89-9	0.05	8.0
105. Heptachlor	76-44-8	0.05	8.0
106. Aldrin	309-00-2	0.05	8.0
107. Heptachlor Epoxide	1024-57-3	0.05	8.0
108. Endosulfan I	959-98-8	0.05	8.0
109. Dieldrin	60-57-1	0.10	16.0
110. 4,4'-DDE	72-55-9	0.10	16.0
111. Endrin	72-20-8	0.10	16.0
112. Endosulfan II	33213-65-9	0.10	16.0
113. 4,4'-DDD	72-54-8	0.10	16.0
114. Endosulfan Sulfate	1031-07-8	0.10	16.0
115. 4,4'-DDT	50-29-3	0.10	16.0
116. Endrin Ketone	53494-70-5	0.10	16.0
117. Methoxychlor	72-43-5	0.5	80.0
118. Chlordane	57-74-9	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

[e]Medium Water Contract Required Detection Limits (CRDL) for Pesticide HSL Compounds are 100 times the individual Low Water CRDL.

[f]Medium Soil/Sediment Contract Required Detection Limits (CRDL) for Pesticide HSL compounds are 15 times the individual Low Soil/Sediment CRDL.

*Detection limits listed for soil/sediment are based on wet weight. The detection limits calculated by the laboratory for soil/sediment, calculated on dry weight basis, as required by the contract, will be higher.

** Specific detection limits are highly matrix dependent. The detection limits listed herein are provided for guidance and may not always be achievable.

TABLE 9-3
INORGANIC PARAMETERS AND
CONTRACT REQUIRED DETECTION LIMITS
(ref. IFB WA85-J838)

Element	Contract Required Detection Level[1,2] (ug/L)
Aluminum	200
Antimony	60
Arsenic	10
Barium	200
Beryllium	5
CAdmium	5
Calcium	5000
Chromium	10
Cobalt	50
Copper	25
Cyanide	10
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

1: Any analytical method specified in SOW Exhibit D may be utilized as long as the documented instrument or method detection limits meet the Contract Required Detection Level (CRDL) requirements. Higher detection levels may only be used in the following circumstance:

If the sample concentration exceeds two 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 level. This is illustrated in the example below:

For lead:
Method in use = ICP
Instrument Detection Limit (IDL) = 40
Sample concentration = 85
Contract Required Detection Level (CRDL) = 5

The value of 85 may be reported even though instrument detection limit is greater than required detection level. The instrument or method detection limit must be documented as described in Exhibit E.

2: These CRDL are the instrument detection limits obtained in pure water that must be met using the procedure in Exhibit E. The detection limits for samples may be considerably higher depending on the sample matrix.

10. DATA REDUCTION, VALIDATION AND REPORTING

Data reduction is the process of converting measurement system outputs to an expression of the parameter which is consistent with the comparability objectives (outlined in Section 5). Calculations made during data reduction by a Contract lab, CEC or Jordan, are described in the U.S. EPA analytical methods.

Validation of measurements is a systematic process of reviewing a body of data to provide assurance that the data are adequate for their intended use. The process includes the following activities:

- o auditing measurement system calibration and calibration verification;
- o auditing quality control activities;
- o screening data sets for outliers;
- o reviewing data for technical credibility vs. the sample site setting;
- o auditing field sample data records and chain-of-custody;
- o checking intermediate calculations; and
- o certifying the process above.

Data validation activities will be documented and records kept of any necessary corrective or remedial action. Laboratory reports of data are edited by comparing with original calculations. Subsequent data tabulations are edited by comparing with the laboratory reports. The data is screened to determine compliance with the quality assurance objectives identified in Section 5.

Jordan's Environmental Laboratory routinely participates in and successfully completes performance audits using reference samples provided by U.S. EPA and other regulatory authorities. Results of these audits will assist in validating the data reported. In addition, system audits of laboratory procedures and data management are conducted by the QAC. Results reported for each sample are verified to assure proper identification by comparing the original sample collection log sheets with chain-of-custody forms and laboratory log books, when possible.

The Contract labs will follow the data reduction, validating and reporting protocol documented by the CLP.

11.0 INTERNAL QUALITY CONTROL

11.1 MEASUREMENT SYSTEMS

Quality control procedures are established for laboratory and field activities. Procedures used in U.S. EPA Contract laboratories, such as analytical duplicates, matrix spike samples, blanks, control charts, internal standards, surrogates and reagent checks are described in detail in the specified analytical methods outlined by the CLP. Special samples to be submitted to the Contract labs for the Metamora Landfill Site RI include:

Type	Media	Number
VOA trip blanks	Water	9
blind replicates	Soil	5
	Water	9
sampler blanks	Water	3
filtration blanks	Water	6

These samples provide a quantitative basis for validating the data reported. Each is described in detail in Section 9 of Jordan's "Standard Sampling and Sample Handling Procedures".

11.2 QUALITY REVIEW OF STUDIES AND REPORTS

The purpose of quality reviews through the course of studies, designs and reports is to ensure that the service, designs and documents produced by each department meet currently accepted professional standards. The level of effort for each project will vary depending on type of project, duration and size. Review of small projects entails periodic discussions between production staff and discipline managers. Quality control on larger projects requires that a review team be selected for more frequent meetings and discussions. Quality control reviews are scheduled on a routine basis, but the option of holding a quality control review at any time is always open.

The time required to plan, schedule, and conduct quality control reviews is considered part of all other design, writing and checking phases of a project. While quality control activities are continuous, each project is divided into phases for quality control reviews. At each phase, the review should include client goals, contractual commitments, technical merit, timing, budget, assignment of appropriate personnel, department coordination, project problem resolution, documentation, and consistency with company policy. Key elements to the success of any quality control review are identification of problem areas, communication to implement solutions, and follow-up.

Quality control during the preparation of studies and reports relies on documentation of data utilized and peer review of conclusions drawn from the assembled data base. The comparability objective established for the project is of particular importance when data are derived from many sources (i.e., the data base is comprised of secondary measurements). Documentation of secondary data typically is accomplished via data verification/tracking checklists with accompanying written criteria describing "acceptable" data to ensure consistency in data selection. This allows all data base components to be traced to the primary generator and forces a review of data quality as the data base is developed. All project personnel are responsible for utilization and monitoring of this process; compliance is audited by the QAC. Upon completion of the data base, data interpretation, evaluation, and report preparation commence. Interpretation may require consultation with Jordan's statistician and/or use of computerized statistical routines. Documentation is also prepared for statistical manipulation methodologies. Data evaluations incorporate peer review to provide broad-based insight to data correlations and interactions.

To enhance the professional quality of the company's studies and reports, the discipline manager will also:

- require that reports refer to and are consistent in scope with the project proposal and contract; and
- require that report language and contents be chosen to foster client's understanding of risks and uncertainties by distinguishing fact from opinion and identifying risks and limitations in a clear and informative manner.

It is anticipated that quality control reviews for the Metamora Landfill Site RI will occur at the following project phases:

- Work Plan Preparation;
- Quality Assurance Project Plan preparation;
- Description of current situation;
- Health and Safety Plan;
- Preinvestigative Evaluation
- RI Report
- Response Objectives
  Remedial Alternatives
- Conceptual Design
- FS Report

12.0 AUDITS

Quality assurance audits are performed to assure and document that quality control measures are being utilized to provide data of acceptable quality and that subsequent calculations, interpretation and other project outputs are checked and validated.

System and performance audits may be conducted by the Quality Assurance Coordinator (QAC). The Quality Review Team (QRT) will conduct project reviews of interpretations and reports which are based on the measurement system outputs. If any of the procedures to assess precision and accuracy described in Section 14.2 indicate potential data problems, an audit may be initiated.

12.1 SYSTEMS AUDIT

A system audit may be conducted on all components of measurement systems to determine proper selection and utilization. The systems audit includes evaluation of both field and laboratory procedures.

Organization and Personnel. The project organization is reviewed for compliance with the proposed organization and for clarity of assigned responsibility. Personnel assigned to the project will be reviewed to determine that assigned responsibility, skill and training of the personnel are properly matched. The Technical Director maintains firsthand knowledge of his team's capabilities and will discuss the organization's efficacy with the QAC. Assigned personnel may be interviewed by the QAC during an audit.

Facilities and Equipment. The audit will address whether field tools and analytical instruments are selected and used to meet requirements specified by the project objectives stated in the QAPP. Equipment and facilities provided for personnel health and safety will also be evaluated. Calibration and documentation procedures for instruments used in the field will receive special attention.

Analytical Methodology. Routine external performance evaluations as well as blind internal performance evaluations are generally conducted. A review of analytical methodology in regard to the data requirements for the project will also be performed. An on-site observation of analyst technique, data reduction and record keeping may be performed if determined necessary. Periodic review of precision and accuracy data is essential.

Sampling and Sample Handling Procedure. An audit of scheduled samples vs samples collected vs samples received for analysis may be performed. Field documentation will be reviewed. If deemed necessary, a site visit will be made to assure that designated control procedures are practiced during sampling activities.

Data Handling. During a system audit, the QAC will review data handling procedures with the TD and Task Leaders. Accuracy, consistency, documentation and appropriate selection of methodologies will be discussed.

12.2 PERFORMANCE AUDIT

These audits are intended primarily for analytical and data generation systems.

12.3 PROJECT AUDIT

Project audits encompass the aspects of both the systems audit and the performance audit. The project audit typically occurs at least once for a short-term project and twice or more often during long-term projects. Timing is keyed to the systems involved and the project objectives.

It is currently anticipated that one project audit will occur for the Metamora Landfill Site RI.

12.4 QA AUDIT REPORT

A written report of the QA audit may be prepared to include:

- an assessment of project team status in each of the major project areas;
- clear statements of areas requiring improvement or problems to be corrected. Recommendation and assistance will be provided regarding proposed corrective actions or system improvements. If no action is required, the report will state that the QA audit was satisfactorily completed;
- a timetable for any corrective action required; and
- a follow-up to assure that recommendations have been implemented.

Figure 12-1 provides an example Quality Assurance Audit Report.

FIGURE 12-1

QUALITY ASSURANCE AUDIT REPORT

Project:_____

Project No.:_____ Quality Assurance Coordinator:_____

Project Aspects Audited:_____

Laboratory/Technical Director:_____

Audit Conducted By:_____ for the period _____ to _____

Date of Audit:_____

Personnel Interviewed:_____

Objectives of the Project Aspects Audited

Sampling and Analytical Requirements

QUALITY ASSURANCE AUDIT REPORT

ADEQUACY/APPROPRIATENESS OF:

Organization and Personnel

Facilities Utilized

Analytical Methodologies

QUALITY ASSURANCE AUDIT REPORT

ADEQUACY/APPROPRIATENESS OF:

Sampling and Sample Handling

Data Handling

Quality Control Measures Utilized

QUALITY ASSURANCE AUDIT REPORT

Quality Assurance Deficiencies

Recommended Corrective Actions and Schedule

Signed Date

Title

Distribution:

Reviewed by Date

Title

13.0 PREVENTIVE MAINTENANCE

13.1 ANALYTICAL INSTRUMENTATION

Preventive maintenance for analytical instrumentation is outlined in the protocol established by the U.S. EPA CLP.

13.2 FIELD INSTRUMENTS

Preventive maintenance of field equipment is performed by analysts and staging area staff and routinely precedes each sampling event; more extensive maintenance is performed on the basis of hours in use. Sampling crews report on the performance of the equipment after each sampling event. Critical spare parts are kept in stock.

14.0 DATA ASSESSMENT

14.1 GENERAL

The purpose of data quality assessment is to assure that data generated under the program are accurate and consistent with project objectives. The quality of data will be assessed based on the precision, accuracy, consistency and completeness of the data that are measured or generated.

Data quality assessment will be conducted in three phases:

Phase 1

Prior to data collection, sampling and analysis procedures are evaluated in regard to their ability to generate the appropriate, technically acceptable information required to achieve project objectives. This QAPP meets this requirement by establishing project objectives defined in terms of parameters, analytical methods, and required sampling protocols.

Phase 2

During data collection, results will be assessed to assure that the selected procedures are efficient and effective and that the data generated provide sufficient information to achieve project objectives. Precision and accuracy of measurement systems will also be evaluated. In general, evaluation of data will be based on performance audits, results of duplicate and spiked sample analyses, and review of completeness objectives.

Documentation may include:

- o number of replicate samples collected;
- o number of replicate, spike and field blank samples analyzed;
- o identification of statistical techniques, if used, to measure central tendency, dispersion, or testing for outliers;
- o use of historical data and its reference; and
- o identification of analytical method.

Dr. Bruce K. Wallin, Technical Director of Jordan's Analytical Laboratory, and Jordan staff under his supervision, will be responsible for any additional evaluation required of data packages.

Phase 3

Throughout the data collection activities, an assessment of the adequacy of the data base generated in regard to completing project objectives will be

undertaken throughout each phase of site work. Recommendations for improved quality control will be developed, if appropriate. In the event that data gaps are identified, the QAC, TPD or QRT may recommend the collection of additional raw data to fully support the project's findings and recommendations.

14.2 PROCEDURES TO ASSESS PRECISION AND ACCURACY

Assessment of precision and accuracy of analytical data is accomplished via review of duplicate analyses (precision) and surrogate spike recovery (accuracy) both in reagent water and sample matrices. Precision is generally expressed as the coefficient of variation (CV). Accuracy is expressed as percent recovery. Precision must be assessed for each matrix since distribution of contaminants may be non-homogeneous, especially in non-water matrices. Precision in samples must be reviewed with knowledge of the matrix and level of analyte present. Corrective action or documentation of substandard precision is a laboratory responsibility. Accuracy, too, must recognize the impact of matrix interferences. Optional surrogate/spike recoveries are generally specified by the analytical method for reagent water under defined conditions. Each method which provides quality control requirements and acceptance criteria also specifies the method of generating the data to be reviewed. It is the laboratory's responsibility to attempt to identify the source of substandard recoveries and either take corrective action or document the cause.

Calculations are presented below:

$$\%R = \frac{\text{observed value}}{\text{theoretical value}} \times 100$$

$$CV = (S/X) \times 100$$

where $\%R$ = percent recovery

CV = coefficient of variation

S = sample standard deviation

X = mean value of data set

Completeness is generally assessed as a percentage of data intended to be generated, and is most often utilized in Phase 3 of the data assessment process.

15.0 CORRECTIVE ACTION

Corrective or preventive action is required when potential or existing conditions are identified that may have an adverse impact on data quantity or quality. Corrective action could be immediate or long-term. In general any member of the program staff who identifies a condition adversely affecting quality can initiate corrective action by notifying his or her supervisor and the QAC. The written communication will identify the condition and explain how it may affect data quality or quantity.

15.1 IMMEDIATE CORRECTIVE ACTION

This type of corrective action is usually applied to spontaneous, non-recurring problems, such as an instrument malfunction. The individual who detects or suspects nonconformance to previously established criteria or protocol in equipment, instruments, data, methods, etc., will immediately notify his/her supervisor. The supervisor and the appropriate task leader will then investigate the extent of the problem and take the necessary corrective steps. If a large quantity of data is affected, the task leader must prepare a memorandum to the Project Manager and the QAC. These individuals will collectively decide how to proceed. If the problem is limited in scope, the task leader will decide on the corrective action measure, document the solution in the appropriate workbook and notify the Project Manager and the QAC in memorandum form.

15.2 LONG-TERM CORRECTIVE ACTION

Long-term corrective action procedures are devised and implemented to prevent the recurrence of a potentially serious problem. The QAC will be notified of the problem and will conduct an investigation to determine the cause, severity and extent of the problem. The QAC will then file a corrective action request with the Project Manager.

In case of dispute between the QAC and the PM, the Responsible Corporate Officer (RCO) will make a final determination for the company.

Corrective actions may also be initiated as a result of other activities, including:

- Performance Audits;
- System Audits;
- Laboratory/field comparison studies; and
- QA program audits.

The QAC will be responsible for documenting all notifications, recommendations, and final decisions. The PM and the QAC will be jointly responsible for notifying program staff and implementing the agreed upon course of action. The QAC will be responsible for verifying the efficacy of the implemented actions. The development and implementation of preventive and corrective actions will be timed so as to not adversely impact either project schedules or subsequent data generation/processing activities to the extent possible. The QAC will also be responsible for developing and implementing routine program controls to minimize the need for corrective action.

16.0 REPORTS TO MANAGEMENT

Summary reports are prepared on a periodic basis to inform management of project status. The reports will include:

- o periodic assessment of measurement data accuracy, precision and completeness;
- o results of performance audits and/or systems audits;
- o significant QA problems and recommended solutions; and
- o status of solutions to any problems previously identified.

In most cases, these reports may be included in monthly project progress reports or the QA Audit Report illustrated in Section 12 may be prepared. Additionally, any incidents requiring corrective action will be fully documented. Procedurally, the QAC will prepare the reports to management. These reports will be addressed to the PM and the Quality Assurance Officer, in addition to the MDNR Project Administrator. The summary of findings shall be factual, concise and complete. Any required supporting information will be appended to the report.

APPENDIX A

GEOPHYSICAL DATA COLLECTION

Three different geophysical techniques will be used at the Metamora Landfill Site: 1) seismic refraction; 2) electrical earth resistivity; and 3) magnetics. Seismic refraction will be used to determine the depth to the water table surface, the depth to the underlying clay layer, and the depth to bedrock. Electrical earth resistivity will be used to confirm the findings of the seismic refraction survey, and also to possibly define areas of inorganic groundwater contamination. The magnetometer survey will be used to define the location of buried metallic objects (presumably drums) at two onsite locations.

Because it is difficult to incorporate the different aspects of geophysical surveys into the main body of a QAPP, this appendix was compiled to make it easier for the reviewer to understand. The following paragraphs include a discussion of the principles, instrumentation, field techniques (including those techniques used to check the data for quality), interpretation, and instrument calibration for each geophysical technique to be used at the Metamora site.

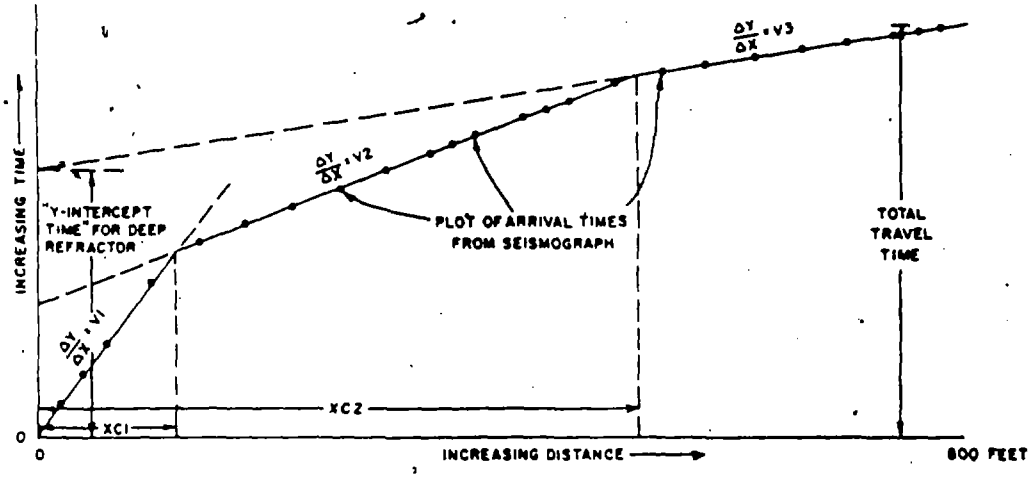
SEISMIC REFRACTION

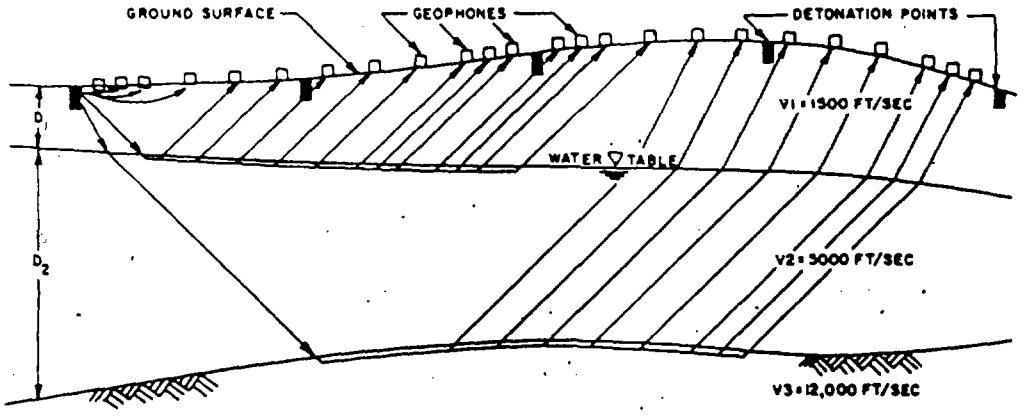
A major factor in quality control of a geophysical survey is the pilot survey. A pilot survey is virtually always conducted prior to a full-scale survey to assure that the method is appropriate for the site conditions and the objectives of the project, and thus will generate good quality data. A pilot survey, consisting of 3,200 linear feet of seismic refraction profiling, will be conducted at the Metamora site prior to the initiation of a full-scale survey which consists of 19,200 linear feet of profiling.

Principles. The principles of seismic refraction are illustrated on Figure AA-1. The technique is an indirect means of determining the depths to a refracting horizon and the thicknesses of major seismic discontinuities overlying a high-velocity refracting horizon.

It is essential to measure the elapsed time of travel for elastic waves from a point source of energy to a series of sensitive listening devices. These listening devices are called geophones, or seismometers, and are spaced at known intervals along a straight line on the ground surface. They are connected to the seismograph by seismic spread cables which are fitted with connectors for the geophones. This instrument array is called a seismic spread.

The seismic waves detected in a seismic refraction survey and used for depth calculations and the identification of materials is called a "P" (compressional) wave. This wave is transmitted through earth materials as a series of compressions and rarefactions. Just as light is bent through a prism (refraction), soundwaves which travel through various earth media are also bent as they travel deeper into the earth. Because they are bent, they eventually return to the surface as refracted seismic waves. If one carefully measures the transit times between the energy source and each geophone, in addition to knowing the distance between the energy source and each geophone,





$$D1 = (XC1/2) * K1$$

$$D2 = (XC2/2) * K2 + D1(K3) \quad \text{where:}$$

$$K1 = ((V2 - V1)/(V2 + V1))^{1/2}$$

$$K2 = ((V3 - V2)/(V3 + V2))^{1/2}$$

$$K3 = (V3 * (V2^2 - V1^2)^{1/2} - V2 * (V3^2 - V1^2)^{1/2}/(V1 * (V3^2 - V2^2)^{1/2})$$

SEISMIC REFRACTION TECHNIQUE

FIGURE AA-1

ECJORDANCO

one can interpret subsurface structure. The thicknesses and velocity values of various soil and rock layers can be computed. In the same manner, seismologists have learned about the interior of the earth by carefully measuring the arrival of seismic waves generated by distant earthquakes.

Instrumentation. The seismic refraction system centers around a seismograph, which is a series of amplifiers (one per geophone) and a device to record the seismic waves, or vibrations at each geophone as a function of time. The system also includes seismic spread cables, an energy source, and the array of geophones. Modern seismographs have the capability of "stacking" or digitally summing the vibrations from multiple events created by an energy source at one location. This capability is referred to as "signal enhancement" and greatly improves data quality under some conditions permitting more reliable interpretation.

Field Techniques. Seismic cables, which have been fabricated with premeasured shotpoint and geophone locations, are positioned along the lines of investigation. Geophones, which have been fitted with a spiked base so as to provide good ground contact, are emplaced at their measured locations. Seismic energy is generated with either a weight impact (sledge hammer) or small buried charges of explosives. If explosives are used, as will be the case at Metamora, shotholes are usually prepared with a driven rod or portable drilling device so as to insure good ground coupling. The explosives are tightly tamped and the depths and amount of explosives used are recorded.

Seismograms are obtained with a portable signal enhancement seismograph which records the wave arrivals from the energy source along the seismic spread, acquiring separate data for each geophone position. Timing lines are provided across the entire recording allowing direct reading of wave arrivals to an accuracy of one millisecond or better. The signal enhancement capability refers to the ability of the instrument to record the seismic waves from several impacts (or explosions), add them electronically, and retain this data in its internal digital memory for later processing and interpretation. The enhanced signal improves data quality and greatly facilitates interpretation.

Generally, several recordings are obtained along each seismic spread; seismographs are generated with the energy source at each end, and others may be obtained by energy generation in the middle, and at other positions along an individual spread as necessary. Continuous profiling is accomplished by having an end shotpoint of one seismic spread coincident with an end or intermediate position shot point of the succeeding spread.

The length of each spread is determined by the required depth of penetration. Seismic spreads of varying lengths can be used in a study; the deeper the required penetration, the longer the spread must be. At Metamora, each seismic spread will be 800 feet long, and for each there will be five detonations at an interval of 200 feet. This will ensure that each seismic spread is reversed (a technique referred to as reverse shooting), and also internally reversed several times for each seismic spread. This procedure is extremely valuable for evaluating data quality because it allows the interpreter to continuously monitor common parameters such as total travel time (i.e., the time of travel of a seismic wave from point A to point B should equal the time of travel from point B to point A), and "y-intercept" time, which is the intercept time on the y-axis for the intercepted "line of

best fit" for time arrivals due to a refracting horizon on a time vs. distance graph. The concepts of "total time" and "y-intercept time" are illustrated on Figure AA-1.

In addition to the five detonations along each seismic spread noted above, there will be an additional "offset" detonation 800 feet off each end of a spread to insure that the deepest refracting horizon is defined with adequate detail. The 40-foot spacing which will be used between geophones will provide good resolution of subsurface seismic layers but will still allow for adequate definition of the deepest refractor with offset shooting. Multiple data sets (detonations) on a single seismic spread also allow an evaluation of the consistency of patterns of "later" arrivals. These can be caused by either undulations of deeper horizons, or, more commonly, by variations in surface topography or seismic velocity changes in the surficial overburden layer.

During the seismic refraction survey at Metamora, the quality of the data will be evaluated in the field in two ways. As data is generated, it will be evaluated subjectively for quality by a careful examination of each individual seismogram. Seismograms of poor quality (perhaps due to outside disturbances such as airplanes, heavy trucks, etc.) will be re-generated. In addition, at the end of each field day, the travel time arrivals will be read by a qualified geophysicist and hand-plotted as a time-distance graph for further evaluation and interpretation.

Interpretation. The data are interpreted by first accurately measuring the individual transit times at each geophone position, then constructing a graph of these times versus their distance from the energy source. The geophysicist then determines by inspection of the time-distance graphs the number of subsurface layers present. Straight line segments of best fit are drawn onto the graph, each layer being represented by a line of different slope. The inverse of the slope of each line is equivalent to the (apparent) velocity value for each layer. The distance from the origin (or energy source) of the "crossover point" between two layers is proportional to the thickness of the overlying layer. A wavefront diagram, seismogram, and corresponding time-distance plot are shown on Figure AA-1. Standard formuli are also included on Figure AA-1 for both 2- and 3-layer cases, although, theoretically, one can obtain a solution for many layers.

The general identification of various materials can often be made if the seismic velocity values are known. Identifications should be based on findings from other engineering studies with similar geologic conditions and on correlations with various test borings taken near seismic lines. At Metamora, the findings of the seismic refraction survey will be compared to geologic materials and layer thicknesses encountered during soil-test borings, and the data from the resistivity survey.

Instrument Calibration. The instruments to be used at Metamora, and their procedures for calibration, are described as follows:

ES-2415F Signal Enhancement Seismograph - This instrument is calibrated by the manufacture prior to purchase and is not calibrated in the field.

Phillip R. Burger Model 1000D Vibration Seismograph - This instrument is calibrated by the manufacture prior to purchase and is not calibrated in the field. The instrument resets itself prior to the initiation of each blast.

ELECTRICAL EARTH RESISTIVITY

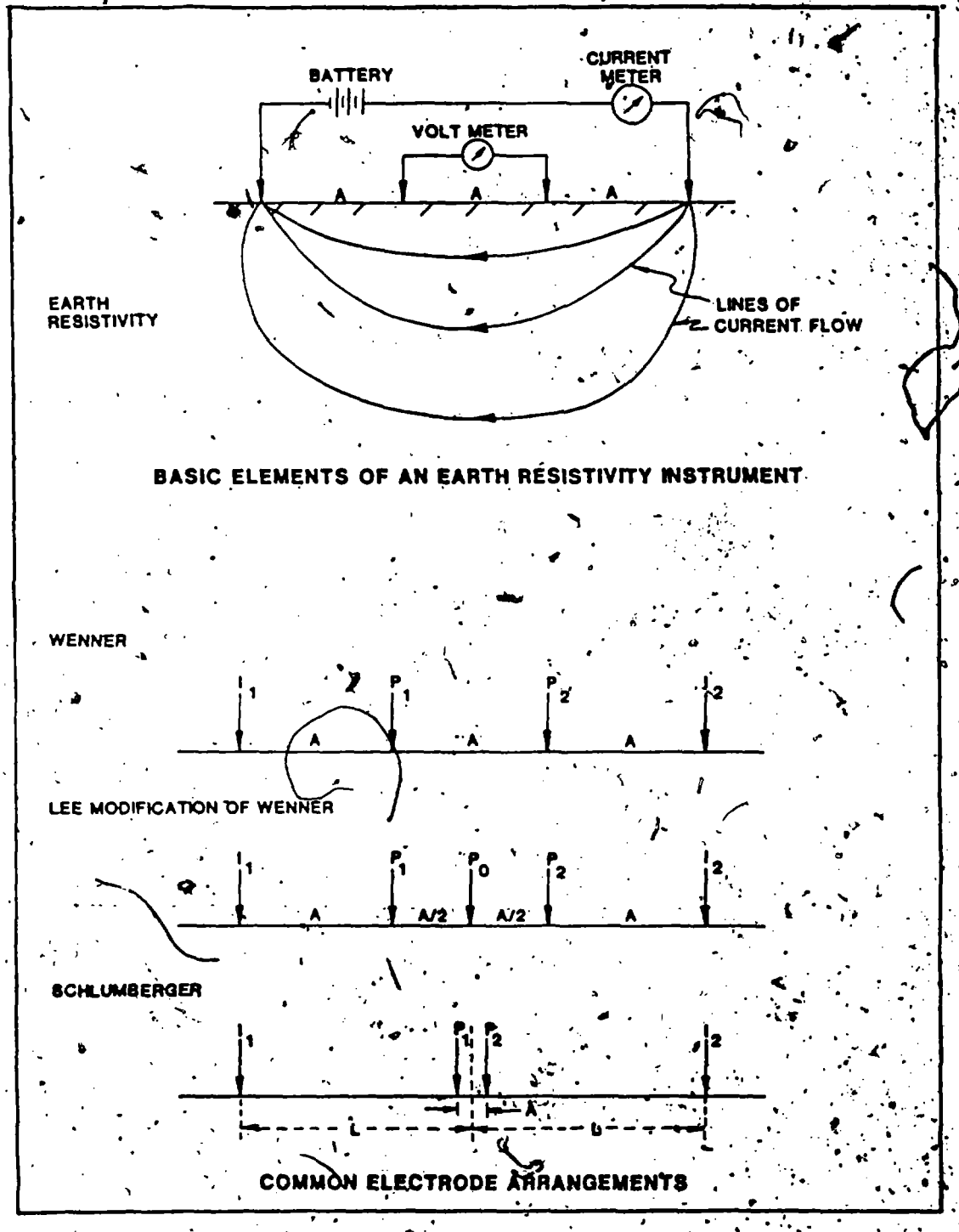
A pilot resistivity survey will be conducted at the Metmora site to ensure that the method is suitable. The pilot survey will consist of 10 vertical electric soundings. If successful, the full-scale survey will consist of up to 46 additional soundings.

Principles. Earth materials are good conductors of electricity in proportion to their content of (1) water or moisture, and (2) dissolved salts or free ions. Thus, massive rock formations such as granite or limestone are poor conductors (show high electrical resistivity) because they contain very little moisture. Clean gravels and clean sands are likewise poor conductors because, even when saturated with clean water, the water tends to be relatively clean and free from dissolved ions. If the gravels or sands are dry, then their resistivity will be even higher. By contrast, moist clays and clay soils contain both water and dissolved ions; hence they are good electrical conductors (low resistivity materials). Other earth materials will have their own characteristic resistivity values.

The earth resistivity method provides a method for shallow subsurface exploration by means of electrical measurements taken at the surface of the earth. Four electrodes are pushed or driven into the ground to a depth of several inches at locations where measurements are desired. Electrical current from a battery or generator flows into the ground between two of the electrodes (see Figure AA-2). The resulting voltage drop produced by this current in the earth is measured across the other two electrodes. Since some earth materials are much better conductors of electricity than others, the voltage drop will be affected differently by different subsurface conditions. Interpretation of earth resistivity readings involves deducing subsurface conditions from the measurements.

The depth of investigation by the earth resistivity method can be controlled by the user. Shallow investigations are carried out by placing the electrodes relatively close together, whereas deeper investigations require increased spacing between the electrodes. Typically, a shallow survey for gravel in the 10 to 20 foot depth range would use electrodes equally spaced along a line at intervals of approximately 30 feet; a deeper survey for mapping bedrock topography at depths of 50 to 75 feet would increase the electrode spacing interval to approximately 100 feet.

Instrumentation. The earth resistivity system centers around a central console which monitors current flow in the earth and is capable of accurately measuring very small changes in voltage potential. The system also consists of an electric power source (which may be DC or low frequency AC, depending on the instrumentation); four electrodes, two of which permit current to flow into the ground, and two to allow measurement of the voltage drop which occurs as a result of the current flow in the ground; and insulated wire for electrical continuity between the electrodes and the central console.



EARTH RESISTIVITY TECHNIQUE
FIGURE AA-2

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Field Techniques. The method commonly employs two data acquisition techniques which are referred to as (1) lateral profiling and (2) vertical sounding. The profiling technique is often used to determine the lateral distribution of suspected high or low resistivity subsurface materials by taking a series of measurements at a regular interval along a traverse where lateral change is anticipated. Usually, such measurements employ the same electrode configuration and separation so that one measurement can be qualitatively correlated with the next. If the same measurement parameters (electrode configuration and separation) are maintained, then the depth of penetration for each measurement will be similar. An application which makes good use of the profiling technique is groundwater contaminant plume delineation downgradient from a source of suspected contamination.

In vertical sounding, the method to be used at Metamora, the objective is to determine the electrical properties of various subsurface materials as a function of depth. This is accomplished by methodically increasing the spacing between the four electrodes thus achieving deeper and deeper penetration. Measurements of this sort will yield the sequence of high and low resistivity layers in the earth materials underlying the electrode array.

There are several different electrode array configurations, but the two most widely used on engineering surveys are the Wenner and Schlumberger arrays (Figure AA-2). There are advantages to each of these array configurations. At the Metamora site, the Wenner array with "a" spacings of 10, 20, 30, 40, 60, 80, 100, 120, 160, 200, 240 and 320 feet will be used for most soundings. Some of the soundings will be carried out to additional "a" spacings of 400, 480, 640, 800, 960 and 1280 (if within the capabilities of the instrument. This will permit an evaluation of the depth to the bedrock.

Some of the soundings will be rotated by 90 degrees, which will serve as an internal check on data consistency and will also provide insight into the homogeneity of geologic conditions. In addition, the Lee modification of the Wenner array will be made to the rotated sounding for additional control on geologic homogeneity.

Interpretation. Interpretation of sounding data can be accomplished in two ways. One can manually plot the (apparent) resistivity values on standard log-log graph paper such that the data points form a curve. This field curve is then compared with standard theoretical curves to produce a solution which consists of a multilayered earth model with up to 4 layers whose thicknesses and resistivity values have been determined. Generally speaking, the more layers a model has, the less accurate will be the manual solution.

Field data can also be input into a computer which compares the field data with a series of theoretical solutions through a process of iteration and arrives at a solution which agrees most closely (in a least squares sense) with the observed field data. Several programs are available which will produce solutions to field data. At Metamora, two programs will be used, TARLEM, written by P.A. Davis, University of Minnesota, and a program developed by Keck Consulting Services, Inc. The results of these two programs will be compared for consistency. The interpreter must check that the computer-derived solution is consistent with any geological data available for the site. At Metamora, boring logs and seismic profiles will be avaiable for correlation with the resistivity sounding data.

Instrument Calibration. The instruments to be used at Metamora, and their procedures for calibration, are described as follows:

Keck Model No. IC-69 Earth Resistivity Instrument - This instrument is not calibrated, but is tested to make sure it is working properly by internal checks which are performed in the field. There is a test function on the instrument that verifys that the ohmeter readings are the same as dictated in manual, and thus working properly. This test check is performed every day. In addition to the test check, the insulated wire used during the survey is examined to assure that no damage has occurred to the insulation. The wire is examined daily as it is unwound from the reels.

MAGNETICS

Magnetometer surveys have previously been conducted at Metamora with good results. Because of this, a pilot survey will not be conducted. The survey will consist of readings over a 2-acre area.

Prineiples. Although the origin of the earth's magnetic field is not well understood, we do know that the earth behaves magnetically as if a large bar magnet were located near its center. The axis of this "magnet" is oriented at a small angle (about 18 degrees) with respect to its axis of rotation. It is this angle which produces the small differences between "true" north and "magnetic" north called "declination." The lines of magnetic force are nearly horizontal at the equator and nearly vertical at the poles. The angle between these lines of force and horizontal at any point on the earth's surface is known as "inclination."

The strength of the magnetic field also varies over the surface of the earth, and is stronger at the poles than at the equator. The strength of the field is approximately 60,000 gammas at the poles and 30,000 gammas at the equator (where 1 gamma = 10^{-5} gauss).

The earth's magnetic field (sometimes referred to as its "ambient" field) is modified locally by both naturally-occurring and man-made magnetic materials. Two types of magnetization contribute to this: induced and remanent.

Induced magnetization refers to the ability of a material to act as a magnet itself thereby enhancing the ambient field. The more the ambient field is enhanced by a material, the greater is the "magnetic susceptibility" for that material.

Remanent or permanent magnetization often predominates over induced magnetization in igneous rocks and metals. (Remanent refers to rocks and permanent to metals). Remanent or permanent magnetization is produced in materials which have been heated above the Curie point allowing magnetic minerals to become aligned with the earth's ambient field before cooling. The remanent field direction is not, in general, parallel to the earth's present field, and may in fact act in an opposite direction. The remanent field combines vectorially with the ambient and induced field components, and any quantitative interpretation of magnetic data should take this into account if such information is available.

Instrumentation. Although many types of magnetometers are available, by far the most widely-used is the "proton precession" type. This device utilizes the precession of spinning protons of hydrogen atoms in a sample of hydrogen-rich fluid (kerosene, alcohol, or water) to measure the total magnetic field intensity.

Protons spinning in an atomic nucleus behave like tiny magnetic dipoles which can be aligned (polarized) by an external magnetic field. The protons are initially aligned parallel to the earth's field. A second, much stronger magnetic field is produced approximately perpendicular to the earth's field by introducing electric current through a coil of wire. The protons become temporarily aligned with this stronger field. When this stronger field is removed, the protons tend to realign themselves with the earth's field; causing them to precess about this direction at a frequency of about 2,000 Hz. The precessing protons will generate a small electric signal in the same coil used to polarize them with a frequency proportional to the total magnetic field intensity and independent of the coil orientation. By measuring the signal frequency, one can obtain the absolute value of the total earth field intensity to an accuracy of 1 gamma or better. The total magnetic field value measured by the proton precession magnetometer is the net vector sum of the ambient earth's field and any local induced and/or remanent (permanent) perturbations.

Field Techniques. In the field, the operator should avoid any sources of high magnetic gradients such as would be caused by power lines, buildings, and any large iron or steel objects. The operator should also avoid carrying any unnecessary metal articles. Magnetic stations are established at an interval which reflects the nature of the survey and the gradients encountered.

At hazardous waste sites, a typical "rough" reconnaissance grid might start out at perhaps a 25-foot interval, and would be closed down to 3 or 5 feet in areas where fine detail is desired. At Metamora, a 100-foot grid system will be used, and all data points will be referenced to this grid. Base station readings should be taken frequently (every hour or so) to provide a check on any diurnal variations and magnetic storms which may occur. Typically, diurnal variations will not exceed a few tens of gammas, but magnetic storms may produce changes in the earth's field of thousands of gammas in a short period of time (the order of hours). At the Metamora site, a continuously-recording magnetic base station will be established to account for diurnal variations. If a magnetic storm occurs, survey operations will cease until the storm is over. Diurnal corrections obtained from the base station will be applied to the raw field data prior to any data processing. This will insure that the magnetic intensity values from traverse to traverse are referenced to the same magnetic baseline.

Interpretation. For typical man-made iron or steel objects, one may quantify estimates for the approximate depth of burial and the amount of metal which produces an observed magnetic perturbation (or anomaly). The size of the anomaly (T) can be expressed as

$$T = \frac{M}{r^n}$$

where M is the magnetic moment of the source, r is the depth to the source, and n is a measure of the rate of decay with distance (n = 3 for a dipole source and 2 for a monopole source).

Assuming a dipole source, the weight of a metal object (in pounds) can be expressed by the following relation

$$Wt. = \frac{Tr}{M}$$

where M is the magnetic moment per pound of iron and varies from approximately 175 to 1750, r is the depth in feet, and T is the anomaly amplitude in gammas.

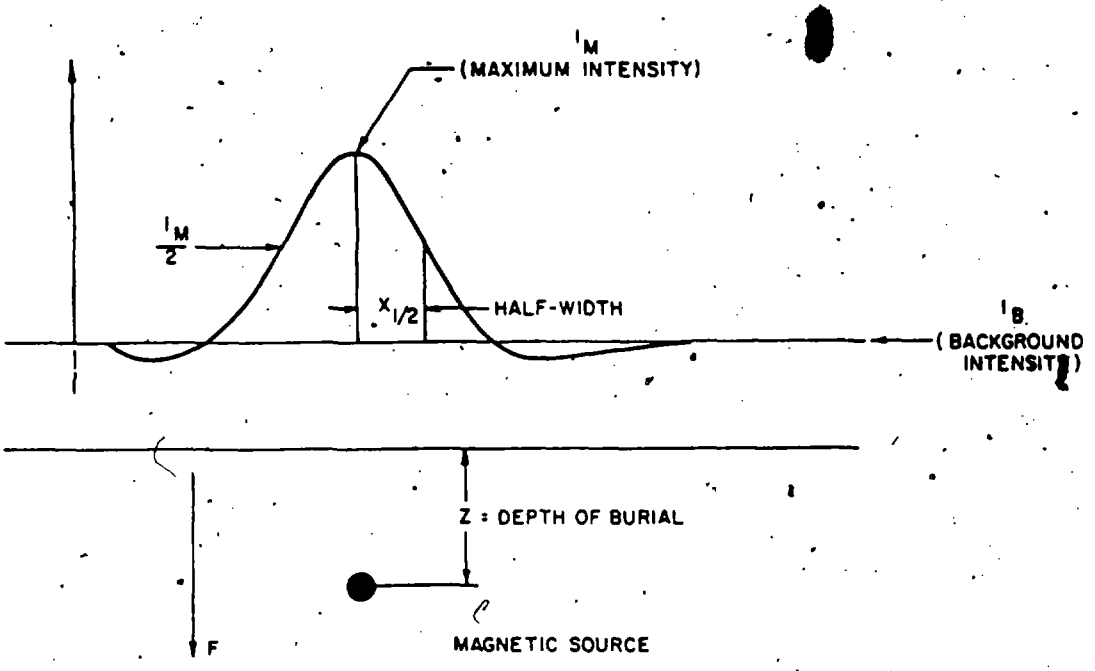
The depth, r, of a magnetic source can be estimated by a number of techniques, but perhaps the simplest is by the "half-width" rule. This states that for simple anomaly sources, the depth to the center of the anomaly is equal to the "half-width" of the anomaly. The half-width is the horizontal distance between the maximum value of the anomaly and the point at which the value is one-half the maximum value (see Figure AA-3).

Instrument Calibration. The instruments to be used at Metamora, and their calibrations procedures, are described below:

Geometrics G-856 Proton Precession Magnetometer (base station) -

EDA Omni IV Tie-line Magnetometer - Magnetometers cannot be effectively calibrated in the field by the operator. The best check available in the field is to check the value of the earth's total magnetic field in a magnetically quiet area with two different instruments. The value should agree within one or two gammas. This procedure is done every day to assure that the instruments are working properly.

DEPTH CALCULATION/METAL QUANTITY
FOR TOTAL FIELD MEASUREMENTS:



T = MAGNETIC ANOMALY INTENSITY

= MAXIMUM ANOMALY INTENSITY MINUS BACKGROUND INTENSITY

$= I_M - I_B$

$$= \frac{M_{fps}}{r^3} = \frac{1.75 \times 10^2 \text{ to } 1.75 \times 10^3}{(1 \text{ to } 2)\, r^3}$$

where "M_{fps}" is the magnetic moment per pound of iron and "r" is the distance between the magnetometer sensor and the object (the depth of burial) "z" is equal to "r" minus the height of the sensor above the ground.

DEPTH CALCULATION FOR GRADIOMETER MEASUREMENTS

$$r = \frac{-nT}{\frac{dT}{dz}}$$

where "n" is the "falloff" factor and generally varies from 1 to 2, depending on the magnetic source, "r" is the separation between the midpoint between the two sensors and the object.

MAGNETOMETER DATA INTERPRETATION
FIGURE AA-3

EC JORDAN CO.

APPENDIX B

COMPATIBILITY TESTING PROCEDURES

During Task 13, Pollutant Characterization, it is estimated that 1,200 drums will be excavated and sampled. In order to stage these drums safely, the contents must be sampled and tested for compatibility characteristics so that drums containing similar wastes can be stored together (and perhaps composited), and drums containing incompatible wastes are segregated.

Great Lakes Environmental (GLE) will assist Jordan by providing earthmoving and drum moving equipment plus personnel during Task 13. GLE will also supply a chemist and onsite laboratory to perform compatibility tests on the waste samples collected during this task. The tests to be performed are as follows:

Radioactivity	Cyanide content
Total organic vapor	Sulfide content
pH	Flammability
Water reactivity/solubility	Chlorides
Oxidation/reduction potential	

The following list is used for general classifications for compositing wastes:

1. Strong acids
2. Strong bases
3. Oxidizers
4. Reducing agents
5. Cyanide/sulfide wastes
6. Water reactives
7. Flammable liquids
8. Halogenated organics
9. Non-halogenated organics
10. PCBs
11. Non-hazardous
12. Radioactives

To place wastes into these categories with the least amount of work, a strict flow chart or decision tree is followed (see Figure AB-1). The tests are performed in a specific sequence with the results of one test determining the next test to be performed. The results lead to an ultimate classification of the sample into one of the classifications listed above.

Before a drum is opened and sampled, it is screened with a radiation detector to determine if radioactive components are present. If so, the drum is classified as radioactive and all necessary safety procedures are used to move and isolate the drum from the rest of the waste materials.

If radioactive components are not present, the organic vapor content inside the drum is determined by using an organic vapor monitor (e.g., photoionization meter). If a reading >2,000 ppm is found, the drum is labeled "potentially explosive", and is segregated from the other drums until further testing can be performed.

After these first two preliminary field tests have been conducted, the drums are sampled and the wastes are segregated based on pH according to the following criteria:

Bases	pH > 10
Acids	pH < 4
Neutral	pH = 5-9

The next step is to check basic and acidic wastes for their oxidation/reduction potential. In addition, basic materials are checked at this time for cyanide and sulfide.

The remaining samples with a neutral pH and/or organics are tested for water reactivity. Depending on the reaction observed, the samples are separated into one of the following classifications:

Water reactive
Water soluble
Water insoluble

Samples classified as water reactive are segregated into a separate group. Water solubles are tested for flammability. Water insolubles are segregated into halogenated and non-halogenated groups. The halogenated samples are checked for chlorides and composited accordingly. Non-halogenated samples are checked for flammability. Non-flammable materials such as oils are checked for PCBs.

Compatibility Test Procedures

The tests described below will provide the information for determining the compatibility of drum wastes. Once drums have been segregated into compatible groups, decisions can be made on compositing and disposal. Some materials, once classified, will not be composited for disposal (e.g., oxidizers, water reactives, etc.).

The following paragraphs describe the procedures for the compatibility tests which will be performed by GLE.

1.) pH Measurement

pH is a measure of the corrosivity of a substance. Materials with a very high pH ($\geq$ 12.5) are considered corrosive. These materials, along with materials with a pH > 7.0, are considered basic or caustic. Examples of caustic materials are sodium hydroxide (NaOH), ammonia (NH_4), and potash (KOH).

If a substance has a very low pH ($\leq$2.0), it is also considered corrosive. Materials with a low pH are called acids. Examples of some strong acids are sulfuric acid (H_2SO_4), hydrochloric acid (HCl), and hydrofluoric acid (HF). Strong acids and strong bases are not compatible.

If a substance is neutral, it has a pH of 7. A substance is generally considered neutral if the pH is between 5 and 9. It is important to remember

that pH is expressed on a logarithmic scale; therefore, pH 5 is 10 times stronger than pH 6, and pH 4 is 100 times stronger than pH 6. One pH unit makes a considerable difference.

Equipment:
- pH test strips
- pH meter (Orion 407 A/F pH meter, or Orion hand held 201 pH meter)
- pH electrode
- pH buffer solutions
- Distilled water
- Kimwipes
- Disposable beakers
- Disposable glass rods

Procedure: (pH strip) This is the most common method used when screening samples. Immerse a glass rod into the sample and spread a small amount on the pH test strip. Wait for 5-10 seconds and allow the color to develop. Compare the color to the chart on the side of the package and record the pH. In some instances, such as highly colored material (paints), it may be difficult to obtain an accurate colormetric reading. A pH meter is used for such samples.

(pH meter) The pH meter is used only for highly colored material, composite samples, or when a very accurate pH is required. pH strips are preferrable because the pH electrode may be damaged by unknown solutions, or may clog frequently. When the electrode becomes clogged, it requires time consuming cleaning and recalibration.

To obtain a reading, simply immerse the electrode in the solution. Wait for the reading to stabilize, and record the indicated value.

2.) Water Reactivity/Solubility

It is very important to determine if a sample will react with water because it is very likely that at some point in time the material will come in contact with water. The procedure is simple and with additional observation, it is extremely informative. Special precautions and handling procedures must be implemented during this test.

Equipment:
- Disposable beakers
- Disposable pipets
- Thermometer
- Glass rods
- Distilled water
- Stainless steel beaker
- Protective shield

Procedure: Make sure all necessary safety equipment is in place. Fill the disposable beaker half full with distilled water, place it in the stainless steel beaker, and place the

thermometer in the disposable beaker. Make sure that the beaker base is resting flat with the open end pointing upwards (away from you). Read the temperature of the water. Carefully add 1 ml or 1 gm of sample to the water and note temperature changes, fuming of any kind, and/or spattering or spitting. If no reaction takes place, stir the sample with a glass rod and look for reactions. If there is still no reaction, stir in another 4 ml or 4 gms, one at a time. If there is still no reaction, add another 5 ml or 5 gms.

A positive result is observed when any of the following occurs: 1) a significant increase in temperature (it is very important that both the water and the sample are at the same initial temperature); 2) gases are generated; or 3) a violent reaction take place (i.e., spattering or spitting).

The solubility of the sample can be determined during this test as well, if the sample is not water reactive. As the sample is stirred into the water in the beaker, observe if the sample is soluble. If not, observe whether it floats or sinks. These observations may not be readily made in the beaker. If so, use a separatory funnel and slowly drop 3-5 ml of non-reactive material (liquid) into the water-filled separatory funnel.

If the sample floats, it is classified as a "non-halogenated organic". If the sample sinks, it is classifed as a "halogenated organic".

3.) Oxidation/Reduction Potential

This test is performed because of the violent reactions that take place when an oxidizing agent comes in contact with easily oxidized material. If an oxidizing material is found on a site, it should be segregated from other materials on the site and disposed of separately.

Equipment:
Orion 407 A/F Multimeter
Redox electrode
0.001 Normal ferrous ammonium sulfate solution
0.001 Normal potassium chromate solution
Heavy polypropylene cup

Procedure: Place 50 ml of 0.001 Normal ferrous ammonium sulfate solution into a 4.5 oz. heavy polypropylene cup. Measure the cell potential of the ferrous ammonium sulfate solution using a millivolt (mV) meter with a platinum sensing electrode and standard reference electrode. Remove the electrodes and add 50 ml. of sample to the ferrous ammonium sulfate solution. Mix the solutions and let stand for one minute. Measure the change in cell potential of the mixture with the millivolt meter. A change of 50 mV in the positive direction indicates the

presence of an oxidizing agent in the sample. Ferrous ammonium sulfate is used in this procedure because it is easily oxidized and the difference in oxidation potential may be measured with the millivolt meter.

To determine the presence of a reducing agent, follow the same procedure using potassium chromate.

If the sample is organic in nature, the mixture may separate into layers. The organic layer of the mixture should be drained off and only the aqueous layer of the mixture is tested. It is important to keep the probes away from organic materials because they will foul and require constant maintenance.

4.) Cyanide/Sulfide Determination

Equipment: Orion 407 A/F Multimeter
Cyanide ion specific electrode
Hydrochloric acid
Lead acetate paper

Cyanide will be determined using the Orion 407 A/F Multimeter and a cyanide ion specific electrode. Using this method enables the determination of cyanide both qualitatively and quantitatively in a sample. The procedure for this method will be determined on a case by case basis taking site specific requirements and possible findings into consideration.

Samples that do not contain cyanide will be tested for sulfide. Acidify the sample with HCl and place a lead acetate paper in the head space of the sample jar. Seal the jar and wait about 2 minutes. If the paper turns dark, the test is positive for sulfide.

5.) Flammability

Equipment: Sand box
Disposable pipet
Disposable beaker
Propane torch, matches, or other ignition source

Procedure: Place 3-5 ml. or mg. of a representative sample into a disposable beaker and place the beaker into a sand box. Slowly pass a lighted torch over the sample (the sample should be at ambient room temperature - 70 to 80 degrees F). If no flame arises, pass the torch over the sample 3-4 more times.

If a flame is observed, the result is positive. The waste is classified as "flammable". If no flame is observed after several passes, the result is negative, and the sample is classified as "non-flammable".

6.) Flame Test (chloride determination)

The flame test (or Beilstein test) is a screening method for chloride. The test is a simple test based on the fact that chlorinated compounds produce a green flame when introduced to a flame.

Equipment: Bunsen burner, or other flame source
Glass rod or pipet

Procedure: Dip the glass rod into the sample so that the rod is coated with the sample. Quickly move the rod from the sample to the flame. Observe the color of the flame when the material on the glass rod burns. A positive result is found when a green flame is observed. A positive result indicates the presence of chloride (Cl > 30%). This indicates the presence of a chlorinated solvent (e.g., methylene chloride, trichloroethene, perchloroethylene). A negative result is found when a green flame is not observed.

APPENDIX C

ANALYTICAL WORK TO BE CONDUCTED BY CLAYTON ENVIRONMENTAL CONSULTANTS

Clayton Environmental Consultants (CEC) will provide support to Jordan during the Metamora project by conducting specific analytical tests. CEC will analyze charcoal tubes used to collect volatile organic chemicals in air samples during Task 9 (Air Investigation) and Task 13 (Pollutant Characterization). These samples will be collected for health and safety reasons (i.e., to assure that proper respiratory protection is being worn), therefore, it is necessary that these samples be analyzed as quickly as possible. To assure fast turn-around time, the samples will be delivered to CEC. CEC will also analyze Tenax tubes used to collect volatile organic chemicals in soil gas samples, if this method is used at the site. Again, a fast turn-around time will be necessary for these samples because the soil gas sampling plan will be driven by the results from previous sampling locations. The last item that CEC will be responsible for will be the analysis of waste samples for EP Toxicity metals and organics, and PCBs. These analyses will be conducted for waste compositing and disposal purposes.

Listed below is a summary of the analyses to be performed by CEC, plus the method and reference for each sample type:

Matrix	Analyte	Method	Reference
Air (charcoal)	total hydrocarbons	GC/FID	NIOSH 127
Soil gas (Tenax)	qualitative	GC/MS	TO-1 EPA-600/4-84-041
Leachate (EP Toxicity)	metals	AA	EPA SW-846
	pesticides	GC/ECD	EPA SW-846
	herbicides	GC/ECD	EPA SW-846
Waste	PCBs	GC/ECD	EPA SW-846

The following attachments are summaries of analytical and quality control procedures for each analysis to be performed by CEC. Also included is a list of the laboratory instrumentation used by CEC in their Southfield office.

APPENDIX C - NIOSH 127 (TOTAL HYDROCARBONS AS HEXANE)

Analyte: Total hydrocarbons as hexane

Method: NIOSH P&CAM 127; NIOSH Manual of Analytical Methods, Second Edition.

Synopsis: The charcoal sample is desorbed in carbon disulfide (CS_2). An aliquot of the CS_2 extract is injected onto a gas chromatograph equipped with a flame ionization detector. Area response of the sample is compared to a hexane reference standard.

Detection Limit: 0.01 milligrams (mg)

Calibration: A four-point calibration for n-hexane is prepared at 0.001, 0.002, 0.003, and 0.007 mg and is analyzed with each sample set. Background is determined by analysis of blanks. Limit of detection is verified by serial dilution.

Quality Control: Duplicate desorption efficiencies for n-hexane are analyzed with each sample set at 0.006, 0.06, and 0.33 mg. Standards and blanks are analyzed every 10 injections. The operation of the chromatographic system is monitored daily by checking/changing septa and cleaning FID.

ORGANIC SOLVENTS IN AIR

Physical and Chemical Analysis Branch

Analytical Method

Analyte:	Organic Solvents (See Table 1)	**Method No.:**	P&CAM 127
Matrix:	Air	**Range:**	For the specific compound, refer to Table 1
Procedure:	Adsorption on charcoal desorption with carbon disulfide, GC		
Date Issued:	9/15/72	**Precision:**	10.5% RSD
Date Revised:	2/15/77	**Classification:**	See Table 1

1. **Principle of the Method**

   1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

   1.2 The charcoal in the tube is transferred to a small, graduated test tube and desorbed with carbon disulfide.

   1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

   1.4 The area of the resulting peak is determined and compared with areas obtained from the injection of standards.

2. **Range and Sensitivity**

   The lower limit in mg/sample for the specific compound at 16 × 1 attenuation on a gas chromatograph fitted with a 10:1 splitter is shown in Table 1. This value can be lowered by reducing the attenuation or by eliminating the 10:1 splitter.

3. **Interferences**

   3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped. Preliminary experiments indicate that high humidity severely decreases the breakthrough volume.

   3.2 When two or more solvents are known or suspected to be present in the air, such information (including their suspected identities), should be transmitted with the sample, since with differences in polarity, one may displace another from the charcoal.

   3.3 It must be emphasized that any compound which has the same retention time as the specific compound under study at the operating conditions described in this method is an interference. Hence, retention time data on a single column, or even on a number of columns, cannot be considered as proof of chemical identity. For this reason it is important that a sample of the bulk solvent(s) be submitted at the same time so that identity(ies) can be established by other means.

3.4 If the possibility of interference exists, separation conditions (column packing, temperatures, etc.) must be changed to circumvent the problem.

4. **Precision and Accuracy**

4.1 The mean relative standard deviation of the analytical method is 8% (11.4).

4.2 The mean relative standard deviation of the analytical method plus field sampling using an approved personal sampling pump is 10% (11.4). Part of the error associated with the method is related to uncertainties in the sample volume collected. If a more powerful vacuum pump with associated gas-volume integrating equipment is used, sampling precision can be improved.

4.3 The accuracy of the overall sampling and analytical method is 10% (NIOSH–unpublished data) when the personal sampling pump is calibrated with a charcoal tube in the line.

5. **Advantages and Disadvantages of the Method**

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method. The method can also be used for the simultaneous analysis of two or more solvents suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal tube exceeds 25% of that found on the front section, the possibility of sample loss exists. During sample storage, the more volatile compounds will migrate throughout the tube until equilibrium is reached (33% of the sample on the backup section).

5.3 Furthermore, the precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. **Apparatus**

6.1 An approved and calibrated personal sampling pump for personal samples. For an area sample, any vacuum pump whose flow can be determined accurately at 1 liter per minute or less.

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The absorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the absorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 lpm.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (20 ft × ⅛ in) with 10% FFAP stationary phase on 80/100 mesh, acid-washed DMCS Chromosorb W solid support. Other columns capable of performing the required separations may be used.

6.5 A mechanical or electronic integrator or a recorder and some method for determining peak area.

6.6 Microcentrifuge tubes: 2.5 ml, graduated.

6.7 Hamilton syringes: 10 μl, and convenient sizes for making standards.

6.8 Pipets: 0.5-ml delivery pipets or 1.0-ml type graduated in 0.1-ml increments.

6.9 Volumetric flasks: 10 ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Spectroquality carbon disulfide (Matheson Coleman and Bell).

7.2 Sample of the specific compound under study, preferably chromatoquality grade.

7.3 Bureau of Mines Grade A helium.

7.4 Prepurified hydrogen.

7.5 Filtered compressed air.

8. Procedure

8.1 **Cleaning of Equipment:** All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.

8.2 **Calibration of Personal Pumps.** Each personal pump must be calibrated with a representative charcoal tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 **Collection and Shipping of Samples**

8.3.1 Immediately before sampling, the ends of the tube should be broken to provide an opening at least one-half the internal diameter of the tube (2 mm).

8.3.2 The small section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be vertical during sampling to reduce channeling through the charcoal.

8.3.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.

8.3.5 The flow, time, and or volume must be measured as accurately as possible. The sample should be taken at a flow rate of 1 lpm or less to attain the total sample volume required. The minimum and maximum sample volumes that should be collected for each solvent are shown in Table 1. The minimum volume quoted must be collected if the desired sensitivity is to be achieved.

8.3.6 The temperature and pressure of the atmosphere being sampled shbuld be measured and recorded.

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

8.3.9 Capped tubes should be packed tightly before they are shipped to minimize tube breakage during shipping

8.3.10 Samples of the suspected solvent(s) should be submitted to the laboratory for qualitative characterization. These liquid bulk samples should not be transported in the same container as the samples or blank tube. If possible, a bulk air sample (at least 50 l air drawn through tube) should be shipped for qualitative identification purposes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a small stoppered test tube. The separating section of foam is removed and discarded; the second section is transferred to another test tube. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, one-half ml of carbon disulfide is pipetted into each test tube. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Tests indicate that desorption is complete in 30 minutes if the sample is stirred occasionally during this period.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 85 cc min. (70 psig) helium carrier gas flow.
2. 65 cc min. (24 psig) hydrogen gas flow to detector.
3. 500 cc min. (50 psig) air flow to detector.
4. 200°C injector temperature.
5. 200°C manifold temperature (detector).
6. Isothermal oven or column temperature — refer to Table 1 for specific compounds.

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blowback or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10 μl syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 μl to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-μl aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back a short distance to minimize evaporation of the sample from the tip of the needle. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below.

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process for a given compound, provided the same batch of charcoal is used. NIOSH has found that the desorption efficiencies for the compounds in Table 1 are between 81% and 100% and vary with each batch of charcoal.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 5-cm, 4-mm I.D. glass tube, flame-sealed at one end (similar to commercially available culture tubes). This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of the compound is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm. The amount injected is usually equivalent to that present in a 10-liter sample at a concentration equal to the federal standard.

At least five tubes are prepared in this manner and allowed to stand for at least overnight to assure complete absorption of the specific compound onto the charcoal. These five tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of compound into 0.5 ml of CS_2 with the same syringe used in the preparation of the sample. These are analyzed with the samples.

The desorption efficiency equals the difference between the average peak area of the samples and the peak area of the blank divided by the average peak area of the standards, or

$$\text{desorption efficiency} = \frac{\text{Area sample} - \text{Area blank}}{\text{Area standard}}$$

9. **Calibration and Standards**

It is convenient to express concentration of standards in terms of mg/0.5 ml CS_2 because samples are desorbed in this amount of CS_2. To minimize error due to the volatility of carbon disulfide, one can inject 20 times the weight into 10 ml of CS_2. For example, to prepare a 0.3 mg/0.5 ml standard, one would inject 6.0 mg into exactly 10 ml of CS_2 in a glass-stoppered flask. The density of the specific compound is used to convert 6.0 mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg 0.5 ml versus peak area.

NOTE: Since no internal standard is used in the method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of known day-to-day variations and variations during the same day of the FID response.

10. **Calculations**

10.1 The weight, in mg, corresponding to each peak area is read from the standard curve for the particular compound. No volume corrections are needed, because the standard curve is based on mg/0.5 ml CS_2 and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

$$\text{Correct mg} = \text{mg}_s - \text{mg}_b$$

where:

mg_s = mg found in front section of sample tube

mg_b = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 The corrected amounts present in the front and backup sections of the same sample tube are added to determine the total measured amount in the sample.

10.4 This total weight is divided by the determined desorption efficiency to obtain the corrected mg per sample.

10.5 The concentration of the analyte in the air sampled can be expressed in mg per m^3.

$$mg/m^3 = \frac{\text{Corrected mg (Section 10.4)} \times 1000 \text{ (liters/m}^3\text{)}}{\text{Air volume sampled (liters)}}$$

10.6 Another method of expressing concentration is ppm (corrected to standard conditions of 25°C and 760 mm Hg)

$$\text{ppm} = mg/m^3 \times \frac{24.45}{MW} \times \frac{760}{P} \times \frac{(T + 273)}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
MW = molecular weight
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

11.1 White, L. D., D. G. Taylor, P. A. Mauer, and R. E. Kupel, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere", Am Ind Hyg Assoc J 31:225, 1970.

11.2 Young, D. M. and A. D. Crowell, Physical Adsorption of Gases, pp. 187-146, Butterworths, London, 1962.

11.3 Federal Register, 37:202:22139-22142, October 18, 1972.

11.4 NIOSH Contract HSM-99-72-98, Scott Research Laboratories, Inc., "Collaborative Testing of Activated Charcoal Sampling Tubes for Seven Organic Solvents", pp. 4-22, 4-27, 1973.

TABLE 1

Parameters Associated With P&CAB Analytical Method No. 127

Organic Solvent	Method Classification	Detection limit (mg/sample)	Sample Volume (liters)[a] Minimum[a]	Maximum[b]	GC Column Temp.(°C)	Molecular Weight
Acetone	D	–	0.5	7.7	60	58.1
Benzene	A	0.01	0.5	55	90	78.1
Carbon tetrachloride	A	0.20	10	60	60	154.0
Chloroform	A	0.10	0.5	13	80	119
Dichloromethane	D	0.05	0.5	3.8	85	84.9
p-Dioxane	A	0.05	1	18	100	88.1
Ethylene dichloride	D	0.05	1	12	90	99.0
Methyl ethyl ketone	B	0.01	0.5	13	80	72.1
Styrene	D	0.10	1.5	34	150	104
Tetrachloroethylene	B	0.06	1	25	130	166
1,1,2-trichloroethane	B	0.05	10	97	150	133
1,1,1-trichloroethane (methyl chloroform)	B	0.05	0.5	13	150	133
Trichloroethylene	A	0.05	1	17	90	131
Toluene	B	0.01	0.5	22	120	92.1
Xylene	A	0.02	0.5	31	100	106

(a) Minimum volume, in liters, required to measure 0.1 times the OSHA standard

(b) These are breakthrough volumes calculated with data derived from a potential plot (11.2) for activated coconut charcoal. Concentrations of vapor in air at 5 times the OSHA standard (11.3) or 500 ppm, whichever is lower, 25°C, and 760 torr were assumed. These values will be as much as 50% lower for atmospheres of high humidity. The effects of multiple contaminants have not been investigated, but it is suspected that less volatile compounds may displace more volatile compounds (See 3.1 and 3.2)

APPENDIX C - TO-1 (QUALITATIVE ORGANICS)

Analyte: Qualitative organics

Method: Thermal desorption gas chromatography/mass spectrometry

Synopsis: The sample is collected in precleaned Tenax sorbent tubes (see cleaning procedure attached) and thoroughly desorbed by heating to 250 °C. The effluent is cryogenically focused in liquid nitrogen. The trap is heated and the trap effluent is analyzed by gas chromatography/mass spectrometry using general scanning techniques.

Detection Limit: Approximately 0.1 microgram/compound

Calibration: Compounds reported as "Target" compounds (see below) are calculated against authentic standards. "Target" compounds are reported as "less than (<)" if not found in the sample.

Benzene	Toluene
Chloroform	Xylene
Dichlorobenzene	Butylatedhydroxytoluene (BHT)
Ethyl benzene	1,1,1-trichloroethane
Limonene	1,1,2-trichloroethene (TCE)
Methylene Chloride	2-butanone (MEK)
Naphthalene	2-pentanone
Tetrachloroethene	4-methyl-2-pentanone (MIBK)

Additional compounds are identified by a forward library search of the combined Wiley-EPA-NIH-NBS Library. They are quantified against the average total-ion-current area of compounds of different types (see attached). Results are blank corrected and are semi-quantitative.

Quality Control:

- Tenax is analyzed before tube preparation to verify contaminant level.
- At least one field blank (or 10%) is analyzed with each sample set.
- A daily external standard of target compounds is analyzed.

Tenax Sorbent Tube Cleaning Procedure

1. Cut glass tubes to 8" lengths with glass cutter.

2. Clean Tenax
   - Extract 6 hours with pentane in a soxhlet extractor.
   - Extract 6 hours with methanol in a soxhlet extractor.
   - Dry completely in hood.
   - Pack into clean column; check for leaks and flowrate.
   - Bake overnight in GC at 270 °C, running nitrogen or inert gas through column.
   - Discard any discolored sorbent.
   - Wash with soap; rinse throrougly with distilled water.

3. Soak glass tubing twice with methylene chloride.

4. Dry at 105 °C for 2 hours in forced air oven.

5. Rinse glass wool in a beaker twice with methylene chloride.

6. Dry at 300 °C in a muffle furnace for 3 hours.

7. Using glass rod, stuff a plug of glass wool about 4" from end of tube.

8. Fill the other end with 300 mg precleaned Tenax.

9. Tap tube to pack sorbent.

10. Put a second plug of glass wool on top of Tenax.

11. Seal the ends of the tubes, using a gas oxygen torch, the same day that tubes are made.

12. Cap with orange caps.

STANDARD NAME: [illegible] | NUMBER: 30100

SOLVENT SOURCE/LOT #: [illegible] | SOLVENT: [illegible] | STORAGE LOCATION: [illegible]

ANALYST NAME: [illegible] | DATE MADE: 1-7-86 | FINAL VOLUME: 10 mL

	COMPOUND	SOURCE	SOURCE CONC	VOL USED	FINAL CONC
1	[illegible]	[illegible]	NEAT	115.5 uL	[illegible]
2	[illegible]	" 310 [illegible]	"	14.5 "	"
3	[illegible]	" [illegible]	"	65.3 "	"
4	[illegible]	ICN	"	66.1 "	"
5	[illegible]	" [illegible]	"	111.9 "	"
6	[illegible]	" [illegible]	"	115.5 "	"
7	[illegible]	" [illegible]	"	114.9 "	"
8	[illegible]	" [illegible]	"	61.6 "	"
9					
10					
11					
12					
13					
14					
15					
16					
17					
18					
19					
20					

VERIFICATION

	VER. CONC	DIFF	%DEV.		VER. CONC	DIFF	%DEV.
1				11			
2				12			
3				13			
4				14			
5				15			
6				16			
7				17			
8				18			
9				19			
10				20			

(ATTACH VERIFICATION CHROMATOGRAMS ON REVERSE SIDE)

STANDARD NAME: [illegible] | NUMBER: 30101

SOLVENT SOURCE/LOT #: [illegible] | SOLVENT: [illegible] | STORAGE LOCATION: [illegible]

ANALYST NAME: [illegible] | DATE MADE: [illegible] | FINAL VOLUME: [illegible]

	COMPOUND	SOURCE	SOURCE CONC	VOL USED	FINAL CONC
1	[illegible]		NEAT	[illegible]	[illegible]
2	[illegible]		"	[illegible]	"
3	[illegible]		"	[illegible]	"
4	[illegible]		"	[illegible]	"
5	[illegible]		"	[illegible]	"
6	[illegible]		"	[illegible]	"
7	[illegible]		"	[illegible]	"
8	[illegible]		"	[illegible]	"
9	[illegible]		"	[illegible]	"
10	[illegible]		"	[illegible]	"
11	[illegible]		"	[illegible]	"
12	[illegible]		"	[illegible]	"
13	[illegible]		"	[illegible]	"
14	[illegible] TRIMETHYL BENZENE	ACROS 040651	1	[illegible]	[illegible]
15					
16					
17					
18					
19					
20					

VERIFICATION

	VER. CONC	DIFF	%DEV.		VER. CONC	DIFF	%DEV.
1				11			
2				12			
3				13			
4				14			
5				15			
6				16			
7				17			
8				18			
9				19			
10				20			

(ATTACH VERIFICATION CHROMATOGRAMS ON REVERSE SIDE)

STANDARD NAME	NUMBER
[illegible]	30102

SOLVENT SOURCE/LOT #	SOLVENT	STORAGE LOCATION
[illegible]	[illegible]	[illegible]

ANALYST NAME	DATE MADE	FINAL VOLUME
[illegible]	[illegible]	[illegible]

	COMPOUND	SOURCE	SOURCE CONC	VOL USED	FINAL CONC
1	2-METHYL PENTANE	PCB	NEAT	[illegible]	10.000 ppm
2	2-METHYL METHYLF	SUPELCO	"	[illegible]	"
3	METHYLCYCLOPENTANE	KITS	"	[illegible]	"
4	2-METHYLHEXANE	MIX	"	[illegible]	"
5	1-NONANOL	↓	"	[illegible]	"
6	HEXENE-1		"	[illegible]	"
7					
8					
9					
10					
11					
12					
13					
14					
15					
16					
17					
18					
19					
20					

VERIFICATION

	* VER. CONC	DIFF	%DEV.		VER. CONC	DIFF	%DEV.
1				11			
2				12			
3				13			
4				14			
5				15			
6				16			
7				17			
8				18			
9				19			
10				20			

(ATTACH VERIFICATION CHROMATOGRAMS ON REVERSE SIDE)

30103

STANDARD NAME | NUMBER

SOLVENT SOURCE/LOT # | SOLVENT | STORAGE LOCATION

ANALYST NAME | DATE MADE | FINAL VOLUME

	COMPOUND	SOURCE	SOURCE CONC.	VOL USED	FINAL CONC
1	2-Methyl-hexane		NBS		
2	Cyclohexane		"		"
3	2-Ethanone		"		"
4	[illegible]		"		"
5	[illegible]		"		"
6					
7					
8					
9					
10					
11					
12					
13					
14					
15					
16					
17					
18					
19					
20					

VERIFICATION

	VER. CONC	DIFF	%DEV.		VER. CONC	DIFF	%DEV.
1				11			
2				12			
3				13			
4				14			
5				15			
6				16			
7				17			
8				18			
9				19			
10				20			

(ATTACH VERIFICATION CHROMATOGRAMS ON REVERSE SIDE)

METHOD TO1

Revision 1.0
April, 1984

METHOD FOR THE DETERMINATION OF VOLATILE ORGANIC COMPOUNDS IN AMBIENT AIR USING TENAX® ADSORPTION AND GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS)

1. Scope

1.1 The document describes a generalized protocol for collection and determination of certain volatile organic compounds which can be captured on Tenax® GC (poly(2,6-Diphenyl phenylene oxide)) and determined by thermal desorption GC/MS techniques. Specific approaches using these techniques are described in the literature (1-3).

1.2 This protocol is designed to allow some flexibility in order to accommodate procedures currently in use. However, such flexibility also results in placement of considerable responsibility with the user to document that such procedures give acceptable results (i.e. documentation of method performance within each laboratory situation is required). Types of documentation required are described elsewhere in this method.

1.3 Compounds which can be determined by this method are nonpolar organics having boiling points in the range of approximately 80° - 200°C. However, not all compounds falling into this category can be determined. Table 1 gives a listing of compounds for which the method has been used. Other compounds may yield satisfactory results but validation by the individual user is required.

2. Applicable Documents

2.1 ASTM Standards:

D1356 Definitions of Terms Related to Atmospheric Sampling and Analysis.

E355 Recommended Practice for Gas Chromatography Terms and Relationships.

2.3 Other documents:

Existing procedures (1-3).
U.S. EPA Technical Assistance Document (4).

3. Summary of Protocol

3.1 Ambient air is drawn through a cartridge containing ~1-2 grams of Tenax and certain volatile organic compounds are trapped on the resin while highly volatile organic compounds and most inorganic atmospheric constituents pass through the cartridge. The cartridge is then transferred to the laboratory and analyzed.

3.2 For analysis the cartridge is placed in a heated chamber and purged with an inert gas. The inert gas transfers the volatile organic compounds from the cartridge onto a cold trap and subsequently onto the front of the GC column which is held at low temperature (e.g. - 70°C). The GC column temperature is then increased (temperature programmed) and the components eluting from the column are identified and quantified by mass spectrometry. Component identification is normally accomplished, using a library search routine, on the basis of the GC retention time and mass spectral characteristics. Less sophistacated detectors (e.g. electron capture or flame ionization) may be used for certain applications but their suitability for a given application must be verified by the user.

3.3 Due to the complexity of ambient air samples only high resolution (i.e. capillary) GC techniques are considered to be acceptable in this protocol.

4. Significance

4.1 Volatile organic compounds are emitted into the atmosphere from a variety of sources including industrial and commercial facilities, hazardous waste storage facilities, etc. Many of these compounds are toxic; hence knowledge of the levels of

such materials in the ambient atmosphere is required in order to determine human health impacts.

4.2 Conventional air monitoring methods (e.g. for workspace monitoring) have relied on carbon adsorption approaches with subsequent solvent desorption. Such techniques allow subsequent injection of only a small portion, typically 1-5% of the sample onto the GC system. However, typical ambient air concentrations of these compounds require a more sensitive approach. The thermal desorption process, wherein the entire sample is introduced into the analytical (GC/MS) system fulfills this need for enhanced sensitivity.

5. Definitions

Definitions used in this document and any user prepared SOPs should be consistent with ASTM D1356(6). All abbreviations and symbols are defined with this document at the point of use.

6. INTERFERENCES

6.1 Only compounds having a similar mass spectrum and GC retention time compared to the compound of interest will interfere in the method. The most commonly encountered interferences are structural isomers.

6.2 Contamination of the Tenax cartridge with the compound(s) of interest is a commonly encountered problem in the method. The user must be extremely careful in the preparation, storage, and handling of the cartridges throughout the entire sampling and analysis process to minimize this problem.

7. Apparatus

7.1 Gas Chromatograph/Mass Spectrometry system - should be capable of subambient temperature programming. Unit mass resolution or better up to 800 amu. Capable of scanning 30-440 amu region every 0.5-1 second. Equipped with data system for instrument control as well as data acquisition, processing and storage.

7.2 Thermal Desorption Unit - Designed to accommodate Tenax cartridges in use. See Figure 2a or b.

7.3 Sampling System - Capable of accurately and precisely drawing an air flow of 10-500 ml/minute through the Tenax cartridge. (See Figure 3a or b.)

7.4 Vacuum oven - connected to water aspirator vacuum supply.

7.5 Stopwatch

7.6 Pyrex disks - for drying Tenax.

7.7 Glass jar - Capped with Teflon-lined screw cap. For storage of purified Tenax.

7.8 Powder funnel - for delivery of Tenax into cartridges.

7.9 Culture tubes - to hold individual glass Tenax cartridges.

7.10 Friction-top can (paint can) - to hold clean Tenax cartridges.

7.11 Filter holder - stainless steel or aluminum (to accommodate 1 inch diameter filter). Other sizes may be used if desired. (optional)

7.12 Thermometer - to record ambient temperature.

7.13 Barometer (optional).

7.14 Dilution bottle - Two-liter with septum cap for standards preparation.

7.15 Teflon stirbar - 1 inch long.

7.16 Gas-tight glass syringes with stainless steel needles - 10-500 µl for standard injection onto GC/MS system.

7.17 Liquid microliter syringes - 5,50 µL for injecting neat liquid standards into dilution bottle.

7.18 Oven - 60 ± 5°C for equilibrating dilution flasks.

7.19 Magnetic stirrer.

7.20 Heating mantel.

7.21 Variac

7.22 Soxhlet extraction apparatus and glass thimbles - for purifying Tenax.

7.23 Infrared lamp - for drying Tenax.

7.24 GC column - SE-30, or alternative coating, glass capillary or fused silica.

7.25 Psychrometer - to determine ambient relative humidity. (optional).

8. Reagents and Materials

8.1 Empty Tenax cartridges - glass or stainless steel (See Figure 1a or b).

8.2 Tenax 60/80 mesh (2,6-diphenylphenylene oxide polymer).

8.3 Glasswool - silanized.

8.4 Acetone - Pesticide quality or equivalent.

8.5 Methanol - Pesticide quality, or equivalent.

8.6 Pentane - Pesticide quality or equivalent.

8.7 Helium - Ultra pure, compressed gas. (99.9999%)

8.8 Nitrogen - Ultra pure, compressed gas. (99.9999%)

8.9 Liquid nitrogen.

8.10 Polyester gloves - for handling glass Tenax cartridges.

8.11 Glass Fiber Filter - one inch diameter, to fit in filter holder. (optional)

8.12 Perfluorotributylamine (FC-43).

8.13 Chemical Standards - Neat compounds of interest. Highest purity available.

8.14 Granular activated charcoal - for preventing contamination of Tenax cartridges during storage.

9. Cartridge Construction and Preparation

9.1 Cartridge Design

9.1.1 Several cartridge designs have been reported in the literature (1-3). The most common (1) is shown in Figure 1a. This design minimizes contact of the sample with metal surfaces, which can lead to decomposition in certain cases. However, a disadvantage of this design is the need to rigorously avoid contamination of the outside portion of the cartridge since the entire surface is subjected to the purge gas stream during the desorption porcess.

Clean polyester gloves must be worn at all times when handling such cartridges and exposure of the open cartridge to ambient air must be minimized.

9.1.2 A second common type of design (3) is shown in Figure 1b. While this design uses a metal (stainless steel) construction, it eliminates the need to avoid direct contact with the exterior surface since only the interior of the cartridge is purged.

9.1.3 The thermal desorption module and sampling system must be selected to be compatible with the particular cartridge design chosen. Typical module designs are shown in Figures 2a and b. These designs are suitable for the cartridge designs shown in Figures 1a and 1b, respectively.

9.2 Tenax Purification

9.2.1 Prior to use the Tenax resin is subjected to a series of solvent extraction and thermal treatment steps. The operation should be conducted in an area where levels of volatile organic compounds (other than the extraction solvents used) are minimized.

9.2.2 All glassware used in Tenax purification as well as cartridge materials should be thoroughly cleaned by water rinsing followed by an acetone rinse and dried in an oven at 250°C.

9.2.3 Bulk Tenax is placed in a glass extraction thimble and held in place with a plug of clean glasswool. The resin is then placed in the soxhlet extraction apparatus and extracted sequentially with methanol and then pentane for 16-24 hours (each solvent) at approximately 6 cycles/hour. Glasswool for cartidge preparation should be cleaned in the same manner as Tenax.

9.2.4 The extracted Tenax is immediately placed in an open glass dish and heated under an infrared lamp for two

hours in a hood. Care must be exercised to avoid over heating of the Tenax by the infrared lamp. The Tenax is then placed in a vacuum oven (evacuated using a water aspirator) without heating for one hour. An inert gas (helium or nitrogen) purge of 2-3 ml/minute is used to aid in the removal of solvent vapors. The oven temperature is then increased to 110°C, maintaining inert gas flow and held for one hour. The oven temperature control is then shut off and the oven is allowed to cool to room temperature. Prior to opening the oven, the oven is slightly pressurized with nitrogen to prevent contamination with ambient air. The Tenax is removed from the oven and sieved through a 40/60 mesh sieve (acetone rinsed and oven dried) into a clean glass vessel. If the Tenax is not to be used immediately for cartridge preparation it should be stored in a clean glass jar having a Teflon-lined screw cap and placed in a desiccator.

9.3 Cartridge Preparation and Pretreatment

9.3.1 All cartridge materials are pre-cleaned as described in Section 9.2.2. If the glass cartridge design shown in Figure 1a is employed all handling should be conducted wearing polyester gloves.

9.3.2 The cartridge is packed by placing a 0.5-1cm glass-wool plug in the base of the cartridge and then filling the cartridge to within approximately 1 cm of the top. A 0.5-1cm glasswool plug is placed in the top of the cartridge.

9.3.3 The cartridges are then thermally conditioned by heating for four hours at 270°C under an inert gas (helium) purge (100 - 200 ml/min).

9.3.4 After the four hour heating period the cartridges are allowed to cool. Cartridges of the type shown in Figure 1a are immediately placed (without cooling) in clean culture tubes having Teflon-lined screw caps with a glasswool cushion at both the top and the bottom. Each tube should be shaken to ensure that the cartridge is held firmly in place. Cartridges of the type shown in Figure 1b are allowed to cool to room temperature under inert gas purge and are then closed with stainless steel plugs.

9.3.5 The cartridges are labeled and placed in a tightly sealed metal can (e.g. paint can or similar friction top container). For cartridges of the type shown in Figure 1a the culture tube, not the cartridge, is labeled.

9.3.6 Cartridges should be used for sampling within 2 weeks after preparation and analyzed within two weeks after sampling. If possible the cartridges should be stored at -20°C in a clean freezer (i.e. no solvent extracts or other sources of volatile organics contained in the freezer).

10. Sampling

10.1 Flow rate and Total Volume Selection

10.1.1 Each compound has a characteristic retention volume (liters of air per gram of adsorbent) which must not be exceeded. Since the retention volume is a function of temperature, and possibly other sampling variables, one must include an adequate margin of safety to ensure good collection efficiency. Some considerations and guidance in this regard are provided in a recent report (5). Approximate breakthrough volumes at 38°C (100°F) in liters/gram of Tenax are provided in Table 1. These retention volume data are supplied only as rough guidance and are subject to considerable variability, depending on cartridge design as well as sampling parameters and atmospheric conditions.

10.1.2 To calculate the maximum total volume of air which can be sampled use the following equation:

$$V_{MAX} = \frac{V_b \times W}{1.5}$$

where

V_{MAX} is the calculated maximum total volume in liters.

V_b is the breakthrough volume for the least retained compound of interest (Table 1) in liters per gram of Tenax.

W is the weight of Tenax in the cartridge, in grams.

1.5 is a dimensionless safety factor to allow for variability in atmospheric conditions. This factor is appropriate for temperatures in the range of 25-30°C. If higher temperatures are encountered the factor should be increased (i.e. maximum total volume decreased).

10.1.3 To calculate maximum flow rate use the following equation:

$$Q_{MAX} = \frac{V_{MAX}}{t} \times 1000$$

where

Q_{MAX} is the calculated maximum flow rate in milliliters per minute.

t is the desired sampling time in minutes. Times greater than 24 hours (1440 minutes) generally are unsuitable because the flow rate required is too low to be accurately maintained.

10.1.4 The maximum flow rate Q_{MAX} should yield a linear flow velocity of 50-500 cm/minute. Calculate the linear velocity corresponding to the maximum flow rate using the following equation:

$$B = \frac{Q_{MAX}}{\pi r^2}$$

where

B is the calculated linear flow velocity in centimeters per minute.

r is the internal radius of the cartridge in centimeters.

If B is greater than 500 centimeters per minute either the total sample volume (V_{MAX}) should be reduced or the sample flow rate (Q_{MAX}) should be reduced by increasing the collection time. If B is less than 50 centimeters per minute the sampling rate (Q_{MAX}) should be increased by reducing the sampling time. The total sample value (V_{MAX}) cannot be increased due to component breakthrough.

10.1.4 The flow rate calculated as described above defines the maximum flow rate allowed. In general, one should collect additional samples in parallel, for the same time period but at lower flow rates. This practice yields a measure of quality control and is further discussed in the literature (5). In general, flow rates 2 to 4 fold lower than the maximum flow rate should be employed for the parallel samples. In all cases a constant flow rate should be achieved for each cartridge since accurate integration of the analyte concentration requires that the flow be constant over the sampling period.

10.2 Sample Collection

10.2.1 Collection of an accurately known volume of air is critical to the accuracy of the results. For this reason the use of mass flow controllers, rather than conventional needle valves or orifices is highly recommended, especially at low flow velocities (e.g. less than 100 milliliters/minute). Figure 3a illustrates a sampling system utilizing mass flow controllers. This system readily allows for collection of parallel samples. Figures 3b shows a commercially available system based on needle valve flow controllers.

10.2.2 Prior to sample collection insure that the sampling flow rate has been calibrated over a range including the rate to be used for sampling, with a "dummy" Tenax cartridge in place. Generally calibration is accomplished using a soap bubble flow meter or calibrated wet test meter. The flow calibration device is connected to the flow exit, assuming the entire flow system is sealed. ASTM Method D3686 describes an appropriate calibration scheme, not requiring a sealed flow system downstream of the pump.

10.2.3 The flow rate should be checked before and after each sample collection. If the sampling interval exceeds four hours the flow rate should be checked at an intermediate point during sampling as well. In general, a rotameter should be included, as showed in Figure 3b, to allow observation of the sampling flow rate without disrupting the sampling process.

10.2.4 To collect an air sample the cartridges are removed from the sealed container just prior to initiation of the collection process. If glass cartridges (Figure 1a) are employed they must be handled only with polyester gloves and should not contact any other surfaces.

10.2.5 A particulate filter and holder are placed on the inlet to the cartridges and the exit end of the cartridge is connected to the sampling apparatus. In many sampling situations the use of a filter is not necessary if only the total concentration of a component is desired. Glass cartridges of the type shown in Figure 1a are connected using teflon ferrules and Swagelok (stainless steel or teflon) fittings. Start the pump and record the following parameters on an appropriate data sheet (Figure 4): data, sampling location, time, ambient temperature, barometric

pressure, relative humidity, dry gas meter reading (if applicable) flow rate, rotameter reading (if applicable), cartridge number and dry gas meter serial number.

10.2.6 Allow the sampler to operate for the desired time, periodically recording the variables listed above. Check flow rate at the midpoint of the sampling interval if longer than four hours.
At the end of the sampling period record the parameters listed in 10.2.5 and check the flow rate and record the value. If the flows at the beginning and end of the sampling period differ by more than 10% the cartridge should be marked as suspect.

10.2.7 Remove the cartridges (one at a time) and place in the original container (use gloves for glass cartridges). Seal the cartridges or culture tubes in the friction-top can containing a layer of charcoal and package for immediate shipment to the laboratory for analysis. Store cartridges at reduced temperature (e.g. - 20°C) before analysis if possible to maximize storage stability.

10.2.8 Calculate and record the average sample rate for each cartridge according to the following equation:

$$Q_A = \frac{Q_1 + Q_2 + \ldots Q_N}{N}$$

where

Q_A = Average flow rate in ml/minute.

$Q_1, Q_2, \ldots Q_N$ = Flow rates determined at beginning, end, and immediate points during sampling.

N = Number of points averaged.

10.2.9 Calculate and record the total volumetric flow for each cartridge using the following equation:

$$V_m = \frac{T \times Q_A}{1000}$$

where

V_m = Total volume sampled in liters at measured temperature and pressure.
T_2 = Stop time.
T_1 = Start time.
T = Sampling time = $T_2 - T_1$, minutes

10.2.10 The total volume (V_s) at standard conditions, 25°C and 760 mmHg, is calculated from the following equation:

$$V_s = V_m \times \frac{P_A}{760} \times \frac{298}{273 + t_A}$$

where

P_A = Average barometric pressure, mmHg
t_A = Average ambient temperature, °C.

11. GC/MS Analysis

11.1 Instrument Set-up

11.1.1 Considerable variation from one laboratory to another is expected in terms of instrument configuration. Therefore each laboratory must be responsible for verifying that their particular system yields satisfactory results. Section 14 discusses specific performance criteria which should be met.

11.1.2 A block diagram of the typical GC/MS system required for analysis of Tenax cartridges is depicted in Figure 5. The operation of such devices is described in 11.2.4. The thermal desorption module must be designed to accommodate the particular cartridge configuration. Exposure of the sample to metal surfaces should be minimized and only stainless steel, or nickel metal surfaces should be employed.

The volume of tubing and fittings leading from the cartridge to the GC column must be minimized and all areas must be well-swept by helium carrier gas.

11.1.3 The GC column inlet should be capable of being cooled to -70°C and subsequently increased rapidly to approximately 30°C. This can be most readily accomplished using a GC equipped with subambient cooling capability (liquid nitrogen) although other approaches such as manually cooling the inlet of the column in liquid nitrogen may be acceptable.

11.1.4 The specific GC column and temperature program employed will be dependent on the specific compounds of interest. Appropriate conditions are described in the literature (1-3). In general a nonpolar stationary phase (e.g. SE-30, OV-1) temperature programmed from 30°C to 200°C at 8°/minute will be suitable. Fused silica bonded phase columns are preferable to glass columns since they are more rugged and can be inserted directly into the MS ion source, thereby eliminating the need for a GC/MS transfer line.

11.1.5 Capillary column dimensions of 0.3 mm ID and 50 meters long are generally appropriate although shorter lengths may be sufficient in many cases.

11.1.6 Prior to instrument calibration or sample analysis the GC/MS system is assembled as shown in Figure 5. Helium purge flows (through the cartridge) and carrier flow are set at approximately 10 ml/minute and 1-2 ml/minute respectively. If applicable, the injector sweep flow is set at 2-4 ml/minute.

11.1.7 Once the column and other system components are assembled and the various flows established the column temperature is increased to 250°C for approximately four hours (or overnight if desired) to condition the column.

11.1.8 The MS and data system are set according to the manufacturer's instructions. Electron impact ionization (70eV) and an electron multiplier gain of approximately 5×10^4 should be employed. Once the entire GC/MS system has been setup the system is calibrated as described in Section 11.2. The user should prepare a detailed standard operating procedure (SOP) describing this process for the particular instrument being used.

11.2 Instrument Calibration

11.2.1 Tuning and mass standarization of the MS system is performed according to manufacturer's instructions and relevant information from the user prepared SOP. Perfluorotributylamine should generally be employed for this purpose. The material is introduced directly into the ion source through a molecular leak. The instrumental parameters (e.g. lens voltages, resolution, etc.) should be adjusted to give the relative ion abundances shown in Table 2 as well as acceptable resolution and peak shape. If these approximate relative abundances cannot be achieved, the ion source may require cleaning according to manufacturer's instructions. In the event that the user's instrument cannot achieve these relative ion abundances, but is otherwise operating properly, the user may adopt another set of relative abundances as performance criteria.

However, these alternate values must be repeatable on a day-to-day basis.

11.2.2 After the mass standarization and tuning process has been completed and the appropriate values entered into the data system the user should then calibrate the entire system by introducing known quantities of the standard components of interest into the system. Three alternate procedures may be employed for the calibration process including 1) direct syringe injection of dilute vapor phase standards, prepared in a dilution bottle, onto the GC column, 2) Injection of dilute vapor phase standards into a carrier gas stream directed through the Tenax cartridge, and 3) introduction of permeation or diffusion tube standards onto a Tenax cartridge. The standards preparation procedures for each of these approaches are described in Section 13. The following paragraphs describe the instrument calibration process for each of these approaches.

11.2.3 If the instrument is to be calibrated by direct injection of a gaseous standard, a standard is prepared in a dilution bottle as described in Section 13.1. The GC column is cooled to -70°C (or, alternately, a portion of the column inlet is manually cooled with liquid nitrogen). The MS and data system is set up for acquisition as described in the relevant user SOP. The ionization filament should be turned off during the initial 2-3 minutes of the run to allow oxygen and other highly volatile components to elute. An appropriate volume (less than 1 ml) of the gaseous standard is injected onto the GC system using an accurately calibrated gas tight syringe.

The system clock is started and the column is maintained at -70°C (or liquid nitrogen inlet cooling) for 2 minutes. The column temperature is rapidly increased to the desired initial temperature (e.g. 30°C). The temperature program is started at a consistent time (e.g. four minutes) after injection. Simultaneously the ionization filament is turned on and data acquisition is initiated. After the last component of interest has eluted acquisiton is terminated and the data is processed as described in Section 11.2.5. The standard injection process is repeated using different standard volumes as desired.

11.2.4 If the system is to be calibrated by analysis of spiked Tenax cartridges a set of cartridges is prepared as described in Sections 13.2 or 13.3. Prior to analysis the cartridges are stored as described in Section 9.3. If glass cartridges (Figure 1a) are employed care must be taken to avoid direct contact, as described earlier. The GC column is cooled to -70°C, the collection loop is immersed in liquid nitrogen and the desorption module is maintained at 250°C. The inlet valve is placed in the desorb mode and the standard cartridge is placed in the desorption module, making certain that no leakage of purge gas occurs. The cartridge is purged for 10 minutes and then the inlet valve is placed in the inject mode and the liquid nitrogen source removed from the collection trap. The GC column is maintained at -70°C for two minutes and subsequent steps are as described in 11.2.3. After the process is complete the cartridge is removed from the desorption module and stored for subsequent use as described in Section 9.3.

11.2.5 Data processing for instrument calibration involves determining retention times, and integrated characteristic ion intensities for each of the compounds of interest. In addition, for at least one chromatographic run, the individual mass spectra should be inspected and compared to reference spectra to ensure proper instrumental performance. Since the steps involved in data processing are highly instrument specific, the user should prepare a SOP describing the process for individual use. Overall performance criteria for instrument calibration are provided in Section 14. If these criteria are not achieved the user should refine the instrumental parameters and/or operating procedures to meet these criteria.

11.3 Sample Analysis

11.3.1 The sample analysis process is identical to that described in Section 11.2.4 for the analysis of standard Tenax cartridges.

11.3.2 Data processing for sample data generally involves 1) qualitatively determining the presence or absence of each component of interest on the basis of a set of characteristic ions and the retention time using a reverse-search software routine, 2) quantification of each identified component by integrating the intensity of a characteristic ion and comparing the value to that of the calibration standard, and 3) tentative identification of other components observed using a forward (library) search software routine. As for other user specific processes, a SOP should be prepared describing the specific operations for each individual laboratory.

12. Calculations

12.1 Calibration Response Factors

12.1.1 Data from calibration standards is used to calculate a response factor for each component of interest. Ideally the process involves analysis of at least three calibration levels of each component during a given day and determination of the response factor (area/nanogram injected) from the linear least squares fit of a plot of nanograms injected versus area (for the characteristic ion). In general quantities of component greater than 1000 nanograms should not be injected because of column overloading and/or MS response nonlinearity.

12.1.2 In practice the daily routine may not always allow analysis of three such calibration standards. In this situation calibration data from consecutive days may be pooled to yield a response factor, provided that analysis of replicate standards of the same concentration are shown to agree within 20% on the consecutive days. One standard concentration, near the midpoint of the analytical range of interest, should be chosen for injection every day to determine day-to-day response reproducibility.

12.1.3 If substantial nonlinearity is present in the calibration curve a nonlinear least squares fit (e.g. quadratic) should be employed. This process involves fitting the data to the following equation:

$$Y = A + BX + CX^2$$

where

Y = peak area
X = quantity of component, nanograms
A,B, and C are coefficients in the equation

12.2 Analyte Concentrations

12.2.1 Analyte quantities on a sample cartridge are calculated from the following equation:

$$Y_A = A + BX_A + CX_A$$

where

Y_A is the area of the analyte characteristic ion for the sample cartridge.

X_A is the calculated quantity of analyte on the sample cartridge, in nanograms.

A,B, and C are the coefficients calculated from the calibration curve described in Section 12.1.3.

12.2.2 If instrumental response is essentially linear over the concentration range of interest a linear equation (C=0 in the equation above) can be employed.

12.2.3 Concentration of analyte in the original air sample is calculated from the following equation:

$$C_A = \frac{X_A}{V_S}$$

where

C_A is the calculated concentration of analyte in nanograms per liter.

V_S and X_A are as previously defined in Section 10.2.10 and 12.2.1, respectively.

13. Standard Preparation

13.1 Direct Injection

13.1.1 This process involves preparation of a dilution bottle containing the desired concentrations of compounds of interest for direct injection onto the GC/MS system.

13.1.2 Fifteen three-millimeter diameter glass beads and a one-inch Teflon stirbar are placed in a clean two-liter glass septum capped bottle and the exact volume is determined by weighing the bottle before and after filling with deionized water. The bottle is then rinsed with acetone and dried at 200°C.

13.1.3 The amount of each standard to be injected into the vessel is calculated from the desired injection quantity and volume using the following equation:

$$W_T = \frac{W_L}{V_I} \times V_B$$

where

W_T is the total quantity of analyte to be injected into the bottle in milligrams

W_I is the desired weight of analyte to be injected onto the GC/MS system or spiked cartridge in nanograms

V_I is the desired GC/MS or cartridge injection volume (should not exceed 500) in microliters.

V_B is total volume of dilution bottle determined in 13.1.1, in liters.

13.1.4 The volume of the neat standard to be injected into the dilution bottle is determined using the following equation:

$$V_T = \frac{W_T}{d}$$

where

V_T is the total volume of neat liquid to be injected in microliters.

d is the density of the neat standard in grams per milliliter.

13.1.6 The bottle is placed in a 60°C oven for at least 30 minutes prior to removal of a vapor phase standard.

13.1.7 To withdraw a standard for GC/MS injection the bottle is removed from the oven and stirred for 10-15 seconds. A suitable gas-tight microber syring warmed to 60°C, is inserted through the septum cap and pumped three times slowly. The appropriate volume of sample (approximately 25% larger than the desired injection volume) is drawn into the syringe and the volume is adjusted to the exact value desired and then immediately injected over a 5-10 seconds period onto the GC/MS system as described in Section 11.2.3.

13.2 Preparation of Spiked Cartridges by Vapor Phase Injection

13.2.1 This process involves preparation of a dilution bottle containing the desired concentrations of the compound(s) of interest as described in 13.1 and injecting the desired volume of vapor into a flowing inert gas stream directed through a clean Tenax cartridge.

13.2.2 A helium purge system is assembled wherein the helium flow 20-30 mL/minute is passed through a stainless steel Tee fitted with a septum injector.. The clean Tenax cartridge is connected downstream of the tee using appropriate Swagelok fittings. Once the cartridge is placed in the flowing gas stream the appropriate volume vapor standard, in the dilution bottle, is injected through the septum as described in 13.1.6. The syringe is flushed several times by alternately filling the syringe with carrier gas and displacing the contents into the flow stream, without removing the syringe from the septum. Carrier flow is maintain through the cartridge for approximately 5 minutes after injection.

13.3 Preparation of Spiked Traps Using Permeation or Diffusion tubes

13.3.1 A flowing stream of inert gas containing known amounts of each compound of interest is generated according to ASTM Method D3609(6). Note that a method of accuracy maintaining temperature within ± 0.1°C is required and the system generally must be equilibrated for at least 48 hours before use.

13.3.2 An accurately known volume of the standard gas stream (usually 0.1-1 liter) is drawn through a clean Tenax cartridge using the sampling system described in Section 10.2.1, or a similar system. However, if mass flow controllers are employed they must be calibrated for the carrier gas used in Section 13.3.1 (usually nitrogen). Use of air as the carrier gas for permeation systems is not recommended, unless the compounds of interest are known to be highly stable in air.

13.3.3 The spiked cartridges are then stored or immediately analyzed as in Section 11.2.4.

14. Performance Criteria and Quality Assurance

This section summarizes quality assurance (QA) measures and provides guidance concerning performance criteria which should be achieved within each laboratory. In many cases the specific QA procedures have been described within the appropriate section describing the particular activity (e.g. parallel sampling).

14.1 Standard Opreating Procedures (SOPs)

14.1.1 Each user should generate SOPs describing the following activities as they are performed in their laboratory:

1) assembly, calibration, and operation of the sampling system,
2) preparation, handling and storage of Tenax cartridges,
3) assembly and operation of GC/MS system including the thermal desorption apparatus and data system, and
4) all aspects of data recording and processing.

14.1.2 SOPs should provide specific stepwise instructions and should be readily available to, and understood by the laboratory personnel conducting the work.

14.2 Tenax Cartridge Preparation

14.2.1 Each batch of Tenax cartridges prepared (as described in Section 9) should be checked for contamination by analyzing one cartridge immediately after preparation. While analysis can be accomplished by GC/MS, many laboratories may chose to use GC/FID due to logistical and cost considerations.

14.2.2 Analysis by GC/FID is accomplished as described for GC/MS (Section 11) except for use of FID detection.

14.2.3 While acceptance criteria can vary depending on the components of interest, at a minimum the clean cartridge should be demonstrated to contain less than one fourth of the minimum level of interest for each component. For most compounds the blank level should be less than 10 nanograms per cartridge in order to be acceptable. More rigid criteria may be adopted, if necessary, within a specific laboratory. If a cartridge does not meet these acceptance criteria the entire lot should be rejected.

14.3 Sample Collection

14.3.1 During each sampling event at least one clean cartridge will accompany the samples to the field and back to the laboratory, without being used for sampling, to serve as a field blank. The average amount of material found on the field blank cartridge may be subtracted from the amount found on the actual samples. However, if the blank level is greater than 25% of the sample amount, data for that component must be identified as suspect.

14.3.2 During each sampling event at least one set of parallel samples (two or more samples collected simultaneously) will be collected, preferably at different flow rates as described in Section 10.1. If agreement between parallel samples is not generally within ± 25% the user should collect parallel samples on a much more frequent basis (perhaps for all sampling points). If a trend of lower apparent concentrations with increasing flow rate is observed for a set

of parallel samples one should consider using a reduced flow rate and longer sampling interval if possible. If this practice does not improve the reproducibility further evaluation of the method performance for the compound of interest may be required.

14.3.3 Backup cartridges (two cartridges in series) should be collected with each sampling event. Backup cartridges should contain less than 20% of the amount of components of interest found in the front cartridges, or be equivalent to the blank cartridge level, whichever is greater. The frequency of use of backup cartridges should be increased if increased flow rate is shown to yield reduced component levels for parallel sampling. This practice will help to identify problems arising from breakthrough of the component of interest during sampling.

14.4 GC/MS Analysis

14.4.1 Performance criteria for MS tuning and mass calibration have been discussed in Section 11.2 and Table 2. Additional criteria may be used by the laboratory if desired. The following sections provide performance guidance and suggested criteria for determining the acceptability of the GC/MS system.

14.4.2 Chromatographic efficiency should be evaluated using spiked Tenax cartridges since this practice tests the entire system. In general a reference compound such as perfluorotoluene should be spiked onto a cartridge at the 100 nanogram level as described in Section 13.2 or 13.3. The cartridge is then analyzed by GC/MS as

described in Section 11.4. The perfluorotoluene (or other reference compound) peak is then plotted on an expanded time scale so that its width at 10% of the peak can be calculated, as shown in Figure 6. The width of the peak at 10% height should not exceed 10 seconds. More stringent criteria may be required for certain applications. The assymmetry factor (See Figure 6) should be between 0.8 and 2.0. The assymmetry factor for any polar or reactive compounds should be determined using the process described above. If peaks are observed that exceed the peak width or assymmetry factor criteria above, one should inspect the entire system to determine if unswept zones or cold spots are present in any of the fittings and is necessary. Some laboratories may chose to evaluate column performance separately by direct injection of a test mixture onto the GC column. Suitable schemes for column evaluation have been reported in the literature (7). Such schemes cannot be conducted by placing the substances onto Tenax because many of the compounds (e.g. acids, bases, alcohols) contained in the test mix are not retained, or degrade, on Tenax.

14.4.3 The system detection limit for each component is calculated from the data obtained for calibration standards. The detection limit is defined as

$$DL = A + 3.3S$$

where

DL is the calculated detection limit in nanograms injected.

A is the intercept calculated in Section 12.1.1 or 12.1.3.

S is the standard deviation of replicate determinations of the lowest level standard (at least three such determinations are required.

In general the detection limit should be 20 nanograms or less and for many applications detection limits of 1-5 nanograms may be required. The lowest level standard should yield a signal to noise ratio from the total ion current response of approximately 5.

14.4.4 The relative standard deviation for replicate analyses of cartridges spiked at approximately 10 times the detection limit should be 20% or less. Day to day relative standard deviation should be 25% or less.

14.4.5 A useful performance evaluation step is the use of an internal standard to track system performance. This is accomplished by spiking each cartridge, including blank, sample, and calibration cartridges with approximately 100 nanograms of a compound not generally present in ambient air (e.g. perfluorotoluene). The integrated ion intensity for this compound helps to identify problems with a specific sample. In general, the user should calculate the standard deviation of the internal standard response for a given set of samples analyzed under identical tuning and calibration conditions. Any sample giving a value greater than $\pm$ 2 standard deviations from the mean (calculated

excluding that particular sample) should be identified as suspect. Any marked change in internal standard response may indicate a need for instrument recalibration.

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APPENDIX C - EPA SW-846 (EP TOXICITY METALS)

Analyte: EP leachate metals

Method: SW-846, EPA Test Methods for Evaluating Solid Wastes - Physical/Chemical Methods, July 1982.

Synopsis: A 100-gram representative sample is extracted in an acetic acid/water solution for 24 hours. The sample and extract are filtered and the filtrate is analyzed for arsenic, barium, cadmium, chromium, lead, mercury, selenium, and silver by atomic absorption spectrophotometry using the following methods:

Analyte	EPA Method No.
Arsenic	7060
Barium	7080
Cadmium	7130
Chromium	7190
Lead	7420
Mercury	7470
Selenium	7740
Silver	7760

Detection Limit:

	milligrams/liter (mg/L)
Arsenic	0.02
Barium	0.5
Cadmium	0.02
Chromium	0.2
Lead	0.2
Mercury	0.002
Selenium	0.02
Silver	0.05

Calibration: A five-point calibration curve is analyzed with each set of samples to establish linearity and limit of detection (see below). Quantitation is performed by a three-point standard-addition plot.

Arsenic	(mg/L)	0.01	0.02	0.03	0.05	0.07	
Barium	(mg/L)	0.5	1	2	5	7	
Cadmium	(mg/L)	0.02	0.1	0.5	1	1.5	
Chromium	(mg/L)	0.2	0.5	1	2	5	7
Lead	(mg/L)	0.2	0.5	1	2	5	7
Mercury	(ug/L)	0.2	0.5	1	2.5	7.5	20
Selenium	(mg/L)	0.01	0.02	0.03	0.05	0.07	
Silver	(mg/L)	0.5	0.1	0.5	1	1.5	

(continued)

Quality Control:

At least one method blank is analyzed with every 10 samples or with each batch of samples submitted, whichever is more frequent.

Duplicate recoveries (spiked reagent blanks) are analyzed with every 20 samples or with each batch of samples submitted, whichever is more frequent (see concentrations listed below).

Arsenic	(mg/L)	0.04
Barium	(mg/L)	2
Cadmium	(mg/L)	1
Chromium	(mg/L)	4
Lead	(mg/L)	4
Mercury	(ug/L)	5
Selenium	(mg/L)	0.04
Silver	(mg/L)	1

At least 10% of the samples are analyzed in duplicate to demonstrate precision.

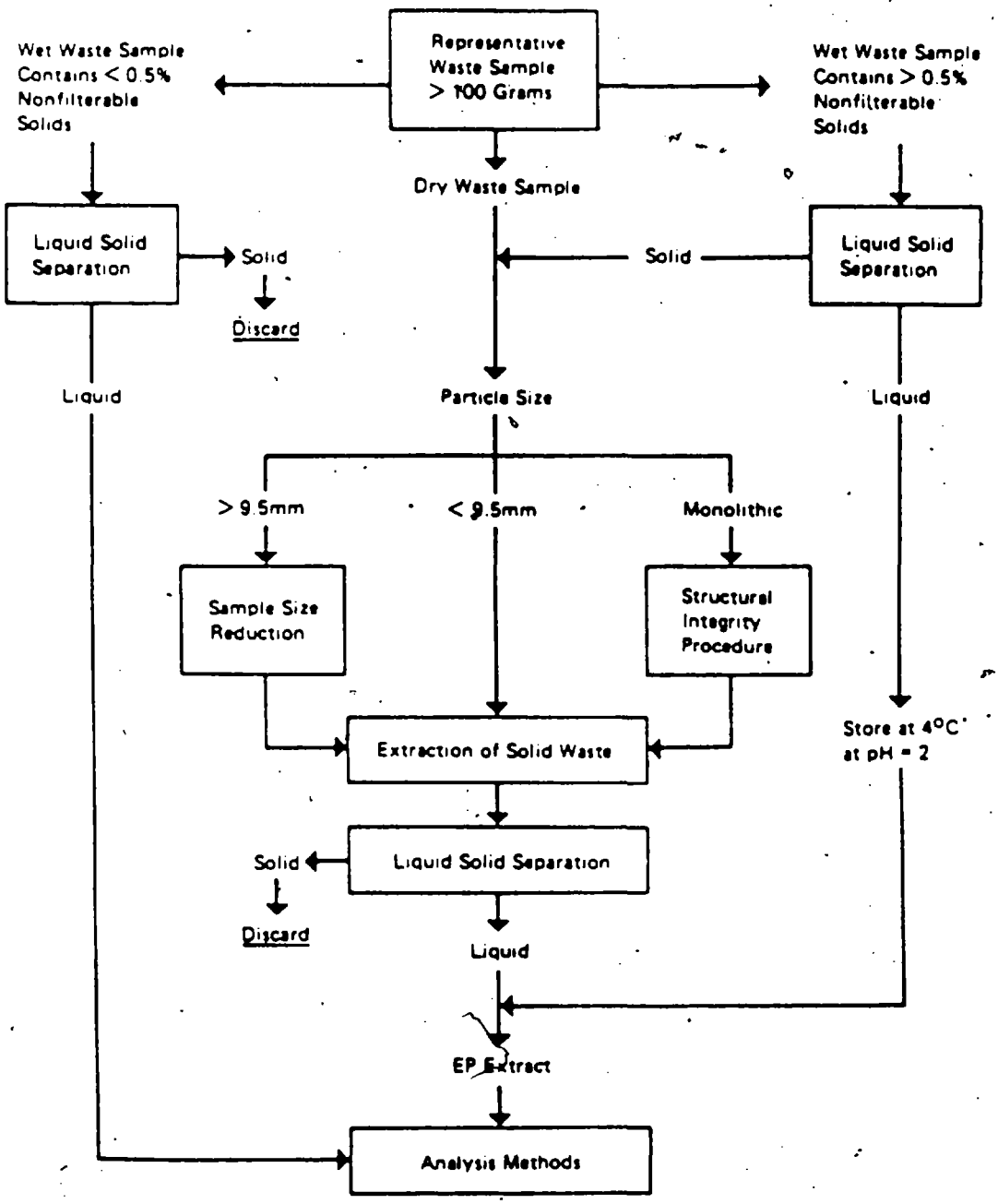


Figure 1. Extraction Procedure Flowchart.

2.1.4 Extraction Procedure Toxicity

Introduction

The Extraction Procedure (EP) is designed to simulate the leaching a waste will undergo if disposed of in a sanitary landfill. This test is designed to simulate leaching that takes place in a sanitary landfill only. It is a laboratory test in which a representative sample of a waste is extracted with distilled water maintained at a pH of 5 using acetic acid. The extract obtained from the EP (the "EP Extract") is then analyzed to determine if any of the thresholds established for the eight elements (arsenic, barium, cadmium, chromium, lead, mercury, selenium, silver), four pesticides (Endrin, Lindane, Methoxychlor, Toxaphene), and two herbicides (2,4,5-trichlorophenoxypropionic acid, 2,4-dichlorophenoxyacetic acid) have been exceeded. If the EP Extract contains any one of the above substances in an amount equal to or exceeding the levels specified in 40 CFR 261.24, the waste possesses the characteristic of Extraction Procedure Toxicity and is a hazardous waste.

Summary of Procedure

The Extraction Procedure consists of five steps (refer to Figure 1):

1. Separation Procedure

A waste containing unbound liquid is filtered and if the solid phase is less than 0.5% of the waste, the solid phase is discarded and the filtrate analyzed for trace elements, pesticides, and herbicides (step 5). If the waste contains more than 0.5% solids, the solid phase is extracted and the liquid phase stored for later use.

2. Structural Integrity Procedure/Particle Size Reduction

Prior to extraction, the solid material must pass through a 9.5-mm (0.375-in.) standard sieve, have a surface area per gram of waste of 3.1 cm^2, or, if it consists of a single piece, be subjected to the Structural Integrity Procedure. The Structural Integrity Procedure is used to demonstrate the ability of the waste to remain intact after disposal. If the waste does not meet one of these conditions it must be ground to pass the 9.5-mm sieve.

3. Extraction of Solid Material

The solid material from step 2 is extracted for 24 hr in an aqueous medium whose pH is maintained at or below 5 using 0.5 N acetic acid. The pH is maintained either automatically or manually. (In acidifying to pH 5, no more than 4.0 g of acid solution per g of material being extracted may be used.)

TABLE 1. MAXIMUM CONCENTRATION OF CONTAMINANTS FOR CHARACTERISTIC OF EP TOXICITY

EPA Hazardous Waste Number	Contaminant	Maximum concentration (mg/l)
D004	Arsenic	5.0
D005	Barium	100.0
D006	Cadmium	1.0
D007	Chromium	5.0
D008	Lead	5.0
D009	Mercury	0.2
D010	Selenium	1.0
D011	Silver	5.0
D012	Endrin (1,2,3,4,10,10-Hexachloro-1 7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1 4-endo, endo-5,8-dimethanonaphthalene)	0.02
D013	Lindane (1,2,3,4,5,6-Hexachlorocyclohexane, gamma isomer	0.4
D014	Methoxychlor (1,1,1-Trichloro-2,2-bis (p-methoxyphenyl)ethane)	10.0
D015	Toxaphene ($C_{10}H_{10}Cl_8$, Technical chlorinated camphene, 67-69% chlorine)	0.5
D016	2,4-D (2,4-Dichlorophenoxyacetic acid)	10.0
D017	2,4,5-TP (Silvex) (2,4,5-Trichlorophenoxypropionic acid)	1.0

4. Final Separation of the Extraction from the Remaining Solid

After extraction, the liquid:solid ratio is adjusted to 20:1 and the mixed solid and extraction liquid are separated by filtration. the solid is discarded and the liquid combined with any filtrate obtained in step 1. This is the EP Extract that is analyzed and compared to the threshold listed in Table 1 of 40 CFR 261.24.

5. Testing (Analysis) of EP Extract

Inorganic and organic species are identified and quantified using the appropriate methods in the 7000 and 8000 series of methods in this manual.

Regulatory Definition

A solid waste exhibits the characteristic of EP toxicity if, using the appropriate test methods described in this manual or equivalent methods approved by the Administrator under the procedures set forth in 40 CFR 260.20 and 260.21, the extract from a representative sample of the waste contains any of the contaminants listed in Table 1 at a concentration equal to or greater than the respective value given in that Table. If a waste contains less than 0.5% filterable solids, the waste itself, after filtering, is considered to be the extract for the purposes of analysis.

A solid waste that exhibits the characteristic of EP toxicity, but is not listed as a hazardous waste in Subpart D, is assigned EPA Hazardous Waste Numbers that correspond to the toxic contaminants causing it to be hazardous. These numbers are specified in Table 1.

METHOD 1310

EXTRACTION PROCEDURE (EP) TOXICITY TEST METHOD AND STRUCTURAL INTEGRITY TEST

1.0 Scope and Application

1.1 The extraction procedure (EP) described in this method is designed to simulate the leaching a waste will undergo if disposed of in an improperly designed sanitary landfill. Method 1310 is applicable to liquid, solid, and multiphasic samples.

2.0 Summary of Method

2.1 If a representative sample of the waste contains more than 0.5% solids, the solid phase of the sample is extracted with deionized water which is maintained at a pH of 5 ± 0.2 using acetic acid. The extract is analyzed to determine if any of the threshold limits listed in Table 1 are exceeded. Table 1 also specifies the approved method of analysis. Wastes that contain less than 0.5% solids are not subjected to extraction, but are directly analyzed and evaluated in a manner identical to that of extracts.

3.0 Interferences

3.1 Potential interferences that may be encountered during analysis are discussed in the individual analytical methods referenced in Table 1.

4.0 Apparatus and Materials

4.1 Extractor: For purposes of this test, an acceptable extractor is one that will impart sufficient agitation to the mixture to (1) prevent stratification of the sample and extraction fluid and (2) ensure that all sample surfaces are continuously brought into contact with well-mixed extraction fluid. Examples of suitable extractors are shown in Figures 1-3 of this method and Section 2.2 (Mobility) of this manual and are available from Associated Designs & Manufacturing Co., Alexandria, Virginia; Glas-Col Apparatus Co., Terre Haute, Indiana; Millipore, Bedford, Massachusetts; and Rexnard, Milwaukee, Wisconsin.

4.2 pH Meter or pH Controller (Chemtrix, Inc., Hillsboro, Oregon is a possible source of a pH controller).

4.3 Filter holder: A filter holder capable of supporting a 0.45-μ filter membrane and able to withstand the pressure needed to accomplish separation. Suitable filter holders range from simple vacuum units to relatively complex systems that can exert up to 5.3 kg/cm^3 (75 psi) of pressure. The type of filter holder used depends upon the properties of the mixture to be filtered. Filter holders known to EPA and deemed suitable for use are listed in Table 2.

TABLE 1. MAXIMUM CONCENTRATION OF CONTAMINANTS FOR CHARACTERISTIC OF EP TOXICITY

Contaminant	Maximum concentration (mg/l)	Analytical method
Arsenic	5.0	7060, 7061
Barium	100.0	7080, 7081
Cadmium	1.0	7130, 7131
Total Chromium	5.0	7190, 7191
Hexavalent Chromium	5.0	7195, 7196, 7197
Lead	5.0	7420, 7421
Mercury	0.2	7470
Selenium	1.0	7740, 7741
Silver	5.0	7760, 7761
Endrin (1,2,3,4,10,10-Hexachloro-1 7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1 4-endo, endo-5,8-dimethanonaphthalene)	0.02	8080
Lindane (1,2,3,4,5,6-Hexachlorocyclohexane, gamma isomer)	0.4	8080
Methoxychlor (1,1,1-Trichloro-2,2-bis (p-methoxyphenyl)ethane)	10.0	8080
Toxaphene ($C_{10}H_{10}Cl_8$, Technical chlorinated camphene, 67-69% chlorine)	0.5	8080
2,4-D (2,4-Dichlorophenoxyacetic acid)	10.0	8150
2,4,5-TP (Silvex) (2,4,5-Trichlorophenoxypropionic acid)	1.0	8150

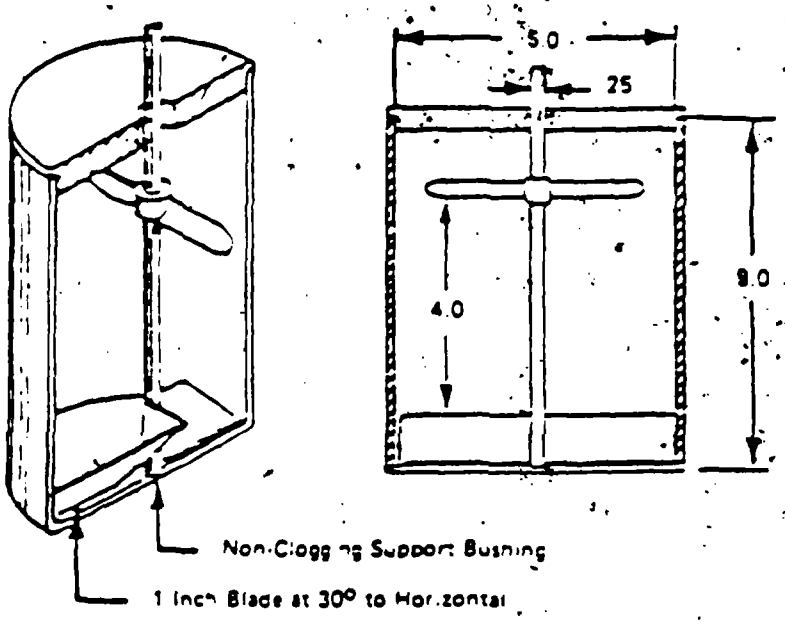


Figure 1. Extractor

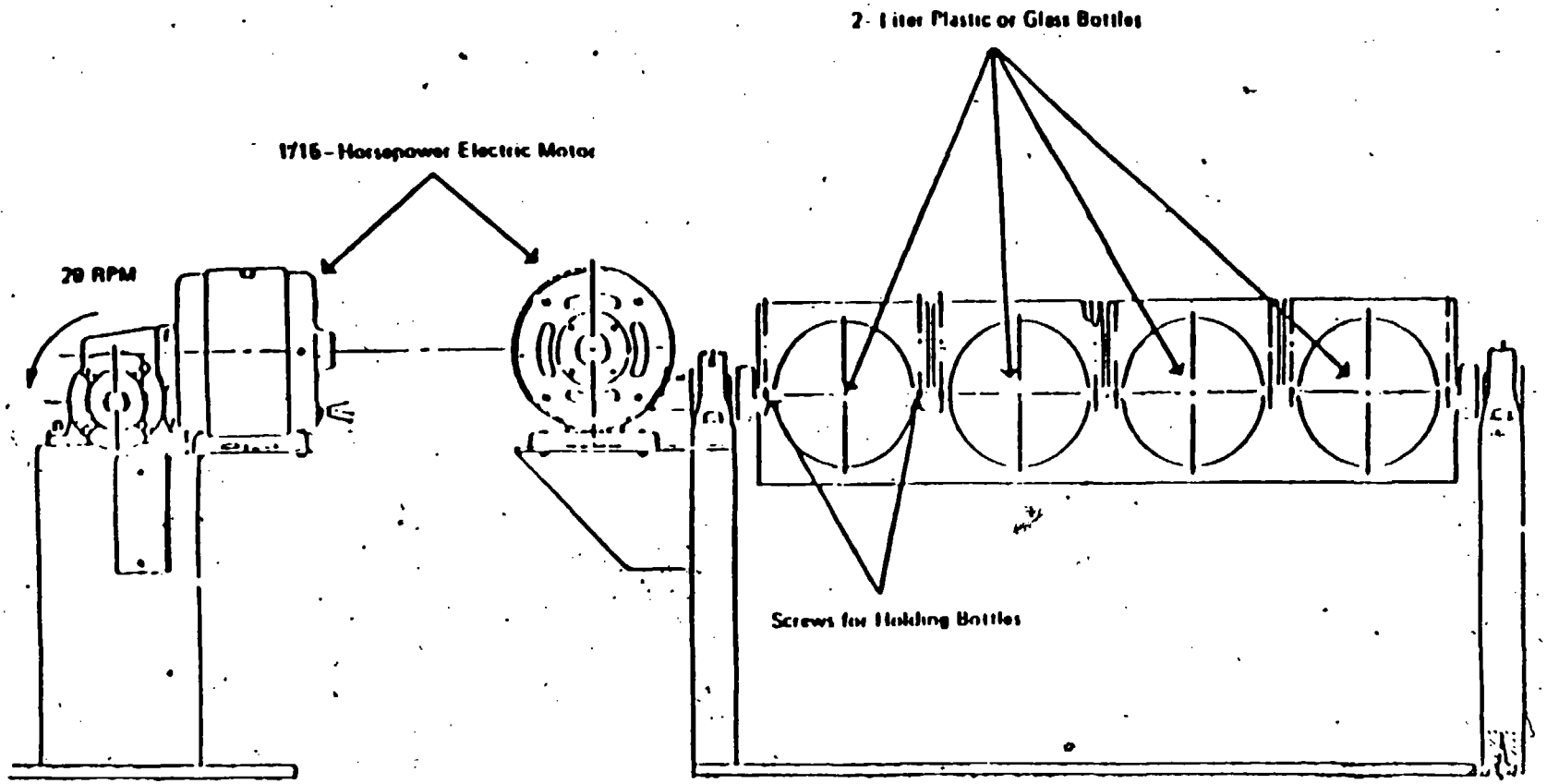


Figure 2 Rotary Extractor

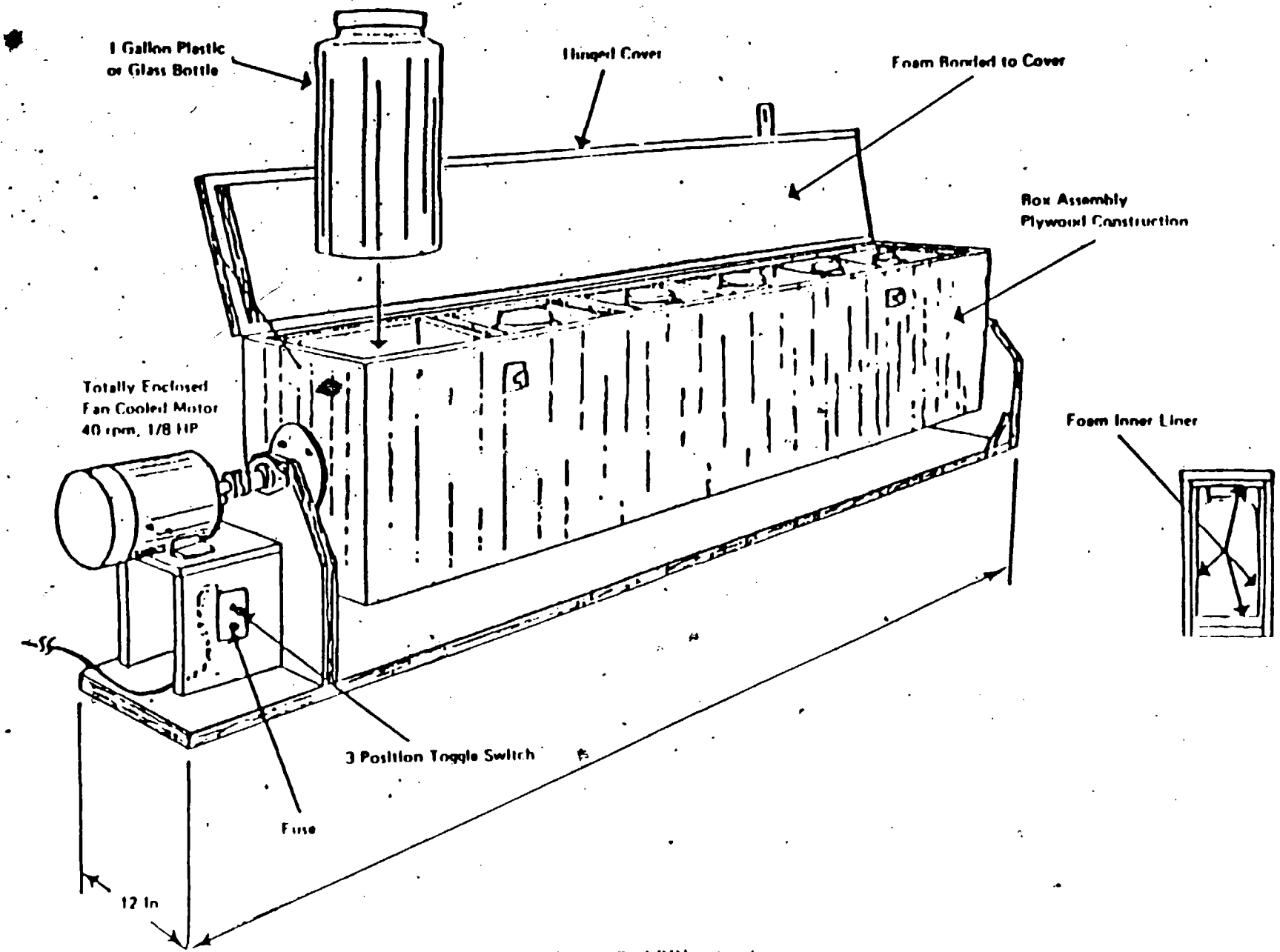


Figure 3. EPRI extractor

4.4 Filter membrane: Filter membrane suitable for conducting the required filtration shall be fabricated from a material which: (1) is not physically changed by the waste material to be filtered, and (2) does not absorb or leach the chemical species for which a waste's EP Extract will be analyzed. Table 3 lists filter media known to the agency and generally found to be suitable for solid waste testing.

4.4.1 In cases of doubt, contact the filter manufacturer to determine if the membrane or the prefilter are adversely affected by the particular waste. If no information is available, submerge the filter in the waste's liquid phase. After 48 hr, a filter that undergoes visible physical change (i.e., curls, dissolves, shrinks, or swells) is unsuitable for use.

TABLE 2. EPA-APPROVED FILTER HOLDERS

Manufacturer	Size	Model No.	Comments
Vacuum Filters			
Nalgene	500 ml	44-0045	Disposable plastic unit, includes prefilter and filter pads, and reservoir; should be used when solution is to be analyzed for inorganic constituents.
Nuclepore	47 mm	410400	
Millipore	47 mm	XX10 047 00	
Pressure Filters			
Nuclepore	142 mm	425900	
Micro Filtration Systems	142 mm	302300	
Millipore	142 mm	YT30 142 HW	

TABLE 3. EPA-APPROVED FILTRATION MEDIA

Supplier	Filter to be used for aqueous systems	Filter to be used for organic systems
Coarse Prefilter		
Gelman	61631, 61635	61631, 61635
Nuclepore	210907, 211707	210907, 211707
Millipore	AP25 035 00, AP25 127 50	AP25 035 00, AP25 127 50
Medium prefilters		
Nuclepore	210905, 211705	210905, 211705
Millipore	AP20 035 00, AP20 124 50	AP20 035 00, AP20 124 50
Fine prefilters		
Gelman	64798, 64803	64798, 64803
Nuclepore	210903, 211703	210903, 211703
Millipore	AP15 035 00, AP15 124 50	AP15 035 00, AP15 124 50
Fine filters (0.45 μm)		
Gelman	60173, 60177	60540 or 66149, 60544 or 66151
Pall	NX04750, NX14225	
Nuclepore	142218	142218[a]
Millipore	HAWP 047 00, HAWP 142 50	FHUP 047 00, FHLP 142 50
Selas	83485-02, 83486-02	83485-02, 83486-02

[a]Susceptible to decomposition by certain polar organic solvents.

4.4.2.1 Prepare a standard solution of the chemical species of interest.

4.4.2.2 Analyze the standard for its concentration of the chemical species.

4.4.2.3 Filter the standard and re-analyze. If the concentration of the filtrate differs from the original standard, the filter membrane leaches or absorbs one or more of the chemical species.

4.5 Structural integrity tester: Having a 3.18-cm (1.25-in.) diameter hammer weighing 0.33 kg (0.73 lb) and having a free fall of 15.24 cm (6 in.) shall be used. This device is available from Associated Design and Manufacturing Company, Alexandria, VA 22314, as Part No. 125, or it may be fabricated to meet the specifications shown in Figure 4.

5.0 Reagents

5.1 Deionized water: Water should be monitored for impurities.

5.2 0.5 N acetic acid: This can be made by diluting concentrated glacial acetic acid (17.5 N). The glacial acetic acid should be of high purity and monitored for impurities.

5.3 Analytical standards should be prepared according to the analytical methods referenced in Table 1.

6.0 Sample Collection, Preservation and Handling

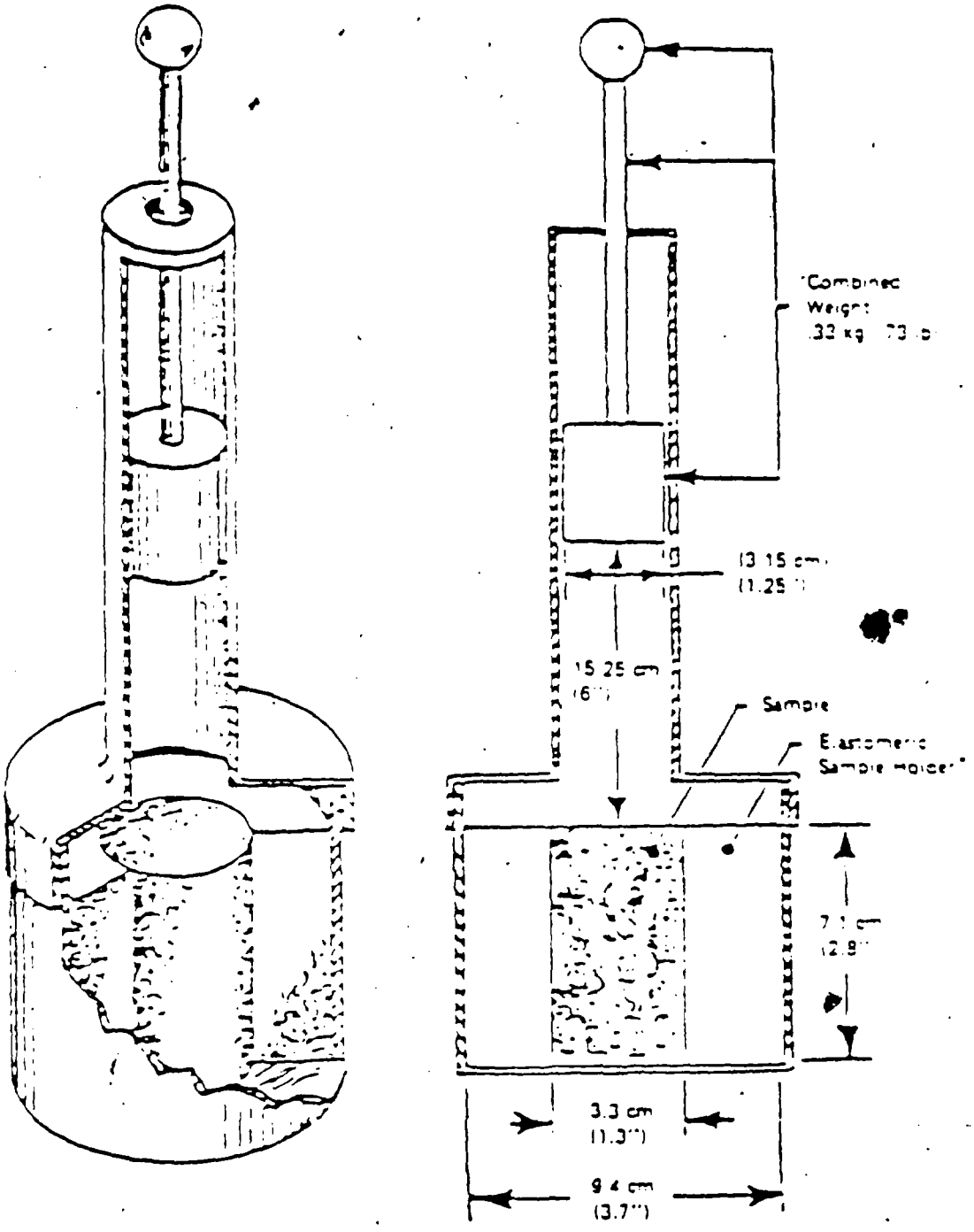
6.1 All samples must be collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 Preservatives must not be added to samples.

6.3 Samples can be refrigerated if it is determined that refrigeration will not affect the integrity of the sample.

7.0 Procedure

7.1 If the waste does not contain any free liquid, go to Section 7.9. If the sample is liquid or multiphase, continue as follows. Weigh filter membrane and prefilter to ±0.01 g. Handle membrane and prefilters with blunt curved-tip forceps or vacuum tweezers, or by applying suction with a pipette.



* Elastomeric sample holder fabricated of material firm enough to support the sample

Figure 4 Compaction tester.

7.2 Assemble filter holder, membranes, and prefilters following the manufacturer's instructions. Place the 0.45-μm membrane on the support screen and add prefilters in ascending order of pore size. Do not prewet filter membrane.

7.3 Weigh out a representative subsample of the waste (100 g minimum).

7.4 Allow slurries to stand to permit the solid phase to settle. Wastes that settle slowly may be centrifuged prior to filtration.

7.5 Wet the filter with a small portion of the waste's or extraction mixture's liquid phase. Transfer the remaining material to the filter holder and apply vacuum or gentle pressure (10-15 psi) until all liquid passes through the filter. Stop filtration when air or pressurizing gas moves through the membrane. If this point is not reached under vacuum or gentle pressure, slowly increase the pressure in 10-psi increments to 75 psi. Halt filtration when liquid flow stops. This liquid will constitute part or all of the extract (refer to Section 7.16). The liquid should be refrigerated until time of analysis.

NOTE: Oil samples or samples which contain oil are treated in exactly the same way as any other sample. The liquid portion of the sample is filtered and treated as part of the EP extract. If the liquid portion of the sample will not filter (this is usually the case with heavy oils or greases) it is carried through the EP extraction as a solid.

7.6 Remove the solid phase and filter media and, while not allowing it to dry, weight to ±0.01 g. The wet weight of the residue is determined by calculating the weight difference between the weight of the filters (Section 7.1) and the weight of the solid phase and the filter media.

7.7 The waste will be handled differently from this point on depending on whether it contains more of less than 0.5% solids. If the sample appears to have less than 0.5% solids, the percent solids will be determined by the following procedure.

7.7.1 Dry the filter and residue at 80° C until two successive weighings yield the same value.

7.7.2 Calculate the percent solids using the following equation:

$$\frac{\text{weight of filtered solid and filters} - \text{tared weight of filters}}{\text{initial weight of waste material}} \times 100 = \% \text{ solids}$$

NOTE: This procedure is only used to determine whether the solid must be extracted or whether it can be discarded unextracted. It

is not used in calculating the amount of water or acid to use in the extraction step. Do not extract solid material that has been dried at 80° C. A new sample will have to be used for extraction if a percent solids determination is performed.

7.8 If the solid comprises less than 0.5% of the waste, discard the solid and proceed immediately to Section 7.17, treating the liquid phase as the extract.

7.9 The solid material obtained from Section 7.5 and all materials that do not contain free liquids should be evaluated for particle size. If the solid material has a surface area per gram of material equal to or greater than 3.1 cm^2 or passes through a 9.5-mm (0.375-in.) standard sieve, the operator should proceed to Section 7.11. If the surface area is smaller or the particle size larger than specified above, the solid material would be prepared for extraction by crushing, cutting or grinding the material so that it passes through a 9.5-mm (0.375-in.) sieve or, if the material is in a single piece, by subjecting the material to the "Structural Integrity Procedure" described in Section 7.10.

7.10 Structural Integrity Procedure (SIP):

7.10.1 Cut a 3.3-cm-diameter by 7.1-cm-long cylinder from the waste material. For wastes that have been treated using a fixation process, the waste may be cast in the form of a cylinder and allowed to cure for 30 days prior to testing.

7.10.2 Place waste into sample holder and assemble the tester. Raise the hammer to its maximum height and drop. Repeat 14 additional times.

7.10.3 Remove solid material from tester and scrape off any particles adhering to sample holder. Weigh the waste to the nearest 0.01 g and transfer it to the Extractor.

7.11 If the sample contains more than 0.5% solids, use the wet weight of the solid phase obtained in Section 7.6 for purposes of calculating the amount of liquid and acid to employ for extraction by using the following equation:

$$W = W_f - W_t$$

where:

W = wet weight in grams of solid to be charged to extractor

W_f = wet weight in grams of filtered solids and filter media

W_t = weight in grams of tared filters.

If the waste does not contain any free liquids, 100 g of the material will be subjected to the extraction procedure.

7.12 Place the appropriate amount of material (refer to Section 7.11) into the extractor and add 16 times its weight of deionized water.

7.13 After the solid material and deionized water are placed in the extractor, the operator should begin agitation and measure the pH of the solution in the extractor. If the pH is greater than 5.0, the pH of the solution should be decreased to 5.0 ± 0.2 by adding 0.5 N acetic acid. If the pH is equal to or less than 5.0, no acetic acid should be added. The pH of the solution should be monitored, as described below, during the course of the extraction and, if the pH rises above 5.2, 0.5 N acetic acid should be added to bring the pH down to 5.0 ± 0.2. However, in no event shall the aggregate amount of acid added to the solution exceed 4 ml of acid per gram of solid. The mixture should be agitated for 24 hr and maintained at 20°-40° C (68°-104° F) during this time. It is recommended that the operator monitor and adjust the pH during the course of the extraction with a device such as the Type 45-A pH Controller manufactured by Chemtrix, Inc., Hillsboro, Oregon 97123 or its equivalent, in conjunction with a metering pump and reservoir of 0.5 N acetic acid. If such a system is not available, the following manual procedure shall be employed.

7.13.1 A pH meter should be calibrated in accordance with the manufacturer's specifications.

7.13.2 The pH of the solution should be checked and, if necessary, 0.5 N acetic acid should be manually added to the extractor until the pH reaches 5.0 ± 0.2. The pH of the solution should be adjusted at 15-, 30-, and 60-min intervals, moving to the next longer interval if the pH does not have to be adjusted more than 0.5 pH units.

7.13.3 The adjustment procedure should be continued for at least 6 hr.

7.13.4 If, at the end of the 24-hr extraction period, the pH of the solution is not below 5.2 and the maximum amount of acid (4 ml per gram of solids) has not been added, the pH should be adjusted to 5.0 ± 0.2 and the extraction continued for an additional 4 hr, during which the pH should be adjusted at 1-hr intervals.

7.14 At the end of the extraction period, deionized water should be added to the extractor in an amount determined by the following equation:

$$V = (20)(W) - 16(W) - A$$

where:

V = ml deionized water to be added

W = weight in g of solid charged to extractor

A = ml of 0.5 N acetic acid added during extraction

7.15 The material in the extractor should be separated into its component liquid and solid phases in the following manner.

7.15.1 Allow slurries to stand to permit the solid phase to settle (wastes that are slow to settle may be centrifuged prior to filtration) and set up the filter apparatus (refer to Section 4.3 and 4.4).

7.15.2 Wet the filter with a small portion of the waste's or extraction mixture's liquid phase. Transfer the remaining material to the filter holder and apply vacuum or gentle pressure (10-15 psi) until all liquid passes through the filter. Stop filtration when air or pressurizing gas moves through the membrane. If this point is not reached under vacuum or gentle pressure, slowly increase the pressure in 10 psi increments to 75 psi. Halt filtration when liquid flow stops.

7.16 The liquids resulting from Sections 7.5 and 7.15 should be combined. This combined liquid (or the waste itself if it has less than 0.5% solids, as noted in Section 7.8) is the extract and should be analyzed for the presence of any of the contaminants specified in Table 1 using the Analytical Procedures designated in Section 7.17.

7.17 The extract will be prepared and analyzed according to the analytical methods specified in Table 1. All of these analytical methods are included in this manual. The method of standard addition will be employed for all metal analyses.

NOTE: If the EP extract includes two phases, concentration of contaminants is determined by using a simple weighted average. For example: An EP extract contains 50 ml of oil and 1,000 ml of an aqueous phase. Contaminant concentrations are determined for each phase. The final contamination concentration is taken to be

$$\frac{(50)(\text{contaminant conc. in oil})}{1{,}050} + \frac{(1{,}000)(\text{contaminant conc. of aqueous phase})}{1{,}050}$$

7.18 The extract concentrations are compared to the maximum contamination limits listed in Table 1. If the extract concentrations are equal to or greater than the respective values, then the waste is considered to be EP toxic.[1]

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[1]Chromium concentrations have to be interpreted differently. A waste containing chromium will be determined to be EP toxic if (1) the waste extract has an initial pH of less than 7 and contains more than 5 mg/l of hexavalent chromium in the resulting extract, or (2) the waste extract has an initial pH greater than 7 and a final pH greater than 7 and contains more than 5 mg/l of hexavalent chromium in the extract, or (3) the waste extract has an initial pH greater than 7 and a final pH less than 7 and contains more than 5 mg/l of total chromium, unless the chromium is trivalent. To determine whether the chromium is trivalent, the sample must be processed according to an alkaline digestion method (Method 3060) and analyzed for hexavalent chromium (Methods 7195, 7196, or 7197).

8.0 Quality Control

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.3 All quality control measures suggested in the referenced analytical methods should be followed.

METHOD 7060

ARSENIC (ATOMIC ABSORPTION, FURNACE TECHNIQUE)

1.0 Scope and Application

1.1 Method 7060 is an atomic absorption procedure approved for determining the concentration of arsenic in wastes, mobility procedure extracts, soils, and groundwater. All samples must be subjected to an appropriate dissolution step prior to analysis.

2.0 Summary of Method

2.1 Prior to analysis by Method 7060, samples must be prepared in order to convert organic forms of arsenic to inorganic forms, to minimize organic interferences, and to convert the sample to a suitable solution for analysis. The sample preparation procedure varies depending on the sample matrix. Aqueous samples are subjected to the acid digestion procedure described in this method. Sludge samples are prepared using the procedure described in Method 3050. For samples containing oils, greases, or waxes, the procedures described in Methods 3030 and 3040 may be applicable.

2.2 Following the appropriate dissolution of the sample, a representative aliquot of the digestate is spiked with a nickel nitrate solution and is placed manually or by means of an automatic sampler into a graphite tube furnace. The sample aliquot is then slowly evaporated to dryness, charred (ashed), and atomized. The absorption of hollow cathode radiation during atomization will be proportional to the arsenic concentration.

2.3 The typical detection limit for this method is 1 µg/l.

3.0 Interferences

3.1 Elemental arsenic and many of its compounds are volatile and therefore samples may be subject to losses of arsenic during sample preparation. Spike samples and relevant standard reference materials should be processed to determine if the chosen dissolution method is appropriate.

3.2 Likewise, caution must be employed during the selection of temperature and times for the dry and char (ash) cycles. A nickel nitrate solution must be added to all digestate prior to analysis to minimize volatilization losses during drying and ashing.

3.3 In addition to the normal interferences experienced during graphite furnace analysis, arsenic analysis can suffer from severe nonspecific absorption and light scattering caused by matrix components during atomization. Arsenic analysis is particularly susceptible to these problems because of its low analytical wavelength (193.7 nm). Simultaneous background correction must be employed to avoid erroneously high results.

3.4 If the analyte is not completely volatilized and removed from the furnace during atomization, memory effects will occur. If this situation is detected by means of blank burns, the tube should be cleaned by operating the furnace at full power at regular intervals in the analytical scheme.

4.0 Apparatus and Materials

4.1 250-ml Griffin beaker.

4.2 10-ml volumetric flasks.

4.3 Atomic absorption spectrophotometer: Single or dual channel, single- or double-beam instrument having a grating monochromator, photomultiplier detector, adjustable slits, a wavelength range of 190 to 800 nm, and provisions for simultaneous background correction and interfacing with a strip chart recorder.

4.4 Arsenic hollow cathode lamp or electrodeless discharge lamp.

4.5 Graphite furnace: Any graphite furnace device with the appropriate temperature and timing controls.

4.6 Strip chart recorder: A recorder is strongly recommended for furnace work so that there will be a permanent record and so that any problems with the analysis such as drift, incomplete atomization, losses during charring, changes in sensitivity, etc., can easily be recognized.

4.7 Pipets: Microliter with disposable tips. Sizes can range from 5 to 1000 µl as required.

5.0 Reagents

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Concentrated nitric acid: Acid should be analyzed to determine levels of impurities. If impurities are detected, all analyses should be blank-corrected.

5.3 Hydrogen peroxide (30%): Oxidant should be analyzed to determine levels of impurities. If impurities are detected, all analyses should be blank-corrected.

5.4 Arsenic standard stock solution (1000 mg/l): Either procure a certified aqueous standard from a supplier (Spex Industries, Alpha Products, or Fisher Scientific) and verify by comparison with a second standard, or dissolve

1.320 g of arsenic trioxide (As_2O_3, analytical reagent grade) or equivalent in 100 ml of Type II water containing 4 g NaOH. Acidify the solution with 20 ml conc. HNO_3 and dilute to 1 liter.

5.5 Nickel nitrate solution (5%): Dissolve 24.780 g of ACS reagent grade $Ni(NO_3)_2 \cdot 6H_2O$ or equivalent in Type II water and dilute to 100 ml.

5.6 Nickel nitrate solution (1%): Dilute 20 ml of the 5% nickel nitrate to 100 ml with Type II water.

5.7 Arsenic working standards: Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. Withdraw appropriate aliquots of the stock solution, add 1 ml of conc. HNO_3, 2 ml of 30% H_2O_2, and 2 ml of the 5% nickel nitrate solution. Dilute to 100 ml with Type II water.

6.0 Sample Collection, Preservation, and Handling

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and distilled deionized water. Plastic and glass containers are both suitable.

6.3 Special containers (e.g., containers used for volatile organic analysis) may have to be used if very volatile arsenic compounds are to be analyzed.

6.4 Aqueous samples must be acidified to a pH of less than 2 with nitric acid.

6.5 Nonaqueous samples shall be refrigerated when possible, and analyzed as soon as possible.

7.0 Procedure

7.1 Sample preparation: Aqueous samples should be prepared in the manner described in Sections 7.1.1-7.1.3. Sludge-type samples should be prepared according to Method 3050, and samples containing oils, greases, or waxes may be prepared according to Methods 3030 or 3040. The applicability of a sample-preparation technique to a new matrix type must be demonstrated by analyzing spiked samples and/or relevant standard reference materials.

7.1.1 Transfer 100 ml of well-mixed sample to a 250-ml Griffin beaker, add 2 ml of 30% H_2O_2 and sufficient conc. HNO_3 to result in an acid concentration of 1% (v/v). Heat for 1 hr at 95° C or until the volume is slightly less than 50 ml.

7.1.2 Cool and bring back to 50 ml with Type II water.

7.1.3 Pipet 5 ml of this digested solution into a 10-ml volumetric flask, add 1 ml of the 1% nickel nitrate solution and dilute to 10 ml with Type II water. The sample is now ready for injection into the furnace.

7.2 The 193.7-nm wavelength line and a background correction system must be employed. Follow the manufacturer's suggestions for all other spectrophotometer parameters.

7.3 Furnace parameters suggested by the manufacturer should be employed as guidelines. Since temperature-sensing mechanisms and temperature controllers can vary between instruments or with time, the validity of the furnace parameters must be periodically confirmed by systematically altering the furnace parameters while analyzing a standard. In this manner, losses of analyte due to higher than necessary temperature settings or losses in sensitivity due to less than optimum settings can be minimized. Similar verification of furnace parameters may be required for complex sample matrices.

7.4 Inject a measured µl aliquot of sample into the furnace and atomize. If the concentration found is greater than the highest standard, the sample should be diluted in the same acid matrix and reanalyzed. The use of multiple injections can improve accuracy and help detect furnace pipetting errors.

7.5 Analyze, by the method of standard additions, all EP extracts, all samples analyzed as part of a delisting petition, and all samples that suffer from matrix interferences.

7.6 Run a check standard after approximately every 10 sample injections. Standards are run in part to monitor the life and performance of the graphite tube. Lack of reproducibility or significant change in the signal for the standard indicates that the tube should be replaced.

7.7 Calculate metal concentrations by (1) the method of standard additions, or (2) from a calibration curve, or (3) directly from the instrument's concentration readout. All dilution or concentration factors must be taken into account. Concentrations reported for multiphased or wet samples must be appropriately qualified (e.g., 5 µg/g dry weight).

7.8 Duplicates, spiked samples, and check standards should be routinely analyzed.

8.0 Quality Control

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.5 Analyze check standards after approximately every 15 samples.

8.6 Run one duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation process.

8.7 Spiked samples or standard reference materials shall be periodically employed to ensure that correct procedures are being followed and that all equipment is operating properly.

8.8 The method of standard additions shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

METHOD 7080

BARIUM (ATOMIC ABSORPTION, DIRECT ASPIRATION METHOD)

1.0 Scope and Application

1.1 Method 7080 is an atomic absorption procedure approved for determining the concentration of barium in wastes, mobility procedure extracts, soils, and groundwater. All samples must be subjected to an appropriate dissolution step prior to analysis.

2.0 Summary of Method

2.1 Prior to analysis by Method 7080, samples must be prepared for direct aspiration. The method of sample preparation will vary according to the sample matrix. Aqueous samples are subjected to an acid digestion procedure (Method 3010). Sludge samples are prepared using the procedure described in Method 3050. For samples containing oils, greases, or waxes, the procedures described in Methods 3030 and 3040 may be applicable.

2.2 Following the appropriate dissolution of the sample, an ionization suppressant is added and a representative aliquot is aspirated into a nitrous oxide/acetylene flame. The resulting absorption of hollow cathode radiation will be proportional to the barium concentration. When possible, background correction should be employed.

2.3 The typical detection limit for this method is 0.1 mg/l; typical sensitivity is 0.4 mg/l.

3.0 Interferences

3.1 High hollow cathode current settings and a narrow spectral band pass must be used since both barium and calcium emit strongly at barium's analytical wavelength.

3.2 Barium undergoes significant ionization in the nitrous oxide/acetylene flame, resulting in a significant decrease in sensitivity. Therefore an ionization suppressant must be added to both standards and samples.

3.3 Samples and standards should be monitored for viscosity differences that may alter the aspiration rate.

3.4 If an air/acetylene flame is used, then the presence of phosphate silicon and aluminum will decrease the sensitivity. This problem can be overcome by adding a releasing agent (e.g., lanthanum) to both samples and standard.

4.0 Apparatus and Materials

4.1 Atomic absorption spectrophotometer: single or dual channel, single- or double-beam instrument, having a grating monochromator, photomultiplier detector, adjustable slits, and provisions for background correction.

4.2 Barium hollow cathode lamp or electrodeless discharge lamp.

4.3 Strip chart recorder (optional).

5.0 Reagents

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Concentrated nitric acid: Acid should be analyzed to determine level of impurities. If impurities are detected, all analyses should be blank-corrected.

5.3 Barium standard stock solution (1000 mg/l): Either procure a certified aqueous standard from a supplier (Spex Industries, Alpha Products, or Fisher Scientific) and verify by comparison with a second standard, or dissolve 1.787 g barium chloride ($BaCl_2 \cdot 2H_2O$ (analytical reagent grade) in Type II water and dilute to 1 liter.

5.4 Potassium chloride solution: Dissolve 95 g potassium chloride (KCl) in Type II water and dilute to 1 liter.

5.5 Lanthanum chloride solution if needed: Dissolve 25 g reagent grade La_2O_3 slowly in 250 ml concentrated HCl. (Reaction can be violent.) Dilute to 500 ml with Type II water.

5.6 Barium working standards: Prepare dilutions of the stock barium solution to be used as calibration standards. To each 100 ml of standard and sample add 2.0 ml potassium chloride solution.

5.7 Air: Cleaned and dried through a suitable filter to remove oil, water, and other foreign substances. The source may be a compressor or a cylinder of industrial-grade compressed air.

5.8 Acetylene: Should be of high purity. Acetone, which is usually present in acetylene cylinders, can be prevented from entering and affecting flame conditions by replacing the cylinder before the pressure has fallen to 50 psig.

6.0 Sample Collection, Preservation, and Handling

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and Type II water. Plastic and glass containers are both suitable.

6.3 Aqueous samples must be acidified to a pH of less than 2 with nitric acid.

6.4 Nonaqueous samples shall be refrigerated when possible, and analyzed as soon as possible.

7.0 Procedure

7.1 Sample preparation: Aqueous samples should be prepared according to Method 3010; sludge-type samples should be prepared according to Method 3050; and samples containing oils, greases, or waxes may be prepared according to Methods 3030 or 3040. The applicability of a sample preparation technique to a new matrix type must be demonstrated by analyzing spiked samples and/or relevant standard reference materials.

7.2 The 553.6-nm wavelength line shall be used.

7.3 A fuel-rich nitrous oxide/acetylene flame shall be used.

7.4 Follow the manufacturer's operating instructions for all other instrument parameters.

7.5 Either (1) run a series of barium standards and construct a calibration curve by plotting the concentrations of the standards against the absorbances or (2) for the method of standard additions, plot added concentration versus absorbance. For instruments that read directly in concentration, set the curve corrector to read out the proper concentration.

7.6 Analyze, by the method of standard additions, all EP extracts, all samples analyzed as part of a delisting petition, and all samples that suffer from matrix interferences.

7.7 Duplicates, spiked samples, and check standards should be routinely analyzed.

7.8 The final calculated concentration should take into account all dilution and concentration factors.

8.0 Quality Control

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.5 Analyze check standards after approximately every 15 samples.

8.6 Run one duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation process.

8.7 Spiked samples or standard reference materials shall be periodically employed to ensure that correct procedures are being followed and that all equipment is operating properly.

8.8 The method of standard additions shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

METHOD 7130

CADMIUM (ATOMIC ABSORPTION, DIRECT ASPIRATION METHOD)

1.0 Scope and Application

1.1 Method 7130 is an atomic absorption procedure approved for determining the concentration of cadmium in wastes, mobility procedure extracts, soils, and groundwater. All samples must be subjected to an appropriate dissolution step prior to analysis.

2.0 Summary of Method

2.1 Prior to analysis by Method 7130, samples must be prepared for direct aspiration. The method of sample preparation will vary according to the sample matrix. Aqueous samples are subjected to acid digestion procedure (Method 3010). Sludge samples are prepared using the procedure described in Method 3050. For samples containing oils, greases, or waxes, the procedures described in Methods 3030 and 3040 may be applicable.

2.2 Following the appropriate dissolution of the sample, a representative aliquot is aspirated into an air/acetylene flame. The resulting absorption of hollow cathode radiation will be proportional to the cadmium concentration. Background correction must be employed for all analyses.

2.3 The typical detection limit for this method is 0.005 mg/l; typical/sensitivity is 0.025 mg/l.

3.0 Interferences

3.1 Nonspecific absorption and light scattering can be significant at the analytical wavelength. Thus background correction is required.

3.2 Samples and standards should be monitored for viscosity differences that may alter the aspiration rate.

4.0 Apparatus and Materials

4.1 Atomic absorption spectrophotometer: Single or dual channel, single- or double-beam instrument, having a grating monochromator, photomultiplier detector, adjustable slits, and provisions for background correction.

4.2 Cadmium hollow cathode lamp or electrodeless discharge lamp.

4.3 Strip chart recorder (optional).

5.0 Reagents

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Concentrated nitric acid: Acid should be analyzed to determine level of impurities. If impurities are detected, all analyses should be blank-corrected.

5.3 Cadmium standard stock solution (1000 mg/l): Either procure a certified aqueous standard from a supplier (Spex Industries, Alpha Products, or Fisher Scientific) and verify by comparison with a second standard, or dissolve 2.282 g cadmium sulfate ($CdSO_4 \cdot 8H_2O$, analytical reagent grade) and dissolve in Type II water or equivalent.

5.4 Cadmium working standards: These standards should be prepared with the same type and same concentration of acid that will be found in the analytical solution.

5.5 Air: Cleaned and dried through a suitable filter to remove oil, water, and other foreign substances. The source may be a compressor or a cylinder of industrial-grade compressed air.

5.6 Acetylene: Should be of high purity. Acetone, which is usually present in acetylene cylinders, can be prevented from entering and affecting flame conditions, by replacing the cylinder before the pressure has fallen to 50 psig.

6.0 Sample Collection, Preservation, and Handling

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and Type II water. Plastic and glass containers are both suitable.

6.3 Aqueous samples must be acidified to a pH of less than 2 with nitric acid.

6.4 Nonaqueous samples shall be refrigerated when possible, and analyzed as soon as possible.

7.0 Procedure

7.1 Sample preparation: Aqueous samples should be prepared according to Method 3010; sludge-type samples should be prepared according to Method 3050; and samples containing oils, greases or waxes may be prepared according

to Methods 3030 or 3040. The applicability of a sample preparation technique to a new matrix type must be demonstrated by analyzing spiked samples and/or relevant standard reference materials.

7.2 The 228.8-nm wavelength line and background correction shall be employed.

7.3 An oxidizing air/acetylene flame shall be used.

7.4 Follow the manufacturer's operating instructions for all other instrument parameters.

7.5 Either (1) run a series of cadmium standards and construct a calibration curve by plotting the concentrations of the standards against the absorbances or (2) for the method of standard additions, plot added concentration versus absorbance. For instruments that read directly in concentration, set the curve corrector to read out the proper concentration.

7.6 Analyze, by the method of standard additions, all EP extracts, all samples analyzed as part of a delisting petition, and all samples that suffer from matrix interferences.

7.7 Duplicates, spiked samples, and check standards should be routinely analyzed.

7.8 Calculate metal concentrations by (1) the method of standard additions, or (2) from a calibration curve, or (3) directly from the instrument's concentration readout. All dilution or concentration factors must be taken into account. Concentrations reported for multiphased or wet samples must be appropriately qualified (e.g., 5 µg/g dry weight).

8.0 Quality Control

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.5 Analyze check standards after approximately every 15 samples.

8.6 Run one duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation process.

8.7 Spiked samples or standard reference materials shall be periodically employed to ensure that correct procedures are being followed and that all equipment is operating properly.

8.8 The method of standard additions shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

METHOD 7190

CHROMIUM (ATOMIC ABSORPTION, DIRECT ASPIRATION METHOD)

1.0 Scope and Application

1.1 Method 7190 is an atomic absorption procedure approved for determining the concentration of chromium in wastes, mobility procedure extracts, soils, and groundwater. All samples must be subjected to an appropriate dissolution step prior to analysis.

2.0 Summary of Method

2.1 Prior to analysis by Method 7190, samples must be prepared for direct aspiration. The method of sample preparation will vary according to the sample matrix. Aqueous samples are subjected to an acid digestion procedure (Method 3010). Sludge samples are prepared using the procedure described in Method 3050. For samples containing oils, greases, or waxes, the procedures described in Methods 3030 and 3040 may be applicable.

2.2 Following the appropriate dissolution of the sample, a representative aliquot is aspirated into an nitrous oxide/acetylene flame. The resulting absorption of hollow cathode radiation will be proportional to the chromium concentration.

2.3 The typical detection limit for this method is 0.05 mg/l; typical sensitivity is 0.25 mg/l.

3.0 Interferences

3.1 The nitrous oxide/acetylene flame is the recommended flame since chromium analysis in an air/acetylene flame suffers from matrix interferences caused by nickel iron and other metals. If an air/acetylene flame must be used it should be lean.

3.2 An ionization interference may occur in the nitrous oxide flame if the samples have a significantly higher amount of alkali salts than the standards. If this interference is encountered, an ionization suppressant should be added to both samples and standards.

3.3 Samples and standards should be monitored for viscosity differences that may alter the aspiration rate.

4.0 Apparatus and Materials

4.1 Atomic absorption spectrophotometer: Single or dual channel, single- or double-beam instrument, having a grating monochromator, photomultiplier detector, adjustable slits, and provisions for background correction.

4.2 Chromium hollow cathode lamp or electrodeless discharge lamp.

4.3 Strip chart recorder (optional).

5.0 Reagents

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Concentrated nitric acid: Acid should be analyzed to determine level of impurities. If impurities are detected, all analyses should be blank-corrected.

5.3 Chromium standard stock solution (1000 mg/l): Either procure a certified aqueous standard from a supplier (Spex Industries, Alpha Products, or Fisher Scientific) and verify by comparison with a second standard, or dissolve 1.923 g of chromium trioxide (CrO_3, reagent grade) in Type II water, acidify with redistilled HNO_3 and dilute to 1 liter.

5.4 Chromium working standards: These standards should be prepared with the same type and same concentration of acid that will be found in the analytical solution.

5.5 Nitrous oxide cylinder.

5.6 Air: Cleaned and dried through a suitable filter to remove oil, water, and other foreign substances. The source may be a compressor or a cylinder of industrial-grade compressed air.

5.7 Acetylene: Should be of high purity. Acetone, which is usually present in acetylene cylinders, can be prevented from entering and affecting flame conditions, by replacing the cylinder before the pressure has fallen to 50 psig.

6.0 Sample Collection, Preservation, and Handling

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and Type II water. Plastic and glass containers are both suitable.

6.3 Aqueous samples must be acidified to a pH of less than 2 with nitric acid.

6.3 Aqueous samples must be acidified to a pH of less than 2 with nitric acid.

7.0 Procedure

7.1 Sample preparation: Aqueous samples should be prepared according to Method 3010; sludge-type samples should be prepared according to Method 3050; and samples containing oils, greases or waxes may be prepared according to Methods 3030 or 3040. The applicability of a sample preparation technique to a new matrix type must be demonstrated by analyzing spiked samples and/or relevant standard reference materials.

7.2 The 357.9-nm wavelength line and background correction shall be employed.

7.3 A fuel-rich nitrous oxide/acetylene flame shall be used.

7.4 Follow the manufacturer's operating instructions for all other instrument parameters.

7.5 Either (1) run a series of chromium standards and construct a calibration curve by plotting the concentrations of the standards against the absorbances or (2) for the method of standard additions, plot added concentration versus absorbance. For instruments that read directly in concentration, set the curve corrector to read out the proper concentration.

7.6 Analyze, by the method of standard additions, all EP extracts, all samples analyzed as part of a delisting petition, and all samples that suffer from matrix interferences.

7.7 Duplicates, spiked samples, and check standards should be routinely analyzed.

7.8 Calculate metal concentrations by (1) the method of standard additions, or (2) from a calibration curve, or (3) directly from the instrument's concentration readout. All dilution or concentration factors must be taken into account. Concentrations reported for multiphased or wet samples must be appropriately qualified (e.g., 5 µg/g dry weight).

8.0 Quality Control

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.5 Analyze check standards after approximately every 15 samples.

8.6 Run one duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation process.

8.7 Spiked samples or standard reference materials shall be periodically employed to ensure that correct procedures are being followed and that all equipment is operating properly.

8.8 The method of standard additions shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

METHOD 7420

LEAD (ATOMIC ABSORPTION, DIRECT ASPIRATION METHOD)

1.0 Scope and Application

1.1 Method 7420 is an atomic absorption procedure approved for determining the concentration of lead in wastes, mobility procedure extracts, and soils. All samples must be subjected to an appropriate dissolution step prior to analysis.

2.0 Summary of Method

2.1 Prior to analysis by Method 7420, samples must be prepared for direct aspiration. The method of sample preparation will vary according to the sample matrix. Aqueous samples are subjected to an acid digestion procedure (Method 3010). Sludge samples are prepared using the procedure described in Method 3050. For samples containing oils, greases, or waxes, the procedures described in Methods 3030 and 3040 may be applicable.

2.2 Following the appropriate dissolution of the sample, a representative aliquot is aspirated into an air/acetylene flame. The resulting absorption of hollow cathode radiation will be proportional to the lead concentration. Background correction must be employed for all analyses.

2.3 The typical detection limit for this method is 0.1 mg/l; typical sensitivity is 0.5 mg/l.

3.0 Interferences

3.1 Background correction is required since nonspecific absorption and light scattering can be significant at the analytical wavelength.

3.2 Samples and standards should be monitored for viscosity differences that may alter the aspiration rate.

4.0 Apparatus and Materials

4.1 Atomic absorption spectrophotometer: Single or dual channel, single- or double-beam instrument, having a grating monochromator, photomultiplier detector, adjustable slits, and provisions for background correction.

4.2 Lead hollow cathode lamp or electrodeless discharge lamp.

4.3 Strip chart recorder (optional).

5.0 Reagents

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Concentrated nitric acid: Acid should be analyzed to determine level of impurities. If impurities are detected, all analyses should be blank-corrected.

5.3 Lead standard stock solution (1000 mg/l): Either procure a certified aqueous standard from a supplier (Spex Industries, Alpha Products, or Fisher Scientific) and verify by comparison with a second standard, or dissolve 1.599 g of lead nitrate, $Pb(NO_3)_2$ (analytical reagent grade), and dissolve in Type II water, acidify with 10 ml redistilled HNO_3, and dilute to 1 liter with Type II water.

5.4 Lead working standards: These standards should be prepared with the same type and same concentration of acid that will be found in the analytical solution.

5.5 Air: Cleaned and dried through a suitable filter to remove oil, water, and other foreign substances. The source may be a compressor or a cylinder of industrial-grade compressed air.

5.6 Acetylene: Should be of high purity. Acetone, which is usually present in acetylene cylinders, can be prevented from entering and affecting flame conditions, by replacing the cylinder before the pressure has fallen to 50 psig.

6.0 Sample Collection, Preservation, and Handling

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and Type II water. Plastic and glass containers are both suitable.

6.3 Aqueous samples must be acidified to a pH of less than 2 with nitric acid.

6.4 Nonaqueous samples shall be refrigerated when possible, and analyzed as soon as possible.

7.0 Procedure

7.1 Sample preparation: Aqueous samples should be prepared according to Method 3010; sludge-type samples should be prepared according to Method 3050; and samples containing oils, greases or waxes may be prepared according

to Methods 3030 or 3040. The applicability of a sample preparation technique to a new matrix type must be demonstrated by analyzing spiked samples and/or relevant standard reference materials.

7.2 The 283.3-nm wavelength line and background correction shall be used.

7.3 An oxidizing air/acetylene flame shall be used.

7.4 Follow the manufacturer's operating instructions for all other instrument parameters.

7.5 Either (1) run a series of lead standards and construct a calibration curve by plotting the concentrations of the standards against the absorbances or (2) for the method of standard additions, plot added concentration versus absorbance. For instruments that read directly in concentration, set the curve corrector to read out the proper concentration.

7.6 Analyze, by the method of standard additions, all EP extracts, all samples analyzed as part of a delisting petition, and all samples that suffer from matrix interferences.

7.7 Duplicates, spiked samples, and check standards should be routinely analyzed.

7.8 Calculate metal concentrations by (1) the method of standard additions, or (2) from a calibration curve, or (3) directly from the instrument's concentration readout. All dilution or concentration factors must be taken into account. Concentrations reported for multiphased or wet samples must be appropriately qualified (e.g., 5 µg/g dry weight).

8.0 Quality Control

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.5 Analyze check standards after approximately every 15 samples.

8.6 Run one duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation process.

8.7 Spiked samples or standard reference materials shall be periodically employed to ensure that correct procedures are being followed and that all equipment is operating properly.

8.8 The method of standard additions shall be used for the analysis of all EP-extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

METHOD 7470

MERCURY (MANUAL COLD-VAPOR TECHNIQUE)

1.0 Scope and Application

1.1 Method 7470 is a cold-vapor atomic absorption procedure approved for determining the concentration of mercury in mobility procedure extracts, aqueous wastes and groundwaters. (Method 7470 can also be used for analyzing certain solid and sludge-type wastes; however, Method 7471 is usually the method of choice for these waste types.) All samples must be subjected to an appropriate dissolution step prior to analysis.

2.0 Summary of Method

2.1 Prior to analysis, the samples must be prepared according to the procedure discussed in this method.

2.2 Method 7470, a cold-vapor atomic absorption technique, is based on the absorption of radiation at 253.7 nm by mercury vapor. The mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (peak height) is measured as a function of mercury concentration.

2.3 The typical detection limit for this method is 0.0002 mg/l.

3.0 Interferences

3.1 Potassium permanganate is added to eliminate possible interference from sulfide. Concentrations as high as 20 mg/l of sulfide as sodium sulfide do not interfere with the recovery of added inorganic mercury from Type II water.

3.2 Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/l had no effect on recovery of mercury from spiked samples.

3.3 Seawaters, brines and industrial effluents high in chlorides require additional permanganate (as much as 25 ml) since, during the oxidation step, chlorides are converted to free chlorine which also absorbs radiation of 253 nm. Care must therefore be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine sulfate reagent (25 ml). In addition, the dead air space in the BOD bottle must be purged before adding stannous sulfate. Both inorganic and organic mercury spikes have been quantitatively recovered from seawater using this technique.

3.4 Certain volatile organic materials that absorb at this wavelength may also cause interference. A preliminary run without reagents should determine if this type of interference is present.

4.0 Apparatus and Materials

4.1 Atomic absorption spectrophotometer or equivalent: Any atomic absoption unit having an open sample presentation area in which to mount the absorption cell is suitable. Instrument settings recommended by the particular manufacturer should be followed. Instruments designed specifically for the measurement of mercury using the cold-vapor technique are commercially available and may be substituted for the atomic absorption spectrophotometer.

4.2 Mercury hollow cathode lamp or electrodeless discharge lamp.

4.3 Recorder: Any multirange variable speed recorder that is compatible with the UV detection system is suitable.

4.4 Absorption cell: Standard spectrophotometer cells 10 cm long having quartz end windows may be used. Suitable cells may be constructed from plexiglass tubing, 1 in. O.D. x 4.5 in. The ends are ground perpendicular to the longitudinal axis and quartz windows (1 in. diameter x 1/16-in. thickness) are cemented in place. The cell is strapped to a burner for support and aligned in the light beam by use of two 2-in. x 2-in. cards. One-in.-diameter holes are cut in the middle of each card. The cards are then placed over each end of the cell. The cell is then positioned and adjusted vertically and horizontally to give the maximum transmittance.

4.5 Air pump: Any peristaltic pump capable of delivering 1 liter air/min may be used. A Masterflex pump with electronic speed control has been found to be satisfactory.

4.6 Flowmeter: Capable of measuring an air flow of 1 liter/min.

4.7 Aeration tubing: A straight glass frit having a coarse porosity. Tygon tubing is used for passage of the mercury vapor from the sample bottle to the absorption cell and return.

4.8 Drying tube: 6-in. x 3/4-in.-diameter tube containing 20 g of magnesium perchlorate or a small reading lamp with 60-W bulb which may be used to prevent condensation of moisture inside the cell. The lamp should be positioned to shine on the absorption cell so that the air temperature in the cell is about 10° C above ambient.

4.9 The cold-vapor generator is assembled as shown in Figure 1.

4.10 The apparatus shown in Figure 1 is a closed system. An open system, where the mercury vapor is passed through the absorption cell only once, may be used instead of the closed system.

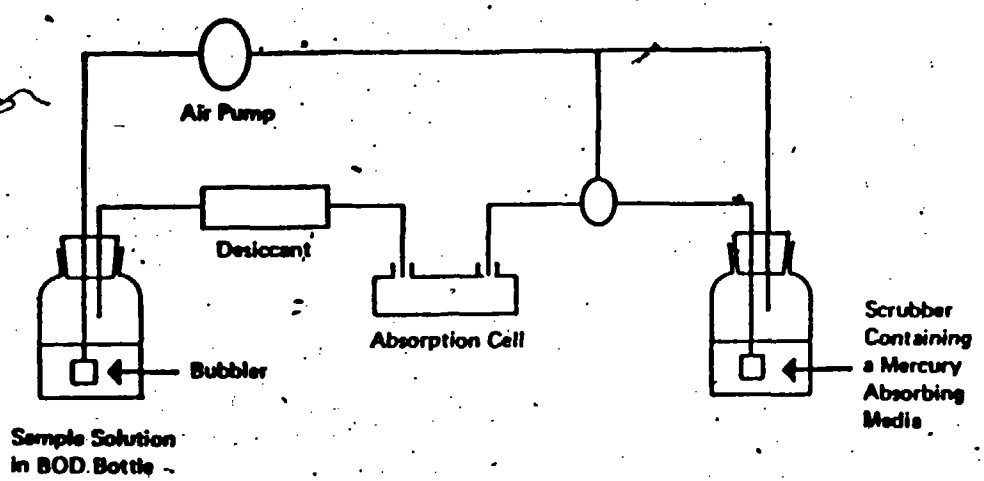

Figure 1. Apparatus for flameless mercury determination.

4.11 Because mercury vapor is toxic, precaution must be taken to avoid its inhalation. Therefore, a bypass has been included in the system to either vent the mercury vapor into an exhaust hood or pass the vapor through some absorbing media, such as:

1. equal volumes of 0.1 M $KMnO_4$ and 10% H_2SO_4
2. 0.25% iodine in a 3% KI solution

A specially treated charcoal that will adsorb mercury vapor is also available from Barnebey and Cheney, E. 8th Ave. and N. Cassidy St., Columbus, Ohio 43219, Cat. #580-13 or #580-22.

5.0 Reagents

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Sulfuric acid, conc.: Reagent grade.

5.3 Sulfuric acid, 0.5 N: Dilute 14.0 ml of conc. sulfuric acid to 1.0 liter.

5.4 Nitric acid, conc.: Reagent grade of low mercury content. If a high reagent blank is obtained, it may be necessary to distill the nitric acid.

5.5 Stannous sulfate: Add 25 g stannous sulfate to 250 ml of 0.5 N sulfuric acid. This mixture is a suspension and should be stirred continuously during use. (Stannous chloride may be used in place of stannous sulfate.)

5.6 Sodium chloride-hydroxylamine sulfate solution: Dissolve 12 g of sodium chloride and 12 g of hydroxylamine sulfate in Type II water and dilute to 100 ml. (Hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate.)

5.7 Potassium permanganate, 5% solution (w/v): Dissolve 5 g of potassium permanganate in 100 ml of Type II water.

5.8 Potassium persulfate, 5% solution (w/v): Dissolve 5 g of potassium persulfate in 100 ml of Type II water.

5.9 Stock mercury solution: Dissolve 0.1354 g of mercuric chloride in 75 ml of Type II water. Add 10 ml of conc. HNO_3 and adjust the volume to 100.0 ml (2 ml = 1 mg Hg).

5.10 Mercury working standard: Make successive dilutions of the stock mercury solution to obtain a working standard containing 0.1 µg per ml. This working standard and the dilutions of the stock mercury solution should be prepared fresh daily. Acidity of the working standard should be maintained at 0.15% nitric acid. This acid should be added to the flask as needed before addition of the aliquot.

6.0 Sample Collection, Preservation, and Handling

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and Type II water. Plastic and glass containers are both suitable.

6.3 Aqueous samples must be acidified to a pH of less than 2 with nitric acid. The suggested maximum holding times for these samples are 38 days in glass containers and 13 in plastic containers.

6.4 Nonaqueous samples shall be refrigerated when possible, and analyzed as soon as possible.

7.0 Procedure

7.1 Sample preparation: Transfer 100 ml, or an aliquot diluted to 100 ml, containing not more than 1.0 µg of mercury, to a 300-ml BOD bottle. Add 5 ml of sulfuric acid and 2.5 ml of conc. nitric acid, mixing after each addition. Add 15 ml of potassium permanganate solution to each sample bottle. Sewage samples may require additional permanganate. Shake and add additional portions of potassium permanganate solution, if necessary, until the purple color persists for at least 15 min. Add 8 ml of potassium persulfate to each bottle and heat for 2 hr in a water bath maintained at 95° C. Cool and add 6 ml of sodium chloride-hydroxylamine sulfate to reduce the excess permanganate. After a delay of at least 30 sec, add 5 ml of stannous sulfate and immediately attach the bottle to the aeration apparatus and continue as described in Section 7.3.

7.2 Standard preparation: Transfer 0-, 0.5-, 1.0-, 2.0-, 5.0-, and 10.0-ml aliquots of the mercury working standard containing 0 to 1.0 µg of mercury to a series of 300-ml BOD bottles. Add enough Type II water to each bottle to make a total volume of 100 ml. Mix thoroughly and add 5 ml of conc. sulfuric acid and 2.5 ml of conc. nitric acid to each bottle. Add 15 ml of $KMnO_4$ solution to each bottle and allow to stand at least 15 min. Add 8 ml of potassium persulfate to each bottle and heat for 2 hr in a water bath maintained at 95° C. Cool and add 6 ml of sodium chloride-hydroxylamine sulfate solution to reduce the excess permanganate. When the solution has been decolorized, wait 30 sec, add 5 ml of the stannous sulfate solution, and immediately attach the bottle to the aeration apparatus and continue as described in Section 7.3.

7.3 Analysis: At this point the sample is allowed to stand quietly without manual agitation. The circulating pump, which has previously been adjusted to a rate of 1 liter/min, is allowed to run continuously. The absorbance will increase and reach a maximum within 30 sec. As soon as the recorder pen levels off (approximately 1 min), open the bypass valve and continue the aeration until the absorbance returns to its minimum value. Close the bypass valve, remove the stopper and frit from the BOD bottle, and continue the aeration.

7.4 Construct a calibration curve by plotting the absorbance of standards versus micrograms of mercury. Determine the peak height of the unknown from the chart and read the mercury value from the standard curve.

7.5 Analyze, by the method of standard additions, all EP extracts, all samples analyzed as part of a delisting petition, and all samples that suffer from matrix interferences.

7.6 Duplicates, spiked samples, and check standards should be routinely analyzed.

7.7 Calculate metal concentrations by (1) the method of standard additions, or (2) from a calibration curve, or (3) directly from the instrument's concentration readout. All dilution or concentration factors must be taken into account. Concentrations reported for multiphased or wet samples must be appropriately qualified (e.g., 5 µg/g dry weight).

8.0 Quality Control

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.5 Analyze check standards after approximately every 15 samples.

8.6 Run one duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation process.

8.7 Spiked samples or standard reference materials shall be periodically employed to ensure that correct procedures are being followed and that all equipment is operating properly.

8.8 The method of standard additions shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

METHOD 7740

SELENIUM (ATOMIC ABSORPTION, FURNACE METHOD)

1.0 Scope and Application

1.1 Method 7740 is an atomic absorption procedure approved for determining the concentration of selenium in wastes, mobility procedure extracts, soils, and groundwater. All samples must be subjected to an appropriate dissolution step prior to analysis.

2.0 Summary of Method

2.1 Prior to analysis by Method 7740, samples must be prepared in order to convert organic forms of selenium to inorganic forms, to minimize organic interferences, and to convert the sample to a suitable solution for analysis. The sample preparation procedure varies depending on the sample matrix. Aqueous samples are subjected to the acid digestion procedure described in this method. Sludge samples are prepared using the procedure described in Method 3050. For samples containing oils, greases, or waxes, the procedures described in Methods 3030 and 3040 may be applicable.

2.2 Following the appropriate dissolution of the sample, a representative aliquot is placed manually or by means of an automatic sampler into a graphite tube furnace. The sample aliquot is then slowly evaporated to dryness, charred (ashed), and atomized. The absorption of hollow cathode radiation during atomization will be proportional to the selenium concentration.

2.3 The typical detection limit for this method is 2 µg/l.

3.0 Interferences

3.1 Elemental selenium and many of its compounds are volatile and therefore samples may be subject to losses of selenium during sample preparation. Spike samples and relevant standard reference materials should be processed to determine if the chosen dissolution method is appropriate.

3.2 Likewise, caution must be employed during the selection of temperature and times for the dry and char (ash) cycles. A nickel nitrate solution must be added to all digestate prior to analysis to minimize volatilization losses during drying and ashing.

3.3 In addition to the normal interferences experienced during graphite furnace analysis, selenium analysis can suffer from severe nonspecific absorption and light scattering caused by matrix components during atomization. Selenium analysis is particularly susceptible to these problems because of its low analytical wavelength (196.0 nm). Simultaneous background correction must be employed to avoid erroneously high results.

3.4 If the analyte is not completely volatilized and removed from the furnace during atomization, memory effects will occur. If this situation is detected, the tube should be cleaned by operating the furnace at full power at regular intervals in the analytical scheme.

3.5 Selenium analysis suffers interference from chlorides (more than 800 mg/l) and sulfate (more than 200 mg/l). The addition of nickel nitrate such that the final concentration is 1% nickel will lessen this interference.

4.0 Apparatus and Materials

4.1 250-ml Griffin beaker.

4.2 10-ml volumetric flasks.

4.3 Atomic absorption spectrophotometer: Single or dual channel, single- or double-beam instrument having a grating monochromator, photomultiplier detector, adjustable slits, a wavelength range of 190 to 800 nm, and provisions for simultaneous background correction and interfacing with a strip chart recorder.

4.4 Selenium hollow cathode lamp or electrodeless discharge lamp.

4.5 Graphite furnace: Any graphite furnace device with the appropriate temperature and timing controls.

4.6 Strip chart recorder: A recorder is strongly recommended for furnace work so that there will be a permanent record and so that any problems with the analysis such as drift, incomplete atomization, losses during charring, changes in sensitivity, etc., can easily be recognized.

4.7 Pipets: Microliter with disposable tips. Sizes can range from 5 to 1000 µl as required.

5.0 Reagents

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Concentrated nitric acid: Acid should be analyzed to determine levels of impurities. If impurities are detected, all analyses should be blank-corrected.

5.3 Hydrogen peroxide (30%): Oxidant should be analyzed to determine levels of impurities. If impurities are detected, all analyses should be blank-corrected.

5.4 Selenium standard stock solution (1000 mg/l): Either procure a certified aqueous standard from a supplier (Spex Industries, Alpha Products, or Fisher Scientific) and verify by comparison with a second standard, or dissolve 0.3453 g of selenious acid (actual assay 94.6% H_2SeO_3, analytical reagent grade) or equivalent in Type II water and dilute to 200 ml.

5.5 Nickel nitrate solution (5%): Dissolve 24.780 g of ACS reagent grade $Ni(NO_3)_2 \cdot 6H_2O$ or equivalent in Type II water and dilute to 100 ml.

5.6 Nickel nitrate solution (1%): Dilute 20 ml of the 5% nickel nitrate to 100 ml with Type II water.

5.7 Selenium working standards: Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. Withdraw appropriate aliquots of the stock solution, add 1 ml of conc. HNO_3, 2 ml of 30% H_2O_2, and 2 ml of the 5% nickel nitrate solution. Dilute to 100 ml with Type II water.

5.8 Air: Cleaned and dried through a suitable filter to remove oil, water, and other foreign substances. The source may be a compressor or a cylinder of industrial-grade compressed air.

5.9 Hydrogen: Suitable for instrumental analysis.

6.0 Sample Collection, Preservation, and Handling

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and Type II water. Plastic and glass containers are both suitable.

6.3 Special containers (e.g., containers used for volatile organic analysis) may have to be used if very volatile selenium compounds are to be analyzed.

6.4 Aqueous samples must be acidified to a pH of less than 2 with nitric acid.

6.5 Nonaqueous samples shall be refrigerated when possible, and analyzed as soon as possible.

7.0 Procedure

7.1 Sample preparation: Aqueous samples should be prepared in the manner described in Sections 7.1.1 to 7.1.3. Sludge-type samples should be prepared according to Method 3050, and samples containing oils, greases, or waxes may be prepared according to Methods 3030 or 3040. The applicability

of a sample-preparation technique to a new matrix type must be demonstrated by analyzing spiked samples and/or relevant standard reference materials.

7.1.1 Transfer 100 ml of well-mixed sample to a 250-ml Griffin beaker, add 2 ml of 30% H_2O_2 and sufficient conc. HNO_3 to result in an acid concentration of 1% (v/v). Heat for 1 hr at 95° C or until the volume is slightly less than 50 ml.

7.1.2 Cool and bring back to 50 ml with Type II water.

7.1.3 Pipet 5 ml of this digested solution into a 10-ml volumetric flask, add 1 ml of the 1% nickel nitrate solution and dilute to 10 ml with Type II water. The sample is now ready for injection into the furnace.

7.2 The 196.0-nm wavelength line and a background correction system must be employed. Follow the manufacturer's suggestions for all other instrument parameters.

7.3 Furnace parameters suggested by the manufacturer should be employed as guidelines. Since temperature-sensing mechanisms and temperature controllers can vary between instruments or with time, the validity of the furnace parameters must be periodically confirmed by systematically altering the furnace parameters while analyzing a standard. In this manner, losses of analyte due to higher than necessary temperature settings or losses in sensitivity due to less than optimum settings can be minimized. Similar verification of furnace parameters may be required for complex sample matrices.

7.4 Inject a measured µl aliquot of sample into the furnace and atomize. If the concentration found is greater than the highest standard, the sample should be diluted in the same acid matrix and reanalyzed. The use of multiple injections can improve accuracy and help detect furnace pipetting errors.

7.5 Analyze, by the method of standard additions, all EP extracts, all samples analyzed as part of a delisting petition, and all samples that suffer from matrix interferences.

7.6 Run a check standard after approximately every 10 sample injections. Standards are run in part to monitor the life and performance of the graphite tube. Lack of reproducibility or significant change in the signal for the standard indicates that the tube should be replaced.

7.7 Duplicates, spiked samples, and check standards should be routinely analyzed.

7.8 Calculate metal concentrations by (1) the method of standard additions, or (2) from a calibration curve, or (3) directly from the instrument's concentration readout. All dilution or concentration factors

must be taken into account. Concentrations reported for multiphased or wet samples must be appropriately qualified (e.g., 5 µg/g dry weight).

8.0 Quality Control

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.5 Analyze check standards after approximately every 15 samples.

8.6 Run one duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation process.

8.7 Spiked samples or standard reference materials shall be periodically employed to ensure that correct procedures are being followed and that all equipment is operating properly.

8.8 The method of standard additions shall be used for the analysis of all TEP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

METHOD 7760

SILVER (ATOMIC ABSORPTION, DIRECT ASPIRATION METHOD)

1.0 Scope and Application

1.1 Method 7760 is an atomic absorption procedure approved for determining the concentration of silver in wastes, mobility procedure extracts, soils, and groundwater. All samples must be subjected to an appropriate dissolution step prior to analysis.

2.0 Summary of Method

2.1 Prior to analysis by Method 7760, samples must be prepared for direct aspiration. The method of sample preparation will vary according to the sample matrix. Aqueous samples are subjected to the acid digestion procedure described in this method. Sludge samples are prepared using the procedure described in Method 3050. For samples containing oils, greases, or waxes, the procedures described in Methods 3030 and 3040 may be applicable.

2.2 Following the appropriate dissolution of the sample, a representative aliquot is aspirated into an air/acetylene flame. The resulting absorption of hollow cathode radiation will be proportional to the silver concentration. Background correction must be employed for all analyses.

2.3 The typical detection limit for this method is 0.01 mg/l; typical sensitivity is 0.06 mg/l.

3.0 Interferences

3.1 Background correction should be employed since nonspecific absorption and light scattering may occur at the analytical wavelength.

3.2 Silver nitrate solutions are light-sensitive and have the tendency to plate out on container walls. Thus silver standards should be stored in brown bottles.

3.3 Silver chloride is insoluble so hydrochloric acid should be avoided unless the silver is already in solution as a chloride complex.

3.4 Samples and standards should be monitored for viscosity differences that may alter the aspiration rate.

4.0 Apparatus and Materials

4.1 Atomic absorption spectrophotometer: Single or dual channel, single- or double-beam instrument, having a grating monochromator, photomultiplier detector, adjustable slits, and provisions for background correction.

4.2 Silver hollow cathode lamp.

4.3 Strip chart recorder (optional).

5.0 Reagents

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Concentrated nitric acid: Acid should be analyzed to determine level of impurities. If impurities are detected, all analyses should be blank-corrected.

5.3 Concentrated ammonium hydroxide (NH_4OH): Base should be analyzed to determine levels of impurities. If impurities are detected, all analyses should be blank-corrected.

5.4 Silver standard stock solution (1000 mg/l): Either procure a certified aqueous standard from a supplier (Spex Industries, Alpha Products or Fisher Scientific) and verify by comparison with a second standard, or dissolve 0.7874 g anhydrous silver nitrate ($AgNO_3$), analytical reagent grade, in Type II water. Add 5 ml conc. HNO_3 and bring to volume in a 500-ml volumetric flask (1 ml = 1 mg Ag).

5.5 Silver working standards: These standards should be prepared with nitric acid and at the same concentrations as the analytical solution.

5.6 Iodine solution, IN: Dissolve 20 g potassium iodide (KI), analytical reagent grade, in 50 ml Type II water. Add 12.7 g iodine (I_2), analytical reagent grade, and dilute to 100 ml. Place in a brown bottle.

5.7 Cyanogen iodide solution: To 50 ml deionized distilled water add 4.0 ml conc. NH_4OH, 6.5 g KCN, and 5.0 ml of iodine solution. Mix and dilute to 100 ml with deionized distilled water. Do not keep longer than 2 weeks. CAUTION: This reagent cannot be mixed with any acid solutions since toxic hydrogen cyanide will be produced.

5.8 Air: Cleaned and dried through a suitable filter to remove oil, water, and other foreign substances. The source may be a compressor or a cylinder of industrial-grade compressed air.

5.9 Acetylene: Should be of high purity. Acetone, which is usually present in acetylene cylinders, can be prevented from entering and affecting flame conditions by replacing the cylinder before the pressure has fallen to 50 psig.

6.0 Sample Collection, Preservation, and Handling

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and Type II water. Plastic and glass containers are both suitable.

6.3 Aqueous samples must be acidified to a pH of less than 2 with nitric acid.

6.4 When possible standards and samples should be stored in the dark and in brown bottles.

6.5 Nonaqueous samples shall be refrigerated when possible, and analyzed as soon as possible.

7.0 Procedure

7.1 Sample preparation: Aqueous samples should be prepared according to Sections 7.2 and 7.3; sludge-type samples should be prepared according to Method 3050; and samples containing oils, greases or waxes may be prepared according to Methods 3030 or 3040. The applicability of a sample preparation technique to a new matrix type must be demonstrated by analyzing spiked samples and/or relevant standard reference materials.

7.2 Preparation of aqueous samples

7.2.1 Transfer a representative aliquot of the well-mixed sample to a Griffin beaker and add 3 ml of conc. HNO_3. Cover the beaker with a watch glass. Place the beaker on a hot plate and cautiously evaporate to near dryness, making certain that the sample does not boil. (DO NOT BAKE.) Cool the beaker and add another 3-ml portion of conc. HNO_3. Re-cover the beaker with a watch glass and return to the hot plate. Increase the temperature of the hot plate so that a gentle reflux action occurs. Note, if the sample contains thiosulfates, this step may result in splatter of sample out of the beaker as the sample approaches dryness. This has been reported to occur with certain photographic type samples.

7.2.2 Continue heating, adding additional acid as necessary, until the digestion is complete (generally indicated when the digestate is light in color or does not change in appearance with continued refluxing). Again, evaporate to near dryness and cool the beaker. Add a small quantity of HNO_3 so that the final dilution contains 0.5% (v/v) HNO_3, and warm the beaker to dissolve any precipitate or residue resulting from evaporation.

7.2.3 Wash down the beaker walls and watch glass with distilled water and, when necessary, filter the sample to remove silicates and other insoluble material that could clog the nebulizer. Adjust the

volume to some predetermined value based on the expected metal concentrations. The sample is now ready for analysis.

7.3 If plating out of AgCl is suspected, the precipitate can be redissolved by adding cyanogen iodide to the sample. CAUTION: This can only be done after digestion to prevent formation of toxic hydrogen cyanide under acid conditions. If cyanogen iodide addition to the sample is necessary, then the standards must be treated in the same manner. CAUTION: cyanogen iodide must not be added to the acidified silver standards. New standards must be made as directed in Sections 5.4 and 5.5 except that the acid addition step must be omitted. Transfer 10 ml of stock solution to a small beaker. Add Type II water to make about 80 ml. Make the solution basic (pH above 7) with ammonium hydroxide. Rinse the pH meter electrodes into the solution with Type II water. Add 1 ml cyanogen iodide and allow to stand 1 hr. Transfer quantitatively to a 100 ml volumetric flask and bring to volume with Type II water.

7.4 The 328.1-nm wavelength line and background correction shall be employed.

7.5 An oxidizing air/acetylene flame shall be used.

7.6 Follow the manufacturer's operating instructions for all other spectrophotometer parameters.

7.7 Either (1) run a series of silver standards and construct a calibration curve by plotting the concentrations of the standards against the absorbances or (2) for the method of standard additions, plot added concentration versus absorbance. For instruments that read directly in concentration, set the curve corrector to read out the proper concentration.

7.8 Analyze, by the method of standard additions, all EP extracts, all samples analyzed as part of a delisting petition, and all samples that suffer from matrix interferences.

7.9 Duplicates, spiked samples, and check standards should be routinely analyzed.

7.10 Calculate metal concentrations by (1) the method of standard additions, or (2) from a calibration curve, or (3) directly from the instrument's concentration readout. All dilution or concentration factors must be taken into account. Concentrations reported for multiphased or wet samples must be appropriately qualified (e.g., 5 µg/g dry weight).

8.0 Quality Control

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.5 Analyze check standards after approximately every 15 samples.

8.6 Run one duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation process.

8.7 Spiked samples or standard reference materials shall be periodically employed to ensure that correct procedures are being followed and that all equipment is operating properly.

8.8 The method of standard additions shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

APPENDIX C - EPA SW-846 (EP TOXICITY PESTICIDES)

Analyte: EP leachate pesticides

Method: SW-846, EPA Test Methods for Evaluating Solid Wastes - Physical/Chemical Methods, July 1982.

Synopsis: The filtrate is extracted three times with methylene chloride, concentrated, passed through alumina for clean-up, and analyzed for endrin, lindane, methoxychlor, and toxaphene by gas chromatography using electron capture detector.

Detection Limit:

	micrograms/liter (ug/L)
Endrin	0.1
Lindane	0.05
Methoxychlor	0.5
Toxaphene	1.0

Calibration: Initial three-point linearity is established (see below). Standards are analyzed after every five samples to monitor linearity.

	nanograms/milliliter (ng/mL)		
Endrin	4.4	22	44
Lindane	1	5	10
Methoxychlor	14	70	140
Toxaphene	100	500	1,000

Quality Control:

- Laboratory blanks are extracted with each batch of different types of samples (water or soil). At least one blank (or 5%) is extracted daily with each batch of samples.
- A surrogate standard (100 ng/mL dibutylchlorendate) is added to all samples and blanks before extraction to monitor recoveries.
- Six matrix spike compounds are added to selected samples to monitor recoveries and precision (see below). A matrix spike and matrix spike duplicate is run with each batch of samples.

	nanograms/liter (ng/L)
Endrin	100
Lindane	1,400
Methoxychlor	500

- All standards are verified against EPA reference standards.

STANDARD OPERATING PROCEDURES
FOR
TRACKING, ANALYSIS, & DOCUMENTATION
OF
HAZARDOUS WASTE SAMPLES

6.0 SAMPLE PREPARATION/SCREENING/EXTRACTION/CLEANUP

Analyses of water and sediment/soil for Pesticides/PCB (P/PCB) and Base, Neutrals, Acids (BNA's) require sample extraction based on EPA Method 608 (Pesticides/PCB) and Method 625 (Base, Neutrals and Acids).

The PM notifies the Sample Extraction Chemist (SEC) when samples need to be extracted with a copy of the LAR form (Fig. 7). The SEC contacts the PA or designated representative, to receive transfer of samples through our Internal Chain of Custody as outlined in 4.2.4 for P/PCB and BNA's. Following sample documentation the samples are taken for extraction to the HWL (Hazardous Waste Laboratory).

6.1 Preparation/Extraction for Pesticides/PCB - Water

6.1.1 Summary of Method

A one-liter sample aliquot is extracted with methylene chloride using a two-liter separatory funnel. The extract is dried by passing it through sodium sulfate, exchanged to hexane, and adjusted to a final volume of 10.0 mL.

6.1.2 Interferences

(1) Interferences may be caused by contamination of solvents, reagents, glassware and other sample processing hardware. Teflon squeeze bottles are used for all solvents. The common flexible plastics should not be used as solvent containers because they may contain phthalates which appear as broad eluting peaks in the chromatogram. ALL GLASSWARE MUST BE RINSED WITH METHYLENE CHLORIDE BEFORE EACH USE.

(2) Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature and diversity of the industrial complex or municipality being sampled.

6.1.3 Apparatus and Materials

A. Glassware

(1) Separatory funnel - 2000-mL, with Teflon-lined stopcock.

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(2) Drying column - 250-mL, 19mm ID, Chromatographic column, without frit (glasswool is used instead of frit to help prevent cross-contamination of sample extracts).

(3) Concentrator tube - Kontes , 10-mL, graduated and calibrated with a glass stopper to prevent evaporation of extracts.

(4) 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.)

(5) Evaporative flask - Kuderna-Danish or equivalent, 500 mL. Attach to concentrator tube with springs.

(6) Snyder column - Kuderna-Danish, three-ball macro or equivalent.

(7) Chromatographic column for alumina - 10-mL serological pipets plugged with a small piece of glass wool in the tip, filled with 3 gm of treated alumina. (To the 6.7 mark)

(8) Vials - amber glass, 14-mL capacity with Teflon-lined screw cap.

B. Supplies and Equipment

(1) Silicon carbide boiling chips - approximately 10/40 mesh. Heat to 400° C for 30 minutes or Soxhlet-extract with methylene chloride.

(2) Water bath, heated with concentric ring cover, capable of temperature control (+/- 2°C), should be used in hood.

(3) Analytical balance - capable of accurately weighing 0.01 gm.

(4) Nitrogen evaporation device with a water bath maintained at 35 - 40°C.

(5) pH meter with glass electrode.

(6) Glass wool- Pyrex, soxhlet-extract for 4 hours in methylene chloride.

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C. Reagents

(1) Reagent water - distilled water.

(2) Acetone, hexane, methylene chloride, Burdick & Jackson grade, or equivalent.

(3) Sodium sulfate (ACS), granular, anhydrous. Purify by soxhlet extracting in methylene chloride for four hours then heating at 400°C for four hours in a shallow tray. Store in a tightly closed glass bottle.

(4) Alumina - Neutral, Super I Woelm. Prepare activity III by adding 7 grams of distilled water to 93 grams of the Super I neutral alumina. Shake in a wrist action shaker for a minimum of two hours; there should be no lumps present. Store in a tightly closed French square bottle.

Test the alumina by adding the BNA surrogates in 1:1 acetone/hexane to the alumina and following steps 6.1.17-6.1.21. The tribromophenol should not be detected by GC/ECD if the alumina and its activation are acceptable. Check recovery of all single component pesticides following the same 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 ketone which is not recovered.

This alumina equivalency test must be performed, and documented, on each fresh batch of alumina.

(5) Sodium hydroxide solution (10N) - Dissolve 40 grams NaOH in 100 mL of distilled water.

(6) Sulfuric acid solution (50%). Slowly add 50 mL of concentrated sulfuric acid to 50 mL of distilled water.

(7) Pesticide surrogate standard spiking solution, stored in refrigerator No. 9 top shelf. The solution is at concentration of 1 ug/1.00 mL of dibutylchlorendate in acetone.

(8) Pesticide matrix standard spiking solution, stored in refrigerator No. 9 top shelf. It is labeled as pesticide matrix spike 0.2 + 0.5 ug/mL of pesticides in methanol.

Note: Check the date of the solution, if it is older than six months, it cannot be used. Discard and request a fresh solution from the Standards Chemist. (Sec 5.0)

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6.1.4 Record in the Extraction log book, Case number, the SMO numbers, CEC job number, lab numbers, the volume, the initial pH for each sample and the lot numbers of the solvents used (see 4.3.1). The unused portion of the sample is returned for storage to the PA and documented using the Internal Chain-of-Custody form. All samples must be returned to the custody of the PA before the end of the working day.

6.1.5 Samples, blanks, surrogates, and matrix spikes should be at room temperature before starting the extraction procedure.

6.1.6 Prepare a matrix lab blank with each set of samples being extracted and for each type of matrix.

6.1.7 Measure 1 liter of sample using a 1-liter graduated cylinder and place in a labeled 2-liter separatory funnel. Measure the initial pH using a pH meter. Pipette 1.0 mL surrogate standard spiking solution into the separatory funnel and mix well. The pH of the sample for Pesticide/PCB extraction should be between 5 and 9 for best results in the recovery of dibutyl chlorendate. The pH can be adjusted using 10 N NaOH or 1:1 H_2SO_4.

Note: If the pH of any sample is above 11 or below 5, notify the PM for instructions before proceding with the extraction.

6.1.8 One sample designated by the PA should be done in duplicate for a matrix spike and matrix spike duplicate recovery, following steps 6.1.7-6.1.20. Spike the two aliquots with 1.0 mL of the pesticide Matrix Spike solution.

6.1.9 Use a 250-mL French square bottle to collect the extracts for each sample. Place a funnel in the bottle with a layer of Na_2SO_4 on glass wool to stop water from getting into the methylene chloride extract.

6.1.10 Add 60 mL of methylene chloride to the separatory funnel and shake the funnel for two minutes, with periodic venting to release excess pressure. Allow the organic layer to separate from the water phase for a minimum of 10 minutes. In case of emulsion, use a centrifuge or filter through glass wool to break the emulsion. If emulsions prevent achievement of an acceptable solvent recovery with separatory funnel extraction, continuous extraction (see 6.2) may be used. Drain the methylene chloride extract through the Na_2SO_4, with multiple rinsing, and into the French square bottle.

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6.1.11 Add a second 60-mL volume of methylene chloride to the sample and repeat step 6.4.6, combining the extracts in the 250-mL French square bottle. Perform a third extraction in the same manner.

6.1.12 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporating flask with springs.

6.1.13 Pour the combined extracts through a drying column containing about 10 cm of anhydrous sodium sulfate and collect the extract in the K-D concentrator. Rinse the French square bottle twice with methylene chloride and pour the rinses through the column. When the extract in the column is 2 cm above the Na_2SO_4, add an additional 30 mL of methylene chloride to the French square bottle and pour the contents through the column to complete the elution.

6.1.14 Add one clean silicon carbide boiling chip to the evaporative flask and attach a three-ball Snyder column. Pre-wet the Snyder column by adding 1 mL of methylene chloride to the top. Place the K-D apparatus on a hot water bath (86°C), so that the lower part of the concentrator tube is immersed in hot water. The time required to complete the concentration is about 20 to 30 minutes. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume is 2 mL, remove the K-D apparatus and allow to drain and cool for at least 10 minutes.

6.1.15 Remove the Snyder column, add 50 mL of hexane and a new boiling chip, and reattach the Snyder column. Pre-wet the column with 1 mL of hexane, mixing the solution carefully. Place the K-D apparatus on the water bath slowly while tilting the K-D apparatus slightly until bubbling starts, then immerse. Concentrate the solvent extract as before. The elapsed time of concentration is 2-4 hours. (Wrap the K-D apparatus with aluminum foil to speed up concentration). 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 4 mL, remove the K-D apparatus and allow it to drain and cool at least 10 minutes.

6.1.16 Remove the Snyder column. If the sample will not concentrate into the concentration tube, transfer the extract to a clean vial and bring up to a known volume. Record the final volume in the extraction log book. Pipette 1/20 of the extract into a Konte tube and proceed to 6.1.18.

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6.1.17 Using the nitrogen blowdown technique, 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. Rinse the internal wall of the tube several times with hexane. Bring the final volume 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 DRY.

6.1.18 Dilute the extract to 1 mL with acetone Prepare an alumina column using a 10-mL serological pipette. Cut the narrow top at approximately the 12-mL marking. Plug the tip with a small piece of glass wool. Rinse the pipette with hexane. Dry, then fill with about 3 grams of treated alumina to the 6.7-mL mark on the pipette.

6.1.19 Transfer the extract to the chromatographic column (alumina column). Rinse the concentrator tube with 1 mL of hexane. Transfer the rinse to the 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.

6.1.20 Adjust the extract to a final volume of 10 mL using the hexane. Transfer the final extract to a 14-mL amber vial. Label it with the case number, SMO number, and the lab number. Store in freezer number 16.

6.1.21 Complete the Extract Control Form (Fig. 11), sign it, and give it to the PA along with the LAR sheet (Fig. 7), keeping a copy of both for extraction records. The pesticide/PCB extracts are ready for analysis.

6.2 Continuous Extraction P/PCB

6.2.1 When experience with a sample from a given source indicates that a serious emulsion problem is encountered in 6.1.10 using a separatory funnel, a continuous extraction should be used.

6.2.2 Measure out a 1-liter sample aliquot into a 1-liter graduated cylinder and place it into the continuous extractor. Pipette 1.0 mL 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 10 N sodium hydroxide and/or 1 : 1 sulfuric acid solution.

6.2.3 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 6.1.12 through 6.1.21.

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6.2.4 If the extracts cannot be concentrated to a final volume of 10 mL, dilute the more concentrated extract to the final volume of the least concentrated extract.

6.2.5 Transfer the extracts to Wheaton vials and cap them securely. Label the pesticide fraction with the case number, SMO number, and the lab number. Store in freezer 16.

6.2.6 Complete the Extract Control Form (Fig.11), sign it, and give it to the P.A along with the LAR sheet (Fig. 7) keeping a copy of both for the extraction records. The sample extracts are ready for GC/MS analysis.

6.3 Preparation/Extraction for BNA's - Water

6.3.1 Summary of Method

A measured volume of sample, approximately one liter, is serially extracted with methylene chloride at a pH greater than 11 and again at a pH less than 2, using a 2-liter separatory funnel. The methylene chloride extracts are dried and concentrated separately to a volume of 1 mL.

6.3.2 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 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, depending upon the nature and diversity of the industrial complex or municipality being sampled.

6.3.3 Apparatus and Equipment

A. Glassware

(1) Separatory funnel - 2,000-mL, with Teflon-lined stopcock.

(2) Drying column - 250-mL, 19-mm ID chromatographic column without coarse frit. (Substitution of a small piece of Pyrex glass wool for the frit will prevent cross contamination of sample extracts.)

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9.0 GC/ECD ANALYSIS OF PESTICIDES/PCBs

9.1 Summary of Method

The hexane extracts of water and sediment/soil are analyzed on a gas chromatograph equipped with an electron capture detector (GC/ECD). A primary analysis performed using a packed column serves as the basis for quantitation. If pesticides or PCBs are tentatively identified, a second GC/ECD confirmation analysis is performed using a capillary column.

9.2 Interferences

Method interferences are caused by contaminants in solvents, reagents, glassware, septa, vial caps, syringes, and other sample processing hardware. These lead to depressed or elevated baselines and interfering peaks in gas chromatograms. All of these materials are routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory method blanks.

9.3 Apparatus and Materials

9.3.1 Glassware

(1) 10,25,50,100, and 250-uL syringes, Hamilton

(2) 1.0-mL volumetric pipet, Pyrex or Corning

(3) 1-mL Wheaton vials for autosampler, with Teflon-coated caps

(4) 10-mL, 100-mL volumetric flasks, Pyrex or Kimax

9.3.2 Equipment

(1) Gas chromatograph - HP5733A GC equipped with Ni^{63}-ECD, HP7671A automatic sampler, HP3392A electronic integrator. The analytical column consists of 6', 4-mm I.D. glass packed with Supelcoport (100/120 mesh) coated with GP 1.5% SP-2250/1.95% SP-2401. This column is used for quantitation.

(2) Gas chromatograph- HP5890A GC equipped with Ni^{63}-ECD, HP7673A automatic sampler, HP3392A electronic integrator. The analytical column consists of a capillary column - DB-5, 30-m x 0.25 mm I.D., 0.25 micron-film thickness,bonded-phase silicone-coated, fused silica - (J&W Scientific). This column is used for confirmation only; it may be used for quantitation only when Toxaphene and DDT are present and are to be quantitated.

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(3) Balance-analytical capable of accurately weighing 0.0001 g.

9.3.3 Reagents

(1) Hexane, pesticide grade (Burdick and Jackson) for making dilutions of sample extracts and preparation of pesticide/PCB working standards.

(2) Acetone, pesticide grade (Fisher)

(3) Methylene chloride, pesticide grade (Fisher)

(4) Working standards are prepared by the Standards Chemist and are stored in Refrigerator #9.

9.4 Instrument Calibration

9.4.1 The gas chromatographic system is calibrated using the external standard technique for all packed columns used for quantitation.

9.4.2 External standard calibration procedure:

(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 CRDL 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 at the beginning of the contract period and each time a new column is installed.

(2) Using 1-uL injections of each calibration standard, tabulate peak height or area responses against the mass injected. The results are used to prepare a calibration curve for each compound.

9.5 GC/ECD Screening

Samples are screened prior to analysis to determine appropriate dilutions to be run in the primary analysis.

9.5.1 Screen water sample extracts at 1/10 dilutions or straight.

9.5.2 Screen water MS/MSD samples at 4/10 dilutions.

9.5.3 Screen soil sample extracts at 1/10 dilutions.

9.5.4 Screen soil MS/MSD samples at 3/20 dilutions.

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9.6 GC/ECD Primary Analysis Quantitation
(performed on the packed column)

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

9.6.2 Inject 1 uL of the sample and standard extract using the autosamplers. Record the volume injected to the nearest 0.05 uL and the total extract volume. NOTE: Dibutyl chlorendate recovery is calculated from the packed column analysis. Matrix spike duplicates are also quantitated on a packed column.

9.6.3 Inject Individual Standard mix A or B and all multi-response pesticides/PCBs at the beginning of each 72-hour sequence. Establish the daily RT window for the pesticides/ PCBs, using the absolute RT from the chromatograms as the mid-point, and the +/-3 times the standard deviation as calculated in SOW, Exhibit E Section 7.2.2, for each compound. Individual Standard mix A or B is analyzed intermittently throughout the analysis. A pesticide outside of the established time window requires immediate investigation and correction before continuing the analysis. Reanalyze all affected samples.

9.6.4 Sample analysis of extracts begins when linearity and degradation requirements specified in SOW, Exhibit E Sections 3.5 and 3.6, have been met. Analyze groups of 5 samples.

Note: The 10% RSD linearity criteria is only required on the column(s) being used for pesticide/PCBs quantitation. If a column is used for surrogate quantitation only, the 10% RSD is required only for dibutyl chlorendate.

9.6.5 Analyze groups of 5 samples. Evaluation mix B or the Individual Standard Mix A or B is alternately reanalyzed after each group. If a multi-response pesticide/PCB is detected in either of the preceding groups of 5 samples, the appropriate multi-response pesticide/PCB is substituted for Individual mix A or B. All standards listed in SOW, 3.6.1.2.3 are included for every case and are analyzed within the same 72-hour period as the samples (with the exception of Aroclors 1221 and 1232 which are on a monthly basis - see footnote in SOW 3.6.1.2.3). If the samples are split between 2 or more instruments, the complete set of standards are analyzed on each instrument with the same 72-hour requirement. All standards must be analyzed prior to the samples to avoid the effects of poor chromatography caused by the injection of a highly concentrated sample.

9.6.6 If it is noted during a 72-hour run that any one of the following GC Performance criteria is being exceeded, stop the run and take corrective action. After corrective action is made, the 72-hour sequence is restarted beginning with standard #1. If it is determined after completion of a 72-hour run that one or more of the criteria are exceeded, repeat the analyses of all sample extracts following the Individual Standard mix exceeding the criteria. These extracts are included in a new 72-hour sequence.

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(1) The calibration Factor for each standard in Individual Standard Mix A or B must not exceed a 20% difference (15% difference 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.

(2) Samples must be repeated if the degradation of DDT and/or endrin exceeds 20% respectively on the daily intermittent analysis of Evaluation Standard Mix B.

(3) All pesticide standards must fall within the established daily retention time windows.

9.6.7 Highly colored extracts may require a dilution.

9.6.8 After the screening and column priming, sample extracts are analyzed according to the following sequence:

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. Tech. 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.

*These may be one mixture (see SOW, paragraph 3.4.3).
**These may be analyzed once a month.

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9.6.9 Repeat the above sequence starting with evaluation Standard Mix B (step 15 above.)

9.6.10 The pesticide/PCB analysis sequence must end with Individual Standard mix A or B regardless of the number of samples analyzed.

9.6.11 The groups of compounds listed in Table 9.1 for Individual Standard Mix A and B are recommended to prevent overlap of compounds on the packed columns.

Table 9.1

Individual Standard Mix A	ng/mL	Individual Standard Mix B	ng/mL
gamma-BHC	5.0	alpha-BHC	4.1
heptachlor	5.0	beta-BHC	8.0
aldrin*	7.0	delta-BHC	6.0
heptachlor epoxide	8.0	aldrin*	7.0
endosulfan I	11.0	4,4'-DDE	11.0
dieldrin	12.0	4,4'-DDD	20.0
endrin aldehyde	25.0	endosulfan sulfate	25.0
4,4'-DDT	25.0	Endrin	22.0
endosulfan II	20.0	endrin ketone	35.1
methoxychlor	70.0	dibutyl chlorendate	50.0
dibutyl chlorendate	50.0		

*For RRT determination.

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

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9.7 Evaluation of Chromatograms

9.7.1 Samples are negative when the peaks, depending on the pesticide's response factor, result in concentrations less than the contract-required detection level (CRDL). The sample is complete at this point; confirmation is not required.

9.7.2 An unknown peak is tentatively identified when its retention time falls within the established retention time window of a corresponding standard that was chromatographed within a 24-hour period and quantitated to be greater than or equal to the CRDL.

9.7.3 PCBs and multi-component pesticides are tentatively identified by pattern recognition and by using retention time windows.

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

(2) If the response for any compound is greater than 100% of full scale, dilute the extract so that the peak will be between 50 and 100% full scale and reanalyze on the packed column. Use this dilution for confirmation and quantiation.

(3) For 10-fold dilutions, inject an aliquot of a dilution 10 fold more concentrated to determine if other compounds of interest are present at lower concentrations.

9.7.4 Quantitation is performed on the primary analysis, except for toxaphene and the DDT series. If DDT exceeds the +/- 10% RSD linearity criteria, then quantitation for any DDE, DDD and DDT in a sample must be on the confirmation analysis. Toxaphene is always quantitated on the confirmation analysis. See paragraphs 3.6.2.4 and 3.7.3.1.3 and Exhibit E in the SOW for special QC requirements for quantitation.

9.7.5 If identification of compounds of interest are prevented by the presence of interferences, further cleanup is required. If sulfur is evident return the sample to the extraction lab for "Sulfur Cleanup".

9.7.6 Return the sample to the extraction lab for gel permeation chromatrography (GPC) clean-up if unknown interferences or poor chromatography are noted only in the sample chromatogram.

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

$$\text{Percent Recovery} = \frac{Q_d}{Q_a} \times 100\%$$

Where:

Q_d= DBC quantity determined by analysis.

Q_a= DBC quantity added to sample.

9.6.8 Calculate matrix spike duplicate recoveries and report on the proper form.

$$\text{Percent Recovery} = \frac{Q_d}{Q_a} \times 100\%$$

Where:

Q_d= DBC quantity determined by analysis.

Q_a= DBC quantity added to sample.

9.8 GC/ECD Confirmation Analysis

Confirmation analysis is used to confirm the presence of all compounds tentatively identified in the Primary Analysis and quantitated at greater than or equal to the CRDL. Therefore, the only standards that are required are the Evaluation Standard mixes (to check linearity and degradation requirements) and standards of all compounds to be confirmed. Linearity criteria on the confirmation column for pesticides is not required unless the column is used for quantitation. The 72-hour sequence is, therefore, modified to fit each case. Quantitation may be performed on the confirmation analysis if DDT and toxaphene are present. If toxaphene or DDT is to be quantitated, additional linearity requirements are specied in the SOW, in paragraph 3.7.3.1.

9.8.1 Table 9.2 summaries the recommended operating conditons for the gas chromatograph. The column selected for confirmation must separate the compounds for confirmation from all other compounds listed in Table 9.2. Separation is greater than or equal to 25% resolution between peaks. NOTE: For GC/MS confirmation refer to SOW paragraph 3.9.

9.8.2 All QC specified in Exhibit E are adhered to, including the linearity check prior to sample analysis. To quantitate toxaphene, substitute 3 concentration levels of toxaphene for the Evaluation Standard mix A, B, or C. If samples contain a combination of single component pesticides and toxaphene, the 3 standards of both the evaluation standard mixture and toxaphene must be included.

9.8.3 Inject 2 uL of the sample extract.

9.8.4 Inject standards for all compounds tentatively identified in SOW 3.6 to establish the daily retention time windows (See SOW, paragraph 3.6.1.1). A pesticide outside of its established retention time window requires immediate investigation and correction before continuing the analysis. All affected samples must be reanalyzed.

9.8.5 Analyze groups of 5 samples with a standard pertaining to the samples after each group (Evaluation mix B is required after each 10 samples). The alternating standard's ratios of the response to the amount injected must be within 20% of each other if quantitation is performed. Deviations larger than 20% require the laboratory to repeat the samples analyzed in between.

9.8.6 Samples are repeated if the degradation of DDT and endrin exceeds 20% on the intermittant evaluation standard mix B. If the samples are split between 2 or more instruments, all standards and blanks pertaining to those samples must be analyzed on each instrument.

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

9.9 Evaluation of Chromatograms

9.9.1 A compound is confirmed if the retention time falls within the retention time window of a corresponding standard that was chromatographed within a 24-hour period. Quantitation must be on the packed column chromatogram (primary or confirmation) that provides the best separation from interfering peaks.

9.9.2 Quantitation of technical chlordane. Weathering and/or different formulations of chlordane may modify the technical chlordane pattern shown in Figure 3. If the chlordane pattern in a sample is similar to Figure 3, use a technical chlordane standard for quantitation. If the pattern is different but gamma and alpha chlordane are present, use gamma and alpha chlordane standards for calculation, total the results, report under technical chlordane but footnote the data as calculated using gamma and alpha chlordane.

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9.10 Calculations

9.10.1 Calculate the concentration in the sample using the following equation for external standards.

(1) Water

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

Where:

A_x = Response for the parameter to be measured.

A_s = Response for the external standard.

V_t = Volume of total extract (uL) (take into account any dilutions)

I_s = Amount of standard injected in nanograms (ng)

V_i = Volume of extract injected (uL)

V_s = Volume of water extracted (mL)

(2) Sediment/Soil
(Dry weight basis)

$$\text{Concentration (ug/kg)} = \frac{(A_x)(I_s)(V_t)}{(A_s)(V_i)(W_s)(D)}$$

Where:

A_x = Response for the parameter to be measured.

A_s = Response for the external standard.

I_s = Amount of standard injected in nanograms (ng)

V_i = Volume of extract injected (uL)

$D = \frac{100 - \%\ \text{moisture}}{100}$ (% moisture from SOW Section II C)

W_s = Weight of sample extracted (gm)

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V_t = Volume of low level total extract (Use 20,000 uL or a factor of this when dilutions are made other than those accounted for below):

a. 1/20 total extract taken for pesticide analysis (derived from 0.5 mL of 10-mL extract).
b. final concentation to 1.0 mL for pesticide analysis.

or,

V_t = Volume of medium level total extract (Use 10,000 uL or a factor of this when dilutions are made.)

9.10.2 For multicomponent mixtures (chlordane, toxaphene and PCBs) match retention times of peaks in the standards with peaks in the sample. Quantitate every identifiable peak (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.

9.10.3 Calculate surrogate and matrix spikes recovery.

$$\text{Percent Recovery} = \frac{Q_d}{Q_a} \times 100\%$$

Where:

Q_d = quantity determined by analysis.

Q_a = quantity added to sample.

Ensure that all dilutions are taken into account. Sediment/soil has a 20 times dilution factor built into the method when accounting for one twentieth (1/20) of extract taken for pesticide analysis and final dilution to 1 mL.

9.10.4 Report results in micrograms per liter or micrograms per kilogram without correction for recovery data. When duplicate and spiked samples are analyzed, report all data obtained with the sample results.

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Table 9.2

Chromatographic Conditions for Pesticides/PCBs

Parameter	Typical Retention Time (min) Column 1*
alpha - BHC	2.77
gamma - BHC	4.90
beta - BHC	3.72
Heptachlor	4.11
delta - BHC	4.32
Aldrin	4.90
Heptachlor epoxide	6.86
Endosulfan I	8.49
4, 4' - DDE	9.53
Dieldrin	10.18
Endrin	12.24
4, 4' - DDD	13.93
Endosulfan II	14.45
4, 4' - DDT	16.68
Endrin aldehyde	18.05
Endosulfan sulfate	21.10
Endrin ketone	29.25
Technical Chlordane	mr
alpha Chlordane	mr
Toxaphene	mr
Aroclor-1016	mr
Aroclor-1221	mr
Aroclor-1232	mr
Aroclor-1242	mr
Aroclor-1248	mr
Arochlor-1254	mr
Arochlor-1260	mr
methoxychlor	30.18
dibutyl chlorendate	27.29

Column 1 conditions: Supelcoport (100/120 mesh) coated with 1.5% SP-2250/1.95% SP-2401 packed in a 1.8 m long x 2 mm ID (6 mm OD) glass column with 5% methane/95% argon carrier gas at a flow rate of 30 mL/min. (HP 5880) Column temperature, isothermal at 210°C.

Capillary column conditions: 30 m x 0.25 mm ID, 0.25 film thickness, fused-silica DB-5, splitless mode, Helium carrier gas: 4 mL/min at 280°C and 25 PSI Septum purge: 15 mL/min, Split vent: none, Initial temperature: 160°C, initial hold - 2 min, Program at 5°C/min, Final temperature: 270°C, final hold - 4 min, Injection port temperature: 225°C

*GC conditions for attached chromatograms (not contract requirements)

mr = multi-response

NOTE: 2 mm ID column with 80/100 mesh does not adequately resolve dibutyl chlorendate and endrin ketone.

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9.11 GS/MS Confirmation of Pesticides

9.11.1 Compounds confirmed by two columns must also be confirmed by GC/MS if the concentration is sufficient for detection by GC/MS as determined by the laboratory-generated detection limits.

(1) The GC/MS normally requires a minimum concentration of 10 ng/uL in tne final extract for each single component compound.

(2) The pesticide extract and associated blank should be analyzed by GC/MS.

(3) The confirmation may be from the GC/MS analysis of the BNA extractables extracts (sample and blank). However, if the compounds are not detected in the BNA extract even though the concentration is high enough, a GC/MS analysis of the pesticide extract is required.

(4) A reference standard of the compound must also be analyzed by GC/MS. The concentration of the reference standard must be at a level that would demonstrate the ability to confirm the pesticides/PCBs identified by GC/ECD.

(5) In the event the GC/MS does not confirm the presence of the pesticides/PCBs identified by GC/ECD, those compounds should be reported as not detected. The minimum detection limits should be adjusted to reflect the interferences. The inability to confirm the compounds by GC/MS should be footnoted on the data sheet.

(6) For GC/MS confirmation of multi-component pesticides and PCBs, required deliverables are spectra of 3 major peaks of multicomponent compounds from samples and standards.

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Table 9.3

Characteristic Ions for Pesticides/PCBs

Parameter	Primary Ion	Secondary Ion(s)
Alpha - BHC	183	181, 109
Beta - BHC	181	183, 109
Delta - BHC	183	181, 109
Gamma-BHC (Lindane)	183	181, 109
Heptachlor	100	272, 274
Aldrin	66	263, 220
Heptachlor Epoxide	353	355, 351
Endosulfan I	195	339, 341
Dieldrin	79	263, 279
4, 4' - DDE	246	248, 176
Endrin	263	82, 81
Endosulfan II	337	339, 341
4, 4' - DDD	235	237, 165
Endrin Aldehyde	67	345, 250
Endosulfan Sulfate	272	387, 422
4, 4' - DDT	235	237, 165
Metnoxychlor	227	228
Chlordane	373	375, 377
Toxaphene	159	231, 233
Aroclor-1016	222	260, 292
Aroclor-1221	190	224, 260
Aroclor-1232	190	224, 260
Aroclor-1242	222	256, 292
Aroclor-1248	292	362, 326
Aroclor-1254	292	362, 326
Aroclor-1260	360	362, 394
Endrin Ketone	317	67, 319

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APPENDIX C - EPA SW-846 (EP TOXICITY HERBICIDES)

Analyte: EP leachate herbicides

Method: SW-846, EPA Test Methods for Evaluating Solid Wastes - Physical/Chemical Methods, July 1982.

Synopsis: A 100-gram representative sample is extracted in an acetic acid/water solution for 24 hours. The methylene chloride extract is derivatized with diazomethane and subsequently analyzed by gas chromatography using an electron capture detector.

Detection Limit:

	micrograms/liter (ug/L)
2,4-D	0.05
2,4,5-TP	0.02

Calibration: Initial three-point linearity is established by analysis of standards as follows:

	nanograms/milliliter (ng/mL)				
2,4-D	10	25	50	100	250
2,4,5-TP	5	10	25	50	100

Standards are analyzed after every five samples to monitor linearity.

Quality Control:

- Laboratory blanks are extracted with each batch of different types of samples (water or soil). At least one blank (or 5%) is extracted daily with each batch of samples.
- Six matrix spike compounds (2,4-D at 1.2 ug/L and 2,4,5-TP at 12 ug/L) are added to selected samples to monitor recoveries and precision. A matrix spike and matrix spike duplicate is run with each batch of samples.
- All standards are verified against EPA reference standards.

METHOD 8150

CHLORINATED HERBICIDES

1.0 Scope and Application

1.1 Method 8150 is a gas chromatographic (GC) method for determining certain chlorinated acid herbicides in groundwater and waste samples. Specifically, Method 8150 may be used to determine the following compounds:

2,4-D
2,4-DB
2,4,5-T
2,4,5-TP
Dalapon
Dicamba
Dichloroprop
Dinoseb
MCPA
MCPP

Since these compounds are produced and used in various forms (i.e., acid, salt, ester, etc.), the method includes a hydrolysis step to convert the herbicide to the acid form prior to analysis.

1.2 When Method 8150 is used to analyze unfamiliar samples, compound identifications should be supported by at least one additional qualitative technique. This method describes analytical conditions for a second gas chromatographic column that can be used to confirm measurements made with the primary column. Section 8.3 provides gas chromatograph/mass spectrometer (GC/MS) criteria appropriate for the qualitative confirmation of compound identifications.

1.3 This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatography and in the interpretation of gas chromatograms. Only experienced analysts should be allowed to work with diazomethane due to the potential hazards associated with its use (explosive, carcinogenic).

2.0 Summary of Method

Method 8150 provides extraction, esterification and gas chromatographic conditions for the analysis of chlorinated acid herbicides in water and waste samples. Spiked samples are used to verify the applicability of the chosen extraction technique to each new sample type. The esters are hydrolyzed with potassium hydroxide and extraneous organic material is removed by a solvent wash. After acidification, the acids are extracted with solvent and converted to their methyl esters using diazomethane as the derivatizing agent. After excess reagent is removed, the esters are determined by gas chromatography

employing an electron capture detector, microcoulometric detector, or electrolytic conductivity detector (2). The results are reported as the acid equivalents.

2.2 The sensitivity of Method 8150 usually depends on the level of interferences rather than on instrumental limitations. Table 1 lists the limits of detection that can be obtained in wastewaters in the absence of interferences. Detection limits for a typical waste sample would be significantly higher.

TABLE 1. CHROMATOGRAPHIC CONDITIONS AND DETECTION LIMITS FOR METHOD 8150 IN WASTEWATER

Parameter	Retention time (min)[a]				Estimated detection limit (µg/l)
	Col. 1a	Col. 1b	Column 2	Column 3	
Dicamba	1.2	--	1.0	--	1.0
2,4-D	2.0	--	1.6	--	1.0
2,4,5-TP	2.7	--	2.0	--	0.1
2,4,5-T	3.4	--	2.4	--	0.1
2,4-DB	4.1	--	--	--	1.0
Dalapon	--	--	--	5.0	1.0
MCPP	--	3.4	--	--	200
MCPA	--	4.1	--	--	200
Dichloroprop	--	4.8	--	--	1.0
Dinoseb	--	11.2	--	--	0.1

[a]Column conditions are as follows:

Column 1a conditions: 95% Argon/5% Methane carrier gas as a flow rate of 70 ml/min. Column temperature isothermal at 185° C.

Column 1b temperature: 140° C for 6 min and then programmed to 200° C at 10°/min.

Column 2 conditions: 95% Argon/5% Methane carrier gas at a flow rate of 70 ml/min. Column temperature isothermal at 185° C.

Column 3 conditions: UHP Nitrogen carrier gas at a flow rate of 25 ml/min. Column temperature programmed from 100° C to 150° C at 10°/min.

3.0 Interferences

3.1 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 gas chromatograms. All these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks as described in Section 8.1.

3.1.1 Glassware must be scrupulously cleaned. Clean all glassware as soon as possible after use by rinsing with the last solvent used in it. This should be followed by detergent washing with hot water and rinses with tap and distilled water. The glassware should then be drained dry and heated in a muffle furnace at 400° C for 15 to 30 min. Some thermally stable materials such as PCB's may not be eliminated by this treatment. Solvent rinses with acetone and pesticide quality hexane may be substituted for the muffle furnace heating. Volumetric ware should not be heated in a muffle furnace. After drying and cooling, glassware should be sealed and stored in a clean environment to prevent any accumulation of dust or other contaminants. Store inverted or capped with aluminum foil.

3.1.2 The use of high purity reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all-glass systems may be required.

3.2 Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from waste to waste, depending upon the nature and diversity of the waste being sampled.

3.3 Organic acids, especially chlorinated acids, cause the most direct interference with the determination. Phenols, including chlorophenols, may also interfere with this procedure.

3.4 Alkaline hydrolysis and subsequent extraction of the basic solution removes many chlorinated hydrocarbons and phthalate esters that might otherwise interfere with the electron capture analysis.

3.5 The herbicides, being strong organic acids, react readily with alkaline substances and may be lost during analysis. Therefore, glassware and glass wool must be acid-rinsed and sodium sulfate must be acidified with sulfuric acid prior to use to avoid this possibility.

3.6 Before processing any samples, the analyst should demonstrate daily through the analysis of an organic-free water or solvent blank that the entire analytical system is interference-free. Standard quality assurance practices should be used with this method. Field replicates should be

collected to validate the precision of the sampling technique. Laboratory replicates should be analyzed to validate the precision of the analysis. Fortified samples should be analyzed to validate the accuracy of the analyses. Where doubt exists over the identification of a peak on the gas chromatogram, confirmatory techniques such as mass spectroscopy should be used. Detection limits for groundwater and EP extracts are given in Table 1. Detection limits for these compounds in wastes should be set at 1 µg/g.

4.0 Apparatus and Materials

4.1 Glassware (all specifications are suggested. Catalog numbers are included for illustration only).

4.1.1 Separatory funnel: 2000-ml, with Teflon stopcock.

4.1.2 Drying column: Chromatographic column 400 mm long x 19 mm I.D. with coarse frit.

4.1.3 Chromatographic column: 300 mm long x 10 mm I.D. with coarse fritted disc at bottom and Teflon stopcock.

4.1.4 Concentrator tube, Kuderna-Danish: 10-ml, graduated. Calibration must be checked at the volumes employed in the test. Ground-glass stopper is used to prevent evaporation of extracts.

4.1.5 Evaporative flask, Kuderna-Danish: 500-ml. Attach to concentrator tube with springs.

4.1.6 Snyder column, Kuderna-Danish: three-ball macro.

4.1.7 Snyder column, Kuderna-Danish: two-ball micro.

4.1.8 Vials: Amber glass, 10- to 15-ml capacity with Teflon-lined screw-cap.

4.1.9 Erlenmeyer flask: Pyrex, 250-ml with 24/40 ground-glass joint.

4.2 Boiling chips: approximately 10/40 mesh. Heat to 400° C for 30 min or Soxhlet extract with methylene chloride.

4.3 Diazald Kit: recommended for the generation of diazomethane (available from Aldrich Chemical Co., Cat. No. 210,025-2).

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

4.5 Glass wool: Acid washed.

4.6 Balance: Analytical, capable of accurately weighing to the nearest 0.0001 g.

4.7 Pipet: Pasteur, glass, disposable (140-mm x 5-mm I.D.).

4.8 Gas chromatograph: Analytical system complete with gas chromatograph suitable for on-column injection and all required accessories including syringes, analytical columns, gases, detector and stripchart recorder. A data system is recommended for measuring peak areas.

4.8.1 Column 1: 180 cm long x 4 mm I.D. glass, packed with 1.5% SP-2250/1.95% SP-2401 on Supelcoport (100/120 mesh) or equivalent.

4.8.2 Column 2: 180 cm long x 4 mm I.D. glass, packed with 5% OV-210 on Gas Chrom Q (100/120 mesh) or equivalent.

4.8.3 Column 3: 180 cm long x 2 mm I.D. glass, packed with 0.1% SP-1000 on 80/100 mesh Carbopak C or equivalent.

4.8.4 Detector: Electron capture. This detector has proven effective in the analysis of wastewaters for the parameters listed in Section 1.1. Guidelines for the use of alternate detectors are provided in Section 7.4.

4.9 Wrist Shaker: Burrel Model 75 or equivalent.

5.0 Reagents

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

5.2 Sodium hydroxide solution (10 N): Dissolve 40 g NaOH in reagent water and dilute to 100 ml.

5.3 Sulfuric acid solution (1:1): Slowly add 50 ml H_2SO_4 (sp. gr. 1.84) to 50 ml of reagent water.

5.4 Sulfuric acid solution (1:3): Slowly add 1 part H_2SO_4 (sp. gr. 1.84) to 3 parts reagent water.

5.5 Hydrochloric acid: (ACS) Mix 1 part of concentrated acid with 9 parts distilled water (v/v).

5.6 Potassium hydroxide solution: 37% aqueous solution (w/v). Prepare with reagent grade potassium hydroxide pellets and distilled water.

5.7 Acetone, hexane, toluene, methanol: Pesticide quality or equivalent.

5.8 Diethyl ether: Nanograde, redistilled in glass if necessary. Must be free of peroxides as indicated by EM Quant test strips (available from Scientific Products Co., Cat. No. P1126-8, and other suppliers). Procedures recommended for removal of peroxides are provided with the test strips. After cleanup, 20 ml ethyl alcohol preservative must be added to each liter of ether.

5.9 Sodium sulfate: (ACS) Granular, acidified as follows: Slurry 100 g sodium sulfate with enough diethyl ether to just cover the solid, then add 0.1 ml of concentrated sulfuric acid. Remove the ether under a vacuum. Mix 1 g of the resulting solid with 5 ml of reagent water and measure the pH of the mixture. It must be below pH 4. Store at 130° C. Several levels of purification may be required in order to reduce background phthalate levels to an acceptable level: (1) Heat 4 hr at 400° C in a shallow tray, (2) Heat 16 hr at 450-400° C in a shallow tray, (3) Soxhlet extract with methylene chloride for 48 hr.

5.10 Carbitol (diethylene glycol monoethyl ether).

5.11 N-methyl (-N-nitroso-p-toluenesulfonamide (Diazald): High purity available from Aldrich Chemical Co.

5.12 5% acidified Na_2SO_4: Use 50 g of acidified anhydrous Na_2SO_4 to every 1000 ml distilled H_2O.

5.13 Stock standard solutions (1.00 µg/µl): Stock standard solutions can be prepared from pure standard materials or purchased as certified solutions.

5.13.1 Prepare stock standard solutions by accurately weighing about 0.0100 g of pure acids. Dissolve the material in pesticide-quality diethyl ether and dilute to volume in a 10-ml volumetric flask. 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 certified by the manufacturer or by an independent source.

5.13.2 Transfer the stock standard solutions into Teflon-sealed screw-cap bottles. Store at 4° C and protect from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.13.3 Stock standard solutions must be replaced after 1 week, or sooner if comparison with check standards indicates a problem.

5.14 Diazomethane solution: Follow generator kit instructions. Store in freezer in glass bottle stoppered with cork. Check for deterioration.

6.0 Sample Collection, Preservation, and Handling

6.1 Grab samples must be collected in glass containers. Conventional sampling practices should be followed; however, the bottle must not be prerinsed with sample before collection. Composite samples should be collected in refrigerated glass containers in accordance with the requirements of the program. Automatic sampling equipment must be as free as possible of Tygon and other potential sources of contamination.

6.2 The samples must be iced or refrigerated at 4° C from the time of collection until extraction.

6.3 All samples must be extracted within 7 days and completely analyzed within 30 days of extraction.

7.0 Procedures

7.1 Sample preparation

7.1.1 Solid extraction

7.1.1.1 Thoroughly mix moist solids and weigh an amount of wet sample equivalent to 50 g of dry weight into 500-ml wide-mouth Erlenmeyer flasks.

7.1.1.2 Acidify solids with reagent grade concentrated hydrochloric acid using 2-3 ml to pH 2. Allow to stand for 15 min with occasional stirring until the pH remains below 2. Add more acid if necessary.

7.1.1.3 Add 20 ml of acetone to each flask containing the acidified sample and clamp the stopper in place. Mix the contents of the flasks for 20 min using the wrist-action shaker. Add 80 ml of redistilled ethyl ether to the same flasks and shake again for 20 min.

7.1.1.4 Decant the extracts into 2-liter separatory funnels containing 250 ml of 5% acidified sodium sulfate. If an emulsion forms, slowly add 5 g of acidified sodium sulfate (anhydrous) until the solvent-water mixture separates. A quantity of acidified

sodium sulfate equal to the weight of the sample may be added if necessary.

7.1.1.5 To ensure adequate recovery, measure the volume of extract into a graduated cylinder at each decanting step before adding the extract to the separatory funnel. If the recovered volume is not better than 75%, an additional extraction must be conducted.

7.1.1.6 Check the pH to ensure that it remains below 2. If the pH is not below 2, add more hydrochloric acid until stabilized. Add 20 ml of acetone to each Erlenmeyer flask containing the sediment and shake on the wrist-action shaker for 10 min. Again, add 80 ml of ethyl ether, shake for 10 min and decant extract into their respective separatory funnels. Repeat this step once more, collecting the acetone-ether extracts in the funnels containing the 5% acidified sodium sulfate solution.

7.1.1.7 Gently mix the content of each separatory funnel for about 1 min and allow the layers to separate. Collect the aqueous phase in a clean beaker and the extract (top layer) in a 500-ml ground-glass Erlenmeyer flask. Reextract the water layer with 25 ml of ethyl ether. Allow the layers to separate and discard the aqueous layer. Combine the ether extracts in the respective Erlenmeyer flasks.

7.1.1.8 Add 30 ml of distilled water to the extract in the Erlenmeyer flasks and refrigerate. Note: This is a good stopping point or, if time permits, continue to step 7.1.1.12.

7.1.1.9 Add 5 ml of 37% (w/w) aqueous potassium hydroxide and boiling chips to the extract in the flask and fit them with a one-ball Snyder column. Evaporate the ethyl ether on the steam bath and continue to heat for 90 min.

7.1.1.10 Remove the flasks from the steam bath, allow them to cool, and transfer the water solutions to 125-ml separatory funnels. Extract the basic solutions once with 40 ml and then twice with 20 ml of redistilled ethyl ether. Allow sufficient time for the layers to separate, and discard the ether layer each time. Note: This is a solvent cleanup step. The phenoxy acid herbicides remain soluble in the aqueous phase as potassium salts.

7.1.1.11 Add 5 ml cold 25% (v/v) sulfuric acid to the contents of each funnel to adjust the pH to 2. Be sure to check the pH at this point. Extract the herbicides once with 40 ml and two more times with 20 ml of ethyl ether.

7.1.1.12 Collect the ether extracts in 125-ml Erlenmeyer flasks containing 1.0 g of acidified anhydrous Na_2SO_4. Stopper and allow the extracts to remain in contact with the acidified Na_2SO_4. Store the samples overnight in the refrigerator. Note: This is a good stopping point.

7.1.1.13 Concentrate extract and perform esterification, starting with step 7.2.2.7.

7.1.2 Liquid extraction

7.1.2.1 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Pour the entire sample into a 2-liter separatory funnel. Check the pH with wide-range pH paper and adjust to pH less than 2 with sulfuric acid (1:1).

7.1.2.2 Add 150 ml diethyl ether to the sample bottle, seal, and shake 30 sec to rinse the walls. Transfer the solvent into the separatory funnel. Extract the sample by shaking the funnel for 2 min with periodic venting to release excess vapor pressure. Allow the organic layer to separate from the water phase for a minimum of 10 min. If the emulsion interface between the layers is more than one-third the size of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration of the emulsion through glass wool, or centrifugation. Drain the water phase into a 1-liter Erlenmeyer flask. Then collect the extract in a 250-ml ground-glass Erlenmeyer flask containing 2 ml of 37% aqueous potassium hydroxide. Approximately 80 ml of the diethyl ether will remain dissolved in the aqueous phase.

7.1.2.3 Extract the sample two more times using 50 ml of diethyl ether each time. Combine the extracts in the Erlenmeyer flask. (Rinse the 1-liter flask with each additional aliquot of extracting solvent.)

7.1.2.4 Add 1 or 2 clean boiling chips to the 250-ml flask, add 15 ml distilled water, and attach a three-ball Snyder column. Prewet the Snyder column by adding 1 ml diethyl ether to the top. Place the apparatus on a hot water bath (60° to 65° C), such that the bottom of the flask is bathed in the water vapor. Although the diethyl ether will evaporate in about 15 min, continue heating for a total of 60 min, beginning from the time the flask is placed in the water bath. Remove the apparatus and let stand at room temperature for at least 10 min.

7.1.2.5 Transfer the solution to a 60-ml separatory funnel using 5 to 10 ml of distilled water. Wash the basic solution twice by shaking for 1 min with 20-ml portions of diethyl ether. Discard the organic phase. The herbicides remain in the aqueous phase.

7.1.2.6 Acidify the contents of the separatory funnel to pH 2 by adding 2 ml of cold (4° C) sulfuric acid (1:3). Test with pH indicator paper. Add 20 ml diethyl ether and shake vigorously for 2 min. Drain the aqueous layer into the 250-ml Erlenmeyer, then pour the organic layer into a 125-ml Erlenmeyer containing about 0.5 g of acidified anhydrous sodium sulfate. Repeat the extraction twice more with 10-ml aliquots of diethyl ether, combining all solvent in the 125-ml flask. Allow the extract to remain in contact with the sodium sulfate for approximately 2 hr.

7.1.2.7 Transfer the ether extract, through a funnel plugged with acid-washed glass wool, into a 500-ml Kuderna-Danish flask equipped with a 10-ml concentrator tube. Use liberal washings of ether. Use a glass rod to crush any caked sodium sulfate during the transfer.

7.1.2.8 Add 1 to 2 clean boiling chips to the flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 ml diethyl ether to the top. Place the K-D apparatus on a hot water bath (60° to 65° C) so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed in vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15 to 20 min. At the proper rate of distillation, the balls of the column will actively chatter but the chambers will not flood. When the apparent volume of liquid reaches 1 ml, remove the K-D apparatus and allow it to drain for at least 10 min while cooling.

7.1.2.9 Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 to 2 ml of diethyl ether. Final volume should be 4.0 ml. The sample is now ready for derivatization with diazomethane to form methyl esters.

7.1.3 Esterification

7.1.3.1 The diazomethane derivatization (1) procedure described below will react efficiently with all of the chlorinated herbicides described in this method and should be used only by experienced analysts, due to the potential hazards associated with its use. Diazomethane is a carcinogen and can explode under certain conditions. The following precautions should be taken:

- Use a safety screen.
- Use mechanical pipetting aides.
- Do not heat above 90° C - EXPLOSION may result.
- Avoid grinding surfaces, ground-glass joints, sleeve bearings, glass stirrers - EXPLOSION may result.
- Store away from alkali metals - EXPLOSION may result.
- Solutions of diazomethane decompose rapidly in the presence of solid materials such as copper powder, calcium chloride, and boiling chips.

7.1.3.2 Instructions for preparing diazomethane are provided with the generator kit.

7.1.3.3 Add 2 ml of diazomethane solution and let sample stand for 10 min with occasional swirling.

7.1.3.4 Rinse inside wall of ampule with several hundred µl of ethyl ether. Take sample to approximately 2 ml to remove excess diazomethane by allowing solvent to evaporate spontaneously (room temperature).

7.1.3.5 Dissolve residue in 5 ml of hexane. Analyze by gas chromatography.

7.2 Gas chromatography conditions

7.2.1 The recommended gas chromatographic column materials and operating conditions for the instrument are:

Parameter	Column
Dicamba	1a,2
2,4-D	1a,2
2,4,5-TP	1a,2
2,4,5-T	1a,2
2,4-DB	1a
Dalapon	3
MCPP	1b
MCPA	1b
Dichloroprop	1b
Dinoseb	1b

Column 1a conditions: 95% Argon/5% Methane carrier gas at a flow rate of 70 ml/min. Column temperature isothermal at 185° C.

Column 1b temperature: 140° C for 6 min and then programmed to 200° C at 10°/min.

Column 2 conditions: 95% Argon/5% Methane carrier gas at a flow rate of 70 ml/min. Column temperature, isothermal at 185° C.

Column 3 conditions: UHP Nitrogen carrier gas at a flow rate of 25 ml/min. Column temperature programmed from 100° to 150° C at 10°/min.

7.2.2 The use of capillary (open-tubular) columns is acceptable if appropriate response and separation can be demonstrated.

7.3 Calibration

7.3.1 Establish gas chromatographic operating parameters equivalent to those indicated above in Table 1. The gas chromatographic system can be calibrated using the external standard technique (Section 7.3.2) or the internal standard technique (Section 7.3.3).

7.3.2 External standard calibration procedure

7.3.2.1 For each parameter of interest, prepare working standards at a minimum of three concentration levels by adding volumes of one or more stock standards to a volumetric flask and diluting to volume with diethyl ether. One of the external standards should be at a concentration near, but above, the method detection limit. The other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector.

7.3.2.2 Prepare calibration standards from the free acids by esterification of the working standards as described under Liquid Extraction, Section 7.1.2. Using injections of 2 to 5 µl of each esterified working standard, tabulate peak height or area responses against the mass injected. The results can be used to prepare a calibration curve for each parameter. Alternatively, the ratio of the response to the mass injected, defined as the calibration factor (CF), can be calculated for each parameter at each standard concentration. If the relative standard deviation of the calibration factor is less than 10% over the working range, linearity through the origin can be assumed and the average calibration factor can be used in place of a calibration curve.

7.3.2.3 The working calibration curve or calibration factor must be verified on each working day by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than ±10%, the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve or calibration factor may be prepared for that parameter.

7.3.3 Internal standard calibration procedure. To use this approach, the analyst must select one or more internal standards similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Due to these limitations, no internal standard applicable to all samples can be suggested.

7.3.3.1 Prepare working standards at a minimum of three concentration levels for each parameter of interest in the acid form by adding volumes of one or more stock standards to a volumetric flask, and dilute to volume with diethyl ether. One of the standards should be at a concentration near, but above, the method detection limit. The other concentrations should correspond to the expected range of concentrations found in real samples, or should define the working range of the detector.

7.3.3.2 Prepare calibration standards from the free acids by esterification of the working standards as described under Liquid Extraction, Section 7.1.2.

7.3.3.3 Prior to injection, add a known constant amount of one or more internal standards to each calibration standard.

7.3.3.4 Using injections of 2 to 5 µl of each calibration standard, tabulate the peak height or area responses against the concentration for each compound and internal standard. Calculate response factors (RF) for each compound as follows:

$$RF = (A_s C_{is})/(A_{is} C_s)$$

where:

A_s = Response for the parameter to be measured.

A_{is} = Response for the internal standard.

C_{is} = Concentration of the internal standard in µg/l.

C_s = Concentration of the parameter to be measured in µg/l.

If the RF value over the working range is constant, less than 10% relative standard deviation, the RF can be assumed to be invariant and the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios, A_s/A_{is} against RF.

7.3.3.5 The working calibration curve or RF must be verified on each working day by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than ±10%, the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve must be prepared for that compound.

7.3.4 Before using any cleanup procedure, the analyst must process a series of standards through the procedure to validate elution patterns and the absence of interferences from the reagents.

7.4 Analysis

7.4.1 Inject 2 to 5 µl of the sample extract using the solvent-flush technique. Smaller (1.0-µl) volumes can be injected if automatic devices are employed. Record the volume injected to the nearest 0.05 µl, and the resulting peak size, in area units.

7.4.2 If the peak area exceeds the linear range of the system, dilute the extract and reanalyze.

7.4.3 If peak detection is prevented by the presence of interferences, further cleanup is required. Before using any cleanup procedure, the analyst must process a series of calibration standards through the procedure to validate elution patterns and the absence of interferences from the reagents.

7.4.4 Examples of chromatograms for chlorophenoxy herbicides are shown in Figures 1 to 3.

8.0 Quality Control

8.1 Before processing any samples, the analyst should demonstrate through the analysis of a distilled water method blank that all glassware and reagents are interference-free. Each time a set of samples is extracted or there is a change in reagents, a method blank should be processed as a safeguard against chronic laboratory contamination.

8.2 Standard quality assurance practices should be used with this method. Field replicates should be collected to validate the precision of

Column 1.5% SP-2250/1.95% SP-2401 on Supelcoport (100/120 Mesh)
Temperature: Isothermal at 185°C
Detector: Electron Capture

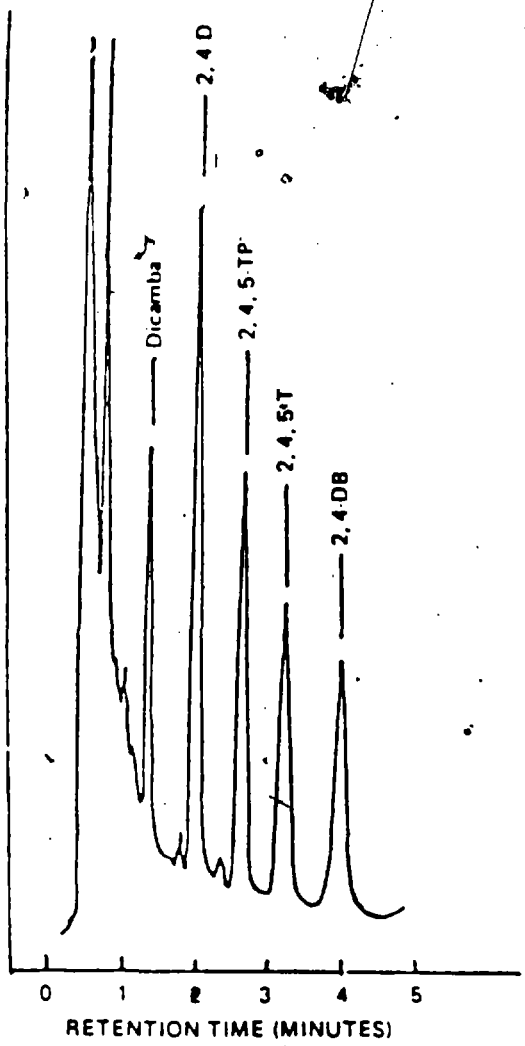

Figure 1. Gas chomatogram of chlorinated herbicides.

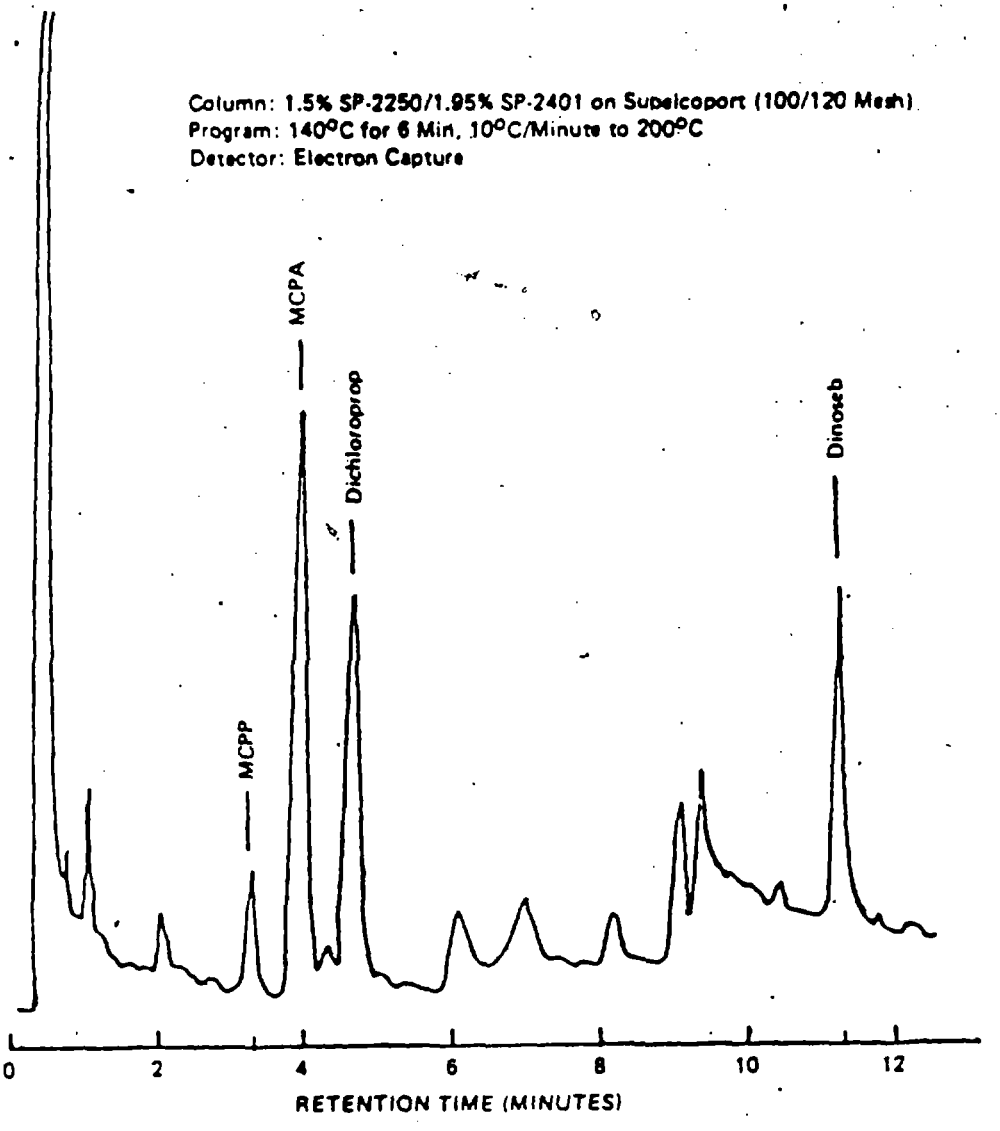

Figure 2. Gas chromatogram of chlorinated herbicides.

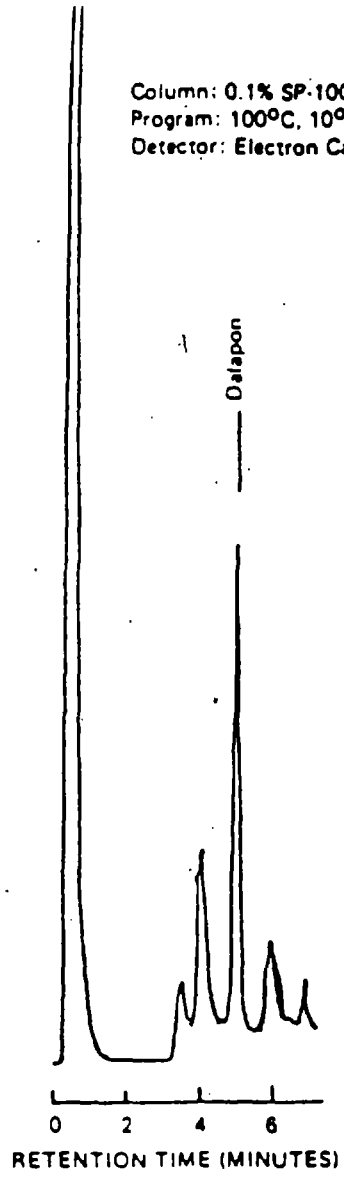

Figure 3. Gas chromatogram of dalapon, column 3.

the sampling technique. Laboratory replicates should be analyzed to validate the precision of the analysis. Fortified waste samples should be analyzed to validate the accuracy of the analysis. Detection limits to be used for groundwater samples are indicated in Table 1. Where doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as mass spectrometry should be used (Section 8.3).

8.3 GC/MS confirmation

8.3.1 GC/MS techniques should be judiciously employed to support qualitative identifications made with this method. The mass spectrometer should be capable of scanning the mass range from 35 amu to a mass 50 amu above the molecular weight of the compound. The instrument must be capable of scanning the mass range at a rate to produce at least 5 scans per peak but not to exceed 3 sec per scan utilizing 70 V (nominal) electron energy in the electron impact ionization mode. A GC-to-MS interface constructed of all-glass or glass-lined materials is recommended. A computer system that allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program should be interfaced to the mass spectrometer.

8.3.2 Gas chromatographic columns and conditions should be selected for optimum separation and performance. The conditions selected must be compatible with standard GC/MS operating practices, such as those described for Method 8250.

8.3.3 At the beginning of each day that confirmatory analyses are to be performed, the GC/MS system must be checked to see that all DFTPP (decafluorotriphenyl phosphine) performance criteria are achieved, as described in Method 8250.

8.3.4 To confirm an identification of a compound, the background-corrected mass spectrum of the compound must be obtained from the sample extract and compared with a mass spectrum from a stock or calibration standard analyzed under the same chromatographic conditions. At least 25 ng of material should be injected into the GC/MS. The following criteria must be met for qualitative confirmation:

1. The molecular ion and all other ions present above 10% relative abundance in the mass spectrum of the standard must be present in the mass spectrum of the sample with agreement to ±10%. For example, if the relative abundance of an ion is 30% in the mass spectrum of the standard, the allowable limits for the relative abundance of that ion in the mass spectrum for the sample would be 20-40%.

2. The retention time of the compound in the sample must be within 6 sec of the retention time for the same compound in the standard solution.

3. Compounds that have very similar mass spectra can be explicitly identified by GC/MS only on the basis of retention time data.

8.3.5 Where available, chemical ionization mass spectra may be employed to aid the qualitative identification process.

8.3.6 Should these MS procedures fail to provide satisfactory results, additional steps may be taken before reanalysis. These steps may include the use of alternate packed or capillary GC columns or additional cleanup.

9.0 References

1. U.S. EPA. 1971. National Pollutant Discharge Elimination System, Appendix A, Fed. Reg., 38, No. 75, Pt. II, Method for Chlorinated Phenoxy Acid Herbicides in Industrial Effluents, Cincinnati, Ohio.

2. Goerlitz, D.G., and W.L. Lamar. 1967. Determination of phenoxy acid herbicides in water by electron capture and microcoulometric gas chromatography. U.S. Geol. Survey Water Supply Paper, 1817-C.

3. Burke, J.A., 1965. Gas chromatography for pesticide residue analysis; some practical aspects. Journal of the Association of Official Analytical Chemists 48:1037.

4. U.S. EPA. 1972. Extraction and cleanup procedure for the determination of phenoxy acid herbicides in sediment. EPA Toxicant and Analysis Center, Bay St. Louis, Mississippi.

APPENDIX C - EPA SW-846 (PCBS)

Analyte: PCB

Method: SW-846, EPA Test Methods for Evaluating Solid Wastes - Physical/Chemical Methods, July 1982.

Synopsis: An aliquot of sample is extracted with organic solvents -- water with methylene chloride and soil with hexane/acetone. The extracts are solvent exchanged into hexane, passed through florisil, acid cleaned, and concentrated for analysis by gas chromatography using a Hall electroconductivity detector.

Detection Limit: 5 micrograms/liter for waters or 300 micrograms/kilogram for soils. Matrix interferences may increase detection limits on samples.

Calibration: A four-point PCB standard (Aroclor 1254) is analyzed after every five samples to monitor linearity (see below).

micrograms/milliliter (ug/mL)
0.5
1.0
2.0
3.5

Quality Control:

- Laboratory blanks are extracted with each batch of different types of samples (water or soil). A minimum of one blank is extracted daily with each batch of samples.
- PCB spikes (Aroclor 1254 @ 20 ug) are added to matrix blanks at a minimum of 10% of all samples to monitor recoveries.
- All standards are verified against EPA reference standards.

METHOD 8080

ORGANOCHLORINE PESTICIDES AND PCB'S

1.0 Scope and Application

1.1 Method 8080 is used to determine the concentration of certain organochlorine pesticides and polychlorinated biphenyls (PCB's) in groundwater, liquid, and solid sample matrices. Specifically, Method 8080 may be used to detect the following substances:

Aldrin	Endrin aldehyde
a-BHC	Heptachlor
B-BHC	Heptachlor epoxide
d-BHC	Kepone
g-BHC (Lindane)	Methoxychlor
Chlordane	Toxaphene
4,4'-DDD	PCB-1016
4,4'-DDE	PCB-1221
4,4'-DDT	PCB-1232
Dieldrin	PCB-1242
Endosulfan I	PCB-1248
Endosulfan II	PCB-1254
Endosulfan sulfate	PCB-1260
Endrin	

1.2 Method 8080 is recommended for use only by, or under the close supervision of, experienced residue analysts.

2.0 Summary of Method

2.1 Method 8080 provides cleanup and chromatographic conditions for the detection of ppb levels of organochlorine pesticides and PCB's. Prior to the use of this method, appropriate sample extraction techniques must be used. Groundwater and other aqueous samples are extracted at a neutral pH with methylene chloride as a solvent using a separatory funnel (Method 3510) or a continuous liquid-liquid extractor (Method 3520). Both neat and diluted organic liquids may be analyzed by direct injection. Solid samples are extracted with hexane:acetone (1:1) using either the Soxhlet extraction (Method 3540) or sonication (Method 3550) procedures. A 2- to 5-µl sample is injected into a gas chromatograph (GC) using the solvent flush technique, and compounds in the GC effluent are detected by an electron capture detector (ECD) or another halogen-specific detector. An aliquot of each sample will be spiked with standards to determine the spike recovery and the limits of detection for that particular sample. It is recommended that the analyst carefully select the compounds used in sample spiking to avoid coelution under the GC conditions given in Table 1. Aroclor 1221 will give minimal interference with the single component pesticides listed in Table 1. Chlordane and toxaphene may require individual spiked sample analysis to yield valid recovery data.

TABLE 1. GAS CHROMATOGRAPHY OF PESTICIDES AND PCB's[a]

Parameter	Retention time (min)		Detection limit[b] (µg/l)
	Column 1[c]	Column 2[d]	
Aldrin	2.40	4.10	0.004
a-BHC	1.35	1.82	0.004
b-BHC	1.90	1.97	0.006
w-BHC	2.15	2.20	0.009
g-BHC (Lindane)	0.70	2.13	0.004
Chlordane	e	e	0.014
4,4'-DDD	7.83	9.08	0.012
4,4'-DDE	5.13	7.15	0.004
4,4'-DDT	9.40	11.75	0.012
Dieldrin	5.45	7.23	0.002
Endosulfan I	4.50	6.20	0.014
Endosulfan II	8.00	8.28	0.004
Endosulfan sulfate	14.22	10.70	0.066
Endrin	6.55	8.10	0.006
Endrin aldehyde	11.82	9.30	0.023
Heptachlor	2.00	3.35	0.004
Heptachlor epoxide	3.50	5.00	0.083
Methoxychlor	18.20	26.60	0.176
PCB-1016	e	e	ND
PCB-1221	e	e	ND
PCB-1232	e	e	ND
PCB-1242	e	e	0.065
PCB-1248	e	e	ND
PCB-1254	e	e	ND
PCB-1260	e	e	ND

ND = not determined.

[a]Taken from reference 6.

[b]Detection limit is calculated from the minimum detectable GC response being equal to five times the GC background noise, assuming a 10-ml final volume of a 1-liter liquid extract, and assuming a GC injection of 5 µl.

[c]Column 1 conditions: Supelcoport 100/120 mesh coated with 1.5% SP-2250/1.95% SP-2401 packed in a 180-cm long x 4-mm I.D. glass column with 5% Methane/95% Argon carrier gas at 60 ml/min flow rate. Column temperature is 200° C.

[d]Column 2 conditions: Supelcoport 100/200 mesh coated with 3% OV-1 in a 180-cm long x 4-mm I.D. glass column with 5% Methane/95% Argon carrier gas at 60 ml/min flow rate. Column temperature is 200° C.

[e]Multiple peak response.

2.2 The sensitivity of Method 8080 usually depends on the level of interferences rather than on instrumental limitations. Table 1 lists the limits of detection that can be obtained in wastewaters in the absence of interferences. Detection limits for a typical waste sample may be significantly higher.

3.0 Interferences

3.1 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of gas chromatograms. All these materials must therefore be demonstrated to be free from interferences under the conditions of the analysis by running method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.

3.2 Interferences coextracted from the samples will vary considerably from waste to waste. While general cleanup techniques are provided as part of this method, unique samples may require additional cleanup approaches to achieve desired sensitivities.

3.3 Glassware must be scrupulously clean. Clean all glassware as soon as possible after use by rinsing with the last solvent used. This should be followed by detergent washing in hot water. Rinse with tap water, distilled water, acetone, and finally pesticide-quality hexane. Heavily contaminated glassware may require treatment in a muffle furnace at 400° C for 15 to 30 min. Some high boiling materials, such as PCB's, may not be eliminated by this treatment. Volumetric ware should not be heated in a muffle furnace. Glassware should be sealed/stored in a clean environment immediately after drying or cooling to prevent any accumulation of dust or other contaminants. Store inverted or capped with aluminum foil.

3.4 Interferences by phthalate esters can pose a major problem in pesticide analysis. These materials elute in the 15% and 50% fractions of the Florisil cleanup. They usually can be minimized by avoiding contact with any plastic materials. The contamination from phthalate esters can be completely eliminated with a microcoulometric or electrolytic conductivity detector.

3.5 Before processing any samples, the analyst should demonstrate daily through the analysis of an organic-free water or solvent blank that the entire analytical system is interference-free. Standard quality assurance practices should be used with this method. Field replicates should be collected to validate the precision of the sampling technique. Laboratory replicates should be analyzed to validate the precision of the analysis. Fortified samples should be analyzed to validate the accuracy of the analyses. Where doubt exists over the identification of a peak on the gas chromatogram, confirmatory techniques such as mass spectroscopy should

be used. Detection limits for groundwater and EP extracts are given in Table 1. Detection limits for these compounds in wastes should be set at 1 µg/g.

4.0 Apparatus and Materials

4.1 Drying column: 20-mm I.D. pyrex chromatographic column with coarse frit.

4.2 Kuderna-Danish (K-D) apparatus

4.2.1 Concentrator tube: 10 ml, graduated. Calibration must be checked at 1.0- and 10.0-ml level. Ground glass stopper (size 19/22 joint) is used to prevent evaporation of extracts.

4.2.2 Evaporative flask: 500 ml. Attach to concentrator tube with springs.

4.2.3 Snyder column: Three-ball macro (Kontes K503000-0121 or equivalent).

4.2.4 Boiling chips: Extracted, approximately 10/40 mesh.

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

4.4 Gas chromatograph: Analytical system complete with gas chromatograph suitable for on-column injection and all required accessories including electron-capture or halogen-specific detector, column supplies, recorder, gases, syringes. A data system for measuring peak areas is recommended.

4.5 Chromatographic column: Pyrex, 400 mm x 25 mm O.D., with coarse fritted plate and Teflon stopcock (Kontes K-42054-213 or equivalent).

5.0 Reagents

5.1 Preservatives

5.1.1 Sodium hydroxide: (ACS) 10 N in distilled water.

5.1.2 Sulfuric acid (1+1): (ACS) Mix equal volumes of conc. H_2SO_4 with distilled water.

5.2 Methylene chloride: Pesticide quality or equivalent.

5.3 Sodium sulfate: (ACS) Granular, anhydrous (purified by heating at 400° C for 4 hr in a shallow tray).

5.4 Stock standards: Prepare stock standard solutions at a concentration of 1.00 µg/µl by dissolving 0.100 g of assayed reference material in pesticide quality isooctane or other appropriate solvent and diluting to volume in a 100-ml ground-glass-stoppered volumetric flask. The stock solution is transferred to ground-glass-stoppered reagent bottles, stored in a refrigerator, and checked frequently for signs of degradation or evaporation, especially just prior to preparing working standards from them.

5.5 Mercury: Triple distilled.

5.6 Hexane: Pesticide residue analysis grade.

5.7 Isooctane (2,2,4-trimethyl pentane): Pesticide residue analysis grade.

5.8 Acetone: Pesticide residue analysis grade.

5.9 Diethyl ether: Nanograde, redistilled in glass if necessary.

5.9.1 Must be free of peroxides as indicated by EM Quant test strips (Test strips are available from EM Laboratories, Inc., 500 Executive Blvd., Elmsford, N.Y. 10523).

5.9.2 Procedures recommended for removal of peroxides are provided with the test strips. After cleanup, 20 ml ethyl alcohol preservative must be added to each liter of ether.

5.10 Florisil: PR grade (60/100 mesh); purchase activated at 1250° F; store in glass containers with glass stoppers or foil-lined screw caps. Before use, activate each batch at least 16 Hr at 130° C in a foil-covered glass container.

6.0 Sample Collection, Preservation, and Handling

6.1 Grab samples must be collected in appropriately cleaned glass containers and the sampling bottle must not be prewashed with the sample before collection. Composite samples should be collected in refrigerated glass containers in accordance with the requirements of the program. Automatic sampling equipment must be free of tygon and other potential sources of contamination.

6.2 The samples must be iced or refrigerated from the time of collection until extraction. Chemical preservatives should not be used in the field unless more than 24 hr will elapse before delivery to the laboratory. If the samples will not be extracted within 48 hours of collection, the sample should be adjusted to a pH range of 6.0-8.0 with sodium hydroxide or sulfuric acid.

6.3 All samples must be extracted within 7 days and completely analyzed within 30 days of collection.

7.0 Procedures

7.1 Sample preparation

7.1.1 Extraction. Extract water samples at a neutral pH with methylene chloride as a solvent using a separatory funnel (Method 3510) or a continuous liquid-liquid extractor (3520). Extract solid samples with hexane:acetone (1:1) using either the Soxhlet extraction (Method 3540) or sonication procedures (Method 3550). Spiked samples are used to verify the applicability of the chosen extraction technique to each new sample type. Each sample must be spiked to determine the % recovery and the limit of detection for that sample.

7.1.2 Florisil column cleanup

7.1.2.1: Add a weight of Florisil (nominally 21 g), predetermined by calibration (Section 7.3) to a chromatographic column. Settle the Florisil by tapping the column. Add sodium sulfate to the top of the Florisil to form a layer 1-2 cm deep. Add 60 ml of hexane to wet and rinse the sodium sulfate and Florisil. Packing the Florisil in a hexane slurry is an alternative method which has proven effective. Just prior to exposure of the sodium sulfate to air, stop the elution of the hexane by closing the stopcock on the chromatography column. Discard the eluate. Adjust the sample extract volume to 10 ml and transfer it from the K-D concentrator tube to the Florisil column. Rinse the tube twice with 1-2 ml hexane, adding each rinse to the column.

7.1.2.2 Place a 500-ml K-D flask and clean concentrator tube under the chromatography column. Drain the column into the flask until the sodium sulfate layer is nearly exposed. Elute the column with 200 ml of 6% ethyl ether in hexane (Fraction 1) using a drip rate of about 5 ml/min. Remove the K-D flask and set aside for later concentration. Elute the column again, using 200 ml of 15% ethyl ether in hexane (Fraction 2), into a second K-D flask. Perform the third elution using 200 ml of 50% ethyl ether in hexane (Fraction 3). The elution patterns for the pesticides and PCB's are shown in Table 2.

7.1.2.3 Concentrate the eluates by standard K-D techniques, as described in the referenced extraction procedures, substituting hexane for the glassware rinses and using the water bath at about 85° C. Adjust final volume to 10 ml with hexane. Analyze by gas chromatography.

TABLE 2. DISTRIBUTION AND RECOVERY OF CHLORINATED PESTICIDES AND PCB's USING FLORISIL COLUMN CHROMATOGRAPHY[a]

Parameter	Percent recovery by fraction[b]		
	1(6%)	2(15%)	3(50%)
Aldrin	100		
a-BHC	100		
B-BHC	97		
w-BHC	98		
g-BHC (Lindane)	100		
Chlordane	100		
4,4'-DDD	99		
4,4'-DDE	98		
4,4'-DDT	100		
Dieldrin	0	100	
Endosulfan I	37	64	
Endosulfan II	0	7	91
Endosulfan sulfate	0	0	106
Endrin	4	96	
Endrin aldehyde	0	68	26
Heptachlor	100		
Heptachlor epoxide	100		
Methoxychlor	100		
Toxaphene	96		
PCB-1016	97		
PCB-1221	97		
PCB-1232	95	4	
PCB-1242	97		
PCB-1248	103		
PCB-1254	90		
PCB-1260	95		

[a]Taken from reference 1.

[b]Eluting solvent composition given in Section 7.1.2.2.

7.2 Gas chromatography conditions. The recommended gas chromatographic columns and operating conditions for the instrument are:

Column 1 conditions: Supelcoport 100/120 mesh coated with 1.5% SP-2250/ 1.95% SP-2401 packed in a 180-cm long x 4-mm I.D. glass column with 5% Methane/95% Argon carrier gas at 60 ml/min flow rate. Column temperature is 200° C.

Column 2 conditions: Supelcoport 100/120 mesh coated with 3% OV-1 in a 180-cm long x 4-mm I.D. glass column with 5% Methane/95% Argon carrier gas at 60 ml/min flow rate. Column temperature is 200° C.

7.3 Calibration

7.3.1 Establish gas chromatographic operating parameters equivalent to those indicated in Table 1. The gas chromatographic system can be calibrated using the external standard technique (Section 7.3.2) or the internal standard technique (Section 7.3.3).

7.3.2 External standard calibration procedure

7.3.2.1 For each parameter of interest, prepare calibration standards at a minimum of three concentration levels by adding volumes of one or more stock standards to a volumetric flask and diluting to volume with isooctane. One of the external standards should be at a concentration near, but above, the method detection limit. The other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector.

7.3.2.2 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 parameter. Alternatively, the ratio of the response to the mass injected, defined as the calibration factor (CF), can be calculated for each parameter at each standard concentration. If the relative standard deviation of the calibration factor is less than 10% over the working range, linearity through the origin can be assumed and the average calibration factor can be used in place of a calibration curve.

7.3.2.3 The working calibration curve or calibration factor must be verified on each working day by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than ±10%, the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve or calibration factor may be prepared for that parameter.

7.3.3 Internal standard calibration procedure. To use this approach, the analyst must select one or more internal standards similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Due to these limitations, no internal standard applicable to all samples can be suggested.

7.3.3.1 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. To each calibration standard, add a known constant amount of one or more internal standards, and dilute to volume with isooctane. One of the standards should be at a concentration near, but above, the method detection limit. The other concentrations should correspond to the expected range of concentrations found in real samples, or should define the working range of the detector.

7.3.3.2 Using injections of 2 to 5 µl of each calibration standard, tabulate the peak height or area responses against the concentration for each compound and internal standard. Calculate response factors (RF) for each compound as follows:

$$RF = (A_s C_{is})/(A_{is} C_s)$$

where:

A_s = Response for the parameter to be measured.

A_{is} = Response for the internal standard.

C_{is} = Concentration of the internal standard in µg/l.

C_s = Concentration of the parameter to be measured in µg/l.

If the RF value over the working range is constant, less than 10% relative standard deviation, the RF can be assumed to be invariant and the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios, A_s/A_{is} against RF.

7.3.3.3 The working calibration curve or RF must be verified on each working day by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than ±10%, the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve must be prepared for that compound.

7.3.4 Florisil standardization. The cleanup procedure described in Section 7.1.2 utilizes Florisil chromatography. Florisil from

different batches or sources may vary in absorption capacity. To determine the amount of Florisil to be used, the absorption capacity of each separate batch of Florisil is measured using lauric acid values (2). The referenced procedure determines the adsorption from hexane solution of lauric acid (mg) per g Florisil. The amount of Florisil to be used for each column is calculated by dividing this factor into 110 and multiplying by 20 g.

7.4 Gas chromatographic analysis

7.4.1 Inject 2-5 µl of the sample extract using the solvent flush technique. Smaller (1.0 µl) volumes can be injected if automatic devices are employed. Record the volume injected to the nearest 0.05 µl, and the resulting peak size, in area units.

7.4.2 If the peak areas exceed the linear range of the system, dilute the extract and reanalyze.

7.4.3 If peak detection is prevented by the presence of interferences, further cleanup is required. Before using any cleanup procedure, the analyst must process a series of calibration standards through the procedure to validate elution patterns and the absence of interferences from the reagents.

7.4.4 Examples of chromatograms for organochlorine pesticides are shown in Figures 1-5.

8.0 Quality Control

8.1 Before processing any samples, the analyst should demonstrate through the analysis of a distilled water method blank that all glassware and reagents are interference-free. Each time a set of samples is extracted or there is a change in reagents, a method blank should be processed as a safeguard against chronic laboratory contamination. The blank samples should be carried through all stages of the sample preparation and measurement steps.

8.2 Standard quality assurance practices should be used with this method. Field replicates should be collected to validate the precision of the sampling technique. Laboratory replicates should be analyzed to validate the precision of the analysis. Fortified samples should be analyzed to validate the sensitivity and accuracy of the analysis. If the fortified waste samples do not indicate sufficient sensitivity to detect less than or equal to 1 µg/g of sample, then the sensitivity of the instrument should be increased or the extract subjected to additional cleanup. Detection limits to be used for groundwater samples are indicated in Table 1. The fortified samples should be carried through all stages of the sample preparation and measurement steps. Where doubt exists over the identification of a peak on the chromatograph, confirmatory techniques such as mass spectroscopy should be used.

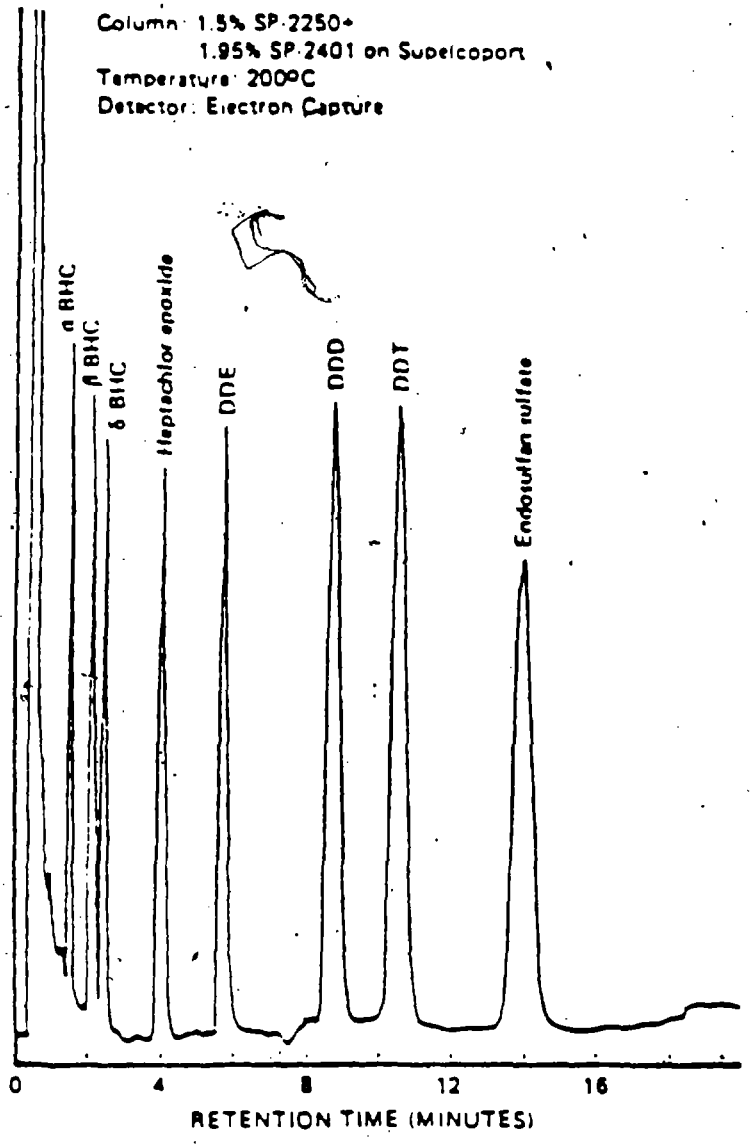

Figure 1. Gas chromatogram of pesticides.

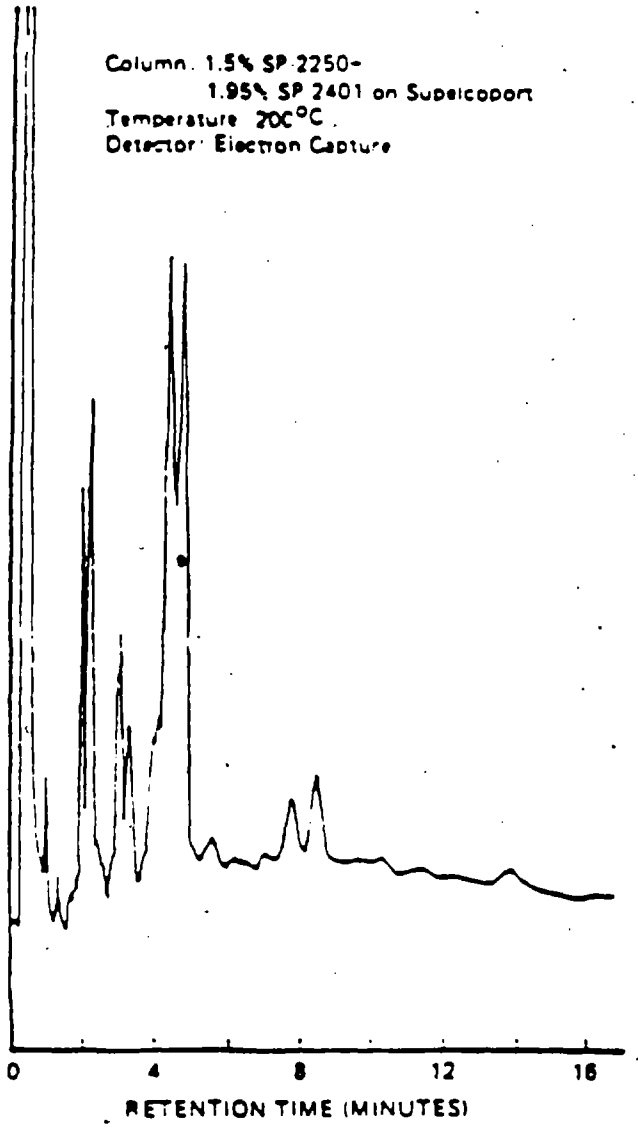

Figure 2. Gas chromatogram of chlordane.

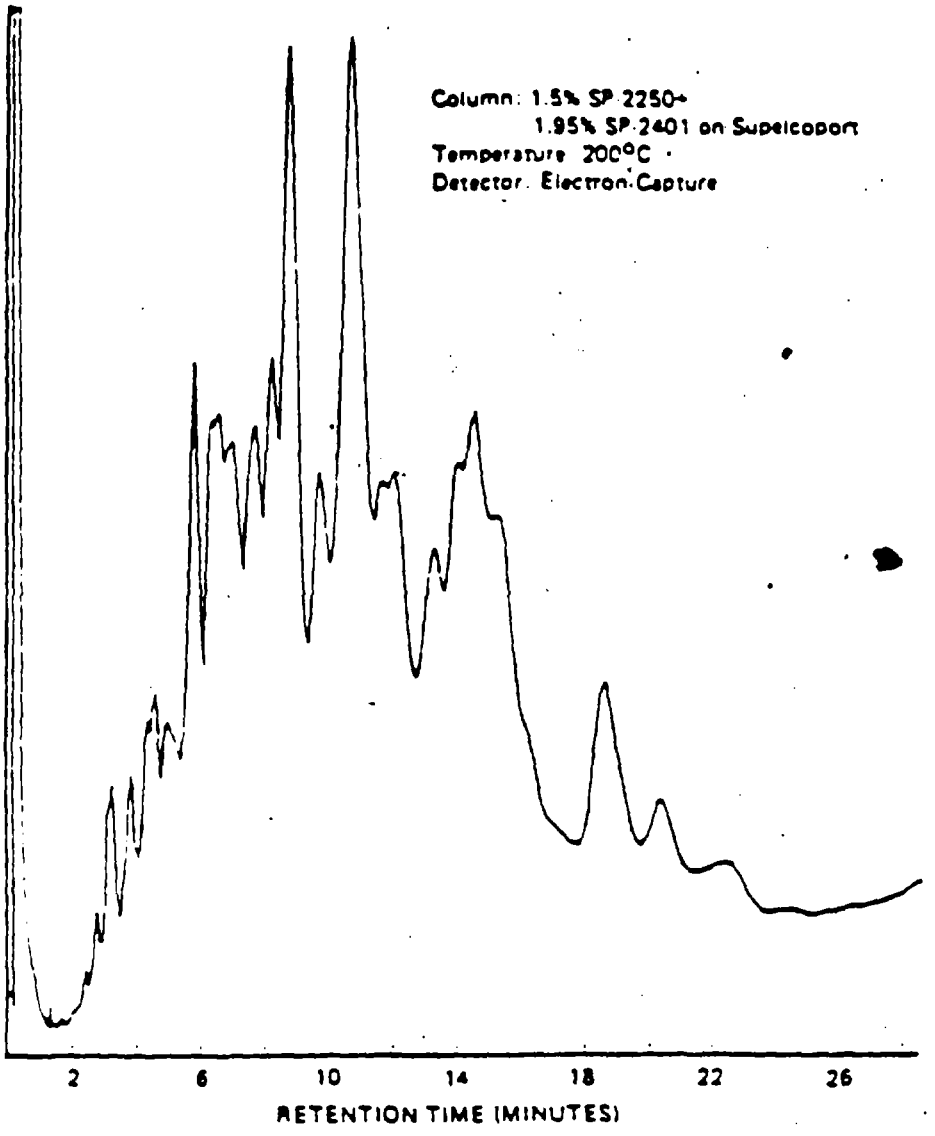

Figure 3. Gas chromatogram of toxaphene.

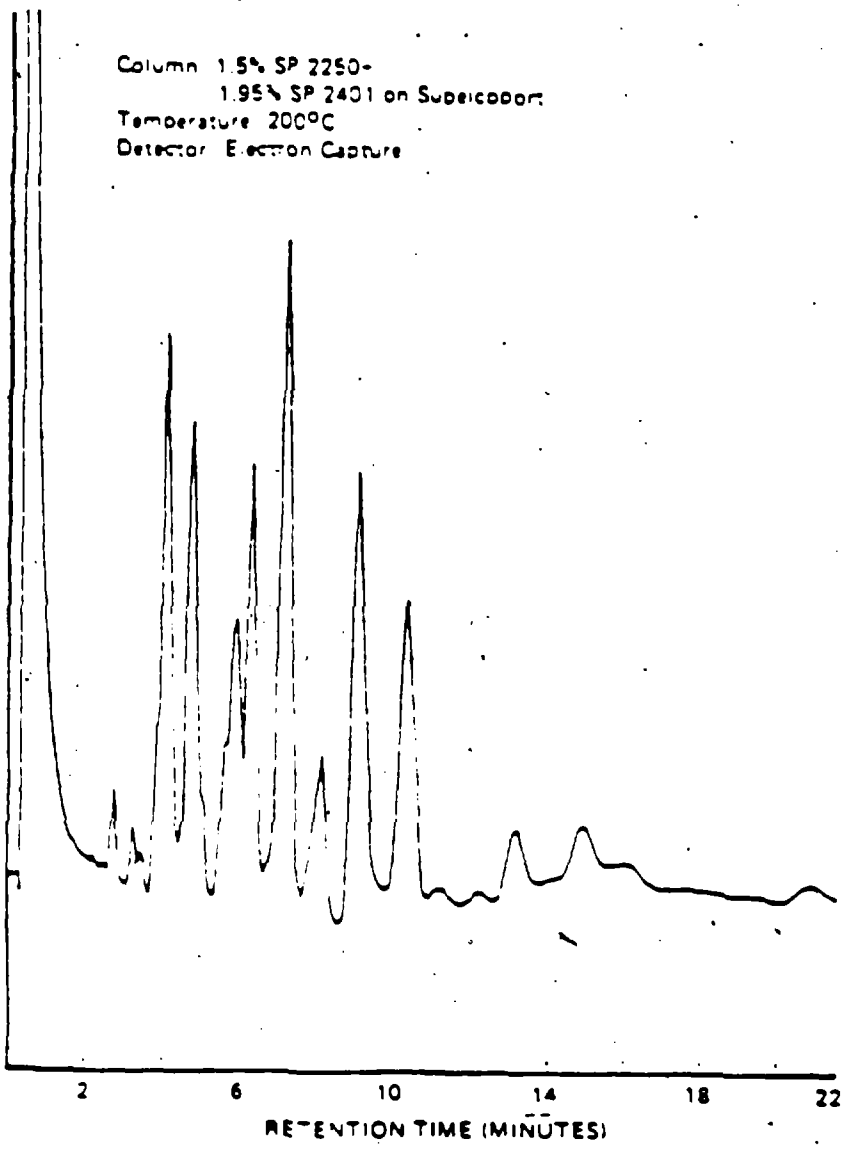

Figure 4. Gas chromatogram of PCB-1254.

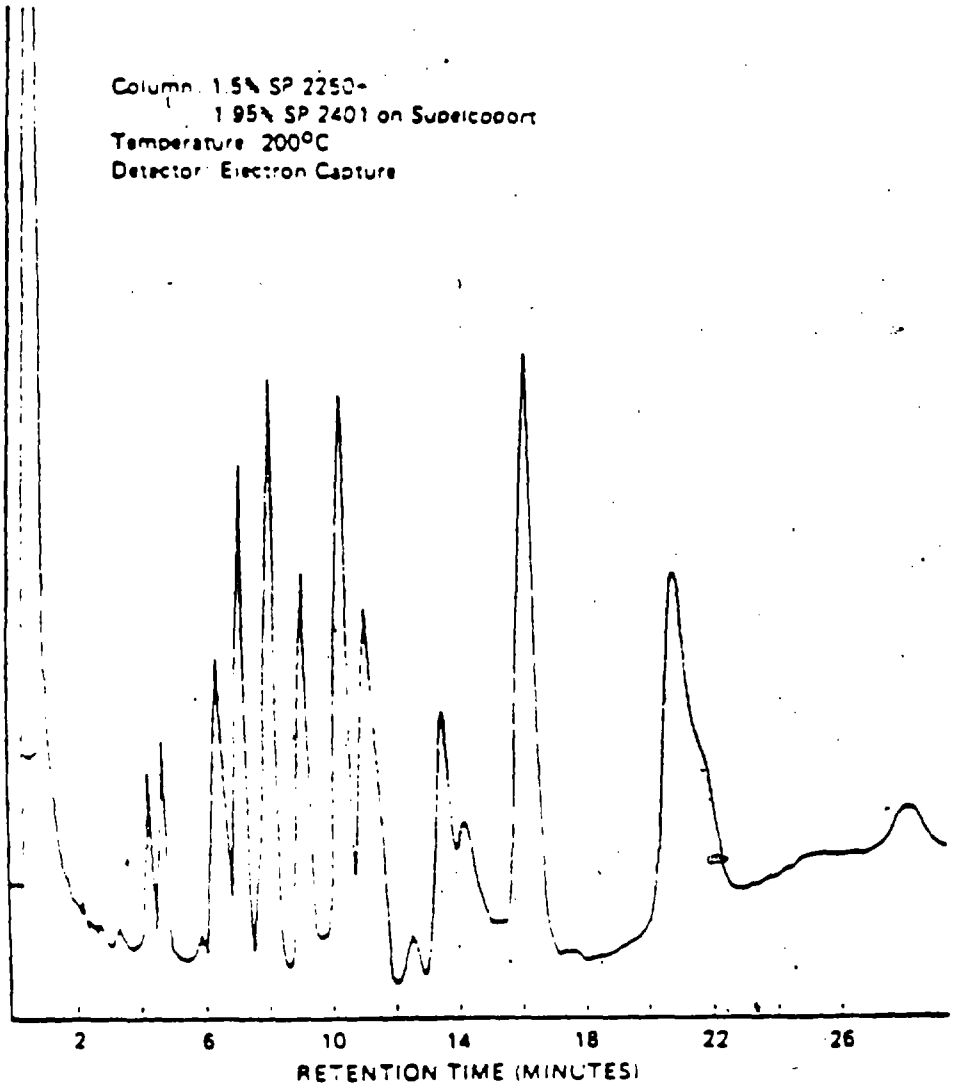

Figure 5 Gas chromatogram of PCB-1260.

8.3 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. The MDL concentrations listed in Table 1 were obtained using reagent water. Similar results were achieved using representative wastewaters. The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

8.4 In a single laboratory, using reagent water and wastewaters spiked at or near background levels, the average recoveries presented in Table 3 were obtained. The standard deviation of the measurement in percent recovery is also included in Table 3.

TABLE 3. SINGLE OPERATOR ACCURACY AND PRECISION

Parameter	Average percent recovery	Standard deviation (%)	Spike range (µg/l)	Number of analyses	Matrix types
Aldrin	89	2.5	2.0	15	3
a-BHC	89	2.0	1.0	15	3
B-BHC	88	1.3	2.0	15	3
w-BHC	86	3.4	2.0	15	3
g-BHC (Lindane)	97	3.3	1.0	15	3
Chlordane	93	4.1	20	21	4
4,4'-DDD	92	1.9	6.0	15	3
4,4'-DDE	89	2.2	3.0	15	3
4,4'-DDT	92	3.2	8.0	15	3
Dieldrin	95	2.8	3.0	15	2
Endosulfan I	96	2.9	3.0	12	2
Endosulfan II	97	2.4	5.0	14	3
Endosulfan sulfate	99	4.1	15	15	3
Endrin	95	2.1	5.0	12	2
Endrin aldehyde	87	2.1	12	11	2
Heptachlor	88	3.3	1.0	12	2
Heptachlor epoxide	93	1.4	2.0	15	3
Toxaphene	95	3.8	200	18	3
PCB-1016	94	1.8	25	12	2
PCB-1221	96	4.2	55-100	12	2
PCB-1232	88	2.4	110	12	2
PCB-1242	92	2.0	28-56	12	2
PCB-1248	90	1.6	40	12	2
PCB-1254	92	3.3	40	18	3
PCB-1260	91	5.5	80	18	3

9.0 References

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2. Mills, P.A. 1968. Variation of florisil activity: simple method for measuring absorbent capacity and its use in standardizing florisil columns. J. Assoc. Official Anal. Chem. 51 (29).

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4. Bellar, T., J. Lichtenburg and S. Lonnesman: 1980. Recovery of organic compounds from environmentally contaminated bottom materials. In Contaminants and sediments; Volume 2, ed. R. Baker, Ann Arbor Science Publ., Inc., Ann Arbor, Michigan.

5. Rodriguez, C., W. McMahon, and K. Thomas. 1980. Method development for determination of polychlorinated hydrocarbons in municipal sludge. EPA Report-600/2-80-029.

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APPENDIX C - STANDARD OPERATING PROCEDURES

STANDARD OPERATING PROCEDURES

FOR

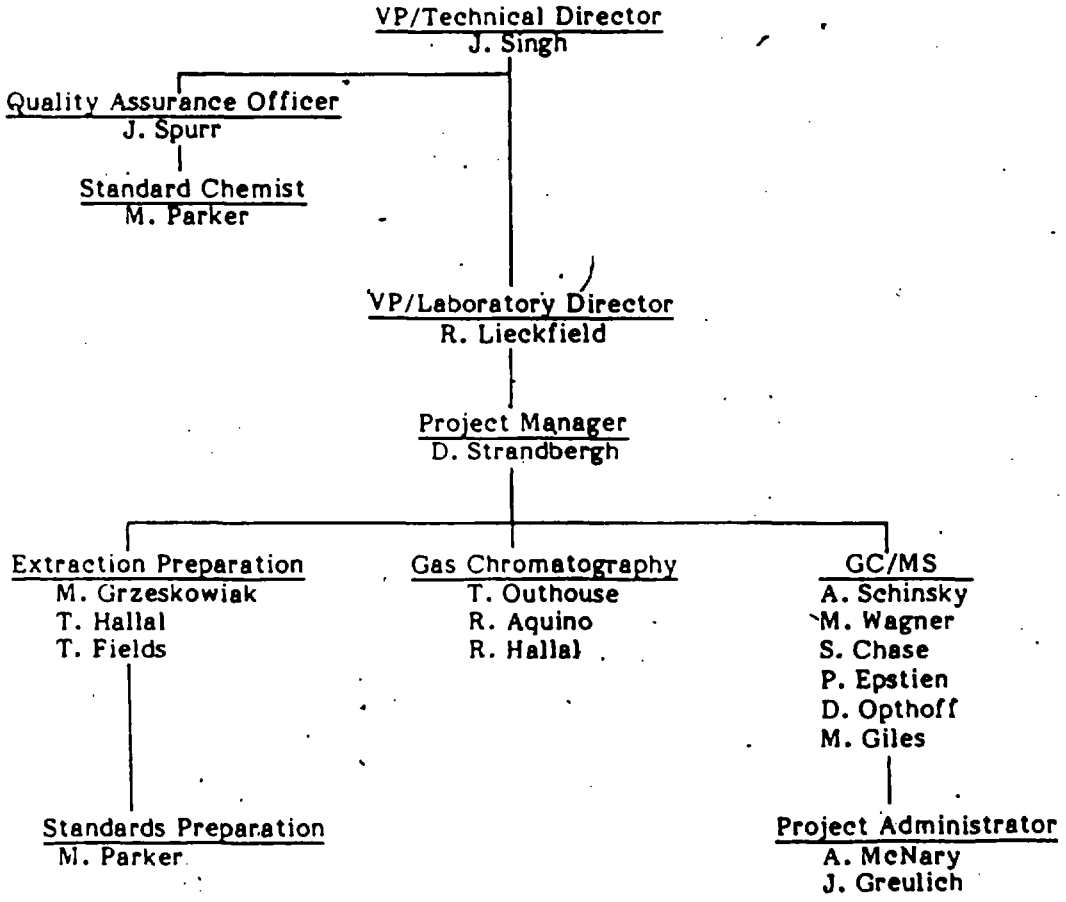
TRACKING, ANALYSIS, & DOCUMENTATION

OF

HAZARDOUS WASTE SAMPLES

1.0 ORGANIZATION

The handling and analysis of hazardous waste samples is the direct responsibility of the Laboratory Department of Clayton Environmental Consultants, Inc. All technical and administrative decisions are the responsibility of the Laboratory Director, who reports to the Corporate Technical Director/Executive Vice President. Quality Assurance (QA) is the responsibility of the QA Officer, who reports directly to the Technical Director. The organization chart shown below illustrates the reporting responsibilities for the conduct of projects considered by this protocol.



Date: 7/15/85

Signature:

3.0 SAMPLE RECEIPT & STORAGE

Purpose: The purpose of this procedure is to ensure the safe and orderly receipt of samples and to define the method of storage used to eliminate sample loss, deterioration, or contamination.

Responsibility: Adherence to this procedure and care of all hazardous waste samples is the responsibility of the HW Project Administrator. He may be assisted by log-in technicians and other laboratory staff, but primary responsibility falls to the PA.

3.1 Sample Receipt

3.1.1 Location: All HW samples are delivered to the north entrance of the building. No coolers or other sample containers are permitted through the personnel entrances and samples are not be transported through the building.

3.1.2 Notification: The PA (or designated representative) is notified in advance by the PM about the case number, the airbill number and the date the samples will arrive. The PA (or designated representative) is advised immediately when the samples arrive. Samples are not to be left unattended. All delivery receipts must be signed by the PA /designated representative.

3.1.3 Inspection: The PA, upon receipt of a sample lot, performs the following steps:

(1) Check the sample shipment information on the delivery receipt against pre-shipment notification. If the information does not agree notify the PM before proceeding.

(2) Check the shipping container for the presence or absence of the custody seal (Fig. 1). The custody seal should have a number, which should appear on the Chain of Custody (Fig. 2), have a signature and be intact. If it does not, make a note in the remark section of the Log-In sheet (Fig. 5).

(3) Examine the shipping container. If it does not appear to be intact, make a note in the remark section (Fig. 5).

(4) Place the shipping container on the lab cart and proceed to the HWL. Place the shipping container under the hood.

(5) Remove the container seal(s) and save for case documentation. Open the shipping container and remove the enclosed documents. They should be in a waterproof bag taped to the inside lid of the container. The bag should contain:

1. Chain of Custody Record (Fig. 2)

2. Traffic Report(s) (SMO Form, Fig. 4).

Date: 7/15/86

Signature: [signature]

(6) Compare the following to the Chain of Custody for agreement.

1. Case number
2. Shipper's name on the airbill
3. Custody seal numbers

(7) Remove the samples from the shipping container. Place them in the hood. Record the following information on the Log-In Sheet (Fig. 5).

1. The sample condition (broken, leaking, etc.)
2. The presence/absence of sample tags (Fig. 1A).
3. The sample tag document control number.

(8) Compare the case number, SMO sample number and tag numbers on the samples to the Chain of Custody Record: (Fig. 2)

1. If these numbers agree, record this on the Log-In sheet.
2. If any of the numbers do not agree, record this on the Log-In Sheet.

(9) Compare the following documents to verify agreement among the information contained on them:

1. Chain of Custody records
2. Sample tags
3. SMO forms (traffic reports)
4. Air bills or bills of lading numbers

(10) If all of the information agrees on all documents, record this on the Log-In Sheet. If there are discrepancies on the forms, notify the Program Manager, who will in turn notify the SMO for clarification. Document the call using the Telephone Record Form (Fig. 6). Logging-in of the samples will continue when descrepancies have been clarified and the PM gives his permission.

010 Date: 7/15/86

 Signature: [signature]

(11) If there are no problems with the sample shipment:

1. Sign the Chain of Custody Record in the appropriate "received by lab" box and record the time and date.
2. Sign and date the SMO Traffic Reports and complete the sample condition column.
3. Record all the information on the Log-In Sheet.
4. Place the samples on the lab cart and proceed to the CLP office.
5. Lock the samples and documents in the CLP office except for the Log-In sheet, which you take to the Computer Center for the pertinent information required to Log-In the samples.

3.1.4 Log-In

The samples are logged in as quickly as possible after sample receipt, at the Computer Center.

(1) Assign a Clayton Job Number from the sequential list in the Computer Job Task Program.

1. Enter the name of the SMO person who will receive the case deliverables.
2. Enter the company name, report address, city, state, and zip.
3. Enter the EPA contract number and Case number.

(2) Prepare a Laboratory Analysis Report (LAR) in the computer Log-In Task Program. The computer assigns a lab number for each sample. A sample of a completed LAR is given in Fig. 7. This is Clayton's internal document, indicating entry of sample and project information. No project may pass through the laboratory without this control.

1. Enter the assigned Job Number
2. Enter in sample description and the sample identification numbers.
3. Enter the sample media "soil" or "water".

011 Date: 7/15/86

 Signature: [signature]

4. Enter the analysis requested using the appropriate code for hazardous waste analysis.

5. Enter the SMO Case Number under special instructions.

6. Print out the LAR and check all information against the Log-In sheet and the Traffic Reports (s).

7. Xerox the appropriate number of copies based on the analyses requested.

(3) Proceed to the CLP locked office and organize samples for storage.

(4) Using the LAR sheet, assign the lab numbers to the appropriate samples.

(5) Remove the sample tags and write the appropriate lab numbers in the "Lab Sample No" box (Fig. 1A).

(6) Lock the samples in the refrigerator except for the VOA's (3.2.2 covers the handling of VOA's).

(7) Place the documents in the document case file (see 4.0 Document Control).

3.2 Sample Storage

3.2.1 Soil samples and water samples for extraction are stored in the locked Beveragaire refrigerator.

3.2.2 Take VOA vials to the GC/MS laboratory to be stored in the designated locked refrigerator.

(1) The PA relinquishes the samples to the GC/MS Operation Chemist.

(2) GC/MS operation chemist signs for the samples on the Internal Chain of Custody Record (Fig. 3), recording the date and time of receipt.

(3) The PA then places this record in the appropriate case document file.

3.2.3 Samples remain in storage until the PM approves the receipt of the sample lot and authorizes analytical activity.

3.2.4 Samples must be protected from light and stored at 4° C from the time of receipt until 60 days after the case has been submitted. Samples may then be appropiately disposed under the PM's direction ✓

3.2.5 Water samples must be extracted within 5 days of receipt and completely analyzed within 40 days of extraction. VOA water samples must be analyzed within 7 days of sample receipt. Soil samples must be extracted within 10 days of sample receipt and completely analyzed within 40 days of extraction. VOA soil samples must be analyzed within 10 days of sample receipt. This does not preclude the contract requirement of 30 or 40-day turnaround of analytical data.

3.2.6 Sample storage areas are locked at all times. The PM, PA, and Lab Manager have the only keys to the storage areas. Either the PM or the PA may designate a substitute for himself in the event of being absent from the laboratory. All such designations are recorded in the PA's tracking log book. Procedures for removing samples from storage for extraction are found in the Chain-of-Custody section (4.0).

3.2.7 Refrigerated storage areas for used and unused portions of samples must be kept at 4° C. The QA officer designates a representative to monitor and record the temperatures of the refrigerators and freezers on a daily basis. Report any variation from approved conditions to the QA officer at once.

3.2.8 Do not store standards or extracts with samples.

ANDARD OPERATING PROCEDURES
FOR
KING, ANALYSIS, & DOCUMENTATION
OF
HAZARDOUS WASTE SAMPLES

L & CHAIN-OF-CUSTODY

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W project:

(1) The PM will notify the PA of pending sample shipment. At this time a document case file is prepared (Fig. 8).

(2) The anticipated date of shipment delivery and the number of samples is entered in the PA's Log Book.

(3) When the samples are delivered, the procedure 3.0 "Sample Receipt and Storage" is followed.

(4) When the samples have been logged-in and stored, all documents received with the shipment are filed in the appropriate document case file.

(5) The document case file is kept in a secure filing cabinet in a secured area. The case file is not removed from the secured area nor are any "originals" from the case file given to other staff. Copies of the case documents may be prepared for authorized personnel.

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ERATING PROCEDURES
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OF
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4.2.2 Clayton maintains legally defensible chain-of-custody security procedures as follows:

(1) Samples are stored in a secure area.

(2) Refrigerators, freezers and other sample storage areas are kept locked.

(3) Samples remain in locked sample storage until they are removed for sample preparation or analysis.

(4) Only the PA, PM, and Lab Manager have keys to the sample storage area(s).

(5) All transfers of samples into and out of storage are documented on an Internal Chain-of-Custody (Fig. 3).

4.2.3 The samples are transferred to the custody of the Sample Extraction Chemist (SEC) or other Analysts when:

(1) Samples have been logged in and all samples and documents have been locked in a secure area.

(2) VOA's have been transferred to GC/MS analyst (Fig. 3).

4.2.4 The Sample Extraction Chemist (SEC) or Analyst will contact the PA or designated representative to receive transfer of samples.

(1) The samples to be prepared are identified by the SEC to the PA by producing the copy of the LAR sheet (Fig. 7) received from the PM which specifies which samples are to be prepped.

(2) The PA transfers the samples from the locked area to the SEC. The SEC must sign in the "Removed By" column of the Internal Chain-of-Custody form (Fig. 3) and complete the "Reason" and "Date/Time" columns.

(3) The SEC must return the samples, or any portion of the samples, to the custody of the PA before the end of the working day. At this time, the PA completes the "Returned To" and "Date/Time" columns. These transactions are recorded in their respective logbooks. Samples may not be left unattended overnight.

(4) These transactions are completed within 5 days of sample receipt for water and within 10 days of sample receipt for soils.

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4.3 Building Security

4.3.1 All Clayton employees wear identification badges. These are standard badges furnished by the company.

4.3.2 All visitors to the Clayton laboratory facility must:

(1) Sign in prior to passing the reception area.

(2) Be issued a "Visitor" badge to be displayed at all times while on the premises.

(3) Be escorted by an authorized Clayton representative while in any of the secure areas.

4.3.3 Any PM, PA, or Technical Staff member may refuse entry to an escorted visitor if, in the opinion of the staff member, entry into the work area may constitute a hazard to the visitor, or other personnel in the area, or may jeopardize the integrity or security of any sample.

4.3.4 Women in any stage of pregnancy will not be permitted into the HWL area.

4.4 Tracking

4.4.1 Tracking of samples and the work is accomplished by a rigorous system of event logging procedures. Each analyst is responsible for maintaining the log books assigned to his area. The system operates as follows:

(1) The P.A. keeps a daily record of all events, including, but not limited to:
1. Sample receipt
2. Sample transfers
3. Data/standards package shipment
4. Collection of documents
5. Communications

From this log, a weekly summary is prepared and forwarded to the PM for his approval and submittal to the Project Officer (SMO).

(2) Each analyst involved in extraction, analysis, or quantitation of samples, standards, or QC samples maintains a permanent log book. The log book contains analytical information from only one case per page.

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(3) Each day, including weekends, is designated by an entry in the log. Data recorded is referenced with the case number, date, and the analyist's signature at the top of the page. If no work is performed by the analyst on a given case, on a given day(s), record the date(s) followed by the entry "No Activity" then sign the logbook on the same line.

(4) When work is performed, the analyst enters information including, but not limited to:

1. Case number
2. Custody activities
3. Sample numbers
4. Process undertaken
5. Results
6. Special conditions

(5) Log books are checked weekly by the PM. He reviews the entries in the logs to ensure that dates, order, signatures, and other critical information is being recorded as required.

(6) Each instrument used for the analysis of HW samples has an instrument maintenance log book. Entries into this book are made whenever parts are changed, or maintenance is performed on the instrument. Manufacturer's reps should be requested to make entries in the log and sign the log when repairs are performed.

(7) All standards logs are kept by the Standards Chemist. Standard preparations are recorded in either of two logbook series. Single component standards are recorded in books with pages numbered 20,000 to 29,999; Multi-component standards are recorded in books with pages numbered 40,000 to 49,999. Each standard mixture has a separate page. This page number then becomes the standard's ID number and is used whenever referencing the standard. Anyone preparing or verifying a standard must record all required information in these logs with the date and his signature. Standard storage locations are also recorded in these logs. The standards log books are reviewed during an onsite visit.

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4.4.2 All logbooks have duplicate pages; the analysts use carbon paper to duplicate each page. When the case package is being prepared, the carbon copies of the appropriate logbook pages are collected, given inventory control numbers, and placed in the case file.

4.4.3 All loose documents related to an HW case are given to the PA for numbering and filing as soon as they become available. No printouts, calculations, worksheets, benchsheets, or other documents shall be left unsecured on a workbench or desk. While incomplete, they are retained in a secure place by the analyst. Once completed, they are turned over to the PA.

4.4.4 All entries in logbooks and other documents are made in ink. If an error is made in a logbook, correct it by crossing a line through the error and entering the corrected information. Any changes made are dated and initialed.

4.4.5 All documentation on a case is cross-checked for consistency. Information on sample tags, custody records, lab bench sheets, personal and instrument logs and relevant data pertaining to each particular sample or case must be consistent throughout the record.

4.5 Report Preparation, Review & Storage

4.5.1 The PA prepares the data packages for submittal. He informs the departments about any documents required for the data package and maintains the document inventory as outlined in 4.0. The PM ensures that the documents are correct prior to their inclusion in the package and verifies their applicability to the case.

4.5.2 When a data package is complete, the PA submits to the PM a completed set, including a table of contents, a cover letter, document inventory sheet, and a data package. The PM reviews the package, signs the necessary forms, and returns the package to the PA for copying, binding and shipping.

4.5.3 The EPA requires that three data packages be submitted. These packages are generated by the PA. Following the approval and signature of the PM, the three submittals are forwarded by express courier to the intended recipients. The original data package is placed in a locked secure storage area for 180 days or until the government requests it.

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 Signature: [signature]

STANDARD OPERATING PROCEDURES
FOR
TRACKING, ANALYSIS, & DOCUMENTATION
OF
HAZARDOUS WASTE SAMPLES

10.0 QUALITY ASSURANCE PROGRAM

Purpose: While the process of sample analysis is under routine control as set forth in Clayton's Quality Assurance Program documents, the handling of hazardous waste samples requires the use of special procedures to ensure the integrity of all data and to facilitate the demonstration that data, calculations, and standards are valid.

Responsibility: The responsibility and authority for monitoring all sample handling and analysis rests with the Quality Assurance Coordinator, who reports directly to the Senior VP/Technical Director. He has the ability to enforce the QA criteria set forth in this document, to allocate the necessary resources to fulfill the contractual requirements, and to regulate the activities of the technical staff, as they impact the quality of data. All quality assurance documentation flows through his office for review, and results may not be released without his approval.

10.1 Standards

The accurate preparation of analytical standards and the control of their use in the analytical process is to be carried out as follows:

10.1.1 A computerized inventory of all "neat" compounds is maintained by the Standards Chemist(SC). The record of each compound includes the following:

1. CAS number
2. Synonyms
3. Supplier
4. Catalog number
5. Lot number
6. Purity
7. Date received
8. Volume or weight
9. Chemical precautions
10. Storage location

Searches for chemical information are possible from a printed alphabetical listing (Figure 10.1) or by direct data base access. The Standards Chemist is responsible for reviewing all chemicals on an annual basis to determine which need to be disposed and reordered.

10.1.2 Stock solutions of standard compounds are prepared and validated by the Standards Chemist. When a solution is prepared from neat material that is less than 96% pure, the concentration must be corrected for its purity.

10.1.3 A standard solution may not be used until its concentration has been verified by GC/ECD (for GC standards) analysis. The standard is verified by analyzing against standard solutions furnished by the U.S. EPA Quality Assurance Materials Bank. These reference solutions are stored below -20 in Freezer #9.

The two solutions must agree within +/- 15% to have a validated concentration. All verification records, including chromatograms, are kept with the preparation records in the standard log books.

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10.1.4 Stock and working solutions for volatile compound standards are prepared monthly. Stock and working levels for gas-phase volatile compounds and 2-chloroethyl vinyl ether are prepared weekly.

Stock and working standards for semi-volatile and PCB/pesticide compounds are prepared at least every six (6) months. Response factors are monitored to detect degradation or evaporation.

10.1.5 Two log book series are maintained for recording CLP standards preparation. Each preparation is recorded on a separate page (Figures 10.2 and 10.3). The pages are numbered according to the following system:

Standard Type	Numbering Series
Single component	20,000 to 29,999
Multi-component	40,000 to 49,999

The standard is labelled with the unique page number and this becomes the "standard number", referenced whenever the standard is used.

10.1.6 Do Not prepare a standard solution without entry in the appropriate log.

10.1.7 When a stock solution or working standard is replaced, the date, time and reason for disposal is noted by the SC on the appropriate page of the standards log. A standard MAY NOT be used following its removal from the standards log.

10.1.8 The PM reviews the standards logs on a weekly basis; the QAC on a monthly basis.

10.2 Equipment Performance Logs

An important part of Clayton's quality assurance program is to provide a detailed record of instrument performance and maintenance for all equipment and instruments used. These records are reviewed at least monthly by the QAC.

10.2.1 Refrigerators/Freezers

(1) Each refrigerator and freezer contains only the items designated for that particular unit (Figure 10.4). This minimizes the possibility of cross-contamination. All units are monitored daily by assigned personnel.

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(2) Temperatures are recorded daily in the temperature log that is attached to the front of each unit (Figure 10.5).

The following guidelines for acceptable temperatures, and corrective actions for unacceptable variations are included in each log.

Refrigerator	Freezer	Action
4°C	-20°C	Normal (no action)
less than 3°C or greater than 6°C	greater than -15°C	Monitor closely
less than 2°C or greater than 8°C	greater than -10°C	Take corrective action

Monitoring closely means to record the temperature several times within the same day, several hours apart. Action first requires notifying the PM or QAC, then making an adjustment to the temperature setting, followed by close monitoring. After this, if there is no improvement and the unit appears to be failing, all contents are transferred to another unit and service is performed on the broken unit.

(3) Completed logs are returned to the QAC for replacement, but are held permanently on file.

10.2.2 Balances

(1) All analytical balances used in the CLP program are checked daily for calibration using a set of class "S" metric weights. All three are "macro-digital" style Mettler balances which are serviced annually.

(2) Records of the calibration checks are kept in a log book stored with each balance (Figure 10.6). Any service or maintenance performed on a balance is noted on a separate maintenance record in the logbook, then cross-referenced in the calibration record.

(3) If the error during the calibration check is greater than +/- 1 of the last readable place, the balance must be recalibrated.

10.2.3 Exhaust Hoods

The exhaust hoods in the Hazardous Materials Lab are equipped with manometers. Manometer readings are recorded daily in the log attached to each hood (Figure 10.7).

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(1) The zero setting must be checked and adjusted before the hood is turned on; the full draw is recorded once the motor has reached full speed.

(2) A 50% drop in the "full performance" reading, or a reading below 0.5 inches of water, requires immediate servicing. Notify the Laboratory Manager if this need arises.

(3) Return a completed log book to the QAC for replacement.

Hoods not equipped with manometers are checked for flow with the door in full, half, and quarter open positions. These measurements are recorded on each hood and are maintained in a log kept by the QAC.

10.2.4, Reagent Water System

Water purification is accomplished by a two-stage system. The "Millipore Milli-Q" system, providing Type I grade water, is preceeded by a "Service D.I. Pretreatment" system which provides Type II grade water. When used in combination, 18 megohms/cm organic-free water is provided on demand at up to 1.5 liters per minute (Figure 10.8).

(1) BEFORE using any Milli-Q water, ALWAYS check the resistivity meter. DO NOT USE THE WATER UNLESS THE METER READS ABOUT 18 meghoms/cm. When first turned on, this should take less than 5 minutes and should remain there until turned off.

(2) The pretreatment water is used for GLASSWARE RINSING ONLY. Two outlets are provided for this purpose above the sinks where glassware is washed.

(3) Water system performance is MONITORED DAILY by reading five indicators installed in the system. These are checked and recorded in a logbook that is attached to the system (Figure 10.9).

(4) Proper operating condititions are described below. The QAC is notified if any of these condititions can not be met.

a. Both pretreatment indicator lights are ON.
b. Resistivity is about 18 megohms/cm.
c. Pressures read less than 30 psi.
d. The difference in pressures is less than 10 psi.

(5) The Milli-Q system cartridges are replaced as needed, typically every 4 to 6 months. A service contract for the pretreatment system provides replacement of the D.I. tanks and 5-um prefilter every 3 months, the carbon tank every 6 months.

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(6) Containers for water are used for short-term storage or for transporting to other parts of the laboratory only. Glass containers are for water used in organics work, polyethylene or polypropylene for water used in inorganics work.

10.2.5 Instrument Logs

Each instrument has two log books. All pages are dated and signed by the analyst performing the work or making the entry. Only bound books are used.

(1) An instrument-run log is maintained as a permanent record of conditions and analytical run sequence.

(2) A maintenance book is kept as a concise record of repair or service required on the instrument. Routine cleaning and maintenance are also noted.

10.3 Glassware Cleaning Procedure

10.3.1 Rinse item thoroughly with warm tap water.

10.3.2 Scrub items with (not in) a 2% solution of RBS-35 cleaning concentrate using an appropriate brush.

10.3.3 Rinse with warm tap water and place in tub of 2% RBS to soak. Soaking of glassware should be done with caution and ONLY after the initial scrub and rinse. Cross-contamination may result from mixing dirty glassware exposed to high levels of contaminants.

10.3.4 Thoroughly scrub the item with the RBS solution.

10.3.5 Thoroughly rinse with warm tap water.

10.3.6 Rinse with distilled water.

10.3.7 Rinse with acetone (from Telfon squeeze bottle) to remove water and trace organics.

10.3.8 Rinse with methylene chloride (from Teflon squeeze bottle) to remove polar compounds.

10.3.9 Rinse with hexane (from Teflon squeeze bottle) to remove non-polar compounds.

10.3.10 Cover open ends of glassware with hexane-rinsed aluminium foil.

10.3.11 Immediately before and after using glassware, rinse exposed surfaces with those solvents used in the analyses.

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10.4 Instrument Tuning

The routine calibration of instruments used in the analysis of HW samples begins with tuning of the GC/MS systems.

10.4.1 Prior to initiating any ongoing data collection, it is necessary to establish that a given GC/MS meets the standard mass spectral abundance criteria. This is accomplished through the analysis of Decafluorotriphenylphospnine (DFTPP) or p-Bromofluorobenzene (BFB). The ion abundance criteria for each calibration compound MUST be met before any samples, blanks, or standards can be analyzed.

10.4.2 Each GC/MS system used for the analysis of semi-volatile or pesticide HSL compounds must be hardware-tuned to meet the abundance criteria listed in Table 10-1 for a 50-ng injection of DFTPP. DFTPP may be analyzed separately or as part of the calibration standard. The criteria must be demonstrated for each twelve (12) hour period. DFTPP is injected to meet this criterion. Post-acquisition manipulation of ion abundance is NOT acceptable. Documentation of the calibraton is provided in the form of a bar graph plot and as a mass listing.

TABLE 10-1: DFTPP KEY IONS AND ION ABUNDANCE CRITERIA

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

10.4.3 Form V (GC/MS Tuning and Mass Calibration) is completed each time an analytical system is tuned. In addition, all samples, standards, blanks, matrix spikes and matrix spike duplicates analyzed during a particular tune are summarized on the bottom of Form V.

10.4.4 p-Bromofluorobenzene (BFB) - The GC/MS system used for the analysis of volatile HSL compounds is hardware-tuned to meet the abundance criteria listed in Table 10-2 for a 50-nanogram injection of BFB. Alternately, add 50 ng of BFB solution to 5.0 mL of reagent or standard solution and analyze according to 5.3.3. This criterion is demonstrated for each twelve (12) hour time period. Post-acquisition manipulation of ion abundance is NOT acceptable. Documentation of the calibration is provided in the form of a bar graph plot and as a mass listing.

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TABLE 10-2: BFB KEY IONS AND ABUNDANCE CRITERIA

Mass	Ion Abundance Criteria
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 the base peak
173	Less than 1.0 percent of the base peak
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

10.4.5 Form V (GC/MS Tuning and Mass Calibration) is completed each time an analytical system is tuned.

10.4.6 Whenever corrective action is taken which may change or affect the tuning criteria for DFTPP or BFB (e.g., ion source cleaning or repair, etc.), the tune is verified irrespective of the 12-hour tuning requirement.

10.4.7 DFTPP and BFB criteria MUST be met before any samples, sample extracts, blanks or standards are analyzed. The twelve (12) hour time period for tuning and calibration criteria begins at the moment of injection of the DFTPP or BFB analysis. The time period ends after twelve (12) hours according to the system clock.

10.5 Initial Calibration

10.5.1 The calibration standards prepared by the Standards Chemist as described in 5.3.3 must meet the following specific concentrations:

(1) Volatile HSL Compounds - Initial calibration of volatile HSL compounds is required at 20, 50, 100, 150 and 200 ug/L. Utilizing the analytical protocol specified in Exhibit D this will result in 100-1000 total ng analyzed. If a sample analyzed saturates at the 200 ug/L concentration level, document it on Form VI and proceed with a four-point initial calibration for that specific analyte.

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 Signature: [signature]

(2) Semi-volatile and Pesticide HSL Compounds - Initial calibration of semi-volatile HSL compounds is required at 20, 50, 80, 120 and 160 total nanograms. Ten compounds: Benzoic Acid, 2, 4-Dinitrophenol, 2,4,5-Trichlorophenol, 2-Nitroaniline, 3-Nitroaniline, 4-Nitroaniline, 4-Nitrophenol, 4,6-Dinitro-2-Methylphenol, and Pentachlorophenol will only require a four-point initial calibraton at 50, 80, 120, and 160 total nanograms since detection at less than 50 nanograms per injection is difficult.

10.5.2 Analyze each calibration standard and tabulate the area of the primary characteristic ion (SOW, Section 5, Table 4 and Table 5) against concentration for each compound including all contract-required surrogate compounds. The relative retention times of each compound in each calibration run should agree within 0.06 relative retention time units except for N-nitrosodimethylamine. Late eluting compounds usually will have much better agreement. N-nitrosodimethylamine MUST be resolved from the solvent.

(1) Using Table 3 and Table 4, calculate the response factors (RF) for each compound at each concentration level using the following equation.

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

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 3.3 or 3.4.

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

C_x = Concentration of the compound to be measured (ng/uL).

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(2) Using the response factors (RF) from the initial calibration, calculate the percent relative standard deviations (%RSD) for compounds labelled as Calibration Check Compounds using the following equation.

$$\%RSD = \frac{o}{\bar{x}} \times 100$$

Where: RSD = Relative Standard Deviation.

o = Standard Deviation of initial 5 response factors (per compound).

$\bar{x}$ = mean of initial 5 response factors (per compounds).

The %RSD for each individual Calibration Check Compound must be less than 30 percent. This criteria must be met for the initial calibration to be valid.

10.5.3 Run a system performance check to insure minimum average response factors are met before the calibration curve is used.

For volatiles, the five System Performance Check Compounds (SPCC's) are: chloromethane, 1,1-dichloroethane, bromoform, 1,1,2,2-tetrachloroethane and chlorobenzene. The minimum acceptable average response factor (RF) for these compounds is 0.300. These compounds typically have RF's of 0.4-0.6 and are used to check compound instability and check for degradation caused by contaminated lines or active sites in the system.

10.5.4 Analyze each calibration standard and tabulate the area of the primary characteristic ion (SOW, Section 5, Table 4 and Table 5) against concentration for each compound including all contract required surrogate compounds. The relative retention times of each compound in each calibration run should agree within 0.06 relative retention time units except for N-nitrosodimethylamine. Late eluting compounds usually will have much better agreement. N-nitrosodimethylamine MUST be resolved from the solvent.

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 Signature:

TABLE 10-3: VOLATILE INTERNAL STANDARDS WITH CORRESPONDING HSL ANALYTES ASSIGNED FOR QUANTITATION

Bromochloromethane	1,4-Difluorobenzene	Chlorobenzene-d_5
Chloromethane	2-Butanone	2-Hexanone
Bromomethane	1,1,1-Trichloroethane	4-Methyl-2-Pentanone
Vinyl Chloride	Carbon Tetrachloride	Tetrachloroetnene
Chloroethane	Vinyl Acetate	1,1,2,2-Tetrachloroetnane
Methylene Chloride	Bromodichlorometnane	Toluene
Acetone	1,2-Dichloropropane	Chlorobenzene
Carbon Disulfide	Trans-1,3-Dichloropropene	Ethylbenze
1,1-Dichloroethene	Trichloroethene	Styrene
1,1-Dichloroethane	Dibromochloromethane	Total Xylenes
Trans-1,2-Dichloroetnene	1,1,2-Trichloroethane	Bromofluorobenzene (surr)
Chloroform	Benzene	Toluene-d_8(surr)
1,2-Dichloroethane	cis-1,3-Dichloropropene	
1,2-Dichloroethane-d_4 (surr)	2-Chloroethyl Vinyl Ether	
	Bromoform	

10.5.5 The System Performance Check Compounds (SPCC's) for BNA'S are: N-Nitroso-Di-n-Propylamine, Hexachloro-cyclopentadiene, 4-Nitrophenol, and 2,4-Dinitrophenol. The minimum acceptable average response factor (RF) for these compounds is 0.050. These compounds (SPCC's) typically have very low RF's (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 caliorated.

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

10.5.7 Once the initial calibration is validated, calculate and report the average response factor (RF) and percent relative standard deviation (%RSD) for all HSL compounds. Prepare a Form VI (Initial Calibration Data) for each instrument used to analyze samples.

Date: 7/15/86

 Signature: Eric Fredericks

10.6 Continuing Calibration

10.6.1 A calibration standard(s) containing all volatile or semi-volatile HSL compounds, including all required surrogates, is run each twelve (12) hours during analysis. Compare the response factor data from the standards 12 hours during analysis. Compare the response factor from the initial calibration for a specific instrument. A system performance check is made each twelve hours. If the SPCC criteria are met, a comparison of response factors is made for all compounds. This is the same check that is applied during the initial calibration (Form VI). If the minimum response factors are not met, the system must be evaluated and corrective action taken before sample analysis begins.

10.6.2 Possible problems include: standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, and active sites in the column or chromatography system. These must be checked before analysis begins. The minimum response factor (RF) for BNA compounds is 0.050. The minimum response factor (RF) for volatile compounds is 0.300.

10.6.3 After the system performance check is met, Calibration Check Compounds listed in Table 10-4 are used to check the validity of the initial calibration. Calculate the percent-difference using the following equation:

$$\% \text{ Difference} = \frac{RF_I - RF_C}{RF_I} \times 100$$

where:

RF_I = average response factor from initial calibration.

RF_C = response factor from current verification check standard..

TABLE 10-4: CALIBRATION CHECK COMPOUNDS

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

10.6.4 If the percent-difference from any compound is greater than 20, it is a warning limit. If the percent difference for each CCC is less than 25%, the initial calibration is validated. If the criteria are not met (greater than 25% difference), for any one calibration check compound, corrective action MUST be taken. Problems similar to those listed under SPCC could affect this criteria. If no source of the problem can be determined after corrective action has been taken, a new initial five point calibration MUST be generated. This criteria MUST be met before sample analysis begins.

10.6.5 The concentration for each volatile HSL compound in the continuing calibration standard(s) is 50 ug/L.

10.6.6 The concentration for each BNA HSL compound in the continuing calibration standard(s) is 50 total nanograms.

10.6.7 Prepare a Form VII for each GC/MS system utilized for each twelve hour time period. Calculate and report the response factor and percent difference (%RSD) for all compounds. Ensure the minimum RF for volatile SPCC's is 0.300 and for semi-volatile SPCC's is 0.050. The percent difference (%RSD) for each CCC compound must be less than 25 percent.

10.7 Method Blank Analysis - VOA'S, BNA'S, Pesticides/PCB'S

The following procedures will be followed to insure the precision and accuracy of the analytical data obtained.

10.7.1 A method blank is a volume of deionized, distilled laboratory water for water samples, or a purified solid matrix (supplied by EMSL-LV) for soil/sediment samples carried through the entire analytical scheme. The method blank volume or weight must be approximately equal to the sample volumes or sample weights being processed.

10.7.2 Method blank analysis must be performed at the following frequency:

(1) For the analysis of volatile HSL compounds, perform a method blank analysis every twelve hours, once per case, or with every twenty (20) samples of similar concentration and/or sample matrix, whichever is more frequent.

(2) For the analysis of BNA or pesticide HSL compounds, perform a method blank analysis once each case, with every twenty (20) samples of similar concentration and/or sample matrix, or whenever samples are extracted, whichever is more frequent.

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10.7.3 It is the analyst's responsibility to ensure that method interferences caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in gas chromatograms be minimized.

10.7.4 An acceptable laboratory method blank should meet the following criteria:

(1) A method blank for volatile analysis should contain no greater than two times (2X) the Contract-Required Detection Limit of common laboratory solvents (common laboratory solvents are: methylene chloride, acetone, benzene, and toluene). The method blank must not contain greater than five times (5X) the CRDL of those compounds previously listed.

(2) A method blank for BNA analysis should contain no greater than two times (2X) the Contract-Required Detection Limit of common phthalate esters. The method blank must not contain greater than five times (5X) the CRDL of any phthalate ester.

(3) A method blank for pesticides/PCB analysis must contain less than the Contract-Required Detection Limit of any single analyte. If a method blank exceeds criteria, the analytical system is out of control. The source of the contamination investigated and appropriate corrective measures are taken before further sample analysis can proceed.

10.7.5 The results of the method blank analyses are reported using the Organic Analysis Data Sheet (Form I) signed in original signature by the PM/designate. In addition, the results from method blanks are summarized on Form IV (Method Blank Summary).

10.7.6 ALL sample concentration data is reported as UNCORRECTED for blanks.

10.8 Surrogate Recovery

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.

10.8.1 Spike each sample (including matrix spike and matrix spike duplicate) and blank with surrogate compounds prior to purging or extraction. The surrogate spiking compounds shown in Table 10-5 are used to fortify each sample or blank with the proper concentrations. Evaluate surrogate spike recovery for acceptance by determining whether the concentration (measured as percent recovery) falls inside the required recovery limits listed in Table 10-6.

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TABLE 10-5: SURROGATE SPIKING COMPOUNDS

Compound	Fraction	Amount in Sample Extract (before any optional dilutions) Low H_2O	Medium H_2O	Low Soil	Medium Soil
Toluene-d_8	VOA	50 ug	50 ug	50 ug	50 ug
4-Bromofluorobenzene	VOA	50 ug	50 ug	50 ug	50 ug
1,2-Dichloroethane-d_4	VOA	50 ug	50 ug	50 ug	50 ug
Nitrobenzene-d_5	BNA	50 ug	50 ug	50 ug	100 ug
2-Fluorobiphenyl	BNA	50 ug	50 ug	50 ug	100 ug
p-Terphenyl-d_{14}	BNA	50 ug	50 ug	50 ug	100 ug
Phenol-d_5	BNA	100 ug	100 ug	100 ug	200 ug
2-Fluorophenol	BNA	100 ug	100 ug	100 ug	200 ug
2,4,6-Tribromophenol	BNA	100 ug	100 ug	100 ug	200 ug
Dibutylchlorendate	Pest.	0.1 ug	0.1 ug	0.1 ug	0.1 ug

TABLE 10-6: EPA CONTRACT-REQUIRED SURROGATE SPIKE RECOVERY LIMITS

Fraction	Surrogate Compound	Low/Medium Water	Low/Medium Soil/Sediment
VOA	Toluene-d_8	88-110	81-117
VOA	4-Bromofluorobenzene	86-115	74-121
VOA	1,2-Dichloroethane-d_4	76-114	70-121
BNA	Nitrobenzene-d_5	35-114	23-120
BNA	2-Fluorobiphenyl	43-116	30-116
BNA	p-Terphenyl-d_{14}	33-141	18-137
BNA	Phenol-d_5	15-094	24-113
BNA	2-Fluorophenol	21-100	26-121
BAN	2,4,6-Tribromophenol	10-123	18-122
Pest.	Dibutylchlorendate	(24-154)*	(20-150)*

* These limits are for advisory purposes only. They are not used to determine if a sample should be reanalyzed. When sufficient data becomes available, the USEPA may set performance based contract required windows.

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10.8.2 When the surrogate recovery of any one surrogate compound is outside of the required surrogate recovery limits (listed in Table 10-6) for a reagent blank, take the following actions:

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

(2) Recalculate or re-inject/re-purge the blank or extract.

(3) Re-extract and re-analyze the blank if the prior two steps do not resolve the problem.

(4) If the measures listed above fail to correct the problem, the analytical system is considered out of control. The problem MUST be corrected before continuing.

10.8.3 If the surrogate recovery of any one surrogate compound is outside of the contract required surrogate recovery limits (listed in Table 7) for a sample, establish that the deviation is not due to laboratory problems. The quality control windows are calculated using program generated analytical data. It is expected that 5-15 percent of the surrogate recovery data may fall outside of these windows, and requires recalculation and/or re-extraction/re-analysis.

10.8.4 Document deviations outside acceptable quality control limits and take the following actions:

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

(2) Recalculate or re-analyze the sample or extract. If re-analysis of the sample or extract solves the problem then only submit the sample data from the analysis with surrogate spike recoveries within the contract windows.

(3) Re-extract and re-analyze the sample if none of the above are a problem.

10.8.5 The surrogate recovery data is summarized on the Surrogate Spike Recovery Form II.

10.9 Matrix Spike/Matrix Spike Duplicate Analysis

In order to evaluate the matrix effect of the sample on the analytical methodology, the USEPA has developed the standard mixes listed in Table 8 to be used for matrix spike and matrix spike duplicate analysis. These compounds are subject to change depending upon availability and suitability for use as matrix spikes.

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10.9.1 Analyze a matrix spike/matrix spike duplicate once each Case, or with every twenty (20) samples of similar concentration and/or similar sample matrix, whichever is greater.

10.9.2 Matrix spiking solutions are prepared by the Standards Chemist. The analytical protocol requires that a uniform amount of matrix spiking solution be added to the sample aliquots prior to extraction. Each method allows for optional dilution steps which must be accounted for when calculating percent recovery of the matrix spike and matrix spike duplicate sample.

TABLE 10-7: MATRIX SPIKING SOLUTIONS

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	

Pesticides		Volatiles	
Heptachlor	Lindane	Chlorobenzene	1,1-Dichloroethene
Aldrin	Endrin	Toluene	Trichloroethene
Dieldrin	4,4'-DDT	Benzene	

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

10.9.4 Calculate individual component recoveries of the matrix spike using the following equation.

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

Where:

SSR = Spike Sample Results

SR = Sample Result

SA = Spike Added from spiking mix

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10.9.5 Calculate the relative percent difference between the matrix spike and matrix spike duplicate. The relative percent differences (RPD) for each component are calculated using the following equation.

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

Where:

RPD = Relative Percent Difference

D_1 = First Sample Value

D_2 = Second Sample Value (duplicate)

10.9.6 The matrix spike (MS) results (concentrations) for non-spiked HSL compounds are reported on Form I (Organic Analysis Data Sheet) and the matrix spike percent recoveries are summarized on Form III (MS/MSD Recovery). The results for non-spiked HSL compounds in the matrix spike duplicate (MSD) analysis are reported on Form I (Organic Analysis Data Sheet) and the percent recovery and the relative percent difference are summarized on Form III (MS/MSD Recovery).

10.9.7 Quantitate pesticides/PCB'S using the external standard quantitation methods. Before performing any sample analysis, determine the retention time window for each pesticide/PCB listed compound and the surrogate spike compound dibutylchlorendate. These retention time windows are used to make tentative identification of pesticides/PCBs during sample analysis.

10.9.8 Prior to establishing retention time windows, the GC operating conditions (oven temperature and flow rate) are adjusted such that 4,4'-DDT has a retention time greater than or equal to 12 minutes on packed GC columns.

10.9.9 Establish retention time windows as follows:

(1) Make three injections of all single-component mixtures, multi-response pesticides/PCBs throughout the course of a 24-hour period.

(2) Verify the retention time shift for dibutylchlorendate in each standard. The retention time shift must be less than a 2 percent difference for packed columns (less than 0.3 percent for capillary column). If this criterion is not met, continue injecting replicate standards to meet criteria.

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10.9.10 Calculate the standard deviation of the three absolute retention times for each single component pesticide. For multiresponse pesticides/PCBs, choose one major peak from the envelope and calculate the standard deviation of the retention time for that peak. Plus or minus three times the standard deviation of the absolute retention times for each pesticides/PCB is used to establish the retention time window; however, experience weighs heavily in the interpretaton of chromatograms. For multiresponse pesticide/PCBs, utilize the retention time window but primarily rely on pattern recognition.

10.9.11 Calculate retention time windows for each pesticide/PCB on each GC column used at the beginning of the program and whenever a new GC column is installed.

10.10 Control Charts For Surrogate, Matrix, and Internal Standard Compounds

Data for all spiked standard recoveries is monitored by using control charts for accuracy and precision. Use of control charts also provides for long term trend analysis (Figure 10.10).

Data is reviewed in terms of both meeting contract required acceptance criteria, and Clayton's internal acceptance limits.

(1) A computerized system of producing control data is used.

(2) Data is input as it is produced and checked for acceptability.

(3) Clayton's acceptance criteria are evaluated and updated on a quarterly basis. A summary table for all spiked compounds is then produced with this new criteria and distributed for use (Figure 10.11).

10.11 Inter Intra-Laboratory QC Samples

Clayton participates in the U.S. Environmental Protection Agency (EPA) Water Pollution and Water Supply Performance Evaluation Study programs. Each program has two rounds per year and provides a method of spotting out-of-control analyses.

To supplement this program frequency, Clayton maintains its own intra-laboratory performance program. Quality assurance sample ampules are provided by the U.S. EPA and submitted on a monthly basis for each analyte type. Target compounds are varied from month to month.

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10.12 Data Review

All analytical data, calculations, standards preparation quantities, and quality control values will be generated and verified in the following manner:

10.12.1 The chemist or analyst makes the primary calculations, entering the results on the appropriate worksheets. No computations are discarded; the equations used and variables entered are retained on the lab benchsheets and a summary of the work is entered in the analyst's logbook.

10.12.2 All work is reviewed by a senior staff member in the department or by the PM. Equations are checked against procedures and contract protocol to determine accuracy. When programmable calculations or computer programs are used, a sample set of variables is checked manually to determine the validity of the program. Particular attention is paid to reasonableness of the data, significant figures, and trends, which may indicate the presence of a lab-induced contaminant.

10.12.3 All department-verified data is submitted to the QAO for review. He is given the summary worksheets, calculations, and supporting information. He will spot check approximately 10% of the calculations and results. He reviews the quality control data to be certain that the criteria have been met for acceptability.

10.12.4 Discrepancies discovered during the review process are reported to the analyst and to the PM. The analyst is responsible for correcting the errors and resubmitting the data. If a discrepancy is found, the entire batch of data in which it was submitted must be reviewed again.

10.12.5 When the data has passed the review of the QAO, it is submitted to the PA for entry into the case file. Data is not available for the case file until it has been approved according to this procedure.

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Signature:

APPENDIX C - INSTRUMENT LIST

LABORATORY INSTRUMENTATION
Southfield Facility

1.0 GAS CHROMATOGRAPHS/MASS SPECTROMETERS (GC/MS)

(S1A) Hewlett Packard 5987 Quadrapole-Type GC/MS System

- Capillary and Packed Column Capabilities
- Electron Impact/Chemical Ionization/Negative Chemical Ionization Source
- Scan Range 1 to 1,000 AMU
- Subambient Cooling
- HP 1000 Data System
- Combined Wiley/NBS Mass Spectral Libraries
- Winchester Disc Drive Data Storage With 132 Mbyte Capacity
- HP 7906 Hard Disc with 20 Mbyte Capacity
- Magnetic Tape (1600 bpi) Archival Storage
- 33-Position HP Autosampler
- Tekmar Liquid Sample Concentrator with Autosampler

(S1B) Hewlett Packard 5985B (5987 upgrade) Quadrapole-Type GC/MS System

- Capillary and Packed Column Capabilities
- Electron Impact/Chemical Ionization Source
- Scan Range 1 to 1,000 AMU
- Subambient Cooling
- HP 1000 Data System
- Combined Wiley/NBS Mass Spectral Libraries
- Winchester Disc Drive Data Storage with 132 Mbyte Capacity
- HP 7906 Hard Disc with 20 Mbyte Capacity
- Magnetic Tape (1600 bpi) Archival Storage
- Thermal Desorber/Cryrogenic Trap
- Tekmar Liquid Sample Concentrator with Autosampler

(S1C) Hewlett Packard 5985B (5987 upgrade) Quadrapole-Type GC/MS System

- Capillary and Packed Column Capabilities
- Electron Impact/Chemical Ionization Source
- Scan Range 1 to 1,000 AMU
- Subambient Cooling
- HP 1000 Data System
- Combined Wiley/NBS Mass Spectral Libraries
- Winchester Disc Drive Data Storage with 132 Mbyte Capacity
- HP 7906 Hard Disc with 20 Mbyte Capacity
- Magnetic Tape (1600 bpi) Archival Storage

2.0 GAS CHROMATOGRAPHS (GC)

(S2A) Hewlett Packard 5711 GC

- Dual Packed Column Capability
- Dual Flame Ionization Detectors (FID)
- Thermal Conductivity Detector (TCD)
- Photoionization Detector (PID)
- 33-Position HP Autosampler
- HP Model 3352B Data System

(S2B) Hewlett Packard 5730 GC

- Dual Packed Column Capability
- Dual Flame Ionization Detectors (FID)
- Electron Capture Detector (ECD)
- 33-Position HP Autosampler
- HP Model 3352B Data System

(S2C) Hewlett Packard 5710 GC

- Dual Packed Column Capability
- Hall Conductivity Detector (HCD)
- Sub-Ambient Cooling
- 60-Position Varian 8000 Autosampler
- Varian Model Vista 401 Data System

(S2D) Hewlett Packard Model 5790 GC

- Packed/Capillary (split/splitless) Column Capability
- Flame Ionization Detector (FID)
- Electron Capture Detector (ECD)
- 99-Position HP Autosampler
- HP Model 3392A Data System

(S2E) Hewlett Packard Model 5880 GC

- Packed Column Capability
- Dual Flame Ionization Detectors (FID)
- Thermionic Detector (NPD)
- Sub-Ambient Cooling
- 33-Position HP Autosampler
- HP Level IV Data System

(S2F) Hewlett Packard Model 5880 GC

- Packed/Capillary (split/splitless) Column Capability
- Dual Flame Ionization Detectors (FID)
- Sub-Ambient Cooling
- 33-Position HP Autosampler
- HP Level IV Data System

(S2G) Hewlett Packard Model 5880 GC

- Packed/Capillary (split/splitless) Column Capability
- Dual Flame Ionization Detectors (FID)
- Thermionic Detector (NPD)
- Sub-Ambient Cooling
- 99-Position HP Autosampler
- HP Level IV Data System

(S2H) Hewlett Packard Model 5890 GC

- Packed/Capillary (split/splitless) Column Capability
- Dual Flame Ionization Detectors (FID)
- Sub-Ambient Cooling
- 99-Position HP Autosampler
- HP Model 3392A Data System

(S2I) Hewlett Packard Model 5890 GC

- Packed/Capillary (split/splitless) Column Capability
- Dual Flame Ionization Detectors (FID)
- Sub-Ambient Cooling
- 99-Position HP Autosampler
- HP Model 3392A Data System

(S2J) Varian 3700 GC

- Dual Packed Capillary Column Capability
- Flame Ionization Detector (FID)
- Hall Conductivity Detector (HCD)
- Flame Photometric Detector (FPD)
- 60-Position Varian 8000 Autosampler
- Varian Vista 401 Data System

(S2K) Tracor 540 GC

- Dual Packed Column Capability
- Hall Conductivity Detector (HCD)
- 60-Position Varian Autosampler
- HP Model 3392A Data System

(S2L) Analytical Instrument Development (AID) Model 511 Portable GC

- Packed Column Capability
- Gas Sampling Loop
- Flame Ionization Detector (FID)
- Flame Photometric Detector (FPD)

(S2M) Analytical Instrument Development (AID) Model 511 Portable GC

- Packed Column Capability
- Gas Sampling Loop
- Flame Ionization Detector (FID)
- Flame Photometric Detector (FPD)
- Electron Capture Detector (ECD)

3.0 HIGH PRESSURE LIQUID CHROMATOGRAPHS (HPLC)

(S3A) Waters Automated System

- Waters Model 720 System Controller (gradient elution capacity)
- Waters Model 6000A Solvent Delivery System
- Waters Model 45 Solvent Delivery System
- Waters Model WISP 710B Autosampler 48-position
- Waters Model 730 Data Module
- Waters Model 440 (Dual Channel) Ultraviolet (UV) Detector
- Waters Model 420-AC Fluorescence Detector
- Waters RCM-100 Radial Compression Module
- Waters Z-Module™ Radial Compression Separation System
- Waters Model U6K Universal Injector

(S3B) Waters Manual System

- Waters Model 660 Solvent Programmer (gradient Elution Capability)
- Waters Model 6000A Solvent Delivery System
- Waters Model 45 Solvent Delivery System
- Waters RCM-100 Radial Compression Module
- Schoeffel Model SF770 Scanning Ultraviolet (UV) Detector
- Waters Model U6K Universal Injector
- Houston Instruments Omniscribe Recorder

4.0 ION CHROMATOGRAPH (IC)

(S4A) Dionex Model 12S IC

- Anion/Cation Capability
- Dual Channel Recorder

5.0 X-RAY DIFFRACTOMETERS (XRD)

(S5A) Rigaku Model D/MAX-IIV X-ray Diffractometer

- Constant Potential X-ray Generator
- Vertical Wide Angle Goniometer With Angular Range of -3 ° to 160 °2θ
- Scintillation Detector
- Copper Target

- Diffracted Beam Monochromator
- Sample Spinner
- 43-Position Autosampler
- Rigaku Model—Data Processing System

(S5B) Norelco Type 120-102-20 X-ray Diffractometer

- Constant Potential X-ray Generator
- Vertical Wide Angle Goniometer With Angular Range of -3 ° to 160 °2θ
- Copper Target
- Scintillation Detector
- Data Processor

6.0 ATOMIC ABSORPTION SPECTROPHOTOMETERS (AAS)

(S6A) Varian Model 975 Atomic Absorption/Emission Spectrophotometer

- GTA-95 Graphite Tube Atomizer with Programmable Autosampler
- Deuterium Arc Background Correction
- Dual Grating Monochromator
- Wide-Range Multi-Alkali Photomultiplier
- Twelve-Position Motorized Lamp-Turret
- In-Built Floppy Disc Memory Capable of Permanently Storing up to 100 Sets of Operating Parameters
- Mercury Cold Vapor Analyzer

(S6B) Perkin Elmer 3030 Atomic Absorption Spectrophotometer

- Deuterium Arc Background Correction
- Electrode Discharge Lamps (EDL)
- Graphite Tube Atomizer with Programmable Autosampler
- Dual Grating Monochromator
- Wide-Range Multi-Alkali Photomultiplier
- Arsenic/Selenium Hydride Generator

(S6C) Instrumentation Laboratory Model IL551 Video 1 Atomic Absorption/Emission Spectrophotometer

- Dual Grating Monochromator
- Extended Range Photomultiplier Tube
- Deuterium Arc Background Correction
- Graphics Display/Internal Data System
- Arsenic/Selenium Hydride Generator
- Mercury Cold Vapor Analyzer

7.0 ULTRAVIOLET/VISIBLE SPECTROPHOTOMETERS (UV/VIS)

(S7A) Perkin Elmer Model Lambda 3A Ultraviolet/Visible Spectrophotometer

(S7B) Bausch and Lomb Spectronic 20 Ultraviolet and Visible Spectrophotometer

(S7C) Bausch and Lomb Spectronic 20 Ultraviolet and Visible Spectrophotometer

8.0 SPECTROFLUOROMETER

(S8A) Farrand Optical Company, Model Mark I Scanning Spectrofluorometer

9.0 OPTICAL MICROSCOPES

(S9A) Olympus Series BH-P-2 Optical Microscope

- Polarized-Light
- Phase-Contrast
- Photomicrography
- Porton Reticle
- Walton/Beckett Graticle
- Berek Compensator

(S9B) Olympus Series BH-P-2 Optical Microscope

- Polarized-Light
- Phase-Contrast
- Photomicrography
- Chalkley Point Array
- Porton Reticle
- Berek Compensator

(S9C) Olympus Series BH-2 Optical Microscope

- Polarized-Light
- Phase-Contrast
- Photomicrography
- Chalkley Point Array
- Porton Reticle
- Berek Compensator

(S9D) Leitz Dialux Optical Microscope

- Polarized-Light
- Phase-Contrast
- Photomicrography

10.0 ELECTRON MICROSCOPES

(S10A) Cambridge Mark 2A Scanning Electron Microscope:

- Separate Recording and Viewing CRTs
- Custom Stage for Accommodating Large Samples
- Digital Equipment Corporation PDP-11 Microcomputer

- Energy-Dispersive Spectrometer Interface EEDS-II EG & G Ortec, with a Computer-Controlled Multi-Channel Spectrum Analyzer (MCA), a Full Color CRT for Data Display, Two Floppy Disk Drives for Storing Spectra
- Denton DBS02 Vacuum Evaporator
- Buehler Metallurgical Specimen Polisher
- Letter-Quality Printer for Generating Hard Data Copy
- Dot Matrix Printer for Reproducing Graphic Displays
- Low Temperature Oxygen Plasma Asher

(S10B) Phillips EM 400T Analytical Transmission Electron Microscope

- Selected Area Electron Diffraction (SAED)
- EG&G Ortec Energy Dispersive Spectrometer

11.0 ELECTROMETRIC EQUIPMENT

(S11A) Orion Research Model 701, pH and Ion Selective Electrode Meter

- Reference Electrodes
- Ion Selective Electrodes Including Ammonia, Chloride, Cyanide, Fluoride, and Fluoroborate Electrodes

(S11B) Sargent-Welch Model LS, pH Meter

(S11C) Sargent-Welch Model DR, pH Meter

(S11D) Hach Chemical Company, Turbidimeter, Model 21004

(S11E) Yellow Springs Instrument Company, Oxygen Meter, Model 54

(S11F) Simpson, Volt-ohm Milliamp Meter, Model 260

(S11G) Hach Chemical Company, Dissolved Solids Meter, Model 2300

12.0 ANALYTICAL BALANCES

(S12A) Cahn Electrobalance™ Model 26

(S12B) Mettler Model H51AR

(S12C) Sartorius Model 2442

(S12D) Mettler Model P1200N

(S12E) Mettler Model AC100

Clayton Environmental Consultants, Inc.

22345 Roethel Drive • Novi, Michigan 48050 • (313) 344-1770

December 4, 1986.

Mr. Matthew Jerue
E.C. JORDAN CO.
17515 West Nine Mile road
Suite 225
Southfield, MI 48075

Subject: Metamora Analytical Quality Assurance Project Plan (QAPP)

Dear Mr. Jerue:

As follow-up to our telephone conversation of November 21, the following provides additional information on performance data for the Metamora analytical program. This information should be used in conjunction with information previously submitted on October 24, 1986, (copy enclosed).

Total Hydrocarbons

Total hydrocarbons refers to a general screening technique commonly used in industrial hygiene. The general method reference is P&CAM 127 - NIOSH Manual of Analytical Methods. The charcoal tube is desorbed in carbon disulfide to extract the organic material. The CS_2 extract is then injected onto a gas chromatograph equipped with a flame ionization detector.

Analysis time is 30 minutes. The net response (total response less solvent response) is quantitated against the response of a hexane standard analyzed with the samples. The result, in hexane equivalents, is reported as "total hydrocarbons".

Instrument conditions, accuracy, and precision data are shown below. Since accuracy and precision data for a general screen is not applicable, target compounds pertinent to the Metamora site are referenced.

Instrument:	Hewlett-Packard 5790 GC
Column:	DB5, 60 meter capillary
Column Temperature:	50 °C for 7 minutes 5 °C /minute 100 ° for 13 minutes

Target Compound	Limit of Detection (micrograms)	Accuracy (%)	Variance
1,1-dichloroethane	1 ug	95	<10
methylene chloride	1 ug	95	<10
1,2-dichloroethane	1 ug	95	<10
toluene	1 ug	95	<10
benzene	1 ug	95	<10
trichloroethylene	1 ug	95	<10

Qualitative Organics

The qualitative analysis of organic compounds will be used if quantifiable results are obtained from the total hydrocarbon screening. The samples will be collected on Tenax and analyzed by thermal desorption/cryrogenic focusing/GC/MS.

Because GC/MS analysis will be used for qualitative purposes, accuracy and precision data would not be applicable.

Instrument conditions are listed below.

Instrument:	Hewlett Packard 5985 GC/MS quadrupole system
Column:	SE 54, 25 me er, capillary
Column Temperature:	30 °C/4 minutes 6 °C/minutes 300 °C/5 minutes

Target Compounds	Limit of Detection (micrograms)
1,1-dichloroethane	0.5
methylene chloride	0.5
1,2-dichloroethane	0.5
toluene	0.5
benzene	0.5
trichloroethylene	0.5

Hazardous Waste Characteristics

Soil and drum samples will be analyzed for EP Toxicity metals, pesticides/herbicides and PCB: Accuracy and precision data is provided in Attachment 1. Instrument and operating conditions are provided below.

EP Leachate Pesticides

Instrument:	Hewlett Packard Model 5790 with electron capture detector
Column:	1/5% SP2250/1.95% SP2401, packed glass, 1.8 meter
Column Temperature:	220 °C

EP Leachate Herbicides

Instrument:	Hewlett-Packard - Model 5790 with electron capture detector
Column:	DB-5, 30 meter Capillary
Column Temperature:	160 °C/2 min. 3.5 °C/min. 270 °C/6.5 min.

PCB

Instrument:	Hewlett-Packard Model 5790 with electron capture detector
Column:	S2100, packed 6 ft. glass
Column Temperature:	140 °C/2 min. 6 °C/min. 240 °C/9 min.

EP Leachate Metals

Analyte	Instrument
Arsenic	Varian 975 (Graphite Furnace)
Barium	P/E 3030 (Flame)
Cadmium	P/E 3030 (Flame)
Chromium	P/E 3030 (Flame)
Lead	P/E 3030 (Flame)
Mercury	P/E 2380 (Cold Vapor)
Selenium	Varian 975 (Graphite Furnace)
Silver	P/E 3030 (Flame)

It is a pleasure to be of assistance to you. Please call if you have any questions.

Sincerely,

Robert Lieckfield Jr., C.I.H.
Manager, Laboratory Services

RL:JS

NUMERICAL OBJECTIVES FOR ACCURACY, PRECISION

. . . . ENVIRONMENTAL SAMPLES . . . .

ANALYTE	MEDIA	ACCURACY AVERAGE	ACCURACY ACCEPTABLE 3s RANGE	PRECISION METHOD	PRECISION ACCEPTABLE DUP. DIFF.
INORGANICS					
Arsenic	liquid	94%	62% - 126%	11%	19%
	EP leachate	99%	58% - 140%	14%	28%
	soil	92%	63% - 120%	10%	31%
Barium	liquid	100%	77% - 122%	8%	12%
	EP leachate	100%	69% - 131%	10%	17%
	soil	97%	72% - 122%	8%	6%
Cadmium	liquid	100%	82% - 119%	6%	7%
	EP leachate	104%	79% - 130%	8%	10%
	soil	99%	86% - 112%	4%	7%
Chromium	liquid	99%	78% - 121%	7%	8%
	EP leachate	100%	75% - 125%	8%	12%
	soil	98%	68% - 128%	10%	6%
Copper	liquid	103%	88% - 117%	5%	6%
	EP leachate	104%	80% - 127%	8%	9%
	soil	97%	79% - 114%	6%	6%
Lead	liquid	101%	85% - 117%	5%	6%
	EP leachate	104%	79% - 128%	8%	12%
	soil	100%	85% - 114%	5%	4%
Mercury	liquid	98%	71% - 126%	9%	16%
	EP leachate	99%	72% - 126%	9%	17%
	soil	100%	73% - 126%	9%	13%
Selenium	liquid	98%	67% - 130%	10%	26%
	EP leachate	99%	64% - 134%	12%	28%
	soil	92%	40% - 144%	17%	30%
Silver	liquid	97%	74% - 120%	8%	10%
	EP leachate	99%	68% - 130%	10%	16%
	soil	95%	77% - 114%	6%	9%
Zinc	liquid	100%	77% - 123%	8%	11%
	EP leachate	106%	75% - 138%	10%	18%
	soil	97%	68% - 126%	10%	12%

ORGANICS

Endrin	liquid (*)	88%	30% - 147%	20%	37%
	EP leachate	98%	68% - 128%	10%	10%
	soil	90%	42% - 139%	24%	45%
Lindane	liquid (*)	80%	32% - 127%	16%	23%
	EP leachate	58%	1% - 116%	20%	16%
	soil	86%	46% - 127%	20%	50%
Methoxychlor	liquid	105%	52% - 158%	18%	12%
	EP leachate	105%	52% - 158%	18%	12%
	soil	105%	52% - 158%	18%	12%
Toxaphene	liquid (*)	84%	41% - 126%	14%	25%
	EP leachate	84%	41% - 126%	14%	25%
	soil	84%	41% - 126%	14%	25%
2,4-D	liquid	62%	1% - 150%	29%	55%
	EP leachate	62%	1% - 150%	29%	55%
	soil	62%	1% - 150%	29%	55%
2,4,5-TP	liquid	78%	1% - 159%	27%	72%
	EP leachate	78%	1% - 159%	27%	72%
	soil	78%	1% - 159%	27%	72%
PCB - 1016	liquid (*)	82%	50% - 114%	11%	20%
	soil	82%	50% - 114%	11%	20%
1221	liquid (*)	96%	15% - 178%	27%	49%
	soil	96%	15% - 178%	27%	49%
1232	liquid (*)	112%	10% - 215%	34%	36%
	soil	112%	10% - 215%	34%	36%
1242	liquid (*)	94%	39% - 150%	18%	24%
	soil	94%	39% - 150%	18%	24%
1248	liquid (*)	98%	38% - 158%	20%	32%
	soil	98%	38% - 158%	20%	32%
1254	liquid (*)	80%	29% - 131%	17%	28%
	soil	80%	29% - 131%	17%	28%
1260	liquid (*)	68%	8% - 127%	20%	21%
	soil	68%	8% - 127%	20%	21%

NOTE: (*) QC Acceptance Criteria found in EPA Method 608

APPENDIX D

PROCEDURES FOR THE 10S50 PORTABLE GAS CHROMATOGRAPH

PHOTOVAC 10S50
INSTRUCTION MANUAL

1.0 INTRODUCTION

This manual provides instruction for operation of the Photovac 10S50 and a protocol for field analysis of water and soil samples for volatile organic compounds. This manual is the product of a three week laboratory study conducted at the E.C. Jordan Company (JORDAN) Environmental Laboratory.

1.1 Objective

The objective of this manual is to provide instruction for the operation of the instrument so as to produce, to the extent possible, data which meets the data quality objectives for site screening of samples.

1.2 Background

Chemical data on groundwater and wastes at the Metamora site have been collected during previous studies. Based on this data, several target compounds have been identified:

- benzene
- toluene
- xylenes
- ethylbenzene
- trans-1,2-dichloroethane
- trichloroethylene (TCE)
- tetrachloroethylene (PCE)
- chloroform
- (1,3)&(1,4)-dichlorobenzene
- (1,1)dichloroethane
- (1,2)dichloroethane
- (1,2)dichloroethylene
- hexachlorobenzene
- methylene chloride
- styrene
- (1,2,4)-trichloroethane
- trichlorofluoromethane

2.0 MOBILIZATION AND SETUP

This section describes the materials needed and the procedure for setting the 10S50 up in the field.

2.1 List of Materials

The 10S50 requires additional support equipment for operation. Carrier gas flow is supplied by a tank of compressed zero-grade air, the volume of which depends on the flow rate and the period of use required. A regulator fitted with a 1/8 inch copper line with a male "quick-connect" fitting (supplied with the machine) are required for connection to the 10S50. A large crescent wrench will be needed for connection of the regulator to the gas cylinder. The 10S50 is equipped with a plotter which requires plotter paper and four colored pens; red, green, black, and blue. These items can be found at Radio Shack or an office supply company. Pen life is a function of level of use and mode of operation (see section 2.3.2.5) and typically last about 2 weeks. The following laboratory equipment is required for standard and sample preparation :

Item	Quantity	Use
Syringes		
1 ul	1	standard preparation
50 ul	2	sample/standard injection
200 ul	2	sample/standard injection
10 ml	2	sample/standard preparation
Needles		
20 gauge	20	for 10 ml syringe
Glassware		
Volumetric Flasks		
100 ml	2	standard/sample dilution
Erlenmeyer Flasks		
500 ml	2	waste/reagent water
VOA vials		
40 ml	200	standard/sample storage
bubble meter	2	gas flow calibration
stop watch	1	gas flow calibration
Miscellaneous		
kimwipes		
small	1 box	general cleaning
pens		
indelible	3	marking VOC vials
Snoop	1 bottle	bubble meter/leak detection
Laboratory Scale		
top loading	1	sample preparation

Standards
(GC PURITY) 1-2 ml each standard preparation

- benzene
- toluene
- xylenes
- ethylbenzene
- trans-1,2-dichloroethane
- trichloroethylene (TCE)
- tetrachloroethylene (PCE)
- chloroform
- (1,3)&(1,4)-dichlorobenzene
- (1,1)dichloroethane
- (1,2)dichloroethane
- (1,2)dichloroethylene
- hexachlorobenzene
- methylene chloride
- styrene
- (1,2,4)-trichloroethane
- trichlorofluoromethane

Additional columns should be kept on hand in an oven at 100 ±10 degrees Celsius with air flowing through them so that they are available for immediate use in case of column saturation. Required equipment:

- o large zero-grade gas cylinder
- o regulator
- o connectors and tubing
- o three columns
- o laboratory oven

2.2 Equipment Setup

2.2.1 Location. The site in which the 10S50 is to be setup for the duration of the project should be chosen carefully. The site should be located as far as possible away from any sources of organic vapor. Screening of the area, inside and out with a PI meter, taking into account daily and weekly fluctuations in activity should help in this decision. The building should have temperature regulation abilities (air conditioning/heating) as the 10S50 is very sensitive to temperature variations. Wide and/or rapid temperature changes could render the instrument unusable for all practical purposes. The interior of the building should be cleared of all possible sources of organic vapor. Any cleaning compounds, air deodorizers, gasoline cans, cars, chemicals or anything that has an odor should be removed and kept clear of the building. Access should be restricted if possible.

At the Metamora site, a separate trailer with temperature regulation abilities will be used to setup the 10S50.

2.2.2 Unpacking. After arrival at the site, the equipment should be carefully unpacked and checked for damage, particularly the glassware and the 10S50, so that if there are any problems, procedures to replace or repair them can be started immediately.

2.2.3 Carrier Gas Supply. The next step is to setup the gas flow systems. In transit, the columns have not had any gas flowing through them and most likely have become contaminated. The columns will have to be flushed out prior to use and this process should be started immediately. The gas cylinders for the 10S50 and the additional columns should be setup out of the way and secured so that they won't fall over. With the gas flow off, the regulators can be attached with a crescent wrench and checked for leaks. If a leak is suspected, applying a soap solution (e.g., Snoop) around the fittings and checking for bubbles will pinpoint leaks.

2.2.3.1 10S50 External Gas Supply Connection.

Gas flow to the column in the 10S50 should be established first.

- Insure that the valve on the regulator is off.
- Connect the copper carrier line to the regulator.
- Open the valve on the gas cylinder and check the pressure in the cylinder on the gauge. This pressure should be between 500 and 3000 psi. If the pressure is below 500 the cylinder will have to be replaced. - Insert the "quick connect" fitting on the copper carrier line into the EXTERNAL CARRIER IN port in the top right hand corner of the 10S50.
- Slowly open the regulator valve until the DELIVERY gauge in the top left hand corner of the 10S50 reads 40 psi. The pressure gauge on the regulator should also read 40 psi. If the gauges don't agree rely on the 10S50's reading. NOTE : A DELIVERY PRESSURE GREATER THAN 40 PSI COULD DAMAGE THE INSTRUMENT.

The column in the instrument now has gas flowing through it. Connect the bubble flow meter to the DETECTOR OUT port and check that this flow does not exceed 60 ml/min (see section 2.3.1 - Setting the Gas Flows). If the instrument is going to be used immediately, you may want to use a fairly high flow rate to purge the column. Generally, the column will have to purge overnight before it is usable. If so, the flow rate should be adjusted to 10 ml/min or less to conserve carrier gas.

2.2.3.2 Backup Columns Gas Supply.

Gas flow for the backup columns is established in a similar manner. Keep in mind that all flow and pressure regulation is done with the pressure regulator on the cylinder and excessive pressure or gas flow rates could damage the columns. Backup column configuration is described in section 7.0.

- Insure that the valve on the regulator is off.
- Connect the carrier line to the regulator.

- Open the valve on the gas cylinder and check the pressure in the cylinder on the gauge. This pressure should be between 500 and 3000 psi. If the pressure is below 500 the cylinder will have to be replaced. Insert the carrier line into the the end of the first column.

- Insert the bubble flow meter into the end of the last column.

- Slowly open the regulator valve and check the flow rate with the bubble meter. Adjust the flow rate to 20 - 40 ml/min.

2.3 Configuring the System

2.3.1 Setting the Gas Flow Rates. The gas flow rate through the instruments column directly affects the retention time of the compounds. In order to identify the compounds for which the instrument has been setup, the gas flow rate must remain constant throughout the course of the project. Consequently at the beginning of each day and throughout the day's run of samples the gas flow rates should be checked via review of standard's retention times. Should retention times vary more than ±5 seconds, the flow rate should be checked with a bubble flow meter. Three flow controls must be adjusted:

- auxiliary valve (backflush outflow)
- VALVE 2 (resting inflow)
- VALVE 1 (sampling inflow)

Proceed as follows:

- Connect the end of the tube on the bubble flow meter to the DETECTOR OUT port.

- Squeeze the rubber bulb on the bottom of the flow meter until some of the soap solution comes up over the gas inlet (CAUTION: Bubble solution is extremely hazardous to the 10S501). A bubble should form and begin to rise in the meter. If no bubble appears and begins to rise you have no air flow. Try turning the YELLOW flow knob on the left side of the instrument counter clock-wise. If you still are not getting a bubble then you need to check the External Carrier Supply setup (see section 2.2.3.1).

- Use the stop watch to time the bubble up the meter. You will be reading milliliters of flow per unit time.

- Adjust the flow by turning the YELLOW flow knob clock-wise to decrease flow and counter clock-wise to increase flow. Set the flow to 10 ml/min.

- Then connect the tube from the bubble flow meter to the flow control valve attached to the AUXILIARY OUT port and adjust this flow to 10 ml/min by screwing the knob on the valve in to decrease flow and out to increase flow.

- Reconnect the bubble meter to the DETECTOR OUT port and check this flow. These two flows are interactive so continue this process until both flows are 10 ml/min.

The third flow to be adjusted has to be done during the analysis. This flow is the flow through the backflush column. Before this can be done the computer has to be configured. If you are unfamiliar with the operation of the computer you may want to go on to section 2.3.2 and set this flow later. Set the EVENTS as follows:

EVENT 1 : START 8.0 STOP 10.0
EVENT 2 : START 0.0 STOP 0.0
EVENT 3 : START 10.0 STOP 25.0
EVENT 4 : START 0.0 STOP 0.0
EVENT 5 : START 10.0 STOP 25.0

This setup will allow you about 40 seconds to set the backflush flow.

- Connect the bubble meter to the DETECTOR OUT port.

- Start a sample run.

- After the pump stops, there will be a surge of air and the bubble will accelerate up the column. After about 2 seconds the flow will slow and stabilize. You now have 40 seconds to adjust this flow to 10 ml/min with the RED flow control knob.

- After about 40 seconds have passed, you will have to stop the run and start over again. This usually takes several starts and stops so you should set the CHART to the "OFF" mode (see section 2.3.2.4) to conserve paper and pens.

Allow the flows to stabilize for about 20 minutes and then recheck them.

2.3.2 Setting Up the Computer. With the gas flowing and the column purged of contaminants the 10350 is now ready to be configured for operation.

2.3.2.1 Power Source

The 10350 can be operated on it's own internal rechargeable battery, by an external 60 Hz, 115 volt A.C. source, or by an external 12 VDC source such as a car battery. To use an external source, simply plug in the power cord to the appropriate receptacle on the left side of the instrument. If the machine is switched on with no power cord plugged in it will automatically work off the battery. To recharge the battery, simply leave the instrument plugged in to the external source. The instrument can be charged while the machine is off unless the batteries are exceptionally low, in which case the instrument should be charged while it is on. The internal battery will operate for about 10 hours between charges depending on the level of use.

2.3.2.2 Starting the 10S50

To start the 10S50 press the ON button. The display will read - LAMP NOT READY PLEASE WAIT. After about three minutes the lamp should come on and display will read - READY ENTER COMMAND. If the lamp does not come on it may have to be replaced.

2.3.2.3 Setting the Valves

In manual operation, the valves are used to provide a signal for injection and to turn the backflush on. The valves are set by the EVENT key. To obtain a listing, press the TEST key and then RETURN. The printer will list the date and the time and two lines of information on the source and the events setup. The events and their settings which should look like this:

EVENT	1	8.0	10.0
EVENT	2	0.0	0.0
EVENT	3	10.0	25.0
EVENT	4	0.0	0.0
EVENT	5	10.0	25.0

To change any of the EVENT settings press the EVENT key when the machine is in ready mode, The display will respond by asking you which event you are concerned with. Enter the number of the event that you want to change and press ENTER. The computer will then ask you if you want LEVEL or PULSE operation. The up and down arrows can be used to toggle between LEVEL and PULSE. Choose LEVEL mode and press ENTER. The ON and OFF levels can then be changed by entering the correct number and pressing ENTER. Anytime the information is already correct the setting can be retained by pressing ENTER. This allows you to view any setting in the computer at anytime without interfering with operation.

2.3.2.4 Setting the Chart

The information that is printed by the plotter after a run can be outputted in four different formats. The formats are:

- CHART OFF - No plot is printed and only the basic information is printed;
- CHART ON - The plot is printed along with the basic information.
- CHART WITH BASELINE - Same as CHART ON except the computer draws the baseline that it used for integration on the plot.
- CHART WITH SETUP - Same as CHART WITH BASELINE except the whole setup is also printed.

The different modes are selected by pressing CHART and then using the arrow keys to switch between modes. It is advisable to use the CHART WITH SETUP mode initially or if conditions are changing frequently. After things have settled down you may want to convert to the CHART WITH BASELINE mode to save on ink, paper and time. After the chart mode has been selected, unless you have chosen the CHART OFF mode, the

display will ask you for the chart speed. This should be set to 1 cm/min. The speed is changed by the arrow keys and set by pressing ENTER.

2.3.2.5 Setting the Plotter Delay and Cycle Time

The CYCLE key is used to set the time when the plotter will turn on and when the analytical run will stop. The plotter delay is generally activated when the analysis starts and the cycle time is set to be slightly longer then the the retention time of the last eluting compound. The plotter delay and the cycle time can be checked by pressing TEST and then ENTER. The setup will be printed out on the plotter. To change the settings press the CYCLE key. The computer will ask you for the plotter delay. If the number on the second line is correct press enter. If not, enter the correct value from the computer keyboard and press ENTER. The computer will then ask you for the analysis time and display some number on the second line. If this number is correct press ENTER. If not, enter the correct number with the keyboard and press ENTER. The computer will then ask you for the cycle time in minutes. The number on the second line should be "0.0". If not, enter a "0" with the keyboard and press ENTER. The computer will then inform you that the cycle function has been disabled and then it will return to ready mode.

2.3.2.6 Setting the Gain

The gain amplifies the signal from the machine by the number of times indicated. In most cases, the gain should be set to 200X. This will provide a dynamic range for PID-appropriate compounds of approximately 5-100 ug/l. Samples with higher concentrations must be diluted into this operating range.

3.0 SAMPLE PREPARATION FOR ANALYSIS

The samples, standards and the blanks should all be prepared for analysis in the same way. All preparations are done in a 40 ml VOA vial. All samples and standards should be stored with the bottle standing on its cap (septum side down) whenever possible to minimize potential volatilization through the cap.

3.1 Liquid Sample Preparation

The sample should be totally filled with liquid with the cap on tightly. The first step is to generate a headspace for analysis. You will need the 10 ml syringe and two clean 20 gauge needles. Rinse the needles and the syringe several times with clean reagent water. Wipe the outside of the needle with a clean kimwipe.

- Insert the needle of the 10 ml syringe through the septum of the VOA vial. Draw the needle back about two or three mls and hold the vacuum.

- Insert a needle into the septum to vent the vacuum generated and allow the syringe to fill.

- Withdraw 10 ml from the vial. Try to maintain a positive pressure on the vial during the extraction process so that air flow through the vent needle is into the vial at all times. As soon as the syringe is full (10 ml) quickly withdraw the vent needle and the syringe and immediately turn the vial over.

All standards, blanks and liquid samples are to be prepared in this way. The key to good results with the 10S50 is cleanliness and consistency.

3.2 Soil Sample Analysis

Soil samples are prepared by placing 10 g of soil in a 40 ml VOA vial and then putting water in until there is a 10 ml headspace left. The best method for doing this is to make up a reference vial with which to compare. To make the reference vial, completely fill a VOC vial with water and use the 10 ml syringe to draw out 10 ml. This vial will then have a 10 ml headspace and can be used to judge how much water to add to the soil already in the vial to leave a 10 ml headspace.

3.3 Drawing a Sample

This procedure is common to both solid and liquid samples. Before a headspace sample is withdrawn:

- The sample should be shaken for 1 minute.
- Then allow the sample to stand for 1 minute with the septum side down.
- Insert the 250 ul syringe through the septum of the vial and purge the syringe with headspace from the sample by filling and discharging the syringe at least three times. Then draw 100 ul of sample into the syringe.

Make sure that the syringe does not draw any liquid or solids into it; only headspace (air sample) may be injected to the 10S50. The sample is now ready for injection into the 10S50.

4.0 INSTRUMENT INITIALIZATION AND CALIBRATION

With the gas flowing through the system and the computer configured, the machine is now ready for calibration. This section will explain how to make a run on the instrument, how to establish a baseline, and how to calibrate the instrument.

4.1 To Start an Analysis

An analysis run is started by pressing the START/STOP button. The display will then ask you whether you want to select the sample (SAMPLE) inlet or the calibration (CAL) inlet. The arrow keys will allow you to toggle between the two modes. Select SAMPLE mode and press return. The plotter will immediately print "START" and a dotted horizontal line and then stop.

At eight seconds you will hear a buzzing sound that will last for two seconds. The END of the buzzing signals when the injection should be made. At the end of the buzzing the plot will start and run for the length of the analysis time. If you want to stop the plot before the analysis time is up, press the STOP button.

4.2 Establishing Background

To distinguish actual signals from background, a baseline must first be established. This is accomplished by running a series of column, syringe and field blanks. These runs should be made at a gain of 200x or the MAXIMUM gain at which the instrument is to be used.

4.2.1 Column Blanks

A column blank will indicate how clean the gas flow path is. A column blank is run by starting an analytical run and making no injection. The plot should be flat and straight with very few small peaks in it. If the plot is "noisy" then there are a number of possibilities. The most likely problem is that the column is contaminated. Another possibility is that the septum is contaminated or leaking. If the septum is known to be old it should be the first thing to be changed since it can be done easily and quickly. If the column blank is still too noisy, the column has to be purged. Depending on time constraints, you can purge the column in the machine or replace the column with one of the backups.

4.2.2 Syringe Blanks

Once a satisfactory baseline has been established (based on column blank results) the next step is to try a syringe blank.
To analyze a syringe blank:

- Purge the 250 ul syringe with ambient air by pumping the plunger several times.
- Draw 100 ul of ambient air into the syringe.
- Insert the syringe into MANUAL INJECTION port 1 located in the bottom left hand corner of the instrument until the needle rests on the septum.
- Initiate an analysis run.
- Immediately after the buzzer stops, plunge the needle through the septum and then make the injection. This motion should be smooth and snappy but, most importantly, it should be done the same way every time whether the the injection is a sample, a standard, or a blank.
- Repeat the procedure until the baseline is acceptable.

If you have trouble getting a good baseline, rinse the syringe with clean reagent water. Be very careful about getting all the water out of the syringe before making another injection. Injection of liquid into the 10350 at anytime could damage the instrument.

4.2.3 Water Blank

The volatile organic analyte (VOA) content of the water being used and the sample vials should be checked regularly. To prepare a water blank, fill a 40 ml VOA vial with the reagent water being used. Then prepare the blank the same way the samples and the standards are prepared (see section 3.1). This is the true background since it is also a combination of the first two blanks. Any large background signals should be noted. Under normal circumstances this blank should be run after each calibration.

4.3 Calibration

4.3.1 Calibration

Calibration of the machine involves both retention time and response factor determination for the expected operating range.

- Prepare a calibration standard.
- Prepare the standard for injection.
- Set the gain to 200X.
- Run the standard.

5.0 SAMPLE ANALYSIS

The machine is now ready to start analyzing samples. The data output is related to the nearest calibration made, either before or after the run. Consequently the run sequence is very important. An analysis log must be maintained.

5.1 Sample Handling

Samples should be collected and handled in the same manner as for standard laboratory analysis (GC/MS). In field screening, close attention should be paid to the portable total organic vapor analyzer readings (e.g., TIP). These readings will be used to screen the samples before analysis to identify samples with high concentration. A high concentration sample could easily contaminate the system; a situation which is very costly in terms of time. The analyst should ask the sampling personnel to note samples that they suspect to be highly contaminated. These readings are taken directly over the sample (water or soil) before it is sealed and are very helpful in avoiding analytical problems.

5.1.1 Sample Holding Times. Under normal circumstances the samples will be analyzed the day that they are taken. In any event the operator should record the date and time of when the sample was taken and when the sample was analyzed.

5.2 Sample Screening

The samples should be analyzed in order of increasing concentration. This ordering is based on the notes the sampling personnel take and the recorded TIP readings. If it is suspected that the contaminant concentration is

high the 10 ml that is withdrawn during preparation of the headspace can be diluted and run at a low gain to determine how much dilution is required to get the response "on scale".

6.0 STANDARD PREPARATION

A concentrated standard solution has been prepared in the laboratory and is labeled primary standard. To prepare this standard solution:

- Rinse a clean 100 ml volumetric flask with the water to be used and then fill it with water. A VOA vial can then be filled for use as the daily field blank. Refill the flask to 100 ml.
- Clean the 1 ul syringe thoroughly with clean reagent water and wipe the needle with a kimwipe.
- Withdraw 1 ul of the concentrated standard. Insert the needle into the flask such that the tip is below the water line and then inject the standard.
- Cap the flask immediately and mix it well.
- Fill VOA vials and store them upside down on ice.

7.0 BACKUP COLUMN SETUP

Frequently, in the course of analyzing samples of unknown concentration, one will slip past even the best screening techniques that is of very high concentration and contaminate the column. The only recourse when this happens is to purge the column with air, preferably at an elevated temperature. To avoid unnecessary delays, backup columns are kept on hand with air flowing through them. The columns should be hooked up in series, connected to the gas cylinder (see section 2.2.3.2) and the columns themselves should be inside the oven. When a column is replaced the remaining backup columns should be first in the series, and the contaminated column should be placed last.

FIELD SCREENING PROCEDURE
FOR VOLATILE ORGANIC COMPOUNDS IN
WATER AND SOIL/SEDIMENT SAMPLES

The following protocol establishes procedures to assure the generation of high quality data from the Photovac Model 10S50 gas chromotograph. This protocol has been utilized previously and has shown that the procedures described are capable of detecting and quantifying the target compounds at the 5 to 100 part per billion range. However, because the instrument utilizes a chromatographic column at ambient temperature, retention time windows and relative response factors must be determined in the field and routinely checked and adjusted throughout the duration of the project.

If, during the course of the project, additional compounds are observed on the instrument output (in addition to the listed target compounds), the attached protocol may be expanded to include calibration of the instrument for those compounds.

1.0 INTRODUCTION

This procedure establishes a method for field screening of soil/sediment and water samples for the target volatile organic compounds listed below using the Photovac model 10S50 gas chromatograph (10S50).

Target Compounds

- trans-1,2-dichloroethene (tDCE)
- benzene
- trichloroethene (TCE)
- toluene
- tetrachloroethene (PCE)
- ethylbenzene
- ortho-xylene (o-xylene)

These compounds have been selected based upon their predominant occurrence in previous sample analyses and their ability to produce characteristic responses on the 10S50.

1.1 Background

The 10S50 is a programmable, portable gas chromatograph capable of detecting a variety of volatile organic compounds in air samples. Other media samples (water, soils) may be screened inferentially by injecting a sample of the headspace in the sample container. Onsite screening of samples being collected during a site investigation can provide valuable information for direction of the detailed site characterization program. To assure the integrity of the data being generated, E.C. Jordan Co. (JORDAN) has developed a Quality Assurance Project Plan (QAPP). This protocol supplements the QAPP specifically for this operation.

1.2 Objective

The objective of this protocol is to establish procedures to assure the generation of high quality data from the 10S50. The quality assurance measures to control the use of that data in achieving project objectives are outlined in the QAPP.

It must be recognized that this protocol is designed to generate data for 1) assisting in selecting the vertical location of well screens and 2) selecting samples for further chemical analysis. Other project objectives will require different protocols.

2.0 SYSTEM SETUP

This protocol has been developed for the Photovac model 10S50 GC/PID system configured (i.e., the choice of column length and materials as well as operating parameters) specifically for the target parameters and project needs of the Metamora Landfill Site investigation. Details of general system operation are presented in the PHOTOVAC 10S50 Operator's Manual (Appendix A).

2.1 Carrier Gas

The carrier gas quality must be "zero-grade" air or better. Air flow should be adjusted to 10 ml/min using a bubble flowmeter. The flows should be allowed to stabilize for twenty minutes and then rechecked. The air flow should be adjusted at the beginning of each analytical event and also when compound retention time variation is indicative of flow rate deviation (see Section 10.4).

2.2 Computer Setup

2.2.1 Events. The event control selects the valve timing for sample introduction and backflushing. The events should be configured as follows:

EVENT 1	8.0	10.0	start/stop sample pump
EVENT 2	0.0	0.0	start/stop calibrant gas flow
EVENT 3	10.0	25.0	open/close valves 2 & 3
EVENT 4	0.0	0.0	open/close valves 1 & 4
EVENT 5	10.0	25.0	open/close valve 5

2.2.2 Chart. The chart control determines the format for the printout of results. There are four modes of operation:

1. CHART OFF
2. CHART ON
3. CHART WITH BASELINE
4. CHART WITH SETUP.

Mode 4 prints out the run results with basic setup information. This mode is useful when first setting up or if the configuration is changing frequently. After the instrument has stabilized (see Section 5.2), mode 3 is satisfactory. The chart speed should be set to 1 cm/min.

2.2.3 Gain Setting. The gain is set at 200. This setting encompasses a dynamic range of approximately 5-100 ug/L for the target volatile compounds.

2.2.4 Sensitivity Setting. The sensitivity determines the change in slope that has to occur to define the edges of the peak. The up and down slope change settings should be set at 5. The peak width (PW) should be set to 5 also.

2.2.5 Area Setting. The area is the minimum number of area counts that the computer will consider for integration and is set at 100 mVS.

2.2.6 Cycle. The cycle control sets the time when the analysis will start and stop. The analysis should start when or soon after the sample is injected and should end shortly after the last eluting compound of interest. For this task the plotter is activated at 10 seconds and is terminated at 500 seconds.

3.0 CALIBRATION

3.1 Establishing a Baseline

The baseline is set at 10 percent of full scale following column equalization (e.g. acceptable column blanks, see Section 5.2).

3.2 Initial Calibration

Initial calibration is a check of the dynamic range in which the instrument is expected to perform for each compound. The initial calibration will consist of a four-point curve generated from standards of 5, 25, 50 and 100 ug/L of each target compound. The standards for initial calibration are prepared fresh before use from a concentrated stock solution prepared in the laboratory (see Section 9.0). The criteria established in Section 10 must be met.

Initial calibration is performed at the beginning of each field event and must be repeated if the instrument fails a continuing calibration standard injection (see Section 3.3) or if the instrument is moved such that initial set-up is again required. If the instrument does not meet the specifications it should be thoroughly checked for any problems. Any problems found and corrected should be fully documented and the calibration rerun until specifications are met.

3.3 Continuing Calibration

Continuing calibration checks are performed periodically to ensure that the machine is still operating within specifications. Continuing calibration is performed with a single standard that is made from a concentrated laboratory stock solution. The standard contains each of the compounds of interest at 50 ug/L. The retention time and specific responses for each target compound must be within the quality control criteria presented in Section 10.

If the compound identification (based upon retention time) fail the criteria, corrective measures are to be instituted and documented. Initial calibration is then repeated until the criteria presented in Section 10 are met. A continuing calibration will be performed at the start of each sequence of

sample runs, at least after every ten samples run (ten percent), and after every noncompliant Matrix Spike/Matrix Spike Duplicate (MS/MSD) (see Section 4). Noncompliant MS/MSD followed by a compliant continuing calibration standard result will be interpreted as documentation of matrix interference for the particular sample in question and no further QA/QC action is required.

4.0 ACCURACY AND PRECISION

4.1 Matrix Effects

The chemical/physical character of some samples may mask some compounds from detection via a particular analysis technique. To determine if the the sample matrix is interfering with compound identification, matrix spike (MS) and matrix spike duplicate (MSD) samples will be run at the five percent level (i.e. every twenty samples). This involves injecting a known standard into duplicates of a triplicate sample aliquot. The concentration of matrix spike will be 50 ug/L for water and 50 ug/kg for soil of each target compound. Refer to reagents (Section 9.3), for details of MS/MSD preparation.

4.2 Accuracy

The percent recovery of the MS/MSD is a measure of the accuracy of the method with respect to the sample matrix and the analysis technique. The percent recovery is calculated as follows:

$$\%R = \frac{Css - Cs}{Ck} \times 100$$

%R = percent recovery;
Ck = known concentration of standard injected into the sample;
Css = concentration in the spiked sample;
Cs = concentration in the unspiked sample.

Recovery criteria are presented in Section 10.3.

4.3 Precision

The precision of the method is measured by determining coefficient of variation of the percent recoveries of the MS/MSD as follows:

$$CV = \frac{S}{M} \times 100$$

Where S = the standard deviation of the duplicate percent recoveries.
M = the mean of the duplicate percent recoveries.

5.0 BLANKS

Blanks are run to ensure that residual contamination from a previous analysis is not carried over to the next sample and that the materials used in the analysis procedure are not themselves contaminated with any of the compounds of concern. Blank sample results for target compounds must be well below the PQL (i.e., 1 ug/L or less) to imply valid analyses. Identification of target

compounds in blanks is an indication of contamination requiring corrective action. The source of contamination must be identified and eliminated before continuing the analytical program. All contamination information must be fully documented in the analytical event log.

5.1 Reagent Water Blank

The reagent water blank checks for contamination in the water and glassware being used for sample and standard preparation. The reagent water blank is prepared by placing the water being used into one of the sample vials and analyzing in the same manner as a sample. Reagent water blanks should be run after every initial or continuing calibration.

5.2 Column Blanks

Column blanks are analyzed to determine if the instrument contains any contamination that may interfere with the analysis. Column blanks are analyzed by starting a sample run with no injection. Column blanks are analyzed at the beginning of the day to establish the baseline. They can also be run in conjunction with syringe blanks (see Section 5.3) to see if the contamination is in the syringe or in the system. Generally, contamination in column blanks are the result of a contaminated column or septum or contaminated carrier gas. The first two items can be replaced in the order of increasing difficulty (first the septum and then the column) to determine if they may be the source of the problem. Unacceptable column blanks are indicated by integrated output (mVS) for the blank runs following valving peaks (i.e., first 20 seconds of recorder output).

5.3 Syringe Blanks

Syringe blanks are analyzed to determine if any residual contamination from a previous injection still exists in the syringe or in the instrument. A syringe blank is prepared by purging the syringe with ambient air several times and then injecting ambient air at the same volume as the samples being run. Syringe blanks must be run between every sample or standard.

6.0 SAMPLE PREPARATION

The samples and the standards will both be prepared for analysis according to the procedure described below. The samples will be collected and preserved according to the protocol outlined in the QAPP for VOA samples. All relevant data must be recorded.

6.1 Water Sample Preparation (Developed from USEPA Region I Protocol)

Water samples are prepared by extracting 10 ml of fluid from a completely full sample vial with a 10 ml gas-tight syringe. The extraction is done through the teflon septum with a vent needle inserted to relieve the vacuum generated. This procedure creates a headspace in the sample vial for equilibration of the volatile organics present. The extraction should be performed so that flow through the vent needle is always into the vial. This can be done by not inserting the vent needle into the septum until after a negative pressure has been applied to the vial with the extraction needle of the gas-tight syringe

and then drawing the liquid out slowly and removing the vent needle, immediately before the fluid extraction is complete. The sample is then shaken for 1 minute and allowed to stand for 1 minute with the septum side down. A headspace sample is then drawn for injection by inserting a 250 ul syringe through the septum and flushing the syringe several times with the headspace in the vial and then drawing 100 µl sample into the syringe. Note that preparing samples in a contaminated atmosphere will lead to sample and blank contamination.

6.2 Soil/Sediment Sample Preparation (Developed from Personal Communication with Dr. T.F. Spittler, USEPA Region I)

The soil/sediment samples are prepared by placing approximately 10 grams of the soil into a sample vial and then filling the vial with water until a 10 ml ± 1 ml headspace remains. The weight of soil/sediment added should be measured to the nearest 0.1 g and water added as quickly as possible to avoid loss of volatiles. The sample will then be shaken for at least one minute or until the soil is evenly dispersed throughout the water. Then the sample will be allowed to sit with the septum side down for 1 minute. The headspace will be sampled in the same manner as water (see Section 6.1).

7.0 ANALYSIS RUN SEQUENCE

In order to ensure that high quality data are produced a specific run sequence must be followed. The outline below is an absolute minimum of what must be done. The frequency of continuing calibrations and MS/MSD runs should be increased if project schedule permits. The run sequence is outlined below: (Note that syringe blanks (Section 5.3) are to be run between each injection).

1. Column blank to establish the baseline.
2. Initial calibration.
3. Continuing calibration check standard.
4. Water blank.
5. 10 samples.
6. Continuing calibration check standard.
7. Water blank.
8. 10 samples (this involves 8 samples + MS/MSD at end).
9. Repeat steps 3-8.
10. The next-to-last samples run are a MS/MSD.
11. Finish the run sequence with a continuing calibration check standard.

8.0 DATA MANAGEMENT

8.1 Initial Calibration

Initial calibration data are subjected to a linear regression analysis using integrated areas (mVS) versus concentration (ug/L) of target compounds. The criteria established in Section 10.1 must be met for initial calibration. Retention times (sec) are obtained for qualitative (compound identification) criteria. If a sample mVS value exceeds the highest mVS value obtained during initial calibration, the sample must be diluted sufficiently to achieve a value within the calibrated range. Note that the PQL rises proportionally with the dilution factor.

8.2 Continuing Calibration

Continuing calibration check standard data are compared with initial calibration data as an indicator of continuing sensitivity (Section 10.2) and maintenance of qualitative criteria (Section 10.4).

8.3 Sample Results

The target compounds elute from the GC column with the approximate retention times given below at 10 cc/minute carrier air flow:

Compound	Retention Time (sec).
tDCE	(To be completed during initial calibration)
benzene	
TCE	
toluene	
PCE	
ethylbenzene	
o-xylene	

Water results are calculated by the following formula:

a) $$ug/L = \frac{mVS}{RF}$$

where mVS = integrator output at appropriate retention time
RF = response factor in mVS per ug/L (slope for linear regression of initial calibration for each of the target compounds)

Soil results are estimated by the following formula:

b) $$ug/kg\ soil = \frac{ug/kg \times 30}{wt.\ soil\ (grams)}$$

where the ug/kg is derived from formula (a) above

9.0 PREPARATION OF STANDARDS

9.1 Primary Standards

Primary standards @ 50 mg/L are prepared in Nanograde methanol as follows:

To 100 ml of Nanograde methanol (MeOH) the following volumes of pure reference standards are added:

Compound	uL/100 ml MeOH
tDCE	4.0
Benzene	5.7
TCE	3.4
toluene	5.8
PCE	3.1
ethylbenzene	5.8
o-xylene	5.7

9.2 Calibration Standards

The primary standard solution (See Section 9.1) is added to 100 mL aliquots of organic-free water as follows to provide working standards:

Per 100 m Water (ug/L)	Target Compounds (ug/L)
10	5
50	25
*100	50
200	100

*Also continuing calibration standard

Calibration standards are prepared fresh daily.

9.3 Matrix Spike

30 ug/L of primary standard (Section 9.1) is added to the sample immediately following withdrawal of liquid to provide headspace.

10.0 QUALITY CONTROL CRITERIA

10.1 Initial Calibration Limits

Compound	Response Factor
tDCE	(To be completed following initial calibration)
Benzene	
TCE	
toluene	
PCE	
ethylbenzene	
o-xylene	

10.2 Continuing Calibration Limits

Compound	Recorder Output (mVS)
tDCE	(To be completed following initial calibration)
benzene	
TCE	
toluene	
PCE	
ethylbenzene	
o-xylene	

10.3 MS/MSD

Acceptance limits for spike recovery: 100 ± 25%

10.4 Qualitative Criteria for Compound Identification

Retention time of last calibration standard for each compound ± 5 seconds.