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French Limited Site
Crosby, Texas

Work Plan - Volume I
Project Activity & Sampling Plan

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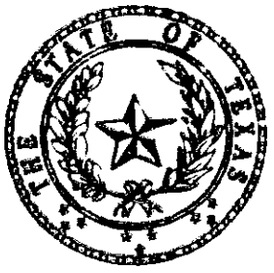

Texas Department of Water Resources

LOCKWOOD, ANDREWS & NEWNAM, INC.

In Asscciation with:

ENVIRONMENTAL SCIENCE AND ENGINEERING, INC.

HARDING LAWSON ASSOCIATES

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WORK PLAN FOR

FRENCH LIMITED SITE

008077

VOLUME I

PROJECT ACTIVITY AND SAMPLING PLAN

Prepared in Cooperation

with the

Texas Department of Water Resources

and the

U.S. Environmental Protection Agency

008077

VOLUME I

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This is Volume I of a four-volume work plan presented to the Texas Department of Water Resources in partial fulfillment of contract requirements on the French Limited Site Studies. The four volumes are as follows:

I. Project Activity and Sampling Plan

II. Project Safety Plan

III. Chain of Custody Plan

IV. Quality Assurance Plan

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VOLUME I

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1.0 SUMMARY

The French Limited Site is an abandoned waste impoundment on a 22.5-acre tract near Crosby, Texas. An unlined disposal pit of approximately 12 acres in size is located on the site. This pit was used to dispose of an estimated 600,000 barrels of industrial wastes from nearby petrochemical industries.

On January 17, 1983, the Texas Department of Water Resources entered into a contract for professional engineering services with Lockwood, Andrews & Newnam, Inc., of Houston, Texas. Associated in this work are Environmental Science and Engineering, Gainesville, Florida, and Harding Lawson Associates, Houston, Texas.

This work plan is prepared to outline the project-related activities, pre-sampling tasks, sampling and analysis, feasibility study tasks and project schedule.

This plan is viewed as flexible in that changes are likely in this plan as work progresses. The location of a given sample, the chemical analyses required, the schedule of events, any or all of these and other items could change during the course of the program. The flexibility in the activities and schedule will permit response to new program needs on a timely basis.

2.0 TECHNICAL APPROACH

A. INTRODUCTION

The work program for the site investigations and feasibility studies of the French Limited site has been structured into major task elements as follows: pre-sampling activities, site investigations, identification of remedial alternatives, assessment of alternatives and reporting requirements. The purpose and objectives of the site investigation and feasibility studies are to:

1. Investigation

Characterize the site in terms of wastes present, magnitude and extent of contamination, rate and direction of any waste migration, target receptors, site geology and hydrology; and

2. Feasibility

Develop and evaluate alternative remedial measures considering technical feasibility, economic factors, environmental impacts, regulatory constraints and timeliness of completion.

B. PRE-SAMPLING ACTIVITIES

1. Historical and Preliminary Data

A review of available historical data and development of a current data base prior to finalizing a sampling and analysis protocol has resulted in comprehensive sampling and analysis programs most responsive to the needs of this site and most cost effective of alternative programs.

a. Site History

The French Limited site is an abandoned surface impoundment on a 22.5-acre tract near Crosby, Texas (Figure 2-1). The site received about 100,000 barrels of industrial waste per year for six years between 1966 and 1972. The property was deeded to the State of Texas following lengthy litigations and French Limited's final bankruptcy in 1973.

The disposal pit covers approximately 12 acres and is located in permeable sands. The pit is unlined, and its approximate boundaries are shown in Figure 2-2.

The site is in the floodplain of the San Jacinto River and has been flooded in 1969, 1973, and 1979. The flood of 1973 flushed some contaminated water out of the pit without any known damage to the downstream ecology. The flood of April, 1979, caused a breach in the north dike of the pit, providing an avenue for the discharge of contaminated sludges into the adjacent swamp north of the pit.

Federal, state, and local sampling teams have determined that the pit contains from 4 to 18 inches (estimated) of highly contaminated sludges containing heavy metals and chlorinated organics (including

It is very important to know how much sludge is in the pit.

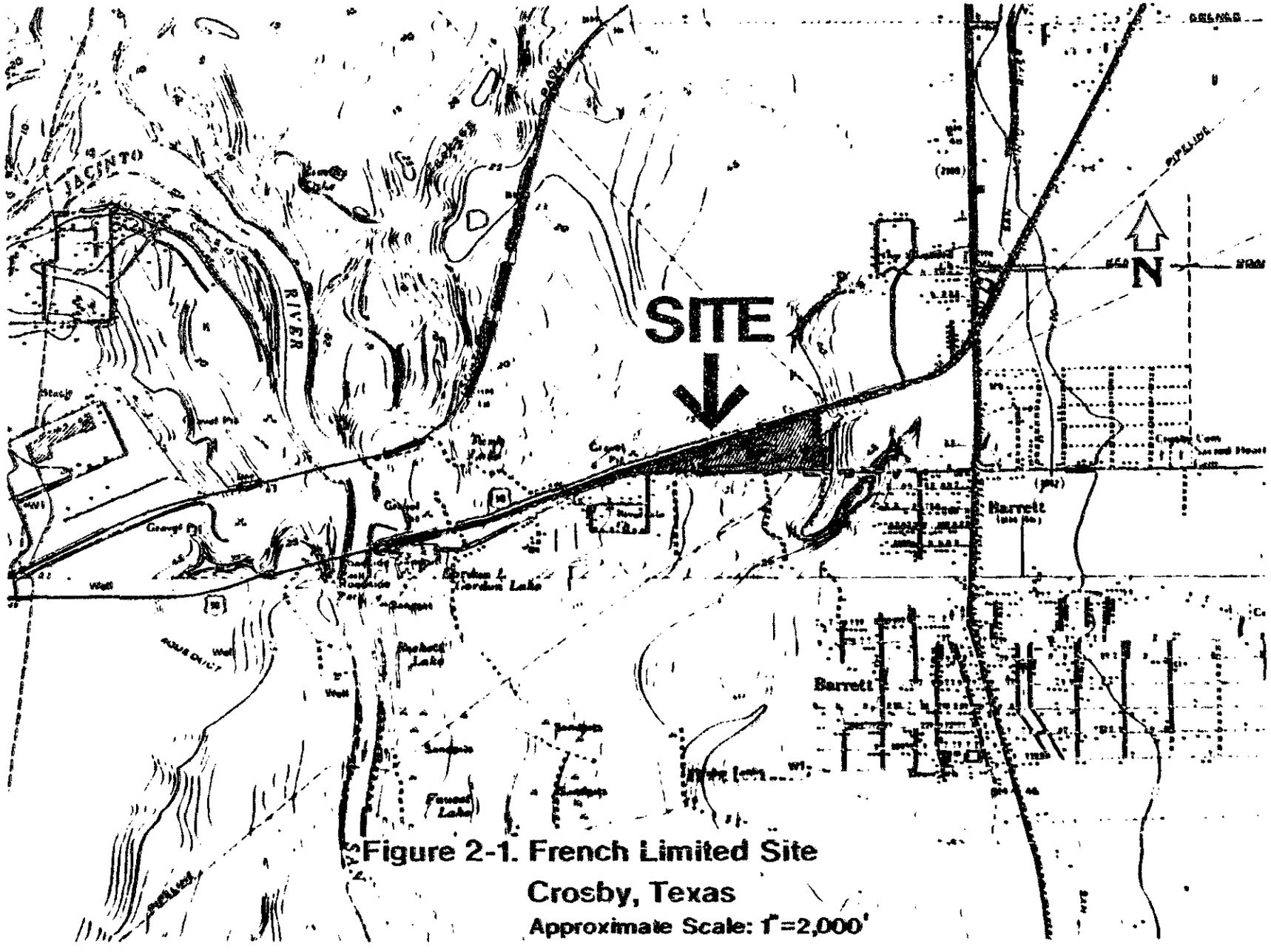

Figure 2-1. French Limited Site
Crosby, Texas
Approximate Scale: 1"=2,000'

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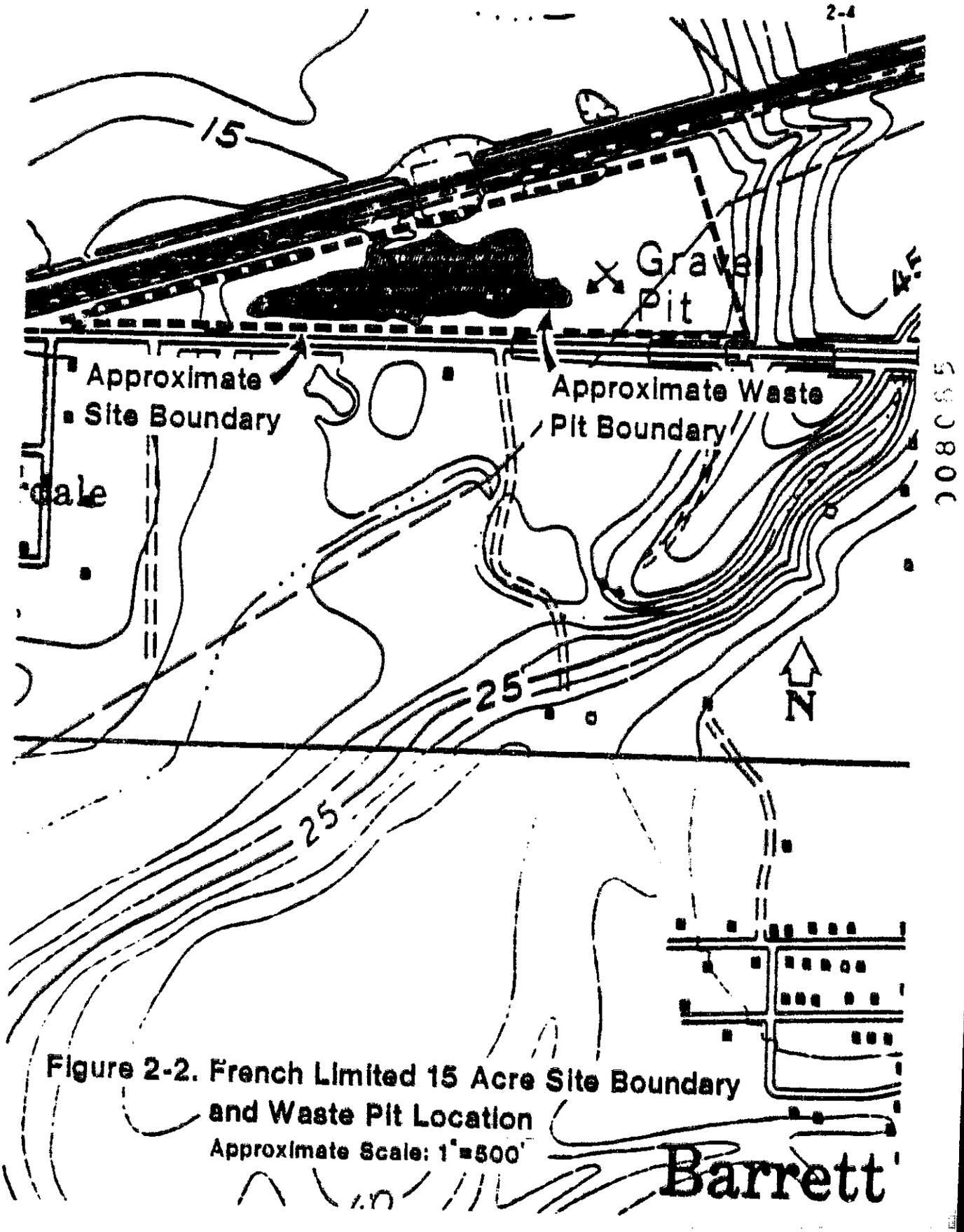

Figure 2-2. French Limited 15 Acre Site Boundary and Waste Pit Location
Approximate Scale: 1"=500'

PCBs). A smaller pit is present on the eastern end of the site which also contains highly contaminated sludges. Groundwater samples taken in October, 1981, from two wells on the site indicate that a variety of acid, volatile, and phenolic compounds were present.

The shallow aquifer beneath the site resides in a broad sandy deposit which is relatively permeable. Some 53 houses in and around the Riverdale subdivision southwest (and apparently downgradient) of the pit depend upon shallow wells (20 to 40 feet deep) into this aquifer for drinking water. Numerous complaints of tastes and odors occurred in the early 1970s near the end of the pit's active operation. The Harris County Pollution Control Board had data in 1979 indicating that the water quality of these shallow residual wells has improved considerably since 1971.

Preliminary remedial actions have been taken since the 1979 flood to repair the dike which was breached and to prevent further discharge of contaminants. A limited effort was recently completed to collect and remove scum and floating oily residues from the swampy area north of the dike and place them back inside the pit.

b. Site Characterization

A comprehensive characterization of the site is necessary to clearly establish those site characteristics that are pertinent to the project. Included in this effort are: boundary and topographic surveys, surface drainage, well inventory, geological, hydrogeological, and hydrological characteristics.

Such characterizations will establish a baseline of available information and data relevant to the project. These site characteristics will serve in subsequent sampling and remedial assessment activities.

(1) Boundary Survey

The purpose of boundary survey will be to clearly define the property and disposal site locations with respect to nearby roadways, highways, and other major features in near proximity to the property. Included will be a survey of major features on the site, the berm for the waste pit, nearby holding ponds, near reaches of the San Jacinto River and the property fencelines. A legal description and deed of the property will be obtained. Such data will be used to generate a comprehensive site map depicting these and other salient features. Permanent boundary markers will be set during these surveys.

This information will be used in subsequent geological, hydrogeological studies and for locating samples of soils, surface waters, groundwaters, vegetation, sludge sediments, etc. A precise sample location strategy is essential to accurate data analysis. This boundary and major features survey will be accomplished by aerial photogrammetry. Only limited ground control will be required.

(2) Topographic Survey

The purpose of the topographic survey (one-foot contours) will be to clearly define the relative elevations of the property and the disposal site's salient features.

Topographic data is vital in the assessment of the extent of contamination, the assessment of remedial actions and the cost-effectiveness analyses of alternative remedial measures. Aerial photography will be used for the topographic survey also.

(3) Well Inventory

The location of domestic water wells in the project vicinity will be an important consideration during the site characterization. Therefore, a field inventory of well locations (both private and public) within an approximately 3/4-mile radius of the French Limited site will be performed. The purpose of the inventory will be to locate existing sources where water samples, hydrogeological and geological information can be obtained to optimize sampling and site investigation activities.

During the well inventory, the following information will be determined where possible: depth of the well; type of construction; the pumping history and usage of the well (drinking, irrigation, livestock or industrial), including any history of known pollution. Where permits are on file, it is expected that the geologic data may be available to indicate the extent of stratification and the presence of a confining clay layer over the underlying deep aquifers. Discussions will be held with the well owners about the possible use of their wells to obtain water samples and determine the groundwater gradient in the area. Accurate survey data will be obtained at these well locations to check the groundwater elevation. Data reviewed to date indicates that privately owned wells in near proximity may have been contaminated by wastes from the site.

(4) Geological Studies

Preliminary site and area geological information can best be obtained from published information, TDWR files and a ground reconnaissance. The published geological maps, fault maps and soils surveys of the Crosby area will be general in nature and/or generally limited to the upper few feet of soil. However, they will be valuable in evaluating the site specific geology with respect to the regional setting. Considering the rural site location and lack of major development in the area, it is expected that the TDWR files will be the best source of site specific geological information. This information will consist of permit application data for the French Limited and Sikes Pit sites as well as logs of monitor wells. It is expected that the well logs obtained during this inventory will also be of some assistance in understanding the regional geology. The Texas Highway Department also has some soil boring data in the area.

Both recent and historic aerial photos will be examined to assist in locating geologic features and conditions which should be examined by field reconnaissance. These photos will be a valuable tool in locating faults which might intersect the site and could affect the groundwater flow or remedial action plans. Some preliminary photo studies already performed indicate that sand pits located southwest of the French Limited site and another southwest of the Riverdale subdivision may be good sources of geologic information by logging the pit sides.

(5) Hydrogeological Studies

Pre-sampling hydrogeological studies will consist of evaluating the groundwater regime based on the data in the existing monitoring wells and private wells identified during an inventory. Accurate ground-surface and water level elevations will be determined at each well where stabilized water levels can be obtained. Current and historical dewatering and water level elevations in the sand pits located south and southwest of the site as well as the nearby San Jacinto River tributaries will also be used in contouring the area ground water elevation.

(6) Hydrological Studies

Historic flood water elevations will be researched to assist in evaluating surface contaminant flow directions. Flood and rain water runoff patterns will assist in determining optimum locations to sample the surface soils and water to check for the extent of the near surface contamination. The historic flood pattern will be utilized not only to study pit migration but also as a valuable tool in planning remedial actions.

2. Site Advance Planning

Prior to completing development of analysis programs, site advance planning is necessary to establish basic program elements for the proper management of personnel safety, sample chain of custody, data storage, quality assurance and community relations. Planning of such elements will help to ensure program continuity.

Meetings with TDWR will be held in the initial phases of the study to ensure that TDWR's ultimate goals and objectives for the work are

EPA must be involved. ! — procedures for EPA input!

clearly detailed. During these meetings, a review of all available data will help to assure that pertinent factors are adequately considered from the start of the program.

a. Safety Contingency Plan

The performance of the objectives of this project in a safe, effective manner is a primary objective of the project team. The corporate commitment to the protection of individuals, property, and the environment is exemplified in the Safety Plan. The Project Safety Plan is contained in Volume II of this Work Plan.

A key individual in implementing the Safety Plan on site is the designated site Safety Officer. He will primarily be responsible for the provisions of the Safety Plan on site.

A detailed Contingency Plan will be prepared as part of the Safety Plan in Volume II to cover emergency evacuation routes and procedures and emergency spill and fire control. The Contingency Plan will be prepared in accordance with state and federal regulations. Copies will be maintained at the site for use by project personnel and for inspection by authorized representatives of the state or federal government.

In the event of an emergency release or spill of hazardous material, the on-site Safety Officer will:

(1) Notify local police and fire departments and local state representatives;

(2) Assess possible hazards to human health and the environment and coordinate all necessary actions including stopping operations to control the emergency situation;

(3) Comply with any state or federal Hazardous Waste Contingency and Emergency Preparedness Plans, and

(4) Order evacuation of all personnel from the site if dangerous situations are perceived to exist.

b. Chain of Custody Plan

A chain of custody program will be developed prior to the field investigations to ensure that samples are collected, handled, and identified in a complete and efficient manner. (See Volume III.)

c. Quality Assurance

Quality assurance encompasses all actions taken by an organization to ensure that the results and conclusions produced by its programs and projects are accurate and reliable. This activity involves two distinct, but related, concepts: quality control (QC) and quality assurance (QA).

Quality control is adherence to the set of policies and procedures which ensure that collected, supporting data are accurate and that the lists of accuracy and precision for the data are known. Quality control involves such operations as documentation adherency to standard operating procedures; proper, documented calibration of equipment; analysis of reference materials; proper training of personnel; calibration and verification of models; review of data; and other functions which check

or prove the reliability of data, calculations, or conclusions. As such, the concept of quality control is one component of quality assurance.

Quality assurance involves audits and review by management to assure that quality control practices and procedures are being properly implemented and that appropriate levels of accuracy, reliability, and comparability are being achieved in all facets of a project: sampling and analyses, calculations and modeling, and reporting of results. A comprehensive QA Program also ensures that all written documents are properly and adequately reviewed.

d. Field Office

A field office in an office trailer will be established during mobilization prior to the site investigation. Electrical and telephone service will be installed in this trailer to provide lighting and communications. This office will provide secure facilities for safety equipment, sampling supplies, and files which are utilized over the course of the field ivestigation. A decontamination station will be located adjacent to the field office to permit cleanup of personnel and equipment which may become contaminated during field activities.

C. SITE INVESTIGATIONS

Details of planned site investigations are contained in Section 4.0 of this document. The purpose and objectives of the site investigations are to characterize the French site in terms of pollutants present, the magnitude and extent of contamination, the rate of waste migration, and other physical site characteristics.

D. FEASIBILITY STUDY

1. General

Following the site investigation, alternatives will be developed which incorporate remedial technologies and cleanup objectives into a comprehensive, site-specific approach. A meeting will be held with TDWR to discuss the objectives of the remedial action and the cleanup criteria. After the meeting, specific recommendations based upon either water quality criteria or upon a pollutant fate analysis could be developed for application at the French Limited site.

Remedial alternatives could entail structural or non-structural strategies, as well as non-cleanup actions such as alternative water supplies or fishing restrictions and no-action options. The development of these alternatives, as well as the selection of site-specific cleanup criteria, will be done in close consultation with the state.

To the extent possible, the feasibility study will be conducted in accordance with the National Oil and Hazardous Substance Contigency Plan as published in the July 16, 1982 Federal Register.

2. Determination of the Appropriate Cleanup Criteria

The remedial action alternatives to be evaluated will be capable of producing an acceptable level of cleanup as defined by criteria established in cooperation with TDWR. These criteria will depend to an extent on the findings of the site investigation and the identification of target receptors. If private wells are threatened by the site or contaminated groundwater migration, the cleanup criteria will be based on established and anticipated drinking water standards.

Data developed during the site investigation coupled with existing data will yield information on the migration of contaminants via surface water and groundwater pathways into the near site environment. The distribution and fate of these contaminants in the aquatic environment may be examined using a simulation model such as the EPA Exposure Analysis Modeling System (EXAMS), developed by Burns et al (1981). This model may be applied to the San Jacinto River and to the "fishing hole" near the U.S. 90 bridge to assess the effectiveness of different remedial alternatives in reducing the exposure by nearby target receptors. Site-specific input could include basin morphometry, flow characteristics, sedimentary organic content, and residual contaminant levels.

3. Development of Remedial Alternatives

In developing remedial alternatives, results of the site investigation report will be examined to determine the extent and types of contamination that have been identified, both onsite and offsite. The relative success of the initial remedial measures which have been completed to date will also be considered. These include the heightening and strengthening of the dikes around the pit, the repair of the dike that washed out during one of the floods, and the cleanup of the material that was washed out of the pit on the west end of the site. This information, in conjunction with the determined appropriate extent of remedial action, will be used to develop the remedial alternatives.

The alternatives that are developed for final remedial action will be of two types: Source Control and Offsite Remedial Action.

a. Source Control

Source control remedial actions will deal with four major areas of contamination: waters within the pit, the contaminated groundwater onsite, the sludges in the pit, and the contaminated soils onsite. The following criteria will be assessed in determining whether and what type of source control remedial actions should be considered:

- o The extent to which substances pose a danger to public health; welfare, or the environment.
- o The extent to which substances are migrating or are contained by either natural or man-made barriers.
- o The experiences and approaches used in similar situations.
- o Environmental effects and welfare concerns.

An initial analysis of the data available on the site is best discussed by looking at each of the four major areas of contamination individually:

(1) Water

Available data indicates that the waste pit waters contain organics and oil and grease; however, no PCB's were detected. The feasibility study will have to address both surface water controls and direct wastewater treatment. Potential surface water controls could include surface seals, surface water diversion and collection systems, grading and revegetation. Potential direct wastewater treatment methods include: biological treatment, chemical treatment and physical treatment.

An analysis of the existing available data indicates likely treatment methods include: air stripping, carbon adsorption, filtration and neutralization.

The water will probably have to be removed from the pit, treated, and either discharged, disposed or returned to the pit.

(2) Groundwater

Available data indicates that the groundwater onsite may not be as contaminated as the leachate plume which has migrated offsite. This is due to the fact that once dumping at the site was halted, various attempts were made to neutralize the water within the pit. Also, the waste within the pit has been diluted due to floods and normal rainfall. Therefore, water leaving the pit now as leachate may be of a higher quality than the leachate produced when the pit was in operation.

In any event, groundwater contamination is of particular concern because once an aquifer has been contaiminated, it can usually not be cleaned up without the expenditure of a great deal of time and money. Potential methods of controlling the groundwater movement offsite are: impermeable barriers, permeable treatment beds, groundwater pumping, or some type of leachate control. The potential treatment techniques for groundwater would be the same as those for the surface waters.

(3) Sludges

Available data indicates that the sludges in the waste pit contain high levels of heavy metals, PCB's and solvent extractable organics. The concentration of these vary throughout the depth of the sludge, with

the highest concentrations in the top layers and the lowest on the bottom.

Relatively few of the hazardous compounds found in the sludges have appeared in the groundwater samples. This indicates that there is very little leaching of those compounds to the groundwater.

(4) Soil

Available data on the site indicates that soil on the inside of the dikes is contaminated with the same compounds that show up in the sludges. This will probably be true throughout the pit. The site investigation could potentially identify other areas onsite where soil has been contaminated. Likely places are the area north of where the dike was breached and the marsh area to the west.

Contaminated soils which require remedial action will probably have to be treated in much the same way as the sludges.

b. Offsite Remedial Action

Existing data indicates that leachate has migrated offsite and has been found in monitoring wells and domestic wells in the area. There have also been several floods on the site which have washed sludge and water out of the pit and onto surrounding property.

Data indicates that groundwater gradient and the majority of the offsite groundwater problems will be to the southwest of the site. The soil and sediments contaminated by the flooding, however, are to the north of the site as this is the major drainage course from the site to

the San Jacinto River. The soil and sediments in this drainage course are likely to be contaminated with PCB's and organics.

(1) Groundwater

As discussed under the source control groundwater section, the leachate plume leaving the site probably varies in quality with distance from the site. The leachate that left the site while the pit was in operation and before any remedial efforts began is probably the most contaminated. The further the leachate plume is from the pit, however, the more dilute it will be. The site investigation will be relied upon extensively to identify the extent and severity of the offsite groundwater contamination. There has likely been some intermingling of the leachate plumes from this site and the Sikes site.

(2) Soils

Existing data indicates that the soils and sediments in the drainage ditch to the north of the site have been contaminated. The potential remedial alternatives for the contaminated offsite soils and sediments would be similar to those onsite.

In both the source control alternatives and offsite remedial action alternatives, air emissions must be considered. There does not presently appear to be a major problem with lateral movement of volatile gases or minor atmospheric emissions. The actual remedial actions, however, could potentially cause serious air quality problems due to stripping of volatile organic compounds or disturbance of the sludges. Potential treatment alternatives include vapor phase adsorption or thermal oxidation.

4. Initial Screening of Alternatives

The remedial action alternatives which are identified will be put through an initial screening to narrow the list of potential alternatives to those which appear to be reasonable for this specific site. The criteria for this initial screening is outlined in the National Oil and Hazardous Substances Contingency Plan as follows:

a. Cost

For each alternative, the cost of installing or implementing the remedial action must be considered, including operation and maintenance costs. An alternative that far exceeds the costs of other alternatives evaluated and that does not provide substantially greater public health or environmental benefit will be excluded from further consideration.

b. Effects of the Alternative

The effect of each alternative should be evaluated in two ways: (i) whether the alternative itself or its implementation has any adverse environmental effects; and (ii) for source control remedial actions, whether the alternative is likely to achieve adequate control of source material, or for offsite remedial actions, whether the alternative is likely to effectively mitigate and minimize the threat of harm to public health, welfare or the environment. If an alternative has significant adverse effects, it will be excluded from further consideration. Only those alternatives that effectively contribute to the protection of public health, welfare, or the environment will be considered further.

c. Acceptable Engineering Practices

Alternatives must be feasible for the location and conditions of the site, applicable to the problem, and represent a reliable means of addressing the problem.

Only those alternatives which are considered reasonable for this specific site will be considered for a detailed feasibility analysis.

→ ...ded and approved upon the evaluation criteria.

E. ASSESSMENT OF ALTERNATIVES

1. General

The reasonable alternatives which survive the initial screening will be subjected to a detailed evaluation. This detailed analysis will consider the factors listed below. The results of the assessment will be tabulated and a recommendation made.

- o Technical Feasibility
- o Economic Feasibility
- o Environmental Acceptability
- o Regulatory Acceptability
- o Potential for Phasing

} list for completeness

2. Technical Feasibility

Each alternative will be described in detail with appropriate figures. In the event that a treatment option is recommended, a determination will be made as to whether treatability studies will be required to confirm the process. The established safety plan and chain of custody procedures will be followed. process should be examined in the feasibility study! *

The analysis of potential groundwater remedial actions will probably require the use of an appropriate groundwater flow model. A model would be appropriate when evaluating slurry walls and various groundwater pumping strategies to reduce or contain offsite contamination. When models are used, they will be calibrated to the extent possible with the observed water quality and quantity data collected during the site investigation.

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The technical feasibility will also consider the methods of construction, site characteristics, effectiveness of any slurry walls, types of liners proposed, leachate collection systems, monitoring, operation and maintenance, final disposal, etc.

3. Economic Feasibility

Once the viable alternatives have been thoroughly defined in the technical review, a cost estimate will be made of the capital cost required to implement each proposed remedial action. Any required monitoring and operation and maintenance costs will also be calculated. These costs will all be calculated on a present worth basis at an accepted discount rate at the time of the study. Information available in Cost Comparisons of Treatment and Disposal Alternatives for Hazardous Wastes, Volumes I and II will be utilized in the economic analysis.

4. Environmental Acceptability

One of the outputs of the technical feasibility analysis will be an estimate of the quantity and quality of contaminants remaining. The environmental acceptability portion of this study will assess each alternative in terms of the extent to which it is expected to effectively mitigate and minimize damage to the public health and the environment. Any adverse environmental impacts will also be considered. This section of the feasibility study will be particularly important to be sure that such problems are mitigated.

5. Regulatory Acceptability

Each alternative will be evaluated to see that all the applicable regulations of the Comprehensive Environmental Response, Compensation

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and Liability Act of 1980 (CERCLA), The National Contingency Plan (NCP), the Clean Water Act (CWA), and the State of Texas are followed. Also to be considered under this section will be the degree to which the alternative is acceptable to the public and the political acceptability of the remedy.

6. Potential for Phasing

Different alternatives will offer a variety of opportunities for phasing the work to accommodate factors such as incremented funding or fast-track requirements. The potential for phasing will be a criterion considered during the feasibility study.

F. REPORTING

Certain submittals will be made as shown below. The type of report or submittal, timing, content and format will be as indicated:

1. Pre-Sampling Submittals

The following materials are to be submitted to TDWR by the dates indicated: - Submit to EPA at the same time.

a. Worker Safety Plan, February 7, 1983, containing safety procedures specifying:

- o Fire Control
- o Spill Prevention/Containment
- o Decontamination
- o Supporting Sampling/Analysis
- o Training Program
- o Communications
- o Twenty-four Hour Entry Control
- o Local Police, Fire, Medical Support
- o Waste Segregation Procedures
- o Potable Water Supply/Sanitary Support
- o Emergency Evacuation Procedures/Alarms
- o Safety Equipment Use, Inspection and Care
- o Laboratory Safety Procedures
- o Safety Officer Responsibility/Authority

b. Quality Assurance Plan, February 7, 1983, containing detailed procedures relative to sampling and analysis programs specifying:

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- o Use of Standards
- o Sample Spikes
- o Precision
- o Accuracy
- o Reproducibility
- o Specific Analytical Procedures
- o Data Management
- o Known Interferences
- o Sample Preservation
- o Laboratory Handling

c. Chain of Custody, February 7, 1983, containing detailed procedures on sample chain of custody, specifying:

- o Sample Collection Procedures
- o Sample Containers
- o Sample Identification
- o Sample Archiving
- o Sample Shipment

d. Site-Specific Sampling, February 7, 1983, containing detailed procedures on site activities, schedule, and sampling.

2. Post-Sampling Submittals

The following materials are to be submitted to TDWR by dates indicated:

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a. Draft Site Investigation Report, June 2, 1983, containing preliminary results of site sampling effort for TDWR review. To be in a technical report format, containing headings similar to the following:

- o Executive Summary
- o Introduction/Background
- o Field Sampling
- o Laboratory Analyses
- o Analytical Results
- o Discussion of Significance
- o Conclusions and Recommendations
- o Appendixes

b. Final Site Investigation Report, July 18, 1983, containing the final results of the site sampling effort with TDWR comments. To be in a technical report format, containing headings similar to those indicated above for the draft report.

c. Draft Feasibility Report, July 31, 1983, containing preliminary evaluation of remedial measures for TDWR review. To be in a technical report format, containing headings similar to the following:

- o Executive Summary
- o Introduction/Background
- o Goals/Objectives
- o Selection Criteria
- o Technical Feasibility
- o Economic Feasibility

- o Environmental Acceptability
- o Regulatory Acceptability
- o Phasing
- o Conclusions and Recommendations
- o Appendixes

d. Final Feasibility Report, October 14, 1983, containing final evaluations and recommendations of remedial measures for site reclamation with TDWR comments. To be in a technical report format, with headings similar to those indicated for the draft report.

3. Periodic Submittals

The following materials are to be submitted to TDWR by dates indicated:

a. Monthly Status Reports, containing pertinent activities including those listed below. Monthly status report format, graphical presentations, etc., will be established in conference with TDWR personnel.

- o Schedule
- o Budget
- o Significant Activities/Analytical Results
- o Changes in Sampling/Analysis Protocols Based on Results to Date
- o Meetings/Conferences/Correspondence
- o Safety Program Summary
- o Quality Assurance Program Summary
- o Problem Areas
- o General Comments

3.0 SCHEDULE AND ORGANIZATION

A. INTRODUCTION

The schedule outlined in this section is based on the required delivery dates stipulated in the professional services contract between TDWR and LAN. Figure 3-1 is a graphical presentation of the project schedule. The major tasks are shown for the three series of work:

100-Series - Pre-Sampling Activities

200-Series - Site Investigations

300-Series - Feasibility Study

B. PROJECT SCHEDULE

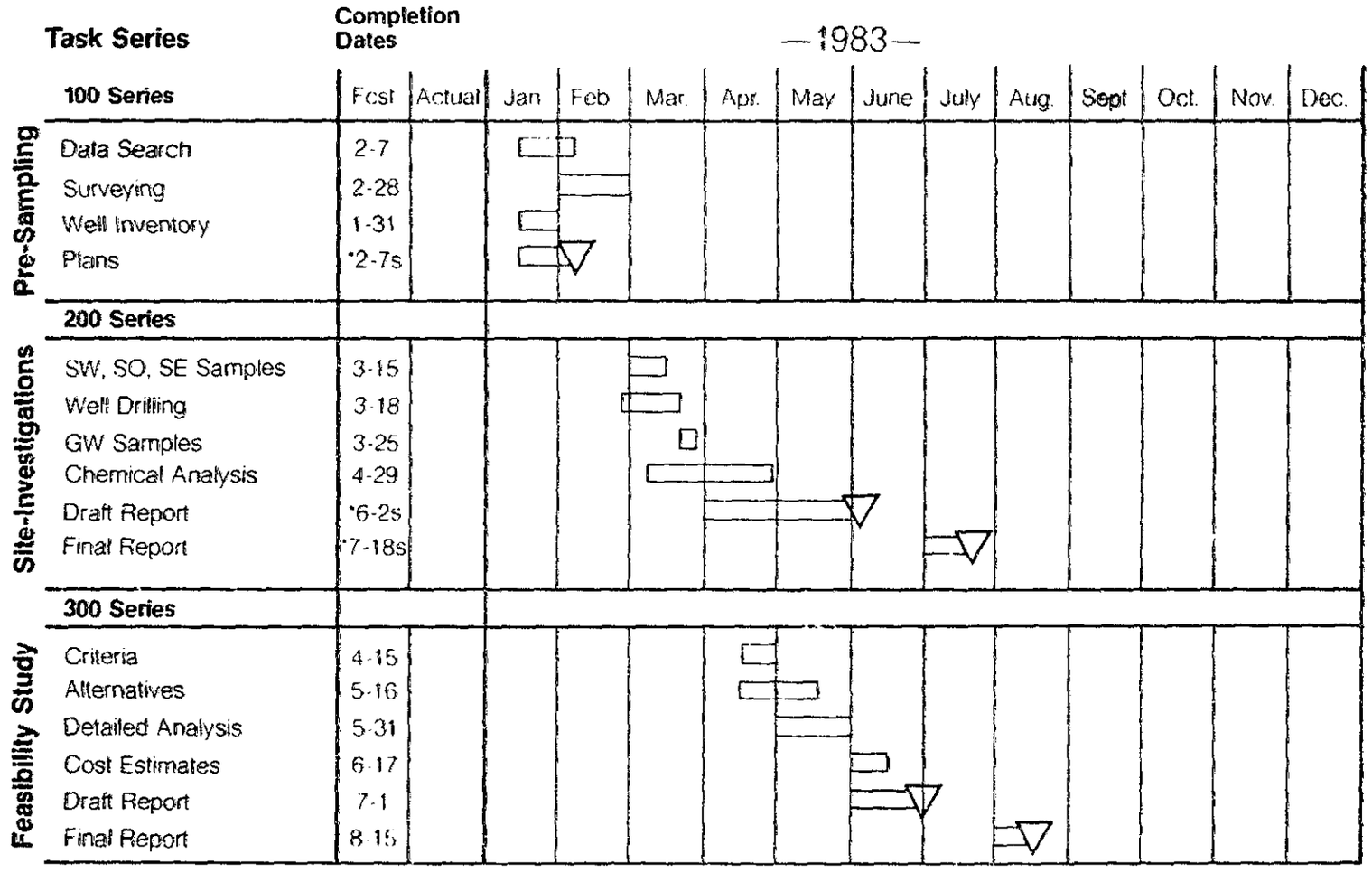
In each series, the forecast completion dates are shown for the major tasks. In those cases where completion of a major task will result in delivery to TDWR of a required product, the required delivery date is indicated in the graph. In those cases where TDWR is to review draft inputs, a 30-day review period has been assumed. The start date for the site feasibility study is flexible. For purposes of this schedule of activities, the feasibility study begins when the draft site investigation report is delivered to TDWR.

C. MANAGEMENT ORGANIZATION

Figure 3-2, the organizational diagram, depicts the management organization for this study.

French Limited Site — Schedule of Major Activities
Texas Department of Water Resources.

Figure 3-1



Notes: * Specific Delivery Dates
200 Series Final Rep .. Completion Date Assumes 30 Day TDWR Review of Draft
300 Series Completion Dates Assumes NTP on 300 Series by TDWR on 4-1-83
300 Series Final Report Completion Date Assumes 30 Day TDWR Review of Draft

008111

MANAGEMENT ORGANIZATION

French Limited Hazardous Waste Disposal Site

Crosby, Texas

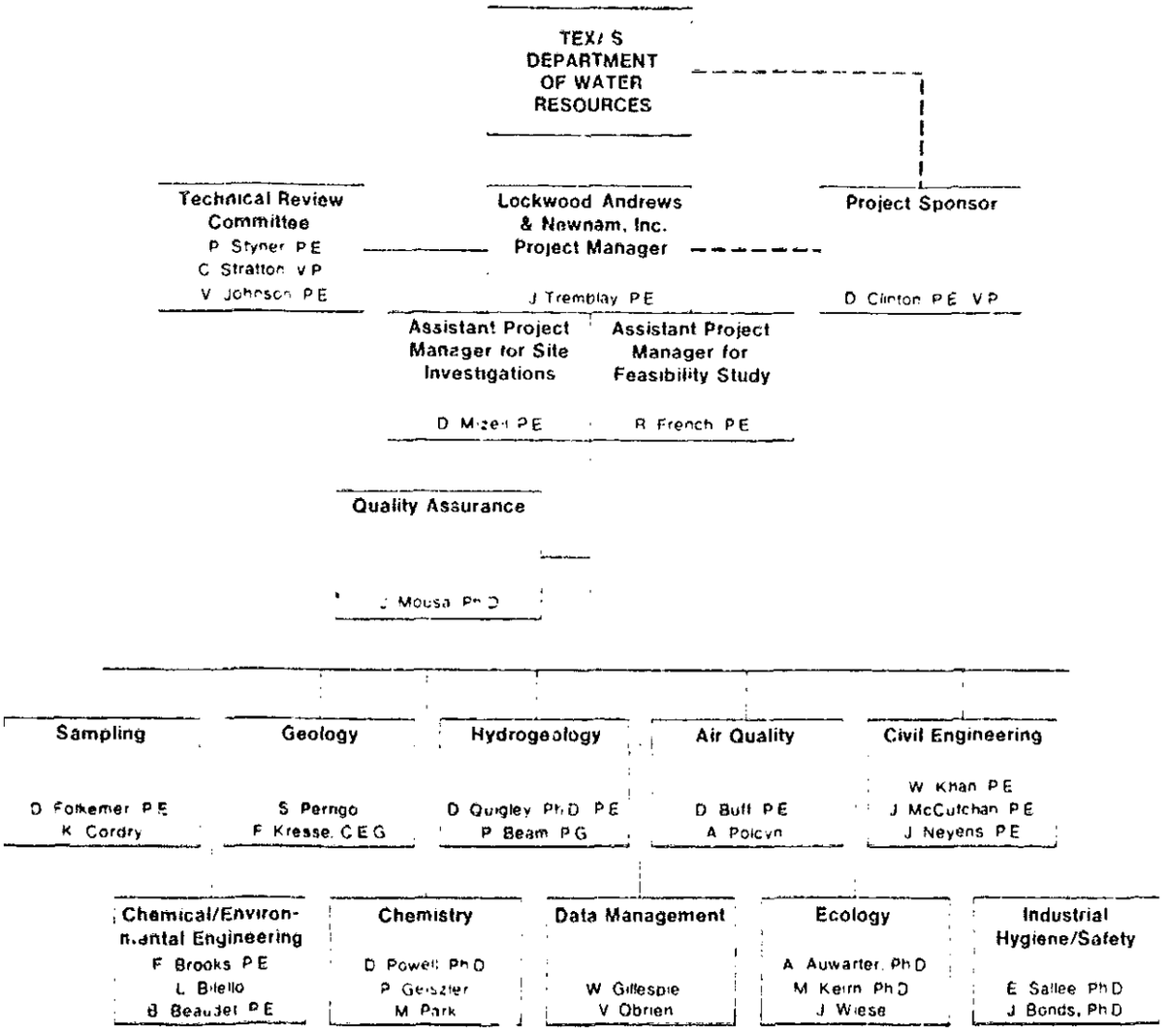


Figure 3-2

008112

4.0 SITE SAMPLING

The engineering feasibility study must be based upon the character and quantities of contaminants and their potential for migration. Thus, the site investigation will entail sampling of environmental media to supplement prior site investigations.

A. SOIL BORINGS/GROUNDWATER

Eleven new soil borings and twelve groundwater samples will be analyzed from the site vicinity. Seven of these groundwater samples will be taken from wells to be installed in bore holes following the boring program. The site selection rationale for these borings and groundwater samples is presented in Table A. The chemical analyses are depicted in Table B.

Borings B001 will be drilled and logged east of the site near the base of the hill in an upgradient direction. A shallow well, approximately 40 feet deep, will be installed in this hole to serve as a background groundwater sample, GW01, These well locations are shown in Figure 4-1. Boring B002 will be a deep boring (about 100 feet deep) just east of the Riverdale Subdivision and will have a well installed afterward (GW02) to provide data of the deeper aquifer. A shallow well (GW07) will be installed close by to form a piezometer cluster with the deep well. Downward vertical gradients can be measured at this cluster, and field permeability tests can be run if appropriate.

Borings B003 and B004 and shallow wells GW03 and GW04 will be installed further east of Riverdale. These wells, coupled with composite

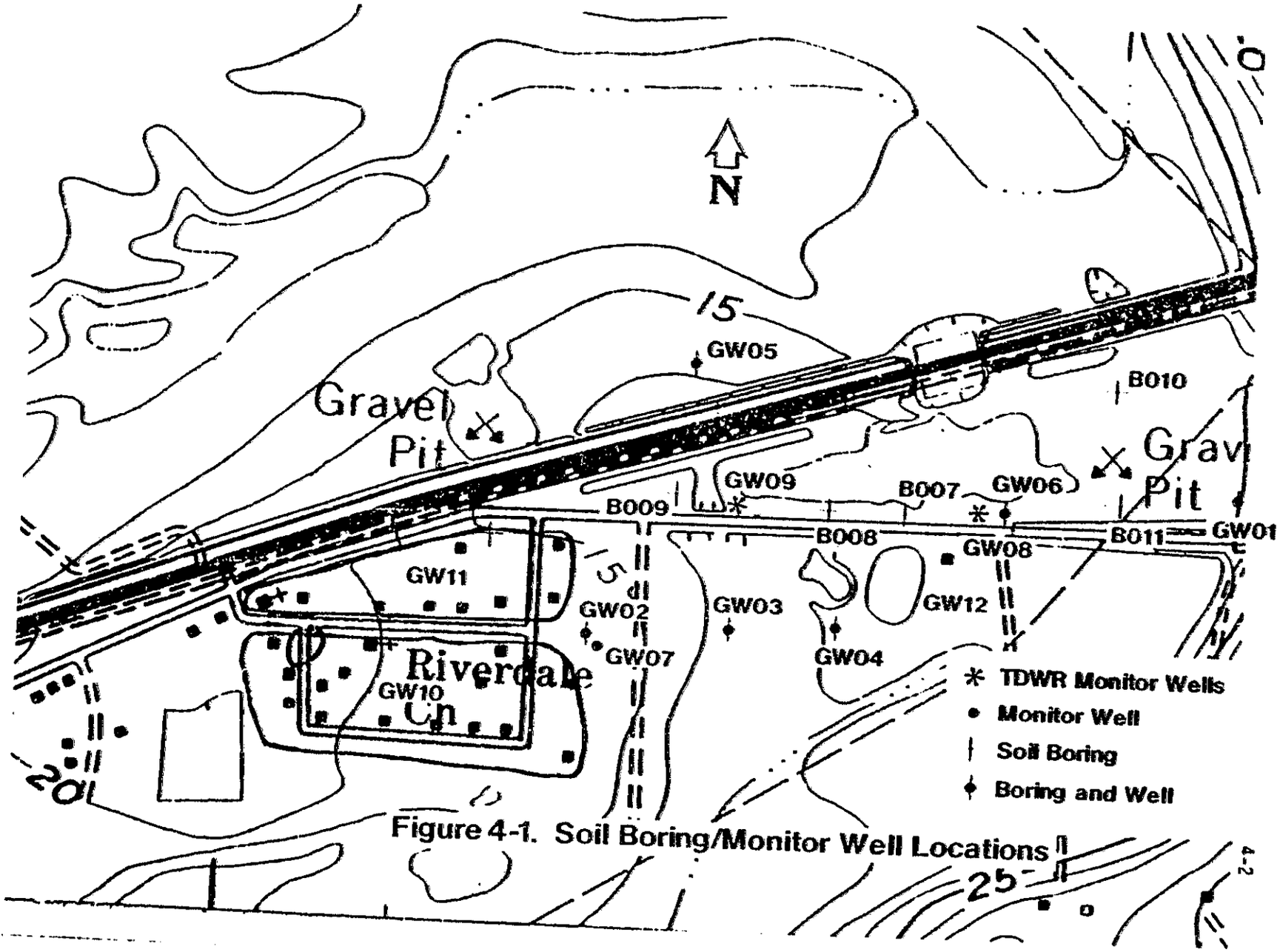


Figure 4-1. Soil Boring/Monitor Well Locations

LOCKWOOD, ANDREWS & NEWNAM, INC.

4-2

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Table A
Well/Boring Site Selection Rationale
French Limited Site

Site Number	Rationale
B001/GW01	Background shallow well upgradient (east) of French Limited.
B002/GW02	Deep well south of Gulf Pump Road, downgradient of French Limited.
B003/GW03	Shallow well south of Gulf Pump Road, downgradient of French Limited, east of B002.
B004/GW04	Shallow well upgradient of B002/3, potentially across gradient from French Limited.
B005/GW05	Shallow well north of U.S. 90, northwest of French Limited, potentially downgradient.
B006/GW06	Deep well adjacent to existing EPA well southeast of main lagoon.
B007 B008 B009	Shallow borings to 40 feet along southern French Limited boundary to define soil characteristics along potential slurry wall alignment.
B010 B011	Shallow borings to 40 feet along eastern boundary to define soils along potential slurry wall alignment.
GW07	Shallow well adjacent to deep well GW02, forming a piezometer cluster downgradient of French Limited, but upgradient from Riverdale Subdivision.
GW08	Existing well southeast of Main Lagoon.
GW09	Existing well southwest of Main Lagoon.
GW10	Composite groundwater sample from about 5 homes with shallow wells in southern half of Riverdale.
GW11	Composite groundwater sample from about 5 homes with shallow wells in northern half of Riverdale.
GW12	Residence well at 915 Gulf Pump Road immediately south and downgradient from French Limited.

Source: ESE, 1983.

008115

Table B
Groundwater Chemical Analysis
French Limited Site

Site Number	Type of Chemical Analysis										
GW01*	A	B	C	D	E	F	G	H	I	J	K
GW02	A	B	C	D	E	-	-	-	-	-	-
GW03	A	B	C	D	E	-	-	-	-	-	-
GW04	A	B	C	D	E	-	-	-	-	-	-
GW05	A	B	C	D	E	F	-	H	I	J	K
GW06	A	B	C	D	E	-	-	-	-	J	K
GW07	A	B	C	D	E	F	G	H	I	-	-
GW08	A	B	C	D	E	F	G	H	I	J	K
GW09	A	B	C	D	E	F	G	H	I	J	K
GO10	A	B	C	D	E	-	G	-	-	-	-
GW11	A	B	C	D	E	-	G	-	-	J	K
GW12	A	B	C	D	E	-	-	-	-	-	-
TOTAL SITES	12	12	12	12	12	5	6	5	5	6	6

* Duplicate samples.

A -- pH
B -- Conductivity
C -- TOE (Total Extractable Organics)
D -- TOC (Total Organic Carbon)
E -- TOX (Total Organic Halogen)
F -- Metals
G -- Total Phenols
H -- PCBs (Pesticides)
I -- GC/MS (Volatiles)
J -- GC/MS (Base Neutral)
K -- GC/MS (Acid)

Source: ESE, 1983.

groundwater samples GW10 and GW11 (in Riverdale) and GW12 will provide insight into groundwater conditions downgradient from the site.

Boring B005 and Well GW05 will be installed north of U.S. 90 to provide comparative water levels against those wells south of the site and to determine groundwater chemistry north of the Main Lagoon. Boring B006 and Well GW06 will be installed into deep strata (approximately 100 feet deep) near the existing EPA well southeast of the waste pit. This well and the existing shallow well will serve as a second piezometer cluster to determine vertical groundwater gradients.

Three shallow borings B007, B008, and B009 will be installed along the south site boundary to provide information on soil layers along a potential slurry wall alignment. Two additional bores (B010 and B011) will be placed along the eastern boundary. Monitoring wells will not be installed in these bore holes.

Groundwater samples GW08 and GW09 will be collected from the existing monitoring wells along the southeast and southwest boundary of the site.

B. SEDIMENTS

Nine sediment samples will be collected for analysis (see Table C). Three samples (SE01, SE02, and SE03) will be composited from the eastern, central, and western zones of the waste pit. Sample SE04 will be taken from the small pit at the eastern end of the site. Samples SE05 and SE06 will be composited along transects across the swamp north of the waste pit. Sample SE07 will be composited beneath the U.S. 90 bridge. Sample SE08

Table C
Sediment Sample
Site Selection Rationale
French Limited Site

Site Number	Rationale
SE01, 02, 03	Waste pit composite samples from east, center, and west zones.
SE04	Composite sample from east pit on French Limited Site.
SE05	Composite or samples taken from swamp along cross section near U.S. 90 bridge.
SE06	Composite of samples taken from swamp along cross section near west end of waste pit.
SE07	Composite of samples taken under U.S. 90 bridge.
SE08	Sample taken from channel centerline north of U.S. 90 at site to be selected.
SE09	Sample from drainage ditch south of Gulf Pump Road and east of Riverdale.

Source: ESE, 1983.

will be taken north of the bridge to indicate whether PCB and heavy organic compounds have been carried off site. Sample SE09 will be collected from the drainage ditch passing southward east of the Riverdale subdivision. These sample locations are shown in Figure 4-2. The laboratory analysis is shown in Table D.

C. SURFACE WATER

Six surface water samples will be collected for analysis (see Table E). Samples SW01 and SW02 will be collected from the waste pit at depths to be selected based on stratification of pH or conductivity. Sample SW03 will be taken from the east pit. Samples SW04, SW05, and SW06 would be composited from the swamp north of the waste pit and beneath the U.S. 90 bridge. These locations are shown in Figure 4-3. Chemical parameters to be analyzed are described in Table F.

In addition to these surface water samples, a survey will be done to determine water stratification and to define bottom contours in the waste pit.

D. SOILS

Recent flood events have dispersed sludge and scum residues into the forested areas in the immediate site vicinity. A site reconnaissance walk-through survey will be done to map areas affected by past flooding. Samples of residues will be composited by area (see Table G). Six soil samples will be collected from areas west (S001), south (S002), east (S003),

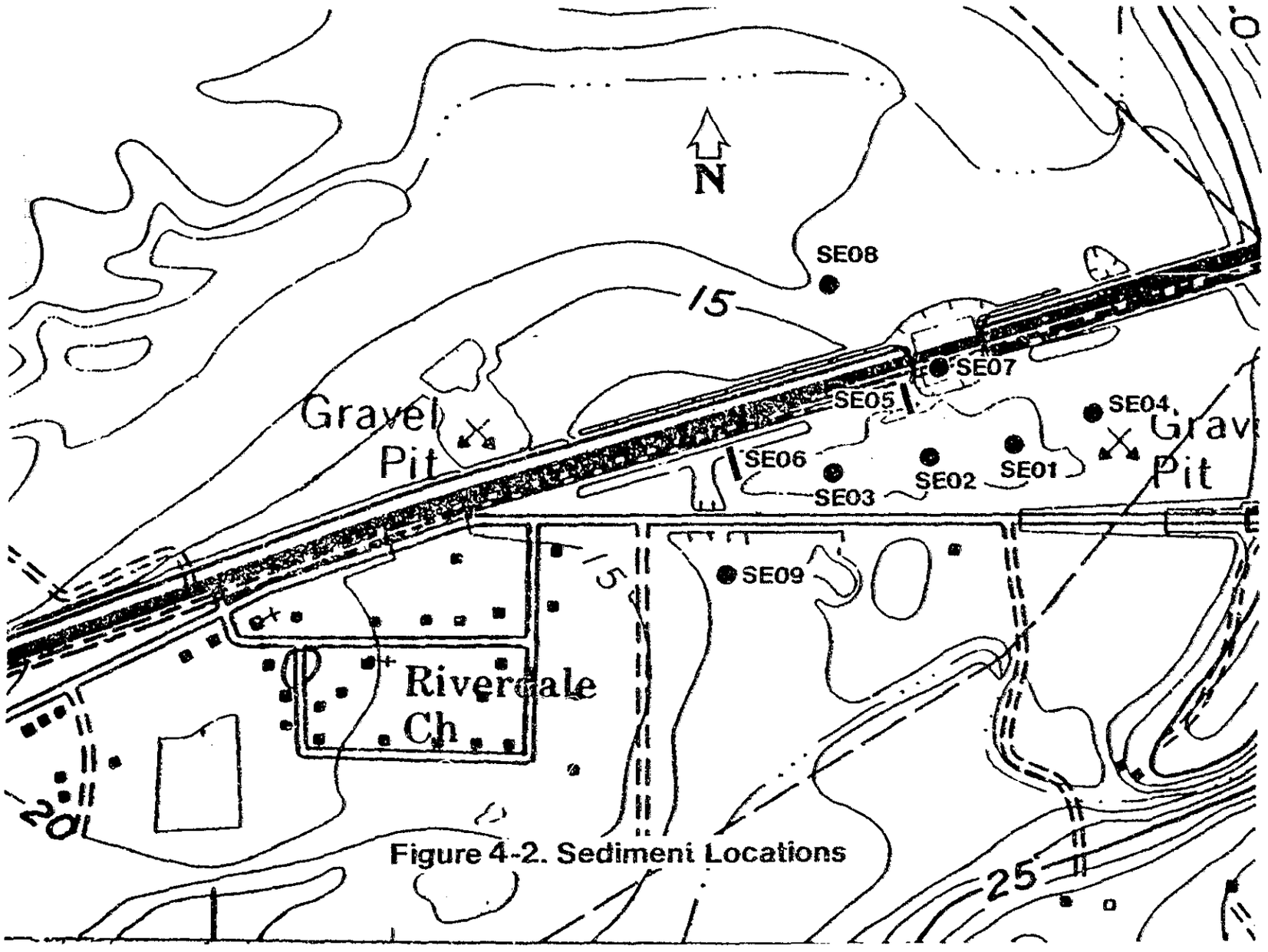


Figure 4-2. Sediment Locations

008120

Table D
Sediment Chemical Analysis
French Limited Site

Site Number	Type of Chemical Analysis										
SE01*	-	-	C	D	E	F	G	H	-	J	K
SE02	-	-	C	D	E	-	G	H	-	-	-
SE03	-	-	C	D	E	F	G	H	-	J	K
SE04	-	-	C	D	E	F	G	H	-	J	K
SE05	-	-	C	D	E	-	G	H	-	-	-
SE06	-	-	C	D	E	F	G	H	-	J	K
SE07	-	-	C	D	E	-	G	H	-	-	-
SE08	-	-	C	D	E	-	-	-	-	-	-
SE09	-	-	C	D	E	-	-	-	-	-	-
TOTAL SITES	0	0	9	9	9	4	7	7	0	4	4

* Duplicate samples.

A -- pH
B -- Conductivity
C -- TOE (Total Extractable Organics)
D -- TOC (Total Organic Carbon)
E -- TOX (Total Organic Halogen)
F -- Metals
G -- Total Phenols
H -- PCBs (Pesticides)
I -- GC/MS (Volatiles)
J -- GC/MS (Base Neutral)
K -- GC/MS (Acid)

Source: ESE, 1983.

Table E
Surface Water Sample
Site Selection Rationale
French Limited Site

Site Number	Rationale
SW01	Eastern end of waste pit at depths to be selected.
SW02	Western end of waste pit at depths to be selected.
SW03	Sample from east pit.
SW04, 05	Samples from swamp northwest of waste pit.
SW06	Beneath U.S. 90 bridge.
--	Survey to determine any stratification of pH or conductivity in waste pit.
--	Bathymetric Survey to determine water depths over grid on waste pit.

Source: ESE, 1983.

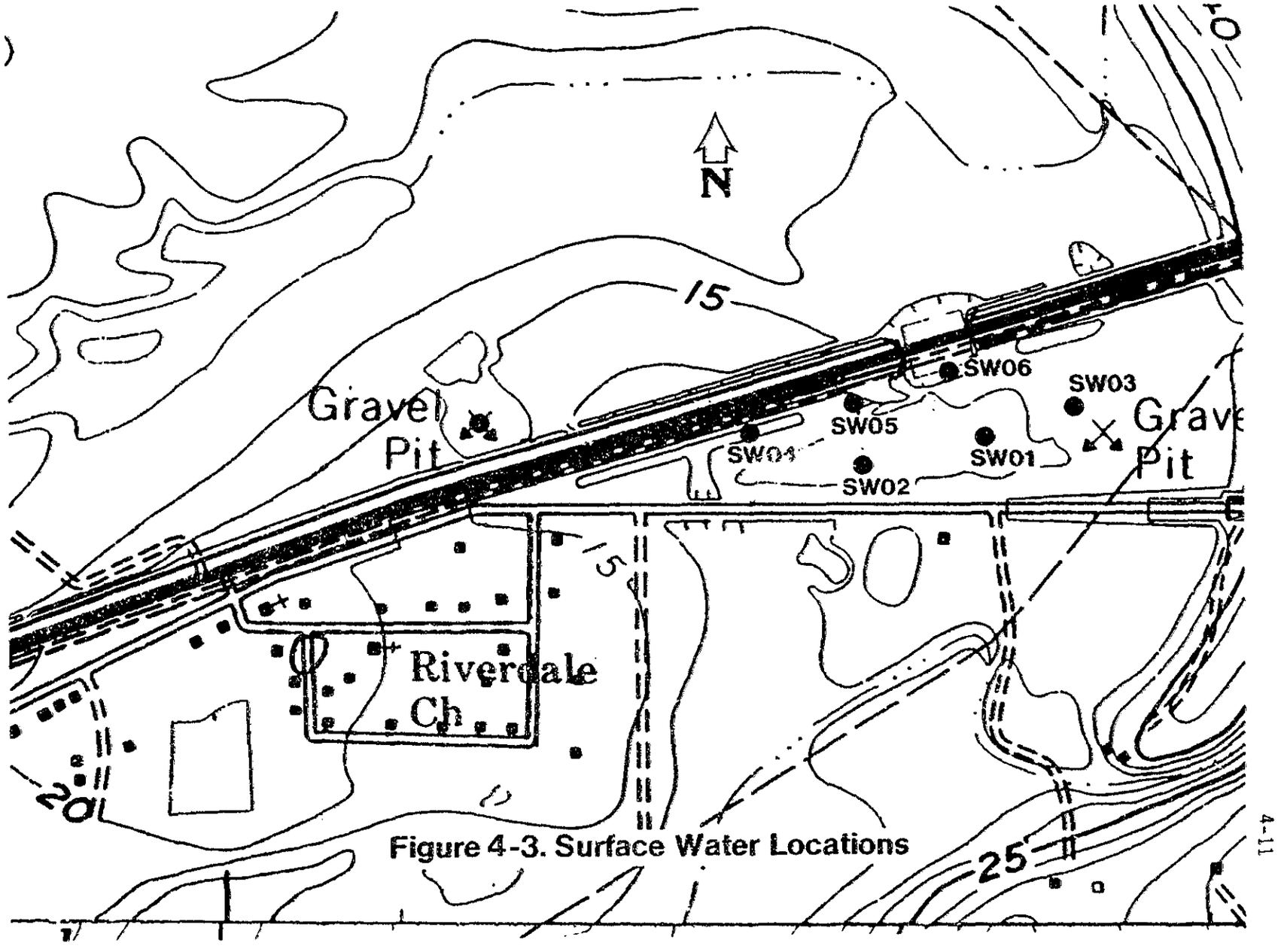


Figure 4-3. Surface Water Locations

008123

Table F
Surface Water Chemical Analysis
French Limited Site

Site Number	Type of Chemical Analysis										
SW01	A	B	C	D	E	F	G	H	I	J	K
SW02	A	B	C	D	E	-	G	H	-	-	-
SW03*	A	B	C	D	E	-	G	-	-	-	-
SW04	A	B	C	D	E	F	G	H	I	J	K
SW05	A	B	C	D	E	-	G	H	-	-	-
SW06	A	B	C	D	E	F	G	H	I	J	K
TOTAL SITES	6	6	6	6	6	3	6	5	3	3	3

* Duplicate samples.

A -- pH
B -- Conductivity
C -- TOE (Total Extractable Organics)
D -- TOC (Total Organic Carbon)
E -- TOX (Total Organic Halogen)
F -- Metals
G -- Total Phenols
H -- PCBs (Pesticides)
I -- GC/MS (Volatiles)
J -- GC/MS (Base Neutral)
K -- GC/MS (Acid)

Source: ESE, 1983.

Table G
Soil Sample
Site Selection Rationale
French Limited Site

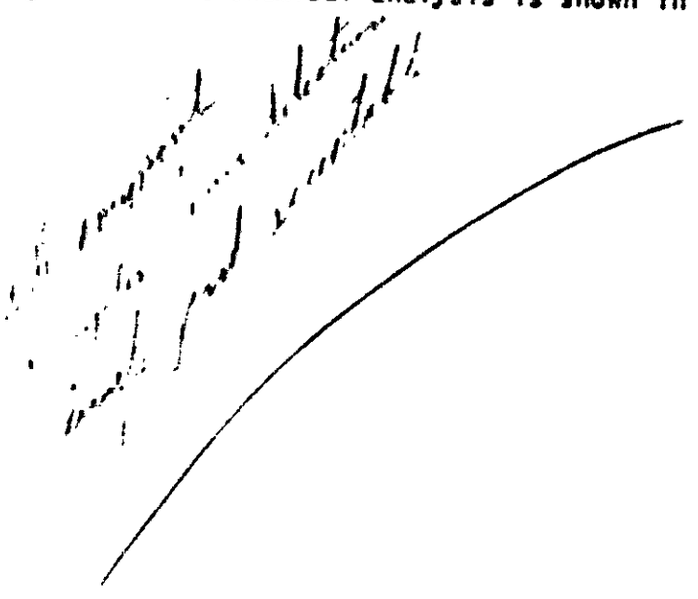
Site Number	Rationale
S001	West end of French Limited Site, seek sludge residue.
S002	Sludge and/or soils along south site boundary.
S003	Sludge and/or soils along east site boundary.
S004	Sludge and/or soils above swamp waterline south of U.S. 90.
S005, 06	Soils north of U.S. 90 in area flooded by past high waters.
--	Site reconnaissance walk-through survey to determine extent of sludge residues on soils above prevailing swamp waterline.

Source: ESE, 1983.

and north (S004, 5, 6) of the waste pit (see Figure 4-4). Chemical analysis are described in Table H.

E. FISH TISSUE

Three composite samples of fish tissue will be taken from the fishing area beneath the U.S. 90 bridge and analyzed to determine if metals and PCBs are accumulating in aquatic organisms (see Table I). The location of this site is shown in Figure 4-4 and chemical analysis is shown in Table J.



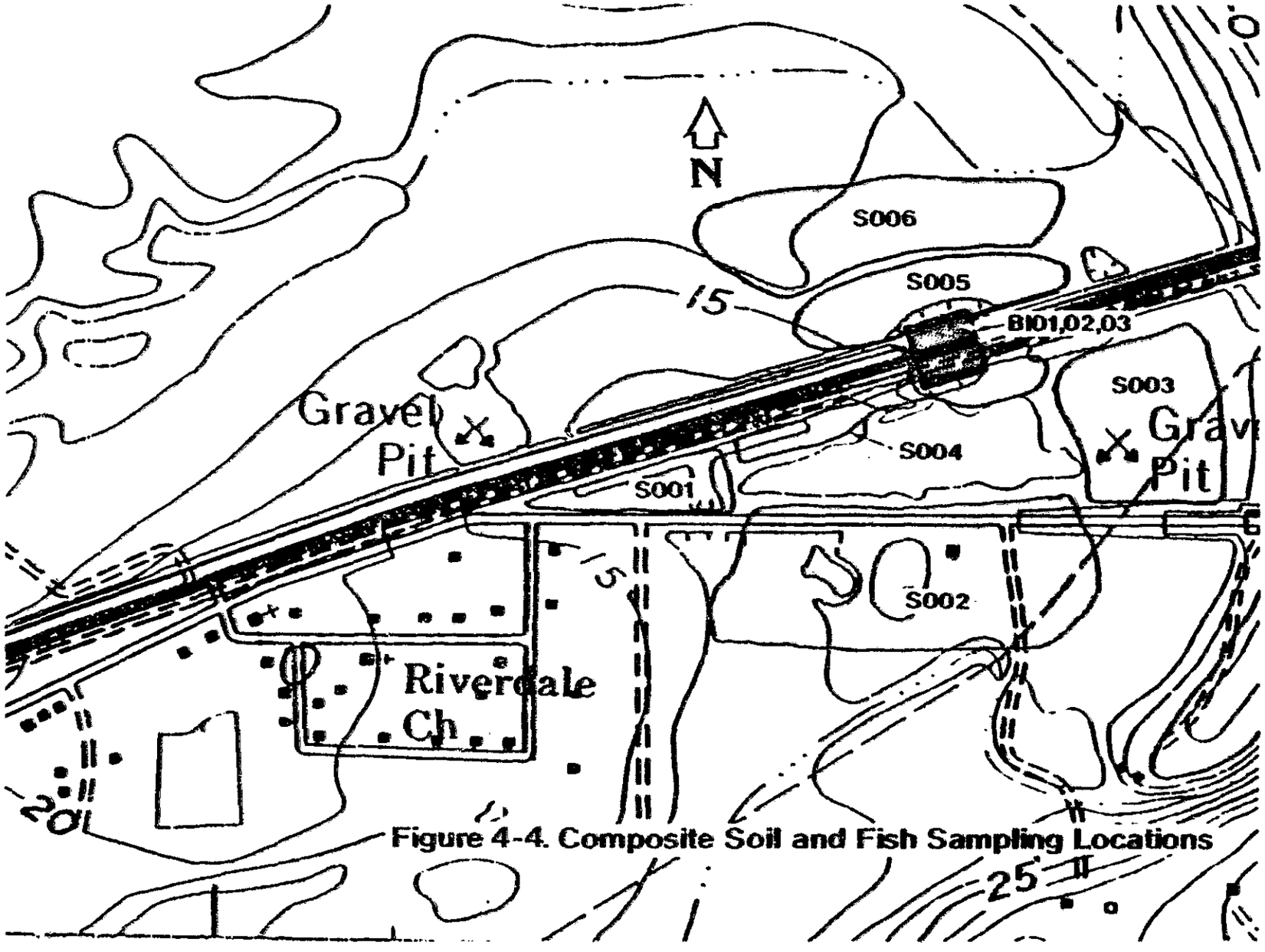


Figure 4-4. Composite Soil and Fish Sampling Locations

008127

Table H
Soils Chemical Analysis
French Limited Site

Site Number	Type of Chemical Analysis										
S001	-	-	C	D	E	F	-	H	-	J	K
S002	-	-	C	D	E	-	-	-	-	-	-
S003	-	-	C	D	E	-	-	-	-	J	K
S004	-	-	C	D	E	-	-	H	-	J	K
S005	-	-	C	D	E	-	-	H	-	J	K
S006*	-	-	C	D	E	-	-	H	-	-	-
TOTAL SITES	0	0	6	6	6	1	0	4	0	4	4

* Duplicate samples.

A -- pH
B -- Conductivity
C -- TOE (Total Extractable Organics)
D -- TOC (Total Organic Carbon)
E -- TOX (Total Organic Halogen)
F -- Metals
G -- Total Phenols
H -- PCBs (Pesticides)
I -- GC/MS (Volatiles)
J -- GC/MS (Base Neutral)
K -- GC/MS (Acid)

Source: ESE, 1983.

008128

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Table I
Biota Samples
Site Selection Rationale
French Limited Site

Site Number	Rationale
8101, 02, 03	Fish specimens beneath U.S. 90 bridge analyzed for bioaccumulation.

Source: ESE, 1983.

Table J
Fish Tissue Chemical Analysis
French Limited Site

Site Number	Type of Chemical Analysis										
FTO1-A	-	-	-	-	-	F	-	H	-	-	-
FTO1-B	-	-	-	-	-	F	-	H	-	-	-
FTO1-C	-	-	-	-	-	F	-	H	-	-	-
TOTAL SITES	0	0	0	0	0	3	0	3	0	0	0

* Duplicate samples.

A -- pH
B -- Conductivity
C -- TOE (Total Extractable Organics)
D -- TOC (Total Organic Carbon)
E -- TOX (Total Organic Halogen)
F -- Metals
G -- Total Phenols
H -- PCBs (Pesticides)
I -- GC/MS (Volatiles)
J -- GC/MS (Base Neutral)
K -- GC/MS (Acid)

Source: ESE, 1983.

5.0 HYDROGEOLOGIC INVESTIGATIONS

The hydrogeological investigation program was developed from a review of existing hydrogeological data. These investigations are intended to substantially improve the existing data base. Details of these programs are provided in the following subsections. Some modifications to the programs may be made as field data collection proceeds.

A. SOIL BORINGS

Soil borings to obtain information regarding the geology and groundwater and to obtain samples for analytical and physical property testing will be performed using truck-mounted or swamp buggy-mounted rotary wash drilling equipment. Rotary wash equipment will be used because of the relatively high water table and sandy soils which are not suited to flight and hollow-auger drilling methods. However, dry auger drilling may be used until groundwater or seepage is encountered. All the borings will be drilled under the direction of a geologist or field engineer who will log the borings and obtain samples of the soils encountered. Undisturbed samples will be obtained at approximately 5-foot intervals by pushing 3-inch diameter Shelby tubes or driving a 3-inch diameter split barrel samler. Because the French Limited pit once contained very acidic waste (pH=2), the pH of each soil sample will be measured in the field to help identify the lateral and vertical extent of the contaminated zone(s) and check that the boring depth is sufficient to penetrate it. Completed boreholes will be logged with a Johnson-Keck SR-3000 resistivity and natural gamma borehole logger to

accurately identify clay and sand layers and for later correlation with other geophysical methods. After the borings are logged. they will be either grouted with a cement bentonite mixture or converted to a groundwater monitoring well. Tube samples from the borings will be returned to the laboratory for geotechnical testing.

Eleven new soil borings are planned for the site vicinity. The site selection rationale for these borings is presented in Table K.

Boring B001 will be drilled and logged east of the site near the base of the hill in an upgradient direction. A shallow well, approximately 40 feet deep, will be installed in this hole to serve as a background groundwater sample, GW01. These well locations are shown in Figure 4-1. Boring B002 will be a deep boring (about 100 feet deep) just east of the Riverdale Subdivision and will have a well installed afterward (GW02) to provide data of the deeper aquifer. A shallow well (GW07) will be installed close by to form a piezometer cluster with the deep well. Downward vertical gradients can be measured at this cluster, and field permeability tests can be run if appropriate.

Borings B003 and B004 and shallow wells GW03 and GW04 will be installed further east of Riverdale. These wells, coupled with composite groundwater samples GW10 and GW11 (in Riverdale) and GW12 will provide insight into groundwater conditions downgradient from the site.

Boring B005 and Well GW05 will be installed north of U.S. 90 to provide comparative water levels against those wells south of the site and to determine groundwater chemistry north of the Main Lagoon. Boring

Table K
Well/Boring Site Selection Rationale
French Limited Site

Site Number	Rationale
B001/GW01	Background shallow well upgradient (east) of French Limited.
B002/GW02	Deep well south of Gulf Pump Road, downgradient of French Limited.
B003/GW03	Shallow well south of Gulf Pump Road, downgradient of French Limited, east of B002.
B004/GW04	Shallow well upgradient of B002/3, potentially across gradient from French Limited.
B005/GW05	Shallow well north of U.S. 90, northwest of French Limited, potentially downgradient.
B006/GW06	Deep well adjacent to existing EPA well southeast of main lagoon.
B007 B008 B009	Shallow borings to 40 feet along southern French Limited boundary to define soil characteristics along potential slurry wall alignment.
B010 B011	Shallow borings to 40 feet along eastern boundary to define soils along potential slurry wall alignment.
GW07	Shallow well adjacent to deep well GW02, forming a piezometer cluster downgradient of French Limited, but upgradient from Riverdale Subdivision.
GW08	Existing well southeast of Main Lagoon.
GW09	Existing well southwest of Main Lagoon.
GW10	Composite groundwater sample from about 5 homes with shallow wells in southern half of Riverdale.
GW11	Composite groundwater sample from about 5 homes with shallow wells in northern half of Riverdale.
GW12	Residence well at 915 Gulf Pump Road immediately south and downgradient from French Limited.

B006 and Well GW06 will be installed into deep strata (approximately 100 feet deep) near the existing EPA well southeast of the waste pit. This well and the existing shallow well will serve as a second piezometer cluster to determine vertical groundwater gradients.

Three shallow borings B007, B008 and B009 will be installed along the south site boundary to provide information on soil layers along a potential slurry wall alignment. Two additional bores (B010 and B011) will be placed along the eastern boundary. Monitoring wells will not be installed in these bore holes.

B. MONITORING WELLS

Eight of the 11 new soil borings will be converted to permanent groundwater monitoring and sampling wells. Both 4-inch and 2-inch diameter monitoring wells will be installed. Four-inch wells will be required where pumping/recovery tests are planned. Tamper-proof security covers will be installed at each monitoring well to prevent unauthorized removal of the well cap. Details of the proposed monitoring well installation procedures are contained in Appendix C.

C. GROUNDWATER LEVEL MEASUREMENTS

Accurate groundwater level measurements will be obtained at each of the new and existing monitoring wells and the accessible private wells during the site investigation. In order to accurately determine the water levels, the elevation of each well casing will be surveyed to the nearest .01 foot.

Water levels in the casing will be measured with an electronic sounding device (Olympic Model 250 well probe), and the elevation of the groundwater will be determined from the permanent casing benchmark. Water level readings will be taken weekly and after periods of heavy rainfall so that the longterm groundwater gradient and flow direction can be determined and changes monitored.

D. FIELD PERMEABILITY TESTS

Field permeability (slug) tests will be performed in the new monitoring wells where the formation permeability is not high (i.e., where nearly instantaneous rising or lowering of the groundwater level in the well can be achieved. A slug test procedure is a rapid means of determining the permeability of an aquifer from the rate that the water level in the well rises after a certain volume (or slug) is suddenly added. The change in water level in each well will be measured with a Paroscientific Digiquartz pressure transducer and the data recorded on a Hewlett Packard digital printer at intervals as close as one second. The theory and procedure for analyzing slug test data developed by Bouwer and Rice (1976) for unconfined aquifers and by Reed (1980) for confined aquifers will be used.

Because of the relatively large screened interval in most of the monitoring wells and the possibility that the alluvial materials are highly permeable, the time required to introduce or remove the slug may not be instantaneous in comparison to the time required for the water level to fall or rise to its equilibrium level. In this case, a pumping/recovery test will be conducted. The pumping/recovery test

will involve pumping the well long enough to achieve a stabilized drawdown and recording the rate of recovery of the water level in the well after pumping has stopped. The quantity of water pumped will be measured using a volumetric flow meter. During recovery of the water table, the in-well pressure changes will be recorded by the pressure transducer. It is anticipated that the pumping/recovery test will be used in the deeper monitoring wells or the highly permeable zones in the shallow monitoring wells.

E. PHYSICAL SOIL ANALYSES

Laboratory testing on selected samples from the soil borings will be performed. The laboratory program will be designed to evaluate the physical properties of the soil for use in contaminant transport modeling and analysis and to provide a correlation between the rings and with field tests. It is anticipated that the following laboratory tests will be performed: constant head permeability on granular soils, falling head permeability on fine-grained materials, Atterberg limits, grain-size analysis, moisture content, dry density, and specific gravity. All tests will be performed according to the current ASTM, EPA, or U.S. Army Corps of Engineers standards (See Appendix C). If required by the Project Safety Plan, the soil samples will be discarded into containers for transport to an approved disposal facility, or be returned to the site for disposal. Table L summarizes the number of analyses initially assumed. The results of laboratory testing will be reviewed by geotechnical engineers, and copies of the laboratory data are sent to corporate Laboratory Director for quality control checks.

Table L
Summary of Laboratory Tests for Physical Soil Properties

Type of Test	Number
Moisture Content	60
Dry Density	60
Atterberg Limits	10
Grain Size Analysis	24
Specific Gravity	10
Permeability	12

F. GEOPHYSICS

Various remote sensing geophysical techniques have been considered to help define the contaminant plume location and reduce the number of soil borings. The techniques consist of electromagnetic (EM) profiling, and electric resistivity profiling. However, our review of existing data and a site inspection indicates that the contaminants may be so dispersed that they cannot be accurately detected by geophysical techniques and that site access is limited by heavy vegetation in many areas. The team has strong geophysical capabilities and is prepared to use remote techniques should additional studies indicate they would be beneficial.

6.0 SAMPLING METHODOLOGIES

A. SAMPLING PROCEDURES

This action presents procedures which are common to the groundwater, surface soils, surface water, sediment, and biological tissue sampling efforts.

Prior to each field trip, a detailed field notebook will be prepared. The notebook will be permanently bound with waterproof sheets. Field data will not be recorded on loose sheets of paper.

The notebook will contain the following contents as a minimum:

(1) Project name,

(2) Project number,

(3) Beginning and ending dates for entries,

(4) Volume number if more than one notebook is used for the project,

(5) Schedule of field activities,

(6) Station locations and maps,

(7) Equipment checklist (to include both sampling and safety equipment),

(8) Equipment calibration information,

(9) Analysis to be performed at each sample station,

(10) Sampling procedures,

(11) Sample shipping information,

(12) Contacts, and

(13) Observations.

Items 1 through 12 will be completed prior to actual field sampling.

Observations taken at each station will consist of:

(1) Station number and location,

(2) Date,

(3) Time (24-hour system),

(4) Weather conditions,

(5) Antecedent weather conditions (if pertinent),

(6) pH, conductivity, and temperature of water samples,

(7) Sample number,

(8) Initials of samplers,

(9) Preservation of samples, and

(10) Other pertinent observations (odor, texture, color, etc.)

At the conclusion of each day in the field, the Field Leader will review each page of the notebook for errors and omissions. He will then date and sign each reviewed page.

B. GROUNDWATER

All wells to be used for groundwater monitoring will be allowed to stabilize a minimum of five days prior to sampling.

Preliminary piezometric data shows the static water level to be within the limits of suction lift (approximately 25 feet of the surface). Should this be the case for both shallow and deep wells, a peristaltic pump will be used for sampling. If the water table is below 25 feet, a PVC bailer with inert ball check valve will be used for sampling. A separate bailer will be used for each well.

The following procedures will be followed during groundwater sampling.

1. Prior to any water removal the water level will be measured and recorded.
2. Before sampling, a minimum of five volumes of water standing in the well casing will be removed. Recharge characteristics of the wells will be noted during drilling. This will enable the sampling team to allow adequate time for slow recharging wells to recover between volume removal and sampling. In most cases, the peristaltic sampling pump and a separate length of Teflon tubing for each well will be used to remove the preliminary volumes. For wells with large volumes of water to be removed (deep 2-inch wells containing over 3 gallons and 4-inch wells) a high speed centrifugal pump will be used to expedite volume removal. If the water table is below the limit of vacuum lift techniques, both the volume removal and sampling will be accomplished with a separate PVC bailer fabricated for each well.
3. If possible, all samples will be collected using a peristaltic pump and Teflon tubing. The intake will be located at the center of the screened interval and the sample evacuated at a slow pumping rate to minimize the aeration of the sample. When the water table falls below the lift limits of the peristaltic pump, a PVC bailer with glass check valve will be used for sampling.
4. Temperature, conductivity and pH will be recorded during sampling using a Hydrolab 4000 field test unit. After the measurements are made the sample of water will be discarded.

5. Residential wells will be sampled after allowing the top to run for two to three minutes. Equal aliquots will be taken from the residential wells that are to be composited. A graduated cylinder will be used to collect the sample and transfer it to the sample container. The cylinder will be rinsed with deionized water followed by a thorough rinse with the water to be sampled.
6. Samples will be properly labeled, preserved and chilled immediately after collection. See Table M for preservation techniques.
7. To minimize the potential of cross-contamination, the following procedures will be followed:
   a. Any equipment exposed to more than one well sample (e.g. a water level indicator) will be thoroughly cleaned with an approved water supply prior to being used at another location.
   b. Disposable gloves will be worn by all sampling personnel. If non-disposable rubber gloves are used during sampling, they will be cleaned with deionized water after sampling.

C. SEDIMENT

Sediment samples will be collected with a Ponar sampler in areas of deep water (3 feet) and by post hole digger in areas of shallow water or for dry sediments. Grab samples at four locations along a cross section will be composited into one sample. This will be done by homogenizing equal portions (visual) of each grab on a clean piece of plastic sheeting and transferring to a glass container with Teflon-lined lids.

Table M
Water Sample Preservation and Volume

Sample Description	Container	Preservation	Volume
TOE in water	Glass	H_2SO_4 to pH <2	1 liter
TOC in water	Cubitainer	Chilled 4°C	500 ml
HPLC screen in water	Glass	Chilled 4°C	1 liter
Metals by ICAP in water (Hg not included)	Cubitainer	HNO_3 to pH <2	1 liter
PCB in water	Glass	Chilled 4°C	1 liter
GCMS in water, VOA	Amber Glass	Chilled 4°C	60 ml
GCMS in water, base neutral	Glass	Chilled 4°C	1 liter
GCMS in water, acid	Glass	Chilled 4°C	1 liter

Source: ESE, 1983.

Samples will be properly labeled and placed on ice immediately after collection.

The Ponar or post hole digger will be cleaned before use at each location by brushing with a wire brush, rinsing with an approved water source, followed by a final rinse with deionized water. The first grab will be discarded at each location as a final cleaning step.

Sediment sampling locations will be accurately located on a map at time of sampling. Tape measures and/or rangefinders will be used to verify station locations with regard to landmarks. The extensions of the cross section will be marked by wooden stakes with sample numbers written on them.

D. SURFACE WATER

Except for the pit proper, all surface water samples will be collected as grab samples at one foot depth or at mid-depth, whichever is less. Samples in streams or ditches will be taken at the cross-sectional point where vertical and lateral mixing produces the most representative sample. Samples from sloughs, ponds and standing water areas will be taken near the center of the water body or midpoint of the cross section.

Water samples will be collected using a pond sampler or peristaltic pump with Teflon tubing suspended from a rod where necessary to minimize wading and boat use. This will also help to assure that the water sample is obtained before the bottom sediments are disturbed.

Surface water samples taken in the pit will be collected by boat. These samples will consist of a composite taken at a minimum of four stations along a cross-section of the pit.

At each station a vertical profile consisting of pH, conductivity, and temperature will be developed using a multi-probe water quality instrument (Hydrolab 4000). An equal aliquot will then be taken at the depth where pH and/or conductivity indicate the highest probability of finding contamination at each station. The aliquot will be obtained by using a peristaltic pump and measured by graduated cylinder. The pump and graduated cylinder will be cleaned by flushing with the water to be sampled at each station.

Station locations will be accurately located on a map at time of sampling. Tape measures and/or rangefinders will be used to verify station locations with regard to landmarks.

Preservation techniques and sample handling will be the same as for the groundwater samples.

E. SOILS

Soil samples will be obtained using a hand trowel. Grab samples at four locations will be composited into one sample. This will be done by homogenizing equal portions (visual) of each grab on a clean piece of plastic sheeting and transferring to glass containers with aluminum foil lined caps.

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Samples will be properly labeled and placed on ice immediately after collection.

Soil sample location will be accurately located on a map at time of sampling. A wooden stake with sample number written on it will be driven near the center of the area where the grabs were taken. Information on distance from stake to individual grab sites will be recorded.

F. BATHYMETRIC SURVEY

The bathymetric survey at French Limited will be made using a boat equipped with a Trisponder microwave navigation system interfaced with an Easterline-Angus data logger. The navigational equipment will continuously record the location of the boat while a fathometer records the depth of water and thickness of sludge beneath the craft. The combined input will be recorded on magnetic tape and a strip chart for back up. A single sludge core will be taken to calibrate the fathometer.

Figure 6-1 depicts the operation of the system, Figure 6-2 shows an example of the type of transects to be made, and Figure 6-3 is an example of the finished bathymetric contour map from a previous project.

G. FISH TISSUE

Fish samples will be collected from the surface water area beneath the U.S. 90 bridge just north of the site. An electroshocking unit will be run from the bank to retrieve fish from the pool. Three samples of fish tissue, each sample composited from one species, will be filleted and frozen for prompt shipment to the laboratory.

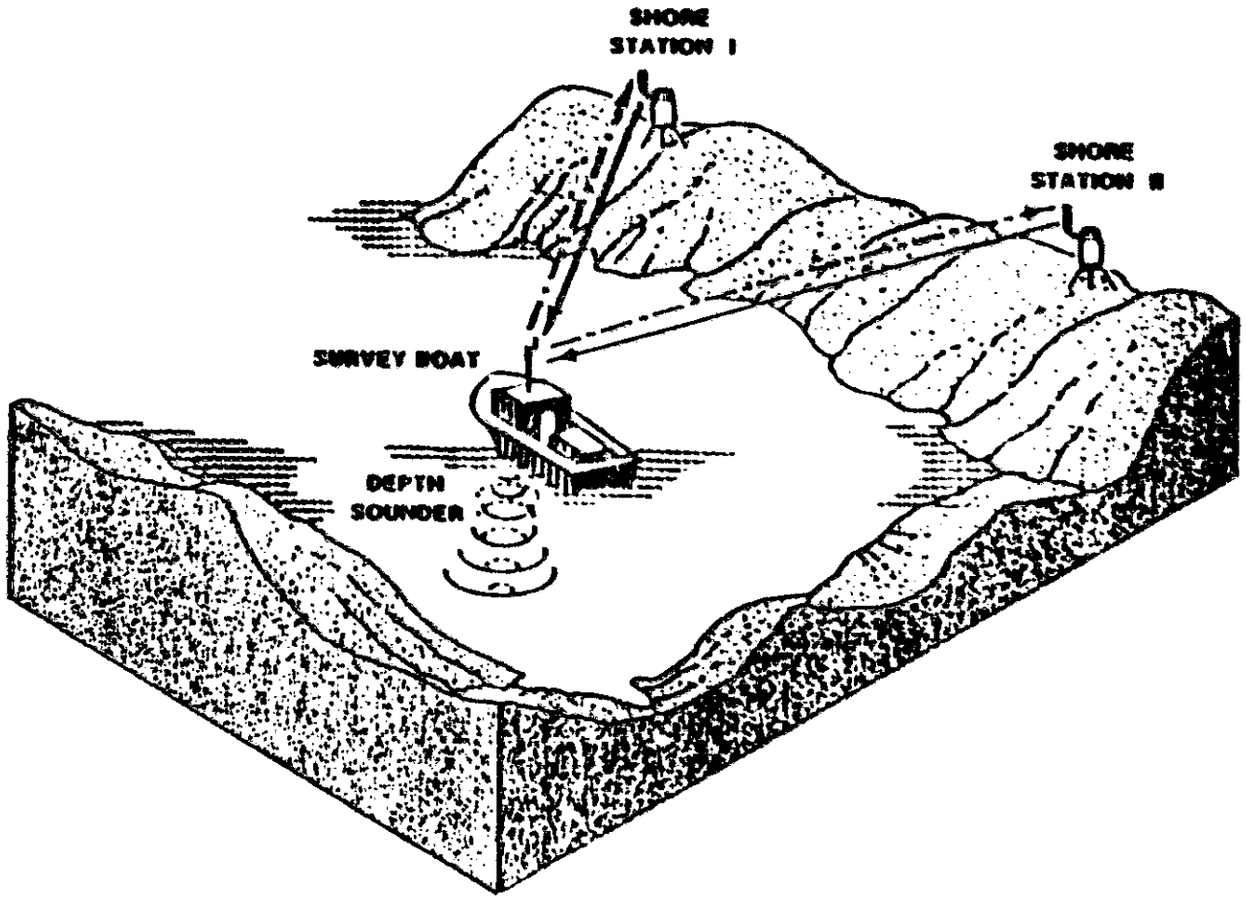

Figure 6-1. Operation of Bathymetric Survey System

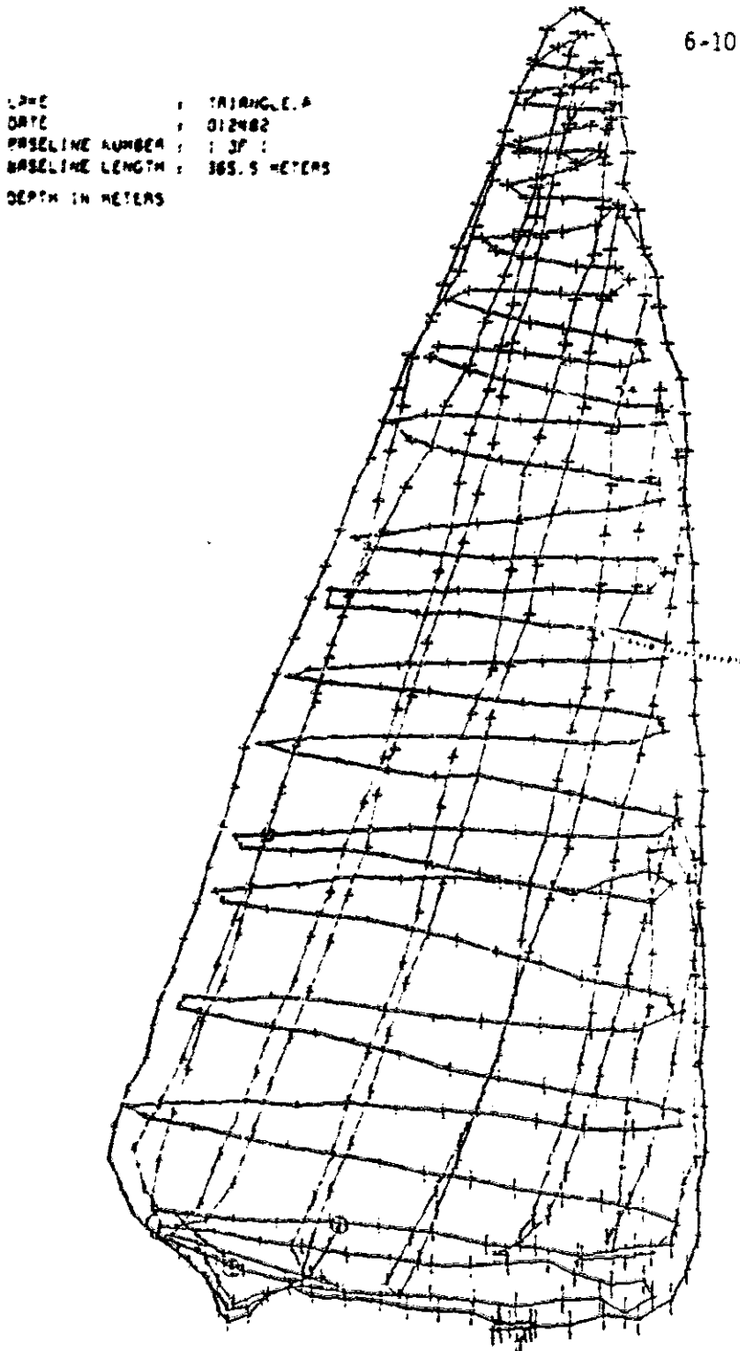

Figure 6-2. Example of Bathymetric Transects

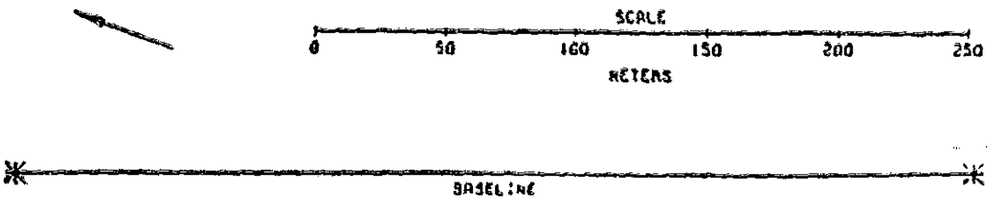

Figure 6-3. Example of Countour Map

A Scientific Collectors Permit will be obtained from the Texas Park and Wildlife Department prior to any fish collection.

Table N
French Limited Samples Analyses

Number of Stations: Analyses	Water					Solids						
	Ground Water 12		Surface Water 6		Total 18	Soil 6		Sediments 9		Fish 3		Total 18
	Station	Dup.	Station	Dup.		Station	Dup.	Station	Dup.	Station	Dup.	
pH	12	1	6	1	20	--	--	--	--	--	--	--
Conductivity	12	1	6	1	20	--	--	--	--	--	--	--
TOE	12	1	6	1	20	6	1	9	1	--	--	17
TOC	12	1	6	1	20	6	1	9	1			17
TOX	12	1	6	1	20	6	1	9	1			17
Metals-ICAP	5	1	3	0	9	4	0	4	1	3	0	12
Phenols	6	1	6	1	14	--	--	7	1	--	--	8
PCBs/Pesticides	5	1	5	0	11	4	1	7	1	3	0	16
GC/MS VOA	5	1	3	0	9	--	--	--	--	--	--	--
GC/MS B/N	6	1	3	0	10	4	0	4	1			9
GC/MS Acid	6	1	3	0	10	4	0	4	1			9

Source: ESE, 1983.

7.0 LABORATORY ANALYSIS

Samples will be analyzed for pH, conductivity, total organic extractables (TOE), total organic carbon (TOC), total organic halides (TOX), metals, phenols, polychlorinated biphenyls (PCBs)/pesticides, volatile organic acids (VOA), base neutrals (B/N), and acid extractables (acids). Summaries of the numbers of analyses by environmental media for each site are presented in Table 4. Table 5 summarizes the analytical methods which will be used for each of the parameters of interest. Copies of each of these methods can be seen in Appendix A. Table 6 lists the analytical holding times and preservatives which will be used for all ground waters and surface waters. Soils, sediments, sludges, and fish will be kept chilled at 4°C until analyzed. There are no required holding times for these matrices, but every effort will be made to extract the samples within 7 days for organic analysis.

<u>In situ</u> parameters, to include pH and conductivity, will be measured to give information as to the conditions of the area at the time of the sampling.

The analytical protocol will be directed towards screening to identify major organic compounds and metals. The screening procedure will include analyzing for TOE, TOC, TOX, metals, and phenols. TOE will be analyzed by freon extraction followed by infrared determination. TOC will be measured by the method of combustion using the Oceanography International Model 915A TOC analyzer. Metals analyses will be carried out on a Jarrel-Ash 1100 Simultaneous Inductively Coupled Argon Plasma Spectrometer (ICAP). This

Table 0
Analytical Methodology

Parameter	Method	Method Reference (Ground Water and Surface Water)	Method Reference (Sediments, Soil, Sludges, and Fish)
pH	Electrometric	1 (150.1)	Not Applicable
Conductivity	Wheatstone Bridge	1 (120.1)	Not Applicable
TOE	Spectrophotometric, Infrared	1 (413.2)	7 (739)
TOC	Combustion	1 (415.1)	1 (415.1)
TOX	Microcoulometric Titration	3 (450.1)	3 (450.1)
Metals	ICAP	2	2
Phenol	Spectrophotometric 4-AAP	1 (420.1)	7 (417)
PCB/pesticides	GC/EC	4 (608)	8
VOA	GCMS	5 (624)	6
B/N	GCMS	5 (625)	6
Acids	GCMS	5 (625)	6

1 Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, March 1979.
2 Federal Register, Vol. 44, No. 233, Monday, December 3, 1979, pp. 69559-69567.
3 EPA, EMSL, Cincinnati, Ohio, November 1980, Method 450.1.
4 EPA, EMSL, Cincinnati, Ohio, July 1982, Method 608.
5 Federal Register, Part III, December 3, 1979, pp. 69526-69552.
6 Extraction and Analysis of Priority Pollutants in Sediment and Soil, EPA, Athens, Georgia, November, 1981.
7 Chemistry Laboratory Manual for Sediment and Elutriate Testing, EPA-905/4-79-014, March 1979.
8 Interim Methods for the Sampling and Analysis of Priority Pollutants in Sediments and Fish Tissue, EPA, EMSL, Cincinnati, Ohio, 1977.

Source: ESE, 1983.

Table P
Analytical Holding Times and Preservatives

Parameter	Holding Time	Preservative
pH	6 hours	Determine onsite
Conductivity	24 hours	Cool, 4°C
TOE	28 days	Cool, 4°C H_2SO_4 pH <2
TOC	28 days	Cool, 4°C H_2SO_4 pH <2
TOX	7 days (until extraction) 30 days (after extraction)	Cool, 4°C
Metals	6 months except Hg 28 days	HNO_3 pH <2
Phenol	28 days	Cool, 4°C H_3PO_4 pH <4 1.0 g $CuSO_4$/L
PCB/Pesticides	7 days (until extraction) 30 days (after extraction)	Cool, 4°C
VOA	7 days (until extraction) 30 days (after extraction)	Cool, 4°C
B/N	7 days (until extraction) 30 days (after extraction)	Cool, 4°C
Acids	7 days (until extraction) 30 days (after extraction)	Cool, 4°C

Source: ESE, 1983.

procedure has the capability of analyzing up to 33 metals simultaneously on a sample. For the initial phase of the survey, the 13 metals listed in Table O will be determined by ICAP. Data for the additional 20 metals will be available for further waste characterization, if needed. Total phenols will be determined spectrophotometrically by the 4-aminoantipyrine (4-AAP) method. TOX will be determined by the microcoulometric-titration method using the Dohrman DX-20 TOX system. Detection limits for the above parameters in both liquid (ground water and surface water) and solid (sediment, soils, and fish) matrices are given in Table Q.

Selected samples will be analyzed by gas chromatography (GC) and gas chromatography/mass spectroscopy (GC/MS) for qualitative and quantitative identification. PCBs/pesticides will be analyzed by GC with electron capture detector. Detection limits for this method are summarized in Method 608, Organochlorine Pesticides and PCBs (see Appendix A). The GC/MS analysis will determine the organic compounds on the priority pollutant list. VOA, B/N, and acid compounds will be analyzed by GC/MS. Detection limits for these compounds are given in Federal Register Methods 624 and 625 (see Appendix A).

Table Q
Analytical Detection Limits

Parameter	Detection Limit Water	Detection Limit Soils, Sediments, and Fish
TOC	0.5 mg/L	500 mg/L
Phenol	5 ug/L	500 mg/kg
Silver	0.003 mg/L	0.3 mg/kg
Arsenic	0.05 mg/L	5.0 mg/kg
Beryllium	0.001 mg/L	0.1 mg/kg
Cadmium	0.002 mg/L	0.2 mg/kg
Chromium	0.005 mg/L	0.5 mg/kg
Copper	0.002 mg/L	0.2 mg/kg
Mercury	0.030 mg/L	3.0 mg/kg
Nickel	0.010 mg/L	1.0 mg/kg
Lead	0.025 mg/L	2.5 mg/kg
Selenium	0.05 mg/L	5.0 mg/kg
Antimony	0.05 mg/L	5.0 mg/kg
Thallium	0.05 mg/L	5.0 mg/kg
Zinc	0.004 mg/L	0.4 mg/kg
TOE	0.2 mg/L	650 mg/kg
TOX	5 ug/L	50 ug/kg

Source: ESE, 1983.

APPENDIX A

SAMPLING AND ANALYTICAL METHODS

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pH

Method 150.1 (Electrometric)

STORET NO.
Determined on site 00400
Laboratory 00403

1. Scope and Application
   1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes
2. Summary of Method
   2.1 The pH of a sample is determined electrometrically using either a glass electrode in combination with a reference potential or a combination electrode
3. Sample Handling and Preservation
   3.1 Samples should be analyzed as soon as possible preferably in the field at the time of sampling.
   3.2 High-purity waters and waters not at equilibrium with the atmosphere are subject to changes when exposed to the atmosphere, therefore the sample containers should be filled completely and kept sealed prior to analysis.
4. Interferences
   4.1 The glass electrode, in general, is not subject to solution interferences from color turbidity, colloidal matter, oxidants, reductants or high salinity.
   4.2 Sodium error at pH levels greater than 10 can be reduced or eliminated by using a "low sodium error" electrode.
   4.3 Coatings of oily material or particulate matter can impair electrode response. These coatings can usually be removed by gentle wiping or detergent washing, followed by distilled water rinsing. An additional treatment with hydrochloric acid (1 + 9) may be necessary to remove any remaining film.
   4.4 Temperature effects on the electrometric measurement of pH arise from two sources. The first is caused by the change in electrode output at various temperatures. This interference can be controlled with instruments having temperature compensation or by calibrating the electrode-instrument system at the temperature of the samples. The second source is the change of pH inherent in the sample at various temperatures. This error is sample dependent and cannot be controlled, it should therefore be noted by reporting both the pH and temperature at the time of analysis.
5. Apparatus
   5.1 pH Meter-laboratory or field model. A wide variety of instruments are commercially available with various specifications and optional equipment.

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5.2 Glass electrode.

5.3 Reference electrode—a calomel, silver-silver chloride or other reference electrode of constant potential may be used.

NOTE 1: Combination electrodes incorporating both measuring and reference functions are convenient to use and are available with solid, gel type filling materials that require minimal maintenance

5.4 Magnetic stirrer and Teflon-coated stirring bar.

5.5 Thermometer or temperature sensor for automatic compensation.

6. Reagents

6.1 Primary standard buffer salts are available from the National Bureau of Standards and should be used in situations where extreme accuracy is necessary.

6.1.1 Preparation of reference solutions from these salts require some special precautions and handling[1] such as low conductivity dilution water, drying ovens, and carbon dioxide free purge gas. These solutions should be replaced at least once each month.

6.2 Secondary standard buffers may be prepared from NBS salts or purchased as a solution from commercial vendors. Use of these commercially available solutions, that have been validated by comparison to NBS standards, are recommended for routine use.

7. Calibration

7.1 Because of the wide variety of pH meters and accessories, detailed operating procedures cannot be incorporated into this method. Each analyst must be acquainted with the operation of each system and familiar with all instrument functions. Special attention to care of the electrodes is recommended.

7.2 Each instrument/electrode system must be calibrated at a minimum of two points that bracket the expected pH of the samples and are approximately three pH units or more apart.

7.2.1 Various instrument designs may involve use of a "balance" or "standardize" dial and/or a slope adjustment as outlined in the manufacturer's instructions. Repeat adjustments on successive portions of the two buffer solutions as outlined in procedure 8.2 until readings are within 0.05 pH units of the buffer solution value.

8. Procedure

8.1 Standardize the meter and electrode system as outlined in Section 7.

8.2 Place the sample or buffer solution in a clean glass beaker using a sufficient volume to cover the sensing elements of the electrodes and to give adequate clearance for the magnetic stirring bar

8.2.1 If field measurements are being made the electrodes may be immersed directly in the sample stream to an adequate depth and moved in a manner to insure sufficient sample movement across the electrode sensing element as indicated by drift free (< 0.1 pH) readings.

8.3 If the sample temperature differs by more than 2°C from the buffer solution the measured pH values must be corrected. Instruments are equipped with automatic or manual

[1]National Bureau of Standards Special Publication 260.

compensators that electronically adjust for temperature differences. Refer to manufacturer's instructions.

8.4 After rinsing and gently wiping the electrodes, if necessary, immerse them into the sample beaker or sample stream and stir at a constant rate to provide homogeneity and suspension of solids. Rate of stirring should minimize the air transfer rate at the air water interface of the sample. Note and record sample pH and temperature. Repeat measurement on successive volumes of sample until values differ by less than 0.1 pH units. Two or three volume changes are usually sufficient.

9. Calculation

9.1 pH meters read directly in pH units. Report pH to the nearest 0.1 unit and temperature to the nearest °C.

10. Precision and Accuracy

10.1 Forty-four analysts in twenty laboratories analyzed six synthetic water samples containing exact increments of hydrogen-hydroxyl ions, with the following results:

pH Units	Standard Deviation pH Units	Accuracy as Bias, %	Accuracy as Bias, pH Units
3.5	0.10	-0.29	-0.01
3.5	0.11	-0.00	
7.1	0.20	+1.01	+0.07
7.2	0.18	-0.03	-0.002
8.0	0.13	-0.12	-0.01
8.0	0.12	+0.16	+0.01

(FWPCA Method Study 1, Mineral and Physical Analyses)

10.2 In a single laboratory (EMSL), using surface water samples at an average pH of 7.7, the standard deviation was ±0.1.

Bibliography

1. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 460, (1975).
2. Annual Book of ASTM Standards, Part 31, "Water", Standard D1293-65, p 178 (1976).

CONDUCTANCE

Method 120.1 (Specific Conductance, umhos at 25°C)

STORET NO. 00095

1. Scope and Application
   1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.
2. Summary of Method
   2.1 The specific conductance of a sample is measured by use of a self-contained conductivity meter, Wheatstone bridge-type, or equivalent.
   2.2 Samples are preferably analyzed at 25°C. If not, temperature corrections are made and results reported at 25°C.
3. Comments
   3.1 Instrument must be standardized with KCl solution before daily use.
   3.2 Conductivity cell must be kept clean.
   3.3 Field measurements with comparable instruments are reliable.
4. Precision and Accuracy
   4.1 Forty-one analysts in 17 laboratories analyzed six synthetic water samples containing increments of inorganic salts, with the following results:

Increment as Specific Conductance	Precision as Standard Deviation	Accuracy as Bias, %	Accuracy as Bias, umhos/cm
100	7.55	-2.02	-2.0
106	8.14	-0.76	-0.8
808	66.1	-3.63	-29.3
848	79.6	-4.54	-38.5
1640	106	-5.36	-87.9
1710	119	-5.08	-86.9

(FWPCA Method Study 1, Mineral and Physical Analyses.)

   4.2 In a single laboratory (EMSL) using surface water samples with an average conductivity of 536 umhos/cm at 25°C, the standard deviation was ±6.
5. References
   5.1 The procedure to be used for this determination is found in:
   Annual Book of ASTM Standards, Part 31, "Water", Standard D1125-64, p 120 (1976).
   Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 71, Method 205, (1975).

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OIL AND GREASE, TOTAL RECOVERABLE

Method 413.2 (Spectrophotometric, Infrared)

STORET NO. 00560

1. Scope and Application
   - 1.1 This method includes the measurement of fluorocarbon-113 extractable matter from surface and saline waters, industrial and domestic wastes. It is applicable to the determination of hydrocarbons, vegetable oils, animal fats, waxes, soaps, greases and related matter.
   - 1.2 The method is applicable to measurement of most light petroleum fuels, although loss of about half of any gasoline present during the extraction manipulations can be expected.
   - 1.3 The method covers the range from 0.2 to 1000 mg/l of extractable material.
   - 1.4 While this method can be used to obtain an estimate of the oil and grease that would be measured gravimetrically, in many cases the estimate more accurately describes the parameter, as it will measure volatiles more effectively and is not susceptible to interferences such as extractable sulfur. It can be used with the Petroleum Hydrocarbon procedure to obtain an oil and grease value and a petroleum hydrocarbon value on the same sample.
2. Summary of Method
   - 2.1 The sample is acidified to a low pH (< 2) and extracted with fluorocarbon-113. The oil and grease is determined by comparison of the infrared absorbance of the sample extract with standards.
3. Definitions
   - 3.1 The definition of oil and grease is based on the procedure used. The source of the oil and/or grease, and the presence of extractable non-oily matter will influence the material measured and interpretation of results.
4. Sampling and Storage
   - 4.1 A representative sample of 1 liter volume should be collected in a glass bottle. If analysis is to be delayed for more than a few hours, the sample is preserved by the addition of 5 ml HCl (6.1) at the time of collection and refrigerated at 4°C.
   - 4.2 Because losses of grease will occur on sampling equipment, the collection of a composite sample is impractical. Individual portions collected at prescribed time intervals must be analyzed separately to obtain the average concentration over an extended period.
5. Apparatus
   - 5.1 Separatory funnel, 2000 ml, with Teflon stopcock.
   - 5.2 Infrared spectrophotometer, scanning. Non-scanning instruments may also be used but can be subject to positive interferences in complex chemical wastewaters.
   - 5.3 Cells, 10 mm, 50 mm, and 100 mm path length, sodium chloride or infrared grade glass.
   - 5.4 Filter paper, Whatman No. 40, 11 cm.

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6. Reagents
   - 6.1 Hydrochloric acid, 1:1. Mix equal volumes of conc. HCl and distilled water.
   - 6.2 Fluorocarbon-113, (1,1,2-trichloro-1,2,2-trifluoroethane), b. p. 48°C.
   - 6.3 Sodium sulfate, anhydrous crystal.
   - 6.4 Calibration mixtures:
     - 6.4.1 Reference oil: Pipet 15.0 ml n-hexadecane, 15.0 ml isooctane, and 10.0 ml chlorobenzene into a 50 ml glass stoppered bottle. Maintain the integrity of the mixture by keeping stoppered except when withdrawing aliquots.
     - 6.4.2 Stock standard: Pipet 1.0 ml reference oil (6.4.1) into a tared 200 ml volumetric flask and immediately stopper. Weigh and dilute to volume with fluorocarbon-113.
     - 6.4.3 Working standards: Pipet appropriate volumes of stock standard (6.4.2) into 100 ml volumetric flasks according to the cell pathlength to be used. Dilute to volume with fluorocarbon-113. Calculate concentration of standards from the stock standard.

7. Procedure
   - 7.1 Mark the sample bottle at the water meniscus for later determination of sample volume. If the sample was not acidified at time of collection, add 5 ml hydrochloric acid (6.1) to the sample bottle. After mixing the sample, check the pH by touching pH-sensitive paper to the cap to insure that the pH is 2 or lower. Add more acid if necessary.
   - 7.2 Pour the sample into a separatory funnel.
   - 7.3 Add 30 ml fluorocarbon-113 (6.2) to the sample bottle and rotate the bottle to rinse the sides. Transfer the solvent into the separatory funnel. Extract by shaking vigorously for 2 minutes. Allow the layers to separate.
   - 7.4 Filter the solvent layer into a 100 ml volumetric flask through a funnel containing solvent-moistened filter paper.

     NOTE: An emulsion that fails to dissipate can be broken by pouring about 1 g sodium sulfate (6.3) into the filter paper cone and slowly draining the emulsion through the salt. Additional 1 g portions can be added to the cone as required.
   - 7.5 Repeat (7.3 and 7.4) twice more with 30 ml portions of fresh solvent, combining all solvent in the volumetric flask.
   - 7.6 Rinse the tip of the separatory funnel, filter paper, and the funnel with a total of 5–10 ml fluorocarbon-113 and collect the rinsings in the flask. Dilute the extract to 100 ml, and stopper the flask.
   - 7.7 Select appropriate working standards and cell pathlength according to the following table of approximate working ranges:

Pathlength	Range
10 mm	2–40 mg
50 mm	0.4–8 mg
100 mm	0.1–4 mg

   - 7.8 Scan standards and samples from 3200 cm^{-1} to 2700 cm^{-1} with fluorocarbon-113 in the reference beam and record the results on absorbance paper. The absorbances of samples

and standards are measured by constructing a straight baseline over the range of the scan and measuring the absorbance of the peak maximum at 2930 cm^{-1} and subtracting the baseline absorbance at that point. For an example of a typical oil spectrum and baseline construction, see Gruenfeld[3]. Non-scanning instruments should be operated according to manufacturer's instructions, although calibration must be performed using the standards described above (6.4). If the absorbance exceeds 0.8 for a sample, select a shorter pathlength or dilute as required.

7.9 Use a calibration plot of absorbance vs. mg oil prepared from the standards to determine the mg oil in the sample solution.

8. Calculation

8.1 mg/l total oil and grease $= \frac{R \times D}{V}$

where:

R = oil in solution, determined from calibration plot, in milligrams.
D = extract dilution factor, if used.
V = volume of sample, determined by refilling sample bottle to calibration line and correcting for acid addition if necessary, in liters.

9. Precision and Accuracy

9.1 The two oil and grease methods in this manual were tested by a single laboratory (EMSL) on sewage. This method determined the oil and grease level in the sewage to be 17.5 mg/l. When 1 liter portions of the sewage were dosed with 14.0 mg of a mixture of #2 fuel oil and Wesson oil, the recovery was 99% with a standard deviation of ±1.4 mg/l.

Bibliography

1. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 516, Method 502B, (1975).
2. American Petroleum Institute, "Manual on Disposal of Refinery Wastes", Vol. IV, Method 733-58 (1958).
3. Gruenfeld, M., "Extraction of Dispersed Oils from Water for Quantitative Analysis by Infrared Spectroscopy", Environ. Sci. Technol. 7, 636 (1973).

Analysis of Sediments and Other Solids for Oil and Grease
CRL Method Number 739

Scope and Application

This method is applicable to the measurement of freon extractable matter from sediments, sludges and other solids which contain relatively non-volatile hydrocarbons, vegetable oils, animal fats, soaps, waxes, greases and related compounds.

This method is not applicable to the measurement of light hydrocarbons that volatilize at temperatures below 70°C. Petroleum fuels from gasoline through #2 fuel oil are completely or substantially lost in the solvent extraction process.

This method is applicable in the range from 650 mg/kg to 100,000 mg/kg.

Summary of Method

The acidified sediment or solid sample is dried with magnesium sulfate monohydrate (avoid heating, which gives low results) and extracted with freon in a soxhlet apparatus for 4 hours.

Equipment

Extraction apparatus, soxhlet.
Vacuum pump or other source of vacuum.
Extraction thimble, paper.

Reagents

a. Hydrochloric acid, HCl, conc.
b. Magnesium sulfate monohydrate: Prepare $MgSO_4H_2O$ overnight
c. Freon (1,1,2-trichloro-1,2,2,-trifluoroethan), boiling point 47°C. The solvent should leave no measurable residue on evaporation; distill if necessary.
d. Grease-free cotton: Extract non-absorbent cotton with freon.

Procedure

In a 150 ml beaker weigh a sample of wet sludge, 20 ± 0.5 g of which the dry-solids content is known. Acidify to pH 2.0 (generally, 0.3 ml conc HCl is sufficient). Add 25 g $MgSO_4H_2O$. Stir to a smooth paste and spread on the sides of the beaker to facilitate subsequent removal. Allow to stand until solidified, 15 to 30 min. Remove the solids and grind in a porcelain mortar. Add the powder to a paper extraction thimble. Wipe the beaker and mortar with small pieces of filter paper moistened with freon and add to the

thimble. Fill the thimble with glass wool or small glass beads. Extract in a Soxhlet apparatus, using freon, at a rate of 20 cycles/hr for 4 hours. If any turbidity of suspended matter is present in the extraction flask, remove by filtering through grease-free cotton into another weighed flask. Rinse flask and cotton with freon. Distill the solvent from the extraction flask in water at 70°C. Place the flask on a warm steam bath for 15 minutes and draw air through the flask by means of an applied vacuum for the final one minute. Cool in a desiccator for exactly 30 minutes and weigh.

Quality Control

One blank and one duplicate of one of the sediments are analyzed with each group of samples. If twenty or more samples are analyzed, a minimum of two duplicates are analyzed.

The analytical balance is calibrated and set at zero before each sample is weighed.

Calculations

Grease and oil as % dry solids

$$= \frac{\text{gain in weight of flask, g} \times 100}{\text{wt. of wet solids, g} \times \% \text{ dry solids}}$$

REFERENCES

1. Standard Methods for the Examination of Water and Wastes, 14th ed., 1975 APHA-AWWA-WPCF, pp. 519-520.

2. EPA Manual, "Methods for Chemical Analysis of Water and Wastes" 1974 Office of Technology Transfer, Wash., D.C., pp. 226-228.

ORGANIC CARBON, TOTAL

Method 415.1 (Combustion or Oxidation)

STORET NO. Total 00680
Dissolved 00681

1. Scope and Application
   1.1 This method includes the measurement of organic carbon in drinking, surface and saline waters, domestic and industrial wastes. Exclusions are noted under Definitions and Interferences.
   1.2 The method is most applicable to measurement of organic carbon above 1 mg/1.
2. Summary of Method
   2.1 Organic carbon in a sample is converted to carbon dioxide (CO_2) by catalytic combustion or wet chemical oxidation. The CO_2 formed can be measured directly by an infrared detector or converted to methane (CH_4) and measured by a flame ionization detector. The amount of CO_2 or CH_4 is directly proportional to the concentration of carbonaceous material in the sample.
3. Definitions
   3.1 The carbonaceous analyzer measures all of the carbon in a sample. Because of various properties of carbon-containing compounds in liquid samples, preliminary treatment of the sample prior to analysis dictates the definition of the carbon as it is measured. Forms of carbon that are measured by the method are:
      A) soluble, nonvolatile organic carbon; for instance, natural sugars.
      B) soluble, volatile organic carbon; for instance, mercaptans.
      C) insoluble, partially volatile carbon; for instance, oils.
      D) insoluble, particulate carbonaceous materials, for instance; cellulose fibers.
      E) soluble or insoluble carbonaceous materials adsorbed or entrapped on insoluble inorganic suspended matter; for instance, oily matter adsorbed on silt particles.
   3.2 The final usefulness of the carbon measurement is in assessing the potential oxygen-demanding load of organic material on a receiving stream. This statement applies whether the carbon measurement is made on a sewage plant effluent, industrial waste, or on water taken directly from the stream. In this light, carbonate and bicarbonate carbon are not a part of the oxygen demand in the stream and therefore should be discounted in the final calculation or removed prior to analysis. The manner of preliminary treatment of the sample and instrument settings defines the types of carbon which are measured. Instrument manufacturer's instructions should be followed.

Approved for NPDES
Issued 1971
Editorial revision 1974

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4. Sample Handling and Preservation

4.1 Sampling and storage of samples in glass bottles is preferable. Sampling and storage in plastic bottles such as conventional polyethylene and cubitainers is permissible if it is established that the containers do not contribute contaminating organics to the samples.
NOTE 1: A brief study performed in the EPA Laboratory indicated that distilled water stored in new, one quart cubitainers did not show any increase in organic carbon after two weeks exposure.

4.2 Because of the possibility of oxidation or bacterial decomposition of some components of aqueous samples, the lapse of time between collection of samples and start of analysis should be kept to a minimum. Also, samples should be kept cool (4°C) and protected from sunlight and atmospheric oxygen.

4.3 In instances where analysis cannot be performed within two hours (2 hours) from time of sampling, the sample is acidified (pH $\leq$ 2) with HCl or H_2SO_4.

5. Interferences

5.1 Carbonate and bicarbonate carbon represent an interference under the terms of this test and must be removed or accounted for in the final calculation.

5.2 This procedure is applicable only to homogeneous samples which can be injected into the apparatus reproducibly by means of a microliter type syringe or pipette. The openings of the syringe or pipette limit the maximum size of particles which may be included in the sample.

6. Apparatus

6.1 Apparatus for blending or homogenizing samples: Generally, a Waring-type blender is satisfactory.

6.2 Apparatus for total and dissolved organic carbon:

6.2.1 A number of companies manufacture systems for measuring carbonaceous material in liquid samples. Considerations should be made as to the types of samples to be analyzed, the expected concentration range, and forms of carbon to be measured.

6.2.2 No specific analyzer is recommended as superior.

7. Reagents

7.1 Distilled water used in preparation of standards and for dilution of samples should be ultra pure to reduce the carbon concentration of the blank. Carbon dioxide-free, double distilled water is recommended. Ion exchanged waters are not recommended because of the possibilities of contamination with organic materials from the resins.

7.2 Potassium hydrogen phthalate, stock solution, 1000 mg carbon/liter: Dissolve 0.2128 g of potassium hydrogen phthalate (Primary Standard Grade) in distilled water and dilute to 100.0 ml.
NOTE 2: Sodium oxalate and acetic acid are not recommended as stock solutions.

7.3 Potassium hydrogen phthalate, standard solutions: Prepare standard solutions from the stock solution by dilution with distilled water.

7.4 Carbonate-bicarbonate, stock solution, 1000 mg carbon/liter: Weigh 0.3500 g of sodium bicarbonate and 0.4418 g of sodium carbonate and transfer both to the same 100 ml volumetric flask. Dissolve with distilled water.

7.5 Carbonate-bicarbonate, standard solution: Prepare a series of standards similar to step 7.3.

NOTE 3: This standard is not required by some instruments.

7.6 Blank solution: Use the same distilled water (or similar quality water) used for the preparation of the standard solutions.

8. Procedure

8.1 Follow instrument manufacturer's instructions for calibration, procedure, and calculation

8.2 For calibration of the instrument, it is recommended that a series of standards encompassing the expected concentration range of the samples be used.

9. Precision and Accuracy

9.1 Twenty-eight analysts in twenty-one laboratories analyzed distilled water solutions containing exact increments of oxidizable organic compounds, with the following results:

Increment as TOC mg/liter	Precision as Standard Deviation TOC, mg/liter	Accuracy as Bias, %	Accuracy as Bias, mg/liter
4.9	3.93	+15.27	+0.75
107	8.32	+ 1.01	+1.08

(FWPCA Method Study 3, Demand Analyses)

Bibliography

1. Annual Book of ASTM Standards, Part 31, "Water", Standard D 2574-79, p 469 (1976).
2. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 532, Method 505, (1975).

TOTAL ORGANIC HALIDE

Method 450.1

Interim

U S. Environmental Protection Agency
Office of Research and Development
Environmental Monitoring and Support Laboratory
Physical and Chemical Methods Branch
Cincinnati, Ohio 45268

November 1980

TOTAL ORGANIC HALIDE

Method 450.1

1. Scope and Application

1.1 This method is to be used for the determination of Total Organic Halides as Cl^- by carbon adsorption, and requires that all samples be run in duplicate. Under conditions of duplicate analysis, the reliable limit of sensitivity is 5 ug/L. Organic halides as used in this method are defined as all organic species containing chlorine, bromine and iodine that are adsorbed by granular activated carbon under the conditions of the method. Fluorine containing species are not determined by this method.

1.2 This is a microcoulometric-titration detection method applicable to the determination of the compound class listed above in drinking and ground waters, as provided under 40 CFR 265.92.

1.3 Any modification of this method, beyond those expressly permitted, shall be considered as major modifications subject to application and approval of alternate test procedures under 40 CFR 260.21.

1.4 This method is restricted to use by, or under the supervision of, analysts experienced in the operation of a pyrolysis/microcolumeter and in the interpretation of the results.

2. Summary of Method

2.1 A sample of water that has been protected against the loss of volatiles by the elimination of headspace in the sampling container, and is free of undissolved solids, is passed through a column containing 40 mg of activated carbon. The column is washed

to remove any trapped inorganic halides, and is then pyrolyzed to convert the adsorbed organohalides to a titratable species that can be measured by a microcoulometric detector.

3. Interferences

3.1 Method interferences may be caused by contaminants, reagents, glassware, and other sample processing hardware. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running method blanks.

3.1.1 Glassware must be scrupulously cleaned. Clean all glassware as soon as possible after use by treating with chromate cleaning solution. This should be followed by detergent washing in hot water. Rinse with tap water and distilled water, drain dry, and heat in a muffle furnace at 400°C for 15 to 30 minutes. Volumetric ware should not be heated in a muffle furnace. Glassware should be sealed and stored in a clean environment after drying and cooling, to prevent any accumulation of dust or other contaminants.

3.1.2 The use of high purity reagents and gases help to minimize interference problems.

3.2 Purity of the activated carbon must be verified before use. Only carbon samples which register less than 1000 ng/40 mg should be used. The stock of activated carbon should be stored in its granular form in a glass container with a Teflon seal. Exposure to the air must be minimized, especially during and after milling and sieving the activated carbon. No more than a two-week supply

should be prepared in advance. Protect carbon at all times from all sources of halogenated organic vapors. Store prepared carbon and packed columns in glass containers with Teflon seals.

3.3 This method is applicable to samples whose inorganic-halide concentration does not exceed the organic-halide concentration by more than 2000 times.

4. Safety

The toxicity or carcinogenicity of each reagent in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current-awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material-handling data sheets should also be made available to all personnel involved in the chemical analysis.

5. Apparatus and Materials (All specifications are suggested. Catalog numbers are included for illustration only).

5.1 Sampling equipment, for discrete or composite sampling

5.1.1 Grab-sample bottle - Amber glass, 250-mL, fitted with Teflon-lined caps. Foil may be substituted for Teflon if the sample is not corrosive. If amber bottles are not available, protect samples from light. The container must be washed and muffled at 400°C before use, to minimize contamination.

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5.2 Adsorption System

5.2.1 Dohrmann Adsorption Module (AD-2), or equivalent, pressurized, sample and nitrate-wash reservoirs.

5.2.2 Adsorption columns - pyrex, 5 cm long X 6-mm OD X 2-mm ID.

5.2.3 Granular Activated Carbon (GAC) - Filtrasorb-400, Calgon-APC, or equivalent, ground or milled, and screened to a 100/200 mesh range. Upon combustion of 40 mg of GAC, the apparent-halide background should be 1000-mg Cl^- equivalent or less.

5.2.4 Cerafelt (available from Johns-Manville), or equivalent - Form this material into plugs using a 2-mm ID stainless-steel borer with ejection rod (available from Dohrmann) to hold 40 mg of GAC in the adsorption columns. CAUTION: Do not touch this material with your fingers.

5.2.5 Column holders (available from Dohrman).

5.2.6 Volumetric flasks - 100-mL, 50-mL.

A general schematic of the adsorption system is shown in Figure 1.

5.3 Dohrmann microcoulometric-titration system (MCTS-20 or DX-20), or equivalent, containing the following components:

5.3.1 Boat sampler.

5.3.2 Pyrolysis furnace.

5.3.3 Microcoulometer with integrator.

5.3.4 Titration cell.

A general description of the analytical system is shown in Figure 2.

5.4 Strip-Chart Recorder.

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6. Reagents

6.1 Sodium sulfite - 0.1 N, ACS reagent grade (12.6 g/L).

6.2 Nitric acid - concentrated.

6.3 Nitrate-Wash Solution (5000 mg NO_3^-/L) - Prepare a nitrate-wash solution by transferring approximately 8.2 gm of potassium nitrate into a 1-litre volumetric flask and diluting to volume with reagent water.

6.4 Carbon dioxide - gas, 99.9% purity.

6.5 Oxygen - 99.9% purity.

6.6 Nitrogen - prepurified.

6.7 70% Acetic acid in water - Dilute 7 volumes of acetic acid with 3 volumes of water.

6.8 Trichlorophenol solution, stock (1 µL = 10 µg Cl^-) - Prepare a stock solution by weighing accurately 1.856 gm of trichlorophenol into a 100-mL volumetric flask. Dilute to volume with methanol.

6.9 Trichlorophenol solution, calibration (1 µL = 500 ng Cl^-) - Dilute 5 mL of the trichlorophenol stock solution to 100 mL with methanol.

6.10 Trichlorophenol standard, instrument-calibration - First, nitrate wash a single column packed with 40 mg of activated carbon as instructed for sample analysis, and then inject the column with 10 µL of the calibration solution.

6.11 Trichlorophenol standard, adsorption-efficiency (100 µg Cl^-/L) - Prepare a adsorption-efficiency standard by injecting 10 µL of stock solution into 1 liter of reagent water.

6.12 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.

6.13 Blank standard - The reagent water used to prepare the calibration standard should be used as the blank standard.

7. Calibration

7.1 Check the adsorption efficiency of each newly-prepared batch of carbon by analyzing 100 mL of the adsorption-efficiency standard, in duplicate, along with duplicates of the blank standard. The net recovery should be within 5% of the standard value.

7.2 Nitrate-wash blanks (Method Blanks) - Establish the repeatability of the method background each day by first analyzing several nitrate-wash blanks. Monitor this background by spacing nitrate-wash blanks between each group of eight pyrolysis determinations.

7.2.1 The nitrate-wash blank values are obtained on single columns packed with 40 mg of activated carbon. Wash with the nitrate solution as instructed for sample analysis, and then pyrolyze the carbon.

7.3 Pyrolyze duplicate instrument-calibration standards and the blank standard each day before beginning sample analysis. The net response to the calibration-standard should be within 3% of the calibration-standard value. Repeat analysis of the instrument-calibration standard after each group of eight pyrolysis determinations, and before resuming sample analysis after cleaning or reconditioning the titration cell or pyrolysis system.

8. Sample Preparation

8.1 Special care should be taken in the handling of the sample to

minimize the loss of volatile organohalides. The adsorption procedure should be performed simultaneously on duplicates.

8.2 Reduce residual chlorine by the addition of sulfite (1 mL of 0.1 M per liter of sample). Addition of sulfite should be done at the time of sampling if the analysis is meant to determine the TOX concentration at the time of sampling. It should be recognized that TOX may increase on storage of the sample. Samples should be stored at 4°C without headspace.

8.3 Adjust pH of the sample to approximately 2 with concentrated HNO_3 just prior to adding the sample to the reservoir.

9. Adsorption Procedure

9.1 Connect two columns in series, each containing 40 mg of 100/200-mesh activated carbon.

9.2 Fill the sample reservoir, and pass a metered amount of sample through the activated-carbon columns at a rate of approximately 3 mL/min. NOTE: 100 mL of sample is the preferred volume for concentrations of TOX between 5 and 500 ug/L; 50 mL for 501 to 1000 ug/L, and 25 mL for 1001 to 2000 ug/L.

9.3 Wash the columns-in-series with 2 mL of the 5000-mg/L nitrate solution at a rate of approximately 2 mL/min to displace inorganic chloride ions.

10. Pyrolysis Procedure

10.1 The contents of each column is pyrolyzed separately. After rinsing with the nitrate solution, the columns should be protected from the atmosphere and other sources of contamination until ready for further analysis.

10.2 Pyrolysis of the sample is accomplished in two stages. The volatile components are pyrolyzed in a CO_2-rich atmosphere at a low temperature to assure the conversion of brominated trihalomethanes to a titratable species. The less volatile components are then pyrolyzed at a high temperature in an O_2-rich atmosphere.

NOTE: The quartz sampling boat should have been previously muffled at 600°C for at least 2 to 4 minutes as in a previous analysis, and should be cleaned of any residue by vacuuming.

10.3 Transfer the contents of each column to the quartz boat for individual analysis.

10.4 If the Dohrmann MC-1 is used for pyrolysis, manual instructions are followed for gas flow regulation. If the MCT-20 is used, the information on the diagram in Figure 3 is used for gas flow regulation.

10.5 Position the sample for 2 minutes in the 200°C zone of the pyrolysis tube. For the MCTS-20, the boat is positioned just outside the furnace entrance.

10.6 After 2 minutes, advance the boat into the 800°C zone (center) of the pyrolysis furnace. This second and final stage of pyrolysis may require from 6 to 10 minutes to complete.

11. Detection

The effluent gases are directly analyzed in the microcoulometric-titration cell. Carefully follow manual instructions for optimizing cell performance.

12. Breakthrough

Because the background bias can be of such an unpredictable nature, it can be especially difficult to recognize the extent of breakthrough of organohalides from one column to another. All second-column measurements for a properly operating system should not exceed 10-percent of the two-column total measurement. If the 10-percent figure is exceeded, one of three events can have happened. Either the first column was overloaded and a legitimate measure of breakthrough was obtained - in which case taking a smaller sample may be necessary; or channeling or some other failure occurred - in which case the sample may need to be rerun; or a high, random, bias occurred and the result should be rejected and the sample rerun. Because knowing which event has occurred may not be possible, a sample analysis should be repeated often enough to gain confidence in results. As a general rule, any analyses that is rejected should be repeated whenever sample is available. In the event that the second-column measurement is equal to or less than the nitrate-wash blank value, the second-column value should be disregarded.

13. Quality Control

13.1 Before performing any analyses, the analyst must demonstrate the ability to generate acceptable accuracy and precision with this procedure by the analysis of appropriate quality-control check samples.

13.2 The laboratory must develop and maintain a statement of method accuracy for their laboratory. The laboratory should update the accuracy statement regularly as new recovery measurements are made.

13.3 It is recommended that the laboratory adopt additional quality-assurance practices for use with this method. The specific practices that would be most productive will depend upon the needs of the laboratory and the nature of the samples. Field duplicates may be analyzed to monitor the precision of the sampling technique. Whenever possible, the laboratory should perform analysis of standard reference materials and participate in relevant performance-evaluation studies.

14. Calculations

OX as Cl^- is calculated using the following formula:

$$1000 \times \frac{(C_1 - C_3) + (C_2 - C_3)}{V} = \text{ug/L Total Organic Halide}$$

where:

C_1 = ug Cl^- on the first column in series

C_2 = ug Cl^- on the second column in series

C_3 = predetermined, daily, average, method-blank value (nitrate-wash blank for a 40-mg carbon column)

V = the sample volume in mL

15. Accuracy and Precision

These procedures have been applied to a large number of drinking-water samples. The results of these analysis are summarized in Tables I and II.

16. Reference

Dressman, R., Najar, G., Redzikowski, R., paper presented at the Proceedings of the American Water Works Association Water Quality Technology Conference, Philadelphia, Dec. 1979.

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TABLE I

PRECISION AND ACCURACY DATA FOR MODEL COMPOUNDS

Model Compound	Dose ug/L	Dose as ug/L Cl	Average % Recovery	Standard Deviation	No. of Replicates
$CHCl_3$	98	88	89	14	10
$CHBrCl_2$	160	106	98	9	11
$CHBr_2Cl$	155	79	86	11	13
$CHBr_3$	160	67	111	8	11
Pentachlorophenol	120	80	93	9	7

TABLE II

PRECISION DATA ON TAP WATER ANALYSIS

Sample	Avg. halide ug Cl/L	Standard Deviation	No. of Replicates
A	71	4.3	8
B	94	7.0	6
C	191	6.1	4

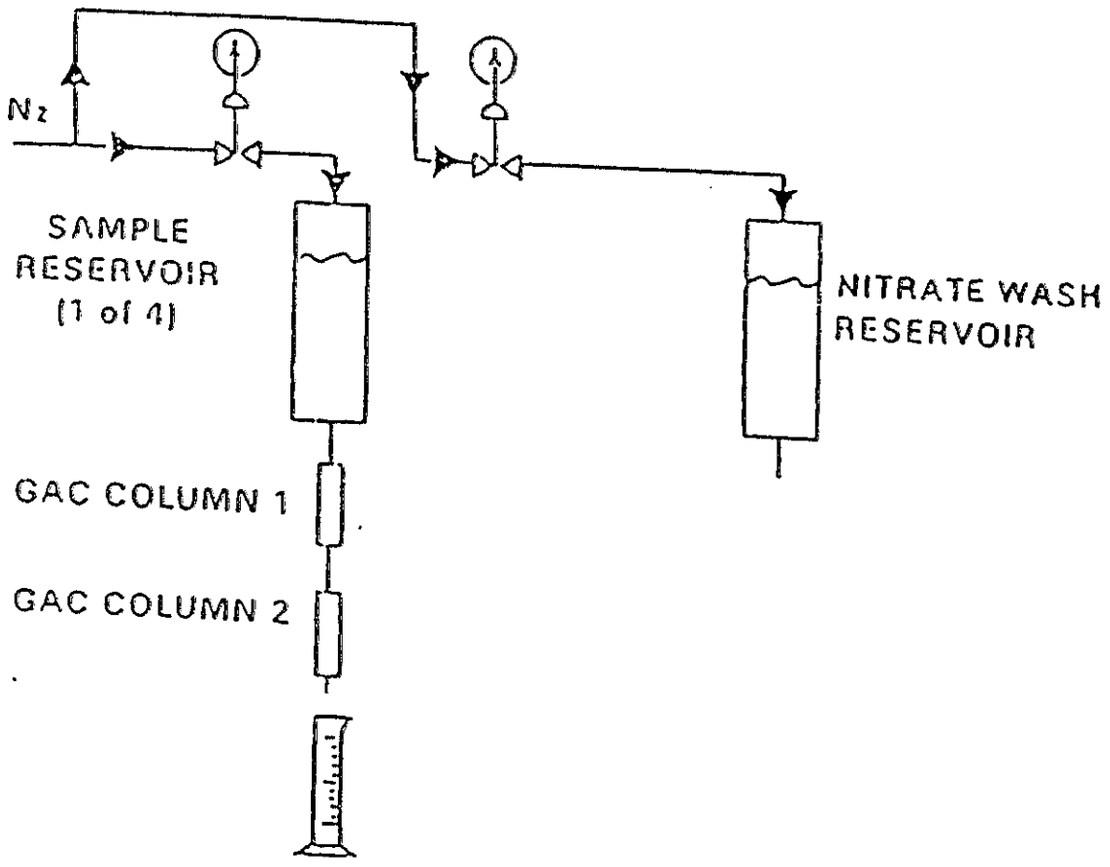

Figure 1. Adsorption Schematic

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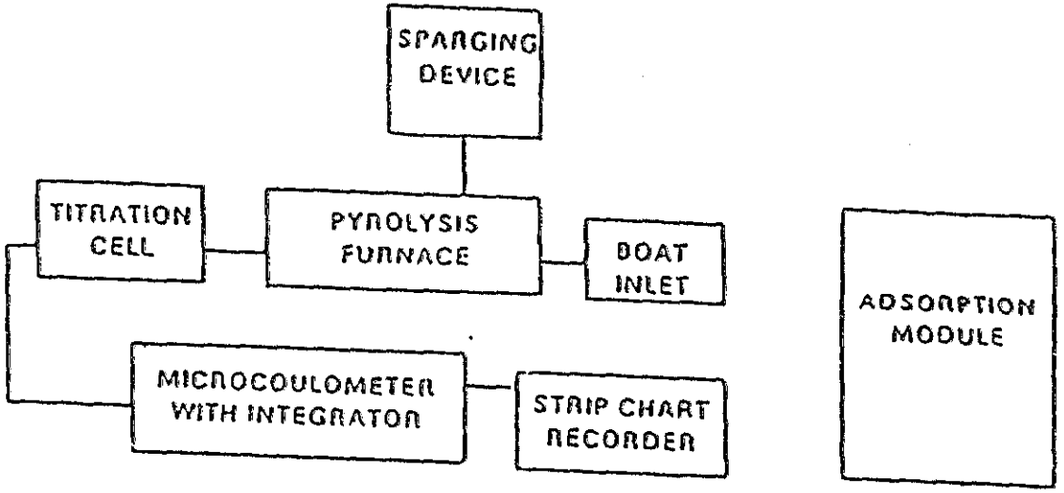

Figure 2. CAOX Analysis System Schematic

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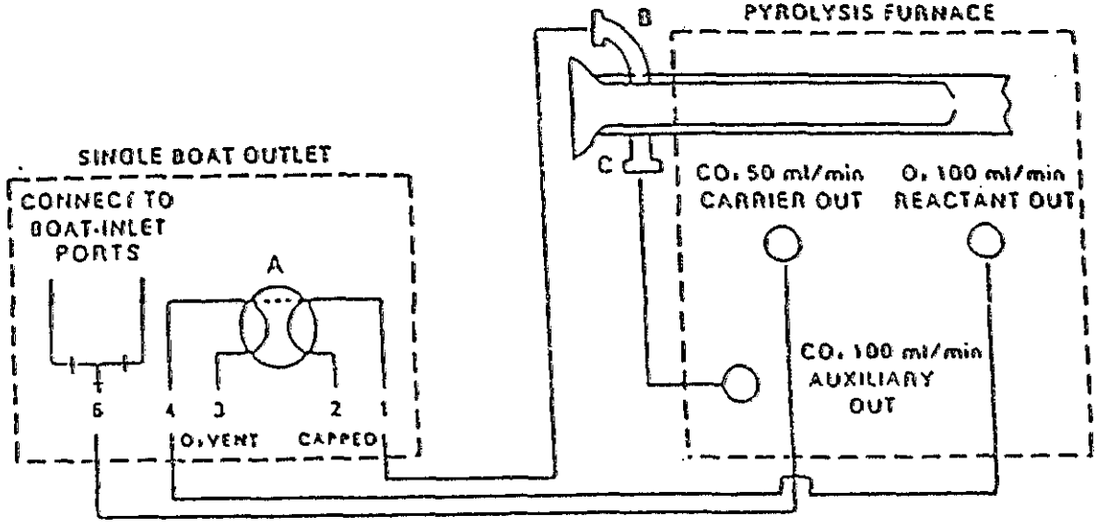

Figure 3. Rear view plumbing schematic for MCTS-20 system. Valve A is set for first-stage combustion. O_2 venting (push/pull valve out). Port B enters inner combustion tube; Port C enters outer combustion tube.

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The following is an example of the results for samples 2 to 30 of a 30 sample study:

Pollutant (µg/l)		Surrogate standard (µg/l)			
Sample	Found	Added	Found	Percent recovery	
2	14	100	80	80	
3	15	100	88	88	
4	20	100	100	100	
5	21	100	107	107	
6	17	100	109	109	
7	16	100	100	100	Update recovery for 8S.*
8	16	100	75	75	Not acceptable, disregard results.
9	14	100	82	82	
10	13	100	83	83	
11	12	100	97	94	Update recovery for 8S.**
12	20	100	85	85	
30	15	100	85	85	Give final statistic on recovery of 8S.

*Includes 28 results, 12 validation, 3 first day and days 2 through 6. Mean = 99. Std. Dev. = 4.8. Acceptable range 85–113%.
**Includes 26 results; day 5 result not included. Mean = 96. Std. Dev. = 4.8. Acceptable range 84–112%.

Appendix IV—Inductively Coupled Plasma Optical Emission Spectrometric Method (ICP) for Trace Element Analysis of Water and Wastes

Inductively Coupled Plasma (ICP) Optical Emission Spectrometric Method for Trace Element Analysis of Water and Wastes

Interim

Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268

October 1978

Foreword

This method has been prepared by the staff of the Environmental Monitoring and Support Laboratory—Cincinnati, with the cooperation of the EPA-ICP Users Group. Their cooperation and support is gratefully acknowledged.

This method represents the current state-of-the-art but as time progresses, improvements are anticipated. Users are encouraged to identify problems and assist in updating the method by contacting the Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268.

Inductively Coupled Plasma (ICP) Optical Emission Spectrometric Method for Trace Element Analysis of Water and Wastes

1. Scope and Application.

1.1 This method may be used for the determination of dissolved, suspended, or total elements in surface water, drinking water, and domestic and industrial wastewaters.

1.2 Dissolved elements are determined in filtered and acidified samples. Appropriate steps must be taken to ensure that potential interference are taken into account when dissolved solids exceed 1500 mg/l. (See 4.2)

1.3 Total elements are determined after appropriate digestion procedures are performed. Since digestion techniques increase the dissolved solids content of the samples, appropriate steps must be taken to correct for potential interference effects.

1.4 Table 1 lists elements for which this method applies along with recommended wavelengths and typical estimated instrumental detection limits. Actual working detection limits are sample dependent and as the sample matrix varies, these concentrations may also vary. In time, other elements may be added as more information becomes available.

1.5 Because of the differences between various makes and models of satisfactory instruments, no detailed instrumental operating instructions can be provided. Instead, the analyst is referred to the instructions provided by the manufacturer of the particular instrument.

Table 1—*Recommended Wavelengths* [1] *and Estimated Instrumental Detection Limits*

Element	Wavelength, nm	Estimated detection limit, µg/l [2]
Aluminum	308.2	40
Arsenic	193.7	53
Barium	455.5	2
Beryllium	313.0	0.3
Boron	249.8	5
Cadmium	226.5	4
Calcium	317.9	10
Chromium	267.7	7
Cobalt	228.6	7
Copper	324.7	6
Iron	259.9	7
Lead	220.3	42
Lithium	670.7	4
Magnesium	279.1	30
Manganese	257.6	2

Table 1—*Recommended Wavelengths* [1] *and Estimated Instrumental Detection Limits*—Continued

Element	Wavelength, nm	Estimated detection limit, µg/l [2]
Molybdenum	202.0	9
Nickel	231.6	15
Potassium	766.5	300 [3]
Selenium	196.0	75
Silica (SiO_2)	288.1	57
Silver	328.0	7
Sodium	589.6	53
Strontium	407.7	0.5
Vanadium	292.4	8
Zinc	213.8	2

[1] The wavelengths listed are recommended because of their sensitivity and overall acceptance. Other wavelengths may be substituted if they can provide the required sensitivity and are treated with the same correction techniques to spectral interference. (See 4.1.1).

[2] The estimated instrumental detection limits as listed are taken from "Inductively Coupled Plasma-Optical Emission Spectroscopy Preliminary Limits," EPA-600/4-79-017. Detection limits are sample dependent and as the sample matrix varies, these concentration values may also vary.

[3] Highly dependent on operating conditions and plasma position.

2. Summary of Method.

2.1 The method describes a technique for the simultaneous or sequential multielement determination of trace elements in solution. The basis of the method is the measurement of atomic emission by an optical spectroscopic technique. Samples are nebulized and the aerosol that is produced is transported to the plasma torch where excitation occurs. Characteristic atomic-line emission spectra are produced by a radio-frequency inductively coupled plasma (ICP). The spectra are dispersed by a grating spectrometer and the intensities of the lines are monitored by photomultiplier tubes. The photocurrents from the photomultiplier tubes are processed and controlled by a computer system. A background correction technique is required to compensate for variable background contribution to the determination of trace elements. Background must be measured adjacent to analyte lines on samples during analysis. Additional interferences named in 4.1 should also be recognized and appropriate corrections made.

3. Definitions.

3.1 *Dissolved*—Those elements which will pass through a 0.45 µm membrane filter.

3.2 *Suspended*—Those elements which are retained by a 0.45 µm membrane filter.

3.3 *Total*—The concentration determined on an unfiltered sample following vigorous digestion (Section 8.3), or the sum of the dissolved plus suspended concentrations (Section 8.1 plus 8.2).

3.4 *Total recoverable*—The concentration determined on an

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[illegible] with hot, dilute mineral acid (Section 9.1).

3.5 *Instrumental detection limit*—The concentration equivalent to a signal, due to the analyte, which is equal to three times the standard deviation of a series of ten replicate measurements of a reagent blank signal at the same wavelength.

3.6 *Sensitivity*—The slope of the analytical curve, i.e. functional relationship between emission intensity and concentration.

3.7 *Instrument check standard*—A multielement standard of known concentrations prepared by the analyst. Should be included in the analytical scheme with a frequency of 10%. (See 8.5.1.)

3.8 *Reference standard*—A solution obtained from an outside source having known, verified values. Must be used initially to verify the calibration standards and analyzed thereafter as a blind sample on a weekly frequency. (See 8.5.2.)

3.9 *Calibration standards*—A series of known standard solutions used by the analyst for calibration of the instrument (i.e., preparation of the analytical curve). (See 8.4.)

3.10 *Linear dynamic range*—The concentration range over which the analytical curve remains linear.

3.11 *Reagent blank*—A volume of deionized, distilled water containing the same acid matrix as the calibration standards carried through the entire analytical scheme. (See 8.5.2.)

3.12 *Calibration blank*—A volume of deionized, distilled water acidified with HNO_3 and HCl. (See 8.5.1.)

3.13 *Method of standard addition*—The standard addition technique involves the use of the unknown and the unknown plus a known amount of standard. (See 8.5.1.)

4. Interferences.

4.1 Several types of interference effects may contribute to inaccuracies in the determination of trace elements. They can be summarized as follows:

4.1.1 *Spectral interferences* can be categorized as (1) overlap of a spectral line from another element; (2) unresolved overlap of molecular band spectra; (3) background contribution from continuous or recombination phenomena; and (4) background contribution from stray light from the line emission of high concentration elements. The first of these effects can be compensated by utilizing a computer correction of the raw data, requiring measurement of the interfering element. The second effect may require selection of an alternate wavelength. The third and fourth effects can usually be compensated by a background correction adjacent to the analyte line.

4.1.2 *Physical interferences* are generally considered to be effects associated with the sample nebulization and transport processes. Such properties as changes in viscosity and surface tension can cause significant inaccuracies especially in samples which may contain high dissolved solids and/or acid concentrations. (See Note 1.) If these types of interferences are operative, they must be reduced by dilution of the sample and/or utilization of standard addition techniques.

Note 1.—The use of a peristaltic pump may lessen these interferences.

4.1.3 *Chemical interferences* are characterized by molecular compound formation, ionization effects and solute vaporization effects. Normally these effects are not pronounced with the ICP technique, however, if observed they can be minimized by careful selection of operating conditions (that is, incident power, observation position, and so forth), by buffering of the sample, by matrix matching, and by standard addition procedures. These types of interferences can be highly dependent on matrix type and the specific analyte element.

4.2 It is recommended that whenever a new or unusual sample matrix is encountered, a series of tests be performed prior to reporting concentration data for analyte elements. These tests, as outlined in 4.2.1 through 4.2.4, will ensure the analyst that neither positive nor negative interference effects are operative on any of the analyte elements thereby distorting the accuracy of the reported values.

4.2.1 *Serial dilution*—If the analyte concentration is sufficiently high (minimally a factor of 10 above the instrumental detection limit after dilution), an analysis of a dilution should agree within 5 percent of the original determination (or within some acceptable control limit (13.3) that has been established for that matrix). If not, a chemical or physical interference effect should be suspected.

4.2.2 *Spike addition*—The recovery of a spike addition added at a minimum level of 10X the instrumental detection limit (maximum 100X) to the original determination should be recovered to within 90 to 110 percent or within the established control limit for that matrix. If not, a matrix effect should be suspected. The use of a standard addition analysis procedure can usually compensate for this effect.

Caution.—The standard addition technique does not detect coincident spectral overlap. If suspected, use of an alternate wavelength or [illegible] with an alternate method [illegible] recommended (See 4.2.3).

4.2.3 *Comparison with alternate method of analysis*—When investigating a new sample matrix, comparison tests may be performed with other analytical techniques such as atomic absorption spectrometry, or other approved methodology.

4.2.4 *Wavelength scanning of analyte line region*—If the appropriate equipment is available, wavelength scanning can be performed to detect potential spectral interferences.

5. Apparatus.

5.1 Inductively Coupled Plasma (ICP) Optical Emission Spectrometer.

5.1.1 Computer controlled atomic emission spectrometer with background correction.

5.1.2 Radiofrequency generator.

5.1.3 Argon gas supply, welding grade or better.

5.2 Operating conditions—Because of the differences between various makes and models of satisfactory instruments, no detailed operating instructions can be provided. Instead, the analyst should follow the instructions provided by the manufacturer of the particular instrument. Sensitivity, instrumental detection limit, precision, linear dynamic range, and interference effects must be investigated and established for each individual analyte line on that particular instrument.

6. Reagents and standards.

6.1 Acids used in the preparation of standards and for sample processing must be ultra-high purity grade or equivalent. Redistilled acids are acceptable.

6.1.1 *Acetic acid*, conc. (sp gr 1.06).

6.1.2 *Aqua regia*: Mix cautiously 3 parts conc. HCl (sp gr 1.19) and 1 part conc. HNO_3 (sp gr 1.41) just before use.

6.1.3 *Hydrochloric acid*, conc. (sp gr 1.19).

6.1.4 *Hydrochloric acid* (1+1): Add 500 ml conc. HCl (sp gr 1.19) to 400 ml deionized, distilled water and dilute to 1 liter.

6.1.5 *Nitric acid*, conc. (sp gr 1.41).

6.1.6 *Nitric acid* (1+1): Add 500 ml conc. HNO_3 (sp gr 1.41) to 400 ml deionized, distilled water and dilute to 1 liter.

6.2 *Deionized, distilled water*: Prepare by passing distilled water through a mixed bed of cation and anion exchange resins. Use deionized, distilled water for the preparation of all reagents, calibration standards and as dilution water.

6.3 *Standard stock solutions* may be purchased or prepared from ultra high purity grade chemicals or metals

...olution: See Note 2). All salts must be ... at 105° C unless otherwise ...ed.

Note 1.—Many metal salts are extremely ...ic and may be fatal if swallowed. Wash ...ds thoroughly after handling.

Typical stock solution preparation ...edures follow:

6.3.1 *Aluminum solution, stock.* 1 ml = 100 µg Al: Dissolve 0.100 g of ...minum metal in an acid mixture of 4 ... of (1+1) HCl and 1 ml of conc. HNO_3 ... a beaker. Warm gently to effect ...lution. When solution is complete, ...ansfer quantitatively to a liter flask, ...d an additional 10 ml of (1+1) HCl ...d dilute to 1,000 ml with deionized, ...stilled water.

6.3.2 *Arsenic solution, stock.* 1 ...l = 100 µg As: Dissolve 0.1320 g of As_2O_3 in 100 ml of deionized, distilled water containing 0.4 g NaOH. Acidify the solution with 2 ml conc. HNO_3 and dilute to 1,000 ml with deionized, distilled water.

6.3.3 *Barium solution, stock.* 1 ml = 100 µg Ba: Dissolve 0.1516 g $BaCl_2$ in 10 ml deionized, distilled water with 1 ml (1+1)HCl. Add 10.0 ml (1+1) HCl and dilute to 1,000 ml with deionized, distilled water.

6.3.4 *Beryllium solution, stock.* 1 ml = 100 µg Be: Dissolve 1.127 g $Be_4O(C_2H_3O_2)_6$ beryllium acetate basic, in a minimum amount of conc. acetic acid. Add 10.0 ml conc. HNO_3 and dilute to 1,000 ml with deionized, distilled water.

6.3.5 *Boron solution, stock.* 1 ml = 100 µg B: Dissolve 0.5716 g anhydrous H_3BO_3 in deionized, distilled water and dilute to 1,000 ml. Because H_3BO_3 loses weight on drying at 105° C, use a reagent meeting ACS specifications and keep the bottle tightly stoppered to prevent the entrance of atmospheric moisture.

6.3.6 *Cadmium solution, stock.* 1 ml = 100 µg Cd: Dissolve 0.1142 g CdO in a minimum amount of (1+1) HNO_3. Heat to increase rate of dissolution. Add 10.0 ml conc. HNO_3 and dilute to 1,000 ml with deionized, distilled water.

6.3.7 *Calcium solution, stock.* 1 ml = 100 µg Ca: Suspend 0.2498 g $CaCO_3$ dried at 180° C for 1 h before weighing in deionized, distilled water and dissolve cautiously with a minimum amount of (1+1) HNO_3. Add 10.0 ml conc. HNO_3 and dilute to 1,000 ml with deionized, distilled water.

6.3.8 *Chromium solution, stock.* 1 ml = 100 µg Cr: Dissolve 0.1923 g of CrO_3 in deionized, distilled water. When ...lution is complete, acidify with 10 ml ...onc. HNO_3 and dilute to 1,000 ml with deionized, distilled water.

6.3.9 *Cobalt solution, stock.* 1 ml = 100 µg Co: Dissolve 0.1407 g Co_3O_4 in a minimum amount of (1+1) HNO_3. Add 10.0 ml conc. HNO_3 and dilute to 1,000 ml with deionized, distilled water.

6.3.10 *Copper solution, stock.* 1 ml = 100 µg Cu: Dissolve 0.1252 g CuO in a minimum amount of (1+1) HNO_3. Add 10.0 ml conc. HNO_3 and dilute to 1,000 ml with deionized, distilled water.

6.3.11 *Iron solution, stock.* 1 ml = 100 µg Fe: Dissolve 0.1430 g Fe_2O_3 in 10 ml deionized, distilled water with 1 ml (1+1) HCl. Add 10.0 ml conc. HNO_3 and dilute to 1,000 ml with deionized, distilled water.

6.3.12 *Lead solution, stock.* 1 ml = 100 µg Pb: Dissolve 0.1598 g $Pb(NO_3)_2$ in a minimum amount of (1+1) HNO_3. Add 10.0 ml conc. HNO_3 and dilute to 1,000 ml with deionized, distilled water.

6.3.13 *Lithium solution, stock.* 1 ml = 100 µg Li: Dissolve 0.5323 g Li_2CO_3 slowly in a minimum amount of (1+1) HNO_3. Add 10.0 ml conc. HNO_3 and dilute to 1,000 ml with deionized, distilled water.

6.3.14 *Magnesium solution, stock.* 1 ml = 100 µg Mg: Dissolve 0.1658 g MgO in a minimum amount of (1+1) HNO_3. Add 10.0 ml conc. HNO_3 and dilute to 1,000 ml with deionized, distilled water.

6.3.15 *Manganese solution, stock.* 1 ml = 100 µg Mn: Dissolve 0.3225 g $Mn(NO_3)_2 \cdot 6H_2O$ (do not dry) in deionized, distilled water. Add 10.0 ml conc. HNO_3 and dilute to 1,000 ml with deionized, distilled water.

6.3.16 *Molybdenum solution, stock.* 1 ml = 100 µg Mo: Dissolve 0.2043 g $(NH_4)_6MoO_4$ in deionized, distilled water and dilute to 1,000 ml.

6.3.17 *Nickel solution, stock.* 1 ml = 100 µg Ni: Dissolve 0.4953 g $Ni(NO_3)_2 \cdot 6H_2O$ in deionized, distilled water. Add 10 ml of conc. HNO_3 and dilute to 1,000 ml with deionized, distilled water.

6.3.18 *Potassium solution, stock.* 1 ml = 100 µg K: Dissolve 0.1907 g KCl, dried at 110° C, in deionized, distilled water dilute to 1,000 ml.

6.3.19 *Selenium solution, stock.* 1 ml = 100 µg Se: Dissolve 0.1727 g H_2SeO_3 in deionized, distilled water and dilute to 1,000 ml.

6.3.20 *Silica solution, stock.* 1 ml = 100 µg SiO_2: *Do not dry.* Dissolve 0.4730 g $Na_2SiO_3 \cdot 9H_2O$ in deionized, distilled water. Add 10.0 ml conc. HNO_3 and dilute to 1,000 ml with deionized, distilled water.

6.3.21 *Silver solution, stock.* 1 ml = 1 µg Ag: Dissolve 0.1575 g $AgNO_3$ in 100 ml of deionized, distilled water and 10 ml conc. HNO_3. Dilute to 1,000 ml with deionized, distilled water.

6.3.22 *Sodium solution, stock.* 1 ml = 100 µg Na: Dissolve 0.2542 g NaCl in deionized, distilled water. Add 10.0 ml conc. HNO_3 and dilute to 1,000 ml with deionized, distilled water.

6.3.23 *Strontium solution, stock.* 1 ml = 100 µg Sr: Dissolve 0.2416 g $Sr(NO_3)_2$ in deionized, distilled water. Add 10.0 ml conc. HNO_3 and dilute to 1,000 ml with deionized, distilled water.

6.3.24 *Vanadium solution, stock.* 1 ml = 100 µg V: Dissolve 0.2297 NH_4VO_3 in a minimum amount of conc. HNO_3. Heat to increase rate of dissolution. Add 10.0 ml conc. HNO_3 and dilute to 1,000 ml with deionized, distilled water.

6.3.25 *Zinc solution, stock.* 1 ml = 100 µg Zn: Dissolve 0.1245 g ZnO in a minimum amount of dilute HNO_3. Add 10.0 ml conc. HNO_3 and dilute to 1,000 ml with deionized, distilled water.

6.4 *Mixed calibration standard solutions*—Prepared mixed calibration standard solutions by combining appropriate volumes of the stock solutions in volumetric flasks. (See 6.4.1 thru 6.4.6) Add 2 ml of (1+1) HNO_3 and 2 ml of (1+1) HCl and dilute to 100 ml with deionized, distilled water. Prior to preparing the mixed standards, each stock solution should be analyzed separately to determine possible spectral interference. Care should be taken when preparing the mixed standards that the elements are compatible and stable. Transfer the mixed standard solutions to a TFE fluorocarbon bottle for storage. Fresh mixed standards should be prepared weekly. Some typical combinations follow:

6.4.1 *Mixed standard solution I*—Iron, manganese, cadmium, lead, and zinc.

6.4.2 *Mixed standard solution II*—Beryllium, copper, strontium, vanadium, and cobalt.

6.4.3 *Mixed standard solution III*—Molybdenum, silica, lithium, and barium.

6.4.4 *Mixed standard solution IV*—Calcium, magnesium, sodium, and potassium.

6.4.5 *Mixed standard solution V*—Aluminum, arsenic, boron, chromium, nickel, and selenium.

6.4.6 *Mixed standard solution VI*—Silver.

6.5 Two types of blanks are required for the analysis. The calibration blank (3.12) is used in establishing the analytical curve while the reagent blank (3.11) is used to correct for possible contamination resulting from varying amounts of the acids used in the sample processing.

6.5.1 *The calibration blank* is prepared by diluting 2 ml of (1+1) HNO_3 and 2 ml of (1+1) HCl to 100 ml with deionized, distilled water. Prepare a sufficient quantity to be used to flush the system between standards and samples.

Hg, La, P, Sb, Sn, Ti, Tl, Y

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6.3.2 *The reagent blank* must contain all the reagents and in the same volumes as used in the processing of the samples. The reagent blank must be carried through the complete procedure and contain the same acid concentration in the final solution as the sample solution used for analysis.

6.4 In addition to the calibration standards, an instrument check standard (3.7) and a reference standard (3.8) are also required for the analyses.

6.4.1 *The instrument check standard* is prepared by the analyst by combining compatible elements at a concentration equivalent to the midpoint of their respective calibration curves. This standard should be included in the analytical scheme with a frequency of 10%.

6.4.2 *The reference standard* should be prepared according to the instructions provided by the supplier. Following initial verification of the calibration standards, analyze weekly.

7. Sample handling and preservation.

7.1 For the determination of trace elements, contamination and loss are of prime concern. Dust in the laboratory environment, impurities in reagents and impurities on laboratory apparatus which the sample contacts are all sources of potential contamination. Sample containers can introduce either positive or negative errors in the measurement of trace elements by (a) contributing contaminants through leaching or surface desorption and (b) by depleting concentrations through adsorption. Thus the collection and treatment of the sample prior to analysis requires particular attention. Laboratory glassware including the sample bottle (whether linear polyethylene, polypropylene or TFE-fluorocarbon) should be thoroughly washed with detergent and tap water; rinsed with (1+1) nitric acid, tap water, (1+1) hydrochloric acid, tap and finally deionized, distilled water in that order. (See Notes 3 and 4).

Note 3.—*Chromic acid may be useful to remove organic deposits from glassware; however, the analyst should be cautioned that the glassware must be thoroughly rinsed with water to remove the last traces of chromium. This is especially important if chromium is to be included in the analytical scheme. A commercial product, NOCHROMIX, available from Godax Laboratories, 6 Varick St., New York, NY 10013, may be used in place of chromic acid. Chromic acid should not be used with plastic bottles.*

Note 4.—If it can be documented through an active analytical quality control program using spiked samples and reagent blanks, that certain steps in the cleaning procedure are not required for routine samples, those steps may be eliminated from the procedure.

7.2 Before collection of the sample a decision must be made as to the type of data desired, that is dissolved, suspended or total, so that the appropriate preservation and pretreatment steps may be accomplished. Filtration, acid preservation, etc., are to be performed at the time the sample is collected or as soon as possible thereafter.

7.2.1 For the determination of dissolved elements the sample must be filtered through a 0.45-μm membrane filter as soon as practical after collection. (Glass or plastic filtering apparatus is recommended to avoid possible contamination.) Use the first 50–100 ml to rinse the filter flask. Discard this portion and collect the required volume of filtrate. Acidify the filtrate with (1+1) HNO_3 to a pH of 2 or less. Normally, 3 ml of (1+1) acid per liter should be sufficient to preserve the sample.

7.2.2 For the determination of suspended elements a measured volume of unpreserved sample must be filtered through a 0.45-μm membrane filter as soon as practical after collection. The filter plus suspended material should be transferred to a suitable container for storage and/or shipment. No preservative is required.

7.2.3 For the determination of total or total recoverable elements, the sample is acidified with 5 ml conc. HNO_3 per liter (pH 2) as soon as possible, preferably at the time of collection. The sample is not filtered before processing.

8. Sample Preparation.

8.1 For the determinations of dissolved elements, the filtered, preserved sample may often be analyzed as received. The acid matrix and concentration of the samples and calibration standards must be the same. If a precipitate formed upon acidification of the sample or during transit or storage, it must be redissolved before the analysis by adding additional acid and/or by heat as described in 8.3.

8.2 For the determination of suspended elements, transfer the membrane filter containing the insoluble material to a 250-ml Griffin beaker and add 3 ml conc. HNO_3. Cover the beaker with a watch glass and heat gently. The warm acid will soon dissolve the membrane. Increase the temperature of the hot plate and digest the material. When the acid has nearly evaporated, cool the beaker and watch glass and add another 3 ml of conc. HNO_3. Cover and continue heating until the digestion is complete, generally indicated by a light colored digestate. Evaporate to near dryness (DO NOT BAKE), cool, add 2 ml of (1+1) HNO_3 and 2 ml HCl (1+1) per 100 ml dilution and warm the beaker gently to dissolve any soluble material. Wash down the watch glass and beaker walls with deionized distilled water and filter the sample to remove insoluble material that could clog the nebulizer. Adjust the volume based on the expected concentrations elements present. This volume will vary depending on the elements to be determined. The sample is now ready for analysis. Concentrations so determined shall be reported as "suspended."

8.3 For the determination of total elements, choose a measured volume well mixed acid preserved sample appropriate for the expected level of elements and transfer to a Griffin beaker. (See Note 5.) Add 3 ml of conc. HNO_3. Place the beaker on a hot plate and evaporate to near dryness cautiously, making certain that the sample does not boil. (DO NOT BAKE. Cool the beaker and add another 3 ml portion of conc. HNO_3. 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. 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 2 ml of 1+1 HNO_3 and 2 ml of 1+1 HCl per 100 ml of final solution and warm the beaker to dissolve any precipitate or residue resulting from evaporation. Wash down the beaker walls and watch glass with deionized distilled water and filter the sample to remove insoluble material that could clog the nebulizer. Adjust the volume based on the expected concentrations elements present. The sample is now ready for analysis. Concentrations so determined shall be reported as "total."

Note 5.—If low determinations of boron a critical, quartz glassware should be used.

8.4 For the determination of total recoverable elements, choose a measured volume of a well mixed, acid preserved sample appropriate for the expected level of elements and transfer to a Griffin beaker. (See Note 5.) Add 1 ml of HNO_3 (1+1) and 2 ml of HCl (1+ to the sample and heat on a steam bath or hot plate until the volume has been reduced to 15–20 ml making certain the sample does not boil. After this treatment the sample is filtered to remove insoluble material that could clog the nebulizer, and the volume adjusted to 100 ml. The sample is then ready for analysis. Concentrations so determined shall be reported as "total."

9. Procedure.

9.1 Set up instrument with proper operating parameters established in Section 5.2. Instrument must be allowed to stabilize for at least 30 min prior to operations.

9.2 Initiate appropriate operating configuration of computer.

9.3 Profile and calibrate instrument according to instrument manufacturer's recommended procedures, using the typical mixed calibration standard solutions described in Section 6.4. Flush the system with the calibration blank (6.5.1) between each standard. (See note 6.) (The use of the average intensity of multiple exposures for both standardization and sample analysis has been found to reduce random error.)

NOTE 6.—For boron concentrations greater than 500 μg/l extended flush times of 1 to 2 minutes may be required.

9.4 Before beginning the sample run, reanalyze the highest mixed calibration standard as if it were a sample. Concentration values obtained should not deviate from the actual values by more than 2 percent (or the established control limits). If they do, follow the recommendations of the instrument manufacturer to correct for this condition.

9.5 Begin the sample run flushing the system with the calibration blank (6.5.1) between each sample. (See Note 6.) Analyze an instrument check standard (6.6.1) each 10 samples.

9.6 If it has been found that methods of standard addition are required, the following procedure is recommended.

9.6.1 The standard addition technique (13.2) involves preparing new standards in the sample matrix by adding known amounts of standard to one or more aliquots of the processed sample solution. This technique compensates for a sample constituent that enhances or depresses the analyte signal thus producing a different slope from that of the calibration standards. It will not correct for additive interference which causes a baseline shift. The simplest version of this technique is the single-addition method. The procedure is as follows. Two identical aliquots of the sample solution, each of volume V_s, are taken. To the first (labeled A) is added a small volume V_s of a standard analyte solution of concentration c_s. To the second (labeled B) is added the same volume V_s of the solvent. The analytical signals of A and B are measured and corrected for nonanalyte signals. The unknown sample concentration c_x is calculated:

$$C_x = \frac{S_B V_s c_s}{(S_A - S_B) V_x}$$

where S_A and S_B are the analytical signals (corrected for the blank) of solutions A and B, respectively. V_s and c_s should be chosen so that S_A is roughly twice S_B on the average. It is best if V_s is made much less than V_x, and thus c_s is much greater than c_x, to avoid excess dilution of the sample matrix. If a separation or concentration step is used, the additions are best made first and carried through the entire procedure. For the results from this technique to be valid, the following limitations must be taken into consideration:

1. The analytical curve must be linear.
2. The chemical form of the analyte added must respond the same as the analyte in the sample.
3. The interference effect must be constant over the working range of concern.
4. The signal must be corrected for any additive interference.

10. Calculation.

10.1 Reagent blanks (6.5.2) should be subtracted from all samples. This is particularly important for digested samples requiring large quantities of acids to complete the digestion.

10.2 If dilutions were performed, the appropriate factor must be applied to sample values.

10.3 Results should be reported to the nearest μg/l, up to three significant figures, except calcium, magnesium, sodium, and potassium which are reported to the nearest 0.1 mg/l.

11. Quality Control (Instrumental).

11.1 Check the instrument standardization by analyzing appropriate quality control check standards as follow:

11.1.1 Analyze the instrument check standard (6.6.1) made up of all the elements of interest at a frequency of 10%. This check standard is used to determine instrument drift. If agreement is not within ± 2% of the expected values or within the established control limits, the analysis is out of control.

11.1.2 For the purpose of verifying interelement and/or background correction factors, analyze a second check standard, prepared in the following manner. Select a representative sample which contains minimal concentrations of the elements of interest. Spike this sample with the analytes of interest at or near 100 μg/l. (For effluent samples of expected high concentrations, spike at an appropriate level.) Values should fall within the established control levels of 1.5 times the standard deviation of the mean value of the check standard. If not, repeat the standardization.

11.1.3 A reference standard (6.6.2) from an outside source, but having known concentration values, should be analyzed as a blind sample on a weekly frequency. Values should be within the established quality control limits. If not, prepare new stock standards.

12. *Precision and Accuracy.*

12.1 In an EPA round phase 1 study, seven laboratories applied the ICP technique to acid-distilled water matrices that had been dosed with various metal concentrates. Table II lists the true value, the mean reported value and the mean % relative standard deviation.

Table II.—*ICP Precision and Accuracy Data*

Element	Sample No. 1			Sample No. 2			Sample No. 3		
	True value μg/l	Mean reported value μg/l	Mean percent RSD	True value μg/l	Mean reported value μg/l	Mean percent RSD	True value μg/l	Mean reported value μg/l	Mean percent RSD
Be	750	733	6.2	20	20	9.8	180	176	5.2
Mn	350	345	2.7	15	15	6.7	100	99	5.3
V	750	749	1.8	70	69	2.9	170	169	1.1
As	750	768	7.5	22	18	23	60	63	17
Cr	150	149	2.8	10	10	18	50	50	3.3
Cu	250	235	5.1	11	11	40	70	67	7.9
Fe	600	594	2.0	20	18	15	180	178	6.0
Al	700	696	5.6	60	62	33	160	161	13
Cd	50	48	13	2.5	2.9	18	14	13	16
Ca	500	512	10	20	20	4.1	120	106	21
Mg	250	245	5.8	30	28	11	60	55	14
Pb	550	528	18	24	30	32	80	80	14
Zn	500	501	5.8	16	18	45	85	82	9.4
Se	40	32	31.8	8	8.5	42	10	8.5	8.3

Not all elements were analyzed by all laboratories.

13 References.

13.1 Winge, R. K., V. J. Peterson, and V. A. Fassel, "Inductively Coupled Plasma-Optical Emission Spectroscopy: Prominent Lines, EPA-600/4-79-017.

13.2 Winefordner, J. D., "Trace Analysis Spectroscopic Methods for Elements," *Chemical Analysis*, Vol. 46, pp. 41-42.

13.3 Handbook for Analytical Quality Control in Water and Wastewater Laboratories, EPA-600/4-79-019.

13.4 Garbarino, J. R. and Taylor, H. E., "An Inductively-Coupled Plasma Optical Emission Spectrometric Method for Routine Water Quality Testing," *Applied Spectroscopy* 33, No. 3 (1979).

13.5 "Methods for Chemical Analysis of Water and Wastes," EPA-600/4-79-020.

Appendix V—Biological Oxygen Demand, Carbonaceous Method 405.1 (5 Days, 20° C)

Biochemical Oxygen Demand—Method 405.1 (5 Days, 20° C)

STORET No. 00310, Carbonaceous 80082

1. Scope and Application.

1.1 The biochemical oxygen demand (BOD) test is used for determining the relative oxygen requirements of municipal and industrial wastewaters. Application of the test to organic waste discharges allows calculation of the effect of the discharges on the oxygen resources of the receiving water. Data from BOD tests are used for the development of engineering criteria for the design of wastewater treatment plants.

1.2 The BOD test is an empirical bioassay-type procedure which measures the dissolved oxygen consumed by microbial life while assimilating and oxidizing the organic matter present. The standard test conditions include dark incubation at 20° C for a specified time period (often 5 days). The actual environmental conditions of temperature, biological population, water movement, sunlight, and oxygen concentration cannot be accurately reproduced in the laboratory. Results obtained must take into account the above factors when relating BOD results to stream oxygen demands.

1.3 To obtain values for only carbonaceous BOD, the procedure (2.2) for inhibiting the nitrogeneous oxygen demand using 2-chloro-6(trichloromethyl) pyridine should be used.

2. Summary of Method.

2.1 The sample of waste, or an appropriate dilution, is incubated for 5 days at 20° C in the dark. The reduction in dissolved oxygen concentration during the incubation period yields a measure of the biochemical oxygen demand.

2.2 Nitrogenous oxygen demand is inhibited by adding approximately 10 mg of 2-chloro-6(trichloromethyl) pyridine to each BOD bottle prior to adding the sample (or diluted sample) for incubation. Results of samples treated with inhibitor are to be reported as Biochemical Oxygen Demand, Carbonaceous, Storet No. 80082.

3. Comments.

3.1 Determination of dissolved oxygen in the BOD test may be made by use of either the Modified Winkler with Full-Bottle Technique or the Probe Method in this manual.

3.2 Additional information relating to oxygen demanding characteristics of wastewaters can be gained by applying the Total Organic Carbon and Chemical Oxygen Demand tests (also found in this manual).

3.3 The use of 60 ml incubation bottles in place of the usual 300 ml incubation bottles, in conjunction with the probe, is often convenient.

4. Precision and Accuracy.

4.1 Eighty-six analysts in fifty-eight laboratories analyzed natural water samples plus an exact increment of biodegradable organic compounds. At a mean value of 2.1 and 175 mg/l BOD, the standard deviation was ±0.7 and ± 28 mg/l, respectively (EPA Method Research Study 3).

4.2 There is no acceptable procedure for determining the accuracy of the BOD test.

5. References

5.1 The procedure to be used for this determination is found in: "Standard Methods for the Examination of Water and Wastewater, 14th edition," p. 543, Method 507 (1975).

5.2 Young, J. C., "Chemical Methods for Nitrification Control," J. Water Poll. Control Fed., 45, p. 637 (1973).

507 Oxygen Demand (Biochemical)

1. Discussion

The biochemical oxygen demand (BOD) determination is an empirical test in which standardized laboratory procedures are used to determine the relative oxygen requirements of wastewaters, effluents, and polluted waters. The test measures the oxygen required for the biochemical degradation of organic material (carbonaceous demand) and the oxygen used to oxidize inorganic material such as sulfides and ferrous iron. It also may measure the oxygen used to oxidize reduced forms of nitrogen (nitrogenous demand) unless oxidation of nitrogenous compounds is prevented by an inhibitor.

The method consists of placing a sample in a full, air-tight bottle and incubating the bottle under specified conditions for a specific time. Dissolved Oxygen (DO) is measured initially and after incubation. The difference in DO is the oxygen used and from it the BOD can be computed.

The bottle size, incubation temperature, and incubation period are all specified. Because most wastewaters contain more oxygen-demanding materials than the quantity of DO in oxygen-saturated water, it is necessary to dilute the sample before incubation to bring the oxygen required and oxygen supply into appropriate balance. Because bacterial growth requires such nutrients as nitrogen, phosphorus, and trace metals, these are added to the dilution water which is buffered to ensure that the pH of the incubated bottle remains in a range suitable for bacterial growth. Complete stabilization of a sample may require a period of incubation too long for practical purposes; therefore, the 5-day period has been accepted as standard.

Measurements of BOD that include both carbonaceous oxygen demand and nitrogenous oxygen demand generally are not useful; therefore, where appropriate, may be an inhibiting chemical used to prevent nitrogenous oxidation. Carbonaceous and nitrogenous demands are measured separately for predicting oxygen suppression in receiving streams and oxygen requirements for treatment plant design and operation.

The inclusion of ammonia in the citation water demonstrates that there is no intent to include the oxygen demand of reduced forms of nitrogen in the BOD test. If this ammonia were oxidized, errors would result because the oxygen use would not be due exclusively to pollutants in the sample.

The extent of oxidation of nitrogenous compounds during the 5-day incubation period depends on the presence of micro-organisms capable of carrying out this oxidation. Such organisms usually are not present in raw sewage or primary effluent in sufficient numbers to oxidize significant quantities of reduced nitrogen forms in the 5-day BOD test. Currently any biological treatment plant effluents contain a significant population of nitrifying organisms. Consequently, oxidation of nitrogenous compounds can occur within such samples and inhibition of nitrification is recommended for all samples of secondary effluent, for samples seeded with secondary effluent, and for samples of polluted waters.

Samples for BOD analysis may undergo significant degradation during storage between collection and analysis. This results in a low BOD value. Minimize reduction of BOD by promptly analyzing the sample or by cooling it to

PHENOLICS, TOTAL RECOVERABLE

Method 420.1 (Spectrophotometric, Manual 4-AAP with Distillation)

STORET NO. 32730

1. Scope and Application
   - 1.1 This method is applicable to the analysis of drinking, surface and saline waters, domestic and industrial wastes.
   - 1.2 The method is capable of measuring phenolic materials at the 5 *ug/l* level when the colored end product is extracted and concentrated in a solvent phase using phenol as a standard.
   - 1.3 The method is capable of measuring phenolic materials that contain more than 50 *ug/l* in the aqueous phase (without solvent extraction) using phenol as a standard.
   - 1.4 It is not possible to use this method to differentiate between different kinds of phenols.
2. Summary of Method
   - 2.1 Phenolic materials react with 4-aminoantipyrine in the presence of potassium ferricyanide at a pH of 10 to form a stable reddish-brown colored antipyrine dye. The amount of color produced is a function of the concentration of phenolic material.
3. Comments
   - 3.1 For most samples a preliminary distillation is required to remove interfering materials.
   - 3.2 Color response of phenolic materials with 4-amino antipyrine is not the same for all compounds. Because phenolic type wastes usually contain a variety of phenols, it is not possible to duplicate a mixture of phenols to be used as a standard. For this reason phenol has been selected as a standard and any color produced by the reaction of other phenolic compounds is reported as phenol. This value will represent the minimum concentration of phenolic compounds present in the sample.
4. Sample Handling and Preservation
   - 4.1 Biological degradation is inhibited by the addition of 1 g/l of copper sulfate to the sample and acidification to a pH of less than 4 with phosphoric acid. The sample should be kept at 4°C and analyzed within 24 hours after collection.
5. Interference
   - 5.1 Interferences from sulfur compounds are eliminated by acidifying the sample to a pH of less than 4 with H_3PO_4 and aerating briefly by stirring and adding $CuSO_4$.
   - 5.2 Oxidizing agents such as chlorine, detected by the liberation of iodine upon acidification in the presence of potassium iodide, are removed immediately after sampling by the addition of an excess of ferrous ammonium sulfate (6.5). If chlorine is not removed, the phenolic compounds may be partially oxidized and the results may be low.

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Agency

Environmental Monitoring and
Support Laboratory
Cincinnati OH 45268

A-40

Research and Development

EPA

Test Method

Organochlorine Pesticides and PCBs — Method 608

1. Scope and Application

1.1 This method covers the determination of certain organochlorine pesticides and PCBs. The following parameters can be determined by this method:

Parameter	STORET No.	CAS No.
Aldrin	39330	309-00-2
α-BHC	39337	319-84-6
β-BHC	39338	319-85-7
δ-BHC	34259	319-86-8
γ-BHC	39340	58-89-9
Chlordane	39350	57-74-9
4,4'-DDD	39310	72-54-8
4,4'-DDE	39320	72-55-9
4,4'-DDT	39300	50-29-3
Dieldrin	39380	60-57-1
Endosulfan I	34361	959-98-8
Endosulfan II	34356	33212-65-9
Endosulfan sulfate	34351	1031-07-8
Endrin	39390	72-20-8
Endrin aldehyde	34366	7421-93-4
Heptachlor	39410	76-44-8
Heptachlor epoxide	39420	1024-57-3
Toxaphene	39400	8001-35-2
PCB-1016	34671	12674-11-2
PCB-1221	39488	11104-28-2
PCB-1232	39492	11141-16-5
PCB-1242	39496	53469-21-9
PCB-1248	39500	12672-29-6
PCB-1254	39504	11097-69-1
PCB-1260	39508	11096-82-5

1.2 This is a gas chromatographic (GC) method applicable to the determination of the compounds listed above in municipal and industrial discharges as provided under 40 CFR 136.1. When this method is used to analyze unfamiliar samples for any or all of the compounds above, 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. Method 625 provides gas chromatograph/mass spectrometer (GC/MS) conditions appropriate for the qualitative and

quantitative confirmation of results for all of the parameters listed above, using the extract produced by this method.

1.3 The method detection limit (MDL, defined in Section 14.1)[1] for each parameter is listed in Table 1. The MDL for a specific wastewater may differ from those listed, depending upon the nature of interferences in the sample matrix.

1.4 The sample extraction and concentration steps in this method are essentially the same as in methods 606, 609, 611 and 612. Thus, a single sample may be extracted to measure the parameters included in the scope of each of these methods. When cleanup is required, the concentration levels must be high enough to permit selection of aliquots as necessary to apply appropriate cleanup procedures. The analyst is allowed the latitude to select gas chromatographic conditions appropriate for the simultaneous measurement of combinations of these parameters.

1.5 Any modification of this method, beyond those expressly permitted, shall be considered as major modifications subject to application and approval of alternate test procedures under 40 CFR 136.4 and 136.5.

1.6 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. Each analyst must demonstrate the ability to generate acceptable results with this method using the procedure described in Section 8.2.

2. Summary of Method

2.1 A measured volume of sample, approximately one-liter, is solvent extracted with methylene chloride using a separatory funnel. The methylene chloride extract is dried and exchanged to hexane, during concentration to a final volume of 10 mL or less. Gas chromatographic conditions are described which permit the separation and measurement of the parameters in the extract by electron capture GC[2].

2.2 The method provides a Florisil column procedure and elemental sulfur removal procedure to aid in the elimination of interferences that may be encountered.

3. Interferences

3.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in gas chromatograms. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks as described in Section 8.6.

3.1.1 Glassware must be scrupulously cleaned[3]. 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 water and distilled water. It should then be drained dry and heated in a muffle furnace at 400 °C for 15 to 30 minutes. Some thermally stable materials, such as PCBs, may not be eliminated by this treatment. Solvent rinses with acetone and pesticide quality hexane may be substituted for the muffle furnace heating. Thorough rinsing with such solvents usually eliminates PCB interference. 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 Interferences by phthalate esters can pose a major problem in pesticide analysis when using the elution capture detector. These compounds generally appear in the chromatogram as large eluting peaks, especially in the 15 and 50% fractions from Florisil. Common flexible plastics contain varying amounts of phthalates. These phthalates are easily extracted or leached from such materials during laboratory operations. Cross contamination of clean glassware routinely occurs when plastics are handled during extraction steps, especially when solvent wetted surfaces are handled. Interferences from phthalates can best be minimized by avoiding the use of plastics in the laboratory. Exhaustive cleanup of reagents and glassware may be required to eliminate background phthalate contamination[4,5]. The interferences from phthalate esters can be avoided by using a microcoulometric or electrolytic conductivity detector.

3.3 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. The cleanup procedures in Section 11 can be used to overcome many of these interferences, but unique samples may require additional cleanup approaches to achieve the MDL listed in Table 1.

4. Safety

4.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified[6-8] for the information of the analyst.

4.2 The following parameters covered by this method have been tentatively classified as known or suspected, human or mammalian carcinogens: 4,4'-DDT, 4,4'-DDD, the BHCs, and the PCBs. Primary standards of these toxic compounds should be prepared in a hood.

5. Apparatus and Materials

5.1 Sampling equipment, for discrete or composite sampling.

5.1.1 Grab sample bottle—Amber glass, one-liter or one-quart volume, fitted with screw caps lined with Teflon. Foil may be substituted for Teflon if the sample is not corrosive. If amber bottles are not available, protect samples from light. The container must be washed, rinsed with acetone or methylene chloride, and dried before use to minimize contamination.

5.1.2 Automatic sampler (optional)—Must incorporate glass sample containers for the collection of a minimum of 250 mL. Sample containers must be kept refrigerated at 4 °C and protected from light during compositing. If the sampler uses a peristaltic pump, a minimum length of compressible

silicone rubber tubing may be used. Before use, however, the compressible tubing should be thoroughly rinsed with methanol, followed by repeated rinsings with distilled water to minimize the potential for contamination of the sample. An integrating flow meter is required to collect flow proportional composites.

6.2 Glassware (All specifications are suggested. Catalog numbers are included for illustration only).

6.2.1 Separatory funnel—2000-mL, with Teflon stopcock.

6.2.2 Drying column—Chromatographic column approximately 400 mm long x 19 mm ID, with coarse frit.

6.2.3 Chromatographic column—Pyrex, 400 mm long x 22 mm ID, with coarse fritted plate and Teflon stopcock (Kontes K-420540 or equivalent).

6.2.4 Concentrator tube, Kuderna-Danish—10-mL, graduated (Kontes K-570050-1025 or equivalent). Calibration must be checked at the volumes employed in the test. Ground glass stopper is used to prevent evaporation of extracts.

6.2.5 Evaporative flask, Kuderna-Danish—500-mL (Kontes K-570001-0500 or equivalent). Attach to concentrator tube with springs.

6.2.6 Snyder column, Kuderna-Danish—three-ball macro (Kontes K-503000-0121 or equivalent).

6.2.7 Vials—Amber glass, 10- to 15-mL capacity, with Teflon-lined screw cap.

6.3 Boiling chips—approximately 10/40 mesh. Heat to 400 °C for 30 minutes or Soxhlet extract with methylene chloride.

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

6.5 Balance—Analytical, capable of accurately weighing 0.0001 g.

6.6 Gas chromatograph—An analytical system complete with gas chromatograph suitable for on-column injection and all required accessories including syringes, analytical columns, gases, detector, and strip-chart recorder. A data system is recommended for measuring peak areas.

6.6.1 Column 1—1.8 m long x 4 mm ID glass, packed with 1.5% SP-2250/1.95% SP-2401 on Supelcoport (100/120 mesh) or equivalent. Column 1 was used to develop the method performance statements in Section 14. Guidelines for the use of alternate column packings are provided in Section 12.1.

6.6.2 Column 2—1.8 m long x 4 mm ID glass, packed with 3% OV-1 on Supelcoport (100/120 mesh) or equivalent.

6.6.3 Detector—Electron capture. This detector has proven effective in the analysis of wastewaters for the parameters listed in the scope, and was used to develop the method performance statements in Section 14. Guidelines for the use of alternate detectors are provided in Section 12.1.

8. Reagents

8.1 Reagent water—Reagent water is defined as a water in which an interferent is not observed at the MDL of each parameter of interest.

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

8.3 Sodium thiosulfate—(ACS). Granular.

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

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

8.6 Ethyl ether—Pesticide quality or equivalent, redistilled in glass if necessary.

8.6.1 Must be free of peroxides as indicated by EM Laboratories Quant test strips (Available from Scientific Products Co., Cat. No. P1126-8, and others suppliers.)

8.6.2 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.

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

8.8 Florisil—PR grade (60/100 mesh); purchase activated at 1250 °F and store in dark in glass containers with glass stoppers or foil-lined screw caps. Before use, activate each batch at least 16 hours at 130 °C in a foil covered glass container.

8.9 Mercury—Triple distilled.

8.10 Copper powder—Activated.

8.11 Stock standard solutions (1.00 µg/µL)—Stock standard solutions can be prepared from pure standard materials or purchased as certified solutions.

8.11.1 Prepare stock standard solutions by accurately weighing about 0.0100 grams of pure material. Dissolve the material in isooctane, 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.

8.11.2 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. Quality control check standards that can be used to determine the accuracy of calibration standards will be available from the U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268.

8.11.3 Stock standard solutions must be replaced after six months, or sooner if comparison with check standards indicate a problem.

7. Calibration

7.1 Establish gas chromatographic operating parameters which produce retention times equivalent to those indicated in Table 1. The gas chromatographic system may be calibrated using the external standard technique (Section 7.2) or the internal standard technique (Section 7.3).

7.2 External standard calibration procedure:

7.2.1 Prepare calibration standards at a minimum of three concentration levels for each parameter of interest by adding volumes of one or more stock standards to a volumetric flask and diluting to volume with isooctane. One of the external standards should be at a concentration near, but above, the MDL and the other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector.

7.2.2 Using injections of 2 to 5 µL of each calibration standard, tabulate peak height or area responses against the mass injected. The results can be used to prepare a calibration curve for each compound. Alternatively, if the ratio of response to amount injected (calibration factor) is a constant over the working range (<10% relative standard deviation, RSD), linearity through the origin can be assumed and the average ratio or calibration factor can be used in place of a calibration curve.

7.2.3 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 must be prepared for that compound.

7.3 Internal standard calibration procedure. To use this approach, the analyst must select one or more internal standards that are 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. Because of these limitations, no internal standard can be suggested that is applicable to all samples.

7.3.1 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 MDL and 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 Using injections of 2 to 5 µL of each calibration standard, tabulate peak height or area responses against concentration for each compound and internal standard, and calculate response factors (RF) for each compound using equation 1.

Eq. 1. $RF = (A_s C_{is})/(A_{is} C_s)$

where:

A_s = Response for the parameter to be measured.

A_{is} = Response for the internal standard.

C_{is} = Concentration of the internal standard, (µg/L).

C_s = Concentration of the parameter to be measured, (µg/L).

If the RF value over the working range is a constant (<10% RSD), 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}, vs. RF.

7.3.3 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.

7.4 The cleanup procedure in Section 11 utilizes Florisil chromatography. Florisil from different batches or sources may vary in absorptive capacity. To standardize the amount of Florisil which is used, the use of lauric acid value[9] is suggested. The referenced procedure determines the adsorption from hexane solution of lauric acid (mg) per gram Florisil. The amount of Florisil to be used for each column is calculated by dividing this factor into 110 and multiplying by 20 g.

7.5 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.

8. Quality Control

8.1 Each laboratory that uses this method is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and the analysis of spiked samples as a continuing check on performance. The laboratory is required to maintain performance records to define the quality of data that is generated. Ongoing performance checks must be compared with established performance criteria to determine if the results of analyses are within accuracy and precision limits expected of the method.

8.1.1 Before performing any analyses, the analyst must demonstrate the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Section 8.2.

8.1.2 In recognition of the rapid advances that are occurring in chromatography, the analyst is permitted certain options to improve the separations or lower the cost of measurements. Each time such modifications are made to the method, the analyst is required to repeat the procedure in Section 8.2.

8.1.3 The laboratory must spike and analyze a minimum of 10% of all samples to monitor continuing laboratory performance. This procedure is described in Section 8.4.

8.2 To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operations.

8.2.1 Select a representative spike concentration for each compound to be measured. Using stock standards, prepare a quality control check sample concentrate in acetone 1000 times more concentrated than the selected concentrations. Quality control check sample concentrates, appropriate for use with this method, will be available from the U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268.

8.2.2 Using a pipet, add 1.00 mL of the check sample concentrate to each of a minimum of four 1000-mL aliquots of reagent water. A representative wastewater may be used in place of the reagent water, but one or more additional aliquots must be analyzed to determine background levels, and the spike level must exceed twice the background level for the test to be valid. Analyze the aliquots according to the method beginning in Section 10.

8.2.3 Calculate the average percent recovery, (R), and the standard deviation of the percent recovery (s), for the results. Wastewater background corrections must be made before R and s calculations are performed.

8.2.4 Using Table 2, note the average recovery (X) and standard deviation (p) expected for each method parameter. Compare these to the calculated values for R and s. If $s > 2p$ or $|X - R| > 2p$, review potential problem areas and repeat the test.

8.2.5 The U.S. Environmental Protection Agency plans to establish performance criteria for R and s based upon the results of interlaboratory testing. When they become available, these criteria must be met before any samples may be analyzed.

8.3 The analyst must calculate method performance criteria and define

the performance of the laboratory for each spike concentration and parameter being measured.

8.3.1 Calculate upper and lower control limits for method performance:

Upper Control Limit (UCL) = R + 3s
Lower Control Limit (LCL) = R − 3s

where R and s are calculated as in Section 8.2.3. The UCL and LCL can be used to construct control charts[10] that are useful in observing trends in performance. The control limits above be replaced by method performance criteria as they become available from the U.S. Environmental Protection Agency.

8.3.2 The laboratory must develop and maintain separate accuracy statements of laboratory performance for wastewater samples. An accuracy statement for the method is defined as R ± s. The accuracy statement should be developed by the analysis of four aliquots of wastewater as described in Section 8.2.2, followed by the calculation of R and s. Alternately, the analyst may use four wastewater data points gathered through the requirement for continuing quality control in Section 8.4. The accuracy statements should be updated regularly[10].

8.4. The laboratory is required to collect a portion of their samples in duplicate to monitor spike recoveries. The frequency of spiked sample analysis must be at least 10% of all samples or one sample per month, whichever is greater. One aliquot of the sample must be spiked and analyzed as described in Section 8.2. If the recovery for a particular parameter does not fall within the control limits for method performance, the results reported for that parameter in all samples processed as part of the same set must be qualified as described in Section 13.5. The laboratory should monitor the frequency of data so qualified to ensure that it remains at or below 5%.

8.5 Before processing any samples, the analyst should demonstrate through the analysis of a one-liter aliquot of reagent water, that all glassware and reagent interferences are under control. Each time a set of samples is extracted or there is a change in reagents, a laboratory reagent blank should be processed as a safeguard against laboratory contamination.

8.6 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field duplicates may be analyzed to monitor the precision of the sampling technique. When doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as gas chromatography with a dissimilar column, specific element detector, or mass spectrometer must be used. Whenever possible, the laboratory should perform analysis of standard reference materials and participate in relevant performance evaluation studies.

9. Sample Collection, Preservation, and Handling

9.1 Grab samples must be collected in glass containers. Conventional sampling practices[11] should be followed, except that the bottle must not be prewashed 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 tubing and other potential sources of contamination.

9.2 The samples must be iced or refrigerated at 4 °C from the time of collection until extraction. If the samples will not be extracted within 72 hours of collection, the sample should be adjusted to a pH range of 5.0 to 9.0 with sodium hydroxide or sulfuric acid. Record the volume of acid or base used. If aldrin is to be determined, add sodium thiosulfate when residual chlorine is present. U.S. Environmental Protection Agency methods 330.4 and 330.5 may be used to measure chlorine residual[12]. Field test kits are available for this purpose.

9.3 All samples must be extracted within 7 days and completely analyzed within 40 days of extraction[2].

10. Sample Extraction

10.1 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Pour the entire sample into a two-liter separatory funnel.

10.2 Add 60 mL methylene chloride to the sample bottle, seal, and shake 30 seconds to rinse the inner surface. Transfer the solvent to the separatory funnel and extract the sample by shaking 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. If the emulsion interface between layers is more than one-third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods. Collect the methylene chloride extract in a 250-mL Erlenmeyer flask.

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

10.4 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporative flask. Other concentration devices or techniques may be used in place of the Kuderna Danish if the requirements of Section 8.2 are met.

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

10.6 Add one or two clean boiling chips to the evaporative flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 mL methylene chloride 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 with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15 to 20 minutes. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 minutes.

10.7 Increase the temperature of the hot water bath to about 80 °C. Momentarily remove the Snyder column, add 50 mL of hexane and a new boiling chip and reattach the Snyder column. Prewet the column by adding about 1 mL of hexane to the top. Concentrate the solvent extract as before. The elapsed time of concentration should be 5 to 10 minutes. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus and allow it to drain and cool at least 10 minutes.

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10.8 Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 to 2 mL of hexane. A 5-mL syringe is recommended for this operation. Stopper the concentrator tube and store refrigerated if further processing will not be performed immediately. If the extracts will be stored longer than two days, they should be transferred to Teflon-sealed screw-cap bottles. If the sample extract requires no further cleanup, proceed with gas chromatographic analysis. If the sample requires cleanup proceed to Section 11.

10.9 Determine the original sample volume by refilling the sample bottle to the mark and transferring the liquid to a 1000-mL graduated cylinder. Record the sample volume to the nearest 5 mL.

11. Cleanup and Separation

11.1 Cleanup procedures may not be necessary for a relatively clean sample matrix. The cleanup procedures recommended in this method have been used for the analysis of various clean waters and industrial effluents. If particular circumstances demand the use of an alternative cleanup procedure, the analyst must determine the elution profile and demonstrate that the recovery of each compound of interest is no less than 85%. The Florisil column allows for a select fractionation of the compounds and will eliminate polar materials. Elemental sulfur interferes with the electron capture gas chromatography of certain pesticides, but can be removed by the techniques described below.

11.2 Florisil column cleanup:

11.2.1 Add a weight of Florisil (nominally 21 g) predetermined by calibration (Section 7.4 and 7.5), 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 to 2 cm deep. Add 60 mL of hexane to wet and rinse the sodium sulfate and Florisil. 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.

11.2.2 Adjust the sample extract volume to 10 mL with hexane and transfer it from the K-D concentrator tube to the Florisil column. Rinse the tube twice with 1 to 2 mL hexane, adding each rinse to the column.

11.2.3 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 (V/V) (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 (V/V)(Fraction 2), into a second K-D flask. Perform the third elution using 200 mL of 50% ethyl ether in hexane (V/V)(Fraction 3). The elution patterns for the pesticides an PCB's are shown in Table 2.

11.2.4 Concentrate the eluates by standard K-D techniques (Section 10.6), 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.

11.3 Elemental sulfur will usually elute entirely in Fraction 1 of the Florisil column cleanup. To remove sulfur interference from this fraction or the original extract, pipet 1.00 mL of the concentrated extract into a clean concentrator tube or Teflon-sealed vial. Add one to three drops of mercury and seal[13]. Agitate the contents of the vial for 15 to 30 seconds. Prolonged shaking (two hours) may be required. If so, this may be accomplished with a reciprocal shaker. Alternatively, activated copper powder may be used for sulfur removal[14]. Analyze by gas chromatography.

12. Gas Chromatography

12.1 Table 1 summarizes the recommended operating conditions for the gas chromatograph. This table includes retention times and MDL that were obtained under these conditions. Examples of the parameter separations achieved by column 1 are shown in Figures 1 to 10. Other packed columns, chromatographic conditions, or detectors may be used if the requirements of Section 8.2 are met. Capillary (open-tubular) columns may also be used if the relative standard deviations of responses for replicate injections are demonstrated to be less than 6% and the requirements of Section 8.2 are met.

12.2 Calibrate the system daily as described in Section 7.

12.3 If the internal standard approach is being used, the internal standard must be added to the sample extract and mixed thoroughly immediately, before injection into the instrument.

12.4 Inject 2 to 5 µL of the sample extract using the solvent-flush technique[15]. Smaller (1.0 µL) volumes can be injected if automatic devices are employed. Record the volume injected to the nearest 0.05 µL, the total extract volume, and the resulting peak size in area or peak height units.

12.5 The width of the retention time window used to make identifications should be based upon measurements of actual retention time variations of standards over the course of a day. Three times the standard deviation of a retention time for a compound can be used to calculate a suggested window size; however, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

12.6 If the response for the peak exceeds the working range of the system, dilute the extract and reanalyze.

12.7 If the measurement of the peak response is prevented by the presence of interferences, further cleanup is required.

13. Calculations

13.1 Determine the concentration of individual compounds in the sample.

13.1.1 If the external standard calibration procedure is used, calculate the amount of material injected from the peak response using the calibration curve or calibration factor in Section 7.2.2. The concentration in the sample can be calculated from equation 2:

Eq. 2. Concentration, µg/L = $\frac{(A)(V_t)}{(V_i)(V_s)}$

where:

A = Amount of material injected, in nanograms.
V_i = Volume of extract injected (µL).
V_t = Volume of total extract (µL).
V_s = Volume of water extracted (mL).

13.1.2 If the internal standard calibration procedure was used, calculate the concentration in the sample using the response factor (RF) determined in Section 7.3.2 and equation 3.

Eq. 3

Concentration, µg/L = $\frac{(A_s)(I_s)}{(A_{is})(RF)(V_o)}$

where:

A_s = Response for the parameter to be measured.
A_{is} = Response for the internal standard.
I_s = Amount of internal standard added to each extract (µg).
V_o = Volume of water extracted, in liters.

13.2 When it is apparent that two or more PCB (Aroclor) mixtures are present, the Webb and McCall procedure[16] may be used to identify and quantify the Aroclors.

13.3 For multicomponent mixtures (chlordane, toxaphene and PCBs) match retention times of peaks in the standards with peaks in the sample. Quantitate every identifiable peak 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.

13.4 Report results in micrograms per liter without correction for recovery data. When duplicate and spiked samples are analyzed, report all data obtained with the sample results.

13.5 For samples processed as part of a set where the laboratory spiked sample recovery falls outside of the control limits in Section 8.3, data for the affected parameters must be labeled as suspect.

14. Method Performance

14.1 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[11]. The MDL concentrations listed in Table 1 were obtained using reagent water[17]. Similar results were achieved using representative wastewaters.

14.2 This method has been tested for linearity of spike recovery from reagent water and has been demonstrated to be applicable over the concentration range from 4 x MDL up to 1000 x MDL with the following exceptions: Chlordane recovery at 4 x MDL was low (60%); Toxaphene recovery was demonstrated linear over the range of 10 x MDL to 1000 x MDL[17].

14.3 In a single laboratory (Southwest Research Institute), using spiked wastewater samples, the average recoveries presented in Table 3 were obtained[14]. Each spiked sample was analyzed in triplicate on two separate days. The standard deviation of the percent recovery is also included in Table 3.

14.4 The U.S. Environmental Protection Agency is in the process of conducting an interlaboratory method study to fully define the performance of this method.

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Table 1. Chromatographic Conditions and Method Detection Limits

Parameter	Retention Time (min.) Column 1	Column 2	Method Detection Limit µg/L
α-BHC	1.36	1.82	0.003
γ-BHC	.70	2.13	0.004
β-BHC	1.80	1.87	0.008
Heptachlor	2.00	3.36	0.003
δ-BHC	2.16	2.20	0.008
Aldrin	2.40	4.10	0.004
Heptachlor epoxide	3.60	8.00	0.003
Endosulfan I	4.80	8.20	0.014
4,4'-DDE	5.13	7.16	0.004
Dieldrin	5.48	7.23	0.002
Endrin	6.56	8.10	0.008
4,4'-DDD	7.83	9.08	0.011
Endosulfan II	8.00	8.28	0.004
4,4'-DDT	8.40	11.76	0.012
Endrin aldehyde	11.82	9.30	0.023
Endosulfan sulfate	14.32	10.76	0.008
Chlordane	mr	mr	0.014
Toxaphene	mr	mr	0.24
PCB-1016	mr	mr	nd
PCB-1221	mr	mr	nd
PCB-1232	mr	mr	nd
PCB-1242	mr	mr	0.088
PCB-1248	mr	mr	nd
PCB-1254	mr	mr	nd
PCB-1260	mr	mr	nd

Column 1 conditions: Supelcoport (100/120 mesh) coated with 1.8% SP-2250/1.65% SP-2401 packed in a 1.8 m long × 4 mm ID glass column with 5% Methane/95% Argon carrier gas at a flow rate of 60 mL/min. Column temperature isothermal at 200°C, except for PCB-1016 through PCB-1248, which should be measured at 180°C.

Column 2 conditions: Supelcoport (100/120 mesh) coated with 3% OV-1 in a 1.8 m long × 4 mm ID glass column with 5% Methane/95% Argon carrier gas at a flow rate of 60 mL/min. Column temperature, isothermal at 200°C, for the pesticides; 140°C for PCB-1221 and 1232; 170°C for PCB-1016 and 1242 to 1268.

mr = Multiple peak response. See Figures 2 thru 10.

nd = Not determined.

Table 2. Distribution of Chlorinated Pesticides and PCBs into Florisil Column Fractions[1]

Parameter	Percent Recovery by Fraction Fraction 1	Fraction 2	Fraction 3
Aldrin	100		
α-BHC	100		
β-BHC	87		
δ-BHC	86		
γ-BHC	100		
Chlordane	100		
4,4'-DDD	88		
4,4'-DDE	98		
4,4'-DDT	100		
Dieldrin	0	100	
Endosulfan I	37	64	
Endosulfan II	0	7	81
Endosulfan sulfate	0	0	106
Endrin	4	96	
Endrin aldehyde	0	86	28
Heptachlor	100		
Heptachlor epoxide	100		
Toxaphene	86		
PCB-1016	87		
PCB-1221	87		
PCB-1232	86	4	
PCB-1242	87		
PCB-1248	103		
PCB-1254	90		
PCB-1260	86		

Eluant composition by fraction:
Fraction 1 – 6% ethyl ether in hexane
Fraction 2 – 15% ethyl ether in hexane
Fraction 3 – 50% ethyl ether in hexane

Table 2. Single Operator Accuracy and Precision

Parameter	Average Percent Recovery	Standard Deviation %	Spike Range (µg/L)	Number of Analyses	Matrix Types
Aldrin	88	2.5	2.0	18	3
α-BHC	88	2.0	1.0	18	3
β-BHC	88	1.3	2.0	18	3
δ-BHC	86	3.4	2.0	18	3
γ-BHC	87	2.3	1.0	18	3
Chlordane	83	4.1	20	21	4
4,4'-DDD	92	1.8	8.0	18	3
4,4'-DDE	88	2.2	3.0	18	3
4,4'-DDT	82	3.3	8.0	18	3
Dieldrin	88	2.8	3.0	18	3
Endosulfan I	86	2.5	3.0	12	2
Endosulfan II	87	2.4	8.0	14	3
Endosulfan sulfate	89	4.1	16	18	3
Endrin	86	2.1	8.0	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	18	3
Toxaphene	86	3.8	200	18	3
PCB-1016	84	1.8	28	12	2
PCB-1221	96	4.2	88-110	12	2
PCB-1232	88	2.4	110	12	2
PCB-1242	83	2.0	28-88	12	2
PCB-1248	80	1.8	40	12	2
PCB-1254	82	3.3	40	18	3
PCB-1260	81	5.5	60	18	3

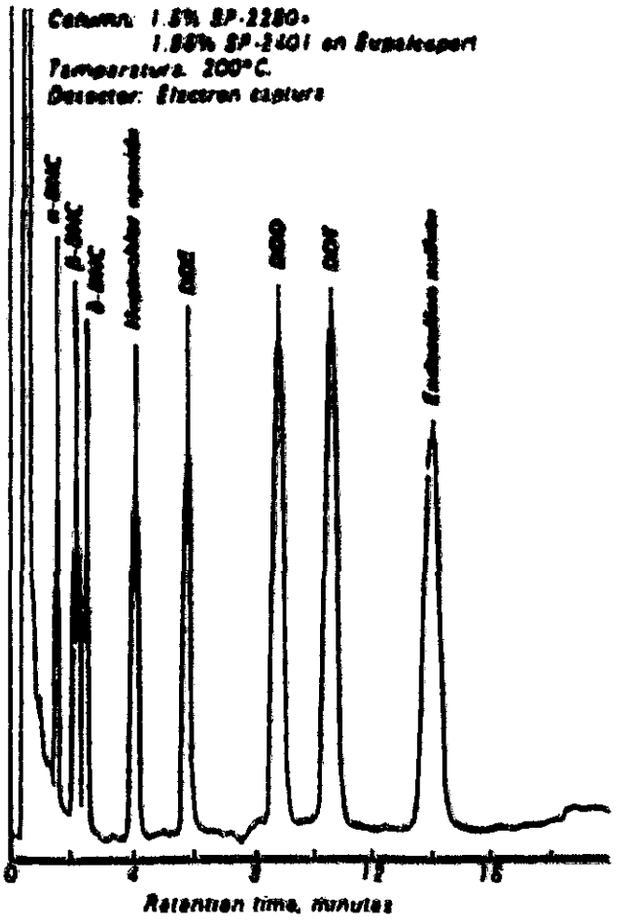

Figure 1. Gas chromatogram of pesticides.

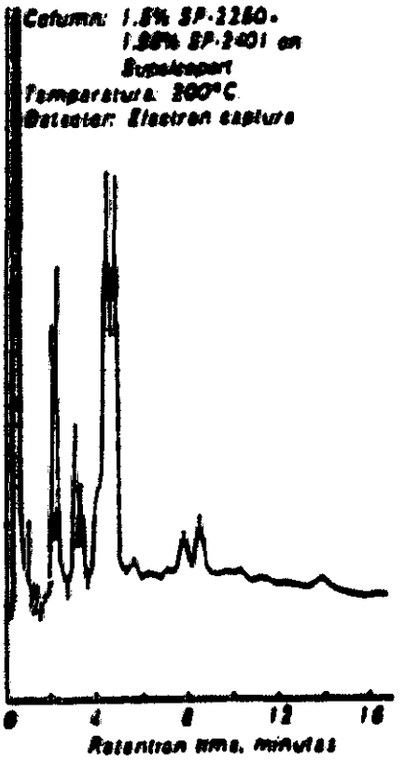

Figure 2. Gas chromatogram of chlordane.

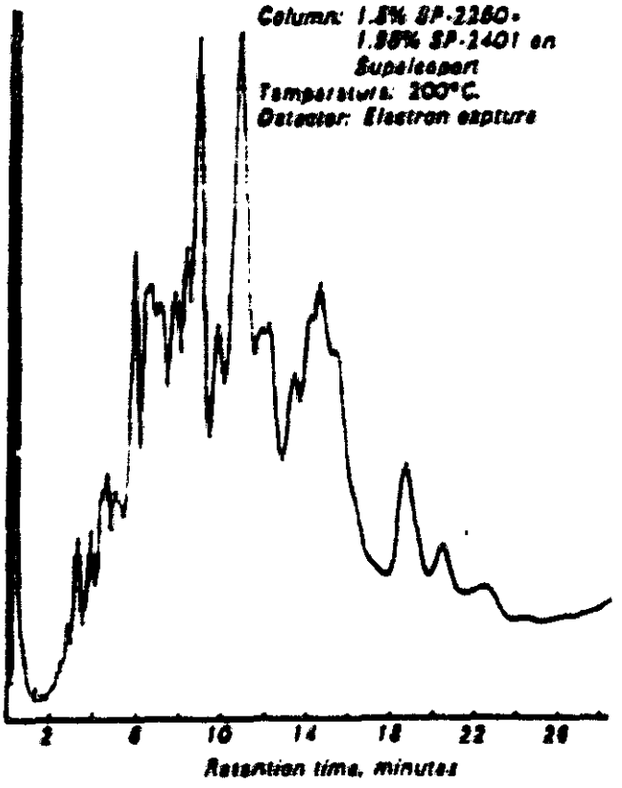

Figure 3. Gas chromatogram of toxaphene.

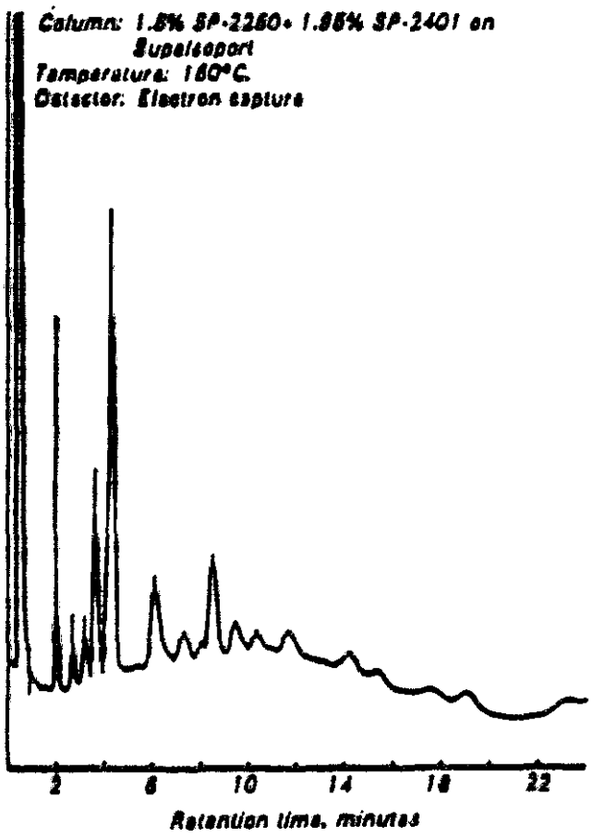

Figure 5. Gas chromatogram of PCB-1221.

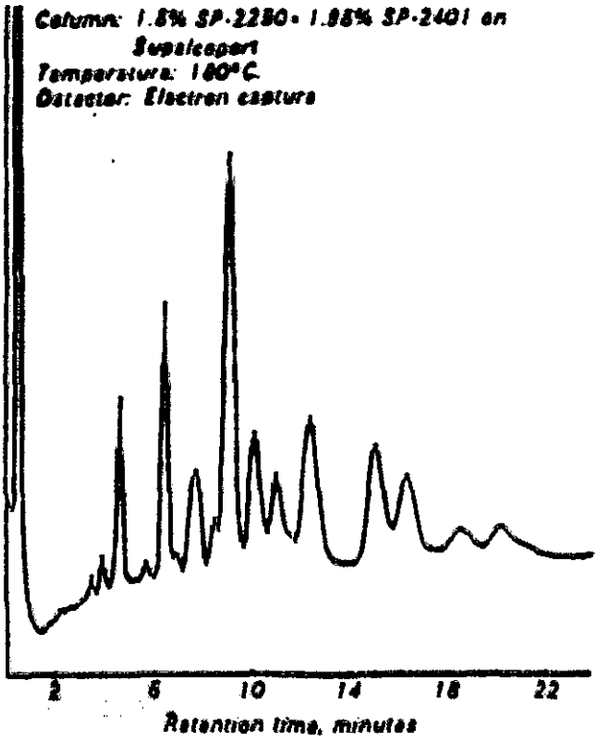

Figure 4. Gas chromatogram of PCB-1016.

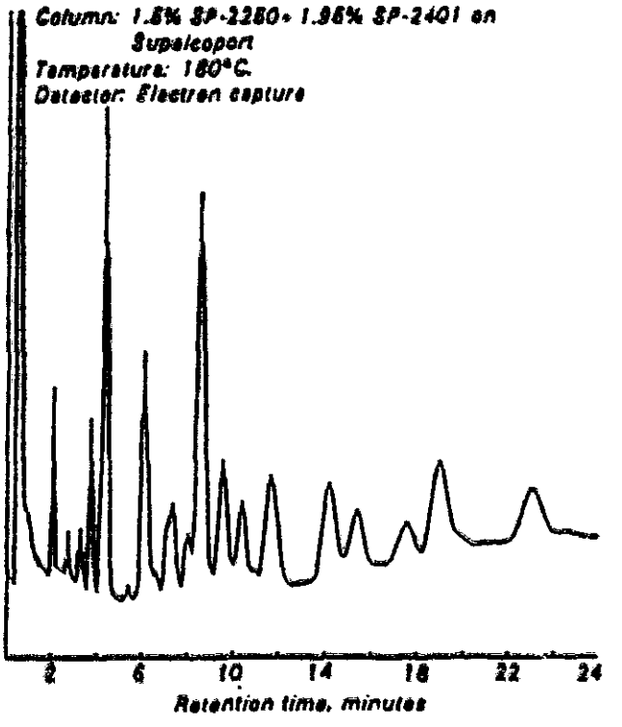

Figure 6. Gas chromatogram of PCB-1232.

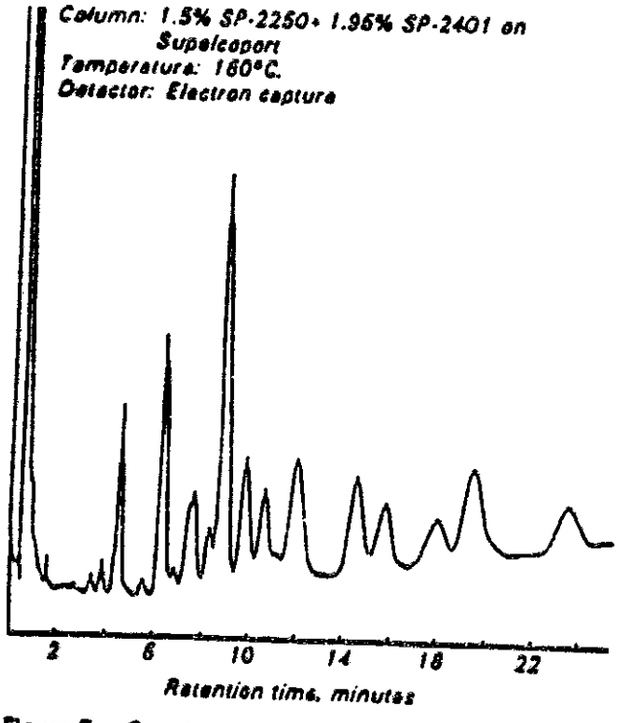

Figure 7. Gas chromatogram of PCB-1242.

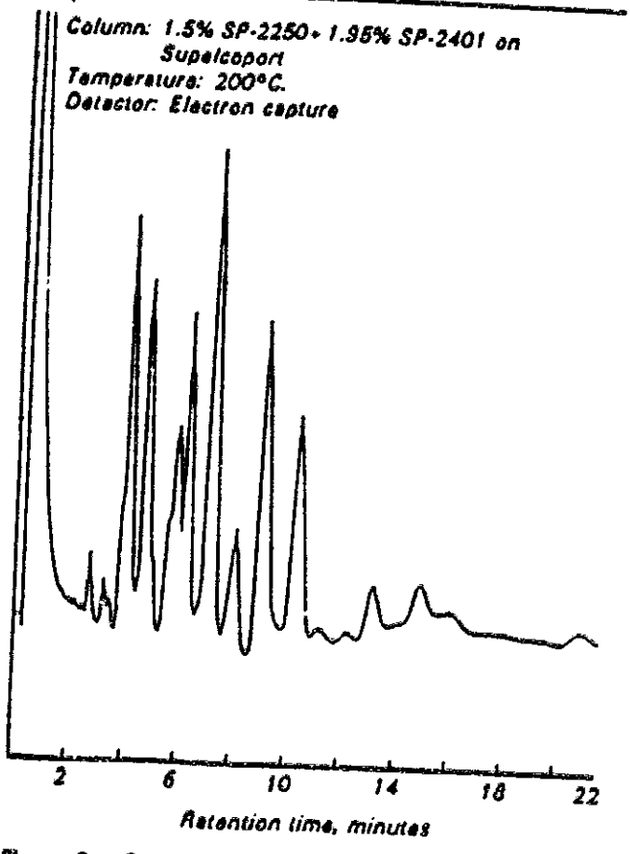

Figure 8. Gas chromatogram of PCB-1254.

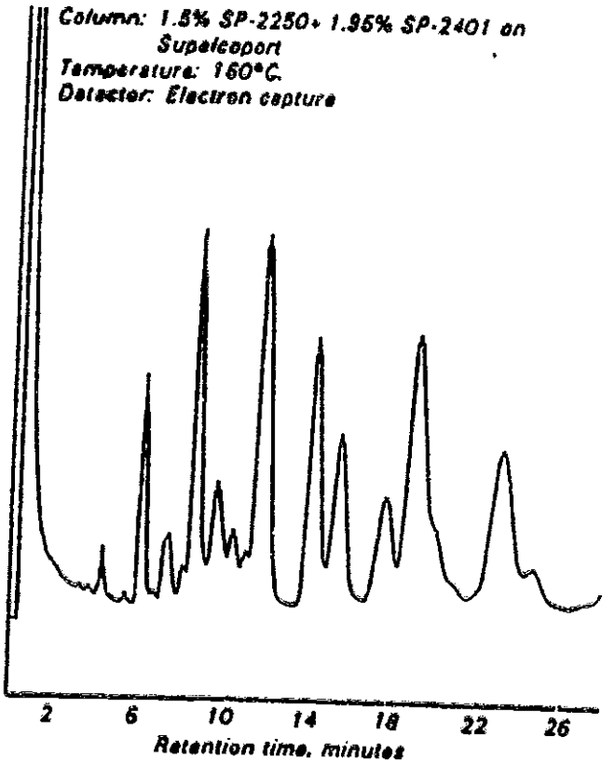

Figure 9. Gas chromatogram of PCB-1248.

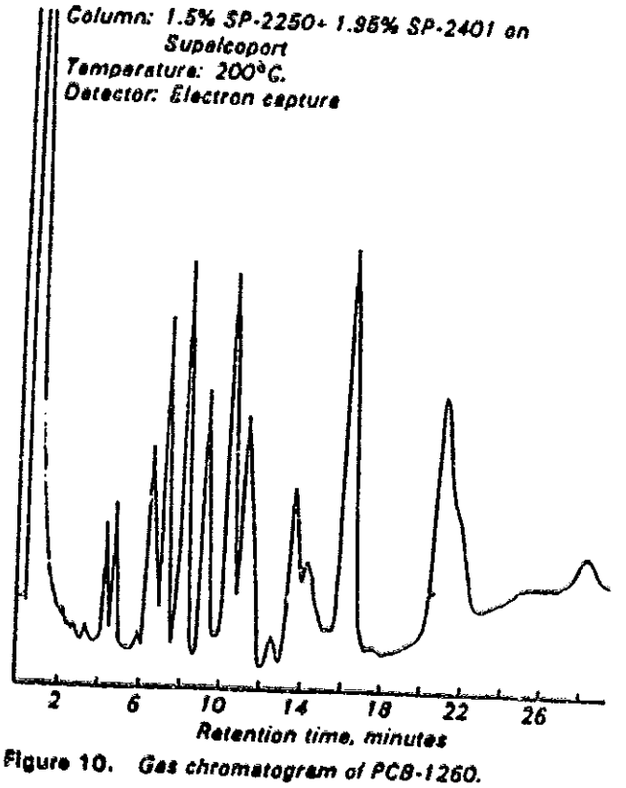

Figure 10. Gas chromatogram of PCB-1260.

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Interim Methods for the Sampling and Analysis of Priority Pollutants in Sediments and Fish Tissue

U. S. Environmental Protection Agency
Environmental Monitoring and Support Laboratory
Cincinnati, Ohio 45268

August 1977
Revised October 1980

FOREWORD

This collection of draft methods for the analyses of fish and sediment samples for the priority pollutants was originally prepared as guidance to the Regional Laboratories. The intention was to update and revise the methods as necessary if and when shortcomings and/or problems were identified. Some problems such as the formation of lead in the "phenol in fish" method have been identified. Consequently, this method has been deleted. Additionally, both the sediment and fish methods for volatile organics by purge and trap analysis have been replaced. Other editorial and technical changes have also been made to the original methods.

It is the intention of the Environmental Monitoring and Support Laboratory - Cincinnati (EMSL-Cincinnati) to update and correct methods as necessary. Consequently, the user of these methods would be performing a service in calling our attention to any problems and in making suggestions to update the methods. Comments should be directed to:

Director, Environmental Monitoring and Support Laboratory
26 W. St. Clair Street
Cincinnati, Ohio 42563

SAMPLE HANDLING

1. Collection

1.1 Samples shall be collected according to recognized procedures. Preferably, all analyses should be performed on the same sample. A minimum of 250 grams are required for the total protocol.

1.2 The recommended container for the sediment sample is a standard one-quart, wide-mouth, screw-cap, glass bottle with a Teflon lid liner. It is particularly important that glassware used in organic residue analyses be scrupulously cleaned before initial use. At the time of collection, the bottle should be filled nearly to the top with the sediment sample. If the sample is collected below a water column, the threads and sealing surfaces should be washed off with sample water. "Top off" the collected sediment sample with sample water and seal with the Teflon-lined screw cap. Maximum effort must be made to seal the sample with a minimum of gaseous headspace. The sample must remain sealed until the aliquots for volatile organics are taken for analyses.

1.3 In the case of small fish, a sufficient number should be combined by sampling site location and species to obtain the minimum weight. The collected samples are wrapped in aluminum foil, labeled with freezer tape, and placed in the freezer chest with dry ice.

2. Preservation

2.1 The sediment sample should be labeled with freezer tape and transferred to the laboratory in an ice chest maintained at or near 4°C. The samples should be processed as soon as possible.

2.2 Fish samples are to be frozen at the time of collection and must remain frozen until the subsamples are taken for purgeable organics.

3. Processing

3.1 Sediment

3.1.1 Decant the water from the top of the sediment. Transfer the sediment into a Pyrex tray and mix thoroughly with a Teflon spatula. Discard sticks, stones, and other foreign objects, if present. Weigh five 10.0-gram portions of the sample into separate 125-ml vials. Using a crimper, tightly secure a septum to each bottle with an aluminum seal. Store these sample aliquots in a freezer until ready for volatile organics analysis.

3.1.2 Determine the percent solids in the sediment by drying a 10-25g portion in a tared evaporating dish, overnight, at 103°C.

Calculate the % solids using the equation:

$$\% \text{ solids} = \frac{A}{B} \times 100$$

where: A = weight of dry residue in grams

B = weight of wet sample in grams

3.1.3 Transfer half of the remaining sediment sample back to the original sample bottle and store at 4°C. This portion will be used for those analyses requiring a wet sample.

Spread the other half of the sample uniformly in the tray and allow to dry at room temperature for four or five days in a contaminant-free environment. When dry - less than 10% water - grind the sample with a large mortar and pestle to a uniform particle size. Discard any foreign objects found during grinding and transfer the powdered sediment into a wide-mouthed glass jar and seal with a Teflon-lined lid. This air-dried sample will be used for those analyses requiring an air-dried sample.

3.2 Fish ⸸

3.2.1 To prepare the fish sample for analytical pretreatment, unwrap and weigh each fish. Combine small fish by site and species until a minimum combined weight of 250g is obtained. Chop the sample into 1-inch chunks using a sharp knife and mallet.

3.2.2 Grind the sample using a large commercial meat grinder that has been precooled by grinding dry ice. Thoroughly mix the ground material. Regrind and mix material two additional times. Clean out any material remaining in the grinder; add this to the sample and mix well.

3.2.3 Weigh five 10.0g portions of the sample into separate 125-ml vials. Using a crimper, tightly secure a septum to each bottle with a seal. Store these sample aliquots in a freezer until ready for volatile organics-analysis.

3.2.4 Transfer the remaining fish sample to a glass container and store in a freezer for later subsampling and analysis.

4. Special Equipment and Materials

4.1 Ice chest.

4.2 Wide-mouth quart bottles with Teflon lid liners.

4.3 Teflon-coated or porcelain spatula.

4.4 Pyrex glass tray, 8x12x2-inch.

4.5 Mortar and pestle (large).

4.6 Knife, heavy blade (or meat cleaver).

4.7 Mallet, plastic faces, 2 to 3 lb.

4.8 Electric meat grinder, 1/2 HP.

4.9 Dry ice.

4.10 Aluminum foil

4.11 Freezer tape, for labels.

4.12 Freezer.

4.13 Vials, 125-ml Hypo-Vials (Pierce Chemical Co., #12995), or equivalent.

4.14 Septa, Tuf-Bond (Pierce #12720), or equivalent.

4.15 Seals, aluminum (Pierce #13214), or equivalent.

4.16 Crimper, hand (Pierce #13212), or equivalent.

Analysis of Sediments for Chlorinated Pesticides, Polychlorinated Biphenyls and Non-polar Neutrals

1. Scope

1.1 The compounds listed in Table I are extracted from air-dried sediment by the Soxhlet extraction technique. The extract is subsequently analyzed for pesticides and PCBs using approved methods (1) as cited in the Federal Register (2). The remaining compounds are determined using the methods described in Appendix II of the Federal Register (3). While the above referenced methods have been proven for pesticides and PCBs, they have not been sufficiently tested through extensive experimentation for the non-polar neutral compounds in Table I.

2. Special Apparatus and Materials

2.1 Soxhlet extractor, 40-mm ID, with 500-ml round bottom flask.

2.2 Kuderna-Danish, 500-ml, with 10-ml graduated receiver and 3-ball Snyder column.

2.3 Chromatographic column - Pyrex, 20-mm ID x approximately 400-mm long, with coarse fritted plate on bottom.

3. Procedure

3.1 Extraction

3.1.1 Weigh 30.0 grams of the previously air-dried sample into a tared 200-ml beaker. Add 3 ml distilled water (10% of

sample weight), mix well and allow to stand for 2 hours while mixing occasionally.

3.1.2 Place about 1/2" of preextracted glass wool in the bottom of the Soxhlet extractor chamber and quantitatively transfer the contents of the beaker into the chamber. Place a second glass wool plug on top of the sample. Wash the 200-ml beaker and all mixing tools several times with a 1:1 hexane/acetone mixture. Cycle the wash mixture through the extractor using a total of 300 ml of the mixed solvent.

3.1.3 Attach the extractor to a 500-ml round bottom flask containing a boiling stone and extract the solids for 16 hours.

3.1.4 After extraction is complete, dry and filter the extract by passing it through a 4" column of hexane-washed sodium sulfate. Wash the 500-ml flask and the sodium sulfate with liberal amounts of hexane. Collect the eluate in a 500-ml K-D evaporative flask with a 10-ml ampul. Concentrate the sample extract to 6-10 ml.

3.2 Cleanup and Separation

3.2.1 Adjust the sample extract volume to 10 ml and clean up the extraction by Florisil column chromatography according to the 304(g) methodology for PCBs (1), part 10.3. For sulfur removal, continue with part 10.5.3.4 of that method. NOTE: If sulfur crystals are present in the extract, separate the crystals from the sample by decantation.

3.2.2 Analyze the Florisil eluates for the pesticides and PCBs appearing in Table I, according to the approved methods (1).

3.2.3 Analyze remaining compounds of Table I, Column C, using the methods described in Appendix II of the Federal Register (3).

3.3 Standard quality assurance protocols should be employed, including blanks, duplicates and dosed samples as described in the "Analytical Quality Control Handbook" (4). Dosing can be accomplished by injecting 1-20 µl of a standard into the homogenized sediment contained in the Soxhlet extractor chamber.

4. Reporting of Data

4.1 Report results in µg/kg on a dry weight basis using the percent moisture values determined earlier. Report all quality control data with the analytical results for the samples.

Analysis of Fish for Chlorinated Pesticides and Polychlorinated Biphenyls

1. Scope

1.1 The chlorinated pesticides and polychlorinated biphenyls (PCBs) listed in Table I are extracted from fish using either method A or B as described below. Method A employs a blender, whereas a Tissumizer or the equivalent is required for Method B. Either procedure results in an extract that can be incorporated directly into the approved procedures (1) for pesticides or PCBs as cited in the Federal Register (2).

2. Special Apparatus and Materials

2.1 Method A Only

2.1.1 Blender, high-speed - Waring Blender, Courdos, Omni-Mixer, or equivalent. Explosion proof model recommended. Quart container is suitable size for routine use.

2.1.2 Buchner funnel - porcelain, 12-cm.

2.1.3 Filter paper - 110 mm sharkskin circles.

2.1.4 Flask, vacuum filtration - 500 ml.

2.2 Method B Only

2.2.1 Tissumizer SDT-182EN (available from Tekmar Company, P. O. Box 37207, Cincinnati, Ohio, 45222), or equivalent.

2.2.2 Centrifuge - capable of handling 100 ml centrifuge tubes.

2.3 Method A & B

2.3.1 Kuderna-Danish concentrator - 500 ml, with 10-ml graduated receiver and 3-ball Snyder column.

2.3.2 Chromatographic column - pyrex, 20 mm ID x approximately 400 mm long, with coarse fritted plate on bottom.

3. Procedures

3.1 Method A

3.1.1 Weigh a 25 to 50g portion of frozen, ground fish and add to a high-speed blender. Add 100g anhydrous Na_2SO_4 to combine with the water present and to disintegrate the sample. Alternately, blend and mix with a spatula until the sample and sodium sulfate are well mixed. Scrape down the sides of the blender jar and break up the caked material with the spatula. Add 150 ml of hexane and blend at high speed for 2 min.

3.1.2 Decant the hexane supernatant through a 12-cm Buchner filter with two sharkskin papers into a 500-ml suction flask. Scrape down the sides of the blender jar and break up the caked material with the spatula. Reextract the residue in the blender jar with two 100 ml portions of hexane, blending 3 min. each time. (After one min. of blending, stop the blender, scrape the material from the sides of the blender jar, and break up the caked material between extractions.)

3.1.3 Decant the hexane supernatants through the Buchner and combine with the first extract. After the last blending, transfer the residue from the blender jar to the Buchner, rinsing the blender jar and material in the Buchner with three 25 to 50 ml portions of hexane. Immediately after the last rinse, press the residue in the Buchner with the bottom of a clean beaker to force out the remaining hexane.

3.1.4 Pour the combined extracts and rinses through a column of anhydrous Na_2SO_4, 20 mm x 100 mm, and collect the eluate in a 500 ml Kuderna-Danish concentrator. Wash the flask and then the column with small portions of hexane and concentrate the extract below 10 ml.

3.2 Method B

3.2.1 Weigh 20.0g of frozen, ground fish and add to a 100-ml centrifuge tube. Add 20 ml of hexane and insert the Tissumizer into the sample. Turn on the Tissumizer and disperse the fish in the solvent for 1 min. Centrifuge and decant the solvent through a column of anhydrous Na_2SO_4, 20 mm x 100 mm, and collect the eluate in a 500-ml Kuderna-Danish concentrator.

3.2.2 Repeat the dispersion twice using a 20-ml aliquot each time, combining all dried portions of solvent in the concentrator. Rinse the Tissumizer and the column with small portions of hexane and concentrate the extract below 10 ml.

3.3 Cleanup and Analysis

3.3.1 Unless prior experience would indicate the fish species fat content is low (less than 3g per extract), the hexane/acetonitrile cleanup procedures described in the reference methods should be followed. In all cases, Florisil column chromatography should be used to clean up the extracts before gas chromatography (1). An electron capture detector is used for final measurement, and results

are calculated in ug/kg. Identifications can be confirmed by GC/MS techniques as described in Appendix II of the Federal Register (3).

3.4 Quality Control

3.4.1 Standard quality assurance protocols should be employed, including blanks, duplicates, and dosed samples as described in the "Analytical Quality Control Handbook (4).

3.4.2 Dose fish sample aliquots by injecting minimum amounts (< 20 µl total) of concentrated pesticide or PCB solutions into the solid subsample 10 to 15 minutes before extraction.

4. Reporting of Data

4.1 Report results in µg/kg on a wet tissue basis. Report all quality control data with the analytical results for the samples.

Base/Neutrals, Acids, [redacted]—Method 625

1. *Scope and Application.*

1.1 This method covers the determination of a number of organic compounds that are solvent extractable and amenable to gas chromatography. The parameters listed in Tables 1, 2 and 3 may be determined by this method.

1.2 This method is applicable to the determination of these compounds in municipal and industrial discharges. It is designed to be used to meet the monitoring requirements of the National Pollutants Discharge Elimination System (NPDES).

1.3 The detection limit of this method is usually dependent upon the level of interferences rather than instrumental limitations. The limits listed in Tables 4, 5, and 6 represent the minimum quantity that must be injected into the system to get confirmation by the mass spectrometric method described below.

1.4 The GC/MS parts of this method are recommended for use only by analysts experienced with GC/MS or under the close supervision of such qualified persons.

2. *Summary of Method.*

2.1 A 1 to 2 liter sample of wastewater is extracted with methylene chloride using separatory funnel or continuous extraction techniques. If emulsions are a problem, continuous extraction techniques should be used. The extract is dried over sodium sulfate and concentrated to a volume of 1 ml using a Kuderna-Danish (K-D) evaporator. Chromatographic conditions are described which allow for the separation of the compounds in the extract.

2.2 Quantitative analysis is performed by GC/MS using either the internal standard or external standard technique.

3. *Interferences.*

3.1 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of chromatograms. All of these materials must 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 source to source, depending upon the diversity of the industrial complex or municipality being sampled.

3.3 The recommended analytical procedure may not have sufficient resolution to differentiate between certain isomeric pairs. These are anthracene and phenanthrene, chrysene and benzo(a)anthracene, and benzo(b)fluoranthene and benzo(k)fluoranthene. The GC retention time and mass spectral data are not sufficiently unique to make an unambiguous distinction between these compounds. Alternative techniques should be used to identify and quantify these specific compounds. See Reference 1.

4. *Apparatus and Materials.*

4.1 Sampling equipment, for discrete or composite sampling.

4.1.1 Grab sample bottle—amber glass, 1-liter to 1-gallon volume. French or Boston Round design is recommended. The container must be washed and solvent rinsed before use to minimize interferences.

4.1.2 Bottle caps—Threaded to fit sample bottles. Caps must be lined with Teflon. Aluminum foil may be substituted if sample is not corrosive.

4.1.3 Compositing equipment—Automatic or manual compositing system. Must incorporate glass sample containers for the collection of a minimum of 1000 ml. Sample containers must be kept refrigerated during sampling. No plastic or rubber tubing other than Teflon may be used in the system.

4.2 Separatory funnel—2000 ml, with Teflon stopcock (Ace Glass 7228-T-72 or equivalent).

4.3 Drying column—A 20 mm ID pyrex chromatographic column equipped with coarse glass frit or glass wool plug.

4.4 Kuderna-Danish (K-D) Apparatus

4.4.1 Concentrator tube—10 ml, graduated (Kontes K-570050-1025 or equivalent). Calibration must be checked. Ground glass stopper (size 19/22 joint) is used to prevent evaporation of extracts.

4.4.2 Evaporative flask—500 ml (Kontes K-57001-0500 or equivalent). Attach to concentrator tube with springs. (Kontes K-662750-0012).

4.4.3 Snyder column—three-ball macro (Kontes K503000-0232 or equivalent).

4.4.4 Snyder column—two-ball micro (Kontes K-569002-0219 or equivalent).

4.4.5 Boiling chips-extracted, approximately 10/40 mesh.

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

4.6 Gas chromatograph—Analytical system complete with gas chromatograph capable of on-column injection and all required accessories including column supplies, gases, etc.

4.6.1 Column 1—For [redacted] and Pesticides a 6-foot glass column (¼ in OD x 2 mm ID) packed with 3% SP-2250 coated on 100/120 Supelcoport (or equivalent).

4.6.2 Column 2—For Acids, a 6-foot glass column (¼ in OD x 2 mm ID) packed with 1% SP-1240 DA coated on 100/120 mesh Supelcoport (or equivalent).

4.7 Mass Spectrometer—Capable of scanning from 35 to 450 a.m.u. every 7 seconds or less at 70 volts (nominal) and producing a recognizable mass spectrum at unit resolution from 50 ng of DFTPP when the sample is introduced through the GC inlet (Reference 2). The mass spectrometer must be interfaced with a gas chromatograph equipped with an injector system designed for splitless injection and glass capillary columns or an injector system designed for on-column injection with all-glass packed columns. All sections of the transfer lines must be glass or glass-lined and must be deactivated. (Use Sylon-CT, Supelco, Inc., or equivalent to deactivate.)

Note.—Systems utilizing a jet separator for the GC effluent are recommended since membrane separators may lose sensitivity for light molecules and glass frit separators may inhibit the elution of polynuclear aromatics. Any of these separators may be used provided that it gives recognizable mass spectra and acceptable calibration points at the limit of detection specified for each individual compound listed in Tables 4, 5, and 6.

4.8 A computer system must be interfaced to the mass spectrometer to allow acquisition of continuous mass scans for the duration of the chromatographic program. The computer system should also be equipped with mass storage devices for saving all data from GC-MS runs. There must be computer software available to allow searching any GC-MS run for specific ions and plotting the intensity of the ions with respect to time or scan number. The ability to integrate the area under any specific ion plot peak is essential for quantification.

4.9 Continuous liquid-liquid extractors—Teflon or glass connecting joints and stopcocks, no lubrication. (Hershberg-Wolf Extractor—Ace Glass Co., Vineland, N.J. P/N 6841-10 or equivalent).

5. *Reagents.*

5.1 Sodium hydroxide—(ACS) 6N in distilled water.

5.2 Sulfuric acid—(ACS) 6N in distilled water.

5.3 Sodium sulfate—(ACS) granular anhydrous (rinsed with methylene chloride (20 ml/g) and conditioned at 400° C for 4 hrs.).

5.6 [illegible] quality or equivalent.

5.8 Stock standards—Obtain stock standard solutions at a concentration of 1.00 µg/µl. For example, dissolve 0.100 grams of assayed reference material in pesticide quality isooctane or other appropriate solvent and dilute to volume in a 100 ml ground glass stoppered volumetric flask. The stock solution is transferred to 15 ml Teflon lined screw cap vials, stored in a refrigerator and checked frequently for signs of degradation or evaporation, especially just prior to preparing working standards from them. Protect PNA standards from light.

6. *Calibration.*

6.1 Prepare calibration standards that contain the compounds of interest, either singly or mixed together. The standards should be prepared at concentrations that will bracket the working ranges of the chromatographic system (two or more orders of magnitude are suggested). If the limit of detection (Tables 4, 5, or 6) can be calculated as 20 ng injected, for example, prepare standards at 1 µg/ml, 10 µg/ml, 100 µg/ml, etc. so that injections of 1–5 µl of the calibration standards will define the linearity of the detector in the working range.

6.2 Assemble the necessary gas chromatographic apparatus and establish operating parameters equivalent to those indicated in Tables 4, 5, and 6. By injecting calibration standards, establish the linear range of the analytical system and demonstrate that the analytical system meets the limits of detection requirements of Tables 4, 5, and 6. If the sample gives peak areas above the working range, dilute and reanalyze.

6.3 Internal Standard Method—The internal standard approach is acceptable for all of the semivolatile organics. The utilization of the internal standard method requires the periodic determination of response factors (RF) which are defined in equation 1.

Eq. 1 $RF = (A_s C_{is})/(A_{is} C_s)$

Where:

A_s is the integrated area or peak height of the characteristic ion for the pollutant standard.

A_{is} is the integrated area or peak height of the characteristic ion for the internal standard.

C_{is} is the amount (µg) of the internal standard.

C_s is the amount (µg) of the pollutant standard.

6.3 The relative response ratio for the pollutants should be known for at least two concentration values—20 ng injected to approximate 10 µg/l and 200 ng injected to approximate the 100 µg/l level (Assuming 1 ml final volume and a 2 µl injection). These compounds that do not respond at either of these levels may be run at concentrations appropriate to their response.

The response factor (RF) should be determined over all concentration ranges of standard (C_s) which are being determined (Generally, the amount of internal standard added to each extract is the same (20 µg) so that C_{is} remains constant.) This should be done by preparing a calibration curve where the response factor (RF) is plotted against the standard concentration (C_s), using a minimum of three concentrations over the range of interest. Once this calibration curve has been determined, it should be verified daily by injecting at least one standard solution containing internal standard. If significant drift has occurred, a new calibration curve must be constructed. To quantify, add the internal standard to the concentrated sample extract no more than a few minutes before injecting into the GC/MS to minimize the possibility of losses due to evaporation, adsorption, or chemical reaction. Calculate the concentration by using the previous equations with the appropriate response factor taken from the calibration curve. Either deuterated or fluorinated compounds can be used as internal standards and surrogate standards. Naphthalene-d_8, anthracene-d_{10}, pyridine-d_5, aniline-d_5, nitrobenzene-d_5, 1-fluoronaphthalene, 2-fluoronaphthalene, 2-fluorobiphenyl, 2,2'-difluorobiphenyl, and 1,2,3,4,5-pentafluorobiphenyl have been used or suggested as appropriate internal standards/surrogates for the base-neutral compounds. Phenol-d_6, pentafluorophenol, 2-perfluoromethyl phenol, and 2-fluorophenol have been used or suggested for the acid compounds. Compounds used as internal standards are not to be used as surrogate standards. The internal standard must be different from the surrogate standards.

6.5 The external standard method can also be used at the discretion of the analyst. Prepare a master calibration curve using a minimum of three standard solutions of each of the compounds that are to be measured. Plot concentrations versus integrated areas or peak heights (selected characteristic ion for GC/MS). One point on each curve should approach the limit of detection (Tables 4, 5, and 6). After the master set of instrument calibration curves have been established, they should be verified daily by injecting at least one standard solution. If significant drift has occurred, a new calibration curve must be constructed.

7. *Quality Control*

7.1 Before processing any samples, demonstrate through the analysis of a 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.

7.2 Standard quality assurance practices should be used with this method. Field replicates should be collected and analyzed to determine the precision of the sampling technique. Laboratory replicates should be analyzed to determine the precision of the analysis. Fortified samples should be analyzed to determine the accuracy of the analysis. Field blanks should be analyzed to check for contamination introduced during sampling and transportation.

8. *Sample Collection, Preservation, and Handling.*

8.1 Grab samples must be collected in glass containers. Conventional sampling practices should be followed, except that 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 free of tygon and other potential sources of contamination.

8.2 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 hours will elapse before delivery to the laboratory. If the samples will not be extracted within 48 hours of collection, they must be preserved as follows:

8.2.1 If the sample contains residual chlorine, add 35 mg of sodium thiosulfate per 1 ppm of free chlorine per liter of sample.

8.2.2 Adjust the pH of the water sample to a pH of 7 to 10 using sodium hydroxide or sulfuric acid. Record the volume of acid or base used.

8.3 All samples must be extracted within 7 days and completely analyzed within 30 days of collection.

9. *Sample Extraction (Base/Neutrals, Acids, and Pesticides).*

9.1 Samples may be extracted by separatory funnel techniques or with a continuous extractor as described in Section 10. Where emulsions prevent acceptable solvent recovery with the separatory funnel technique, the analyst must use the continuous extractor.

9.2 The details of the extraction technique should be adjusted according to the sample volume. The technique described below assumes a sample

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volume of 1000 ml for volumes approximating 1-liter, the volume of extraction solvent should be adjusted to 250, 100, and 100 ml for the serial extraction of the base neutrals, and 200, 100, and 100 ml for the acids.

9.3 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Pour the entire sample into a two-liter separatory funnel. Adjust the pH of the sample with 6N NaOH to 11 or greater. Use multirange pH paper for the measurements. Proceed to Section 10 if continuous extraction is used.

9.4 Add 60 ml methylene chloride to the sample bottle, cap, and shake 30 seconds to rinse the walls. Transfer the solvent into the separatory funnel, and extract the sample by shaking the funnel for two minutes with periodic venting to release excess vapor pressure. Allow the organic layer to separate from the water phase for a minimum of ten minutes. If the emulsion interface between layers is more than one-third the size of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration of the emulsion through glass wool, or centrifugation. (If the emulsion cannot be broken, that is, recovery is less than 80% of the added solvent corrected for the water solubility of methylene chloride, transfer the sample, solvent, and emulsion into a continuous extractor and proceed as described in Section 10). Collect the methylene chloride extract in a 250-ml Erlenmeyer flask.

9.5 Add a second 60-ml volume of methylene chloride to the sample bottle and complete the extraction procedure a second time, combining the extracts in the Erlenmeyer flask.

9.6 Perform a third extraction in the same manner. Pour the combined extract through a drying column containing 3–4 inches of anhydrous sodium sulfate, and collect it in a 500 ml K–D flask equipped with 10 ml concentrator tube. Rinse the Erlenmeyer with 20 to 40 ml of methylene chloride. Pour this through the drying column. Seal, label as base/neutral fraction, and proceed with the acid extraction. If the extract must be stored overnight before analysis by GC/MS, it may be transferred to a 2 ml serum vial equipped with a Teflon-lined rubber septum and crimp cap.

9.7 Acid (Phenols) Extraction—Adjust the pH of the water, previously extracted for base-neutrals, with 6N H_2SO_4 to 2 or below. Serially extract with 60, 60 and 60 ml portions of distilled-in-glass methylene chloride. Collect and combine the extracts in a 250-ml Erlenmeyer flask then dry by passing through a column of anhydrous sodium sulfate. Rinse the Erlenmeyer with 20 to 40 ml of methylene chloride and pour through the drying column. Seal, label acid fraction and prepare for concentration.

9.8 Concentrate the extracts (Base/Neutrals and Acids) in a 500 ml K–D flask equipped with a 10 ml concentrator tube.

9.9 Add 1 to 2 clean boiling chips to the flask and attach a three-ball macro-Snyder column. Prewet the Snyder column by adding about 1 ml methylene chloride through the top. Place the K–D apparatus on a warm water bath (60 to 65°C) so that the concentrator tube is partially immersed in the water, and the entire lower rounded surface of the flask is bathed with water vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15 to 20 minutes. At the proper rate of distillation the balls of the column actively chatter but the chambers do not flood. When the liquid has reached an apparent volume 1 ml, remove the K–D apparatus and allow the solvent to drain for at least 10 minutes while cooling. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 to 2 ml of methylene chloride. A 5-ml syringe is recommended for this operation.

9.10 Add a clean boiling chip and attach a two-ball micro-Snyder column to the concentrator tube in 9.8. Prewet the column by adding about 0.5 ml methylene chloride through the top. Place the K–D apparatus on a warm water bath (60 to 65°C) so that the concentrator tube is partially immersed in the water. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 5–10 minutes. At the proper rate of distillation the balls of the column actively chatter but the chambers do not flood. When the liquid reaches an apparent volume of about 0.5 ml, remove the K–D from the water bath and allow the solvent to drain and cool for at least 10 minutes. Remove the micro-Snyder column and rinse its lower joint into the concentrator tube with approximately 0.2 ml of methylene chloride. Adjust the final volume to 1.0 ml, seal, and label as acid fraction.

9.11 Determine the original sample volume by refilling the sample bottle to the mark and transferring the liquid to a 1,000-ml graduated cylinder. Record the sample volume to the nearest 5 ml.

10. *Emulsions/Continuous Extraction.*

10.1 Place 500 to 750 ml of methylene chloride in the extractor and 250–500 ml methylene chloride in the distilling flask.

10.2 Add the aqueous sample (pH 11 or greater) to the extractor. Add blank water as necessary to operate the extractor and extract for 24 hours. Remove the distilling flask and pour the contents through a drying column containing 7 to 10 cm of anhydrous sodium sulfate. Collect the methylene chloride in a 500 ml K–D evaporator flask equipped with a 10 ml concentrator tube. Seal, label as the base/neutral fraction, and concentrate as per sections 9.8 to 9.10.

10.3 Adjust the pH of the sample in the continuous extractor to 2 or below using 6N sulfuric acid. Charge a clean distilling flask with 500 ml of methylene chloride. Extract for 24 hours. Remove the distilling flask and pour the contents through a drying column containing 7 to 10 cm of anhydrous sodium sulfate. Collect the methylene chloride layer on a K–D evaporator flask equipped with a 10 ml concentrator tube. Label as the acid fraction. Concentrate as per sections 9.8 to 9.10.

11. *Calibration of the GC–MS System.*

11.1 At the beginning of each day, the mass calibration of the GC–MS system must be checked and adjusted if necessary to meet DFTPP specifications (11.3). Each day base-neutrals are measured, the column performance specification (12.1) with benzidine must be met. Each day the acids are measured, the column performance specification (12.1) with pentachlorophenol must be met. DFTPP can be mixed in solution with either of these compounds to complete two specifications with one injection, if desired.

11.2 To perform the mass calibration test of the GC–MS system, the following instrumental parameters are required:

Electron energy—70 volts (nominal).
Mass range—35 to 450 a.m.u.
Scan time—1 second or less.

11.3 *GC–MS system calibration*—Evaluate the system performance each day that it is to be used for the analysis of samples or blanks by examining the mass spectrum of DFTPP. Inject a solution containing 50 ug DFTPP and check to insure that performance criteria listed in Table 10 are met. If the system performance criteria are not met, the analyst must retune the spectrometer and repeat the performance check. The performance criteria must be met before any samples or standards may be analyzed.

12. *Gas Chromatography-Mass Spectrometry of Base/Neutral Fraction.*

[illegible] that base/neutral analyses are to be performed, inject 100 nanograms of benzidine either separately or as part of a standard mixture that may also contain 50 ng of DFTPP. The tailing factor for benzidine should be less than 3. Calculation of the tailing factor is given in Reference 2 and described in Figure 8.

12.2 Establish chromatographic conditions equivalent to those in Tables 4 and 5. Included in these tables are estimated retention times and sensitivities that can be achieved by this method. Examples of the separations achieved by these columns are shown in Figures 1 and 3 through 7.

12.3 Program the GC/MS to operate in the Extracted Ion Current Profile (EICP) mode, and collect EICP for the three ions listed in Tables 7 and 8 for each compound being measured. Operating in this mode, calibrate the system response for each compound as described in Section 6, using either the internal or external standard procedure.

12.4 If the internal standard approach is being used, the analyst may not add the standard to sample extracts until immediately before injection into the instrument. Mix thoroughly.

12.5 Inject 2 to 5 µl of the sample extract. The solvent-flush technique is preferred. If external calibration is employed, record the volume injected to the nearest 0.05 µl. If the response for any ion exceeds the linear range of the system, dilute the extract and reanalyze.

12.6 Qualitative and quantitative measurements are made as described in Section 14. When the extracts are not being used for analysis, store them in vials with unpierced septa in the dark at 4° C.

13. *Gas Chromatography/Mass Spectrometry of Acid Fraction.*

13.1 At the beginning of each day that acid fraction analyses are to be performed, inject 50 nanograms of pentachlorophenol either separately or as part of a standard mixture that may also contain DFTPP. The tailing factor for pentachlorophenol should be less than 5. Calculation of the tailing factor is given in Reference 2 and described in Figure 8.

13.2 Establish chromatographic conditions equivalent to those in Table 6. Included in this table are estimated retention times and sensitivities that can be achieved by this method. An example of the separation achieved by the column is shown in Figure 2.

13.3 Program the GC/MS to operate in the Extracted Ion Current Profile mode, and collect EICP for the three ions listed in Table 9 for each phenol being measured. Operating in this mode, [illegible] compound as described in Section 6 using either the internal or external standard procedure.

13.4 If the internal standard approach is being used, the analyst may not add the standard to sample extracts until immediately before injection into the instrument. Mix thoroughly.

13.5 Inject 2 to 5 µl of the sample extract. The solvent-flush technique is preferred. If external standard calibration is employed, record the volume injected to the nearest 0.05 µl. If the response for any ion exceeds the linear range of the system, dilute the extract and reanalyze.

13.6 Qualitative and quantitative measurements are made as described in Section 14. When the extracts are not being used for analysis, store them in vials with unpierced septa in the dark at 4° C.

14. *Qualitative and Quantitative Determination.*

14.1 To qualitatively identify a compound, obtain an Extracted Ion Current Profile (EICP) for the primary ion and the two other ions listed in Tables 7, 8, or 9. The criteria below must be met for a qualitative identification.

14.1.1 The characteristic ions for the compound must be found to maximize in the same or within one spectrum of each other.

14.1.2 The retention time of the experimental mass spectrum must be within ±60 seconds of the retention time of the authentic compound.

14.1.3 The ratios of the three EICP peak heights must agree within ±20% with the ratios of the relative intensities for these ions in a reference mass spectrum. The reference mass spectrum can be obtained from either a standard analyzed through the GC–MS system or from a reference library.

14.1.4 Structural isomers that have very similar mass spectra can be explicitly identified only if the resolution between the isomers in a standard mix is acceptable. Acceptable resolution is achieved if the valley height between isomers is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

14.2 In samples that contain an inordinate number of interferences the chemical ionization (CI) mass spectrum may make identification easier. In Tables 7 and 8 characteristic CI ions for most of the compounds are given. The use of chemical ionization MS to support EI is encouraged but not required.

14.3 When a compound has been identified, the quantification of that compound will be based on the integrated area from the specific ion plot of the first listed characteristic ion in Tables 7, 8 and 9. If the sample produces an interference for the first listed ion, use a secondary ion to quantify. Quantification will be done by the external or internal standard method.

14.4 Internal Standard—By adding a constant known amount of internal standard (C_{is} in µg) to every sample extract, the concentration of pollutant (C_x) is µg/l in the sample is calculated using equation 2.

Eq. 2 $$C_x = \frac{(A_x)(C_{is})}{(A_{is})(RF)(Vo)}$$

Where: V_o is the volume of the original sample in liters, and the other terms are defined as in Section 6.3.

14.5 External Standard—The concentration of the unknown can be calculated from the slope and intercept of the calibration curve. The unknown concentration can be determined using equation 3.

Eq. 3

$$\text{Micrograms/liter} = \text{ng/ml} = \frac{(A)(V_t)}{(V_i)(V_s)}$$

where:

A = mass of compound from calibration curve (ng).
V_t = volume of extract injected (µl).
V_t = volume of total extract (µl).
V_s = volume of water extracted (ml).

14.6 Report all results to two significant figures. Report results in micrograms per liter (Base/Neutrals and Acids) without correction for recovery data. When duplicate and spiked samples are analyzed, all data obtained should be reported.

14.7 In order to minimize unnecessary GC–MS analysis of method blanks and field blanks, the field blank may be screened on a FID–GC equipped with the appropriate SP–2250 or SP–1240 DA columns.

15. References

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Table 1.—*Base-Neutral Extractables*

Compound	STORET No.
Acenaphthene	34205
Acenaphthylene	34200
Anthracene	34220
Benzo(a)anthracene	34526
Benzo(b)fluoranthene	34230
Benzo(k)fluoranthene	34242
Benzo(a)pyrene	34247
Benzo(g,h,i)perylene	34521
Benzidine	39120
Bis(2-chloroethyl)ether	34273
Bis(2-chloroethoxy)methane	34278
Bis(2-ethylhexyl)phthalate	39100
Bis(2-chloroisopropyl)ether	34283
4-Bromophenyl phenyl ether	34636
Butyl benzyl phthalate	34292
2-Chloronaphthalene	34581
4-Chlorophenyl phenyl ether	34641
Chrysene	34320
Dibenzo(a,h)anthracene	34556
Di-n-butylphthalate	39110
1,3-Dichlorobenzene	34566
1,4-Dichlorobenzene	34571
1,2-Dichlorobenzene	34536
3,3'-Dichlorobenzidine	34631
Diethylphthalate	34336
Dimethylphthalate	34341
2,4-Dinitrotoluene	34611
2,6-Dinitrotoluene	34626
Di-n-octylphthalate	34596
1,2-Diphenylhydrazine	34346
Fluoranthene	34376
Fluorene	34381
Hexachlorobenzene	39700
Hexachlorobutadiene	34391
Hexachloroethane	34396
Hexachlorocyclopentadiene	34386
Indeno(1,2,3-cd)pyrene	34403
Isophorone	34408
Naphthalene	39250
Nitrobenzene	34447
N-Nitrosodimethylamine	34438
N-Nitrosodi-n-propylamine	34428
N-Nitrosodiphenylamine	34433
Phenanthrene	34461
Pyrene	34469
2,3,7,8-Tetrachlorodibenzo-p-dioxin	34675
1,2,4-Trichlorobenzene	34551

Table 2.—*Acid Extractables*

Compound	STORET No.
4-Chloro-3-methylphenol	34452
2-Chlorophenol	34586
2,4-Dichlorophenol	34601
2,4-Dimethylphenol	34606
2,4-Dinitrophenol	34616
2-Methyl-4,6-dinitrophenol	34657
2-Nitrophenol	34591
4-Nitrophenol	34646
Pentachlorophenol	39032
Phenol	34694
2,4,6-Trichlorophenol	34621

Table 3.—*Pesticide Extractables*

Compound	STORET No.
Aldrin	39330
α-BHC	39337
β-BHC	39338
γ-BHC	39340
δ-BHC	39356
Chlordane	39350
4,4'-DDD	39310
4,4'DDE	39320
4,4'DDT	39300
Dieldrin	39380
Endosulfan I	34361
Endosulfan II	34356
Endosulfan Sulfate	34351
Endrin	39390
Endrin Aldehyde	34366
Heptachlor	39410
Heptachlor Epoxide	39420
Toxaphene	39400
PCB-1016	34671
PCB-1221	39488
PCB-1232	39492
PCB-1242	39496
PCB-1248	39500
PCB-1254	39504
PCB-1260	39506

Table 4.—*Gas Chromatography of Base/Neutral Extractables*

Compound	Retention time # (min.)	Limit of detection ## ng injected	Limit of detection ## µg/l
1,3-Dichlorobenzene	7.4	20	10
1,4-Dichlorobenzene	7.8	20	10
Hexachloroethane	8.4	20	10
Bis(2-chloroethyl)ether	8.4	20	10
1,2-Dichlorobenzene	8.4	20	10
Bis(2-chloroisopropyl)ether	8.3	20	10
N-Nitroso-di-n-propyl amine		20	10
Nitrobenzene	11.1	20	10
Hexachlorobutadiene	11.4	20	10
1,2,4-Trichlorobenzene	11.6	20	10
Isophorone	11.9	20	10
Naphthalene	12.1	20	10
Bis(2-chloroethoxy) methane	12.2	20	10
Hexachlorocyclopentadiene	13.9	20	10
2-Chloronaphthalene	15.8	20	10
Acenaphthylene	17.4	20	10
Acenaphthene	17.8	20	10
Dimethyl phthalate	18.3	20	10
2,6-Dinitrotoluene	18.7	20	10
Fluorene	18.5	20	10
4-Chlorophenyl phenyl ether	18.5	20	10
2,4-Dinitrotoluene	18.6	20	10
1,2-Diphenyl hydrazine*	20.1	20	10
Diethyl phthalate	20.1	20	10
N-nitrosodiphenyl amine**	20.5	20	10
Hexachlorobenzene	21.0	20	10
4-Bromophenyl phenyl ether	21.2	20	10
Phenanthrene	22.8	20	10
Anthracene	22.8	20	10
Di-n-butyl phthalate	24.7	20	10
Fluoranthene	26.5	20	10
Pyrene	27.3	20	10
Benzidine	28.8	20	10
Butyl benzyl phthalate	29.8	20	10
Bis(2-ethylhexyl) phthalate	30.6	20	10
Chrysene	31.5	20	10
Benzo(a)anthracene	31.5	20	10
3,3'-Dichlorobenzidine	32.2	20	10
Di-n-octyl phthalate	32.5	20	10
Benzo(b)fluoranthene	34.8	20	10
Benzo(k)fluoranthene	34.8	20	10
Benzo(a)pyrene	36.4	20	10
Indeno(1,2,3-cd)pyrene	42.7	50	25
Dibenzo(a,h)anthracene	43.2	50	25
Benzo(g,h,i)perylene	45.1	50	25
N-Nitrosodimethylamine			
Bis(chloromethyl)ether			
2,3,7,8-Tetrachlorodibenzo-p-dioxin			

A six foot glass column (¼ in. OD x 2 mm ID) packed with 3% SP-2250 coated on 100/120 mesh Supelcoport. Carrier gas: helium at 30 ml per min. Temperature program: Isothermal for 4 minutes at 50° C, then 8° per min to 270° C. Hold at 270° C for 30 minutes. If desired, capillary or SCOT columns may be used.

This is a minimum level at which the entire analytical system must give mass spectral confirmation. (Nanograms injected is based on a 2 µl injection of a one liter sample that has been extracted and concentrated to a volume of 1.0 ml.)

*Detected as aldehydrene.

**Detected as diphenylamine.

Table 5.—*Gas Chromatography of Pesticide Extractables*

Compound	Retention time (min)*	Limit of detection# ng injected	Limit of detection# µg/l
α-bhc	21.1	40	10
β-bhc	22.4	40	10
δ-bhc	23.4	40	10
Heptachlor	23.4	40	10
γ-bhc	23.7	40	10
Aldrin	24.0	40	10
Heptachlor epoxide	25.8	40	10
Endosulfan I	26.4	40	10
Dieldrin	27.2	40	10
4,4'-DDE	27.2	40	10
Endrin	27.9	40	10
Endosulfan II	28.6	40	10
4,4'-DDD	28.6	40	10
4,4'-DDT	29.3	40	10
Endosulfan sulfate	29.8	40	10
Chlordane	28 to 30		
Toxaphene	25 to 34		
PCB-1242	20 to 32		
PCB-1254	23 to 32		

*6 foot glass column (¼ in. OD x 2 mm ID) packed with 3% SP-2250 coated on 100/120 mesh Supelcoport. Carrier gas: helium at 30 ml per min. Temperature program: Isothermal for 4 minutes at 50° C, then 8° per minute to 270°. Hold at 270° C for 30 minutes. If desired, capillary or SCOT columns may be used.

#This is a minimum level at which the entire analytical system must give mass spectral confirmation. (Nanograms injected is based on a 4 µl injection of a one-liter sample that has been extracted and concentrated to a volume of 1.0 ml.

Table 6.—*Gas Chromatography of Acid Extractables*

Compound	Retention time* (min)	Limit of detection# ng injected	Limit of detection# µg/l
2-Chlorophenol	6.8	60	25
2-Nitrophenol	8.4	60	25
Phenol	8.0	60	25
2,4-Dimethylphenol	8.4	60	25
2,4-Dichlorophenol	9.8	60	25
2,4,6-Trichlorophenol	11.8	60	25
4-Chloro-3-methylphenol	13.2	60	25
2,4-Dinitrophenol	15.8	500	250

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Table 6.—Gas chromatographic data for Acid Extractables—Continued

Compound	Retention time[1] (min)	Limit of detection[2] ng injected	µg/l
2-Methyl-4,6-dinitrophenol	16.2	500	250
Pentachlorophenol	17.5	50	25
4-Nitrophenol	20.3	50	25

[1] 6 foot glass column (1/4 in. OD × 2 mm ID) packed with 1% SP-1240 DA coated on 100/120 mesh Supelcoport. Carrier gas: helium at 30 ml per min. Temperature program: 2 min isothermal at 70°, then 8° per min to 200° C. If desired, capillary or SCOT columns may be used.

[2] This is a minimum level at which the entire analytical system must give mass spectral confirmation. Nanograms injected is based on a 2 µl injection of a one liter sample that has been extracted and concentrated to 1.0 ml.

Table 7.—Base/Neutral Extractables Characteristic Ions

Compound	Characteristic ions					
	Electron impact			Chemical ionization (methane)		
1,3-Dichlorobenzene	146	148	113	146	148	150
1,4-Dichlorobenzene	146	148	113	146	148	150
Hexachloroethane	117	201	199	199	201	203
Bis(2-chloroethyl) ether	93	63	95	63	107	109
1,2-Dichlorobenzene	146	148	113	146	148	150
Bis(2-chloroisopropyl) ether	45	77	79	77	135	137
N-Nitrosodipropyl amine	130	42	101	.....	.....	
Isophorone	82	95	138	139	167	178
Nitrobenzene	77	123	65	124	152	164
Hexachlorobutadiene	225	223	227	223	225	227
1,2,4-Trichlorobenzene	180	182	145	181	183	209
Naphthalene	128	129	127	129	157	169
Bis(2-chloroethoxy) methane	93	65	123	65	107	137
Hexachlorocyclopentadiene	237	235	272	235	237	239
2-Chloronaphthalene	162	164	127	153	181	203
Acenaphthylene	152	151	153	152	153	181
Acenaphthene	154	153	152	154	155	183
Dimethyl phthalate	63	194	164	151	163	164
2,6-Dinitrotoluene	165	63	121	63	211	223
Fluorene	166	165	167	166	167	195
4-Chlorophenyl phenyl ether	204	206	141	.....	.....	.....
2,4-Dinitrotoluene	165	89	163	183	211	223
1,2-Diphenylhydrazine[1]	77	93	105	185	213	225
Diethylphthalate	149	177	150	177	223	251
N-Nitrosodiphenylamine[1]	169	168	167	169	170	198
Hexachlorobenzene	284	142	249	284	286	288
4-Bromophenyl phenyl ether	248	250	141	249	251	277
Phenanthrene	178	179	176	178	179	207
Anthracene	178	179	176	178	179	207
Dibutyl phthalate	149	150	104	149	205	279
Fluoranthene	202	101	100	203	231	243
Pyrene	202	101	100	203	231	243
Benzidine	184	92	185	185	213	225
Butyl benzyl phthalate	149	91	.....	149	299	327
Bis(2-ethyl hexyl) phthalate	149	167	279	149	.....	.....
Chrysene	228	226	229	228	229	257
Benzo(a)anthracene	228	229	226	228	229	257
3,3'-Dichlorobenzidine	252	254	126	.....	.....	.....
Dioctyl phthalate	149	.....	.....	.....	.....	.....
Benzo(b)fluoranthene	252	253	125	252	253	281
Benzo(k)fluoranthene	252	253	125	252	253	281
Benzo(a)pyrene	252	253	125	252	253	281
Indeno(1,2,3-c,d)pyrene	276	138	277	276	277	305
Dibenzo(a,h)anthracene	278	139	279	278	279	307
Benzo(g,h,i)perylene	276	138	277	276	277	305
N-Nitrosodimethyl amine	42	74	44	.....	.....	.....
Bis(chloromethyl) ether	45	49	51	.....	.....	.....
2,3,7,8-Tetrachlorodibenzo-p-dioxin	.....	322	320	59	.....	.....
Deuterated anthracene(d-10)[2]	188	94	80	189	217	.....

[1] Detected as azobenzene.
[2] Detected as diphenylamine.
[3] Suggested internal standard.

Table 8.—*Pesticides Characteristic Ions*

Compound	Characteristic ions electron impact		
a-BHC	183	181	109
g-BHC	183	181	109
b-BHC	181	183	109
heptachlor	100	272	274
d-BHC	183	109	181
aldrin	66	263	220
heptachlor epoxide	353	355	351
endosulfan I	201	203	276
dieldrin	79	263	279
4,4'-DDE	246	248	176
4,4'-DDD	235	165	237
endrin	81	263	82
endosulfan II	201	203	276
4,4'-DDT	235	237	165
endosulfan sulfate	272	387	422
chlordane [1]	373	375	377
toxaphene [2]	231	233	235
PCB-1242 [2]	224	260	294
PCB-1254 [2]	294	330	362

[1] Characteristic of alpha and gamma forms of chlordane.
[2] These compounds are mixtures of various isomers.

Table 9.—*Acid Extractable Characteristic Ions*

Compound	Characteristic ions					
	Electron impact			Chemical ionization (methane)		
2-Chlorophenol	128	64	130	129	131	157
2-Nitrophenol	139	65	109	140	168	122
Phenol	94	65	66	95	123	125
2,4-Dimethylphenol	122	107	121	123	151	163
2,4-Dichlorophenol	162	164	98	163	165	167
2,4,6-Trichlorophenol	196	198	200	197	199	201
4-Chloro-3-methyl phenol	142	107	144	143	171	183
2,4-Dinitrophenol	184	63	154	185	213	225
2-Methyl-4,6-Dinitrophenol	198	182	77	199	227	239
Pentachlorophenol	266	264	268	267	265	269
4-Nitrophenol	65	139	109	140	168	122
Anthracene (d-10) [1]	188	94	80	189	217	

[1] Suggested internal standard.

Table 10.—*OFTPP Key Ions and Ion Abundance Criteria*

Mass:	Ion abundance criteria
51	30 to 60 percent of mass 198.
68	Less than 2 percent of mass 69.
70	Less than 2 percent of mass 69.
127	40 to 60 percent of mass 198.
197	Less than 1 percent of mass 198.
198	Base peak, 100 percent relative abundance.
199	5 to 9 percent of mass 198.
275	10 to 30 percent of mass 198.
365	Greater than 1 percent of mass 198.
441	Present but less than mass 443.
442	Greater than 40 percent of mass 198.
443	17 to 23 percent of mass 442.

BILLING CODE 6560-61-M

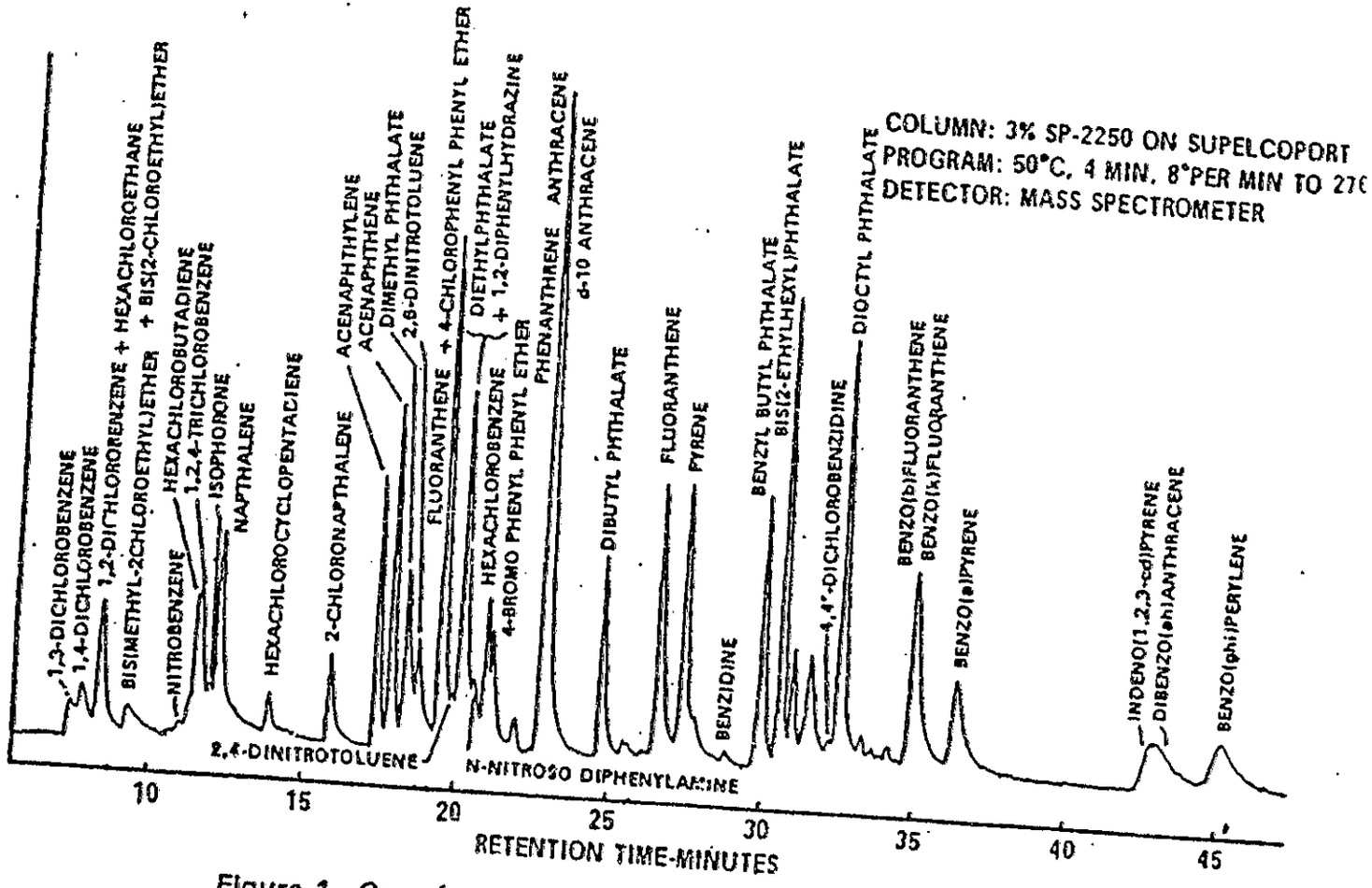

Figure 1. Gas chromatogram of base/neutral fraction

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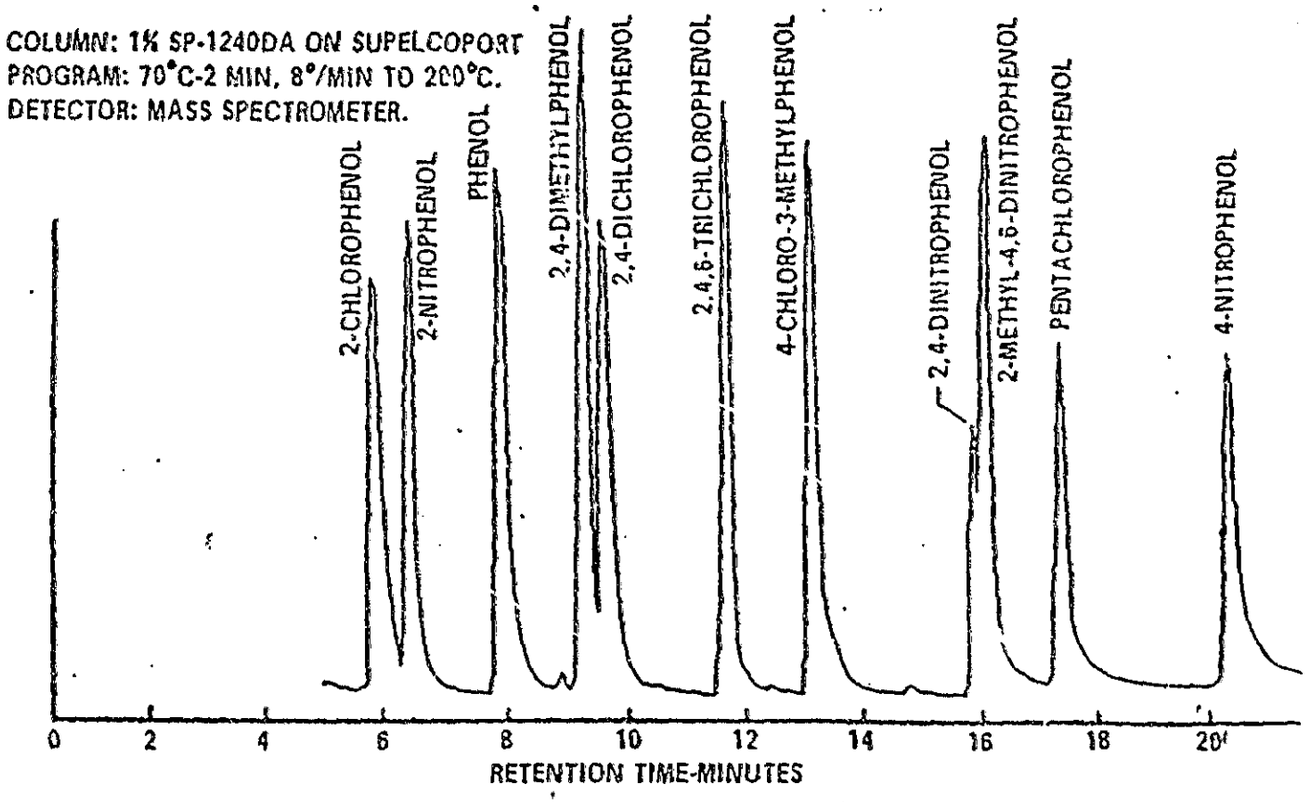

Figure 2. Gas chromatogram of acid fraction

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Method 624

Scope and Application

1.1 This method is designed to determine volatile organic materials that are amenable to the purge and trap method. The parameters listed in Table 1 may be determined by this method.

1.2 This method is applicable to the determination of these compounds in municipal and industrial discharges. It is designed to be used to meet the monitoring requirements of the National Pollutants Discharge Elimination System (NPDES).

1.3 The detection limit of this method is usually dependent upon the level of interferences rather than instrumental limitations. The limits listed in Table 2 represent sensitivities that can be achieved in wastewaters.

1.4 The GC/MS parts of this method are recommended for use only by persons experienced in GC/MS analysis or under the close supervision of such qualified persons.

1.5 The trapping and chromatographic procedures described do not apply to the very volatile pollutant, dichlorodifluoromethane. An alternative three stage trap containing charcoal is to be used if this compound is to be analyzed. See EPA Method 601 and Reference 1. Primary ion for quantitative analysis of this compound is 101. The secondary ions are 85, 87, and 103.

1.6 Although this method can be used for measuring acrolein and acrylonitrile, the purging efficiencies are low and erratic. For a more reliable quantitative analysis of these compounds, use direct aqueous injection (Ref. 4–6) or EPA Method 603, Acrolein and Acrylonitrile, EMSL, Cincinnati, Ohio.

2. *Summary of Method.*

2.1. A sample of wastewater is purged with a stream of inert gas. The gas is bubbled through a 5 ml water sample contained in a specially designed purging chamber. The volatile organics are efficiently transferred from the aqueous phase into the gaseous phase where they are passed through a sorbent bed designed to trap out the organic volatiles. After purging is complete, the trap is backflushed while being rapidly heated in order to thermally desorb the components into the inlet of a gas chromatograph. The components are separated via the gas chromatograph and detected using a mass spectrometer which is used to provide both qualitative and quantitative information. The chromatographic conditions as well as typical mass spectrometer operating parameters are given.

3. *Interferences.*

3.1 Interferences contributed from the samples will vary considerably from source to source, depending upon the diversity of the industrial complex or municipality being sampled. Impurities in the purge gas and organic compounds out gassing from the plumbing ahead of the trap account for the majority of contamination problems. The analytical system must be demonstrated to be free from interferences under the conditions of the analysis by running method blanks. Method blanks are run by charging the purging device with organic-free water and analyzing it in a normal manner. The use of non-TFE plastic tubing, non-TFE thread sealants, or flow controllers with rubber components in the purging device should be avoided.

3.2 Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride) through the septum seal into the sample during shipment and storage. A field blank prepared from organic-free water and carried through the sampling and handling protocol can serve as a check on such contamination.

3.3 Cross contamination can occur whenever high level and low level samples are sequentially analyzed. To reduce cross contamination, it is recommended that the purging device and sample syringe be rinsed out twice, between samples, with organic-free water. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of organic-free water to check for cross-contamination. For samples containing large amounts of water soluble materials, suspended solids, high boiling compounds, or high organohalide levels, it may be necessary to wash out the purging device with a soap solution, rinse with distilled water, and then dry in a 105°C oven between analyses.

4. *Apparatus and Materials.*

4.1. Sampling equipment, for discrete sampling.

4.1.1 Vial, with cap—40 ml capacity screw cap (Pierce #13075 or equivalent). Detergent wash and dry vial at 105°C for one hour before use.

4.1.2 Septum—Teflon-faced silicone (Pierce #12722 or equivalent). Detergent wash and dry at 105°C for one hour before use.

4.2 Purge and trap device—The purge and trap equipment consists of three separate pieces of apparatus: a purging device, a trap, and a desorber. The complete device is available commercially from several vendors or can be constructed in the laboratory according to the specifications of Bellar and Lichtenberg (Ref. 2,3). The sorbent trap consists of ⅛ in. O.D. (0.105 in. I.D.) x 25 cm long stainless steel tubing packed with 15 cm of Tenax-GC (60/80 mesh) and 8 cm of Davison Type-15 silica gel (35–60 mesh). See figures 1 through 4. Ten centimeter traps may be used providing that the recoveries are comparable to the 25 cm traps.

4.3 Gas chromatograph—Analytical system complete with a temperature programmable gas chromatograph suitable for on-column injection and all required accessories including an analytical column.

4.3.1 Column 1—An 8 ft. stainless steel column (⅛ in. OD x 0.90 to 0.105 in ID) packed with 1% SP-1000 coated on 60/80 mesh Carbopack B preceded by a 5-cm precolumn packed with 1% SP-1000 coated on 60/80 mesh Chromosorb W. A glass column (¼ in OD x 2 mm ID) may be substituted. The precolumn is necessary only during conditioning.

4.3.2 Column 2—An 8 ft. stainless steel column (⅛ in OD x 0.09 to 0.105 in ID) packed with 0.2% Carbowax 1500 coated on 60/80 mesh Carbopack C preceded by a 1 ft. stainless steel column (⅛ in. OD x 0.09 to 0.105 in. ID) packed with 3% Carbowax 1500 coated on 60/80 mesh Chromosorb W. A glass column (¼ in. OD x 2 mm ID) may be substituted. The precolumn is necessary only during conditioning.

4.4 Syringes—glass, 5-ml hypodermic with Luer-Lok tip (3 each).

4.5 Micro syringes—10, 25, 100 µl

4.6 2-way syringe valve with Luer ends (3 each, Teflon or Kel-F).

4.7 Syringe—5 ml gas-tight with shut-off valve.

4.8 8-inch, 20-gauge syringe needle—One per each 5-ml syringe.

4.9 Mass Spectrometer—capable of scanning from 20–260 in six seconds or less at 70 volts (nominal), and producing a recognizable mass spectrum at unit resolution from 50 ng of DFTPP when injected through the GC inlet. The mass spectrometer must be interfaced with a gas chromatograph equippad with an all-glass, on-column injector system designed for packed column analysis. All sections of the transfer lines must be glass or glass-lined and deactivated. Use Sylon-CT, Supelco, (or equivalent) to deactivate. The GC/MS interface can utilize any separator that gives recognizable mass spectra (background corrected) and acceptable calibration points at the limit of detection specified for each compound in Table 2.

4.10 A computer system should be interfaced to the mass spectrometer to allow acquisition of continuous mass scans for the duration of the chromatographic program. The computer system should also be equipped with mass storage devices for saving all data from GC-MS runs. There must be

searching any GC/MS run for specific ions and plotting the intensity of the ions with respect to time or scan number. The ability to integrate the area under a specific ion plot peak is essential for quantification.

5. *Reagents.*

5.1 Sodium thiosulfate—(ACS) Granular.

5.2 *Trap Materials*

5.2.1 Porous polymer packing 60/80 mesh *chromatographic grade* Tenax GC (2,6-diphenylene oxide).

5.2.2 Silica gel-(35–60 mesh)—

5.2.2 Three percent OV-1 on Chromosorb-W 60/80 mesh. Davison, grade-15 or equivalent.

5.3 Activated carbon—Filtrasorb-200 (Calgon Corp.) or equivalent.

5.4 Organic-free water

5.4.1 *Organic-free water* is defined as water free of interference when employed in the purge and trap procedure described herein. It is generated by passing tap water or well water through a carbon filter bed containing about 1 lb. of activated carbon.

5.4.2 A water system (Millipore *Super-Q or equivalent) may* be used to generate organic-free deionized water.

5.4.3 Organic-free water may also be prepared by boiling water for 15 minutes. Subsequently, while maintaining the temperature at 90°C, bubble a contaminant-free inert gas *through the water for one hour.* While still hot, transfer the water to a narrow mouth screw cap bottle equipped with a Teflon seal.

5.5 Stock standards (2 mg/ml)—Prepare stock standard solutions in methanol using assayed liquids or gases as appropriate. Because of the toxicity of some of the organohalides, primary *dilutions of these materials should* be prepared in a hood. A NIOSH/MESA approved toxic gas respirator should be worn when the analyst handles high concentrations of such materials.

5.5.1 Place about 9.8 ml of methanol into a 10 ml ground glass stoppered *volumetric flask. Allow the flask to* stand, unstoppered, for about 10 minutes *or until all alcohol wetted surfaces have* dried. Tare the flask to the nearest 0.1 mg.

5.5.2 Add the assayed reference material:

5.5.2.1 Liquids—using a 100 µl syringe, immediately add 2 to 3 drops of *assayed reference material* to the flask, then reweigh. Be sure that the drops fall directly into the alcohol without contacting the neck of the flask.

5.5.2.2 Gases—To prepare standards of bromomethane, chloroethane, chloromethane, and vinyl chloride, fill a [illegible] reference standard to the 5.0-ml mark. Lower the needle to 5 mm above the *methyl alcohol menicus. Slowly inject* the reference standard into the neck of the flask (the heavy gas will rapidly dissolve into the methyl alcohol).

5.5.3 Reweigh the flask, dilute to volume, stopper, then mix by inverting the flask several times. Transfer the standard solution to a 15-ml *screw-cap* bottle equipped with a Teflon cap liner.

5.5.4 *Calculate* the concentration in mg per ml (equivalent to µg per µl) from the net gain in weight.

5.5.5 Store stock standards at 4° C. Prepare fresh standards every second day for the four gases and 2-chloroethylvinyl ether. All other *standards must be replaced with fresh* standards each week.

5.6 Surrogate Standard Dosing Solution—From stock standard solutions prepared as above, add a volume to give 1000 µg each of bromochloromethane, 2-bromo-1-chloropropane, and 1,4-dichlorobutane to 40 ml of organic-free water contained in a 50-ml volumetric flask, mix and dilute to volume. Prepare a fresh surrogate standard dosing solution weekly. Dose the surrogate standard mixture into every 5-ml sample and reference standard analyzed.

6. Calibration.

6.1 Using the stock standards, prepare secondary dilution standards of the compounds of interest, either singly or mixed together in methanol. The standards should be at concentrations such that the aqueous standards prepared in 6.2 will bracket the working range of the chromatographic system. If the limit of detection listed in Table 2 is 10 µg/l, for example, prepare secondary methanolic standards at 100 µg/l, and 500 µg/l, so that aqueous standards prepared from these secondary calibration standards, and the primary standards, will define the linearity of the detector in the working range.

6.2 Using both the primary and secondary dilution standards, prepare calibration standards by carefully adding 20.0 µl of the standard in methanol to 100, 500, or 1000 ml of organic-free water. A 25 µl syringe (Hamilton 702N or equivalent) should be used for this operation. These aqueous standards must be prepared fresh daily.

6.3 Assemble the necessary gas chromatographic and mass spectrometer apparatus and establish operating parameters equivalent to those indicated in Table 2. By injecting secondary dilution standards, establish the linear range of the analytical system for each compound and demonstrate that the analytical system meets the [illegible] 2.

6.4 Assemble the necessary purge and trap device. Pack the trap as shown in Figure 2 and condition overnight at a nominal 180° C by backflushing with an inert gas flow of at least 20 ml/min. Daily, prior to use, condition the traps for 10 minutes by backflushing at 180° C. Analyze aqueous calibration standards (6.2) according to the purge and trap procedure in Section 9. Compare the *responses to those obtained by injection* of standards (6.3), to determine the analytical precision. The analytical precision of the analysis of aqueous standards must be comparable to data presented by Bellar and Lichtenberg (1978, Ref. 1) before reliable sample *analysis may begin.*

6.5 Internal Standard Method—The internal standard approach is acceptable for the purgeable organics. The utilization of the internal standard method requires the periodic determination of response factors (RF) which are defined in equation 1.

Eq. (1) $RF = (A_s C_{is})/(A_{is} C_s)$

Where:

A_s *is the integrated area or peak height of* the characteristic ion for the priority pollutant standard.

A_{is} is the integrated area or peak height of the characteristic ion for the internal standard.

C_{is} is the amount of the internal standard in µg.

C_s is the amount of the pollutant standard in µg.

The relative response ratio for each pollutant *should be known for* at least two concentration values—50 ng injected to approximate 10 µg/l and 500 ng to approximate the 100 µg/l level. Those compounds that do not respond at either of these levels may be run at concentrations appropriate to their *response. The response factor (RF) must* be determined over all concentration ranges of standard (C_s) which are being determined. (Generally, the amount of internal standard added to each extract is the same so that C_{is} remains constant.) This should be done by *preparing a calibration curve where the* response factor (RF) is plotted against the standard concentration (C_s). Use a minimum of three concentrations over the range of interest. Once this calibration curve has been determined, it should be verified daily by injecting at *least one standard solution containing* internal standard. If significant drift has occurred, a new calibration curve must be constructed.

Note.—EPA, through its contractors and *certain of its Regional* Laboratories, is currently evaluating selected compounds for

6.6 The external standard method can also be used at the discretion of the analyst. Prepare a master calibration curve using a minimum of three standard solutions of each of the compounds that are to be measured. Plot concentrations versus integrated areas or peak heights (selected characteristic ion for GC/MS). One point on each curve should approach the method detection limit. After the master set of instrument calibration curves have been established, they should be verified daily by injecting at least one standard solution. If significant drift has occurred, a new calibration curve must be constructed.

7. *Quality Control.*

7.1 Before processing any samples, the analyst should daily demonstrate, through the analysis of an organic-free water method blank, that the entire analytical system is interference-free.

7.2 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 accuracy of the analysis.

7.3 The analyst should maintain constant surveillance of both the performance of the analytical system and the effectiveness of the method in dealing with each sample matrix by determining the precision of the method in blank water and spiking each 5-ml sample, standard, and blank with surrogate halocarbons.

7.3.1 Determine the precision of the method by dosing blank water with the compounds selected as surrogate standards—bromochloromethane, 2-bromo-1-chloropropane, and 1,4-dichlorobutane—and running replicate analyses. Calculate the recovery and its standard deviation. These compounds represent early, middle, and late eluters over the range of the pollutant compounds.

7.3.2 The sample matrix can affect the purging efficiencies of individual compounds; therefore, each sample must be dosed with the surrogate standards and analyzed in a manner identical to the internal standards in blank water. If the recovery of the surrogate standard shows a deviation greater than two standard deviations (7.3.1), repeat the dosed sample analyses. If the deviation is again greater than two standard deviations, dose another aliquot of the same sample with the compounds of interest at approximately two times the [illegible] compounds using these data.

8. *Sample Collection, Preservation, and Handling.*

8.1 Grab samples must be collected in glass containers having a total volume greater than 20 ml. Fill the sample bottles in such a manner that no air bubbles pass through the sample as the bottle is being filled. Seal the bottles so that no air bubbles are entrapped in it. Maintain the hermetic seal on the sample bottle until time of analysis.

8.2 The sample must be iced or refrigerated from the time of collection until extraction. If the sample contains residual chlorine, add sodium thiosulfate preservative (10 μg/40 ml) to the empty sample bottles just prior to shipping to the sample site. Fill with sample just to overflowing, seal the bottle, and shake vigorously for 1 minute.

8.3 All samples must be analyzed within 7 days of collection.

9. *Sample Extraction and Gas Chromatography.*

9.1 Remove standards and samples from cold storage (approximately an hour prior to an analysis) and bring to room temperature by placing in a warm water bath at 20–25°C.

9.2 Adjust the purge gas (nitrogen or helium) flow rate to 40 ml/min. Attach the trap inlet to the purging device, and set the device to the purge mode. Open the syringe valve located on the purging device sample introduction needle.

9.3 Remove the plunger from a 5 ml syringe and attach a closed syringe valve. Open the sample bottle (or standard) and carefully pour the sample into the syringe barrel until it overflows. Replace the syringe plunger and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5.0 mL. Since this process of taking an aliquot destroys the validity of the sample for future analysis, the analyst should fill a second syringe at this time to protect against possible loss of data. Add 5.0 μl of the surrogate spiking solution (7.3) through the valve bore, then close the valve.

9.4 Attach the syringe-valve assembly to the syringe valve on the purging device. Open the syringe valve and inject the sample into the purging chamber.

9.5 Close both valves and purge the sample for 12.0 ±.05 minutes.

9.6 After the 12-minute purge time, attach the trap to the chromatograph, and adjust the device to the desorb mode. Introduce the trapped materials to the GC column by rapidly heating the trap to 180°C while backflushing the [illegible] cannot be achieved, the gas chromatographic column must be used as a secondary trap by cooling it to 30°C (or subambient, if problems persist) instead of the initial program temperature of 45°C.

9.7 While the trap is being desorbed into the gas chromatograph, empty the purging chamber using the sample introduction syringe. Wash the chamber with two 5-ml flushes of organic-free water. After the purging device has been emptied, continue to allow the purge gas to vent through the chamber until the frit is dry, and ready for the next sample.

9.8 After desorbing the sample for four minutes, recondition the trap by returning the purge and trap device to the purge mode. Wait 15 seconds then close the syringe valve on the purging device to begin gas flow through the trap. Maintain the trap temperature at 180°C. After approximately seven minutes, turn off the trap heater and open the syringe valve to stop the gas flow through the trap. When cool, the trap is ready for the next sample. (Note: If this bake out step is omitted, the amount of water entering the GC/MS system will progressively increase causing deterioration of and potential shut down of the system.)

9.9 The analysis of blanks is most important in the purge and trap technique since the purging device and the trap can be contaminated by residues from very concentrated samples or by vapors in the laboratory. Prepare blanks by filling a sample bottle with organic-free water that has been prepared by passing distilled water through a pretested activated carbon column. Blanks should be sealed, stored at 4°C, and analyzed with each group of samples.

10. *Gas Chromatography—Mass Spectrometry.*

10.1 Table 2 summarizes the recommended gas chromatographic column materials and operting conditions for the instrument. Included in this table are estimated retention times and sensitivities that should be achieved by this method. An example of the separation achieved by Column 1 is shown in Figure 5.

10.2 GC–MS Determination—Suggested analytical conditions for determination of the pollutants amenable to purge and trap, using the Tekmar LCS-1 and GC/MS are given below. Operating conditions vary from one system to another; therefore, each analyst must optimize the conditions for each purge and trap and GC/MS system.

10.3 Purge Parameters.

Sample size—5.0 ml
Purge gas—Helium, high purity grade
Purge time—12 minutes.
Purge flow—40 ml/min.
Trap dimensions—⅛ in. O.D. (0.105 in. I.D.)x25 cm long.
Trap sorbent—Tenax-GC, 60/80 mesh (15 cm), plus Type 15 silica gel, 35/60 mesh (8 cm).
Desorption flow—20 ml/min.
Desorption time—4 min.
Desorption temperature—180° C.

10.4 Mass Spectrometer Parameters.

Electron energy—70 volts (nominal).
Mass range—20–27, 33–260 amu.
Scan time—6 seconds or less.

10.5 Calibration of the gas chromatography-mass spectrometry (GC-MS system—Evaluate the system performance each day that it is to be used for the analysis of samples or blanks by examining the mass spectrum of DFTPP or BFB.

10.5.1 To use DFTPP, remove the analytical column and substitute a column more appropriate to the boiling point of the reference compound (e.g. 3% SP-2250 on Supelcoport). Inject a solution containing 50 ng DFTPP and check to insure that the performance criteria listed in Table 3 are met.

10.5.2 To use BFB, inject a solution containing 20 ng BFB and check to insure that the performance criteria listed in Table 4 are met.

10.5.3 If the system performance criteria are not met for either test, the analyst must retune the spectrometer and repeat the performance check. The performance criteria must be met before any samples or standards may be analyzed.

10.6 Analyze an internal or external calibration standard to develop response factors for each compound.

11. *Qualitative and Quantitative Determination.*

11.1 To qualitatively identify a compound, obtain an Extracted Ion Current Profile (EICP) for the primary ion and at least two other ions (if available) listed in Table 5. The criteria below must be met for a qualitative identification.

11.1.1 The characteristic ions for the compound must be found to maximize in the same or within one spectrum of each other.

11.1.2 The retention time at the experimental mass spectrum must be within ±60 seconds of the retention time of the authentic compound.

11.1.3 The ratios of the three EICP peak heights must agree within ±20% with the ratios of the relative intensities for these ions in a reference mass spectrum. The reference mass spectrum can be obtained from either a standard analysis through the [illegible] from a reference library.

11.1.4 Structural isomers that have very similar mass spectra can be explicitly identified only if the resolution between the isomers in a standard mix is acceptable. Acceptable resolution is achieved if the valley height between isomers is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

11.2 The primary ion listed in Table 5 is to be used to quantify each compound. If the sample produces an interference for the primary ion, use a secondary ion to quantify.

11.3 For low concentrations, or direct aqueous injection of acrylonitrile and acrolein, the characteristic masses listed for the compounds in Table 5 may be used for selected ion monitoring (SIM). SIM is the use of a mass spectrometer as a substance selective detector by measuring the mass spectrometric response at one or several characteristic masses in real time.

11.4 Internal Standard Method Calculations—By adding a constant known amount of internal standard (C_{is} in μg) to every sample extract, the concentration of the pollutant (C_o) in μg/l in the sample is calculated using equation 2.

$$\text{Eq. (2)} C_o = \frac{(A_o)(C_{is})}{(A_{is})(RF)(V_o)}$$

Where:

V_o is the volume of the original sample in liters, and the other terms are defined as in Section 6.5. To quantify, add the internal standard to the 5.0 ml sample no more than a few minutes before purging to minimize the possibility of losses due to evaporation, adsorption, or chemical reaction. Calculate the concentration by using the previous equations with the appropriate response factor taken from the calibration curve.

11.5 External Standard Method Calculations—The concentration of the unknown can be calculated from the slope and intercept of the multiple point calibration curve. The unknown concentration can be determined using equation 3.

$$\text{Eq. (3) micrograms per liter} = \text{ng/ml} = \frac{(A)}{(V_o)}$$

Where:

A = Mass of compound from calibration curve (ng/5 ml).

V_o = volume of water purged (5 ml).

11.6 An alternate external standard approach for purgeables utilizes a single point calibration. Prepare and analyze a reference standard that closely [illegible] compound in a sample. Calculate the concentration in the sample using Equation 4.

$$\text{Eq. 4 micrograms per liter} = \frac{(A)(B)}{(C)}$$

Where:

A = area of the unknown
B = concentration of standard (μg/l)
C = area of the standard.

11.7 Report all results to two significant figures. When duplicate and spiked samples are analyzed, all data obtained should be reported. Report results in micrograms per liter without correction for recovery data.

12. *References.*

1. "The Analysis of Halogenated Chemical Indicators of Industrial Contamination in Water by the Purge and Trap Method," U.S. EPA, Environmental Monitoring and Support Laboratory, Cincinnati, OH, 45268, Dec. 1978.

2. "Symposium on Measurement of Organic Pollutants in Water and Wastewater," ASTM Special Publication, 1979 (In Press).

3. "Determining Volatile Organics at Microgram-per-Liter Levels by Gas Chromatography," T. A. Bellar and J. J. Lichtenberg, *Jour. AWWA, 66*, 739–744, Dec. 1974.

4. ASTM Annual Standards—Water, part 31, Method D2908 "Standard Recommended Practice for Measuring Water by Aqueous-Injection Gas Chromatography."

5. ASTM Annual Standards—Water, part 31, Method D3371 "Tentative Method of Test for Nitriles in Aqueous Solution of Gas Liquid Chromatograph."

6. "Direct Analysis of Water Samples for Organic Pollutants with Gas Chromatography-Mass Spectrometry," Harris, L. E., Budde, W. L., and Eichelberger, J. W. *Anal. Chem., 46*, 1912 (1974).

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1. "Sampling and Analysis Procedures for Screening of Industrial Effluents for Priority Pollutants," March 1977 (revised April 1977). USEPA, Effluent Guidelines Division, Washington, D.C. 20460.

2. "Proceedings: Seminar on Analytical Methods for Priority Pollutants," Volume 1—Denver, Colorado, November 1977; Volume 2—Savannah, Georgia, May 1978; Volume 3—Norfolk, Virginia, March 1979; USEPA, Effluent Guidelines Division, Washington, D.C. 20460.

Table 1

Parameter	STORET No.
Acrolein	34210
Acrylonitrile	34215
Benzene	34230
Bromomethane	34413
Bromodichloromethane	32101
Bromoform	32104
Carbon Tetrachloride	32102
Chlorobenzene	34301
Chloroethane	34311
2-Chloroethylvinyl ether	34576
Chloroform	32106
Chloromethane	34418
Dibromochloromethane	34105
1,1-Dichloroethane	34496

Parameter	STORET No
1,2-Dichloroethane	34531
1,1-Dichloroethene	34501
trans-1,2-Dichloroethene	34546
1,2-Dichloropropane	34541
cis-1,3-Dichloropropene	34561
trans-1,3-Dichloropropene	34561
Ethylbenzene	34371
Methylene chloride	34423
1,1,2,2-Tetrachloroethane	34516
Tetrachloroethene	34475
1,1,1-Trichloroethane	34506
1,1,2-Trichloroethane	34511
Trichloroethene	39180
Trichlorofluoromethane	34486
Toluene	34010
Vinyl chloride	39175

Table 2.—*Gas Chromatography of Organics by Purge and Trap*

Compound	Retention time (minutes)		Limit of detection [3] (µg/l)
	Col. 1 [1]	Col. 2 [2]	
chloromethane	1.50	2.10	10
bromomethane	2.17	2.50	10
vinyl chloride	2.67	2.57	10
chloroethane	3.33	2.82	10
methylene chloride	5.25	4.03	10
trichlorofluoromethane	7.18	5.14	10
1,1-dichloroethane	7.92	5.25	10
bromochloromethane (SS)	8.46	6.31	
1,1-dichloroethane	8.30	6.48	10
trans-1,2-dichloroethene	10.06	6.81	10
chloroform	10.68	7.70	10
1,2-dichloroethane	11.40	8.29	10
1,1,1-trichloroethane	12.60	8.28	10
carbon tetrachloride	13.02	9.45	10
bromodichloromethane	13.65	10.38	10
1,2-dichloropropane	14.82	11.30	10
trans-1,3-dichloropropene	15.22	11.70	10
trichloroethene	15.60	11.86	10
dibromochloromethane	16.48	12.66	10
1,1,2-trichloroethane	16.52	12.68	10
cis-1,3-dichloropropene	16.53	12.68	10
benzene		12.85	10
2-chloroethylvinyl ether	18.00	13.71	10
2-bromo-1-chloropropane (SS)		13.82	
bromoform	19.20	15.41	10
1,1,2,2-tetrachloroethane	21.62	17.70	10
tetrachloroethene	21.67	17.44	10
1,4-dichlorobutane (SS)		18.13	
toluene		18.53	10
chlorobenzene	24.18	20.57	10
ethylbenzene		25.06	10
acrolein			[4]100
acrylonitrile			[4]100

[1]Eight ft. stainless steel column (1/8 in. OD×0.1 in. ID) packed with 1% SP-1000 coated on 60/80 mesh Carbopack B preceded by a 1 ft. stainless steel column (1/8 in. OD×0.1 in. ID) packed with 1% SP-1000 coated on 60/80 mesh Chromosorb W. (A glass column (1/4 in. OD×2 mm ID) may be substituted). Carrier gas helium at 40 ml/min. Temperature program: 3 min isothermal at 45° C, then 8°/min to 220°, hold at 220° for 15 minutes.

[2]Eight ft. stainless steel column (1/8 in. OD×0.1 in. ID) packed with 0.2% Carbowax 1500 coated on 60/80 mesh Carbopack C preceded by a 1 ft. stainless steel column (1/8 in. OD×0.1 in. ID) packed with 3% Carbowax 1500 coated on 60/80 mesh Chromosorb W. A glass column (1/4 in. OD×2 mm ID) may be substituted. Carrier gas: helium at 40 ml/min. Temperature program: 3 min. isothermal at 60° C then 6°/min to 180°, hold at 180 until all compounds elute.

[3]This is a minimum level at which the entire system must give recognizable mass spectra and acceptable calibration points.

[4]Sensitivity refers to either this method or direct aqueous injection GC–FID (Ref. 4,5,6).

Mass	Ion abundance criteria
50	26 to 40 pct of mass 95
75	50 to 70 pct of mass 95
95	Base peak, 100 pct relative abundance
96	5 to 9 pct of mass 95
173	Less than 1 pct of mass 95
174	70 to 90 pct of mass 95
175	5 to 9 pct of mass 95
176	70 to 90 pct of mass 95
177	5 to 9 pct of mass 95

Mass	Ion abundance criteria
51	30 to 60 pct of mass 198
68	Less than 2 pct of mass 69
70	Less than 2 pct of mass 69
127	40 to 60 pct of mass 198
197	Less than 1 pct of mass 198
198	Base peak, 100 pct relative abundance
199	5 to 9 pct of mass 198
275	10 to 30 pct of mass 198
365	Greater than 1 pct of mass 198
441	Present but less than mass 443
442	Greater than 40 pct of mass 198
443	17 to 23 pct of mass 442

Table 5.—*Characteristic Ions of Volatile Organics*

Compound	EI Ions				Primary ion
chloromethane	50	52			50
bromomethane	94	96			94
vinyl chloride	62	64			62
chloroethane	64	66			64
methylene chloride	49	51	84	86	84
trichlorofluoromethane	101	103			101
1,1-dichloroethene	61	96	98		96
bromochloromethane (SS)	49	130	128	51	128
1,1-dichloroethane	63	65	83		63
	65	88	100		
trans-1,2-dichloroethane	61	96	98		96
chloroform	83	85			83
1,2-dichloroethane	62	64	98	100	98
1,1,1-trichloroethane	97	99	117	119	97
carbon tetrachloride	117	119	121		117
bromodichloromethane	82	85	127	129	127
1,2-dichloropropene	63	65	112	114	112
trans-1,3-dichloropropene	75	77			75
trichloroethene	95	97	130	132	130
dibromochloromethane	129	127	208	206	127
cis-1,3-dichloropropene	75	77			75
1,1,2-trichloroethane	83	85	97		
	99	132	134		97
benzene	78				78
2-chloroethylvinyl ether	63	65	106		106
2-bromo-1-chloropropane (SS)	77	79	156		77
bromoform	171	173	175	250	173
	252	254	256		
tetrachloroethenbs	129	131	164	166	164
1,1,2,2-tetrachloroethane	83	85	131	133	
	168	168			168
1,4-dichlorobutane (SS)	55	90	92		55
toluene	91	92			92
chlorobenzene	112	114			112
ethylbenzene	91	106			106
acrolein	26	27	55	56	56
acrylonitrile	26	51	52	53	53

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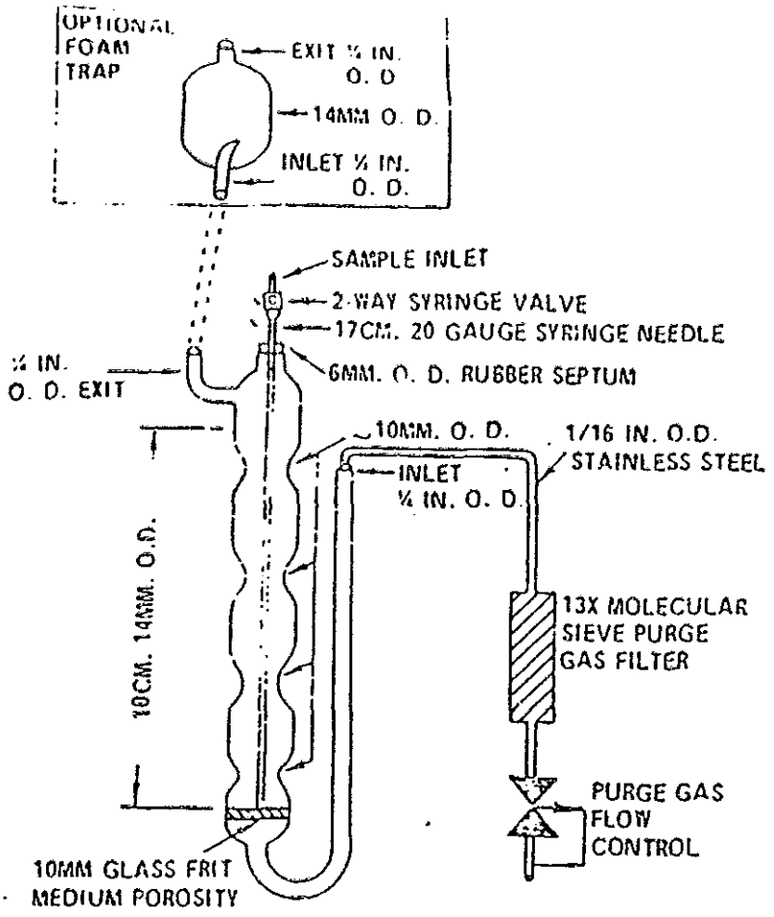

Figure 1. Purging device

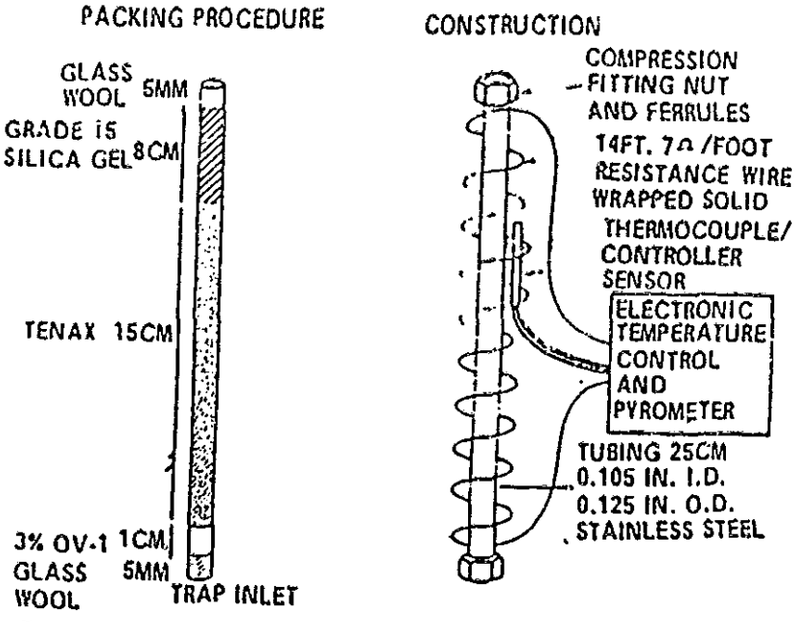

Figure 2. Trap packings and construction to include desorb capability

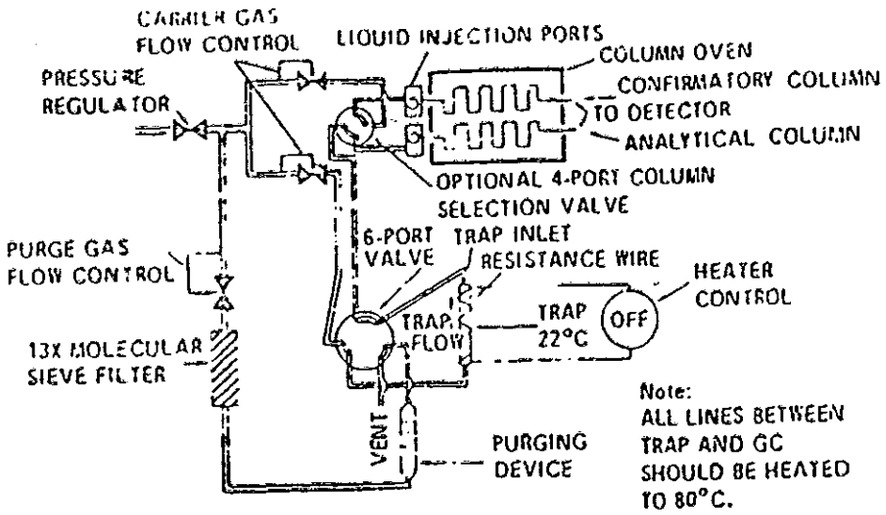

Figure 3. Schematic of purge and trap device - purge mode

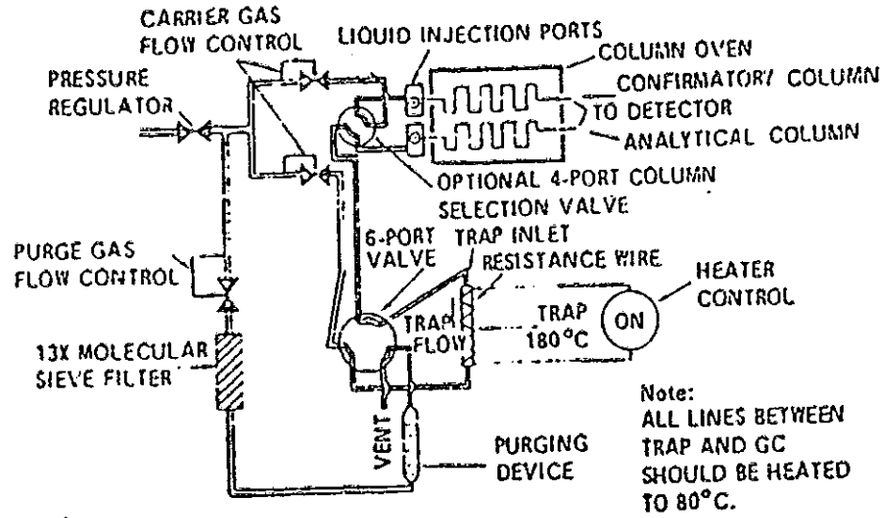

Figure 4. Schematic of purge and trap device - desorb mode

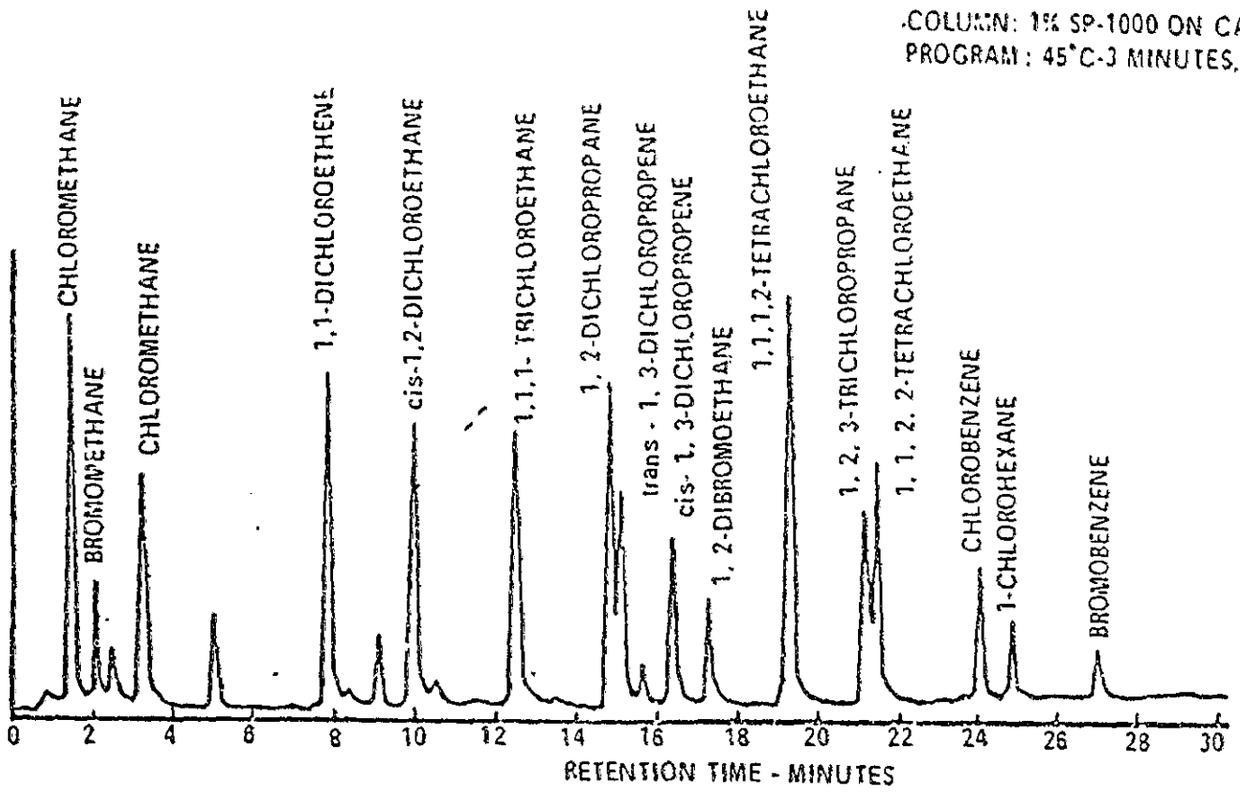

Figure 5. Gas chromatogram of volatile organics by purge and trap

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Laboratory Services Branch
U.S. Environmental Protection Agency
S&A Division
Athens, GA 30613

ATTACHMENT 3

EXTRACTION AND ANALYSIS OF
PRIORITY POLLUTANTS IN SEDIMENT & SOIL

1. Scope and Application

1.1 This method covers the determination of priority pollutants in soils and sediment.

1.2 The limit of detection for this method is usually dependent upon the level of interferences rather than instrumental limitations. Where interferances are not a problem, the limit of detection for most compounds analyzed by GC/MS is 5,000 µg/kg. (5 ppm)

1.3 This method is recommended for use only by experienced residue analysts or under the close supervision of such qualified persons.

2. Summary of Method

A 30 gm portion of sample is mixed with anhydrous sodium sulfate and extracted with 1:1 CH_2Cl_2-acetone using an ultrasonic probe. The extract is filtered, dried, concentrated and cleaned up using gel permeation chromatography. The cleaned up extract is concentrated and divided into two portions. One portion is retained in methylene chloride for screening on GC/FID and analysis on GC/MS for base/neutral/acid compounds. The other portion is exchanged into hexane for pesticide analysis on GC/EC.

3. Interferences

3.1 See Appendix I for general interferences.

3.2 Organic material found naturally in solids interferes with the analysis of pesticides and must be removed by gel permeation chromatography.

4. Apparatus and Material

4.1 Oven, drying.

4.2 Desiccator.

4.3 Crucibles, porcelain, squat form, Size or equivalent.

4.4 Disposable pipets - for transferring extracts.

4.5 Sonicator Cell Disruptor - Heat Systems - Ultrasonics, Inc., with a 3/4" high gain probe, 375 watt or equivalent.

4.6 Beakers, 400-ml.

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4.8 Drying tubes - 180 mm X 25 mm.

4.9 Pyrex Glass Wool

4.9.1 Untreated with acid.

4.9.2 Washed with acidic acetone.

4.10 Tubes with screwcaps - 150 X 15 mm (used for VOA analysis).

4.11 Furnace, muffle.

4.12 Buchner funnels.

4.13 Filter paper

4.14 Kuderna-Danish (K-D) apparatus.

4.14.1 Concentrator tube - 10 ml, graduated (Kontes K - 570040-1025 or equivalent).

4.14.2 Evaporative flask - 500 ml (Kontes - K - 570001-0500 or equivalent).

4.14.3 Snyder column - three-ball macro (Kontes K - 503000-0121 or equivalent).

4.15 Boiling chips - Baryl saddles (Fisher, 91915) crushed.

4.16 Device for nitrogen blowdown for final extract concentration.

4.17 Water bath - Heated, with concentric ring cover, capable of temperature control (± 2°C).

4.18 Vials, 2 ml for GC auto sampler.

4.19 Gas Chromatograph - Analytical system complete with gas chromatograph suitable for on-column injection and all required accessories including flame ionization detector, electron capture detector, Hall electrolytic conductivity detector, thermionic N/P detector, column supplies, recorders, gases, and syringes.

4.19.1 Base/neutral column and analytical conditions - Chromosorb W (100/120), coated with 3% OV-17 packed in a 6' X 2mm ID pyrex glass column. Use ultra pure nitrogen at a flow rate of 30 ml/min. Column temperature is held at 80°C for 2 min., programmed to 290 at 8°/min., and held at 290°C for 16 min. (see figure 1 for chromatogram).

4.19.2 Acid colum and analytical conditions - Supelcoport (100/200) coated with 1% SP-1240 DA, packed in a 4'-long X 2mm ID pyrex glass column. Use ultra pure nitrogen carrier gas at a flow rate of 30 ml/min. Column temperature held at 80°C for 2 min. programmed to 290°C at 8°C/min., and held at 290°C for 16 min. (see figure 2 for chromatogram).

4.19.3 Pesticide column and analytical conditions. Supelcoport (100/120 mesh) coated with 1.5% SP-2250/ 1.95% SP-2401, packed in a 6-ft. X 4 mm ID pyrex glass column. Use Argon 95%/methane 5%, carrier gas at a flow rate of 60 ml/min. Column temperature, isothermal at 200°C.

4.20 Gas Chromatograph/Mass Spectrometer, Finnigan 3200 & INCOS 2300 Data System.

4.20.1 Purge-and-Trap - Chemical Data System - 310 or equivalent.

4.20.2 VOA column and analytical conditions - Carbopack B (60/80 mesh) coated with 1% SP-1000 packed in a 10 ft. X 2 mm ID pyrex glass column. Use ultra pure helium carrier gas at a flow rate of 30 ml/min. Column temperature is held at 50°C per 4 min. programmed to 210°C and held for 11 min. (see figure 3 for chromatogram).

4.21 Gas Chromatograph/Mass Spectrometer, Finnigan 4000 and INCOS 2300 Data System. Scanned form 33-450a m u with a scan time of 3 m sec./a m u. Operated in the electron ionization mode.

4.21 GC column - Same as listed in 4.20.1 and 4.20.2 or 30 meter SE-54 fused silica capilllary column, 0.32 mm i.d. (see figure 4 for chromatogram and Table I for conditions).

4.22 Gal permeation chromatograph (GPC) Analytical Biochemical Labs, Inc. GPC Autoprep 1002 or equivalent including:

4.22.1 25 mm ID X 600 - 700 mm glass column packed with 70 gm of Bio-Beads SX-3.

4.22.2 Syringe, 10 ml with luer lok fitting.

4.22.3 Syringe filter holder - stainless steel and TFE, Gelman 4310 or equivalent.

4.22.4 Analytical balance for GPC calibration using corn oil.

5. Reagents

5.1 Sodium Sulfate - anhydrous and reagent grade, heated at 500°C for a minimum of two hours, cooled in a desiccator, and stored in a glass bottle. Baker anhydrous powder, catalog # 73898 or equivalent.

5.2 Hexane and methylene chloride (CH_2Cl_2) - Pesticide quality and distilled in glass.

5.3 Acetone - Pesticide quality and distilled in glass.

5.5 GPC calibration solutions:

5.5.1 Corn oil - 200 mg/ml in dichlormethane.

5.5.2 bis(2-ethylhexylphthalate) and pentachlorophenol - 4.0 mg/ml in dichloromethane.

5.6 Methanol - Pesticide quality and distilled in glass.

5.7 Reagent water - water in which an interferent is not observed at the method detection of the parameters of interest.

5.8 Surrogate standards - Naphthalene d_8, Nitrobenzene d_5, phenol d_6 and pentafluorophenol - all at 1 ng/µl in acetone.

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6. Quality Control

See Section 8, p. 2. of Laboratory Services Branch Operations and Quality Control manual.

7. Sample Extraction

7.1 Decant and discard the water layer over the sediment. Mix samples thoroughly, especially composited samples. Discard any foreign objects such as sticks, leaves, and rocks.

7.2 Weigh 5 gms. of sample into a 150 X 15-mm, screw-cap tube, for volatile organic analysis. This must be done in a room free of volatile organic compounds.

7.3 Weigh 30 gms. of sample into a 400-ml beaker and add 30 gms of anhydrous sodium sulfate. Mix well and allow to dry to a sandy texture. Do not allow to set more than 2-3 minutes to avoid loss of volatile extractables. Add surrogates and solvent immediately.

7.4 Immediately after weighing the sample for extraction, weigh 5-10 gm. of the partically-dried sediment into a tared crucible. Determine the percent solids by drying overnight at 103°. Allow to cool in a desiccator for half an hour before weighing. If percent volatile solids is to be determined, place the oven-dried sample into a muffle furnace and ignite at 550°C for 60 minutes. Allow to cool in a desiccator before weighing.

7.5 Add 100 ml of 1:1 CH_2Cl_2 ; acetone to the sample.

7.6 Place the probe about 1/2" below the surface of the solvent but above the sediment layer.

7.7 Sonicate for 3 min. at full power with pulse set at 50%.

7.8 Decant the solvent into a Buchner funnel. Repeat 7.5-7.6 twice more.

7.9 Pour the entire sample into the Buchner funnel and rinse with hexane.

7.10 Concentrate the extract to 1 ml using the KD apparatus to concentrate the extract to 5-7 ml and N_2 blowdown for the final concentration.

8.0 Extract cleanup by GPC.

8.1 GPC Setup and Calibration

8.1.1 Packing the column - Place 50 to 60 g of Bio Beads SX-3 in a 400 ml beaker. Cover the beads with dichloromethane and allow the beads to swell overnight (before packing the columns). Transfer the swelled beads to the column and start pumping solvent through the column, from bottom to top, at 5.0 ml/min. After approximately 1 hour, adjust the pressure on the column to 7 to 10 psi and pump an additional 4 hours to remove air from the column. Adjust the column pressure periodically as required to maintain 7 to 10 psi.

8.1.2 Calibration of the column - Load 5 ml of the corn oil solution into sample loop No. 1 and 5 ml of the phthalate/phenol solution into loop No. 2. Inject the corn oil and collect 10 ml fractions (i.e., change fraction at 2 minute

intervals) for 36 minutes. Inject the phthalate-phenol solution and collect 15 ml fractions for 60 minutes. Determine the corn oil elution pattern by evaporation of each fraction to dryness followed by a gravimetric determination of the residue. Analyze the phthalate-phenol fractions by GC/FID on the SP-2250-DA columns or the SE-54 capillary column. Plot the concentration of each component in each fraction versus total eluant volume (or time) from the injection points. Choose a "dump time" which allow ≥ 85% removal of the corn oil and ≥ 85% recovery of the bis(2-ethylhexyl)-phthalate. Choose the "collect time" to extend at least 10 minutes after the elution of pentachlorophenol. "Wash" the column at least 15 minutes between samples. Typical parameters selected are: Dump time, 24 minutes (120 ml), collect time, 33 minutes (165 ml), and wash time, 15 minutes (75 ml). The column can also be calibrated by the use of a 254 nm UV detector in place of gravimetric and GC analyses of fractions. Measure the peak areas at various elution times to determine appropriate fractions.

8.2 GPC Extract Cleanup

Prefilter or load all extracts via the filter holder to avoid particulates that might cause flow stoppage. Load four consecutive 5.0 ml aliquots for extracts at 25 ml or one . ml aliquot for extracts at 10 ml. Purge the sample loading tubing thoroughly with solvent between extracts. After especially dirty extracts, run a GPC blank (i.e., dichloromethane) to check for carry-over. Process the extracts using the dump, collect, and wash parameters determined from the calibration and collect the cleaned extracts in 400 ml beakers tightly covered with aluminum foil. Concentrate the cleaned extracts, combining collected fractions from multiple injections, to approximately 10 ml using Kuderna-Danish evaporators and then to 1 ml using N_2 blowdown. Transfer 0.5 ml of the cleaned extract to a 2 ml GC vial and dilute with 0.5 ml of methylene chloride. Label B/N/A and 4 ml final volume. Reconnect the KD 500 ml flask to the concentrator tube containing the other 0.5 ml of extract and add 20-30 ml of hexane. Add a boiling chip and snyder column and place it back on the steam bath to eliminate the methylene chloride. use N_2 blowdown to reduce volume to 1 ml. Transfer to 2 ml GC vial and label Pest. and 4 ml final volume. Intensely colored extracts may require a second GPC cleanup.

9.0 Analysis by Gas Chromatography

9.1 Gas Chromatograph/Flame Ionization Screening of B/N/A Extracts

9.1.1 The B/N/A extracts are screened on GC/FID using the B/N column. If nothing is present as per 9.1.2, then the extract should also be screened on the acid column.

9.1.2 Calculate the FID response of 50 ng of hexachlorobenzene (HBC) for B/N compounds and 100 ng of pentachlorophenol (PCP) for A compounds. (The GC/MS requires about 50 ng HCB and 100 ng PCP to give a complete mass spectra.)

9.1.2.1 If any peaks are present that are > the response calculated in 9.1.2, calculate the concentration of the largest peak.

9.1.2.1.1 If concentration is >5,000 µg/kg (dry-weight basis), analyze by GC/MS.

9.1.2.1.2 If concentration is <5,000 µg/kg, report as <5,000 µg/kg.

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9.1.2.2 If all peaks are <the responses required in 9.1.2, record the minimum detection limit in the master log.

9.1.3 Analyze all blanks and spikes and record precision-and-accuracy data in the QC log book.

9.2 Gas Chromatograph/Electron Capture Analysis of Pesticide Extracts

9.2.1 A 10X dilution of most samples will provide adquate minimum detection limits for most samples such as MDSD, EGD, and waste-site samples. However, if pesticides or PCB's are detected on a hazardous waste site, then sediment samples from drainage areas should be run as sensitive as possible.

9.2.2 Analyze all blanks and spikes and record precision-and-accuracy data in the QC book.

10 Volatile Organic Analysis

10.1 Add 5-ml of reagent water already spiked with the surrogate/internal standard mix to the VOA tube. Replace the cap and shake the contents until the solids are dispersed throughout the water.

10.2 Immediately place the tube on the purge-and-trap apparatus and heat at 55°C for 12 minutes while purging (see figure 5).

10.3 The volatiles are trapped on a 24" tenax trap and backflushed onto the GC column at 180°C for 4 min. while the column is held at room temperature (50°C). Run fine wire up purge tube to insure it is not plugged with material from sample, during backflush. The GC is then programmed to 210°C at 8°C/min. and held for 11 min.

10.4 The volatile compounds are identified and quantified by the MS computer system.

11 Calculations

11.1 Percent Dry Solids

$$\frac{\text{gm of dried sample}}{\text{gm of sample}} \times 100 = \% \text{ dry solids}$$

11.2 Percent Volatile Solids

$$\frac{\text{gm of dried sample}}{\text{gm of sample}} - \text{gm of ignited sample} = \text{gm of volatile solids.}$$

11.3 Concentration of Pesticide in Sediment

% dry solids X gm sample extracted = gm of dry sample extracted.

$$\frac{\mu\text{l of sample extract injected}}{\mu\text{l of sample extract}} \times \text{gm of dry sample extracted} = \text{gm of dry sample injected.}$$

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$$\frac{\text{ng of pesticide}}{\text{gm of dry sample injected}} = \text{ug/kg of pesticide}$$

12. Data Reporting

Report all data in ug/kg, calculated on a dry-weight basis.

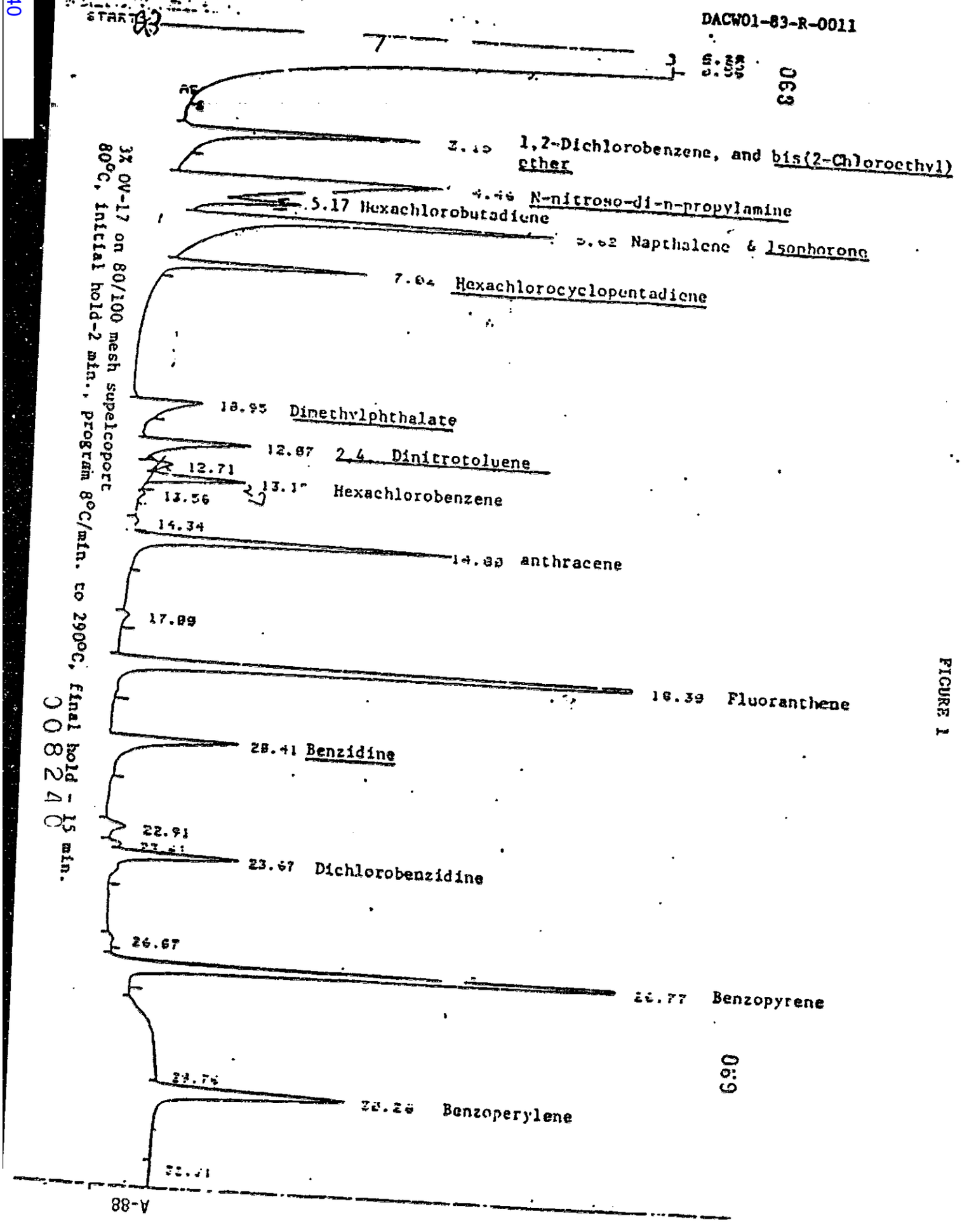
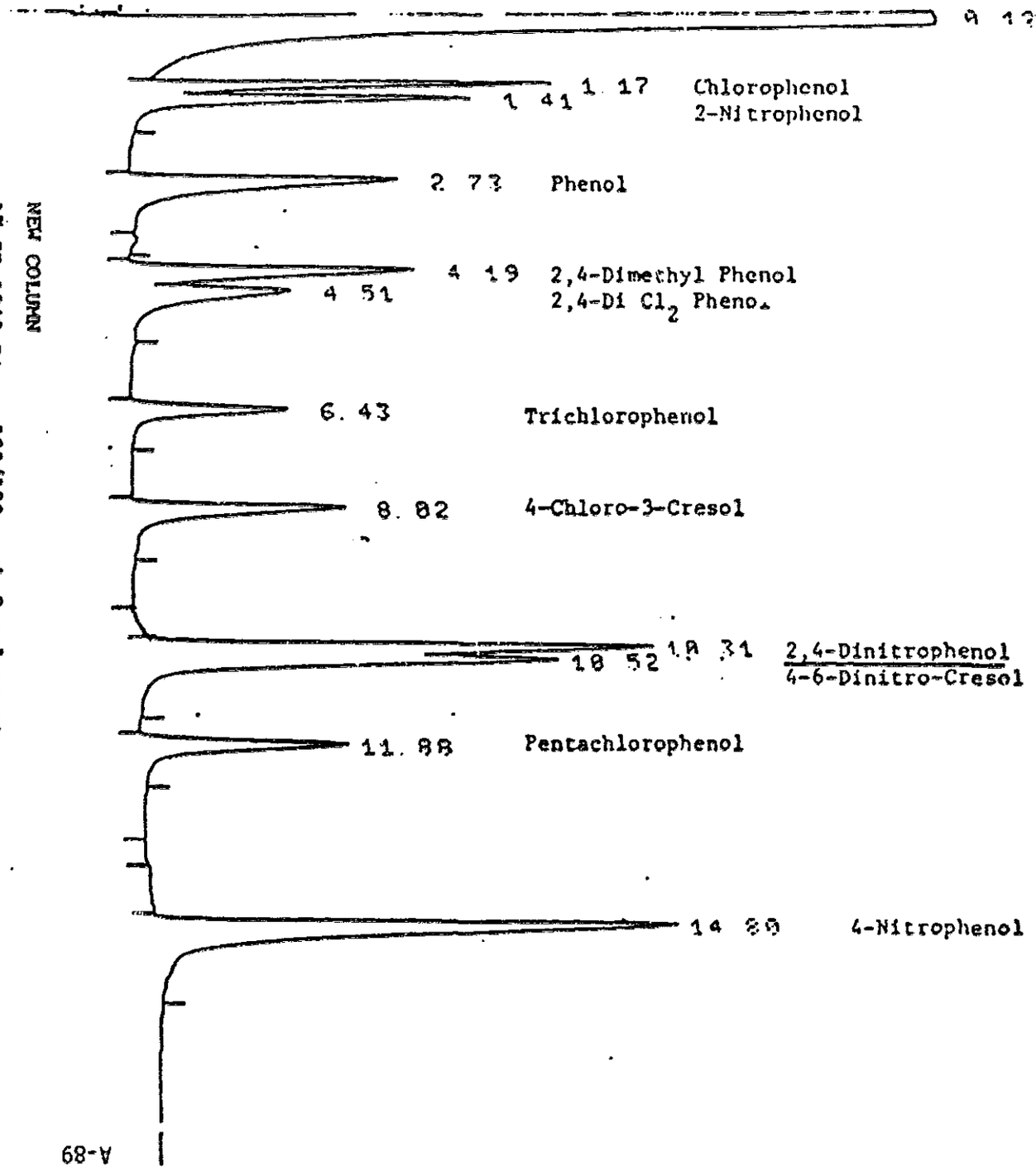

1,2-Dichlorobenzene, and bis(2-Chloroethyl) ether
N-nitroso-di-n-propylamine
5.17 Hexachlorobutadiene
Napthalene & Isophorone
7.64 Hexachlorocyclopentadiene
Dimethylphthalate
2,4 Dinitrotoluene
Hexachlorobenzene
anthracene
Fluoranthene
Benzidine
Dichlorobenzidine
Benzopyrene
Benzoperylene
3% OV-17 on 80/100 mesh supelcoport
80°C, initial hold-2 min., program 8°C/min. to 290°C, final hold - 15 min.

FIGURE 1



NEW COLUMN

1% SP-1240 DA on 100/120-mesh Supelcoport
4-ft.X ¼" OD X 2-mm ID Pyrex glass columns
Oven temperature = 80°C 2-min initial hold, then 8°/min., to 180°C, final

ACID COMPOUNDS

013

FIGURE 3

DACW01-83-R-0011

PURGEABLE COMPOUNDS

1% SP-1000 on Carbopack B

10-ft. X ¼" OD X 2mm ID, Pyrex Glass Column

Program 50° X 210°C by 8°C/Min.

A-90

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FIGURE 4

CAPILLARY COLUMN RUN OF BASE/NEUTRAL AND
ACID PRIORITY POLLUTANT COMPOUNDS

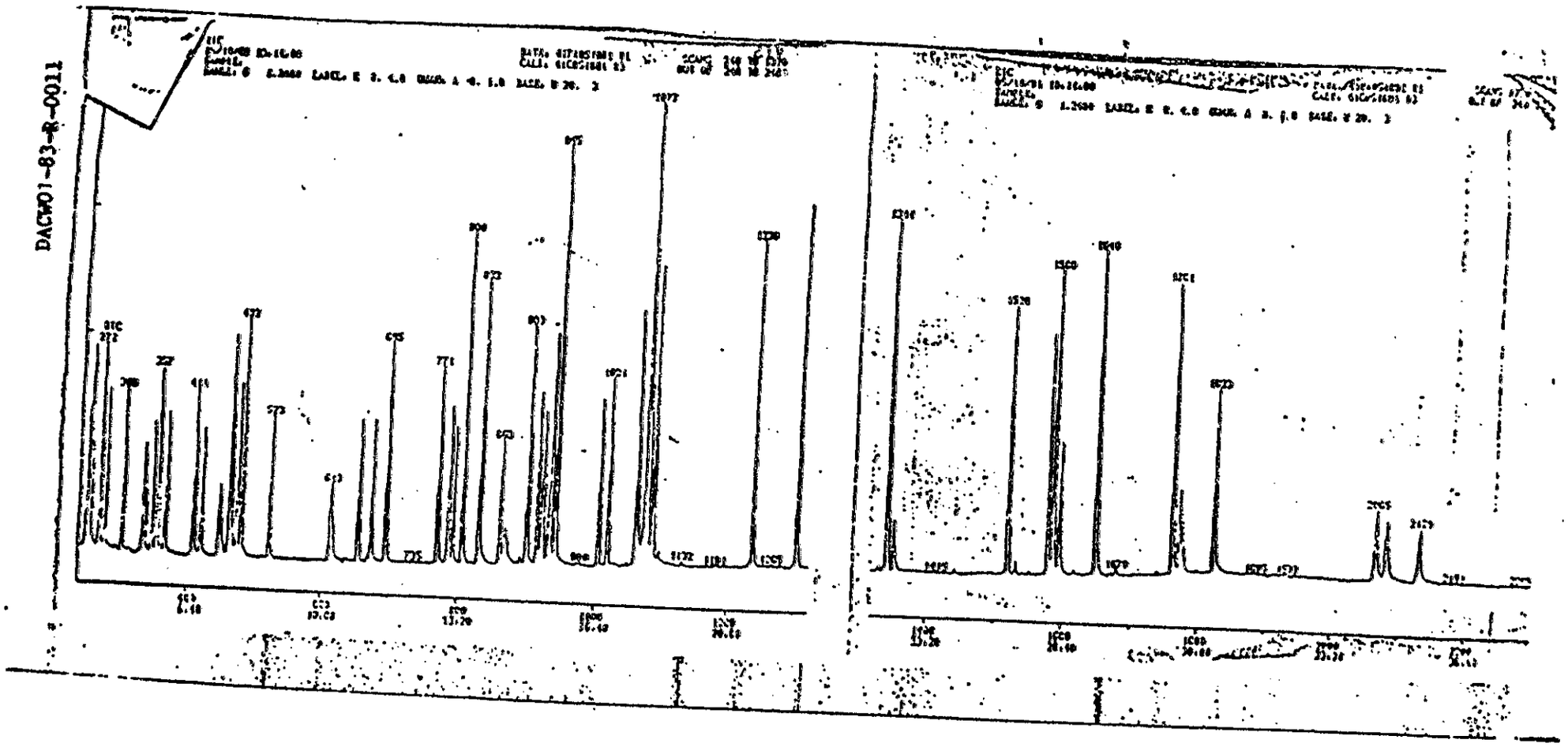

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TABLE I

Capillary Column Conditions

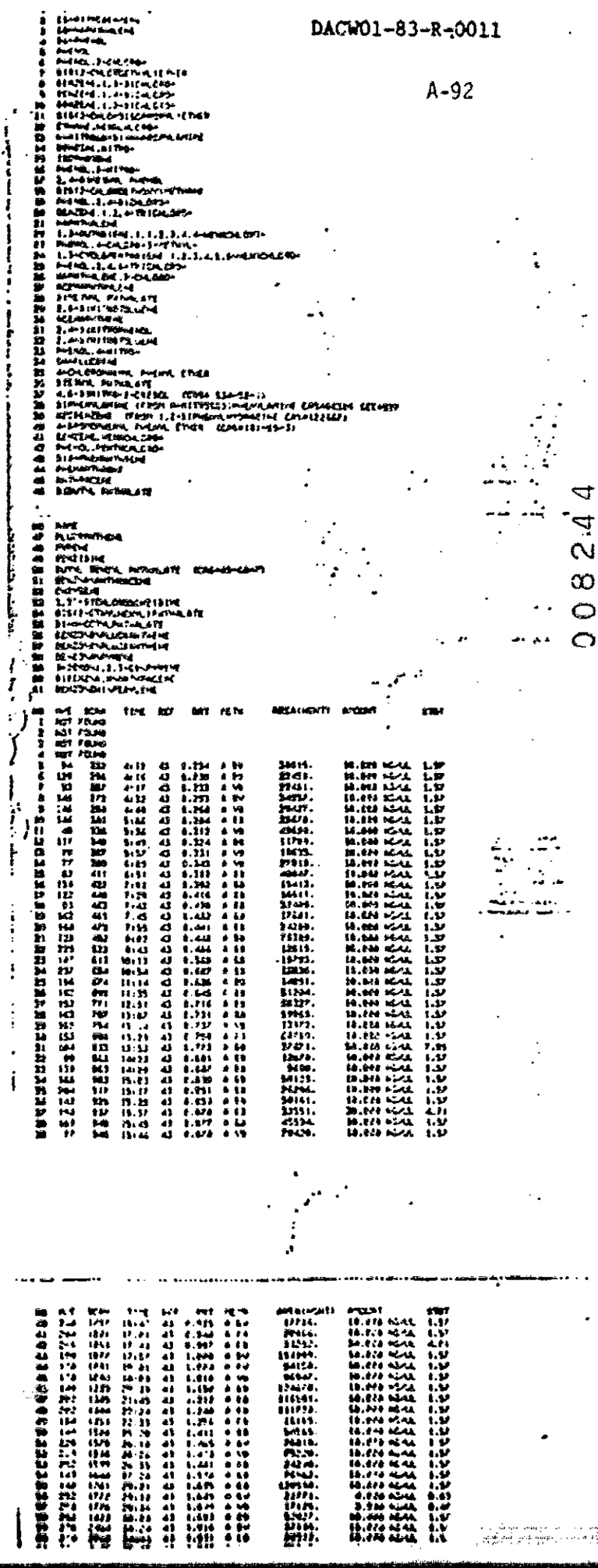
30M. SE-54 fused silica
0.32 mm i.d. from J & W Scientific
film thickness - 0.25 µM

Injection - Splitless w/split open after 1 minute. Split flow 30 ml/min

Injection temperature - 225°C
Sweep - 10 ml/minute
pressure, 14 psi
Column program 50-270° @ 8°/min.
Initial hold 2 min., final hold 12 min.

2 µl injection, most compounds
10 ng/µl (see quan. list attached)

Cap. column interfaced directly into source on mass spec (no separator)



APPENDIX B

INSTALLATION OF GROUNDWATER MONITORING SYSTEM

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HARDING LAWSON ASSOCIATES

INSTALLATION OF GROUNDWATER MONITORING WELL SYSTEM

We recommend that the installation of groundwater monitoring wells meet the following specifications:

1. A geologist/engineer shall supervise the installation of the wells. As a minimum, soils samples shall be obtained in the zone to be screened. In most instances, soils samples should be obtained from overlying zones, as well. These samples shall be inspected by the geologist/engineer to verify the nature of the permeable strata. The geologist/engineer shall record information obtained on depth to water encountered during and following drilling.

2. Wells should be drilled by auger. If rotary drilling is necessary, clear fluid techniques are preferred. If a heavy drilling fluid becomes necessary, U.O.P. Johnson Revert drilling fluid should be used, or an equal quality food grade, organic, low solids, self-destroying drilling fluid.

3. Casing should be a minimum of 4 inch diameter threaded PVC pipe (non-solvent welded) such as TIMCO Geotechnical Grade, Schedule 40 or 80. In certain instances, smaller diameter casing may be appropriate.

4. The screen portion of the well casing shall be factory slotted PVC screen, Teflon or Stainless Steel, with threaded connections.

5. Each well should be screened for the entire thickness of the permeable strata.

6. A granular filter (sand, pea gravel, etc.) of appropriate design should be placed for the entire length of the permeable strata.

7. A geotextile fabric filter of appropriate design shall be insalled on the outside of the screeen. Examples of materials of appropriate engineering properties are contained in the Fibretex series of geotextiles (manufactured by Crown Zellerbach).

8. The annular space between the well casing and the bore hole above the "monitor zone" (zone of saturation) shall be completely backfilled and sealed with an impermeable material such as pure bentonite clay with no additives.

9. The top 12 to 18 inches of the casing below grade shall have concrete placed around it in a wedge configuration.

10. The well shall have a removeable cap to provide access and to prevent entrance of rainwater or external contamination.

11. The well casing shall extend a minimum of 18 inches above ground.

12. After the completion of each well, the well should be developed by pumping, bailing or surging.

13. A means of positive identification shall be provided for each well.

14. During construction, particular care must be taken so that the well does not inadvertantly become contaminated from external sources.

15. In the event an obvious zone of heavy contamination is found during drilling, all the boring residuals should be collected for adequate disposal, at the owner's expense.

16. The driller shall decontaminate the drill auger by appropriate cleaning procedures upon completion of the project and after drilling through any obvious zones of contamination. This practice will minimize hole-to-hole cross contamination.

17. A report will be prepared at the completion of the monitoring well installations containing installation details for each monitoring well, and summarizing installation procedures. The report will contain the following information for each well and be signed by a professional engineer:

    - well location on a suitable map
    - designated identification number of each well
    - ground elevation, with reference datum or benchmark noted (optional)
    - drilling method
    - drill hole diameter
    - borehole log
    - bottom of borehole elevation or depth
    - casing size and material
    - type of screen and mesh size
    - elevation or depth of the bottom of screen

- elevation or depth of top of screen
- type of backfill
- top and bottom elevation or depth of backfill
- top of casing elevation (optional)
- general and miscellaneous information such as date of well completion, weather conditions, on-site supervisor and drilling contractor.

18. All of our work will be done in accordance with client's safety procedures or HLA safety procedures, whichever are stricter.

Optional features which should be considered include:

1. Installation of a locking cover or some other tamper-proof device to prevent unauthorized removal of the well cap.

2. Construction of traffic barriers, such as steel posts, concrete bumpers, or similar devices to protect the well casing from physical damage.

3. Installation of a dedicated bailer in each well to assist in purging and sampling each well. This would eliminate the need to clean the sampler and lines between sampling different wells.

4. Surveying to establish the ground surface and top of casing elevations at each well.

APPENDIX C

PHYSICAL SOIL PROPERTY ANALYSIS

Type of Test	Test Procedure
Moisture Content	ASTM D2216
Dry Density	Volumetric, with Moisture Content
Atterberg Limits	ASTM D423, D424
Grain Size Analysis	ASTM D422
Specific Gravity	ASTM D854
Permeability	Backpressure Saturation Falling Head (see attached)

TEST PROCEDURES FOR PERMEABILITY TESTING WITH BACKPRESSURE SATURATION USING FALLING HEAD APPARATUS

General

This test procedure is based on the referenced procedures and almost 20 years of permeability testing experience at Harding-Lawson Associates.

Limitations

This testing procedure shoudl not be used for determining the permeabilities of soils having a coefficient of permeability greater than about 10^{-3} centimeters per second (cm/sec). The size of lines and permeabilities of the porous stones and filter papers are the limiting factors. Each permeability unit should be checked to determine its limit. The actual limit of a given unit should be about one-half magnitude lower than the permeability of the unit without soil.

Equipment

1. Permeability test cells are of two types: triaxial cells and fluid cells modified by HLA. Both are manufactured by Karol-Warner Inc. of highland Park, New Jersey.

2. The burettes and associated plumbing are designed and constructed by HLA.

3. A constant volume pore pressure measuring device manufactured by Karol-Warner or an electronic transducer with digital readout designed and constructed by HLA is used to determine pore pressure responses (B-value).

Equipment Preparation

Connect top and bottom heads to cell with interior lines. Connect one side of top to one side of bottom with exterior jumper. Place porous stones in plastic heads and trim filter papers and place on stones. Fill saturation burette(s) with distilled water* by placing saturation lead in the water source, connecting a full vacuum on the top of the burettes and opening shut-off valves until burettes are near full. Leave vacuum on until vibration of burette does not free additional air (approximately 1/2 hour).

Specimen Preparation and Setup

Prior to preparation the sample should be visually inspected to determine if microbiologic growth is present. If some is present, the amount should be determined. If the growth as developed since the sample was obtained, the affected soil should not be used in the test.

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*The type of fluid used can be important as permeabilities can vary depending on the properties of the fluid. If at all possible, the actual fluid which will be percolating through the soil should be used such as water from a formation or leachate. Use of distilled water may result in permeabilities which are lower than permeabilities obtained when the actual pore fluids are used.

A sufficient amount of the end of the sample should be trimmed to remove any disturbed or remolded soil. Trim one end of sample to a flat plane at 90 degrees to centerline of tube. Do not alter sample permeability or density any more than necessary during trimming, i.e. do not smear (remold) ends of sample excessively. Place sample in extruder with trimmed end covered with filter paper and extrude an appropriate length and trim other end as above. Record weight to 0.1 gram, height to 0.05 inch, and circumference to .05 inch.

Estimated Permeability (cm/sec)	Approximate Specimen Height (inches)
10^{-3}	3-4
10^{-5}	2
10^{-7}	1
10^{-9}	0.5

Place sample in test cell with filter papers at both ends. Always use two membranes, each with an average thickness of 0.015" and three O-rings at each end of sample.

Equipment Setup

Assemble cell being sure 'O'-ring seals in top and bottom are clean. Tighten three main nuts on chamber posts evenly and securely to prevent leaking. Install strain dial reaction arm on tall chamber post and secure clamp or install strain dial on piston and secure piston clamp in position over piston and post depending on which unit is being used. Set strain dial initially at 0.20 with piston seated on sample. Then raise piston to approximately 0.000 (to allow swell) and tighten piston clamp securely.

Connect chamber fluid source to bottom of chamber and top of chamber to bottom of external burette with top of burette open to atmosphere. Pressure fluid source to approximately 4 psi until fluid fills chamber and rises in burette to 3/4 level and shut off flow. Be sure air pockets are out of cell, exterior lines and burettes. Remove connection to source. An alternate method is with gravity flow.

Seepage Saturation

Relatively permeable specimens should be seepage saturated from bottom to top until some flow occurs at top of sample. Less permeable samples should have some seepage to initiate saturation and remove air around periphery and from ends of sample.

Seepage saturate by connecting bottom of large internal burette (top open to atmosphere) to one internal line to bottom of sample. Connect approximately 4-6" of vacuum to top of sample. If no source of controlled vacuum is available, seepage can be obtained by pressurizing the cell to 4 psi, the saturation burette to 2 pis and leaving the top of the sample at atmosphere. Continue seepage saturation for about 2 hours or until a constant flow occurs for a relatively permeable specimen and until flow ceases for low permeability specimens.

Backpressure Saturation

Before changing to backpressure saturation, remove excess air from internal lines, fittings and specimen heads by connecting one side of bottom head to saturation source and the other side to a controlled vacuum of 4-6" mercury. Draw water through until air bubbles move out and then connect

other side of top block to vacuum to clear air from system. Some agitation and tilting of the cell may be necessary to complete removal. Remove vacuum before using all water from source. If no controlled vacuum is available, proceed as outlined under seepage saturation. There should be no air visible in lines or heads before starting backpressure saturation.

Start backpressure saturation by closing drainage (saturation burette). Set chamber pressure at 4 psi and backpressure at 2 psi and null pore pressure device (if used). Record exterior and saturation burette levels before opening drainage valve. Allow 30 minutes to one hour between pressure increments of 5 psi.* Always maintain a maximum of 2 psi or more positive pressure differential between chamber and backpressure.

To check the saturation progress, confirm chamber and backpressures, and close drainage. Record pore pressure (u) which is zero at this point + backpressure. Increase chamber pressure to 20 psi and null pore pressure device (if used) and record new u + backpressure. Compute change in u + backpressure and ratio of pore pressure Δ to chamber pressure

$$\Delta \left(\frac{\Delta u}{\Delta \rho} = B\right)$$

Saturation is assumed at B value of at least 95 percent. Do not perform this check unless soil is close to 100 percent saturation. Measurement of the B value may not give a true indication of saturation for very hard specimens or rock. For these cases, one of the following can be used.

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*10 psi increments sometimes are more efficient and can be used if soil is not too far from saturation.

1. The applied backpressure is theoretically large enough to cause 98 percent saturation

2. The coefficient of saturation is not increased by significantly increasing the backpressure, or

3. A significant increase in backpressure does not cause additional water to be forced into the specimen.

Typically a backpressure of 100 psi or less is required for saturating most soils. The amount of backpressure needed can be reduced somewhat by increasing the seepage saturation time. A backpressure of 100 psi should not cause any significant deformation of the soil particles that would affect permeability (Ref. __).

After saturation, leave drainage closed (except for consolidated test) and increase chamber pressure above backpressure to desired confining or consolidation pressure.* If specimen is to be consolidated, open drainage and record time rate information as necessary.

Determine Rate of Water Flow Through Specimen

Prior to the start of this part of the test (1) the water levels in the two small diameter interval burettes should be adjusted to give a differential of about 50 cc; (2) the jumper connecting the top and bottom of the specimen should be disconnected. The burette with the highest head should be connected to the bottom of the specimen and the burette with the low head should be connected to the top of the specimen.

*As an alternative, the specimen could be consolidated prior to saturation to reduce the effects of swelling.

Once the specimen is saturated and the burettes are properly connected, the rate portion of the test can begin. The date, starting time and initial water levels should be recorded on HLA permeability laboratory form. Periodic readings should be taken; the time intervals will depend on the permeability of the specimen; however, there should be at least six additional readings taken subsequent to the initial one.

No correction for evaporation is necessary since the tops of the two burettes used are connected. Hence both columns are exposed to the same vapor pressures.

Equipment Takedown

After test, remove all pressures from system and connect bottom of cell to chamber fluid source. Empty cell with approximately 4 psi on external burette. Remove all lines and pore pressure device from cell. Remove cell from loading machine and dismantle. Dry all parts thoroughly and remove internal lines from sample.

Sample Takedown

Remove membrane, filter papers, stones and blocks from specimen. Trim perimeter and ends from specimen and dry internal wedge for final moisture content. Wash trimmings and all other pieces into pan to obtain total dry weight of solids.

Calculations

After oven drying, add dry soils to obtain total weight of solids. Calculate final moisture content. Use total weight of solids and original sample weight to calculate original moisture content and weight of water.

Use total weight of solids and final moisture content to calculate final weight of water (which is equal to final void volume).

Calculate original volume from original area and length. Calculate final volume from external burette changes during saturation and apparatus corrections. Calculate volume of solids with assumed (tested) specific gravity. Calculate volume of voids and void ratio from above information. Calculate volume of voids and void ratio from above information. Calculate dry density from weight of solids and original and final volume. Calculate percentage of saturation from water and void volumes.

Calculate end area before test with final volume and height and finally calculate the permeability using the following:

6. Apparatus
   - 6.1 Distillation apparatus, all glass consisting of a 1 liter pyrex distilling apparatus with Graham condenser.
   - 6.2 pH meter.
   - 6.3 Spectrophotometer, for use at 460 or 510 nm.
   - 6.4 Funnels.
   - 6.5 Filter paper.
   - 6.6 Membrane filters.
   - 6.7 Separatory funnels, 500 or 1,000 ml.
   - 6.8 Nessler tubes, short or long form.

7. Reagents
   - 7.1 Phosphoric acid solution, 1 + 9: Dilute 10 ml of 85% H_3PO_4 to 100 ml with distilled water.
   - 7.2 Copper sulfate solution: Dissolve 100 g $CuSO_4 \cdot 5H_2O$ in distilled water and dilute to 1 liter.
   - 7.3 Buffer solution: Dissolve 16.9 g NH_4Cl in 143 ml conc. NH_4OH and dilute to 250 ml with distilled water. Two ml should adjust 100 ml of distillate to pH 10.
   - 7.4 Aminoantipyrine solution: Dissolve 2 g of 4AAP in distilled water and dilute to 100 ml.
   - 7.5 Potassium ferricyanide solution: Dissolve 8 g of $K_3Fe(CN)_6$ in distilled water and dilute to 100 ml.
   - 7.6 Stock phenol solution: Dissolve 1.0 g phenol in freshly boiled and cooled distilled water and dilute to 1 liter. 1 ml = 1 mg phenol.
   - 7.7 Working solution A: Dilute 10 ml stock phenol solution to 1 liter with distilled water. 1 ml = 10 ug phenol.
   - 7.8 Working solution B: Dilute 100 ml of working solution A to 1000 ml with distilled water. 1 ml = 1 ug phenol.
   - 7.9 Chloroform

8. Procedure
   - 8.1 Distillation
     - 8.1.1 Measure 500 ml sample into a beaker. Lower the pH to approximately 4 with 1 + 9 H_3PO_4 (7.1), add 5 ml $CuSO_4$ solution (7.2) and transfer to the distillation apparatus. Omit adding H_3PO_4 and $CuSO_4$ if sample was preserved as described in 4.1.
     - 8.1.2 Distill 450 ml of sample, stop the distillation, and when boiling ceases add 50 ml of warm distilled water to the flask and resume distillation until 500 ml have been collected.
     - 8.1.3 If the distillate is turbid, filter through a prewashed membrane filter.
   - 8.2 Direct photometric method
     - 8.2.1 Using working solution A (7.7), prepare the following standards in 100 ml volumetric flasks.

ml of working solution A	Conc. ug/l
0	0.0
0.5	50.0
1.0	100.0
2.0	200.0
5.0	500.0
8.0	800.0
10.0	1000.0

8.2.2 To 100 ml of distillate or an aliquot diluted to 100 ml and/or standards, add 2 ml of buffer solution (7.3) and mix. The pH of the sample and standards should be 10 ±0.2.

8.2.3 Add 2.0 ml aminoantipyrine solution (7.4) and mix.

8.2.4 Add 2.0 ml potassium ferricyanide solution (7.5) and mix.

8.2.5 After 15 minutes read absorbance at 510 nm.

8.3 Chloroform extraction method

8.3.1 Using working solution B (7.8), prepare the following standards. Standards may be prepared by pipetting the required volumes into the separatory funnels and diluting to 500 ml with distilled water.

ml of working solution B	Conc. ug/l
0.0	0.0
3.0	6.0
5.0	10.0
10.0	20.0
20.0	40.0
25.0	50.0

8.3.2 Place 500 ml of distillate or an aliquot diluted to 500 ml in a separatory funnel. The sample should not contain more than 25 ug phenol

8.3.3 To sample and standards add 10 ml of buffer solution (7.3) and mix. The pH should be 10 ±0.2.

8.3.4 Add 3.0 ml aminoantipyrine solution (7.4) and mix.

8.3.5 Add 3.0 ml potassium ferricyanide solution (7.5) and mix.

8.3.6 After three minutes, extract with 25 ml of chloroform (7.9). Shake the separatory funnel at least 10 times, let $CHCl_3$ settle, shake again 10 times and let chloroform settle again.

8.3.7 Filter chloroform extracts through filter paper. Do not add more chloroform.

8.3.8 Read the absorbance of the samples and standards against the blank at 460 nm.

9. Calculation

9.1 Prepare a standard curve by plotting the absorbance value of standards versus the corresponding phenol concentrations.

9.2 Obtain concentration value of sample directly from standard curve.

10. Precision and Accuracy

10.1 Using the extraction procedure for concentration of color, six laboratories analyzed samples at concentrations of 9.6, 48.3, and 93.5 ug/l. Standard deviations were ±0.99, ±3.1 and ±4.2 ug/l, respectively

10.2 Using the direct photometric procedure, six laboratories analyzed samples at concentrations of 4.7, 48.2 and 97.0 mg/l. Standard deviations were ±0.18, ±0.48 and ±1.58 mg/l, respectively

Bibliography

1. Annual Book of ASTM Standards, Part 31, "Water", Standard D1783-70, p553 (1976).
2. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p574-581, Method 510 through 510C, (1975).

Determination of Phenols in Sediments and Other Solids
CRL Method 417

Scope and Application

This method is applicable to the determination of phenolic compounds (except paracresols and similar parasubstituted phenols) in sediments and other solids.

Summary of Method

Phenolic compounds are manually distilled to remove interferances. The distillate reacts with buffered ferricyanide and 4 aminoantipyrine spectrophotometrically at 505 nm. An automated system is used for the color development and measurement.

Equipment

Distillation apparatus, consisting of a 500 Pyrex flat-bottom distilling flask and a Graham condenser.

250 ml or 500 ml Erlenmeyer flasks calibrated at 200 ml.

Technicon Autoanalyzer II System (See CRL Method 408, Attached)

Analytical Balance

Heating Mantles or Burners

Reagents

$CuSO_4/H_3PO_4$ Solution, 5%

12% H_2SO_4

Other Reagents - See CRL Method 408 (Attached)

Procedure

1. Steam out the distillation flasks before each use by boiling distilled water in the flasks without water running through the condenser.

2. Weigh accurately 1 to 2 grams of wet, well-mixed sediment.

3. Transfer to the distillation flask.

4. Add 100 ml of distilled water and 2 ml of 5% $CuSO_4/H_3PO_4$ solution.

5. Distill 100 ml of sample (20-35 ml of distilled water may be added to assure distillation of 100 ml of sample into the erlenmyer flask).

6. Add 1 ml of 10% H_2SO_4 and proceed with analysis using CRL Method No. 408. (Samples may be stored at 4°C for a maximum of three weeks if necessary).

Quality Control

A field blank which contains $CuSO_4/H_3PO_4$, one or more standards and a duplicate of one of the samples, are analyzed with each group of samples. If twenty or more samples are analyzed, a minimum of two field blanks, standards and duplicates are analyzed.

The analytical balance is set to zero before each sample is weighed.

The manufacturers instructions are followed for operation of the Technicon Autoanalyzer.

Calculation

$$\text{ug/kg Phenol (dry basis)} = \frac{\text{reading in ug/l} \times 1000 \text{ from Method 408} \times 100}{(\text{orig. wt. in grams}) \times \text{decimal fraction of \% solids}}$$

References

1. "Manual of Methods for Chemical Analysis of Water and Wastes", United States Environmental Protection Agency, Office of Technology Transfer, 1974, Washington, DC, p. 241-242.