UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
REGION 1
1 CONGRESS STREET, SUITE 1100
BOSTON, MASSACHUSETTS 02114-2023

February 10, 2004

RECEIVED
D.E.M. / O.W.M.
2004 FEB 12 A 11:

Mapleville Main, Inc.
c/o Richard B. Hodgson
8677 Batesville Road
Afton, VA 22920

Dear Mr. Hodgson:

I am writing to inform you of a United States Environmental Protection Agency (EPA) Region 1 decision regarding the Bolliden Metech, Inc. site located in Providence, Rhode Island (EPA Identification Number: RID981885023). In accordance with the Superfund Memorandum of Agreement (SMOA), dated 13 February 1997, between the Rhode Island Department of Environmental Management (RI DEM) and EPA, the EPA Superfund program has completed its investigation of this site. On 10 February 2004, EPA determined that a No Further Federal Remedial Action Planned (NFRAP) decision was appropriate. On February 10, 2004 the site was archived (removed) from EPA's Comprehensive Environmental Response, Compensation and Liability Information System (CERCLIS) database. (Sites archived from CERCLIS are maintained as historical records to ensure Superfund program investigations are not needlessly repeated in the future).

The Boliden Metech, Inc. site has been reviewed by the Superfund Site Assessment and Removal programs, and EPA has concluded that, based upon currently available information, this site should be archived from CERCLIS. This action is intended to underscore EPA's finding that the Boliden Metech, Inc. site is not an appropriate candidate for inclusion on the National Priorities List (NPL or "Superfund List"), and that EPA does not anticipate taking any further action at this site. This decision does not necessarily mean that there is no hazard associated with this site; sites with archive decisions may still warrant other federal or state program action. However, the decision to archive this site does mean that it is not judged to be a candidate for NPL consideration, and that EPA considers the RI DEM to be the lead agency overseeing hazardous waste compliance at this site. You may contact Ms. Cynthia Gianfrancesco of the RI DEM at (401) 222-2797 x7126 to verify the status of this property under the state's hazardous waste program.

Finally, archive decisions may be changed in consultation with the state, based upon new information or substantially altered site conditions. Such significantly changed circumstances could result in a recommendation for NPL proposal at a later time. In such an instance, the property owner would be notified and the site would be returned to the CERCLIS database.

If you have any questions, I may be reached at (617) 918-1377.

Sincerely,

Gerardo Millán-Ramos, M.S.
Site Assessment Manager
Office of Site Remediation and Restoration

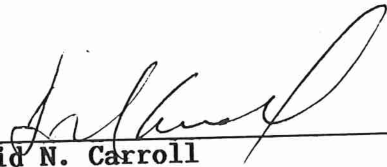
C:\Data\Wp\BolidenMetecharchlet

cc: Ms. Cynthia Gianfrancesco, RI DEM

QUALITY ASSURANCE PROJECT PLAN

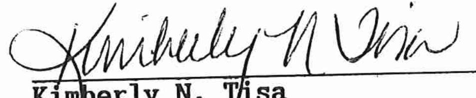
Boliden Metech, Inc.
Allens Avenue Facility
Providence, Rhode Island

BOLIDEN METECH, INC.

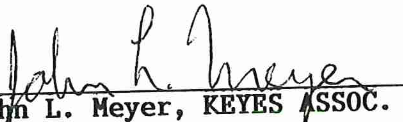


David N. Carroll
Project Manager
VP - Manufacturing

UNITED STATES



Kimberly N. Tisa
EPA Region 1



John L. Meyer, KEYES ASSOC.
Quality Assurance Officer

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1.0 PROJECT DESCRIPTION

The purpose of this project is to develop a Scope of Work (SOW) to verify adequate remediation of PCB contamination at Boliden Metech's (Boliden) Allens Avenue facility in Providence, Rhode Island to an action level (AL) of 10 parts per million (PPM). This Scope of Work is being developed in order to satisfy certain requirements of the consent agreement (Civil Docket 89-0208-T) between Boliden and the US Environmental Protection Agency (EPA). The Scope of Work is consistent with the cleanup standards and guidelines set forth in the PCB Spill Cleanup Policy, (40 CFR Part 761, Subpart G, and the EPA guidance document "Verification of PCB Spill Cleanup by Sampling and Analysis" (EPA Document No. EPA-560-5-85-026).

The Allens Avenue site is located adjacent to the Providence River on approximately 6.5 acres of land. The site had been used for the shredding of scrap computer components from 1980 to 1989. Under the EPA consent agreement, Boliden will remove all piles of shredded scrap containing greater than 50 ppm PCB, and will remediate PCB contamination of the site's cover material, building surface areas, and other on site facilities such as concrete pads and the shredder unit.

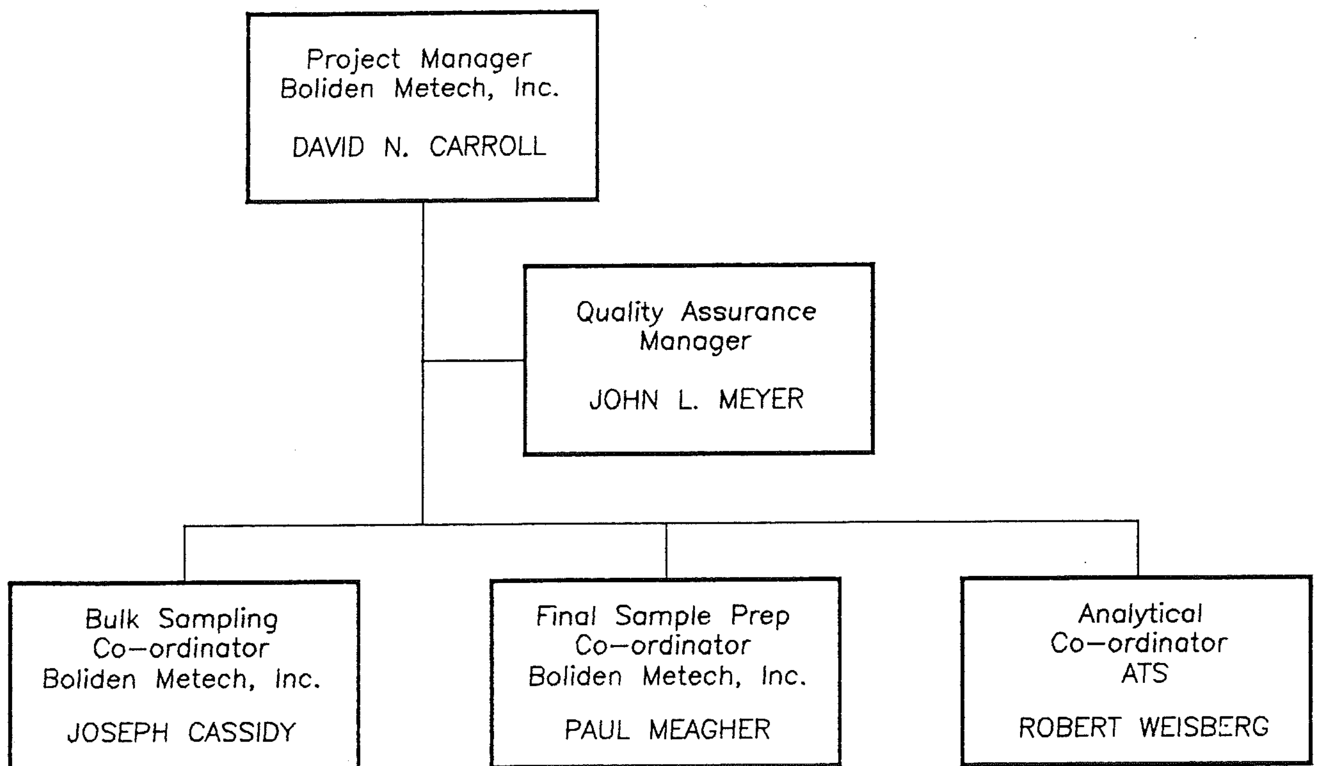
This Scope of Work will cover sampling and analysis to verify adequate remediation of PCB contamination. The proposed remediation will consist of removal of all cover material containing a PCB concentration of 10 ppm or greater and cleaning of building surfaces, shredder components, and concrete pad surfaces to remove PCB's to achieve a concentration of less than 10 ug/100 cm^2.

2.0 PROJECT ORGANIZATION

All field sampling and laboratory operations for this project will be directed by the Boliden Metech Project Coordinator. The project organization is depicted in Figure 2.2.

The Project Manager insures that the performance of each operational component is consistent with the quality goals of the project. The Quality Assurance Manager is independent of all operational activities and prepares quality process monitoring reports for the Project Manager.

2.2 ORGANIZATION CHART



2.3 ASSIGNMENT OF RESPONSIBILITIES

The primary objective of this Scope of Work is to ensure that a quality monitoring and feedback system is in place that will result in the production of data of known quality. Overall quality assessments will communicate to the Field, Laboratory and Project QA Manager. When deficiencies are detected, these assessments serve as the basis for corrective action.

The following tabulations provide a listing of the quality related responsibilities of the Project Manager, Quality Assurance Manager and other key project personnel.

PROJECT MANAGER

BOLIDEN METECH, INC.

Primary responsibilities of the Project Coordinator will include the overall supervision of the following:

1. QUALITY ASSURANCE RESPONSIBILITIES:
   - A. The project manager is responsible for implementing the SOW and complying with the SOW goals. He requires similar compliance by all subordinates.
   - B. He ensures that all field and laboratory operations under his control are in compliance with the quality assurance objectives as described in this SOW.
   - C. He ensures compliance with the quality requirements of methods and procedures as written.
   - D. He is responsible for compliance with any corrective action measures for process deficiencies which are identified by the QA Manager through audit processes or data quality indicators.
   - E. He ensures that all documentation related to quality criteria such as field and laboratory logbooks, chronicles and raw or processed data are maintained in an orderly manner.

2. OPERATIONS RESPONSIBILITIES
   - A. Site preparation and sample scheme layout.
   - B. Composite sampling design layout of site and buildings.
   - C. Composite sampling process and custody documentation.
   - D. Field and sample reports.
   - E. Transportation of individual samples to final preparation site.
   - F. Process and preparation reports of individual sample homogenization and compositing.
   - G. Transportation and chain of custody records to analytical lab.

OPERATING RESPONSIBILITIES (Cont.)

3. Provide a copy of the SOW to all subordinate project management personnel and ensure their understanding of the duties for which they are responsible.

4. Coordination with Project Manager US EPA with regards to all aspects of the SOW.

PROJECT QUALITY ASSURANCE MANAGER

The Quality Assurance Director is independent of all personnel directly involved in sampling data production activities. He reports to the Boliden Metech Project Coordinator. He is responsible for monitoring the quality assurance program described in this Scope of Work and for ensuring that all operational personnel have copies of the Scope and have been thoroughly familiarized with all quality processes.

1. Responsible for monitoring all quality activities of the sampling and analysis program.
2. Responsible for assessing the compliance of the field sampling operation and laboratory within requirement of the QA project plan.
3. Responsible for performing system and performance audit of field sampling and laboratory activities.
4. Reporting the results of systems audits, performance audits and performance evaluation samples to the project coordinator.
5. Recommending corrective action for quality process deficiencies to the project manager.
6. Monitoring corrective action implementation and providing feedback on their effectiveness to the project manager.
7. Receiving and evaluating all final data reports prior to their release to the USEPA Project Manager.

FIELD SAMPLING - COORDINATOR

The supervisor of the field sampling in Providence is responsible for the following:

1. SOW Responsibilities
   A. Instruction to all workers, subcontractors as to the contents and function of this SOW.
   B. Compliance with all provisions of the SOW.
   C. Implementation of any corrective actions as directed by the Project Manager.

2. Direct supervision of all field operations in Providence including:

   A. A site preparation and sample plan layout
   B. Individual sampling, collection, preparation, and transportation
   C. Field Report generation
   D. Chain of custody documentation preparation and implementation
   E. Equipment availability and readiness
   F. Site work as directed by the Project Coordinator

3. Notification to all contractors and subcontractors as to the content of the Consent Decree when their services are performed in conjunction with the Consent Decree.

4. Movement of all materials within the site.

FINAL SAMPLE PREPARATION COORDINATOR

The responsibilities of the Final Sample Preparation Supervisor are as follows:

1. SOW Responsibilities
   A. Instruction to all workers and subcontractors as to the contents and function of this Scope of Work
   B. Compliance with all provisions of the Scope of Work
   C. Implementation of any corrective actions as directed by the Project Manager

2. Direct supervision of all sample preparation including:
   A. Receipt and verification of the individual ground cover samples from the field sample supervisor.
   B. Final preparation of the samples through the Jar mill and final compositing procedures.
   C. Documentation of the processes described in Item 2.
   D. Chain of custody documentation and transportation to the analytical lab of final composite samples.
   E. Performance of the above to be in accordance of this scope of work.

ANALYTICAL COORDINATOR

The supervisor will be responsible for all laboratory activities performed in analyzing samples from the site.

The Analytical Supervisor will ensure that all laboratory staff have copies of the sample collection methods and are familiar with the custody, preparation and analysis requirements as detailed in this scope of work.

ANALYTICAL COORDINATOR (Cont.)

The Analytical Supervisor will:

1. Verify the receipt and chain of custody documentation of all samples received from the Final Composite Sample Supervisor on field sample supervisor.
2. Monitor all laboratory activities and quality assurance/quality control measurements.
3. Ensure that corrective actions in compliance with method specifications are implemented when appropriate.
4. Report results of QA/QC and sample measurements to Project Coordinator and Assurance Supervisor.

QUALITY ASSURANCE OBJECTIVES FOR MEASUREMENT DATA

Composite samples collected at Boliden Metech's Allens Avenue facility will be analyzed for PCBs using Electron Capture Device (ECD) Gas Chromatography (GC/ECD). Composite samples will include soil and wipe samples from the site's yard, concrete pads, shredder, DLA tank, and buildings. This data will be used to determine if PCB contamination at the site has been remediated to below the 10 ppm and/or 10ug/100 cm^2 action level. Results from GC/ECD analysis is to be the basis for all further remediation and disposal actions.

The quality assurance objectives for measurement data obtained from the analysis of composite samples of soil, wipe and concrete using a modification of the method entitled "The Sampling and Analysis of Non-homogeneous Solids for Polychlorinated Biphenyls". Primary modifications of this method include field collection methods, and use of EPA methods 8080 for sample analysis by GC/ECD. The sampling and compositing methods are described in Section 6.0.

The quality of the analytical process will be routinely checked through the analysis of quality control (QC) reference samples and matrix spike duplicate samples. Method performance for each field sample will be monitored through the use of surrogate spikes.

QUALITY ASSURANCE OBJECTIVES FOR MEASUREMENT DATA

The accuracy of the measurement data will be evaluated by comparing the percent recovery of QC check samples containing pre-established concentrations of PCB to the statistically based control limits which have been established for the method. A duplicate spiked field sample will be analyzed routinely for each batch of less than 20 samples. Spike recoveries will be assessed to determine method accuracy, efficiency and matrix interference effects. The matrix spike duplicates will also be used to assess precision. Analytical precision will be expressed as relative percent difference between results of matrix spike duplicate samples.

A single blind performance evaluation (PE) sample will be introduced into the laboratory with every batch of 20 samples. This PE sample will be prepared from homogenized sand mixed with PCB's to achieve a known concentration. The PCB concentrations of the PE sample will be determined through laboratory analysis. The PE sample will be used to monitor the analytical system's performance on a sample of "known" concentration.

Field duplicate samples will be collected from each sample site by collection of ample representative material from each sample point. Duplicate field samples will be run for analysis at a frequency of 1 duplicate per 20 field samples. Duplicate wipe samples will be collected from the area adjacent to the primary wipe sample. Hexane used in the wipe sampling will be analyzed along with the clean wipe medium as a blank. The duplicate field sample will be analyzed using the procedures described in this method as an indication of the precision of the sampling and homogenization sequence. Precision will be expressed as relative percent difference (RPD) for the mean of the replicate pairs.

Duplicate aliquot samples will be randomly selected from a quadrant or portion of each sampled area for parallel analysis.

Duplicate aliquot samples will be run for analysis at a frequency of 1 every 20 field samples.

A PCB surrogate (decachlorobiphenyl) will be added to the sample prior to extraction. Surrogate recovery will be compared to the established recovery criteria for the method (80 - 120% recovery is considered acceptable).

Field data from this project will be evaluated for completeness, representativeness, and comparability to insure that the data can be used for its intended purpose. These evaluations will be based on the criteria that has been established for each quality indicator.

Field data will be considered to be valid from a comparability viewpoint, if the acceptance criteria for accuracy and precision and any other method-specified quality criteria are achieved and are consistent with the original data quality objectives. Each laboratory analyst will validate laboratory data using the established criteria to minimize the amount of statistically invalid data produced. Acceptable quality control performance will enable the data user to make decisions regarding the PCB concentration of each composite sample in relation to the 10 ppm action limit for PCBs.

The data representativeness evaluation is based on achieving the relative percent difference (RPD) criteria that has been established for field duplicates. If these criteria are achieved, the techniques used for field sampling, homogenization, and compositing will have produced samples which accurately represent the site's condition.

Data completeness is a function of achieving the quality criteria that has been established for the analysis of field samples. Complete-

ness is expressed in terms of frequency percentage that this criteria was achieved. For this investigation, all criteria for field sample quality must be achieved before the data can be used for its designated purpose. The precision and accuracy criteria for quality parameters is presented in Table 2.1

TABLE 2.1

PRECISION AND ACCURACY CRITERIA FOR QUALITY PARAMETERS

Blank Spike Accuracy Parameter	Control Interval
2,4,4′ Trichlorobiphenyl	82 - 113%
2,2′3,3′4,4′ Hexachlorobiphenyl	87 - 119%

Matrix Spike Accuracy: Parameter	Control Interval
2,4,4′ Trichlorobiphenyl	61 - 134%
2,2′3,3′,4,4′ Hexachlorobiphenyl	63 - 143%

Matrix Spike Precision: Parameter	Relative % Difference
2,4,4′ Trichlorobiphenyl	30
2,2′3,3′,4,4′ Hexachlorobiphenyl	30

Duplicate Aliquot Precision: Parameter	Relative % Difference
Total X PCBs (Aroclors)′ >2ppm	32
Total X PCBs (Aroclors) <2ppm	47

Field Duplicate Precision: Parameter	Relative % Difference
Total X PCBs (Aroclors) >2ppm	32
Total X PCBs (Aroclors <2ppm	47

Performance Evaluation Accuracy: Parameter	Recovery Criteria**
Total Aroclor (1242 + 1254)	+/- 30%

* Detected PCBs apply to concentrations below the quantitation limit that are capable of being qualitatively identified. Less accurate quantitative values can be assigned to these PCBs based on extrapolation of the calibration curve.

** Determined by USEPA review of performance evaluation data.

RPD based on difference from ODL concentration of 2 ppm.

QUALITY ASSURANCE OBJECTIVES FOR MEASUREMENT DATA (Cont.)

The method sensitivity requirements (Operational Detection Limit - ODL) are based upon regulatory program requirements. This method has been designed to produce accurate data for Aroclor PCBs in the composited ground cover and wipe samples at concentrations above and below 2 ppm. This concentration is selected as the ODL. The ODL for groundwater samples will be 4 ppb.

The ODL is defined as the lowest concentration of a target analyte that can be accurately determined, using the calibration curve that has been developed for the method. The response factor for the calibration standard at the ODL must meet the RPD criteria for the calibration curve to produce accurate data.

3.0 VERIFICATION SAMPLING PLAN PROCEDURES

3.1 COVER MATERIAL SAMPLING, SAMPLE COLLECTION, PREPARATION, AND HOMOGENIZATION

Sampling and Compositing Plan

Verification of adequate remediation of the project site's cover material will be conducted via a composite sampling scheme which is illustrated in Figure 3.1. Sampling will commence immediately upon removal of product piles. Sampling, analysis, and reporting of results are anticipated to take from 4 - 6 weeks. This scheme divides the site into four major quadrants (North, South, East, and West). Each major quadrant is further subdivided into 8 minor quadrants (North', South', East', and West'). Minor quadrants are bisected into two subquadrants (A,B). Each minor subquadrant contains 6 individual sample site cells, with a sample point located at the cell's center. Individual samples will be collected from each cell within the minor subquadrants (6 cells) homogenized and composited for analysis, giving 32 composite samples each composed of material from 6 individual cells.

Sample Collection and Preparation

Field Collection: Both primary and duplicate samples will be collected from an area within 3 to 5 feet from each sample cell center, using a Bobcat excavator. Samples will be collected using the excavator bucket to remove all material between 0-12" within the sample point. Excavation depth will be measured to ensure proper depth. Previous studies of background conditions at the site by Cahill Associates indicated that the contamination did not extend below 12" from the surface. Material from each sample site will be placed on a Tyvex covered plywood sheet and mixed with a shovel. Large stones or pieces of metal and other debris will be excluded from the sample. Portions of the site underneath the metal cleaning building and the concrete pad will be sampled by coring through the concrete and extracting a sample of the underlying soil.

The excavator bucket and shovel will be steam cleaned between each sample in order to prevent cross-contamination. Steam cleaning condensate and rinsate from equipment will be collected and held for analysis. Each individual sample will be at least 2.5 pounds in size, and will be placed into a pre-weighed, pre-cleaned, labeled container for transfer to Boliden's Mapleville, RI plant for homogenization and compositing. Containers will be pre-cleaned and pre-weighed amber glass with teflon-lined lids. The containers will be supplied by the analytical laboratory. Duplicate samples will be collected for homogenization, compositing, and analysis.

All buildings on site were constructed prior to use of the site for shredding PCB containing material. Therefore, sampling material below the building slabs is unnecessary. The roof of the shredder building will be removed and disposed of as PCB contaminated waste. Sampling of the building frame is detailed in Section 3.4.

3.2 SAMPLE PROCESSING & HOMOGENIZATION

Individual bulk samples from each cell are processed in a Jar Mill for homogenization and particle size reduction using batch processing procedures. The integrity of each sample site is maintained during this process to ensure the homogenized sample adequately represents each site.

1. Weigh and verify contents of covered containers containing the individual bulk sample.

2. Manually remove the large, unmillable pieces of metal from the sample prior to jar milling. Place the unmillable material into previously weighed, wide mouth, 2.5-gallon glass jars labeled with the proper sample identification number. Re-weigh the jars containing the unmillable material and

record the weight. (Appendix 3, The Sampling and Analysis of Non-homogeneous Solids for Polychlorinated Biphenyls, Sections 8.2.1.1 and 11.1.6)

NOTE: Occasionally, large, unmillable metal chunks may be present in the sample. These chunks must be removed from the sample prior to jar milling. The weight of this material will be deducted from the beginning sub-sample weight and disregarded if less than 10% of the total. If the weight of any large metal pieces is greater that 10%, they will be treated separately.

3. The individual bulk samples are processed through a Jar Mill for further size reduction to -35° mesh and homogenization.

EQUIPMENT DECONTAMINATION:

Residual contamination of the jar milling equipment may occur during the sample homogenization process.

The jar milling equipment will be decontaminated prior to processing composted sample borings from a different sub-quadrant by processing inert materials through the equipment used in the size reduction procedure.

1. Empty all sample material from the milling equipment.
2. Process approximately two volumes (approximately 3 cubic feet) of previously analyzed cleansing sand through the mill.
3. Collect a ten percent aliquot of the processed cleansing sand by C3Q. Fill and 8-ounce jar with an aliquot of the cleansing sand.

4. Label each sample aliquot and retain it for PCB analysis to verify the absence of cross contamination between processing episodes if needed.

FINAL SAMPLE PRESERVATION AND STORAGE

The likelihood of significant biodegradation of PCBs in the sub-quadrant samples before the final sample extraction is remote. To minimize any potential degradation, homogenized samples will be stored at 4°C in 8-ounce, wide-mouth, amber glass jars until extraction. There is not any preservation requirement for unhomogenized samples.

NOTE: All samples must be extracted within 14 days of collection.

Transport the refrigerated final samples to the analytical laboratory for final analysis.

SAMPLE CONTAINERS

Insulated sample containers will be provided for the transportation of sample bottles to the laboratory for analysis. The containers meet or exceed all protocol requirements (i.e., EPA, ASTM, States) for shipping. Chain-of-custody seals and forms will be provided to ensure complete documentation during sample transport, sampling and analysis.

The laboratory will provide ice packs for each container to ensure that proper preservation temperature is maintained during the shipping process. After collection, it is recommended that all sample containers be chilled with ice prior to shipment.

Sample Compositing: Compositing of samples from individual cells will be performed after homogenization and particle size reduction, in order to produce a more representative composite for analysis.

Compositing will be performed by a progressive cone and quartering method to produce a composite sample of 100 grams for analysis. This method is as follows: (See Appendix A)

1. Individually cone and quarter the homogenized sample from each sample cell within the minor quadrants to produce two 100 gram sub-samples. Place the 100 gram samples in eight ounce amber jars. One 100 gram sample will be used for compositing. Retain the other sample for later analysis if the individual cell must be tested. Retain the remaining homogenized material as a reserve sample.

2. Composite 100 gram homogenized sub-samples from each sample cell in order to produce a 1800 gram composite sample.

3. Cone and quarter the composite sample to produce two 100 gram composite sub samples. Place these sub-samples in two, eight ounce amber jars. One sample will be sent to the laboratory for analysis; the other will be retained for further analysis, if required.

<u>Wipe Sample Compositing</u>: Wipe samples will be collected using pesticide-grade hexane-soaked gauze pads which have been precleaned by soxhlet hexane extraction. A 100 cm^2 area will be sampled using an aluminum foil mask cut to contain the 100 cm^2 sample area. The masked area will be thoroughly wiped vertically and horizontally with the gauze pad using stainless steel tongs held with a pthalate-free glove. The tongs will be rinsed between wipes. Individual samples will be composited in the field by placing them in pre-cleaned brown glass

pre-weighed containers with a teflon lid. Each composite sample will be batch extracted for analysis.

No more than two pads will be placed in one container, in order to allow for their easy removal. Multiple containers may be used for a single composite sample.

SAMPLE CONTAINER CLEANING

New, properly cleaned sample containers will be provided for sample collection. These containers will be prepared by the laboratory or purchased from a commercial vendor who can document their cleanliness. The vendor-prepared bottles which are used routinely are prepared according to US EPA CLP protocol. The glassware cleaning procedures employed by the laboratory for sample containers are outlined below.

Bottle Caps:

* All bottle caps are Teflon lined
* New bottle caps are rinsed with de-ionized water, allowed to air dry in racks, then placed on bottles

Amber Glass Bottles:

* 1 Liter, 500 ml, 250 ml
* Rinsed with de-ionized water
* All bottles are baked at 200°F for 30 minutes prior to capping and use.

3.3 CONCRETE PAD SAMPLING AND COMPOSITING

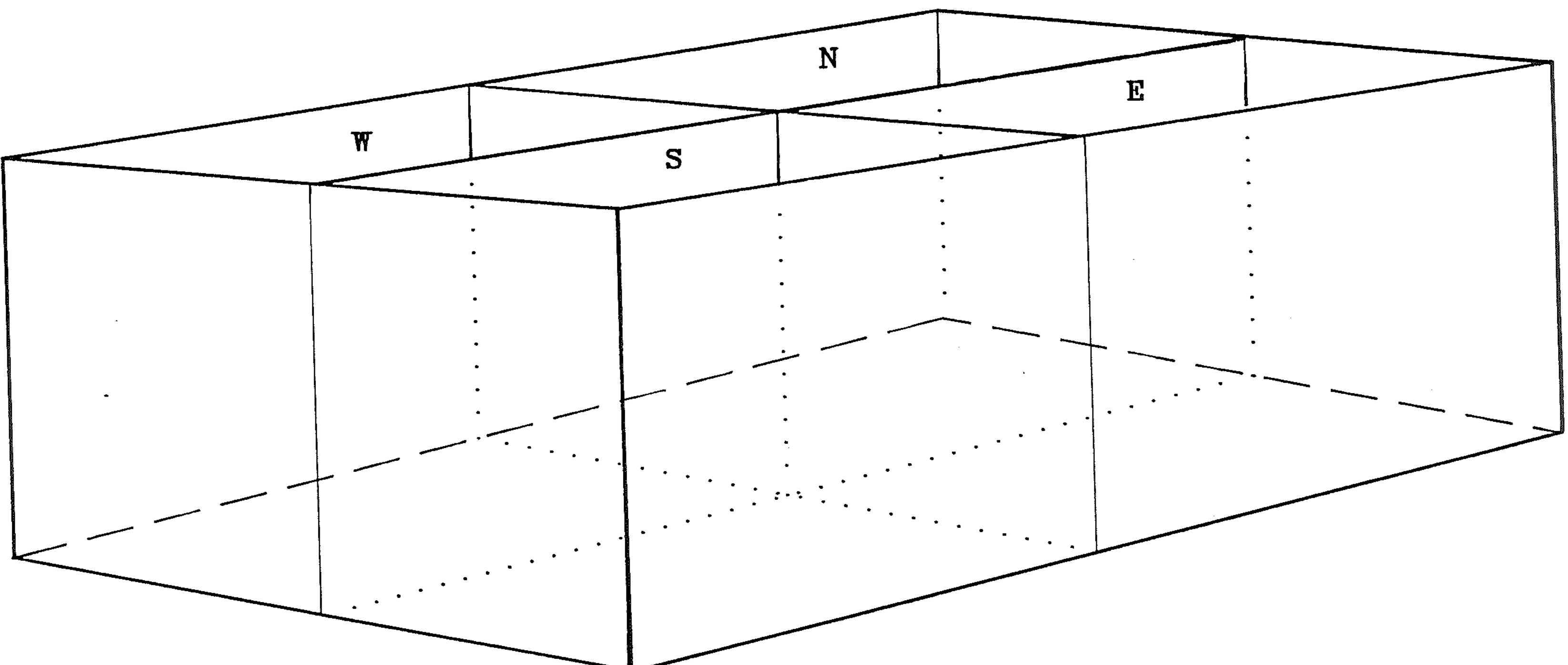
Sample Collection and Compositing: Six individual sample sites will be placed on the concrete pad which is located in the yard area. The concrete pad on the site will be wipe sampled. Wipe sample methods are described in Section 3.2 (Page 19 of 79). If there is evidence that liquid PCB's have permeated the concrete surface cores will be collected for analysis. Cores will be collected to a depth of 3" at wipe sample locations. Coring equipment will be steam cleaned and rinsed between samples to prevent cross-contamination. Condensate and rinsate from sampling equipment will be collected and held for analysis, if required. Duplicate cores will be collected for homogenization, compositing, and analysis. Cores will be placed in clean, pre-weighed containers and transported to Boliden's Mapleville facility for homogenization and compositing. Cores will be homogenized and composited according to the method described for cover material. One 100 gram composited concrete pad core sample will be sent to the laboratory for analysis, whereas the other will be retained as a reserve.

3.4 METAL CLEANING BUILDING

Sample Collection and Compositing: The metal cleaning building will be divided into four major quadrants. Each major quadrant will include floor and girder areas for sampling (see Figure 3.2). The insulation and metal skin of the metal cleaning building will be disassembled and land filled as PCB contaminated waste. Therefore, it will not be sampled. Individual building components such as stairs and the control room will be treated as separate sample areas. The sampling plan for each area within the building is as follows:

Figure 3.2

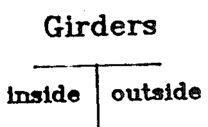
Sampling Plan
Metal Cleaning Building
Boliden Metech – Allens Ave. Facility
Providence, Rhode Island



Sample Separately
Control Room – 12 points
Stairs – 8 points
Shredder – 24 points
(12 Inside and 12 Outside)

4 Major Quadrants
4 Composite Sample Quadrants
Walls – 16 Points/Quadrant
Floor – 8 Points/Quadrant
Ceiling – 8 Points/Quadrant
Girders – 16 Points/Quadrant

Girders



1. Inside
   Top
   Bottom
2. Outside
   Top
   Bottom

3.4 METAL CLEANING BUILDING (Cont.)

Floor Area: Floor areas of each quadrant will contain 6 individual sample sites. The concrete floor of the building will be sampled by wipe sampling and by coring to a depth of 3 inches. If evidence of PCB permeation of the concrete exists, cores of the floor will be collected at wipe sample locations to a depth of 3 inches. Coring equipment will be steam cleaned and rinsed between samples to prevent cross-contamination. Condensate and rinsate will be collected and held for analysis, if required. Duplicate cores will be collected, composited and analyzed. Cores will be homogenized and composited according to the method described for cover material. One 100 gram composited concrete floor core sample will be sent to the laboratory for analysis, whereas the other will be retained as a reserve.

Control Room: The control room will be divided into five sections (four walls and floor). One composite wipe sample of four points each will be collected from each section. On walls, two sample points will be on upper half of the wall and two sample points will be on the lower half. The floor will be divided in half, with one sample point on each half. Reserve wipe samples will be collected and held for further analysis, if required. A sample blank composed of unused hexane soaked sterile gauze pads will be prepared and analyzed.

3.4 METAL CLEANING BUILDING (Cont.)

Girders: Each quadrant contains approximately 5 girders. Girders within each quadrant will be subdivided into inside and outside facing sections. The inside and outside sections of the girders will be further subdivided into top and bottom portions. (See Figure 3.2) The tops and bottoms of the girders within each quadrant will each have a total of 6 equally spaced individual sample points for inside and outside sections. Within each quadrant, wipe samples of the sample points along the inside top and bottom and the outside top and bottom of the girders will be taken, using clean hexane soaked uniform size sterile gauze pads (3" x 3") and composited on site. Duplicate wipe samples will be collected, composited and analyzed. Reserve samples will be collected and retained for further analysis. A sample blank composed of unused hexane-soaked sterile gauze pads will be prepared and analyzed.

Stairs: The metal cleaning building contains 2 staircases. One staircase has 15 treads, whereas the other has 18 treads. Three sample points will be located along each staircase. These samples will be on the stair treads with one sample on the bottom stair, one on the top stair, and one in the middle. Wipe samples of the stairway sample points will be taken using clean hexane soaked uniform size sterile gauze pads (3" x 3") and composited on site. Duplicate wipe samples will be collected, composited, and analyzed. Reserve samples will be collected and and retained for further analysis. A sample blank composed of unused hexane-soaked sterile wipes will be prepared and analyzed.

3.5 SHREDDER UNIT

The shredder unit will be divided into seven interior and seven exterior composite samples. The individual composits will each contain four individual sample points. Wipe samples of the shredder unit sample points will be taken using clean hexane soaked uniform size sterile gauze pads (3" x 3") and composited on site. Duplicate wipe samples will be collected, composited, and analyzed. Reserve samples will be collected and retained for further analysis. A sample blank composed of unused hexane-soaked wipes will be prepared and analyzed.

3.6 DLA TANK

Sample Collection and Compositing: The DLA tank will be divided into two sample quadrants: One for the tank's entire inside, one for the entire outside. A total of 10 composites will be analyzed; four on the outside and six on the inside. Sample points on the outside of the tank will be located in the following manner:

Lower Half of Tank

- Two sample points north
- Two sample points south

Top Half of Tank

- Two sample points east
- Two sample points west

Sample points on the inside of the tank will be located in the following manner:

Upper Half of Tank

- Two sample points north
- Two sample point south

3.6 DLA TANK (Cont.)

Lower Half of Tank

- Two sample points east
- Two sample points west

Tank Bottom

- Two sample points in northern half
- Two sample points in southern half

Wipe samples will be taken of each individual sample point and composited in the field for analysis. Wipe samples will be performed using clean hexane-soaked sterile gauze pads of uniform size (3" x 3"). Duplicate wipe samples will be collected, composited, and analyzed. Reserve samples will be collected and retained further analysis. A sample blank composed of unused hexane-soaked sterile gauze pads will be prepared and analyzed.

3.7 INSTALLATION OF GROUNDWATER MONITORING WELLS

Upon adequate remediation of the site to the prescribed Action Level, 8 groundwater monitoring wells will be installed at the Boliden site in order to assess the post remediation PCB concentrations within the site's groundwater. Six wells will be installed along the site's borders, with the upgradient and downgradient borders of the site having two wells each. Two additional wells will be installed within the central portions of the site; one in the west central portion and one in the east central portion. Drill augers will be steam cleaned between wells to prevent cross-contamination. Well locations are illustrated in Figure 3.1. Wells will be constructed of 2" PVC and

will be installed such that the 10′ screen section is 5′ above and 5′ below the average water table. The screen will be sandpacked with medium sand and grouted with bentonite each well will have a steel locking cap. See Figure 3.3 for well construction details.

3.8 SAMPLING OF GROUNDWATER FROM MONITORING WELLS:

Wells will be developed and allowed to rest for 48 hours. After the resting period, three volumes of water will be removed from the wells and a groundwater sample collected. Sample collection will be via Teflon coated bailers. Individual bailers will be used for each well. Groundwater samples will be placed in quart-sized glass jars with Teflon lined caps and transported to the laboratory for analysis. Samples will be split to include filtered and non-filtered samples. Samples will be analyzed for PCBs according to EPA 8080 protocols. An action level for remediation of any groundwater PCB contamination will be mutually agreed upon by Boliden and EPA based on results of groundwater sample analysis.

3.9 ANALYSIS INTERPRETATION, INDICATION OF ADEQUATE REMEDIATION

A decision tree has been developed for interpretation of composite sample analysis from each area to be remediated. PCB concentrations which indicate a clean or not clean area have been established according to the number of individual sample points in each composite sample, using the formula presented in Section IV.A.2b 4. of EPA Document number EPA 560/5-85-026. This formula is used to calculate a PCB concentration which is indicative of compliance with the established cleanup level, taking into account the probability of false positive analysis results. An action level of 10 ppm was used in these calculations. The formula is as follows:

$$\frac{(0.8)\ (10) + (2.576)\ (0.3)\ (0.8)\ (10)}{\text{Number of samples composited}}$$

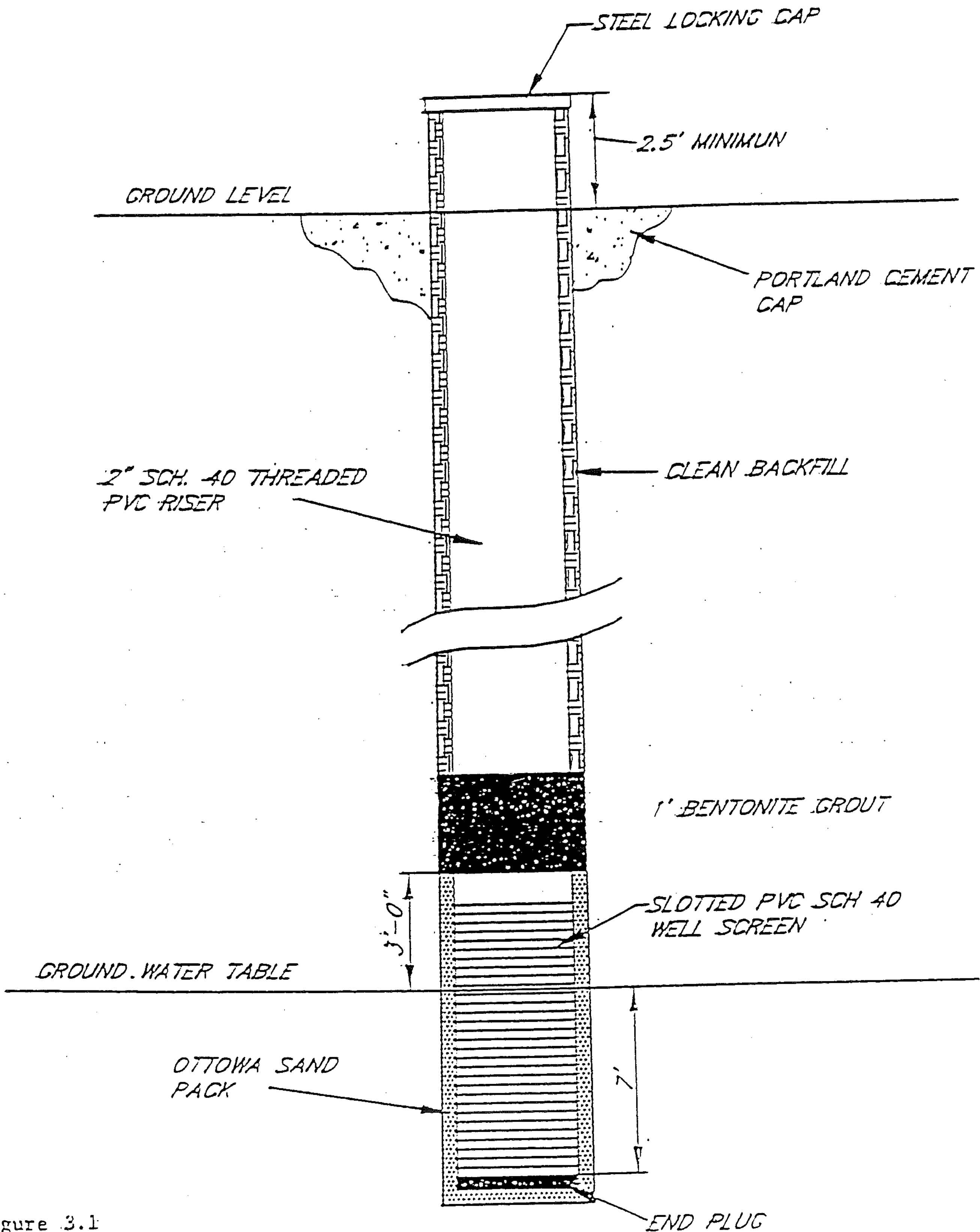


Figure 3.1

3.9 ANALYSIS INTERPRETATION, ETC. (Cont.)

Where:

0.8 is the accuracy of the analytical method

0.3 is the standard deviation of the analytical method

10 ppm (solid samples) on 10 ug/100 cm^2 (wipe samples) is the allowable limit for a single sample

2.576 is a coefficient from the standard normal distribution

Table 3.1 presents the number of composite samples, Allowable Concentration Limits (ACL) and further analysis of recomposited or individual samples and associated ACL.

1. Site ground cover: Based upon a composite sample number of 6 and an action limit of 10 ppm, a PCB concentration of < 2.36 ppm indicates that sample area is adequately remediated. PCB concentrations greater than or equal to 2.36 ppm indicate that the site is not adequately remediated. If an area is indicated to not be adequately remediated, the individual homogenized samples from each of the 6 cells will be recomposited into three composite samples of 2 cells each. A PCB concentration of 7.09 ppm indicates an adequate remediation. Recomposited samples with PCB concentrations equal to or greater than 7.09 ppm will be individually sampled. Individual samples with PCB concentrations less than 10 ppm indicate adequate remediation, whereas those with concentrations greater than or equal to 10 ppm do not comply with the action level and will require further remediation. The decision tree for the ground cover analysis is illustrated in Figure 3.4.

TABLE 3.1

COMPOSITE AND INDIVIDUAL SAMPLE ALLOWABLE CONCENTRATION LIMITS

AREA	FIRST COMPOSITE NO. INDIVIDUAL SAMPLES PER COMPOSITE	ACL**	RECOMPOSITE NO. OF COMPOSITES		NO. OF CELLS/POINTS	ACL**	INDIVIDUAL SAMPLES ACL**
GROUND COVER	6*	< 2.36+	3	OF	2	< 7.09+	< 10#
CONCRETE PAD	6*	< 2.63#		NO		--	< 10#
METAL CLEANING BUILDING							
FLOOR	6*	< 2.36#		NO		--	< 10#
GIRDERS							
(INSIDE)	6*	< ---	3	OF	2	< 7.09#	< 10#
(OUTSIDE)	6*	< ---	3	OF	2	< 7.09#	< 10#
CONTROL ROOM (per sections)	4*	< 3.54#		NO		--	< 10#
STAIRS	3*	< 4.73#		NO		--	< 10#
SHREDDER UNIT							
(7 AREAS INSIDE)	4*	< 3.54#		NO		--	< 10#
(7 AREAS OUTSIDE)	4*	< 3.54#		NO		--	< 10#
DLA TANK (INSIDE)	6*	< 2.36#		NO		--	< 10#
(OUTSIDE)	4*	< 3.55#		NO		--	< 10#

* SAMPLES PER QUADRANT

** ALLOWABLE CONCENTRATION LIMIT TO ENSURE A CONCENTRATION < 10 PPM OR 10 UG/100 CM^2 FOR ALL INDIVIDUAL SAMPLES.

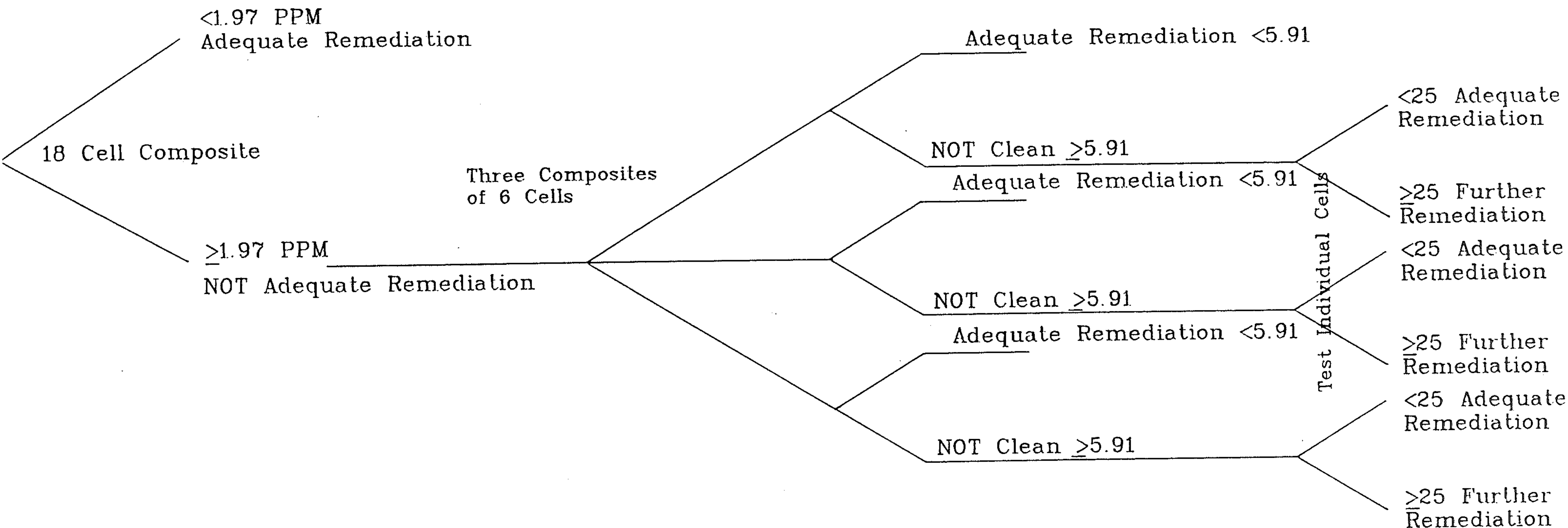
\+ CONCENTRATION IN PARTS PER MILLION (PPM)

\# CONCENTRATION IN UG/100 CM^2

Figure 3.4

Decision Tree

Adequate Remediation of Groundcover
Boliden Metech – Allens Ave.
Providence, Rhode Island



Adequate Remediation AL 18 CEll Composite
(0.8)(25)+(2.576)(0.3)(0.8)(25) = 35.46 PPM/18 = 1.97 PPM
Adequate Remediation AL 6 Cell Composite
(0.8)(25)+(2.576)(0.3)(0.8)(25) = 35.46 PPM/6 = 5.91 PPM

3.9 **ANALYSIS INTERPRETATION, ETC. (Cont.)**

2. Concrete Pad: A PCB concentration of < 2.63 ug/100 cm² will indicate that the concrete pad is in compliance with the 10 ug/100 cm² action limit, and is adequately remediated. If the composite sample analysis results show a PCB concentration greater or equal to 2.63 ug/100 cm², individual samples will be analyzed. PCB concentrations < 10 ug/100 cm² will be considered adequately remediated. Sample points showing PCB concentrations greater than or equal to 10 ug/100 cm² PCB will undergo further remediation.

3. Metal Cleaning Building: The skin and insulation of the metal cleaning building will be removed from the site as PCB-contaminated waste. Composite wipe samples will be collected from the ceiling (four samples) and walls (eight samples) in order to assess the level of contamination prior to disposal.

4. Floor Area: A PCB concentration of < 2.36 ug/100 cm² will indicate that the concrete floor is in compliance with the 10 ug/100 cm² action limit and is adequately remediated. If the composite sample analysis results show a concentration greater than or equal to 2.36 ug/100 cm², individual samples will be analyzed. Areas with concentrations < 10 ug/100 cm² will be considered adequately remediated. Sample points showing greater PCB concentrations than 10 ug/100 cm² will undergo further remediation.

5. Girders: A PCB concentration of < 2.36 ug/100 cm² will indicate that the girders are in compliance with the 10 ug/100 cm² action limit and are adequately remediated. If the composite sample analysis results show a concentration greater or equal to 2.36 ug/100 cm², individual samples will be recomposited to three composite samples

3.9 ANALYSIS INTERPRETATION, ETC. (Cont.)

of 2 wipes each. A PCB concentration of <7.09 ug/100 cm^2 will indicate adequate remediation, whereas a concentration of > 7.09 ug/100cm^2 will indicate that individual samples must be analyzed. Areas with PCB concentrations < 10 ug/100 cm^2 will be considered adequately remediated. Sample points showing PCB concentrations greater than or equal to 10 ug/100 cm^2 will undergo further remediation.

6. Control Room: A PCB concentration of < 3.54 10 ug/100 cm^2 will indicate that the control room is in compliance with the 10 ug/100 cm^2 action limit and is adequately remediated. If the composite sample analysis results show a concentration greater than or equal to 3.54 10 ug/100 cm^2, individual samples will be collected. Individual samples from areas with PCB concentrations < 10 ug/100 cm^2 will be considered adequately remediated. Areas with sample points showing PCB concentrations greater than or equal to 10 ug/100 cm^2 PCB will undergo further remediation.

7. Stairs: A PCB concentration < 4.73 ug/100 cm^2 will indicate that the stairs are in compliance with the 10 ug//100 cm^2 action limit and are adequately remediated. If the composite sample analysis results show a concentration greater than or equal to 4.73 ug/100 cm^2, individual samples will be analyzed. Individual samples in areas with concentrations < 10 ug/100 cm^2 will be considered adequately remediated. Areas with sample points showing PCB concentrations greater than or equal to 10 ug/100 cm^2 will undergo further remediation.

3.9 ANALYSIS INTERPRETATION, ETC. (Cont.)

8. Control Room: A PCB concentration of <3.54 ug/100 cm^2 will indicate that the control room is in compliance with 10 ug/100 cm^2 action limit and is adequately remediated. If the composite sample analysis results show a concentration greater than or equal to 3.54 ug/100 cm^2, individual samples will be collected. Individual samples from areas with PCB concentrations < 10 ug/100 cm^2 will be considered adequately remediated. Areas with sample points showing PCB concentrations greater than or equal to 10 ug/100 cm^2 PCB will undergo further remediation.

9. Stairs: A PCB concentration <4.73 ug/100 cm^2 will indicate that the stairs are in compliance with the 10 ug/100 cm^2 action limit and are adequately remediated. If the composite sample analysis results show a concentration greater than or equal to 4.73 ug/100 cm^2, individual samples will be analyzed. Individual samples in areas with concentrations 10 ug/100 cm^2 will be considered adequately remediated. Areas with sample points showing PCB concentrations greater than or equal to 10 ug/100 cm^2 further remediation.

3.9 ANALYSIS INTERPRETATION, ETC. (Cont.)

8. Shredder: A PCB concentration of < 3.54 ug/100 cm^2 will indicate that the shredder unit is in compliance with the 10 ug/100 cm^2 action limit and is adequately remediated. If the composite sample analysis results show a concentration greater or equal to 3.54 10 ug/100 cm^2, individual samples will be analyzed. Areas with individual samples having PCB concentrations < 10 ug/100 cm^2 will be considered adequately remediated. Sample points showing PCB concentrations greater than or equal to 10 ug/100 cm^2 will undergo further remediation.

9. DLA Tank: A PCB concentration of 2.36 ug/100 cm^2 will indicate that the outside of the tank is in compliance with the 10 ug/100 cm^2 action limit and is adequately remediated. A PCB concentration of < 2.36 ug/100 cm^2 will indicate that the inside of the tank is in compliance with the 10 ug/100 cm^2 action limit and are adequately remediated. If the composite sample analysis results show a PCB concentration greater than or equal to 2.36 ug/100 cm^2 (inside) or 3.55 ug/100 cm^2 (outside), individual samples will be analyzed. Areas with PCB concentrations < 10 ug/100 cm^2 will be considered adequately remediated. Sample points showing PCB concentrations greater than or equal to 10 ug/100 cm^2 will undergo further remediation.

4.0 SAMPLE CUSTODY

Successful analysis depends on the capability to produce valid data and to demonstrate data validity. Proper sample collection, preservation, storage, handling, labeling, and chain-of-custody procedures are necessary.

4.1 SAMPLE CONTAINERS AND PRESERVATION

All sample kits (pre-cleaned sample containers, preservatives, chain-of custody records and tapes, and shipping containers) will be supplied by the Laboratory.

Upon receipt of these sampling kits and prior to final sample preparation, the Final Prep coordinator will inspect each sample kit for completeness and integrity of materials. The laboratory will be notified immediately if the kit does not pass inspection (e.g., breakage, visible uncleanliness, or inadequate number of bottles). Corrective action will be taken so that all quality goals are met.

4.2 FIELD LOG BOOK

Each sampling team will maintain a detailed log book for recording information that is not recorded on sample log sheets or other documentation. All entries in this log will be accompanied by the signature of the author and the date of entry, the project name and number, and the location. At the beginning of each sampling day, the designated team member will start the daily log by entering the date and time, the pile or locations to be samples, field team present, and any potential problems.

4.2 FIELD LOG BOOK (Cont.)

During the day, the following information, at a minimum, should be recorded:

- o Changes in weather conditions;
- o Any unusual circumstances;
- o Subcontractor progress and/or problems, results of subcontractor inspections;
- o Communications with other project members, press representatives, or observers;
- o Any sampling procedures that do not conform to the QA plan;
- o Identification of quality assurance samples (blanks, duplicates, and spikes);
- o Equipment problems, repairs, or maintenance;
- o A list of any photographs taken.

4.3 SAMPLE IDENTIFICATION

Each sample will be labeled at the time of sampling. A copy of the sample container label is presented as Figure 4.1. The following information will be recorded on the label in permanent ink:

- o Project name and number,
- o Sample identification number,
- o Sample type,
- o Date and time sample collected,
- o Signature of person who collected the sample.

Each sample will be labeled in the field at the time of sampling. Containers into which the individual sample material are placed will be sealed with Chain-of-Custody seals or tape and have Boliden Metech labels (Figure 4.2) affixed. Sample identifications will be based on sampled portions of the site and facilities and sample site locations.

Figure 4.1

ANALYTICAL TESTING SERVICES LABEL

ANALYTICAL TESTING SERVICES (401) 232-1420

CLIENT/SOURCE	☐ GRAB ☐ COMPOSITE
CLIENT SAMPLE IDENTIFICATION	DATE:
ATS SAMPLE LOG NUMBER	TIME:
ANALYSIS REQUESTED	PRESERVATIVE:
	COLLECTOR(S):

FIGURE 4.2 BOLIDEN METECH LABEL

Boliden Metech, Inc.

Sample Description

____

____

Plant ____________________ Location ____________________

Date ____/____/____ Sampled By ____________________

Time ____________________ Sample ID No. ____________________

Remarks ______________________________________

____

____

____

4.3 SAMPLE IDENTIFICATION (Cont.)

Sample numbers assigned to bulk individual ground cover samples will consist of a three component Alpha Numeric Sample Location Number, a two digit Dash Number and an additional alpha character to distinguish recomposite samples; e.g., NN'A1-01-I.

a. The three Cell Component Sample Location Number references the cell from which the sample was taken (N'N'A1).

b. The two-digit Number (-01 or -02) will distinguish field duplicate samples.

c. The Roman Numeral character (I, II, III, or IV) will distinguish recomposited samples. These will be assigned to recomposited sample aliquots by the Final Prep Coordinator.

Wipe samples will be designated by an alpha-numeric number designating the structure, quadrant (if applicable), and portion of structure sampled, and sample point. Table 4.2 presents wipe sample alpha-numeric designations for structures and facilities to be sampled. The two-digit dash number and additional alpha character will correspond to the same designations as the ground cover samples.

4.4 CHAIN-OF-CUSTODY PROCEDURES

Chain-of-custody procedures are intended to maintain and permanently document sample possession from the time of collection to disposal, in accordance with federal guidelines. A sample is considered to be under a person's custody if:

- It is in that person's possession,
- It is in that person's view, after being in that person's possession,
- It was in that person's possession and was locked up by them to prevent tampering, or
- It has been placed in a designated or secure area by that person.

TABLE 4.2

ALPHA-NUMERIC SAMPLE IDENTIFICATIONS FOR STRUCTURES AND FACILITIES AT THE BOLIDEN METECH ALLENS AVENUE FACILITY

PROVIDENCE, RI

Metal Cleaning Bldg Designation = M		Quadrants N,S,E,W or Composite No.	Sample # Point
Floor	MF	N,S,E,W	1-6
Girders	MGIT - Inside Top	N,S,E,W	1-6
	MGIB - Inside Bottom	N,S,E,W	1-6
	MGOT - Outside Top	N,S,E,W	1-6
	MGOB - Outside Bottom	N,S,E,W	1-6
Control Room	MR	I-IV	1-4
Stairs	MS	I-II	1-3
Shredder Unit	SI - Inside	I-VII	1-4
	SO - Outside	I-VII	1-4
DLA Tank	DI - Inside	I-VI	1-4
	DO - Outside	I-IV	1-4
Concrete Pad	CP	N,S,E,W	1-2

4.4 CHAIN-OF-CUSTODY PROCEDURES (Cont.)

The chain-of-custody record will be initiated in the field for all samples collected. Figure 4.3 shows a copy of the chain-of-custody record. At a minimum, the following information shall be recorded on the form:

- o Signature of custodian,
- o Date of signature,
- o Sample site identification,
- o Sampling date and time,
- o Sample identification,
- o Sample description,
- o Process/Analysis to be performed
- o Chain-of-custody tape number, and
- o Method of shipment and courier name(s) in the remarks box, if applicable.

The Field Sampling Coordinator will sign the chain-of-custody record; enter the date, time and chain-of-custody seal numbers; tear off and file the back copy with the appropriate sampling log. The sample documentation will be placed in a sealed plastic bag and accompany the containers to the Boliden Metech facility in Mapleville, RI.

The Final Preparation Coordinator will sign and date the chain-of-custody form when he assumes custody of the drums and again when he has relinquished custody after processing. The shipper's waybill or airbill will be retained by the last custodian prior to shipment.

Figure 4.5

ANALYTICAL TESTING SERVICES INC. - CHAIN OF CUSTODY

27 THURBER BOULEVARD - SMITHFIELD, RI 02917-1859 (401)232-1420

CUSTOMER INFORMATION

CUSTOMER ________________

ADDRESS ________________

TELEPHONE ________________

PROJECT ________________

PROJECT MANGER ________________

PROJECT LOCATION ________________

P.O. NUMBER ________________

REPORT INFORMATION

SEND REPORT TO ________________

DATE REPORT REQUIRED ________________

RUSH BY FAX TO: ________________

PROJECT INFORMATION

TURNAROUND (CALENDAR DAYS, CONFIRM WITH LAB)

2 5 7 14 21 OTHER ____

DELIVERABLES: RESULTS ONLY 21E CLP

TIER I TIER II-ECRA TASA OTHER ________

IF QUESTIONS ARISE ABOUT SAMPLES/ANALYSES CALL:

NAME ________________

TELEPHONE ________________

SAMPLE INFORMATION AND ANALYTICAL REQUESTS

LAB ID CODE	SAMPLE IDENTIFICATION	COLLECTED DATE	COLLECTED TIME	SAMPLE TYP	SAMPLE MAT	Preserv NONE	HNO_3	H_2SO_4	HCl	NaOH	OTHER	ANALYSES	COMMENTS

TYP: GRAB, COMPOSITE OR OTHER; MAT: SOLID, LIQUID, COMBINED, OTHER; PLEASE ENTER NUMBER OF CONTAINERS UNDER TYPE OF PRESERVATIVE

CUSTODY

SAMPLER ________________ DATE ________

RECEIVED ________________ TIME ________

RELINQUISHED ________________ DATE ________

RECEIVED ________________ TIME ________

RELINQUISHED ________________ DATE ________

RECEIVED ________________ TIME ________

COMMENTS, REQUESTS OR REMARKS

4.4 CHAIN-OF-CUSTODY PROCEDURES (Cont.)

The laboratory sample custodian will receive and sign the form for the laboratory, and record the date, time, and chain-of-custody tape numbers. The laboratory log-in record will explicitly state the condition of the chain-of-custody seal, any evidence of damage, whether the seal is air-tight, and the completeness of accompanying records. After inspection, each sample will be logged in and assigned a unique laboratory sample identification number. In addition, the following information will be entered in the logging system for each sample:

- Field sample identification number,
- Laboratory sample identification number,
- Date received,
- Project name and number,
- Collection date,
- Sample type,
- Condition of sample,
- Temperature of sample cooler (if samples were stored on ice),
- Analysis to be performed, and
- Assigned storage location.

The laboratory sample custodian will notify the laboratory project director if samples are received that are damaged, warm, frozen, or incompletely documented. The laboratory project director will contact the lab program coordinator who will decide on the disposition of these samples.

After sample log-in is complete, a copy of the chain-of-custody record, with laboratory sample numbers and notations of any discrepancies, will be sent to the program coordinator. The original chain-of-custody form will be filed in the laboratory with the shipper's waybill or airbill attached.

4.5 SAMPLE HANDLING AND SHIPMENT

Final samples will be packed in coolers with blue ice or an equivalent cooling agent and in appropriate packing materials to prevent breakage in accordance with SOP 7510 - Packaging and Shipping of Samples (Appendix B). Samples to be hand-delivered will be packed with blue ice and promptly delivered to the laboratory. Samples will be cooled to 4°C from the time of collection until commencement of the analytical procedure. Sample handling in the laboratory will follow EPA procedural protocols described in Appendix B. Records of sample shipments will be retained by the sample custodian including copies of chain-of-custody records, and shipper's airbills or waybills.

4.6 SAMPLE DISPOSAL

All milled samples and contaminated sampling equipment will be returned to Boliden for disposal in an appropriate manner. Sampling equipment and decontamination waste greater than 10 ppm or 10 ug/100 cm^2 will be disposed of as PCB waste by a licensed hazardous waste contractor. Samples containing concentrations of PCBs greater than the 10 ppm action level will be disposed of using an approved hazardous waste management contractor. Sand and water resulting from monitoring well installation and development which is contaminated with PCB's above the 10 ppm action level will be disposed of as PCB waste, using an approved hazardous waste contractor.

Sample extracts will be held by Analytical Testing Services (ATS) for 180 days prior to disposal. After 180 days, ATS will dispose of the extracts using an approved hazardous waste management contractor.

4.7 DOCUMENT CONTROL

Control of and accounting for documents generated during the course of the project is achieved by assigning the responsibility for

document issuance and archiving to key project personnel. Table 4.4 lists the key documentation for the field program and the corresponding parties for issuing, executing, and archiving. The field notebooks, field sample logs, and a copy of the chain-of-custody records will remain in the possession of the Bulk Sampling Coordinator or designee until conclusion of the field sampling event. A copy of the chain-of-custody records after sample log-in will be mailed to the

Project Manager. Upon completion of the sampling program, all records will be given to the Project Manager to be placed in the project file.

4.7 DOCUMENT CONTROL (Cont.)

Correction on any document shall be accomplished by crossing out the error with a single line and initialing and dating the correction. This includes, but is not limited to, field sampling logs, field notebooks, laboratory notebooks, sample labels, and chain-of-custody forms.

In addition, all documentation for the project will either be recorded in indelible ink in reproduction quality or will be photocopied promptly upon completion and the photocopies dated. All records will be signed by the person completing them. Any problems encountered and corrective actions used to mitigate the problems will be documented as part of the field and analytical activities, where applicable.

TABLE 4.4
DOCUMENT RESPONSIBILITY

	ISSUANCE	EXECUTION	ARCHIVING
Field Notebooks	QA Officer	Field Sampling Team Final Sample Preparation Coordinator	QA Officer
Sample Log Sheets	Field Coordinator	Field Sampling Team Final Sample Preparation Coordinator	Project Manager
Chain-of-Custody Records	Laboratory Project Director	Field Sampling Team Final Sample Preparation Coordinator	Project Manager and Laboratory Project Director
Chain-of-Custody Seals	Laboratory Project Director	Field Sampling Team Final Sample Preparation Coordinator	-----
Shipper's Waybills	Sampling Team Leader	-----	Project Manager

5.0 CALIBRATION PROCEDURES AND FREQUENCY

Demonstration and documentation of acceptable instrument calibration is a mandatory requirement for performing qualitative and quantitative analysis of PCBs in soil or unhomogenized solids. The laboratory will meet the established method criteria and for instrument calibration and calibration verification at the method specified frequency before proceeding with sample analysis (Appendix B, Analysis of PCBs and Pesticides by electron capture detector gas chromatograph [GC/ECD] method 8080). Traceable reference material will be used for standards preparation.

5.1 STANDARD RECEIPT AND TRACEABILITY

Aroclor standards will be traceable to USEPA sources. In cases where USEPA traceable standards cannot be obtained, standards will be obtained from the National Institute of Standards and Technology (NIST).

All PCB and internal standard reference materials delivered to the laboratory are received in a designated receiving area. Upon receipt of this material, the person verifying the contents of the shipment will date and initial each container as it is checked in. This person also arranges for the appropriate distribution of the materials. Dates and initials will be marked as specified above with a label indicating date received, opened, and expiration. This label will not cover any area of or obstruct the original container label.

The person who opens a new standards container will also mark the opening date upon the special label. Documentation of the following items are mandatory: lot number of the materials used, manufacturer or supplier, purity, date prepared, balance used (as applicable) and the initials of the person preparing the reagent. This documentation is available should any problems or suspicions concerning the prepared reagent develop. The PCB standards to be employed can be found in Appendix A.

5.2 CALIBRATION

Initial calibration will be performed before any samples are analyzed and may be required intermittently throughout sample analyses as dictated by the results of continuing calibration checks. After a successful initial calibration, a continuing calibration check will be performed and the beginning and end of each twelve hour period during which analyses are performed. Calibration levels will include the Instrument Detection Limit (IDL), the level used to identify clean (below action level) composite samples, the level to identify dirty

p

(above action level) samples, and two intermediate values. All work will be performed in accordance with Method 8000 as published in Test Methods for the Physical and Chemical Evaluation of Solid Waste, SW - 846 third edition as amended.

5.3 ANALYSIS RUN LOGS

All information pertaining to the analysis of calibration standards, continuing calibration standards (check), and samples must be recorded in a log book with sequentially numbered pages. The log book data must include (at a minimum) the date of analysis, instrument identification, analyst signature, lot numbers of all standards analyzed, the name and/or log number of the standard or sample analyzed, date file name, auto sampler position, dilution value, and injection time.

6.0 ANALYTICAL PROCEDURES

The analytical procedure to be employed for this investigation is The Sampling and Analysis of Non-homogeneous Solids for Polychlorinated Biphenyls, as modified to reflect procedures promulgated in methods 8080 of SW-846. The analytical method is being applied to ground cover and wipe samples to determine that they comply with the
10 ppm clean up criteria.

The analytical method for this phase is electron capture detection gas chromatography (GC/ECD). The method is applicable to PCBs that occur as single congeners or as Aroclor mixtures. A packed column will be used in the analysis. No problems with Arochlor identification or PCB degradation are anticipated through the use of this method. Option 2 of Method 8080B will be used to quantify PCB/arochlor concentrations. [This option uses 3 to 5 major peaks for quantification.] The laboratory participating in this project has sufficient facilities and hardware resources to perform the analysis of soil for PCBs. Results will be reported as Arochlors and total PCBs. The facility and instrumentation resources is listed in Appendix B.

7.0 DATA REDUCTION, VALIDATION & REPORTING

7.1 INTRODUCTION

Data reduction, validation and reporting procedures will be employed to convert raw analytical data into qualitative and quantitative analytical data concerning the concentration of PCBs in the remaining soil and on the remaining structural surfaces at the Boliden Metech Allens Avenue site in Providence, RI. The processes include calculation of raw data into final concentration units, reviewing results for accuracy, and assembling the report contents for delivery in its final form.

7.2 GAS CHROMATOGRAPHY-ELECTRON CAPTURE DATA REDUCTION

Analyst Responsibilities. The analyst will be responsible for verifying instrument performance prior to initiating the analysis. This includes verifying that calibration linearity criteria has been achieved and that the instrument is free from contamination.

The analyst will verify that all criteria is maintained throughout the analysis, including verification that instrumental response has not

changed and that all deadlines for calibration checks contamination checks (blanks) have been met.

The analyst will be responsible for verifying that all quality control data associated with the instrument operation and with the sample analysis batch are within control limits and for taking first level corrective action where indicated.

The analyst will review all acquired data to verify that all qualitative identifications were performed correctly. The analyst will also review quantitative data to insure that the concentration of the individual PCB analysis, detected in the sample, have not exceeded the limits of the calibration range, and for reporting this if it occurs. The alternatives are to accept the sample is dirty or to perform dilution analysis.

The analyst will complete the transfer of the initial qualitative data from the quantitation report to the final reporting table. The analyst will also review the final data report to insure that reported values were corrected for initial weight and volume and that all supporting information is included with the results table.

Documentation. The analyst will verify that all information regarding sample preparation has been recorded in the appropriate laboratory notebook or on the appropriate chronicle. He will be responsible for recording all information relating to his activities during the analysis of any QC or field samples, including the analysis of calibration standards.

He will be responsible for producing hard copies of all chromatograms, quantitation reports, and QC instrument reports that pertain to the analysis of any sample batch.

The source of all reagents and equipment used in the analysis will be documented.

The analyst will verify that data produced during the analysis and recorded on magnetic media is appropriately identified. He will record the identity of the correct data files in a notebook or on a chronicle

which will enable him to reconstruct the analysis, if required. He will also verify that all data associated with the analysis in magnetic file format is transferred to magnetic tape for long-term storage.

[**Results Calculation Equations.** Quantitation will be based on the five major peak areas for the Aroclor that is identified.]

Data entry. The analyst performing the final data review will also perform all data entry tasks. Data entry will be accomplished using manual entry. The completed reporting table will be reviewed by the analyst for accuracy.

The analyst will verify that all qualitative and quantitative data procedures have been performed within the criteria of the method. The analyst will assemble the finalized results table and the appropriate supporting data for secondary review and inclusion in the final report.

7.3 VALIDATION DATA

Validation processes will consist of two separate activities designed to ensure that the analytical results meet the quality criteria of the method and that the analysis performed is consistent with the objectives of the investigation. The first step in the process will be an integrity check of all raw data. The second process will be a validity check or performance verification that the QC results have met the established criteria.

Data Integrity. Data integrity checks will be performed during several difference steps of the analytical process. However, the majority of the steps will be performed by the analyst during the data review. Key integrity checks will be performed as follows:

> **Raw Data Entry:** Raw data documentation will be required for samples received, sample preparation activities, instrumental response data, reagent control and standards control. Review of the raw data entry will be performed at the bench level by a

second analyst and/or at report generation. Managerial data reviews and Quality Assurance data reviews will include the verification of raw data entry.

Extraction Logs: Extraction logs will be checked as a part of the raw data entry.

Instrument Logs: Instrument logs will be checked as a part of the raw data entry.

Calibration Integrity: Calibration integrity will be routinely reviewed by the analyst. This review will be performed for each calibration curve and continuing calibration check to verify that method acceptance criteria for relative retention time and sensitivity have been achieved before proceeding with the analysis.

Legal Chain of Custody: Legal chain of custody will be maintained for all laboratory documents. Secondary review will be performed routinely for custody documentation.

Data Validity

Laboratory QC Checks: Quality control checks for data validity will be performed at the bench level and are the responsibility of the analyst. Before proceeding with the analysis or data reporting, the analyst will review data against pre-existing criteria before proceeding with the next step in the analytical process. If criteria are not achieved, the analyst will be responsible for instituting the required corrective action. The criteria used for accepting or rejecting data based on laboratory QC data are described in the analytical method in Appendix B.

The QC checks performed by the analyst include the following:

Blanks: The analyst will be responsible for verifying that the blank criteria is achieved before proceeding with the analysis.

Calibration: The analyst will verify that the method calibration criteria has been achieved before proceeding with sample analysis. He will perform corrective action on the analytical system if the calibration criteria is not achieved.

Spikes: For each type of spike, the analyst will be responsible for comparing the results of the spiked samples to established method criteria. Dependent upon the type of spike and the results, the analyst will either proceed with the analysis, perform corrective action to the analytical system or repeat the analysis.

Duplicates: If precision criteria for duplicate analysis is not achieved, the analyst will perform the required corrective action before proceeding with the analysis or reporting the data.

Surrogate Recovery: Surrogate (decachlorobiphenyl) recovery will be compared to the established recovery criteria for the method. Recovery of 80 - 120 percent of the surrogate is considered acceptable. If criteria is not achieved, the analyst will be responsible for performing method specific action. He will not proceed with sample analysis if the recovery indicates problems with the analytical system.

Calibration Checks: Instrument calibration will be verified by the analyst according to the method criteria. If criteria is not achieved, the analyst will repeat the calibration check procedure or recalibrate the system as required before proceeding with analysis of field samples. If system corrective action is indicated, the analyst will be responsible for performing the required corrective action.

Chromatography Checks: Checks of the chromatographic system will be performed by the analyst before performing field sample analysis. If the chromatographic criteria is not achieved, the analyst will be responsible for performing all required corrective action to the chromatographic system.

7.4 DATA REPORTING

The analyst will be responsible for initiating the data reporting process. Manual data will be compiled by the analyst and transcribed to the report tables. The printed table will be compared to the hand transcribed original by a second person to insure correctness prior to assembly into the sample data report. PCB data will be reported for each analysis performed. A separate report will be generated for the filed duplicate samples which contains table 7.4.1. The RPD data for the field duplicate will be included in the QC summary. A discussion of the sampling and analysis of additional cells based on field duplicate data will be included in the report cover letter.

Data Report Contents: Specific information will be compiled into the final data report for each ground cover and wipe sample. This information will enable the data user to verify that all quality criteria have been achieved and that all operational criteria for the execution of the method have been performed. Table 7.4.1 lists the contents of the final data report to be assembled for each set of field samples.

Table 7.4.1
Data Report Contents

- A cover letter which describes the samples and summarized any analytical anomalies.
- A data results table which summarizes the concentrations of PCBs as Aroclors.
- Summary tables for all laboratory QC data, including the reagent blank, QC spike and matrix spike duplicate.
- Chromatographic separation and stability criteria summary.
- Surrogate recovery summary table.
- Calibration and continuing calibration summaries for all standards.
- Quantitation reports for the field samples and all QC samples.
- Chromatograms for all field samples and laboratory QC samples.

The analyst will also be responsible for data reporting when automated systems are employed. Extract concentration data will be generated manually. The analyst will enter dilution information, sample size data, and moisture data into the computer system. The additional information will be used to calculate the final results which will be automatically calculated. The printed table will be reviewed by the analyst to insure that manual data entry was correct and that the final reported value incorporated all necessary sample related information. The completed form will be included in the final report.

The completed report is forwarded to the analytical officer for final review and sign-off. The analytical officer then forwards the report to the QA manager for review of all QC and performance data before the report is sent through the project manager to all USEPA project managers.

7.5 DATA STORAGE

General Storage Requirements: All raw data produced during the analysis of samples will be retained by the laboratory to ensure that all steps in the analytical process can be traced and verified if necessary long after the analysis has been completed and the results reported to the client. Raw data and any additional report-related information will be stored for a minimum period of seven (7) years. This information will be stored in a secure area within the laboratory. Data archival and storage will be managed by a designated individual who controls the access to stored information.

Types of Information Stored: The information retained for long term storage will include all sample reports, any raw data stored on magnetic media, raw data which cannot be stored on magnetic media and processed QC data not reported to the client. This data will be logged for storage immediately after the final report is sent to the client.

General Storage Conditions: All retained information will be stored in a secured area within the facility. All hard-copy information will be stored on-site at the laboratory or off-site at a commercial document storage facility equipped with a professional security system.

8.0 FIELD AND LABORATORY QUALITY CONTROL CHECKS

8.1 Field Operations

A field sampling quality control program will be employed to insure that all field samples collected for analysis adequately represent each cell (either soil or wipe sample). This program consists of the analysis of field blanks, equipment rinsings, filed duplicates, and duplicate aliquots. Each of the field QC checks which will be employed are listed below.

Table 8.1

Field Quality Control Checks

Field Blanks: PCB free reagent water which is provided to the client by the laboratory and is transferred to an additional clean sample container while at the field sampling location. Field blanks are used to evaluate environmental and procedural effects of the sampling event and to determine if cross contamination occurred during the sampling event. They are analyzed for PCBs using the analytical procedures specified for this investigation only if PCB cross contamination is suspected to have occurred during the sampling event.

Wipe Sample Media Blanks: A sample of the sterile gauze pad saturated with hexane will be analyzed for PCBs in order to determine if wipe sampling media is contaminated.

Equipment Risings: Prior to collecting samples from an cell, the field sampling shovel and the auger are steam cleaned. After sampling each cell, the shovel and auger or concrete core device are again steam cleaned. The condensate from the steam cleaning is collected and analyzed for PCBs following the procedures outlined in the method to insure that cross contamination of equipment does not occur between samplings. This will only be performed where composites are determined to not be clean.

Field Duplicates: Duplicate samples will be collected from every ninth sample cell or point and analyzed only if the composite that contains that cell or point is not clean. Duplicate wipe samples will be collected adjacent to primary wipe samples.

Duplicate Aliquots: One randomly selected composite will be selected from a quadrant or portion of each sampled area of the site for parallel analysis.

8.2 Laboratory Quality Control Checks

The method which will be employed for these analyses contains control systems to insure that valid qualitative and quantitative data is produced during the analysis of field samples. As further assurance that these method systems are in control, ongoing internal QC checks are routinely performed during the analysis of all samples. The responsibility for internal analytical QC checks rests with the laboratory analyst. The type, frequency and acceptance criteria for QC checks performed are based on the analytical method. The QC checks which will be employed for this project are presented in Table 8.2. The data from these checks will be used by the analyst to fine tune the analytical process and take corrective action where required. They will also be employed by the QA staff to monitor the data for systematic analytical problems.

Table 8.2
Quality Control Check Samples

Method Blank: A blank used to check "reagent" or "process" introduced PCB contamination. Method blanks will be analyzed with each batch of samples (up to a maximum of twenty samples/batch).

QC Check Standard: A PCB free solid matrix (fired sand) which is spiked with a PCB congener standard and processed through the selected analytical method is used to verify method performance. Check standards will be analyzed with each batch of samples (up to a maximum of twenty samples/batch).

Spiked Duplicate Samples: Duplicate aliquots of the same field sample which are spiked with a mixture of PCB congeners and analyzed using the selected method. The spike recovery data is used to determine if the accuracy criteria has been achieved. The relative percent difference (RPD) between the two values is used to check analytical precision.

Single Blind Performance Evaluation Checks: A single blind performance evaluation (PE) sample will be introduced into the laboratory with every batch of twenty samples. This PE sample consists of homogenized sand that will be mixed with PCBs to attain a known concentration. The PE will be used to monitor the performance of the analytical system on a known concentration sample.

9.0 SYSTEMS AUDITS AND PERFORMANCE AUDITS

Field and laboratory audits will be performed on a regularly scheduled basis throughout the duration of this project. These audits will evaluate the implementation of the quality assurance program that has been established for this investigation and an evaluation of the actual quality control parameters being used by field and laboratory personnel. This information will be obtained through a combination of system audits and performance audits.

9.1 SYSTEMS AUDITS

Systems audit will be employed to inspect sample collection and homogenization activities conducted in the field and to review the data generation, quality control and support systems of the analytical laboratory. This inspection and compliance review will include all activities related to the requirements established for the field and laboratory quality assurance program as follows:

- o Assessment of degree of compliance with the quality assurance objectives of the program as established in this Scope of Work and associated Quality Assurance Project Plan (QAPP).
- o An assessment of field QC activities including field sample collection of duplicates, duplicate aliquots, field blanks, equipment blanks and the field documentation system.
- o A review of all field and laboratory sample handling procedures including chain-of-custody procedures.
- o A detailed performance audit of the analytical program as implemented for PCB analysis during this investigation.
- o An assessment of all laboratory procedures including instrument calibration, data collection and reduction, data review and approval process, internal QC program and QC documentation.
- o Continuing compliance with corrective actions identified in a previous audit of the facility and activities.

9.1 SYSTEMS AUDITS (Cont.)

System audits will be performed by the project QA manager. The audit schedule will coincide with ongoing field and laboratory activities at regular intervals throughout the project.

A copy of the systems audit report will be submitted to the field coordinator, laboratory manager and project manager. The audit report will identify any QA system deficiencies. The appropriate manager must immediately implement corrective action for the deficiencies and respond in writing to each of the items and document all corrective actions taken. The manager is required to verbally respond to all audit deficiencies no later than two weeks from the issuance of the audit report. Copies of the managers response will be forwarded to the project manager.

Implementation of all corrective action is the responsibility of the facility operations manager. The QA manager will monitor the corrective action for each previously identified deficiency to insure compliance.

9.2 PERFORMANCE AUDITS

Performance audits will be routinely employed during ongoing field sample collection and laboratory analysis to insure that the criteria that has been established for all quantitative quality control checks are being achieved. These checks include quality parameters for the determination of accuracy, precision and representativeness of all field and laboratory activities as follows:

9.2 PERFORMANCE AUDITS (Cont.)

- **Equipment Rinse Condensates:** The condensate from the steam cleaning of sample collection equipment will be collected and analyzed for PCB's following the procedures outlined in the method to insure that cross contamination of equipment does not occur between scrap pile samplings.

- **Field Duplicates:** Duplicate field samples will be collected from all sample cells and analyzed using the procedures describes in this method and evaluated to determine the precision of the sampling procedure.

- **Duplicate Aliquots:** One randomly selected composite will be selected from a quadrant or portion of each sampled area of the site for parallel analysis.

9.2.1 INTERNAL LABORATORY QC MONITORING

The laboratory will perform the analysis of all samples following the procedures described in the referenced method. The method includes specific control parameters which go beyond instrument performance criteria that was used to evaluate method performance. Method performance is based on the analysis of specific QC samples which provide quantitative date on laboratory contamination and analytical precision and accuracy as indicators of performance. These QC samples will be analyzed each time sample analysis is performed.

The performance parameters for the referenced method includes the following QC samples:

Method Blanks: A blank will be used to check "reagent" or "process" introduced PCB contamination for each batch of samples (up to a maximum of 20 samples/batch).

QC Check Standard: A PCB spiked free solid matrix (fired sand) which is processed through the referenced analytical method. The recovery (accuracy) data is used to verify method performance against expected performance. Check standards will be analyzed with each batch of samples (up to a maximum of 20 samples/batch).

Spiked Duplicate Samples: Duplicate aliquots of the same field sample which are spiked with a PCB mixture and analyzed using the selected method. The spike recovery data is used to determine if the accuracy criteria has been achieved. The relative percent difference (RPD) between the two values is used to check analytical precision.

Surrogate Recovery: A PCB surrogate (decachlorobiphenyl) will be added to the samples prior to extraction in accordance with the analytical method. If surrogate recovery criteria is not achieved, appropriate corrective actions will be taken to identify and resolve any problems with the analytical system.

Date generated for all control parameters will be compared to existing criteria by the analyst. Corrective action will be performed by the analyst when necessary. All performance-related data will be monitored by the Analytical Coordinator. The analyst will report the QA/QC results for each sample set to the Analytical Coordinator prior to final report preparation for each sample set. The Analytical Coordinator will review these results and verify that all method criteria have been met.

The Project QA Manager will periodically review all performance data.

9.2.2 CONTROL CHARTS

Control charts will be generated by the laboratory for all QC parameters pertaining to accuracy measurements and updated on a daily basis. A copy of the control charts for each monitored parameter will be forwarded to the QA manager on a monthly basis. The charts will be reviewed by the laboratory staff and the QA manager for trends which indicate problems within the analytical system. The laboratory manager will investigate method performance problems based on control chart data for corrective action purposes.

10.0 LABORATORY PREVENTIVE MAINTENANCE

Preventive maintenance will be performed on the GC/ECD system prior to every 12-hour analysis sequence. Maintenance will include replacing the septum in the injection port in accordance with laboratory preventive maintenance SOP.

Instrumental maintenance, difficulties and corrective actions will be documented in the instrument run log.

The system is maintained under a full service contract from the manufacturer. This contract insures timely response to system difficulties beyond the scope of routine laboratory maintenance. Manufacturer maintains a full inventory of critical spare parts as part of this service contract.

The ECD is wiped on a semi-annual basis to insure integrity of the radioactive source.

The column will be replaced if the chromatographic performance criteria cannot be achieved and routine column maintenance procedures do not correct the problem.

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

All data from the determination of PCBs in ground cover, wipe samples and concrete cores will be assessed for accuracy, precision, representativeness and completeness. This assessment will be performed by evaluating the data for the quality parameters of the method to determine if they are consistent with pre-established operational criteria. The procedures for performing this evaluation are described in Appendix 3, The Sampling and Analysis of Non-homogeneous Solids for Polychlorinated Biphenyls, Section 10. We have modified this methodology to be consistent with EPA methods 8080 and 8081, using GC/ECD. This assessment is the basis for determining if the data can be used for their intended decision making purposes.

11.1 DATA ACCURACY

Data accuracy will be characterized by the degree of agreement of a measured value to the accepted true value. Accuracy assessments will be used to established the bias present in the data.

The accuracy objective for this investigation is to meet or exceed the criteria that have been established for the referenced method. Accuracy determinations will be performed for PCB contamination performance evaluation samples and laboratory spiked PCBs.

Accuracy assessments will be performed at two separate review levels. The GC/ECD analysts will evaluate laboratory spikes for accuracy using a first level data review. The analysts will compare spiked data results to the established acceptance criteria. The analytical coordinator and project QA Manager will evaluate the results of the single blind performance evaluation samples to the established acceptance criteria.

The accuracy of sample data will be based on the results of spiked blank samples, matrix spiked samples, performance evaluation samples and surrogate spiked samples. Recovery will be calculated by the analyst and compared to the established acceptance/rejection criteria. If the current laboratory performance does not meet the established control criteria, the analytical coordinator will notify the Project QA Manager and an investigation will be performed to determine the causes for the deviation. Corrective action will be implemented by the analyst as necessary.

Spike accuracy will be calculated as follows:

$$\text{Accuracy, } R = \frac{(X - T)}{K} \times 100$$

K = Known addition of the spiked compound
X = Analytical result from the spiked sample
T = Analytical result from the unspiked aliquot
R = Accuracy = % Recovery

For each type of spiked sample (blank, matrix spike, surrogate spike), control charts will be developed. Control limits will initially be based on the results of the method validation study. The limits will be updated as additional recovery data for each type of spiked sample is accumulated. Limits are then calculated based on the following calculations:

Standard deviation (SD) will be the parameter used to define the variation among several recovery samples, the SD values will be used to establish upper and lower warning and control limits.

SD = The square root of: $\frac{(Ri - R)^2}{(n - 1)}$

Where:

SD = standard deviation of % recovery
Ri = observed value
R = mean or average of all observations
n = number of observations

Control limits for recoveries:

UCL = X + 3 SD
LCL = X - 3 SD
UWL = X + 2 SD
LWL = X - 2 SD

Where:

UCL = Upper Control Limit
LCL = Lower Control Limit
UWL = Upper Warning Limit
LWL = Lower Warning Limit

11.2 DATA PRECISION

Data precision will be characterized by the degree of agreement of a measured value for a tested parameter in a given sample to another measured value for the same parameter in a different aliquot of the same sample. Precision assessment will be used to establish the control status of field sample collection activities, sample homogenization processing and sample analysis.

11.2 DATA PRECISION (Cont.)

The precision objective for this investigation is to meet or exceed the criteria specified in the referenced method for all precision measurements. Precision measurements will be performed for field sampling and laboratory activities.

Precision assessments will be performed by the analyst for laboratory precision parameters which pertain to method execution using a first level data review. The analyst will compare data results to the established acceptance criteria. The analyst, analytical coordinator or project QA Manager will review precision data for parameters related to field sample collection and homogenization. When precision criteria is not achieved, an investigation will be performed to determine the causes for the deviation. Corrective action will be implemented by the analyst, analytical coordinator or the project QA Manager as necessary.

To evaluate the precision of acquired data, field duplicate samples, duplicate field sample aliquots and matrix spike/matrix spike duplicates (MS/MSD) samples will be employed. Precision will be calculated by the analyst, analytical coordinator or project QA Manager and compared to the established acceptance/rejection criteria.

Simple precision for duplicate field sample aliquots and MS/MSDs will be calculated as follows:

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

RPD = Relative Percent Difference
A = Replicate conc 1
B = Replicate conc 2

Precision for field duplicate sample will be calculated as follows:

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

RPD = Relative Percent Difference
A = Mean PCB conc, field duplicate sample pair 1
B = Mean PCB conc, field duplicate sample pair 2

Completeness: Completeness will be characterized by the frequency that the quality criteria for all field and method quality criteria meet the established method specifications. Completeness is numerically expressed using the following equation:

$$\text{Completeness} = \frac{\text{Total Sample QC Criteria Achieved}}{\text{Total Sample QC criteria}} \times 100$$

Completeness assessment will be used to assess the usability of the laboratory data for the intended decision making processes.

Representativeness: Representativeness will be defined as the degree in which a collected sample portrays the PCB content of each individual composited sample. Representativeness assessments will be based on achieving the RPD criteria that has been established for field duplicate sample and duplicate field sample aliquots.

12. CORRECTIVE ACTION

For the purpose of this investigation, corrective action is defined as those activities which are necessary to rectify out of control field sampling activities or laboratory analytical operations. Corrective action activities are intended to adjust the process to assure that 11 control parameters satisfy performance specifications. The operational objective for this investigation is to implement appropriate corrective action when and where necessary to insure that valid data is produced.

Corrective actions may be initiated for either field or laboratory activities. Specific quality parameters are designed to indicate which areas of project has been affected. Therefore, corrective actions may be initiated by field technicians, laboratory analysts, laboratory managers or the project Quality Assurance Manager.

If data for a quality parameter indicates that a possible field sampling or analytical problem exists, an investigation will be performed to assess the situation. In necessary, appropriate steps will be taken to correct the problem.

Quality control checks will be evaluated by conducting an initial sample batch run for the specific purpose of checking the quality control procedures established for this project. The results of this initial sample batch analysis will be used solely for this purpose.

12.1 QUALITY INDICATORS

The analytical method includes specific control parameters which are designed to detect systematic operational deficiencies. These control parameters are designed to isolate the deficiency to either sample collection or laboratory analytical operations. Unacceptable performance for these control parameters dictates that corrective action be initiated as follows.

Field Sampling: Quality parameters which may indicate a need for corrective action in field sampling activities are included in the following list.

- **Field Blanks:** PCB free reagent water blanks will be analyzed for PCBs using the analytical procedures specified for this investigation if PCB cross contamination is suspected to have occurred during the sampling event. If the results of the analysis indicate PCB cross contamination, all field samples containing PCBs above the regulatory limit will require recollection and re-analysis.

- **Equipment Rinse Condensates:** The equipment rinse condensate extracts from equipment steam cleaning will be analyzed for PCB to determine if PCB cross contamination occurred during the sample collection step if the PCB value for the previous sample contains PCBs and the next sample contains PCBs at concentrations more than 10 ppm. If PCB cross contamination has occurred and has biased the data for a composite sample, the sample cells will be resampled, recomposited and re-analyzed.

- **Field Duplicates:** Field duplicate samples will be homogenized and analyzed to determine the precision of the sampling procedure. If the data from the analysis of field duplicates does not meet the relative percent difference criteria for duplicate pairs, the field duplicates for each sample will be analyzed. The average concentration from the respective replicates (two sets of replicate pairs) will be reported as the PCB concentration for that respective replicate. If the RPD criteria for the mean value of the first duplicate pair satisfies the sampling precision criteria, no additional field duplicates will be analyzed or collected.

- **Duplicate Aliquots:** One randomly selected composite will be selected from a quadrant or portion of each sampled area of the site for parallel analysis.

Procedures to resolve quality deficiencies associates with field quality control samples will be implemented when all laboratory corrective action options have been exhausted. These options may include complete sample re-extraction, repreparation, analysis, clean-up, dilutions or matrix modifications. The corrective action performed will be documented with the analytical results.

Method Application. Quality parameters which indicate a need for corrective action for laboratory activities are detailed in the following list.

- **Method Blank:** A blank will be analyzed to check for "reagent" or "process" introduced PCB contamination. If PCBs are detected in the blank at concentrations above the operational detection limit, and PCBs are detected in sample extracts, the entire sample batch will be re-extracted and re-analyzed.

- **QC Check Standard:** A PCB free solid matrix (fired sand) will be spiked with a PCB congener standard and analyzed to verify method performance. If the recovery does not meet the performance expectation, the analytical system will be inspected to isolate systematic problems affecting method accuracy. Corrective action will be taken to remedy identified deficiencies. The corrective action will be evaluated to determine its impact on the field data. The evaluation will indicate if the data can be used without qualification, requires qualification on an individual sample basis, or requires re-extraction and re-analysis.

- **Spiked Duplicate Samples:** Duplicate aliquots of field samples will be spiked with PCB congeners and analyzed to determine if the accuracy criteria has been achieved. The relative percent difference (RPD) between the two values will be used to check analytical precision. If the accuracy criteria is not achieved, sample extracts will be re-analyzed. If the deficiency is not rectified, other quality parameters will be evaluated to determine if the deficiency is related to sample matrix interference or method execution. If the precision criteria is not achieved, sample extracts will be re-analyzed. If the deficiency is not rectified, other quality parameters will be evaluated to determine if the deficiency is related to sample matrix interferences or method execution.

- **Performance Evaluation Samples:** A double blind performance evaluation (PE) sample will be introduced into the laboratory with every analytical batch of 20 samples or less. The PE sample will be composed of homogenized sand mixed with PCB to achieve a known concentration. The USEPA project manager and quality assurance officer will review the data from the analysis of this sample to determine if the results meet the pre-established control criteria.

12.1 QUALITY INDICATORS (Cont.)

- **Performance Evaluation Samples:** (Cont.)
  If the reported total PCB values are within 30 percent of the total values expected from an EPA check sample, the laboratory will be approved to continue sample analysis. If the results indicate that deviations from performance expectations have occurred, the USEPA project manager will notify the QA manager who will stop all laboratory work and will initiate an investigation to determine the cause of the deviation. The QA manager will recommend corrective actions to address detected systematic laboratory deficiencies. Corrective action items will be evaluated to determine their impact on the affected field data set. The evaluation will indicate if the data can be used without qualification, require qualification on an individual sample basis, or require re-extraction and re-analysis. The analytical coordinator is responsible for implementing all corrective action. The laboratory will be approved to continue work once the corrective action has been implemented.

An entire batch of samples may require corrective action if QC criteria are not achieved. The analytical coordinator has the decision responsibility for actions which include re-analysis or re-extraction. The analytical coordinator will review both sets of data where applicable to determine if the deficiencies have been resolved.

12.2 QUALITY ASSURANCE REVIEW

In addition to the corrective actions dictated by control parameter variances and audit revealed operational deficiencies, the analytical method contains numerous instrumentation performance checks. Corrective action for these items are within the analyst's control and are routinely addressed during day to day operations. These items are listed in Table 12.4.1 with the corrective action requirements.

Table 12.4.1

Additional Analytical Method Performance Checks

Method QC Specification	Recommended Corrective Action
Initial Calibration	Evaluation of instrument sensitivity, calibration linearity and gas chromotographic resolution. Re-analyze Standards. Check instrument systems, resolve all instrument problems, re-analyze standards, if still unacceptable, then remake standards. Check against external reference as necessary.
Continuing Calibration	Continuing check of instrument sensitivity, calibration linearity, and gas chromotographic resolution. Re-analyze standard to verify. Check response. Re-calibrate and re-analyze samples from the last acceptable calibration check. Perform corrective action indicated for initial calibration as needed.

12.3 PERFORMANCE AUDIT IDENTIFIED DEFICIENCIES

Operational deficiencies in field activities or laboratory operations identified through performance or systems audits and performance evaluation studies also qualify for corrective action. Copies of audit reports or performance evaluation results will be distributed to the analytical coordinator and the project manager with recommendations for corrective action. Corrective action recommendations are subsequently initiated at the operations level. The corrective action is formally documented in a written response to the project QA Manager. Follow up audits will be performed to assure that the non-conformances identified have been eliminated.

12.4 CORRECTIVE ACTION CATEGORIES AND RESPONSIBILITIES

Corrective action for this investigation are generally categorized as system adjustments, operational procedure adjustments or training deficiencies. The Quality Assurance Manager is responsible for recommending corrective action to the project manager and the analytical coordinator. Additionally, the Quality Assurance Manager will monitor corrective action implementation and provide feedback to the project manager.

13. QUALITY ASSURANCE REPORTS TO MANAGEMENT

The objective of the quality assurance program for this investigation is to insure that the established operational system has been implemented according to plan and is producing laboratory data that achieves the quality objectives of the project. The program includes feedback mechanisms which enables management to determine if these objectives have been achieved. An essential component of the feedback system is the communication pathways which insure that management obtains quality information promptly and consistently. To achieve this objective, a formal reporting process will be employed to inform project management of the quality status of all operational components. This information will enable management to take prompt corrective action when required.

13.1 SYSTEMS REPORTS

System reports will be generated on a formal and informal basis. Systems inspections will be performed for sample collection and homogenization activities conducted in the field and for the data generation, quality control and support systems of the analytical laboratory. These inspections will be performed by the field coordinator and the analytical coordinator. Summaries of these evaluations will be submitted to the project QA Manager and the project manager. Internal audits will also be used as a source of system status information. All system related information will be used to fine tune field and laboratory activities to insure that the project objectives are achieved.

Bi-Weekly Reports. On a bi-weekly basis, the facility manager will verbally report the QA program status to the project QA Manager. The project QA Manager uses this information to assess program progress and elevate issues of concern to higher status levels for adjustment or corrections. The items which will be discussed in weekly status report are described in Figure 13.1.1.

Monthly Updates. The project QA Manager will generate a written monthly report which summarizes the QA program issues and QC performance issues for the project. This report will also include copies of the control charts along with a discussion of the trends indicated by the charts. A solution will be proposed which includes an execution date for all identified deficiencies. The report will be copied to the project manager, the laboratory manager, and the USEPA project manager. The laboratory manager will use the monthly report to assess project related quality problems and to take the necessary corrective action to resolve the issue. A copy of the monthly report outline is displayed in Figure 13.1.2.

Audit Reports. System audit reports will be derived from internal audit processes. Internal audits will be scheduled on a bi-monthly basis. Audit reports will be prepared by the project QA Manager for distribution to the field coordinator, analytical coordinator and project manager. These individuals will be responsible for correcting any deficiencies in their area identified in the report.

Figure 13.1.1
Bi-Weekly Quality Assurance Status Report

Field Activities

I. Field Activity Review
   A. Field samples collected
      1. Sample collection & homogenization review
   B. QA samples collected
      1. Duplicates collected
         a. Analytical data
      2. Field replicates collected
         a. Analytical data
      3. Decontamination blanks

II. Corrective Action
   A. Identified
   B. Implemented

Laboratory Activities

I. Laboratory Activity Review
   A. Samples analyzed
   B. Systematic problems
   C. Corrective action
   D. Method performance
      1. Matrix spike/matrix spike duplicate
      2. QC blanks
      3. Performance evaluation samples

II. Corrective action
   A. Identified
   B. Implemented

Figure 13.1.2
Monthly Quality Assurance Report

I. Critical Problems: Problem description and corrective action course. Logic in decision process and confidence on implementation.
   A. Corrective action responses
   B. Corrective action implementation monitoring
   C. Method Precision & Accuracy Assessment
   D. Performance Evaluation Samples
      1. PE report received (Score)
      2. Corrective action (if necessary)

13.2 PERFORMANCE REPORTS

Performance reports will focus on the evaluation of quantitative analytical indicators which reflect data quality. Performance data will be derived from the analysis of quality control samples as indicators of field and laboratory quality. The evaluation will be based on established method criteria. The laboratory analyst will have the responsibility for making corrective action decisions based on method quality indicators.

The analytical coordinator and project QA Manager are responsible for identifying deficiencies in sample collection and homogenization procedures. Field activity evaluation will also be based on a comparison of data from quality indicators with established method criteria.

There will be several other performance monitoring mechanisms which will enable project management to assess the quality of the data produced in the field and the laboratory. Each of these items is described in the following.

Performance Limits. Method accuracy data will be collected for performance evaluation samples, spiked parameters and retained in a QC database. This data will be used to develop performance-based control criteria which will be used by the analyst as a guide in determining if problems have occurred during the execution of the method. If performance problems are indicated, the analyst will execute the appropriate corrective action decisions.

Control Chart Review. Method accuracy data will will be extracted from the database and plotted against the previously calculated control criteria. This data will be reviewed by the project QA Manager to determine if systematic problems have been occurring during sample analysis. If systematic problems are indicated, the QA Manager and the analytical coordinator will investigate the problem to determine the source and implement corrective action.

Performance Evaluation Samples. Performance evaluation samples are samples which are artificially contaminated with known concentrations of PCBs. The constituents and concentrations of the performance evaluation samples are known to the analyst. These samples will be analyzed with every sample batch to assess laboratory accuracy against an established precision standard. Performance evaluation data reports will be evaluated by the analytical coordinator and project QA Manager. The project QA Manager will also send a report copy to the project manager. If the performance deficiencies are detected, the QA Manager works with the analytical coordinator on the corrective action required to eliminate the deficiency. The corrective action will be documented and a copy sent to the project manager.

13.3 QUALITY ASSURANCE PROJECT PLAN CHANGES

Situations may occur in the field and laboratory which require modification of the Quality Assurance Project Plan. If this situation occurs, the manager in charge of the affected operation must immediately be notified. He, in turn, immediately notifies the project manager and the project QA Manager.

The project QA Manager is responsible for immediately contacting the USEPA project manager to obtain approval to proceed before the QAPjP modification is implemented. If the USEPA project manager approves the modification, the project QA Manager must document the change(s) as an amendment to the QAPjP and distribute copies of the change to all parties involved with the project.

14.0 LABORATORY QUALIFICATIONS AND CERTIFICATIONS

The analytical laboratory selected to perform the analysis of samples from the site is Analytical Testing Service, Inc. (ATS) of Smithfield, Rhode Island. ATS maintains the equipment, facilities, personnel, and certifications required to analyze the samples in a manner consistent with EPA protocols and this SOW. Laboratory certifications are presented in Appendix C, whereas resumes of personnel are presented in Appendix D.

Appendix A

Cone and Quartering

APPENDIX A

Cone and Quartering

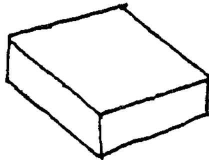
Once the individual sample borings are prepared in accordance with Sections 6.1.1 through 6.1.4 of this SOW, the material will be sampled in the following manner.

Material is coned on a Tyvex covered plywood sheet in a manner as depicted in Figure 1.

Fig. 1

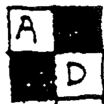
After coning is completed, the sample is spread in a square pattern (Figure 2) to an even thickness. (1-2 inches)

Fig. 2



With a square trowel, a path is cut in the shape of a cross passing the center point of the leveled pile creating 4 equal quadrants. The alternate corners shown in Figure 3 (A and D) are removed from the layout and reconed and the process is repeated with the exception that the B and C quadrants being removed after the next quartering process.

Fig. 3

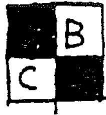


Quadrant A & D
Reconed

Cone and Quartering (Cont'd)

Quadrant A + D from previous page

Fig. 4



The configuration of the final sample step is shown in Figure 4. The process is repeated until a sample size of 100 grams is obtained. Which alternate corners are designated as the reserve samples are dependent upon the number of repetitions required to achieve an optimum sample size of 100 grams.

100-gram individual samples are then mixed together to form an 1800 gram composite sample, and the cone and quarterly operation is repeated to produce a 100-gram composite sample.

Appendix B

Analytical Methods

ORGANIC EXTRACTION AND SAMPLE PREPARATION

1.0 SCOPE AND APPLICATION

1.1 The 3500 Methods are procedures for quantitatively extracting nonvolatile and semivolatile organic compounds from various sample matrices. Cleanup and/or analysis of the resultant extracts are described in Chapter Four, Sections 4.2.2 and 4.3, respectively.

1.2 Method 3580 describes a solvent dilution technique that may be used on non-aqueous nonvolatile and semivolatile organic samples prior to cleanup and/or analysis.

1.3 The 5000 Methods are procedures for preparing samples containing volatile organic compounds for quantitative analysis.

1.4 Refer to the specific method of interest for further details.

2.0 SUMMARY OF METHOD

2.1 3500 Methods: A sample of a known volume or weight is solvent extracted. The resultant extract is dried and then concentrated in a Kuderna-Danish apparatus. Other concentration devices or techniques may be used in place of the Kuderna-Danish concentrator if the quality control requirements of the determinative methods are met (Method 8000, Section 8.0).

2.2 5000 Methods: Refer to the specific method of interest.

3.0 INTERFERENCES

3.1 Samples requiring analysis for volatile organic compounds, can be contaminated by diffusion of volatile organics (particularly chlorofluorocarbons and methylene chloride) through the sample container septum during shipment and storage. A field blank prepared from reagent water and carried through sampling and subsequent storage and handling can serve as a check on such contamination.

3.2 Solvents, reagent, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required. Refer to Chapter One for specific guidance on quality control procedures.

3.3 Interferences coextracted from the samples will vary considerably from source to source. If analysis of an extracted sample is prevented due to interferences, further cleanup of the sample extract may be necessary. Refer to Method 3600 for guidance on cleanup procedures.

3.4 Phthalate esters contaminate many types of products commonly found in the laboratory. Plastics, in particular, must be avoided because phthalates are commonly used as plasticizers and are easily extracted from plastic materials. Serious phthalate contamination may result at any time if consistent quality control is not practiced.

3.5 Glassware contamination resulting in analyte degradation: Soap residue on glassware may cause degradation of certain analytes. Specifically, aldrin, heptachlor, and most organophosphorous pesticides will degrade in this situation. This problem is especially pronounced with glassware that may be difficult to rinse (e.g., 500-mL K-D flask). These items should be hand-rinsed very carefully to avoid this problem.

4.0 APPARATUS AND MATERIALS

4.1 Refer to the specific method of interest for a description of the apparatus and materials needed.

5.0 REAGENTS

5.1 Refer to the specific method of interest for a description of the solvents needed.

5.2 Stock standards: Stock solutions may be prepared from pure standard materials or purchased as certified solutions.

5.2.1 **Purgeable stock standards**: Prepare stock standards 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.

5.2.1.1 Place about 9.8 mL of methanol in a 10-mL tared ground-glass-stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 min or until all alcohol-wetted surfaces have dried. Weigh the flask to the nearest 0.1 mg.

5.2.1.2 Using a 100-uL syringe, immediately add two or more drops of assayed reference material to the flask, then reweigh. The liquid must fall directly into the alcohol without contacting the neck of the flask.

5.2.1.3 Reweigh, dilute to volume, stopper, then mix by inverting the flask several times. Calculate the concentration in micrograms per microliter (ug/uL) from the net gain in weight. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

5.2.1.4 Transfer the stock standard solution into a Teflon-sealed screw-cap bottle. Store, with minimal headspace, at -10°C to -20°C and protect from light.

5.2.1.5 All standards must be replaced after 1 month, or sooner if comparison with check standards indicates a problem.

5.2.2 Semivolatile stock standards: Base/neutral and acid stock standards are prepared in methanol. Organochlorine pesticide standards are prepared in acetone.

5.2.2.1 Stock standard solutions should be stored in Teflon-sealed containers at 4°C. The solutions should be checked frequently for stability. These solutions must be replaced after six months, or sooner if comparison with quality control check samples indicate a problem.

5.3 Surrogate standards: A surrogate standard (i.e., a chemically inert compound not expected to occur in an environmental sample) should be added to each sample, blank, and matrix spike sample just prior to extraction or processing. The recovery of the surrogate standard is used to monitor for unusual matrix effects, gross sample processing errors, etc. Surrogate recovery is evaluated for acceptance by determining whether the measured concentration falls within the acceptance limits. Recommended surrogates for different analyte groups follow; however, these compounds, or others that better correspond to the analyte group, may be used for other analyte groups as well. Normally three or more standards are added for each analyte group.

5.3.1 Base/neutral and acid surrogate spiking solutions: The following are recommended surrogate standards.

Base/neutral	Acid
2-Fluorobiphenyl	2-Fluorophenol
Nitrobenzene-d_5	2,4,6-Tribromophenol
Terphenyl-d_{14}	Phenol-d_6

5.3.1.1 Prepare a surrogate standard spiking solution in methanol that contains the base/neutral compounds at a concentration of 100 ug/mL, and the acid compounds at 200 ug/mL for water and sediment/soil samples (low- and medium-level). For waste samples, the concentration should be 500 ug/mL for base/neutrals and 1000 ug/mL for acids.

5.3.2 Organochlorine pesticide surrogate spiking solution: The following are recommended surrogate standards for organochlorine pesticides.

Organochlorine pesticides

Dibutylchlorendate (DBC)
2,4,5,6-Tetrachloro-meta-xylene (TCMX)

5.3.2.1 Prepare a surrogate standard spiking solution at a concentration of 1 ug/mL in acetone for water and sediment/soil samples. For waste samples, the concentration should be 5 ug/mL.

5.3.3 **Purgeable surrogate spiking solution:** The following are recommended surrogate standards for volatile organics.

Purgeable organics

p-Bromofluorobenzene
1,2-Dichloroethane-d_4
Toluene-d_8

5.3.3.1 Prepare a surrogate spiking solution (as described in Paragraph 5.2.1 or through secondary dilution of the stock standard) in methanol containing the surrogate standards at a concentration of 25 ug/mL.

5.4 Matrix spike standards: Select five or more analytes from each analyte group for use in a spiking solution. The following are recommended matrix spike standard mixtures for a few analyte groups. These compounds, or others that better correspond to the analyte group, may be used for other analyte groups as well.

5.4.1 **Base/neutral and acid matrix spiking solution:** Prepare a spiking solution in methanol that contains each of the following base/neutral compounds at 100 ug/mL and the acid compounds at 200 ug/mL for water and sediment/soil samples. The concentration of these compounds should be five times higher for waste samples.

Base/neutrals	Acids
1,2,4-Trichlorobenzene	Pentachlorophenol
Acenaphthene	Phenol
2,4-Dinitrotoluene	2-Chlorophenol
Pyrene	4-Chloro-3-methylphenol
N-Nitroso-di-n-propylamine	4-Nitrophenol
1,4-Dichlorobenzene	

5.4.2 **Organochlorine pesticide matrix spiking solution:** Prepare a spiking solution in acetone or methanol that contains the following pesticides in the concentrations specified for water and sediment/soil. The concentration should be five times higher for waste samples.

Pesticide	Concentration (ug/mL)
Lindane	0.2
Heptachlor	0.2
Aldrin	0.2
Dieldrin	0.5
Endrin	0.5
4,4'-DDT	0.5

5.4.3 **Purgeable matrix spiking solution**: Prepare a spiking solution in methanol that contains the following compounds at a concentration of 25 ug/mL.

Purgeable organics

1,1-Dichloroethene
Trichloroethene
Chlorobenzene
Toluene
Benzene

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to the Organic Analyte Chapter, Section 4.1.

7.0 PROCEDURE

7.1 Semivolatile organic sample extraction: Water, soil/sediment, sludge, and waste samples requiring analysis for base/neutral and acid extractables and/or organochlorine pesticides must undergo solvent extraction prior to analysis. This manual contains four methods that may be used for this purpose: Method 3510; Method 3520; Method 3540; and Method 3550. The method that should be used on a particular sample, is highly dependent upon the physical characteristics of that sample. Therefore, review these four methods prior to choosing one in particular. Appropriate surrogate standards and, if necessary, matrix spiking solutions are added to the sample prior to extraction for all four methods.

7.1.1 **Method 3510**: Applicable to the extraction and concentration of water-insoluble and slightly water-soluble organics from aqueous samples. A measured volume of sample is solvent extracted using a separatory funnel. The extract is dried, concentrated and, if necessary, exchanged into a solvent compatible with further analysis. Method 3520 should be used if an emulsion forms between the solvent-sample phases, which can not be broken up by mechanical techniques.

7.1.2 **Method 3520**: Applicable to the extraction and concentration of water-insoluble and slightly water-soluble organics from aqueous samples. A measured volume of sample is extracted with an organic solvent in a continuous liquid-liquid extractor. The solvent must have a density greater than that of the sample. The extract is dried, concentrated and, if necessary, exchanged into a solvent compatible with further analysis. The limitations of Method 3510 concerning solvent-sample phase separation do not interfere with this procedure.

7.1.3 **Method 3540**: This is a procedure for extracting nonvolatile and semivolatile organic compounds from solids such as soils, sludges, and wastes. A solid sample is mixed with anhydrous sodium sulfate, placed into an extraction thimble or between two plugs of glass wool, and extracted using an appropriate solvent in a Soxhlet extractor. The extract is dried, concentrated and, if necessary, exchanged into a solvent compatible with further analysis.

7.1.4 **Method 3550**: This method is applicable to the extraction of nonvolatile and semivolatile organic compounds from solids such as soils, sludges, and wastes using the technique of sonication. Two procedures are detailed depending upon the expected concentration of organics in the sample; a low concentration and a high concentration method. In both, a known weight of sample is mixed with anhydrous sodium sulfate and solvent extracted using sonication. The extract is dried, concentrated and, if necessary, exchanged into a solvent compatible with further analysis.

7.1.5 **Method 3580**: This method describes the technique of solvent dilution of non-aqueous waste samples. It is designed for wastes that may contain organic chemicals at a level greater than 20,000 mg/kg and that are soluble in the dilution solvent.

7.2 Volatile organic sample preparation: There are three methods for volatile sample preparation: Method 5030; Method 5040; and direct injection. Method 5030 is the most widely applicable procedure for analysis of volatile organics, while the direct injection technique may have limited applicability to aqueous matrices.

7.2.1 **Method 5030**: This method describes the technique of purge-and-trap for the introduction of purgeable organics into a gas chromatograph. This procedure is applicable for use with aqueous samples directly and to solids, wastes, soils/sediments, and water-miscible liquids following appropriate preparation. An inert gas is bubbled through the sample, which will efficiently transfer the purgeable organics from the aqueous phase to the vapor phase. The vapor phase is swept through a sorbent trap where the purgeables are trapped. After purging is completed, the trap is heated and backflushed with the inert gas to desorb the purgeables onto a gas chromatographic column. Prior to application of the purge-and-trap procedure, all samples (including blanks, spikes, and duplicates) should be spiked with surrogate standards and, if required, with matrix spiking compounds.

7.2.2 **Method 5040**: This method is applicable to the investigation of sorbent cartridges from volatile organic sampling train (VOST).

7.3 Sample analysis: Following preparation of a sample by one of the methods described above, the sample is ready for further analysis. For samples requiring volatile organic analysis, application of one of the three methods described above is followed directly by gas chromatographic analysis (Methods 8010, 8015, 8020, or 8030). Samples prepared for semivolatile analysis may, if necessary, undergo cleanup (See Method 3600) prior to application of a specific determinative method.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific guidance on quality control procedures.

8.2 Before processing any samples, the analyst should demonstrate through the analysis of a reagent water blank that all glassware and reagents are interference free. Each time a set of samples are processed, a method blank(s) should be processed as a safeguard against chronic laboratory contamination. The blank samples should be carried through all stages of the sample preparation and measurement.

8.3 Surrogate standards should be added to all samples when specified in the appropriate determinative method in Chapter Four, Section 4.3.

8.4 A reagent blank, a matrix spike, and a duplicate or matrix spike duplicate must be performed for each analytical batch (up to a maximum of 20 samples) analyzed.

8.5 For GC or GC/MS analysis, the analytical system performance must be verified by analyzing quality control (QC) check samples. Method 8000, Section 8.0 discusses in detail the process of verification; however, preparation of the QC check sample concentrate is dependent upon the method being evaluated.

8.5.1 **Volatile organic QC check samples:** QC check sample concentrates containing each analyte of interest are spiked into reagent water (defined as the QC check sample) and analyzed by purge-and-trap (Method 5030). The concentration of each analyte in the QC check sample is 20 ug/L. The evaluation of system performance is discussed in detail in Method 8000, beginning with Paragraph 8.6.

8.5.2 **Semivolatile organic QC check samples:** To evaluate the performance of the analytical method, the QC check samples must be handled in exactly the same manner as actual samples. Therefore, 1.0 mL of the QC check sample concentrate is spiked into each of four 1-L aliquots of reagent water (now called the QC check sample), extracted, and then analyzed by GC. The variety of semivolatile analytes which may be analyzed by GC is such that the concentration of the QC check sample concentrate is different for the different analytical techniques presented in the manual. Method 8000 discusses in detail the procedure of verifying the detection system once the QC check sample has been prepared. The concentrations of the QC check sample concentrate for the various methods are as follows:

8.5.2.1 Method 8040 - Phenols: The QC check sample concentrate should contain each analyte at a concentration of 100 ug/mL in 2-propanol.

8.5.2.2 Method 8060 - Phthalate esters: The QC check sample concentrate should contain the following analytes at the following concentrations in acetone: butyl benzyl phthalate, 10 ug/mL; bis(2-ethylhexyl)phthalate, 50 ug/mL; di-n-octylphthalate, 50 ug/mL; and any other phthalate at 25 ug/mL.

8.5.2.3 Method 8080 - Organochlorine pesticides and PCBs: The QC check sample concentrate should contain each single-component analyte at the following concentrations in acetone: 4,4'-DDD, 10 ug/mL; 4,4'-DDT, 10 ug/mL; endosulfan II, 10 ug/mL; endosulfan sulfate, 10 ug/mL; and any other single-component pesticide at 2 ug/mL. If the method is only to be used to analyze PCBs, chlordane, or toxaphene, the QC check sample concentrate should contain the most representative multicomponent parameter at a concentration of 50 ug/mL in acetone.

8.5.2.4 Method 8090 - Nitroaromatics and Cyclic Ketones: The QC check sample concentrate should contain each analyte at the following concentrations in acetone: each dinitrotoluene at 20 ug/mL; and isophorone and nitrobenzene at 100 ug/mL.

8.5.2.5 Method 8100 - Polynuclear aromatic hydrocarbons: The QC check sample concentrate should contain each analyte at the following concentrations in acetonitrile: naphthalene, 100 ug/mL; acenaphthylene, 100 ug/mL; acenaphthene, 100 ug/mL; fluorene, 100 ug/mL; phenanthrene, 100 ug/mL; anthracene, 100 ug/mL; benzo(k)fluoranthene 5 ug/mL; and any other PAH at 10 ug/mL.

8.5.2.6 Method 8120 - Chlorinated hydrocarbons: The QC check sample concentrate should contain each analyte at the following concentrations in acetone: hexachloro-substituted hydrocarbons, 10 ug/mL; and any other chlorinated hydrocarbon, 100 ug/mL.

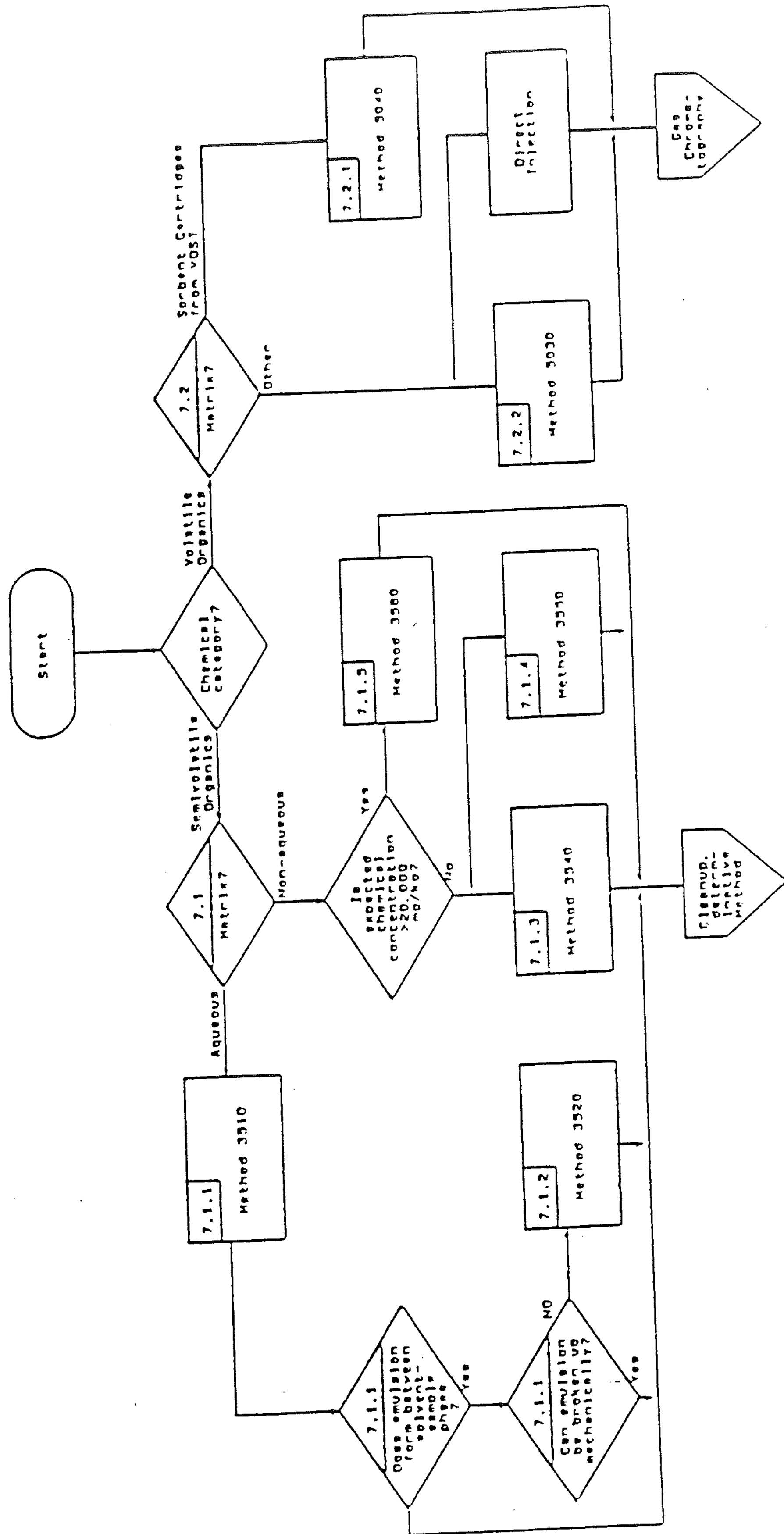
9.0 METHOD PERFORMANCE

9.1 The recovery of surrogate standards is used to monitor unusual matrix effects, sample processing problems, etc. The recovery of matrix spiking compounds indicates the presence or absence of unusual matrix effects.

9.2 The performance of this method will be dictated by the overall performance of the sample preparation in combination with the analytical determinative method.

10.0 REFERENCES

10.1 None required.


METHOD 3500
ORGANIC EXTRACTION AND SAMPLE PREPARATION
Start
Chemical category?
Volatile Organics
Semivolatile Organics
7.2 Matrix?
Sorbent Cartridges from VOST
Other
7.2.1 Method 5040
7.2.2 Method 5030
Direct Injection
Gas Chroma-tography
7.1 Matrix?
Aqueous
Non-aqueous
7.1.1 Method 3510
Is expected chemical concentration >20,000 mg/kg?
Yes
No
7.1.5 Method 3580
7.1.4 Method 3550
7.1.3 Method 3540
7.1.2 Method 3520
Cleanup, determinative Method
7.1.1 Does emulsion form between solvent-sample phase ?
Yes
7.1.1 Can emulsion be broken up mechanically?
NO
Yes

METHOD 3550

SONICATION EXTRACTION

1.0 SCOPE AND APPLICATION

1.1 Method 3550 is a procedure for extracting nonvolatile and semivolatile organic compounds from solids such as soils, sludges, and wastes. The sonication process ensures intimate contact of the sample matrix with the extraction solvent.

1.2 The method is divided into two sections, based on the expected concentration of organics in the sample. The low concentration method (individual organic components of $\leq$20 mg/kg) uses a larger sample size and a more rigorous extraction procedure (lower concentrations are more difficult to extract). The high concentration method (individual organic components of >20 mg/kg) is much simpler and therefore faster.

1.3 It is highly recommended that the extracts be cleaned up prior to analysis. See Cleanup, Section 4.2.2 of Chapter Four, for applicable methods.

2.0 SUMMARY OF METHOD

2.1 Low concentration method: A 30-g sample is mixed with anhydrous sodium sulfate to form a free-flowing powder. This is solvent extracted three times using sonication. The extract is separated from the sample by vacuum filtration or centrifugation. The extract is ready for cleanup and/or analysis following concentration.

2.2 High concentration method: A 2-g sample is mixed with anhydrous sodium sulfate to form a free-flowing powder. This is solvent extracted once using sonication. A portion of the extract is removed for cleanup and/or analysis.

3.0 INTERFERENCES

3.1 Refer to Method 3500.

4.0 APPARATUS AND MATERIALS

4.1 Apparatus for grinding: If the sample will not pass through a 1-mm standard sieve or cannot be extruded through a 1-mm opening, it should be processed into a homogeneous sample that meets these requirements. Fisher Mortar Model 155 Grinder, Fisher Scientific Co., Catalogue Number 8-323, or an equivalent brand and model, is recommended for sample processing. This grinder should handle most solid samples, except gummy, fibrous, or oily materials.

4.2 Sonication: A horn-type sonicator equipped with a titanium tip should be used. The following sonicator, or an equivalent brand and model, is recommended:

> Ultrasonic cell disrupter: Heat Systems - Ultrasonics, Inc., Model W-385 (475 watt) sonicator or equivalent (Power wattage must be a minimum of 375 with pulsing capability and No. 200 1/2" Tapped Disrupter Horn) plus No. 207 3/4" Tapped Disrupter Horn, and No. 419 1/8" Standard Tapered microtip probe.

4.3 Sonabox: Recommended with above disrupters for decreasing cavitation sound (Heat Systems - Ultrasonics, Inc., Model 432B or equivalent).

4.4 Apparatus for determining percent moisture:

4.4.1 Oven: Drying.

4.4.2 Desiccator.

4.4.3 Crucibles: Porcelain.

4.5 Pasteur glass pipets: Disposable, 1-mL.

4.6 Beakers: 400-mL.

4.7 Vacuum filtration apparatus:

4.7.1 Buchner funnel.

4.7.2 Filter paper: Whatman No. 41 or equivalent.

4.8 Kuderna-Danish (K-D) apparatus:

4.8.1 Concentrator tube: 10-mL graduated (Kontes K-570050-1025 or equivalent).

4.8.2 Evaporator flask: 500-mL (Kontes K-570001-0500 or equivalent).

4.8.3 Snyder column: Three-ball macro (Kontes K-503000-0121 or equivalent).

4.8.4 Snyder column: Two-ball micro (Kontes K-569001-0219 or equivalent).

4.9 Boiling chips: Solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).

4.10 Water bath: Heated, with concentric ring cover, capable of temperature control ($\pm 5^\circ C$). The bath should be used in a hood.

4.11 Balance: Top-loading, capable of accurately weighing 0.01 g.

4.12 Vials and caps: 2-mL for GC auto-sampler.

4.13 Glass scintillation vials: At least 20-mL, with screw-cap and Teflon or aluminum foil liner.

4.14 Spatula: Stainless steel or Teflon.

4.15 Drying column: 20-mm I.D. Pyrex chromatographic column with Pyrex glass wool at bottom and a Teflon stopcock.

NOTE: Fritted glass discs are difficult to decontaminate after highly contaminated extracts have been passed through. Columns without frits may be purchased. Use a small pad of Pyrex glass wool to retain the adsorbent. Prewash the glass wool pad with 50 mL of acetone followed by 50 mL of elution solvent prior to packing the column with adsorbent.

4.16 Syringe: 5-mL.

5.0 REAGENTS

5.1 Sodium sulfate: Anhydrous and reagent grade, heated at 400°C for 4 hr, cooled in a desiccator, and stored in a glass bottle. Baker anhydrous powder, catalog #73898, or equivalent.

5.2 Extraction solvents: Methylene chloride:acetone (1:1, v:v), methylene chloride, hexane (pesticide quality or equivalent).

5.3 Exchange solvents: Hexane, 2-propanol, cyclohexane, acetonitrile (pesticide quality or equivalent).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 Sample handling:

7.1.1 Sediment/soil samples: Decant and discard any water layer on a sediment sample. Mix sample thoroughly, especially composited samples. Discard any foreign objects such as sticks, leaves, and rocks.

7.1.2 Waste samples: Samples consisting of multiphases must be prepared by the phase separation method in Chapter Two before extraction. This procedure is for solids only.

7.1.3 Dry waste samples amenable to grinding: Grind or otherwise subdivide the waste so that it either passes through a 1-mm sieve or can be extruded through a 1-mm hole. Introduce sufficient sample into the grinding apparatus to yield at least 10 g after grinding.

7.2 <u>Determination of percent moisture</u>: In certain cases, sample results are desired based on a dry-weight basis. When such data is desired, a portion of sample for moisture determination should be weighed out at the same time as the portion used for analytical determination.

7.2.1 Immediately after weighing the sample for extraction, weigh 5-10 g of the sample into a tared crucible. Determine the percent moisture by drying overnight at 105°C. Allow to cool in a desiccator before weighing:

$$\frac{\text{g of sample} - \text{g of dry sample}}{\text{g of sample}} \times 100 = \%\ \text{moisture}$$

7.3 <u>Determination of pH</u> (if required): Transfer 50 g of sample to a 100-mL beaker. Add 50 mL of water and stir for 1 hr. Determine the pH of sample with glass electrode and pH meter while stirring. Discard this portion of sample.

7.4 <u>Extraction method for samples expected to contain low concentrations of organics and pesticides</u> ($\lesssim$20 mg/kg):

7.4.1 The following step should be performed rapidly to avoid loss of the more volatile extractables. Weigh approximately 30 g of sample into a 400-mL beaker. Record the weight to the nearest 0.1 g. Non-porous or wet samples (gummy or clay type) that do not have a free-flowing sandy texture must be mixed with 60 g of anhydrous sodium sulfate using a spatula. The sample should be free-flowing at this point. Add 1 mL of surrogate standards to all samples, spikes, and blanks (see Method 3500 for details on the surrogate standard solution and the matrix spike solution). For the sample in each analytical batch selected for spiking, add 1.0 mL of the matrix spiking standard. For base/neutral-acid analysis, the amount added of the surrogates and matrix spiking compounds should result in a final concentration of 100 ng/uL of each base/neutral analyte and 200 ng/uL of each acid analyte in the extract to be analyzed (assuming a 1 uL injection). If Method 3640, Gel-permeation cleanup, is to be used, add twice the volume of surrogates and matrix spiking compounds since half of the extract is lost due to loading of the GPC column. Immediately add 100 mL of 1:1 methylene chloride:acetone.

7.4.2 Place the bottom surface of the tip of the #207 3/4 in. disruptor horn about 1/2 in. below the surface of the solvent, but above the sediment layer.

7.4.3 Sonicate for 3 min, with output control knob set at 10 and with mode switch on Pulse and percent-duty cycle knob set at 50%. Do <u>NOT</u> use microtip probe.

7.4.4 Decant and filter extracts through Whatman No. 41 filter paper using vacuum filtration or centrifuge and decant extraction solvent.

7.4.5 Repeat the extraction two or more times with two additional 100-mL portions of solvent. Decant off the extraction solvent after each sonication. On the final sonication, pour the entire sample into the Buchner funnel and rinse with extraction solvent.

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

7.4.7 Dry the extract by passing it through a drying column containing about 10 cm of anhydrous sodium sulfate. Collect the dried extract in a K-D concentrator. Wash the extractor flask and sodium sulfate column with 100-125 mL of extraction solvent to complete the quantitative transfer.

7.4.8 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 (80-90°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 10-15 min. 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 min.

7.4.9 If a solvent exchange is required (as indicated in Table 1), momentarily remove the Snyder column, add 50 mL of the exchange solvent and a new boiling chip, and re-attach the Snyder column. Concentrate the extract as described in Paragraph 7.4.8, raising the temperature of the water bath, if necessary, to maintain proper distillation.

7.4.10 Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1-2 mL of methylene chloride or exchange solvent. If sulfur crystals are a problem, proceed to Method 3660 for cleanup. The extract may be further concentrated by using the technique outlined in Paragraph 7.4.11 or adjusted to 10.0 mL with the solvent last used.

7.4.11 Add a clean boiling chip and attach a two-ball micro-Snyder column to the concentrator tube. Prewet the column by adding approximately 0.5 mL of methylene chloride or exchange solvent through the top. Place the apparatus in the hot water bath. Adjust the vertical position and the water temperature, as required, to complete the concentration in 5-10 min. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood. When the liquid

TABLE 1. SPECIFIC EXTRACTION CONDITIONS FOR VARIOUS DETERMINATIVE METHODS

Determinative method	Extraction pH	Exchange solvent required for analysis	Exchange solvent required for cleanup	Volume of extract required for cleanup (mL)	Final extract volume for analysis (mL)
8040[a]	as received	2-propanol	hexane	1.0	1.0, 10.0[b]
8060	as received	hexane	hexane	2.0	10.0
8080	as received	hexane	hexane	10.0	10.0
8090	as received	hexane	hexane	2.0	1.0
8100	as received	none	cyclohexane	2.0	1.0
8120	as received	hexane	hexane	2.0	1.0
8140	as received	hexane	hexane	10.0	10.0
8250[a,c]	as received	none	-	-	1.0
8270[a,c]	as received	none	-	-	1.0
8310	as received	acetonitrile	-	-	1.0

[a]To obtain separate acid and base/neutral extracts, Method 3650 should be performed following concentration of the extract to 10.0 mL.

[b]Phenols may be analyzed, by Method 8040, using a 1.0 mL 2-propanol extract by GC/FID. Method 8040 also contains an optional derivatization procedure for phenols which results in a 10 mL hexane extract to be analyzed by GC/ECD.

[c]The specificity of GC/MS may make cleanup of the extracts unnecessary. Refer to Method 3600 for guidance on the cleanup procedures available if required.

reaches an apparent volume of approximately 0.5 mL, remove the apparatus from the water bath and allow to drain and cool for at least 10 min. Remove the micro-Snyder column and rinse its lower joint into the concentrator tube with approximately 0.2 mL of appropriate solvent. Adjust the final volume to the volume required for cleanup or for the determinative method (see Table 1).

7.4.12 Transfer the concentrated extract to a clean screw-cap vial. Seal the vial with a Teflon-lined lid and mark the level on the vial. Label with the sample number and fraction and store in the dark at 4°C until ready for analysis or cleanup.

7.5 Extraction method for samples expected to contain high concentrations of organics (>20 mg/kg):

7.5.1 Transfer approximately 2 g (record weight to the nearest 0.1 g) of sample to a 20-mL vial. Wipe the mouth of the vial with a tissue to remove any sample material. Record the exact weight of sample taken. Cap the vial before proceeding with the next sample to avoid any cross contamination.

7.5.2 Add 2 g of anhydrous sodium sulfate to sample in the 20-mL vial and mix well.

7.5.3 Surrogate standards are added to all samples, spikes, and blanks (see Method 3500 for details on the surrogate standard solution and on the matrix spike solution). Add 2.0 mL of surrogate spiking solution to sample mixture. For the sample in each analytical batch selected for spiking, add 2.0 mL of the matrix spiking standard. For base/neutral-acid analysis, the amount added of the surrogates and matrix spiking compounds should result in a final concentration of 200 ng/uL of each base/neutral analyte and 400 ng/uL of each acid analyte in the extract to be analyzed (assuming a 1 uL injection). If Method 3640, Gel-permeation cleanup, is to be used, add twice the volume of surrogates and matrix spiking compounds since half the extract is lost due to loading of the GPC column.

7.5.4 Immediately add whatever volume of solvent is necessary to bring the final volume to 10.0 mL considering the added volume of surrogates and matrix spikes. Disrupt the sample with the 1/8-in. tapered microtip ultrasonic probe for 2 min at output control setting 5 and with mode switch on pulse and percent duty cycle of 50%. Extraction solvents are:

1. Nonpolar compounds, i.e., organochlorine pesticides and PCBs: hexane.

2. Extractable priority pollutants: methylene chloride.

7.5.5 Loosely pack disposable Pasteur pipets with 2- to 3-cm Pyrex glass-wool plugs. Filter the extract through the glass wool and collect

5.0 mL in a concentrator tube if further concentration is required. Follow Paragraphs 7.4.6 through 7.4.12 for details on concentration. Normally, the 5.0 mL extract is concentrated to 1.0 mL.

7.5.6 The extract is ready for cleanup or analysis, depending on the extent of interfering co-extractives.

8.0 QUALITY CONTROL

8.1 Any reagent blanks or matrix spike samples should be subject to exactly the same analytical procedures as those used on actual samples.

8.2 Refer to Chapter One for specific quality control procedures and Method 3500 for extraction and sample preparation procedures.

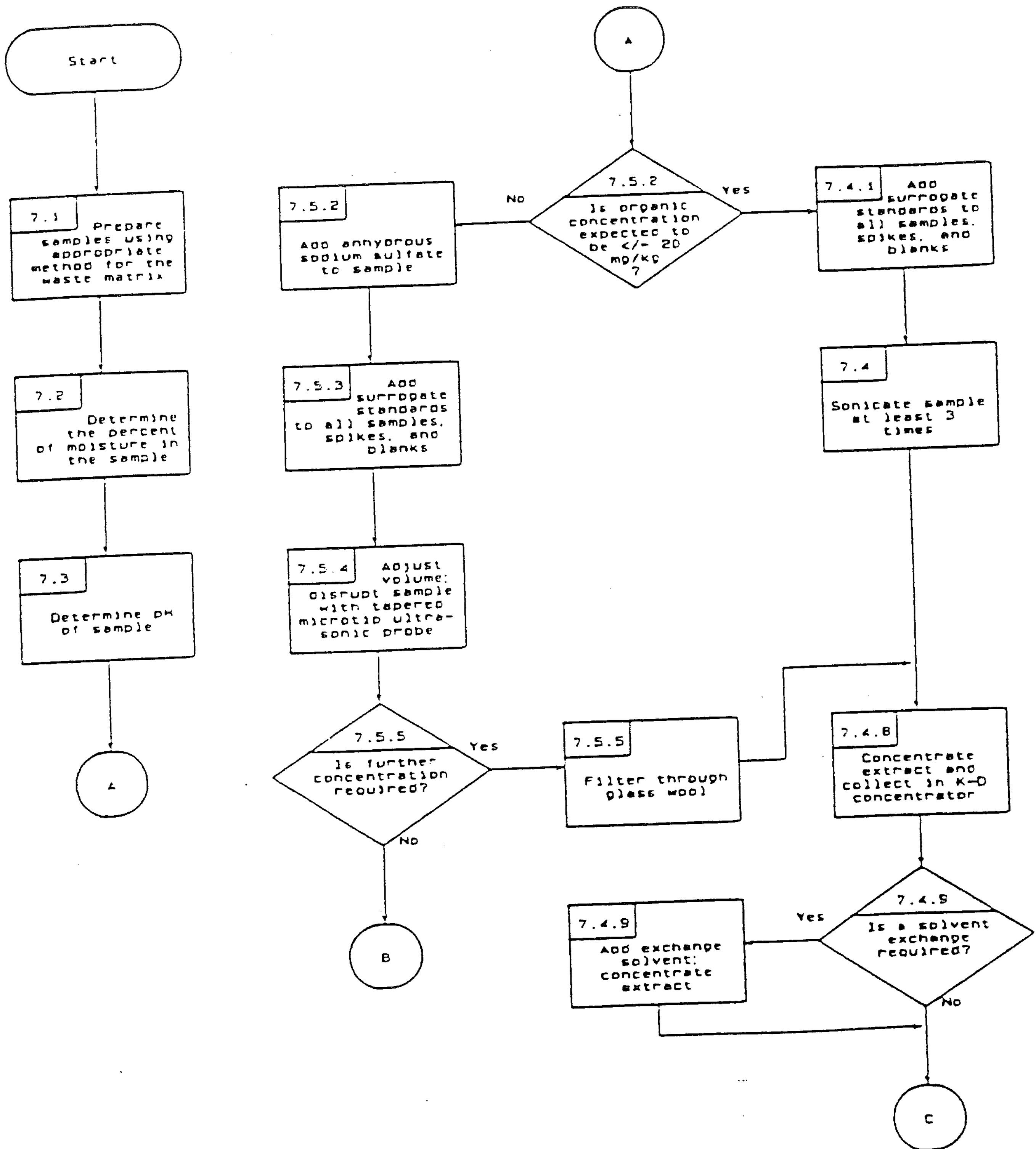
9.0 METHOD PERFORMANCE

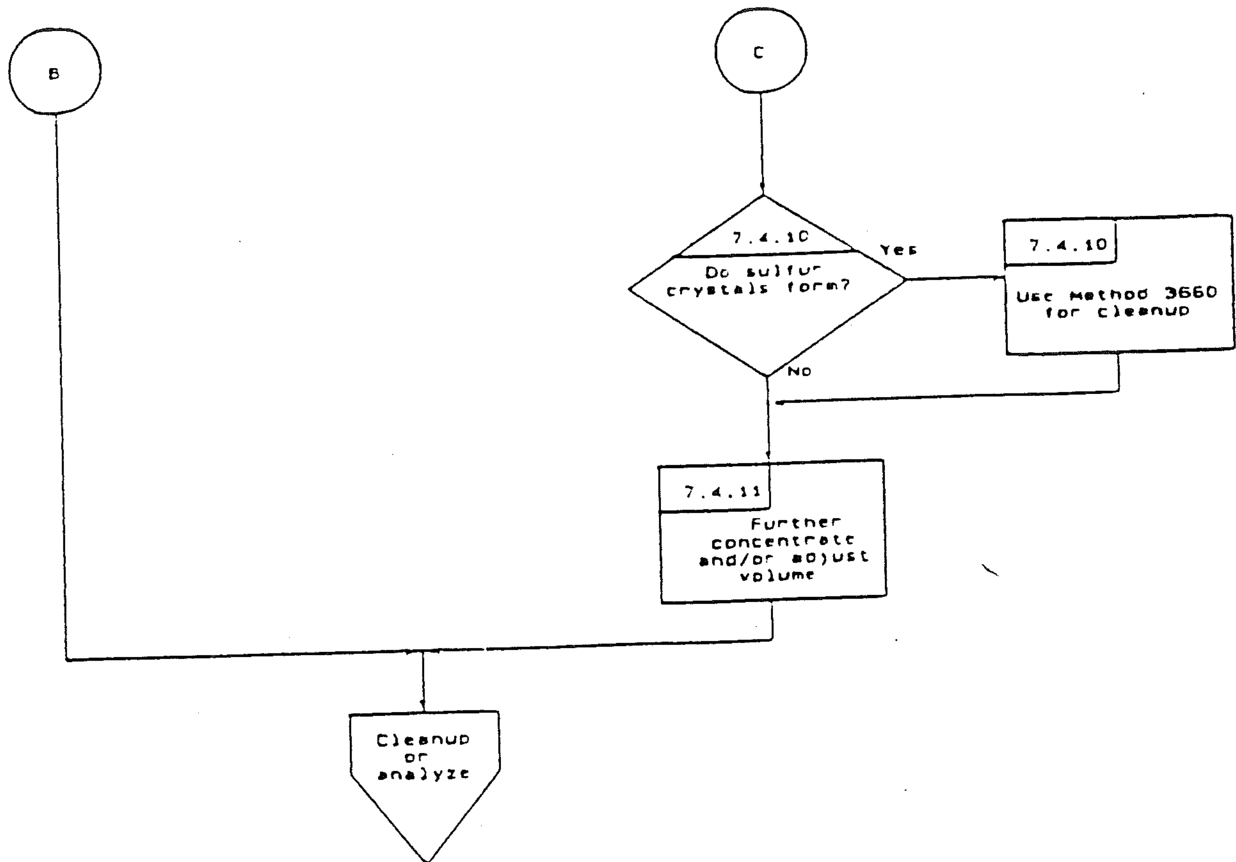
9.1 Refer to the determinative methods for performance data.

10.0 REFERENCES

1. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.

2. U.S. EPA, Interlaboratory Comparison Study: Methods for Volatile and Semi-Volatile Compounds, Environmental Monitoring Systems Laboratory, Office of Research and Development, Las Vegas, NV, EPA 600/4-84-027, 1984.


Start
7.1
Prepare samples using appropriate method for the waste matrix
7.2
Determine the percent of moisture in the sample
7.3
Determine pH of sample
A
A
7.5.2
Is organic concentration expected to be </- 20 mg/kg ?
No
Yes
7.5.2
Add anhydrous sodium sulfate to sample
7.5.3
Add surrogate standards to all samples, spikes, and blanks
7.5.4
Adjust volume: disrupt sample with tapered microtip ultra-sonic probe
7.5.5
Is further concentration required?
Yes
No
B
7.5.5
Filter through glass wool
7.4.1
Add surrogate standards to all samples, spikes, and blanks
7.4
Sonicate sample at least 3 times
7.4.8
Concentrate extract and collect in K-D concentrator
7.4.9
Is a solvent exchange required?
Yes
No
7.4.9
Add exchange solvent; concentrate extract
C


B
C
7.4.10
Do sulfur crystals form?
Yes
No
7.4.10
Use Method 3660 for cleanup
7.4.11
Further concentrate and/or adjust volume
Cleanup or analyze

METHOD 3600

CLEANUP

1.0 SCOPE AND APPLICATION

1.1 General

1.1.1 Injection of extracts into a gas or liquid chromatograph can cause extraneous peaks, deterioration of peak resolution and column efficiency, and loss of detector sensitivity and can greatly shorten the lifetime of expensive columns. The following techniques have been applied to extract purification: partitioning between immiscible solvents; adsorption chromatography; gel permeation chromatography; chemical destruction of interfering substances with acid, alkali, or oxidizing agents; and distillation. These techniques may be used individually or in various combinations, depending on the extent and nature of the co-extractives.

1.1.2 It is an unusual situation (e.g. with some water samples) when extracts can be directly determined without further treatment. Soil and waste extracts often require a combination of cleanup methods. For example, when analyzing for organochlorine pesticides and PCBs, it may be necessary to use gel permeation chromatography (GPC), to eliminate the high boiling material and a micro alumina or Florisil column to eliminate interferences with the analyte peaks on the GC/ECD.

1.2 Specific

1.2.1 Adsorption column chromatography - Alumina (Methods 3610 and 3611), Florisil (Method 3620), and silica gel (Method 3630) are useful for separating analytes of a relatively narrow polarity range away from extraneous, interfering peaks of a different polarity.

1.2.2 Acid-base partitioning - Useful for separating acidic or basic organics from neutral organics. It has been applied to analytes such as the chlorophenoxy herbicides and phenols.

1.2.3 Gel permeation chromatography (GPC) - The most universal cleanup technique for a broad range of semivolatile organics and pesticides. It is capable of separating high molecular-weight material from the sample analytes. It has been used successfully for all the semivolatile base, neutral, and acid compounds associated with the EPA Priority Pollutant and the Superfund Hazardous Substance Lists. GPC is usually not applicable for eliminating extraneous peaks on a chromatogram which interfere with the analytes of interest.

1.2.4 Sulfur cleanup - Useful in eliminating sulfur from sample extracts, which may cause chromatographic interference with analytes of interest.

1.2.5 Table 1 indicates the recommended cleanup techniques for the indicated groups of compounds. This information can also be used as guidance for compounds that are not listed. Compounds that are chemically similar to these groups of compounds should follow a similar elution pattern.

2.0 SUMMARY OF METHOD

2.1 Refer to the specific cleanup method for a summary of the procedure.

3.0 INTERFERENCES

3.1 Analytical interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware. All of these materials must be routinely demonstrated to be free of interferences, under the conditions of the analysis, by running laboratory reagent blanks.

3.2 More extensive procedures than those outlined in the methods may be necessary for reagent purification.

4.0 APPARATUS AND MATERIALS

4.1 Refer to the specific cleanup method for apparatus and materials needed.

5.0 REAGENTS

5.1 Refer to the specific cleanup method for the reagents needed.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Step 4.1.

7.0 PROCEDURE

7.1 Prior to using the cleanup procedures, samples should undergo solvent extraction. Chapter Two, Step 2.3.3, may be used as a guide for choosing the appropriate extraction procedure based on the physical composition of the waste and on the analytes of interest in the matrix (see also Method 3500 for a general description of the extraction technique). For some organic liquids, extraction prior to cleanup may not be necessary.

7.2 In most cases, the extracted sample is then analyzed by one of the determinative methods available in Step 4.3 of this chapter. If the analytes of interest are not able to be determined due to interferences, cleanup is performed.

7.3 Many of the determinative methods specify cleanup methods that should be used when determining particular analytes (e.g. Method 8060, gas chromatography of phthalate esters, recommends using either Method 3610

(Alumina column cleanup) or Method 3620 (Florisil column cleanup) if interferences prevent analysis). However, the experience of the analyst may prove invaluable in determining which cleanup methods are needed. As indicated in Section 1.0 of this method, many matrices may require a combination of cleanup procedures in order to ensure proper analytical determinations.

7.4 Guidance for cleanup is specified in each of the methods that follow. The amount of extract cleanup required prior to the final determination depends on the selectivity of both the extraction procedure and the determinative method and the required detection limit.

7.5 Following cleanup, the sample is concentrated to whatever volume is required in the determinative method. Analysis follows as specified in the determinative procedure (Step 4.3 of this Chapter).

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures.

8.2 The analyst must demonstrate that the compounds of interest are being quantitatively recovered by the cleanup technique before the cleanup is applied to actual samples.

8.2 For sample extracts that are cleaned up, the associated quality control samples (e.g. spikes, blanks, replicates, and duplicates) must also be processed through the same cleanup procedure.

8.3 The analysis using each determinative method (GC, GC/MS, HPLC) specifies instrument calibration procedures using stock standards. It is recommended that cleanup also be performed on a series of the same type of standards to validate chromatographic elution patterns for the compounds of interest and to verify the absence of interferences from reagents.

9.0 METHOD PERFORMANCE

9.1 Refer to the specific cleanup method for performance data.

10.0 REFERENCES

10.1 Refer to the specific cleanup method.

TABLE 1.
RECOMMENDED CLEANUP TECHNIQUES FOR INDICATED GROUPS OF COMPOUNDS

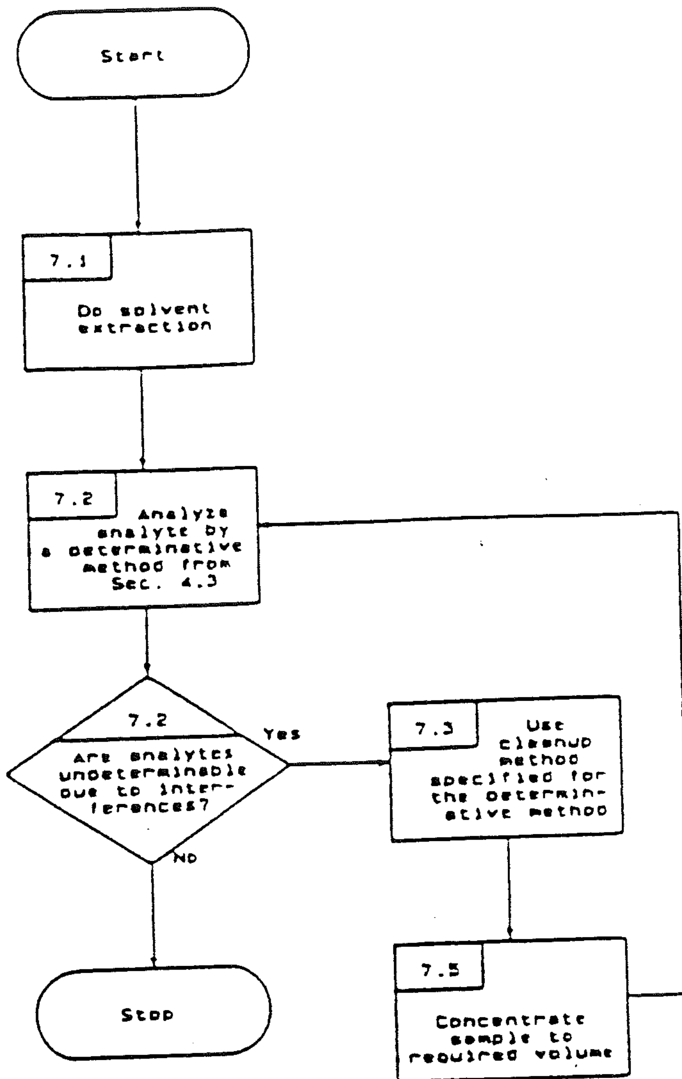
Analyte Group	Determinative[a] Method	Cleanup Method Option
Phenols	8040	3630[b], 3640, 3650, 8040[c]
Phthalate esters	8060	3610, 3620, 3640
Nitrosamines	8070	3610, 3620, 3640
Organochlorine pesticides & PCBs	8080	3620, 3640, 3660
Nitroaromatics and cyclic ketones	8090	3620, 3640
Polynuclear aromatic hydrocarbons	8100	3611, 3630, 3640
Chlorinated hydrocarbons	8120	3620, 3640
Organophosphorous pesticides	8140	3620
Chlorinated herbicides	8150	8150[d]
Priority pollutant semivolatiles	8250, 8270	3640, 3650, 3660
Petroleum waste	8250, 8270	3611, 3650

a The GC/MS Methods, 8250 and 8270, are also appropriate determinative methods for all analyte groups, unless lower detection limits are required.

b Cleanup applicable to derivatized phenols.

c Method 8040 includes a derivatization technique followed by GC/ECD analysis, if interferences are encountered using GC/FID.

d Method 8150 incorporates an acid-base cleanup step as an integral part of the method.


Start
7.1
Do solvent extraction
7.2
Analyze analyte by a determinative method from Sec. 4.3
7.2
Are analytes undeterminable due to interferences?
Yes
No
7.3
Use cleanup method specified for the determinative method
7.5
Concentrate sample to required volume
Stop

METHOD 3620

FLORISIL COLUMN CLEANUP

1.0 SCOPE AND APPLICATION

1.1 Florisil, a registered tradename of the Floridin Co., is a magnesium silicate with acidic properties. It is used for general column chromatography as a cleanup procedure prior to sample analysis by gas chromatography.

1.2 General applications: Cleanup of pesticide residues and other chlorinated hydrocarbons; the separation of nitrogen compounds from hydrocarbons; the separation of aromatic compounds from aliphatic-aromatic mixtures; and similar applications for use with fats, oils, and waxes (Floridin). Additionally, Florisil is considered good for separations with steroids, esters, ketones, glycerides, alkaloids, and some carbohydrates (Gordon and Ford).

1.3 Specific applications: This method includes guidance for cleanup of sample extracts containing the following analyte groups: phthalate esters; nitrosamines; organochlorine pesticides; nitroaromatics; haloethers; chlorinated hydrocarbons; and organophosphorous pesticides.

2.0 SUMMARY OF METHOD

2.1 The column is packed with the required adsorbent, topped with a water adsorbent, and then loaded with the sample to be analyzed. Elution is effected with a suitable solvent(s) leaving the interfering compounds on the column. The eluate is then concentrated.

3.0 INTERFERENCES

3.1 A reagent blank should be performed for the compounds of interest prior to the use of this method. The level of interferences must be below the method detection limit before this method is performed on actual samples.

3.2 More extensive procedures than those outlined in this method may be necessary for reagent purification.

4.0 APPARATUS AND MATERIALS

4.1 Beaker: 500-mL.

4.2 Chromatographic column: 300-mm long x 10-mm I.D. or 400-mm long x 20-mm I.D., to be specified in Paragraph 7.0; with Pyrex glass wool at bottom and a Teflon stopcock.

NOTE: Fritted glass discs are difficult to decontaminate after highly contaminated extracts have been passed through. Columns without frits

may be purchased. Use a small pad of Pyrex glass wool to retain the adsorbent. Prewash the glass wool pad with 50 mL of acetone followed by 50 mL of elution solvent prior to packing the column with adsorbent.

4.3 Kuderna-Danish (K-D) apparatus

4.3.1 **Concentrator tube:** 10-mL, graduated (Kontes K-570050-1025 or equivalent). Ground-glass stopper is used to prevent evaporation of extracts.

4.3.2 **Evaporation flask:** 500-mL (Kontes K-570001-0500 or equivalent). Attach to concentrator tube with springs.

4.3.3 **Snyder column:** Three-ball macro (Kontes K-503000-0121 or equivalent).

4.3.4 **Snyder column:** Two-ball micro (Kontes K-569001-0219 or equivalent).

4.4 Muffle furnace.

4.5 Reagent bottle: 500-mL.

4.6 Water bath: Heated, with concentric ring cover, capable of temperature control (±5°C). The bath should be used in a hood.

4.7 Boiling chips: Solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).

4.8 Erlenmeyer flasks: 50- and 250-mL.

5.0 REAGENTS

5.1 Florisil: Pesticide residue (PR) grade (60/100 mesh); purchase-activated at 1250°F (677°C), stored in glass containers with ground-glass stoppers or foil-lined screw caps.

5.1.1 **Deactivation of Florisil:** for cleanup of phthalate esters. To prepare for use, place 100 g of Florisil into a 500-mL beaker and heat for approximately 16 hr at 40°C. After heating, transfer to a 500-mL reagent bottle. Tightly seal and cool to room temperature. When cool add 3 mL of reagent water. Mix thoroughly by shaking or rolling for 10 min and let stand for at least 2 hr. Keep the bottle sealed tightly.

5.1.2 **Activation of Florisil:** for cleanup of nitrosamines, organochlorine pesticides and PCBs, nitroaromatics, haloethers, chlorinated hydrocarbons, and organophosphorous pesticides. Just before use, activate each batch at least 16 hr at 130°C in a glass container loosely covered with aluminum foil. Alternatively, store the Florisil in an oven at 130°C. Cool the Florisil before use in a desiccator.

(Florisil from different batches or sources may vary in adsorptive capacity. To standardize the amount of Florisil which is used, the use of lauric acid value is suggested. The referenced procedure determines the adsorption from hexane solution of lauric acid (mg) per g of Florisil. The amount of Florisil to be used for each column is calculated by dividing 110 by this ratio and multiplying by 20 g (Mills).)

5.2 Sodium sulfate (ACS): Granular, anhydrous (purified by heating at 400°C for 4 hr in a shallow tray).

5.3 Eluting solvents:

5.3.1 Diethyl ether: Pesticide quality or equivalent.

5.3.1.1 Must be free of peroxides as indicated by EM Quant test strips (available from EM Laboratories Inc., 500 Executive Boulevard, Elmsford, NY 10523).

5.3.1.2 Procedures recommended for removal of peroxides are provided with the test strips. After cleanup, 20 mL ethyl alcohol preservative must be added to each liter of ether.

5.3.2 Acetone; hexane; methylene chloride; pentane; petroleum ether (boiling range 30-60°C): Pesticide quality or equivalent.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 Phthalate esters:

7.1.1 Reduce the sample extract volume to 2 mL prior to cleanup. The extract solvent must be hexane.

7.1.2 Place 10 g of Florisil into a 10-mm I.D. chromatographic column. Tap the column to settle the Florisil and add 1 cm of anhydrous sodium sulfate to the top.

7.1.3 Preelute the column with 40 mL of hexane. The rate for all elutions should be about 2 mL/min. Discard the eluate and, just prior to exposure of the sodium sulfate layer to the air, quantitatively transfer the 2-mL sample extract onto the column using an additional 2 mL of hexane to complete the transfer. Just prior to exposure of the sodium sulfate layer to the air, add 40 mL of hexane and continue the elution of the column. Discard this hexane eluate.

7.1.4 Next, elute the column with 100 mL of 20% ethyl ether in hexane (v/v) into a 500-mL K-D flask equipped with a 10-mL concentrator tube. Concentrate the collected fraction. No solvent exchange is necessary. Adjust the volume of the cleaned-up extract to whatever volume is required (10 mL for Method 8060) and analyze by gas chromatography. Compounds that elute in this fraction are:

Bis(2-ethylhexyl)phthalate
Butyl benzyl phthalate
Di-n-butyl phthalate
Diethyl phthalate
Dimethyl phthalate
Di-n-octyl phthalate

7.2 Nitrosamines:

7.2.1 Reduce the sample extract volume to 2 mL prior to cleanup.

7.2.2 Place 22 g of activated Florisil into a 20-mm I.D. chromatographic column. Tap the column to settle the Florisil and add about 5 mm of anhydrous sodium sulfate to the top.

7.2.3 Preelute the column with 40 mL of ethyl ether/pentane (15:85) (v/v). Discard the eluate and, just prior to exposure of the sodium sulfate layer to the air, quantitatively transfer the 2-mL sample extract onto the column using an additional 2 mL of pentane to complete the transfer.

7.2.4 Elute the column with 90 mL of ethyl ether/pentane (15:85) (v/v) and discard the eluate. This fraction will contain the diphenylamine, if it is present in the extract.

7.2.5 Next, elute the column with 100 mL of acetone/ethyl ether (5:95) (v/v) into a 500-mL K-D flask equipped with a 10-mL concentrator tube. This fraction will contain all of the nitrosamines listed in the scope of the method.

7.2.6 Add 15 mL of methanol to the collected fraction, concentrate using pentane to prewet the K-D column and set the water bath at 70 to 75°C. When the apparatus is cool, remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 to 2 mL of pentane. Analyze by gas chromatography.

7.3 Organochlorine pesticides, haloethers, and organophosphorous pesticides (see Tables 1 and 2 for fractionation patterns of compounds tested):

7.3.1 Reduce the sample extract volume to 10 mL prior to cleanup. The extract solvent must be hexane.

7.3.2 Add a weight of Florisil (nominally 20 g), predetermined by calibration, to a 20-mm I.D. chromatographic column. Settle the Florisil by tapping the column. Add anhydrous 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 chromatographic column. Discard the eluate.

7.3.3 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 1-2 mL hexane, adding each rinse to the column.

7.3.4 Place a 500-mL K-D flask and clean concentrator tube under the chromatographic 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. All of the haloethers are in this fraction. 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 a third elution using 200 mL of 50% ethyl ether in hexane (v/v) (Fraction 3), and a final elution with 200 mL of 100% ethyl ether (Fraction 4), into separate K-D flasks.

7.3.5 Concentrate the eluates by standard K-D techniques using the water bath at about 85°C (75°C for Fraction 4). Adjust the final volume to whatever volume is required (1-10 mL). Analyze by gas chromatography.

7.4 Nitroaromatics and isophorone:

7.4.1 Reduce the sample extract volume to 2 mL prior to cleanup.

7.4.2 Prepare a slurry of 10 g activated Florisil in methylene chloride/hexane (1:9) (v/v) and place the Florisil into a 10-mm I.D. chromatographic column. Tap the column to settle the Florisil and add 1 cm of anhydrous sodium sulfate to the top. Adjust the elution rate to about 2 mL/min.

7.4.3 Just prior to exposure of the sodium sulfate layer to the air, quantitatively transfer the sample extract onto the column using an additional 2 mL of hexane to complete the transfer. Just prior to exposure of the sodium sulfate layer to the air, add 30 mL of methylene chloride/hexane (1:9) (v/v) and continue the elution of the column. Discard the eluate.

7.4.4 Next, elute the column with 30 mL of acetone/methylene chloride (1:9) (v/v) into a 500-mL K-D flask equipped with a 10-mL concentrator tube. Concentrate the collected fraction, while exchanging the solvent to hexane. To exchange the solvent, reduce the elution solvent to about 10 mL. Add 50 mL of hexane, a fresh boiling chip, and return the reassembled K-D apparatus to the hot water bath. Adjust the

TABLE 1

DISTRIBUTION OF CHLORINATED PESTICIDES, PCBs, AND HALOETHERS INTO FLORISIL COLUMN FRACTIONS

Parameter	Percent Recovery by Fraction[a]		
	1	2	3
Aldrin	100		
α-BHC	100		
β-BHC	97		
δ-BHC	98		
γ-BHC	100		
Chlordane	100		
4,4'-DDD	99		
4,4'-DDE	98		
4,4'-DDT	100		
Dieldrin	0	100	
Endosulfan I	37	64	
Ensosulfan II	0	7	91
Endosulfan sulfate	0	0	106
Endrin	4	96	
Endrin aldehyde	0	68	26
Haloethers	R		
Heptachlor	100		
Heptachlor epoxide	100		
Toxaphene	96		
PCB-1016	97		
PCB-1221	97		
PCB-1232	95	4	
PCB-1242	97		
PCB-1248	103		
PCB-1254	90		
PCB-1260	95		

[a]Eluant composition: Fraction 1 - 6% ethyl ether in hexane
Fraction 2 - 15% ethyl ether in hexane
Fraction 3 - 50% ethyl ether in hexane

R = Recovered (no percent recovery data presented).

SOURCE: U.S. EPA and FDA data.

TABLE 2

DISTRIBUTION OF ORGANOPHOSPHOROUS PESTICIDES INTO FLORISIL COLUMN FRACTIONS

Parameter	Percent Recovery by Fraction[a]			
	1	2	3	4
Azinophos methyl			20	80
Bolstar (Sulprofos)	ND	ND	ND	ND
Chlorpyrifos	>80			
Coumaphos	NR	NR	NR	
Demeton	100			
Diazinon		100		
Dichlorvos	NR	NR	NR	
Dimethoate	ND	ND	ND	ND
Disulfoton	25-40			
EPN		>80		
Ethoprop	V	V	V	
Fensulfothion	ND	ND	ND	ND
Fenthion	R	R		
Malathion		5	95	
Merphos	V	V	V	
Mevinphos	ND	ND	ND	ND
Monochrotophos	ND	ND	ND	ND
Naled	NR	NR	NR	
Parathion		100		
Parathion methyl		100		
Phorate	0-62			
Ronnel	>80			
Stirophos (Tetrachlorvinphos)	ND	ND	ND	ND
Sulfotepp	V	V		
TEPP	ND	ND	ND	ND
Tokuthion (Prothiofos)	>80			
Trichloronate	>80			

[a]Eluant composition: Fraction 1 - 200 mL of 6% ethyl ether in hexane
Fraction 2 - 200 mL of 15% ethyl ether in hexane
Fraction 3 - 200 mL of 50% ethyl ether in hexane
Fraction 4 - 200 mL of 100% ethyl ether

R = Recovered (no percent recovery information presented) (U.S. FDA).
NR = Not recovered (U.S. FDA).
V = Variable recovery (U.S. FDA).
ND = Not determined.

SOURCE: U.S. EPA and FDA data.

final volume of the cleaned-up extract to whatever volume is required (1-10 mL). Compounds that elute in this fraction are:

2,4-Dinitrotoluene
2,6-Dinitrotoluene
Isophorone
Nitrobenzene.

Analyze by gas chromatography.

7.5 Chlorinated hydrocarbons:

7.5.1 Reduce the sample extract volume to 2 mL prior to cleanup. The extract solvent must be hexane.

7.5.2 Place 12 g of Florisil into a 10-mm I.D. chromatographic column. Tap the column to settle the Florisil and add 1 to 2 cm of anhydrous sodium sulfate to the top.

7.5.3 Preelute the column with 100 mL of petroleum ether. Discard the eluate and, just prior to exposure of the sodium sulfate layer to the air, quantitatively transfer the sample extract to the column by decantation and subsequent petroleum ether washings. Discard the eluate. Just prior to exposure of the sodium sulfate layer to the air, begin eluting the column with 200 mL of petroleum ether and collect the eluate in a 500-mL K-D flask equipped with a 10-mL concentrator tube. This fraction should contain all of the chlorinated hydrocarbons:

2-Chloronaphthalene
1,2-Dichlorobenzene
1,3-Dichlorobenzene
1,4-Dichlorobenzene
Hexachlorobenzene
Hexachlorobutadiene
Hexachlorocyclopentadiene
Hexachloroethane
1,2,4-Trichlorobenzene.

7.5.4 Concentrate the fraction, using hexane to prewet the column. When the apparatus is cool, remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with hexane. Adjust the final volume of the cleaned-up extract to whatever volume is required (1-10 mL). Analyze by gas chromatography.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures and Method 3600 for cleanup procedures.

8.2 The analyst should demonstrate that the compounds of interest are being quantitatively recovered before applying this method to actual samples.

8.3 For sample extracts that are cleaned up using this method, the associated quality control samples should also be processed through this cleanup method.

9.0 METHOD PERFORMANCE

9.1 Table 1 indicates the distribution of chlorinated pesticides, PCB's, and haloethers in various Florisil column fractions.

9.2 Table 2 indicates the distribution of organophosphorous pesticides in various Florisil column fractions.

10.0 REFERENCES

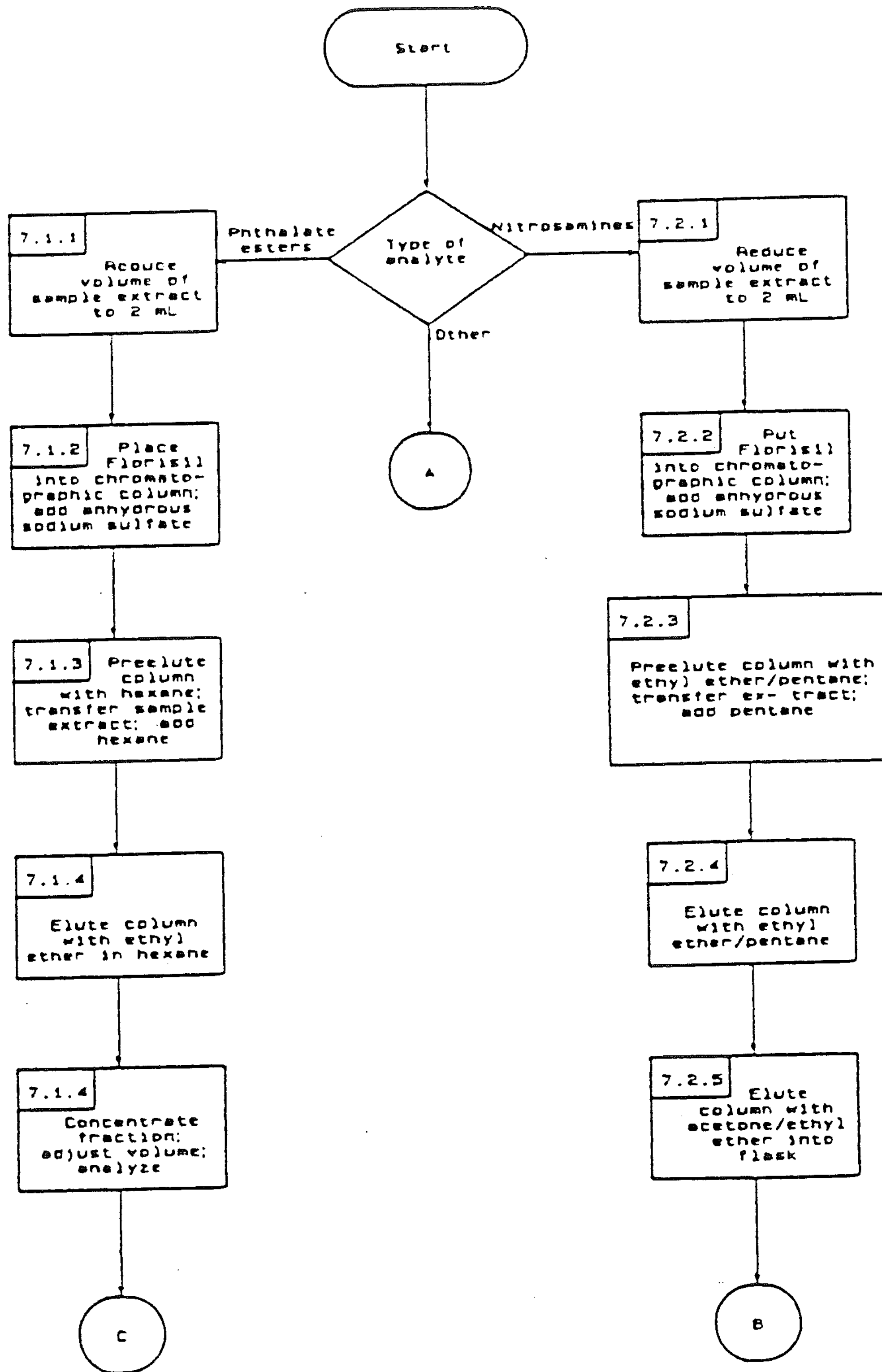
1. Gordon, A.J. and R.A. Ford, The Chemist's Companion: A Handbook of Practical Data, Techniques, and References (New York: John Wiley & Sons, Inc.), pp. 372, 374, and 375, 1972.

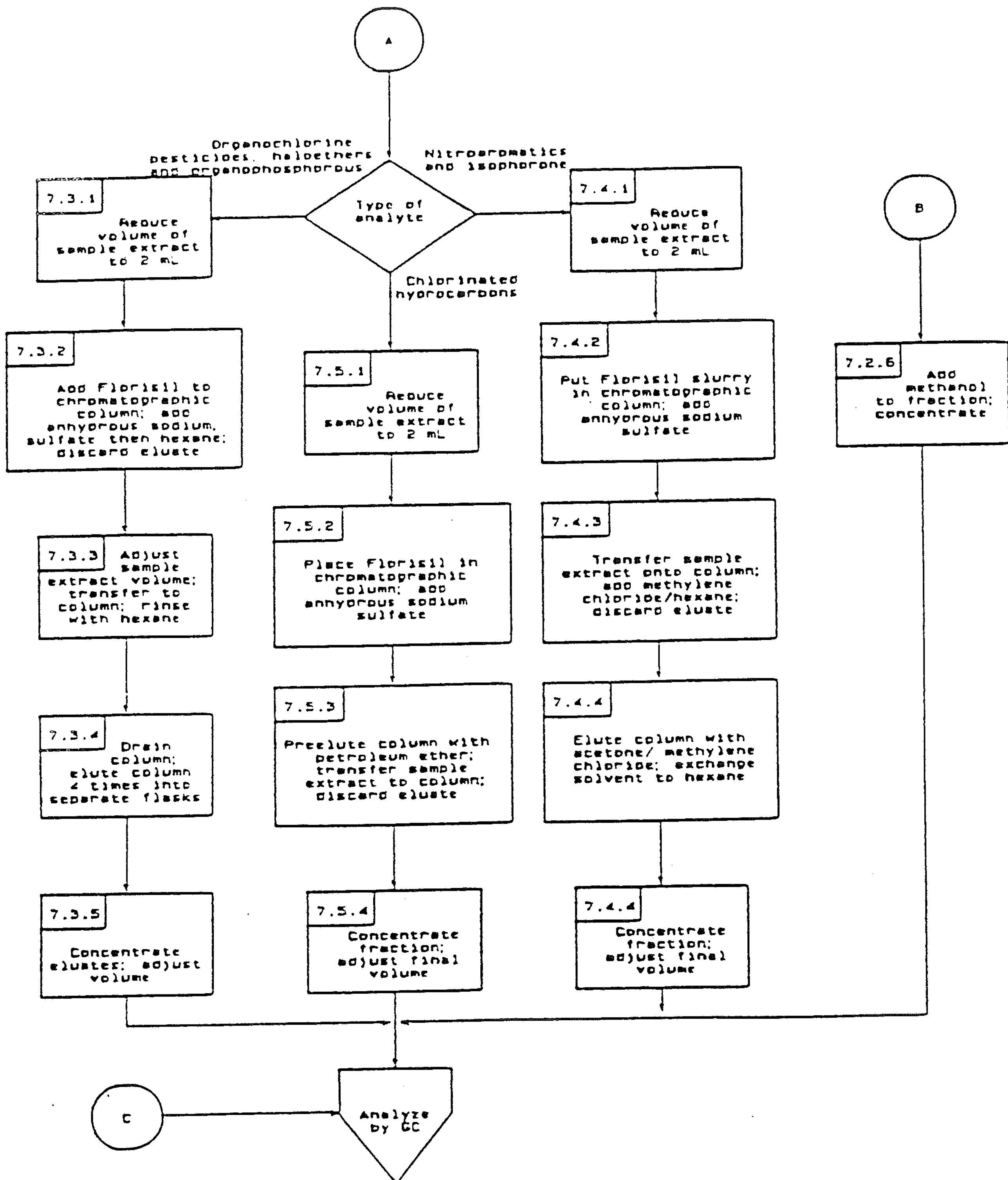
2. Floridin of ITT System, Florisil: Properties, Application, Bibliography, Pittsburgh, Pennsylvania, 5M381DW.

3. Mills, P.A., "Variation of Florisil Activity; Simple Method for Measuring Absorbent Capacity and its use in Standardizing Florisil Columns," Journal of the Association of Official Analytical Chemists, 51, 29, 1968.

4. U.S. Food and Drug Association, Pesticides Analytical Manual (Volume 1), July 1985.

5. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.


Start
Type of analyte
Phthalate esters
Nitrosamines
Other
7.1.1
Reduce volume of sample extract to 2 mL
7.1.2
Place Florisil into chromato-graphic column; add anhydrous sodium sulfate
7.1.3
Preelute column with hexane; transfer sample extract; add hexane
7.1.4
Elute column with ethyl ether in hexane
7.1.4
Concentrate fraction; adjust volume; analyze
C
A
7.2.1
Reduce volume of sample extract to 2 mL
7.2.2
Put Florisil into chromato-graphic column; add anhydrous sodium sulfate
7.2.3
Preelute column with ethyl ether/pentane; transfer ex- tract; add pentane
7.2.4
Elute column with ethyl ether/pentane
7.2.5
Elute column with acetone/ethyl ether into flask
B


A
Organochlorine pesticides, haloethers and organophosphorous
Type of analyte
Nitroaromatics and isophorone
Chlorinated hydrocarbons
7.3.1
Reduce volume of sample extract to 2 mL
7.3.2
Add Florisil to chromatographic column; add anhydrous sodium sulfate then hexane; discard eluate
7.3.3
Adjust sample extract volume; transfer to column; rinse with hexane
7.3.4
Drain column; elute column 4 times into separate flasks
7.3.5
Concentrate eluates; adjust volume
7.5.1
Reduce volume of sample extract to 2 mL
7.5.2
Place Florisil in chromatographic column; add anhydrous sodium sulfate
7.5.3
Preelute column with petroleum ether; transfer sample extract to column; discard eluate
7.5.4
Concentrate fraction; adjust final volume
7.4.1
Reduce volume of sample extract to 2 mL
7.4.2
Put Florisil slurry in chromatographic column; add anhydrous sodium sulfate
7.4.3
Transfer sample extract onto column; add methylene chloride/hexane; discard eluate
7.4.4
Elute column with acetone/ methylene chloride; exchange solvent to hexane
7.4.4
Concentrate fraction; adjust final volume
B
7.2.6
Add methanol to fraction; concentrate
C
Analyze by GC

METHOD 3660

SULFUR CLEANUP

1.0 SCOPE AND APPLICATION

1.1 Elemental sulfur is encountered in many sediment samples (generally specific to different areas in the country), marine algae, and some industrial wastes. The solubility of sulfur in various solvents is very similar to the organochlorine and organophosphorous pesticides; therefore, the sulfur interference follows along with the pesticides through the normal extraction and cleanup techniques. In general, sulfur will usually elute entirely in Fraction 1 of the Florisil cleanup (Method 3620).

1.2 Sulfur will be quite evident in gas chromatograms obtained from electron capture detectors, flame photometric detectors operated in the sulfur or phosphorous mode, and Coulson electrolytic conductivity detectors in the sulfur mode. If the gas chromatograph is operated at the normal conditions for pesticide analysis, the sulfur interference can completely mask the region from the solvent peak through Aldrin.

1.3 Three techniques for the elimination of sulfur are detailed within this method: (1) the use of copper powder; (2) the use of mercury; and (3) the use of tetrabutylammonium-sulfite. Tetrabutylammonium-sulfite causes the least amount of degradation of a broad range of pesticides and organic compounds, while copper and mercury may degrade organophosporous and some organochlorine pesticides.

2.0 SUMMARY OF METHOD

2.1 The sample to undergo cleanup is mixed with either copper, mercury, or tetrabutylammonium (TBA)-sulfite. The mixture is shaken and the extract is removed from the sulfur cleanup reagent.

3.0 INTERFERENCES

3.1 Removal of sulfur using copper:

3.1.1 The copper must be very reactive; therefore, all oxides of copper must be removed so that the copper has a shiny, bright appearance.

3.1.2 The sample extract must be vigorously agitated with the reactive copper for at least one minute.

4.0 APPARATUS AND MATERIALS

4.1 Mechanical shaker or mixer: Such as the Vortex Genie.

4.2 Pipets: Disposable, Pasteur type.

4.3 Centrifuge tubes: Calibrated, 12-mL.

4.4 Glass bottles or vials: 10-mL and 50-mL, with Teflon-lined screw-caps.

5.0 REAGENTS

5.1 Reagent water: Reagent water is defined as water in which an interferent is not observed at the method detection limit of the compounds of interest.

5.2 Nitric acid: Dilute.

5.3 Acetone, hexane, 2-propanol: Pesticide quality or equivalent.

5.4 Copper powder: Remove oxides by treating with dilute nitric acid, rinse with distilled water to remove all traces of acid, rinse with acetone and dry under a stream of nitrogen. (Copper, fine granular Mallinckrodt 4649 or equivalent).

5.5 Mercury: Triple distilled.

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

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 Removal of sulfur using copper:

7.1.1 Concentrate the sample to exactly 1.0-mL in the Kuderna-Danish tube.

7.1.2 If the sulfur concentration is such that crystallization occurs, centrifuge to settle the crystals, and carefully draw off the sample extract with a disposable pipet leaving the excess sulfur in the K-D tube. Transfer the extract to a calibrated centrifuge tube.

7.1.3 Add approximately 2 g of cleaned copper powder (to the 0.5 mL mark) to the centrifuge tube. Mix for at least 1 min on the mechanical shaker.

7.1.4 Separate the extract from the copper by drawing off the extract with a disposable pipet and transfer to a clean vial. The volume remaining still represents 1.0 mL of extract.

NOTE: This separation is necessary to prevent further degradation of the pesticides.

7.2 Removal of sulfur using mercury:

NOTE: Mercury is a highly toxic metal and therefore, must be used with great care. Prior to using mercury, it is recommended that the analyst become acquainted with proper handling and cleanup techniques associated with this metal.

7.2.1 Concentrate the sample extract to exactly 1.0 mL.

7.2.2 Pipet 1.0 mL of the extract into a clean concentrator tube or Teflon-sealed vial.

7.2.3 Add one to three drops of mercury to the vial and seal. Agitate the contents of the vial for 15-30 sec. Prolonged shaking (2 hr) may be required. If so, use a mechanical shaker.

7.2.4 Separate the sample from the mercury by drawing off the extract with a disposable pipet and transfer to a clean vial.

7.3 Removal of sulfur using TBA-sulfite:

7.3.1 Concentrate the sample extract to exactly 1.0 mL.

7.3.2 Transfer the 1.0 mL to a 50-mL clear glass bottle or vial with a Teflon-lined screw-cap. Rinse the concentrator tube with 1 mL of hexane, adding the rinsings to the 50-mL bottle.

7.3.3 Add 1.0 mL TBA-sulfite reagent and 2 mL 2-propanol, cap the bottle, and shake for at least 1 min. If the sample is colorless or if the initial color is unchanged, and if clear crystals (precipitated sodium sulfite) are observed, sufficient sodium sulfite is present. If the precipitated sodium sulfite disappears, add more crystalline sodium sulfite in approximately 100-mg portions until a solid residue remains after repeated shaking.

7.3.4 Add 5 mL distilled water and shake for at least 1 min. Allow the sample to stand for 5-10 min. Transfer the hexane layer (top) to a concentrator tube and use the K-D technique to concentrate the extract to 1.0 mL.

7.4 Analyze the cleaned up extracts by gas chromatography (see the determinative methods, Section 4.3 of this chapter).

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures and Method 3600 for cleanup procedures.

8.2 All reagents should be checked prior to use to verify that interferences do not exist.

9.0 METHOD PERFORMANCE

9.1 Table 1 indicates the effect of using copper and mercury to remove sulfur on the recovery of certain pesticides.

10.0 REFERENCES

1. Loy, E.W., private communication.

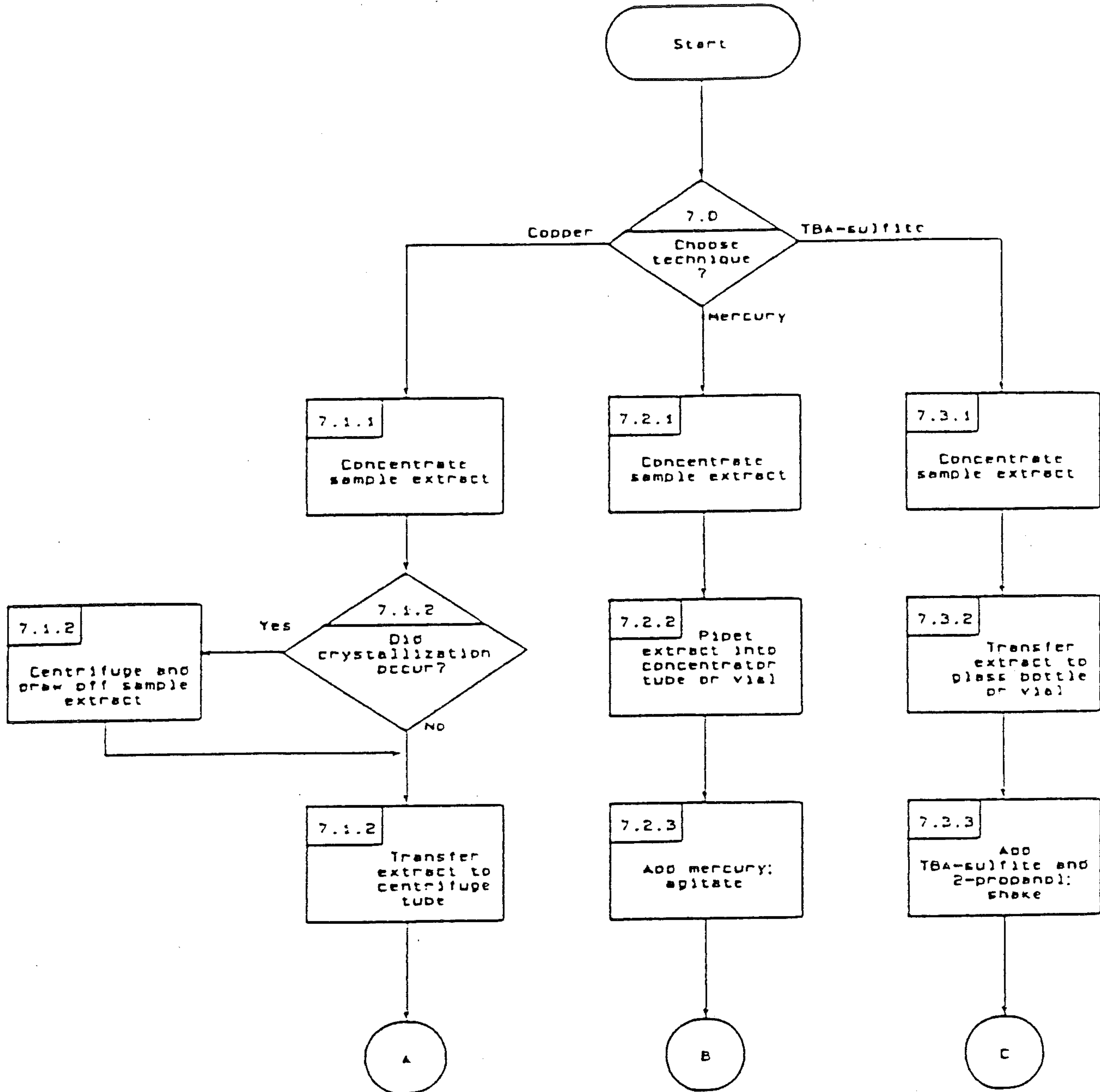
2. Goerlitz, D.F. and L.M. Law, Bulletin for Environmental Contamination and Toxicology, 6, 9 (1971).

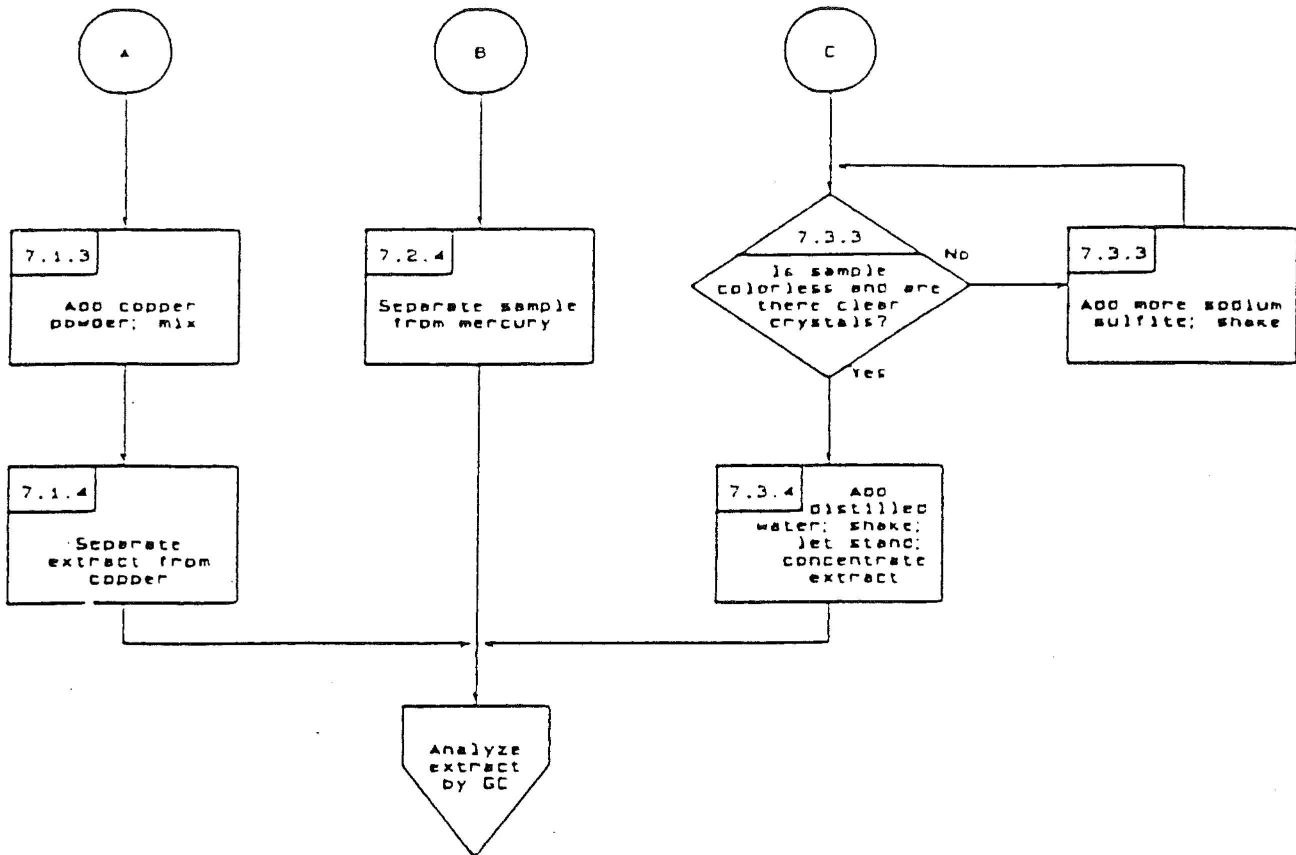
3. U.S. EPA Contract Laboratory Program, Statement of Work for Organic Analysis, Revision, July 1985.

Table 1. EFFECT OF MERCURY AND COPPER ON PESTICIDES

Pesticide	Percent Recovery[a] using: Mercury	Copper
Aroclor 1254	97.10	104.26
Lindane	75.73	94.83
Heptachlor	39.84	5.39
Aldrin	95.52	93.29
Heptachlor epoxide	69.13	96.55
DDE	92.07	102.91
DDT	78.78	85.10
BHC	81.22	98.08
Dieldrin	79.11	94.90
Endrin	70.83	89.26
Chlorobenzilate	7.14	0.00
Malathion	0.00	0.00
Diazinon	0.00	0.00
Parathion	0.00	0.00
Ethion	0.00	0.00
Trithion	0.00	0.00

[a] Percent recoveries cited are averages based on duplicate analyses for all compounds other than for Aldrin and BHC. For Aldrin, four and three determinations were averaged to obtain the result for mercury and copper, respectively. Recovery of BHC using copper is based on one analysis.


Start
7.0
Choose technique ?
Copper
Mercury
TBA-sulfite
7.1.1
Concentrate sample extract
7.1.2
Did crystallization occur?
Yes
No
7.1.2
Centrifuge and draw off sample extract
7.1.2
Transfer extract to centrifuge tube
A
7.2.1
Concentrate sample extract
7.2.2
Pipet extract into concentrator tube or vial
7.2.3
Add mercury; agitate
B
7.3.1
Concentrate sample extract
7.3.2
Transfer extract to glass bottle or vial
7.3.3
Add TBA-sulfite and 2-propanol; shake
C


A
B
C
7.1.3
Add copper powder; mix
7.2.4
Separate sample from mercury
7.3.3
Is sample colorless and are there clear crystals?
No
Yes
7.3.3
Add more sodium sulfite; shake
7.1.4
Separate extract from copper
7.3.4
Add distilled water; shake; let stand; concentrate extract
Analyze extract by GC

METHOD 8000

GAS CHROMATOGRAPHY

1.0 SCOPE AND APPLICATION

1.1 Gas chromatography is a quantitative analytical technique useful for organic compounds capable of being volatilized without being decomposed or chemically rearranged. Gas chromatography (GC), also known as vapor phase chromatography (VPC), has two subcategories distinguished by: gas-solid chromatography (GSC), and gas-liquid chromatography (GLC) or gas-liquid partition chromatography (GLPC). This last group is the most commonly used, distinguished by type of column adsorbent or packing.

1.2 The gas chromatographic methods are recommended for use only by, or under the close supervision of, experienced residue analysts.

2.0 SUMMARY OF METHOD

2.1 Each organic analytical method that follows provides a recommended technique for extraction, cleanup, and occasionally, derivatization of the samples to be analyzed. Before the prepared sample is introduced into the GC, a procedure for standardization must be followed to determine the recovery and the limits of detection for the analytes of interest. Following sample introduction into the GC, analysis proceeds with a comparison of sample values with standard values. Quantitative analysis is achieved through integration of peak area or measurement of peak height.

3.0 INTERFERENCES

3.1 Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. To reduce carryover, the sample syringe or purging device must be rinsed out between samples with water or solvent. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of a solvent blank or of water to check for cross contamination. For volatile 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 syringe or purging device with a detergent solution, rinse it with distilled water, and then dry it in a 105°C oven between analyses.

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph - Analytical system complete with gas chromatograph suitable for on-column injections and all required accessories, including detectors, column supplies, recorder, gases, and syringes. A data system for measuring peak height and/or peak areas is recommended.

4.2 Gas chromatographic columns - See the specific determinative method. Other packed or capillary (open-tubular) columns may be used if the requirements of Step 8.6 are met.

5.0 REAGENTS

5.1 See the specific determinative method for the reagents needed.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Step 4.1.

7.0 PROCEDURE

7.1 Extraction - Adhere to those procedures specified in the referring determinative method.

7.2 Cleanup and separation - Adhere to those procedures specified in the referring determinative method.

7.3 The recommended gas chromatographic columns and operating conditions for the instrument are specified in the referring determinative method.

7.4 Calibration

7.4.1 Establish gas chromatographic operating parameters equivalent to those indicated in Section 7.0 of the determinative method of interest. Prepare calibration standards using the procedures indicated in Section 5.0 of the determinative method of interest. Calibrate the chromatographic system using either the external standard technique (Step 7.4.2) or the internal standard technique (Step 7.4.3).

7.4.2 External standard calibration procedure

7.4.2.1 For each analyte of interest, prepare calibration standards at a minimum of five concentration levels by adding volumes of one or more stock standards to a volumetric flask and diluting to volume with an appropriate solvent. One of the external standards should be at a concentration near, but above, the method detection limit. The other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector.

7.4.2.2 Inject each calibration standard using the technique that will be used to introduce the actual samples into the gas chromatograph (e.g. 2-5-uL injections, purge-and-trap, etc.). Tabulate peak height or area responses against the mass injected. The results can be used to prepare a calibration curve for each analyte. Alternatively, for samples that are introduced into the gas chromatograph using a syringe, the ratio of the response to the amount injected, defined as the calibration factor (CF), can be calculated for each analyte at each standard concentration. If the percent relative standard deviation (%RSD) of the calibration factor is less than 20% over the working range, linearity through the origin can be assumed, and the average calibration factor can be used in place of a calibration curve.

$$\text{Calibration factor} = \frac{\text{Total Area of Peak}^{*}}{\text{Mass injected (in nanograms)}}$$

*For multiresponse pesticides/PCBs use the total area of all peaks used for quantitation.

7.4.2.3 The working calibration curve or calibration factor must be verified on each working day by the injection of one or more calibration standards. The frequency of verification is dependent on the detector. Detectors, such as the electron capture detector, that operate in the sub-nanogram range are more susceptible to changes in detector response caused by GC column and sample effects. Therefore, more frequent verification of calibration is necessary. The flame ionization detector is much less sensitive and requires less frequent verification. If the response for any analyte varies from the predicted response by more than ± 15%, a new calibration curve must be prepared for that analyte.

$$\text{Percent Difference} = \frac{R_1 - R_2}{R_1} \times 100$$

where:

R_1 = Calibration Factor from first analysis.

R_2 = Calibration Factor from succeeding analyses.

7.4.3 Internal standard calibration procedure

7.4.3.1 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. Due to these limitations, no internal standard applicable to all samples can be suggested.

7.4.3.2 Prepare calibration standards at a minimum of five concentration levels for each analyte 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 an appropriate solvent. One of the standards should be at a concentration near, but above, the method detection limit. The other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector.

7.4.3.3 Inject each calibration standard using the same introduction technique that will be applied to the actual samples (e.g. 2- to 5-uL injection, purge-and-trap, etc.). Tabulate the peak height or area responses against the concentration of each compound and internal standard. Calculate response factors (RF) for each compound as follows:

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

where:

A_s = Response for the analyte to be measured.

A_{is} = Response for the internal standard.

C_{is} = Concentration of the internal standard, ug/L.

C_s = Concentration of the analyte to be measured, ug/L.

If the RF value over the working range is constant (< 20% 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} versus RF.

7.4.3.4 The working calibration curve or RF must be verified on each working day by the measurement of one or more calibration standards. The frequency of verification is dependent on the detector. Detectors, such as the electron capture detector, that operate in the sub-nanogram range are more susceptible to changes in detector response caused by GC column and sample effects. Therefore, more frequent verification of calibration is necessary. The flame ionization detector is much less sensitive and requires less frequent verification. If the response for any analyte varies from the predicted response by more than $\pm$ 15%, a new calibration curve must be prepared for that compound.

7.5 Retention time windows

7.5.1 Before establishing windows, make sure the GC system is within optimum operating conditions. Make three injections of all single component standard mixtures and multiresponse products (i.e. PCBs) throughout the course of a 72-hour period. Serial injections over less than a 72-hour period result in retention time windows that are too tight.

7.5.2 Calculate the standard deviation of the three absolute retention times for each single component standard. For multiresponse products, choose one major peak from the envelope and calculate the standard deviation of the three retention times for that peak. The peak chosen should be fairly immune to losses due to degradation and weathering in samples.

7.5.2.1 Plus or minus three times the standard deviation of the absolute retention times for each standard will be used to define the retention time window; however, the experience of the analyst should weigh heavily in the interpretation of chromatograms. For multiresponse products (i.e. PCBs), the analyst should use the retention time window but should primarily rely on pattern recognition.

7.5.2.2 In those cases where the standard deviation for a particular standard is zero, the laboratory must substitute the standard deviation of a close eluting, similar compound to develop a valid retention time window.

7.5.3 The laboratory must calculate retention time windows for each standard on each GC column and whenever a new GC column is installed. The data must be retained by the laboratory.

7.6 Gas chromatographic analysis

7.6.1 Introduction of organic compounds into the gas chromatograph varies depending on the volatility of the compound. Volatile organics are primarily introduced by purge-and-trap (Method 5030). However, there are limited applications where direct injection is acceptable. Use of Method 3810 or 3820 as a screening technique for volatile organic analysis may be valuable with some sample matrices to prevent overloading and contamination of the GC systems. Semivolatile organics are introduced by direct injection.

7.6.2 The appropriate detector(s) is given in the specific method.

7.6.3 Samples are analyzed in a set referred to as an analysis sequence. The sequence begins with instrument calibration followed by sample extracts interspersed with multilevel calibration standards. The sequence ends when the set of samples has been injected or when qualitative and/or quantitative QC criteria are exceeded.

7.6.4 Direct Injection - Inject 2-5 uL of the sample extract using the solvent flush technique. Smaller (1.0-uL) volumes can be injected if automatic devices are employed. Record the volume injected to the nearest 0.05 uL and the resulting peak size in area units or peak height.

7.6.5 If the responses exceed the linear range of the system, dilute the extract and reanalyze. It is recommended that extracts be diluted so that all peaks are on scale. Overlapping peaks are not always evident when peaks are off scale. Computer reproduction of chromatograms, manipulated to ensure all peaks are on scale over a 100-fold range, are acceptable if linearity is demonstrated. Peak height measurements are recommended over peak area integration when overlapping peaks cause errors in area integration.

7.6.6 If peak detection is prevented by the presence of interferences, further cleanup is required.

7.6.7 Examples of chromatograms for the compounds of interest are frequently available in the referring analytical method.

7.6.8 Calibrate the system immediately prior to conducting any analyses (see Step 7.4). A midlevel standard must also be injected at intervals specified in the method and at the end of the analysis sequence. The calibration factor for each analyte to be quantitated, must not exceed a 15% difference when compared to the initial standard of

the analysis sequence. When this criteria is exceeded, inspect the GC system to determine the cause and perform whatever maintenance is necessary (see Step 7.7) before recalibrating and proceeding with sample analysis. All samples that were injected after the sample exceeding the criteria must be reinjected.

7.6.9 Establish daily retention time windows for each analyte. Use the absolute retention time for each analyte from Step 7.6.8 as the midpoint of the window for that day. The daily retention time window equals the midpoint ± three times the standard deviation determined in Step 7.5.

7.6.9.1 Tentative identification of an analyte occurs when a peak from a sample extract falls within the daily retention time window. Normally, confirmation is required: on a second GC column, by GC/MS if concentration permits, or by other recognized confirmation techniques. Confirmation may not be necessary if the composition of the sample matrix is well established by prior analyses.

7.6.9.2 Validation of GC system qualitative performance: Use the midlevel standards interspersed throughout the analysis sequence (Step 7.6.8) to evaluate this criterion. If any of the standards fall outside their daily retention time window, the system is out of control. Determine the cause of the problem and correct it (see Step 7.7).

7.7 Suggested chromatography system maintenance - Corrective measures may require any one or more of the following remedial actions.

7.7.1 Packed columns - For instruments with injection port traps, replace the demister trap, clean, and deactivate the glass injection port insert or replace with a cleaned and deactivated insert. Inspect the injection end of the column and remove any foreign material (broken glass from the rim of the column or pieces of septa). Replace the glass wool with fresh deactivated glass wool. Also, it may be necessary to remove the first few millimeters of the packing material if any discoloration is noted, also swab out the inside walls of the column if any residue is noted. If these procedures fail to eliminate the degradation problem, it may be necessary to deactivate the metal injector body (described in Step 7.7.3) and/or repack/replace the column.

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

7.7.3 Metal injector body - Turn off the oven and remove the analytical column when the oven has cooled. Remove the glass injection port insert (instruments with off-column injection or Grob). Lower the

injection port temperature to room temperature. Inspect the injection port and remove any noticeable foreign material.

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

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

7.8 Calculations

7.8.1 External standard calibration - The concentration of each analyte in the sample may be determined by calculating the amount of standard purged or injected, from the peak response, using the calibration curve or the calibration factor determined in Step 7.4.2. The concentration of a specific analyte is calculated as follows:

Aqueous samples

$$\text{Concentration (ug/L)} = [(A_x)(A)(V_t)(D)]/[(A_s)(V_i)(V_s)]$$

where:

A_x = Response for the analyte in the sample, units may be in area counts or peak height.

A = Amount of standard injected or purged, ng.

A_s = Response for the external standard, units same as for A_x.

V_i = Volume of extract injected, uL. For purge-and-trap analysis, V_i is not applicable and therefore = 1.

D = Dilution factor, if dilution was made on the sample prior to analysis. If no dilution was made, D = 1, dimensionless.

V_t = Volume of total extract, uL. For purge-and-trap analysis, V_t is not applicable and therefore = 1.

V_s = Volume of sample extracted or purged, mL.

Nonaqueous samples

$$\text{Concentration (ng/g)} = [(A_x)(A)(V_t)(D)]/[(A_s)(V_i)(W)]$$

where:

> W = Weight of sample extracted or purged, g. The wet weight or dry weight may be used, depending upon the specific applications of the data.

> A_x, A_s, A, V_t, D, and V_i have the same definition as for aqueous samples.

7.8.2 Internal standard calibration - For each analyte of interest, the concentration of that analyte in the sample is calculated as follows:

Aqueous samples

$$\text{Concentration (ug/L)} = [(A_x)(C_{is})(D)]/[(A_{is})(RF)(V_s)]$$

where:

> A_x = Response of the analyte being measured, units may be in area counts or peak height.

> C_{is} = Amount of internal standard added to extract or volume purged, ng.

> D = Dilution factor, if a dilution was made on the sample prior to analysis. If no dilution was made, D = 1, dimensionless.

> A_{is} = Response of the internal standard, units same as A_x.

> RF = Response factor for analyte, as determined in Step 7.4.3.3.

> V_s = Volume of water extracted or purged, mL.

Nonaqueous samples

$$\text{Concentration (ug/kg)} = [(A_s)(C_{is})(D)]/[(A_{is})(RF)(W_s)]$$

where:

> W_s = Weight of sample extracted, g. Either a dry weight or wet weight may be used, depending upon the specific application of the data.

> A_s, C_{is}, D, A_{is}, and RF have the same definition as for aqueous samples.

8.0 QUALITY CONTROL

8.1 Each laboratory that uses these methods is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and an ongoing analysis of spiked samples to evaluate and document quality data. The laboratory must maintain records to document the quality of the data

generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. When results of sample spikes indicate atypical method performance, a quality control check standard must be analyzed to confirm that the measurements were performed in an in-control mode of operation.

8.2 Before processing any samples, the analyst should demonstrate, through the analysis of a reagent blank, that interferences from the analytical system, glassware, and reagents are under control. Each time a set of samples is extracted or there is a change in reagents, a reagent water blank should be processed as a safeguard against chronic laboratory contamination. The blank samples should be carried through all stages of the sample preparation and measurement steps.

8.3 For each analytical batch (up to 20 samples), a reagent blank, matrix spike, and replicate or matrix spike replicate must be analyzed (the frequency of the spikes may be different for different monitoring programs). The blank and spiked samples must be carried through all stages of the sample preparation and measurement steps.

8.4 The experience of the analyst performing gas chromatography is invaluable to the success of the methods. Each day that analysis is performed, the daily calibration sample should be evaluated to determine if the chromatographic system is operating properly. Questions that should be asked are: Do the peaks look normal?; Is the response obtained comparable to the response from previous calibrations? Careful examination of the standard chromatogram can indicate whether the column is still good, the injector is leaking, the injector septum needs replacing, etc. If any changes are made to the system (e.g. column changed), recalibration of the system must take place.

8.5 Required instrument QC

8.5.1 Step 7.4 requires that the %RSD vary by < 20% when comparing calibration factors to determine if a five point calibration curve is linear.

8.5.2 Step 7.4 sets a limit of ± 15% difference when comparing daily response of a given analyte versus the initial response. If the limit is exceeded, a new standard curve must be prepared.

8.5.3 Step 7.5 requires the establishment of retention time windows.

8.5.4 Step 7.6.8 sets a limit of ± 15% difference when comparing the initial response of a given analyte versus any succeeding standards analyzed during an analysis sequence.

8.5.5 Step 7.6.9.2 requires that all succeeding standards in an analysis sequence must fall within the daily retention time window established by the first standard of the sequence.

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

8.6.1 A quality (QC) check sample concentrate is required containing each analyte of interest. The QC check sample concentrate may be prepared from pure standard materials or purchased as certified solutions. If prepared by the laboratory, the QC check sample concentrate must be made using stock standards prepared independently from those used for calibration.

8.6.1.1 The concentration of the QC check sample concentrate is highly dependent upon the analytes being investigated. Therefore, refer to Method 3500, Section 8.0 for the required concentration of the QC check sample concentrate.

8.6.2 Preparation of QC check samples

8.6.2.1 Volatile organic analytes (Methods 8010, 8020, and 8030) - The QC check sample is prepared by adding 200 uL of the QC check sample concentrate (Step 8.6.1) to 100 mL of water.

8.6.2.2 Semivolatile organic analytes (Methods 8040, 8060, 8080, 8090, 8100, and 8120) - The QC check sample is prepared by adding 1.0 mL of the QC check sample concentrate (Step 8.6.1) to each of four 1-L aliquots of water.

8.6.3 Four aliquots of the well-mixed QC check sample are analyzed by the same procedures used to analyze actual samples (Section 7.0 of each of the methods). For volatile organics, the preparation/analysis process is purge-and-trap/gas chromatography. For semivolatile organics, the QC check samples must undergo solvent extraction (see Method 3500) prior to chromatographic analysis.

8.6.4 Calculate the average recovery ($\bar{x}$) in ug/L, and the standard deviation of the recovery (s) in ug/L, for each analyte of interest using the four results.

8.6.5 For each analyte compare s and $\bar{x}$ with the corresponding acceptance criteria for precision and accuracy, respectively, given the QC Acceptance Criteria Table at the end of each of the determinative methods. If s and $\bar{x}$ for all analytes of interest meet the acceptance criteria, the system performance is acceptable and analysis of actual samples can begin. If any individual s exceeds the precision limit or any individual $\bar{x}$ falls outside the range for accuracy, then the system performance is unacceptable for that analyte.

<u>NOTE</u>: The large number of analytes in each of the QC Acceptance Criteria Tables present a substantial probability that one or more will fail at least one of the acceptance criteria when all analytes of a given method are determined.

8.6.6 When one or more of the analytes tested fail at least one of the acceptance criteria, the analyst must proceed according to Step 8.6.6.1 or 8.6.6.2.

8.6.6.1 Locate and correct the source of the problem and repeat the test for all analytes of interest beginning with Step 8.6.2.

8.6.6.2 Beginning with Step 8.6.2, repeat the test only for those analytes that failed to meet criteria. Repeated failure, however, will confirm a general problem with the measurement system. If this occurs, locate and correct the source of the problem and repeat the test for all compounds of interest beginning with Step 8.6.2.

8.7 The laboratory must, on an ongoing basis, analyze a reagent blank and a matrix spiked replicate for each analytical batch (up to a maximum of 20 samples/batch) to assess accuracy. For soil and waste samples where detectable amounts of organics are present, replicate samples may be appropriate in place of spiked replicates. For laboratories analyzing one to ten samples per month, at least one spiked sample per month is required.

8.7.1 The concentration of the spike in the sample should be determined as follows:

8.7.1.1 If, as in compliance monitoring, the concentration of a specific analyte in the sample is being checked against a regulatory concentration limit, the spike should be at that limit or 1 to 5 times higher than the background concentration determined in Step 8.7.2, whichever concentration would be larger.

8.7.1.2 If the concentration of a specific analyte in a water sample is not being checked against a limit specific to that analyte, the spike should be at the same concentration as the QC reference sample (Step 8.6.2) or 1 to 5 times higher than the background concentration determined in Step 8.7.2, whichever concentration would be larger. For other matrices, the recommended spiking concentration is 20 times the PQL.

8.7.1.3 For semivolatile organics, it may not be possible to determine the background concentration levels prior to spiking (e.g. maximum holding times will be exceeded). If this is the case, the spike concentration should be (1) the regulatory concentration limit, if any; or, if none (2) the larger of either 5 times higher than the expected background concentration or the QC reference sample concentration (Step 8.6.2). For other matrices, the recommended spiking concentration is 20 times the PQL.

8.7.2 Analyze one unspiked and one spiked sample aliquot to determine percent recovery of each of the spiked compounds.

8.7.2.1 Volatile organics - Analyze one 5-mL sample aliquot to determine the background concentration (B) of each analyte. If necessary, prepare a new QC reference sample concentrate (Step 8.6.1)

appropriate for the background concentration in the sample. Spike a second 5-mL sample aliquot with 10 uL of the QC reference sample concentrate and analyze it to determine the concentration after spiking (A) of each analyte. Calculate each percent recovery (p) as 100(A - B)%/T, where T is the known true value of the spike.

8.7.2.2 Semivolatile organics - Analyze one sample aliquot (extract of 1-L sample) to determine the background concentration (B) of each analyte. If necessary, prepare a new QC reference sample concentrate (Step 8.6.1) appropriate for the background concentration in the sample. Spike a second 1-L sample aliquot with 1.0 mL of the QC reference sample concentrate and analyze it to determine the concentration after spiking (A) of each analyte. Calculate each percent recovery (p) as 100(A - B)%/T, where T is the known true value of the spike.

8.7.3 Compare the percent recovery (p) for each analyte in a water sample with the corresponding criteria presented in the QC Acceptance Criteria Table found at the end of each of the determinative methods. These acceptance criteria were calculated to include an allowance for error in measurement of both the background and spike concentrations, assuming a spike to background ratio of 5:1. This error will be accounted for to the extent that the analyst's spike to background ratio approaches 5:1. If spiking was performed at a concentration lower than the QC reference sample concentration (Step 8.6.2), the analyst must use either the QC acceptance criteria presented in the Tables, or optional QC acceptance criteria calculated for the specific spike concentration. To calculate optional acceptance criteria for the recovery of an analyte: (1) Calculate accuracy (x') using the equation found in the Method Accuracy and Precision as a Function of Concentration Table (appears at the end of each determinative method), substituting the spike concentration (T) for C; (2) calculate overall precision (S') using the equation in the same Table, substituting x' for $\bar{x}$; (3) calculate the range for recovery at the spike concentration as $(100x'/T) \pm 2.44(100S'/T)\%$.

8.7.4 If any individual p falls outside the designated range for recovery, that analyte has failed the acceptance criteria. A check standard containing each analyte that failed the criteria must be analyzed as described in Step 8.8.

8.8 If any analyte in a water sample fails the acceptance criteria for recovery in Step 8.7, a QC reference standard containing each analyte that failed must be prepared and analyzed.

<u>NOTE</u>: The frequency for the required analysis of a QC reference standard will depend upon the number of analytes being simultaneously tested, the complexity of the sample matrix, and the performance of the laboratory. If the entire list of analytes given in a method must be measured in the sample in Step 8.7, the probability that the analysis of a QC check standard will be required is high. In this case the QC check standard should be routinely analyzed with the spiked sample.

8.8.1 Preparation of the QC check sample - For volatile organics, add 10 uL of the QC check sample concentrate (Step 8.6.1 or 8.7.2) to 5 mL of water. For semivolatile organics, add 1.0 mL of the QC check sample concentrate (Step 8.6.1 or 8.7.2) to 1 L of water. The QC check sample needs only to contain the analytes that failed criteria in the test in Step 8.7. Prepare the QC check sample for analysis following the guidelines given in Method 3500 (e.g. purge-and-trap, extraction, etc.).

8.8.2 Analyzed the QC check sample to determine the concentration measured (A) of each analyte. Calculate each percent recovery (p_s) as 100 (A/T)%, where T is the true value of the standard concentration.

8.8.3 Compare the percent recovery (p_s) for each analyte with the corresponding QC acceptance criteria found in the appropriate Table in each of the methods. Only analytes that failed the test in Step 8.7 need to be compared with these criteria. If the recovery of any such analyte falls outside the designated range, the laboratory performance for that analyte is judged to be out of control, and the problem must be immediately identified and corrected. The result for that analyte in the unspiked sample is suspect and may not be reported for regulatory compliance purposes.

8.9 As part of the QC program for the laboratory, method accuracy for each matrix studied must be assessed and records must be maintained. After the analysis of five spiked samples (of the same matrix type) as in Step 8.7, calculate the average percent recovery ($\bar{p}$) and the standard deviation of the percent recovery (s_p). Express the accuracy assessment as a percent recovery interval from $\bar{p} - 2s_p$ to $\bar{p} + 2s_p$. If $\bar{p}$ = 90% and s_p = 10%, for example, the accuracy interval is expressed as 70-110%. Update the accuracy assessment for each analyte on a regular basis (e.g. after each five to ten new accuracy measurements).

8.10 To determine acceptable accuracy and precision limits for surrogate standards the following procedure should be performed.

8.10.1 For each sample analyzed, calculate the percent recovery of each surrogate in the sample.

8.10.2 Once a minimum of thirty samples of the same matrix have been analyzed, calculate the average percent recovery (p) and standard deviation of the percent recovery (s) for each of the surrogates.

8.10.3 For a given matrix, calculate the upper and lower control limit for method performance for each surrogate standard. This should be done as follows:

Upper Control Limit (UCL) = p + 3s
Lower Control Limit (LCL) = p - 3s

8.10.4 For aqueous and soil matrices, these laboratory established surrogate control limits should, if applicable, be compared with the control limits listed in Tables A and B of Methods 8240 and 8270,

respectively. The limits given in these methods are multi-laboratory performance based limits for soil and aqueous samples, and therefore, the single-laboratory limits established in Step 8.10.3 must fall within those given in Tables A and B for these matrices.

8.10.5 If recovery is not within limits, the following is required.

- Check to be sure there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.

- Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.

- Reextract and reanalyze the sample if none of the above are a problem or flag the data as "estimated concentration."

8.10.6 At a minimum, each laboratory should update surrogate recovery limits on a matrix-by-matrix basis, annually.

8.11 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 assess the precision of the environmental measurements. 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 analyze standard reference materials and participate in relevant performance evaluation studies.

9.0 METHOD PERFORMANCE

9.1 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. The MDL concentrations listed in the referring analytical methods were obtained using water. Similar results were achieved using representative wastewaters. The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

9.2 Refer to the determinative method for specific method performance information.

10.0 REFERENCES

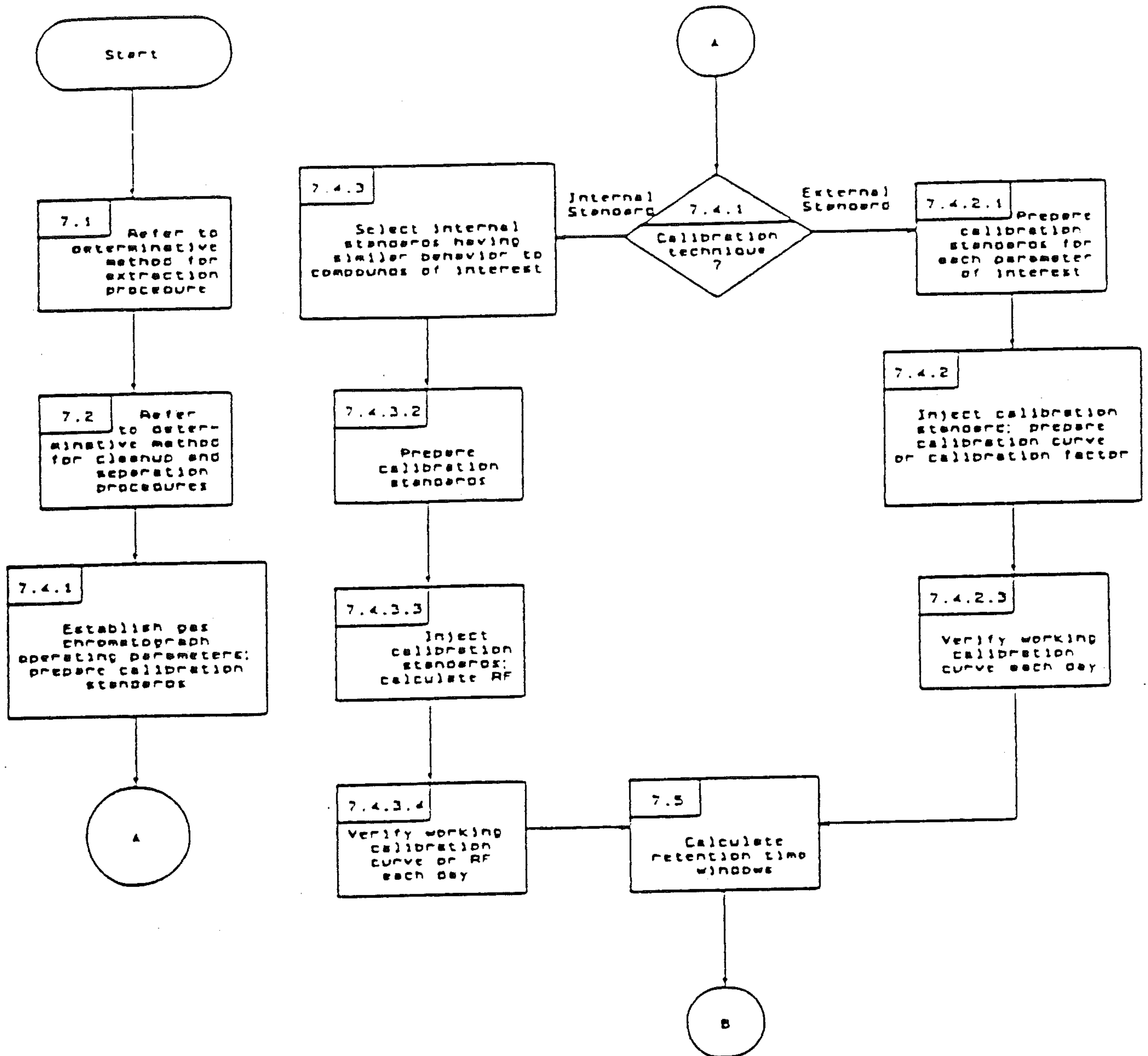
1. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.

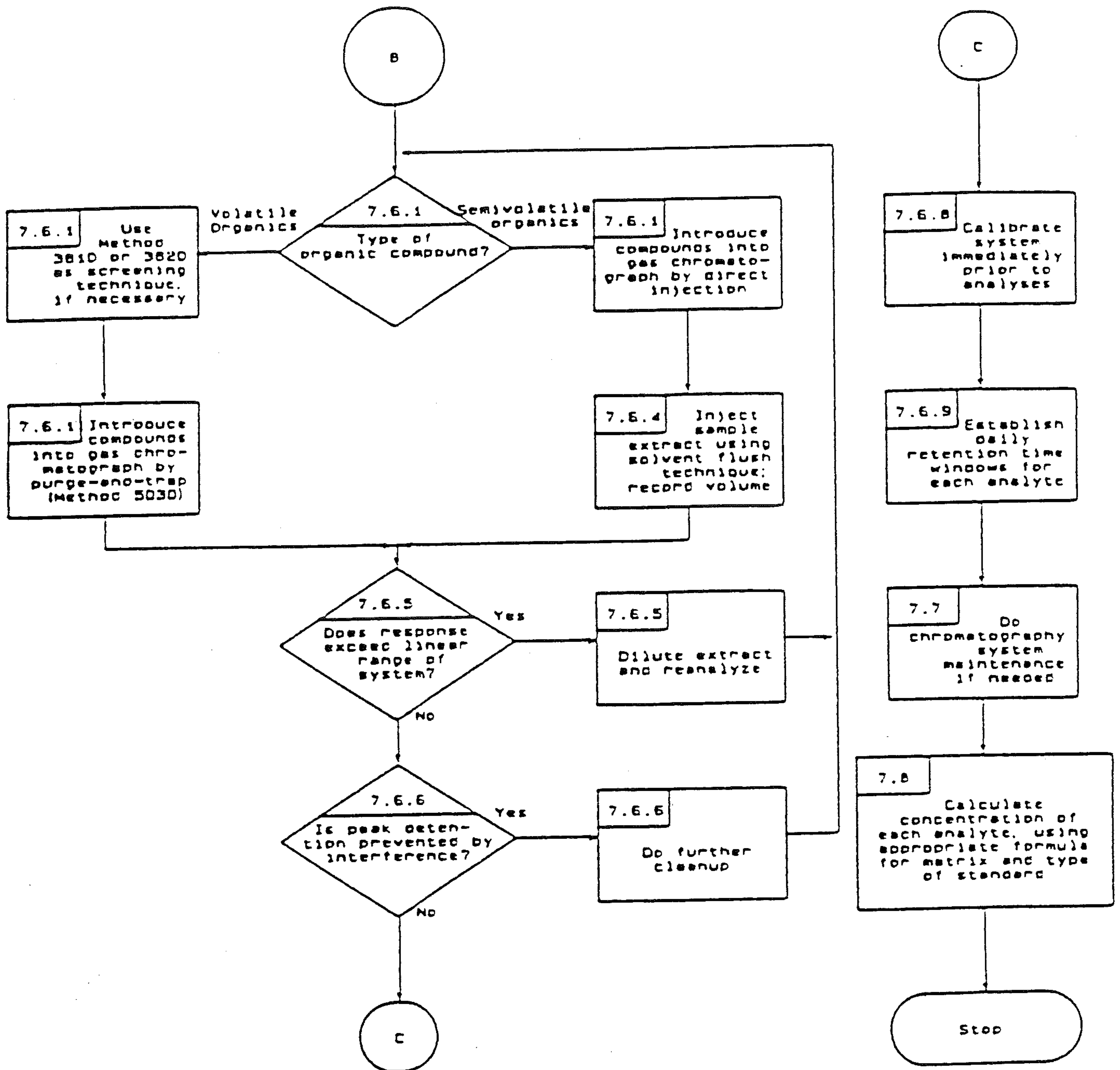
2. U.S. EPA 40 CFR Part 136, Appendix B. "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.

3. U.S. EPA Contract Laboratory Program, Statement of Work for Organic Analysis, July 1985, Revision.

4. Rohrbough, W.G.; et al. Reagent Chemicals, American Chemical Society Specifications, 7th ed.; American Chemical Society: Washington, DC, 1986.

5. 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water"; ASTM: Philadelphia, PA, 1985; D1193-77.


Start
7.1 Refer to determinative method for extraction procedure
7.2 Refer to determinative method for cleanup and separation procedures
7.4.1 Establish gas chromatograph operating parameters; prepare calibration standards
A
A
7.4.1 Calibration technique ?
Internal Standard
External Standard
7.4.3 Select internal standards having similar behavior to compounds of interest
7.4.3.2 Prepare calibration standards
7.4.3.3 Inject calibration standards; calculate RF
7.4.3.4 Verify working calibration curve or RF each day
7.4.2.1 Prepare calibration standards for each parameter of interest
7.4.2 Inject calibration standard; prepare calibration curve or calibration factor
7.4.2.3 Verify working calibration curve each day
7.5 Calculate retention time windows
B


B
7.6.1
Type of organic compound?
Volatile Organics
Semivolatile organics
7.6.1 Use Method 3810 or 3820 as screening technique, if necessary
7.6.1 Introduce compounds into gas chromatograph by direct injection
7.6.1 Introduce compounds into gas chromatograph by purge-and-trap (Method 5030)
7.6.4 Inject sample extract using solvent flush technique; record volume
7.6.5
Does response exceed linear range of system?
Yes
No
7.6.5 Dilute extract and reanalyze
7.6.6
Is peak detection prevented by interference?
Yes
No
7.6.6 Do further cleanup
C
C
7.6.8 Calibrate system immediately prior to analyses
7.6.9 Establish daily retention time windows for each analyte
7.7 Do chromatography system maintenance if needed
7.8 Calculate concentration of each analyte, using appropriate formula for matrix and type of standard
Stop

METHOD 8080B

ORGANOCHLORINE PESTICIDES AND POLYCHLORINATED BIPHENYLS BY GAS CHROMATOGRAPHY

1.0 SCOPE AND APPLICATION

1.1 Method 8080 is used to determine the concentration of various organochlorine pesticides and polychlorinated biphenyls (PCBs). The following compounds can be determined by this method:

Compound Name	CAS No.[a]
Aldrin	309-00-2
α-BHC	319-84-6
β-BHC	319-85-7
δ-BHC	319-86-8
γ-BHC (Lindane)	58-89-9
Chlordane (technical)	12789-03-6
4,4'-DDD	72-54-8
4,4'-DDE	72-55-9
4,4'-DDT	50-29-3
Dieldrin	60-57-1
Endosulfan I	959-98-8
Endosulfan II	33212-65-9
Endosulfan sulfate	1031-07-8
Endrin	72-20-8
Endrin aldehyde	7421-93-4
Heptachlor	76-44-8
Heptachlor epoxide	1024-57-3
4,4'-Methoxychlor	72-43-5
Toxaphene	8001-35-2
Aroclor-1016	12674-11-2
Aroclor-1221	11104-28-2
Aroclor-1232	11141-16-5
Aroclor-1242	53469-21-9
Aroclor-1248	12672-29-6
Aroclor-1254	11097-69-1
Aroclor-1260	11096-82-5

a Chemical Abstract Services Registry Number.

1.1 Table 1 lists the method detection limit for each compound in organic-free reagent water. Table 2 lists the estimated quantitation limit (EQL) for other matrices.

2.0 SUMMARY OF METHOD

2.1 Method 8080 provides gas chromatographic conditions for the detection of ppb concentrations of certain organochlorine pesticides and PCBs. Prior to the use of this method, appropriate sample extraction techniques must be used. Both neat and diluted organic liquids (Method 3580, Waste Dilution) may be analyzed by direct injection. A 2 to 5 µL sample is injected into a gas chromatograph (GC) using the solvent flush technique, and compounds in the GC effluent are detected by an electron capture detector (ECD) or an electrolytic conductivity detector (HECD).

2.2 The sensitivity of Method 8080 usually depends on the concentration of interferences rather than on instrumental limitations. If interferences prevent detection of the analytes, Method 8080 may also be performed on samples that have undergone cleanup. Method 3620, Florisil Column Cleanup, by itself or followed by Method 3660, Sulfur Cleanup, may be used to eliminate interferences in the analysis.

3.0 INTERFERENCES

3.1 Refer to Methods 3500, 3600, and 8000.

3.2 Interferences by phthalate esters can pose a major problem in pesticide determinations when using the electron capture detector. These compounds generally appear in the chromatogram as large late-eluting peaks, especially in the 15% and 50% fractions from the Florisil cleanup. 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 contact with any plastic materials. Exhaustive cleanup of reagents and glassware may be required to eliminate background phthalate contamination. The contamination from phthalate esters can be completely eliminated with a microcoulometric or electrolytic conductivity detector.

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph

4.1.1 Gas Chromatograph: Analytical system complete with gas chromatograph suitable for on-column injections and all required accessories, including detectors, column supplies, recorder, gases, and syringes. A data system for measuring peak heights and/or peak areas is recommended.

4.1.2 Columns

4.1.2.1 Column 1: Supelcoport (100/120 mesh) coated with 1.5% SP-2250/1.95% SP-2401 packed in a 1.8 m x 4 mm ID glass column or equivalent.

4.1.2.2 Column 2: Supelcoport (100/120 mesh) coated with 3% OV-1 in a 1.8 m x 4 mm ID glass column or equivalent.

4.1.3 Detectors: Electron capture (ECD) or electrolytic conductivity detector (HECD).

4.2 Kuderna-Danish (K-D) apparatus:

4.2.1 Concentrator tube: 10 mL, graduated (Kontes K-570050-1025 or equivalent). A ground-glass stopper is used to prevent evaporation of extracts.

4.2.2 Evaporation flask: 500 mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs, clamps, or equivalent.

4.2.3 Snyder column: Three ball macro (Kontes K-503000-0121 or equivalent).

4.2.4 Snyder column: Two ball micro (Kontes K-569001-0219 or equivalent).

4.2.5 Springs - 1/2 inch (Kontes K-662750 or equivalent).

4.3 Boiling chips: Solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).

4.4 Water bath: Heated, with concentric ring cover, capable of temperature control ($\pm$5°C). The bath should be used in a hood.

4.5 Volumetric flasks, Class A: 10, 50, and 100 mL, ground-glass stopper.

4.6 Microsyringe: 10 μL.

4.7 Syringe: 5 mL.

4.8 Vials: Glass, 2, 10, and 20 mL capacity with Teflon-lined screw caps or crimp tops.

4.9 Balances: Analytical, 0.0001 g and Top loading, 0.01 g.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Solvents

5.3.1 Hexane, C_6H_{14} - Pesticide quality or equivalent.

5.3.2 Acetone, CH_3COCH_3 - Pesticide quality or equivalent.

5.3.3 Toluene, $C_6H_5CH_3$ - Pesticide quality or equivalent.

5.3.4 Isooctane, $(CH_3)_3CCH_2CH(CH_3)_2$ - Pesticide quality or equivalent.

5.4 Stock standard solutions:

5.4.1 Prepare stock standard solutions at a concentration of 1000 mg/L by dissolving 0.0100 g of assayed reference material in isooctane and diluting to volume in a 10 mL volumetric flask. A small volume of toluene may be necessary to put some pesticides in solution. Larger volumes can be used at the convenience of the analyst. When compound purity is assayed to be 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards can be used at any concentration if they are certified by the manufacturer or by an independent source.

5.4.2 Transfer the stock standard solutions into vials with Teflon-lined screw caps or crimp tops. Store at 4°C and protect from light. Stock standards should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.4.3 Stock standard solutions must be replaced after one year, or sooner if comparison with check standards indicates a problem.

5.5 Calibration standards: Calibration standards at a minimum of five concentrations for each parameter of interest are prepared through dilution of the stock standards with isooctane. One of the concentrations should be at a concentration near, but above, the method detection limit. The remaining concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the GC. Calibration solutions must be replaced after six months, or sooner, if comparison with check standards indicates a problem.

5.6 Internal standards (if internal standard calibration is used): 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.

5.6.1 Prepare calibration standards at a minimum of five concentrations for each analyte of interest as described in Section 5.5.

5.6.2 To each calibration standard, add a known constant amount of one or more internal standards, and dilute to volume with isooctane.

5.6.3 Analyze each calibration standard according to Section 7.0.

5.7 Surrogate standards: The analyst should monitor the performance of the extraction, cleanup (when used), and analytical system and the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard, and organic-free reagent water blank with pesticide surrogates. Because GC/ECD data are much more subject to interference than GC/MS, a secondary surrogate is to be used when sample interference is apparent. Two surrogate standards (tetrachloro-m-xylene (TCMX) and decachlorobiphenyl) are added to each sample; however, only one need be calculated for recovery. Proceed with corrective action when both surrogates are out of limits for a sample (Section 8.3). Method 3500 indicates the proper procedure for preparing these surrogates.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1. Extracts must be stored under refrigeration and analyzed within 40 days of extraction.

7.0 PROCEDURE

7.1 Extraction:

7.1.1 Refer to Chapter Two for guidance on choosing the appropriate extraction procedure. In general, water samples are extracted at a neutral, or as is, pH with methylene chloride, using either Method 3510 or 3520. Solid samples are extracted using either Method 3540 or 3550.

7.1.2 Prior to gas chromatographic analysis, the extraction solvent must be exchanged to hexane. The exchange is performed during the K-D procedures listed in all of the extraction methods. The exchange is performed as follows.

7.1.2.1 Following K-D of the methylene chloride extract to 1 mL using the macro-Snyder column, allow the apparatus to cool and drain for at least 10 min.

7.1.2.2 Increase the temperature of the hot water bath to about 90°C. Momentarily remove the Snyder column, add 50 mL of hexane, a new boiling chip, and reattach the macro-Snyder column. Concentrate the extract using 1 mL of hexane to prewet the Snyder column. Place the K-D apparatus on the water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature, as required, to complete concentration in 5-10 min. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 min.

7.1.2.3 Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1-2 mL of hexane. A 5 mL syringe is recommended for this operation. Adjust the extract volume to 10.0 mL. Stopper the concentrator tube and store refrigerated

at 4°C, if further processing will not be performed immediately. If the extract will be stored longer than two days, it should be transferred to a vial with a Teflon-lined screw cap or crimp top. Proceed with gas chromatographic analysis if further cleanup is not required.

7.2 Gas chromatography conditions (Recommended):

7.2.1 Column 1:

Carrier gas (5% methane/95% argon) flow rate:	60 mL/min
Column temperature:	200°C isothermal

When analyzing for the low molecular weight PCBs (PCB 1221-PCB 1248), it is advisable to set the oven temperature to 160°C.

7.2.2 Column 2:

Carrier gas (5% methane/95% argon) flow rate:	60 mL/min
Column temperature:	200°C isothermal

When analyzing for the low molecular weight PCBs (PCB 1221-PCB 1248), it is advisable to set the oven temperature to 140°C.

7.2.3 When analyzing for most or all of the analytes in this method, adjust the oven temperature and column gas flow so that 4,4'-DDT has a retention time of approximately 12 min.

7.3 Calibration: Refer to Method 8000 for proper calibration techniques. Use Table 1 and especially Table 2 for guidance on selecting the lowest point on the calibration curve.

7.3.1 The procedure for internal or external calibration may be used. Refer to Method 8000 for a description of each of these procedures.

7.3.2 Because of the low concentration of pesticide standards injected on a GC/ECD, column adsorption may be a problem when the GC has not been used for a day. Therefore, the GC column should be primed or deactivated by injecting a PCB or pesticide standard mixture approximately 20 times more concentrated than the mid-concentration standard. Inject this prior to beginning initial or daily calibration.

7.4 Gas chromatographic analysis:

7.4.1 Refer to Method 8000. If the internal standard calibration technique is used, add 10 µL of internal standard to the sample prior to injection.

7.4.2 Method 8000 provides instructions on the analysis sequence, appropriate dilutions, establishing daily retention time windows, and identification criteria. Include a mid-concentration standard after each group of 10 samples in the analysis sequence.

<u>Note:</u> A 72 hour sequence is not required with this method.

7.4.3 Examples of GC/ECD chromatograms for various pesticides and PCBs are shown in Figures 1 through 5.

7.4.4 Prime the column as per Section 7.3.2.

7.4.5 DDT and endrin are easily degraded in the injection port if the injection port or front of the column is dirty. This is the result of buildup of high boiling residue from sample injection. Check for degradation problems by injecting a mid-concentration standard containing only 4,4'-DDT and endrin. Look for the degradation products of 4,4'-DDT (4,4'-DDE and 4,4'-DDD) and endrin (endrin ketone and endrin aldehyde). If degradation of either DDT or endrin exceeds 20%, take corrective action before proceeding with calibration, by following the GC system maintenance outlined in of Method 8000. Calculate percent breakdown as follows:

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

$$\text{\% breakdown for Endrin} = \frac{\text{Total endrin degradation peak area (endrin aldehyde + endrin ketone)}}{\text{peak areas (endrin + aldehyde + ketone)}} \times 100$$

7.4.6 Record the sample volume injected and the resulting peak sizes (in area units or peak heights).

7.4.7 Using either the internal or external calibration procedure (Method 8000), determine the identity and quantity of each component peak in the sample chromatogram which corresponds to the compounds used for calibration purposes.

7.4.8 If peak detection and identification are prevented due to interferences, the hexane extract may need to undergo cleanup using Method 3620. The resultant extract(s) may be analyzed by GC directly or may undergo further cleanup to remove sulfur using Method 3660.

7.5 Cleanup:

7.5.1 Proceed with Method 3620, followed by, if necessary, Method 3660, using the 10 mL hexane extracts obtained from Section 7.1.2.3.

7.5.2 Following cleanup, the extracts should be analyzed by GC, as described in the previous sections and in Method 8000.

7.6 Quantitation of Multiple Component Analytes:

7.6.1 Scope (excerpted from U.S. FDA, PAM): Residues which are mixtures of two or more components present problems in measurement. When they are found together, e.g., toxaphene and DDT, the problem of quantitation becomes even more difficult. Suggestions are offered in the

following sections for handing toxaphene, chlordane, PCB, DDT, and BHC.

7.6.2 Toxaphene: Quantitative calculation of toxaphene or strobane is difficult, but reasonable accuracy can be obtained. To calculate toxaphene on GC/ECD: (a) adjust the sample size so that the major toxaphene peaks are 10-70% of full-scale deflection (FSD); (b) inject a toxaphene standard that is estimated to be within ±10 ng of the sample; (c) quantitate using the five major peaks or the total area of the toxaphene pattern.

7.6.2.1 To measure total area, construct the baseline of standard toxaphene between its extremities; and construct the baseline under the sample, using the distances of the peak troughs to baseline on the standard as a guide. This procedure is made difficult by the fact that the relative heights and widths of the peaks in the sample will probably not be identical to the standard.

7.6.2.2 A series of toxaphene residues have been calculated using the total peak area for comparison to the standard and also using the area of the last four peaks only, in both sample and standard. The agreement between the results obtained by the two methods justifies the use of the latter method for calculating toxaphene in a sample where the early eluting portion of the toxaphene chromatogram shows interferences from other substances such as DDT.

7.6.3 Chlordane is a technical mixture of at least 11 major components and 30 or more minor components. Trans- and cis-chlordane (alpha and gamma), respectively, are the two major components of technical chlordane. However, the exact percentage of each in the technical material is not completely defined, and is not consistent from batch to batch.

7.6.3.1 The GC pattern of a chlordane residue may differ considerably from that of the technical standard. Depending on the sample substrate and its history, residues of chlordane can consist of almost any combination of: constituents from the technical chlordane, plant and/or animal metabolites, and products of degradation caused by exposure to environmental factors such as water and sunlight.

7.6.3.2 When the chlordane residue does not resemble technical chlordane, but instead consists primarily of individual, identifiable peaks, quantitate the peaks of alpha-chlordane, gamma-chlordane, and heptachlor separately against the appropriate reference materials, and report the individual residues.

7.6.3.3 When the GC pattern of the residue resembles that of technical chlordane, the analyst may quantitate chlordane residues by comparing the total area of the chlordane chromatogram using the five major peaks or the total area. If the heptachlor epoxide peak is relatively small, include it as part of the total chlordane area for calculation of the residue. If heptachlor and/or heptachlor epoxide are much out of proportion, calculate these separately and subtract their areas from the total area to give a corrected

chlordane area. (Note that octachlor epoxide, a metabolite of chlordane, can easily be mistaken for heptachlor epoxide on a nonpolar GC column.)

7.6.3.4 To measure the total area of the chlordane chromatogram, proceed as in Section 7.6.2 on toxaphene. Inject an amount of technical chlordane standard which will produce a chromatogram in which the major peaks are approximately the same size as those in the sample chromatograms.

7.6.4 Polychlorinated biphenyls (PCBs): Quantitation of residues of PCB involves problems similar to those encountered in the quantitation of toxaphene, strobane, and chlordane. In each case, the chemical is made up of numerous compounds which generate multi-peak chromatograms. Also, in each case, the chromatogram of the residue may not match that of the standard.

7.6.4.1 Mixtures of PCBs of various chlorine contents were sold for many years in the U.S. by the Monsanto Co. under the trade name Aroclor (1200 series and 1016). Although these Aroclors are no longer marketed, the PCBs remain in the environment and are sometimes found as residues in foods, especially fish.

7.6.4.2 Since standards are not generally available for all of the congeners of chlorinated biphenyl, PCB residues are quantitated by comparison to one or more of the Aroclor materials, depending on the chromatographic pattern of the residue. A choice must be made as to which Aroclor or mixture of Aroclors will produce a chromatogram most similar to that of the residue. This may also involve a judgement about what proportion of the different Aroclors to combine to produce the appropriate reference material.

7.6.4.3 PCB Quantitation option #1- Quantitate the PCB residues by comparing the total area of the chlorinated biphenyl peaks to the total area of peaks from the appropriate Aroclor(s) reference materials. Measure the total area or height response from the common baseline under all the peaks. Use only those peaks from the sample that can be attributed to chlorobiphenyls. These peaks must also be present in the chromatogram of the reference materials. A mixture of Aroclors may be required to provide the best match of the GC patterns of the sample and reference.

7.6.4.4 PCB Quantitation option #2- Quantitate the PCB residues by comparing the responses of 3 to 5 major peaks in each appropriate Aroclor standard with the peaks obtained from the chlorinated biphenyls in the sample extract. The amount of Aroclor is calculated using each of the major peaks, and the results of the 3 to 5 determinations are averaged. Major peaks are defined as those peaks in the Aroclor standards that are at least 30% of the height of the largest Aroclor peak. Later eluting Aroclor peaks are generally the most stable in the environment.

7.6.5 Hexachlorocyclohexane (BHC, from the former name, benzene hexachloride): Technical grade BHC is a cream-colored amorphous solid

with a very characteristic musty odor; it consists of a mixture of six chemically distinct isomers and one or more heptachlorocyclohexanes and octachlorocyclohexanes. Commercial BHC preparations may show a wide variance in the percentage of individual isomers present. Quantitate each isomer (α, β, γ, and δ) separately against a standard of the respective pure isomer.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures. Quality control to validate sample extraction is covered in Method 3500 and in the extraction method utilized. If extract cleanup was performed, follow the QC in Method 3600 and in the specific cleanup method.

8.2 Mandatory quality control to evaluate the GC system operation is found in Method 8000.

8.2.1 The quality control check sample concentrate (Method 8000) should contain each single-component parameter of interest at the following concentrations in acetone: 4,4'-DDD, 10 mg/L; 4,4'-DDT, 10 mg/L; endosulfan II, 10 mg/L; endosulfan sulfate, 10 mg/L; endrin, 10 mg/L; and any other single-component pesticide, 2 mg/L. If this method is only to be used to analyze for PCBs, chlordane, or toxaphene, the QC check sample concentrate should contain the most representative multi-component parameter at a concentration of 50 mg/L in acetone.

8.2.2 Table 3 indicates the calibration and QC acceptance criteria for this method. Table 4 gives method accuracy and precision as functions of concentration for the analytes of interest. The contents of both Tables should be used to evaluate a laboratory's ability to perform and generate acceptable data by this method.

8.3 Calculate surrogate standard recovery on all samples, blanks, and spikes. Determine if the recovery is within limits (limits established by performing QC procedures outlined in Method 8000).

8.3.1 If recovery is not within limits, the following are required.

8.3.1.1 Check to be sure that there are no errors in the calculations, surrogate solutions or internal standards. If errors are found, recalculate the data accordingly.

8.3.1.2 Check instrument performance. If an instrument performance problem is identified, correct the problem and re-analyze the extract.

8.3.1.3 If no problem is found, re-extract and re-analyze the sample.

8.3.1.4 If, upon re-analysis, the recovery is again not within limits, flag the data as "estimated concentration".

8.4 GC/MS confirmation: Any compounds confirmed by two columns may also be confirmed by GC/MS if the concentration is sufficient for detection by GC/MS as determined by the laboratory generated detection limits.

8.4.1 The GC/MS would normally require a minimum concentration of 10 ng/µL in the final extract, for each single-component compound.

8.4.2 The pesticide extract and associated blank should be analyzed by GC/MS as per Section 7.0 of Method 8270.

8.4.3 The confirmation may be from the GC/MS analysis of the base/neutral-acid extractables extracts (sample and blank). However, if the compounds are not detected in the base/neutral-acid extract even though the concentration is high enough, a GC/MS analysis of the pesticide extract should be performed.

8.4.4 A reference standard of the compound must also be analyzed by GC/MS. The concentration of the reference standard must be at a level that would demonstrate the ability to confirm the pesticides/PCBs identified by GC/ECD.

9.0 METHOD PERFORMANCE

9.1 The method was tested by 20 laboratories using organic-free reagent water, drinking water, surface water, and three industrial wastewaters spiked at six concentrations. Concentrations used in the study ranged from 0.5 to 30 µg/L for single-component pesticides and from 8.5 to 400 µg/L for multi-component parameters. Single operator precision, overall precision, and method accuracy were found to be directly related to the concentration of the parameter and essentially independent of the sample matrix. Linear equations to describe these relationships for a flame ionization detector are presented in Table 4.

9.2 The accuracy and precision obtained will be determined by the sample matrix, sample-preparation technique, optional cleanup techniques, and calibration procedures used.

10.0 REFERENCES

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TABLE 1.
GAS CHROMATOGRAPHY OF PESTICIDES AND PCBs[a]

Analyte	Retention time (min) Col. 1	Col. 2	Method Detection limit (μg/L)
Aldrin	2.40	4.10	0.004
α-BHC	1.35	1.82	0.003
β-BHC	1.90	1.97	0.006
δ-BHC	2.15	2.20	0.009
γ-BHC (Lindane)	1.70	2.13	0.004
Chlordane (technical)	e	e	0.014
4,4'-DDD	7.83	9.08	0.011
4,4'-DDE	5.13	7.15	0.004
4,4'-DDT	9.40	11.75	0.012
Dieldrin	5.45	7.23	0.002
Endosulfan I	4.50	6.20	0.014
Endosulfan II	8.00	8.28	0.004
Endosulfan sulfate	14.22	10.70	0.066
Endrin	6.55	8.10	0.006
Endrin aldehyde	11.82	9.30	0.023
Heptachlor	2.00	3.35	0.003
Heptachlor epoxide	3.50	5.00	0.083
Methoxychlor	18.20	26.60	0.176
Toxaphene	e	e	0.24
PCB-1016	e	e	nd
PCB-1221	e	e	nd
PCB-1232	e	e	nd
PCB-1242	e	e	0.065
PCB-1248	e	e	nd
PCB-1254	e	e	nd
PCB-1260	e	e	nd

[a]U.S. EPA. Method 617. Organochlorine Pesticides and PCBs. Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268.

e = Multiple peak response.

nd = not determined.

TABLE 2.
DETERMINATION OF ESTIMATED QUANTITATION LIMITS (EQLs) FOR VARIOUS MATRICES[a]

Matrix	Factor[b]
Ground water	10
Low-concentration soil by sonication with GPC cleanup	670
High-concentration soil and sludges by sonication	10,000
Non-water miscible waste	100,000

a Sample EQLs are highly matrix-dependent. The EQLs listed herein are provided for guidance and may not always be achievable.

b EQL = [Method detection limit (Table 1)] X [Factor (Table 2)]. For non-aqueous samples, the factor is on a wet-weight basis.

TABLE 3.
QC ACCEPTANCE CRITERIA[a]

Analyte	Test conc. (µg/L)	Limit for s (µg/L)	Range for $\bar{x}$ (µg/L)	Range P, P_s (%)
Aldrin	2.0	0.42	1.08-2.24	42-122
α-BHC	2.0	0.48	0.98-2.44	37-134
β-BHC	2.0	0.64	0.78-2.60	17-147
δ-BHC	2.0	0.72	1.01-2.37	19-140
γ-BHC	2.0	0.46	0.86-2.32	32-127
Chlordane	50	10.0	27.6-54.3	45-119
4,4'-DDD	10	2.8	4.8-12.6	31-141
4,4'-DDE	2.0	0.55	1.08-2.60	30-145
4,4'-DDT	10	3.6	4.6-13.7	25-160
Dieldrin	2.0	0.76	1.15-2.49	36-146
Endosulfan I	2.0	0.49	1.14-2.82	45-153
Endosulfan II	10	6.1	2.2-17.1	D-202
Endosulfan Sulfate	10	2.7	3.8-13.2	26-144
Endrin	10	3.7	5.1-12.6	30-147
Heptachlor	2.0	0.40	0.86-2.00	34-111
Heptachlor epoxide	2.0	0.41	1.13-2.63	37-142
Toxaphene	50	12.7	27.8-55.6	41-126
PCB-1016	50	10.0	30.5-51.5	50-114
PCB-1221	50	24.4	22.1-75.2	15-178
PCB-1232	50	17.9	14.0-98.5	10-215
PCB-1242	50	12.2	24.8-69.6	39-150
PCB-1248	50	15.9	29.0-70.2	38-158
PCB-1254	50	13.8	22.2-57.9	29-131
PCB-1260	50	10.4	18.7-54.9	8-127

s = Standard deviation of four recovery measurements, in µg/L.

$\bar{x}$ = Average recovery for four recovery measurements, in µg/L.

P, P_s = Percent recovery measured.

D = Detected; result must be greater than zero.

[a]Criteria from 40 CFR Part 136 for Method 608. These criteria are based directly upon the method performance data in Table 4. Where necessary, the limits for recovery have been broadened to assure applicability of the limits to concentrations below those used to develop Table 4.

TABLE 4.
METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION[a]

Analyte	Accuracy, as recovery, x′ (μg/L)	Single analyst precision, s_r' (μg/L)	Overall precision, S′ (μg/L)
Aldrin	0.81C+0.04	$0.16\bar{x}-0.04$	$0.20\bar{x}-0.01$
α-BHC	0.84C+0.03	$0.13\bar{x}+0.04$	$0.23\bar{x}-0.00$
β-BHC	0.81C+0.07	$0.22\bar{x}+0.02$	$0.33\bar{x}-0.95$
δ-BHC	0.81C+0.07	$0.18\bar{x}+0.09$	$0.25\bar{x}+0.03$
γ-BHC	0.82C-0.05	$0.12\bar{x}+0.06$	$0.22\bar{x}+0.04$
Chlordane	0.82C-0.04	$0.13\bar{x}+0.13$	$0.18\bar{x}+0.18$
4,4′-DDD	0.84C+0.30	$0.20\bar{x}-0.18$	$0.27\bar{x}-0.14$
4,4′-DDE	0.85C+0.14	$0.13\bar{x}+0.06$	$0.28\bar{x}-0.09$
4,4′-DDT	0.93C-0.13	$0.17\bar{x}+0.39$	$0.31\bar{x}-0.21$
Dieldrin	0.90C+0.02	$0.12\bar{x}+0.19$	$0.16\bar{x}+0.16$
Endosulfan I	0.97C+0.04	$0.10\bar{x}+0.07$	$0.18\bar{x}+0.08$
Endosulfan II	0.93C+0.34	$0.41\bar{x}-0.65$	$0.47\bar{x}-0.20$
Endosulfan Sulfate	0.89C-0.37	$0.13\bar{x}+0.33$	$0.24\bar{x}+0.35$
Endrin	0.89C-0.04	$0.20\bar{x}+0.25$	$0.24\bar{x}+0.25$
Heptachlor	0.69C+0.04	$0.06\bar{x}+0.13$	$0.16\bar{x}+0.08$
Heptachlor epoxide	0.89C+0.10	$0.18\bar{x}-0.11$	$0.25\bar{x}-0.08$
Toxaphene	0.80C+1.74	$0.09\bar{x}+3.20$	$0.20\bar{x}+0.22$
PCB-1016	0.81C+0.50	$0.13\bar{x}+0.15$	$0.15\bar{x}+0.45$
PCB-1221	0.96C+0.65	$0.29\bar{x}-0.76$	$0.35\bar{x}-0.62$
PCB-1232	0.91C+10.79	$0.21\bar{x}-1.93$	$0.31\bar{x}+3.50$
PCB-1242	0.91C+10.79	$0.21\bar{x}-1.93$	$0.31\bar{x}+3.50$
PCB-1248	0.91C+10.79	$0.21\bar{x}-1.93$	$0.31\bar{x}+3.50$
PCB-1254	0.91C+10.79	$0.21\bar{x}-1.93$	$0.31\bar{x}+3.50$
PCB-1260	0.91C+10.79	$0.21\bar{x}-1.93$	$0.31\bar{x}+3.50$

x′ = Expected recovery for one or more measurements of a sample containing concentration C, in μg/L.

s_r' = Expected single analyst standard deviation of measurements at an average concentration of $\bar{x}$, in μg/L.

S′ = Expected interlaboratory standard deviation of measurements at an average concentration found of $\bar{x}$, in μg/L.

C = True value for the concentration, in μg/L.

$\bar{x}$ = Average recovery found for measurements of samples containing a concentration of C, in μg/L.

Figure 1
Gas Chromatogram of Pesticides

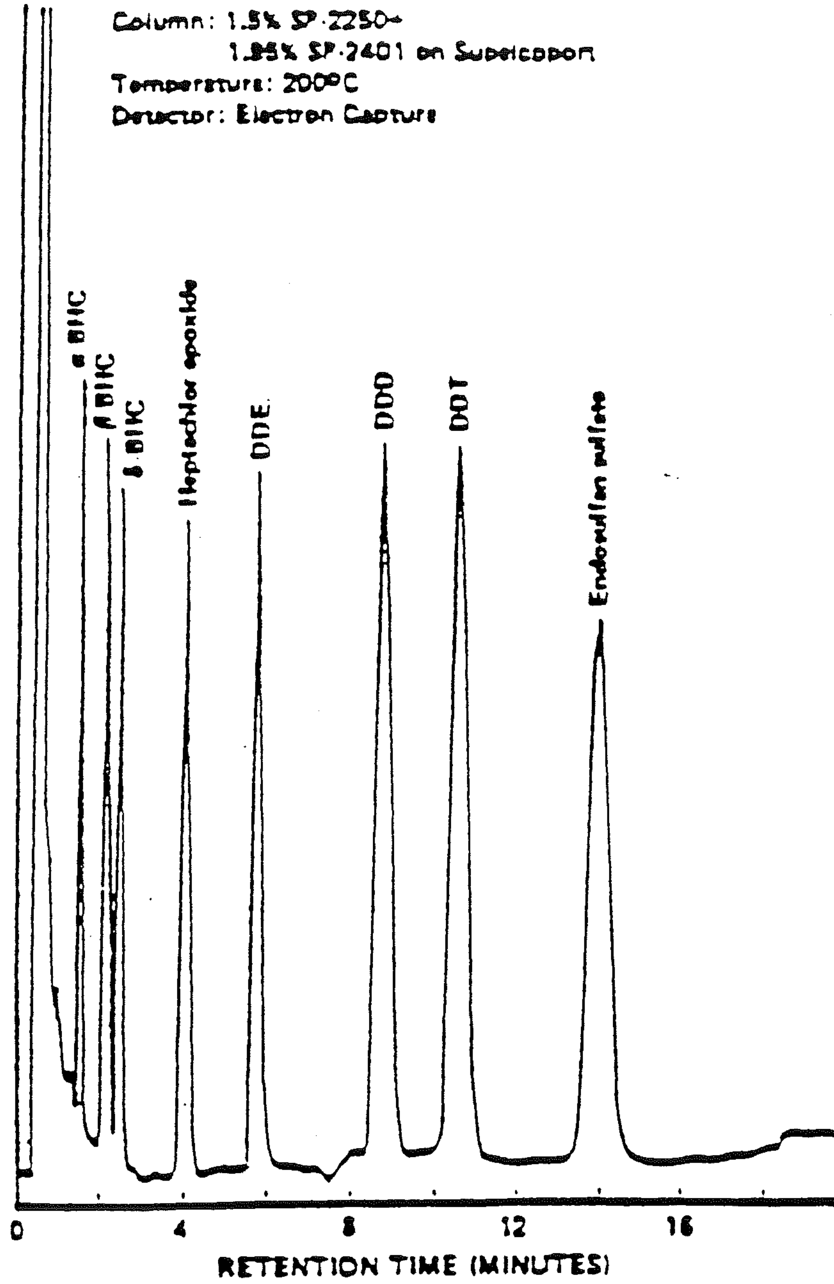


Figure 2
Gas Chromatogram of Chlordane

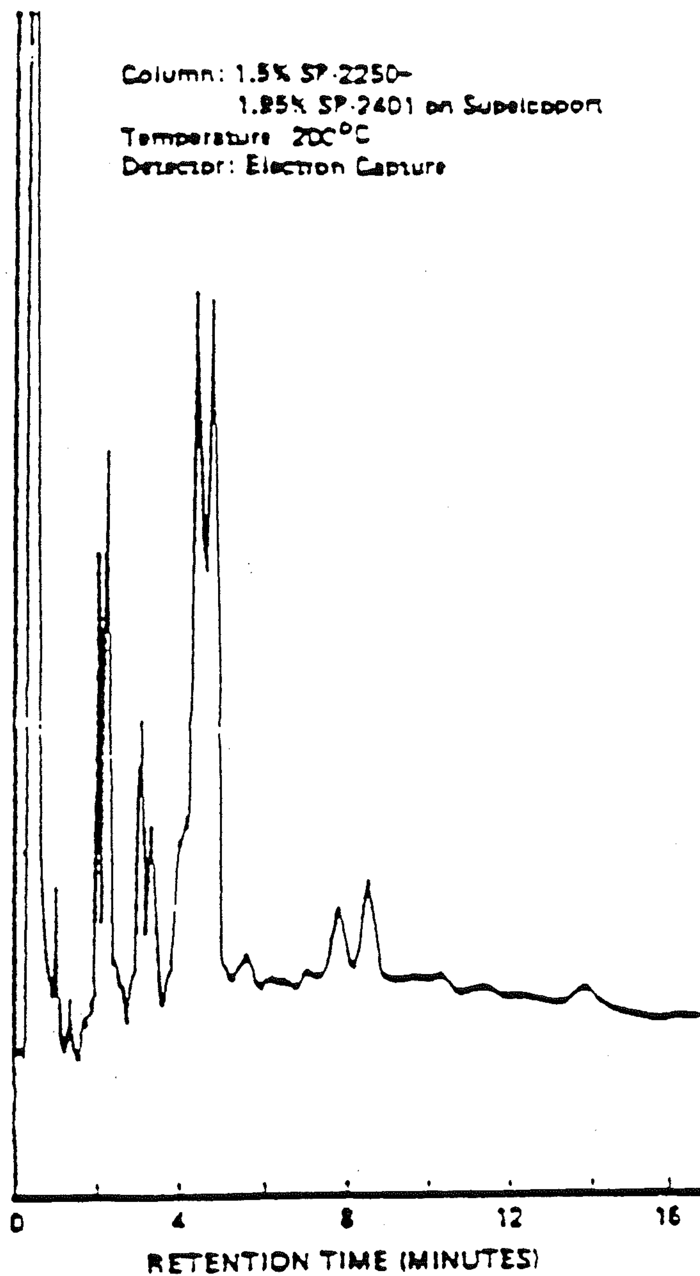


Figure 3
Gas Chromatogram of Toxaphene

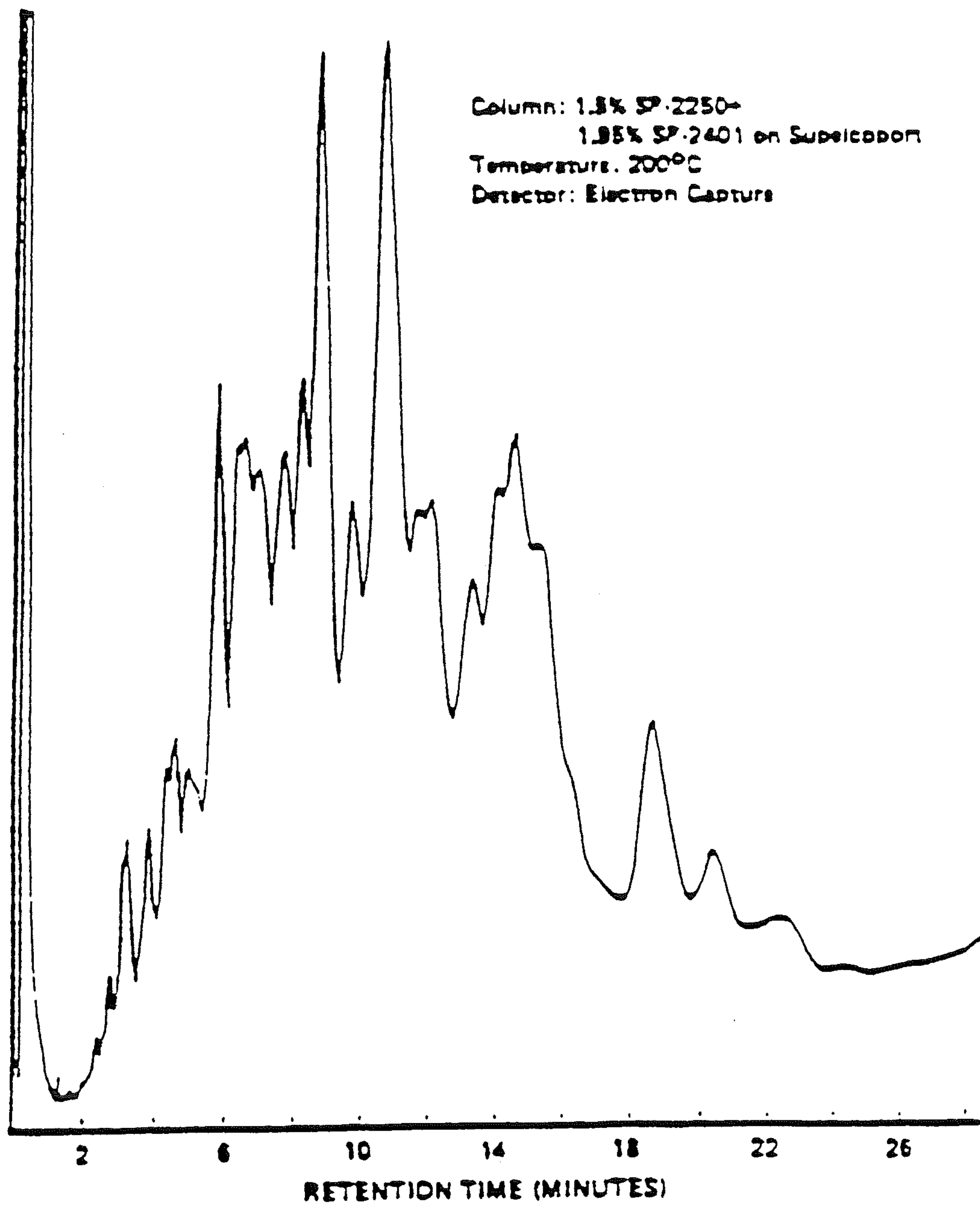


Figure 4
Gas Chromatogram of Aroclor 1254

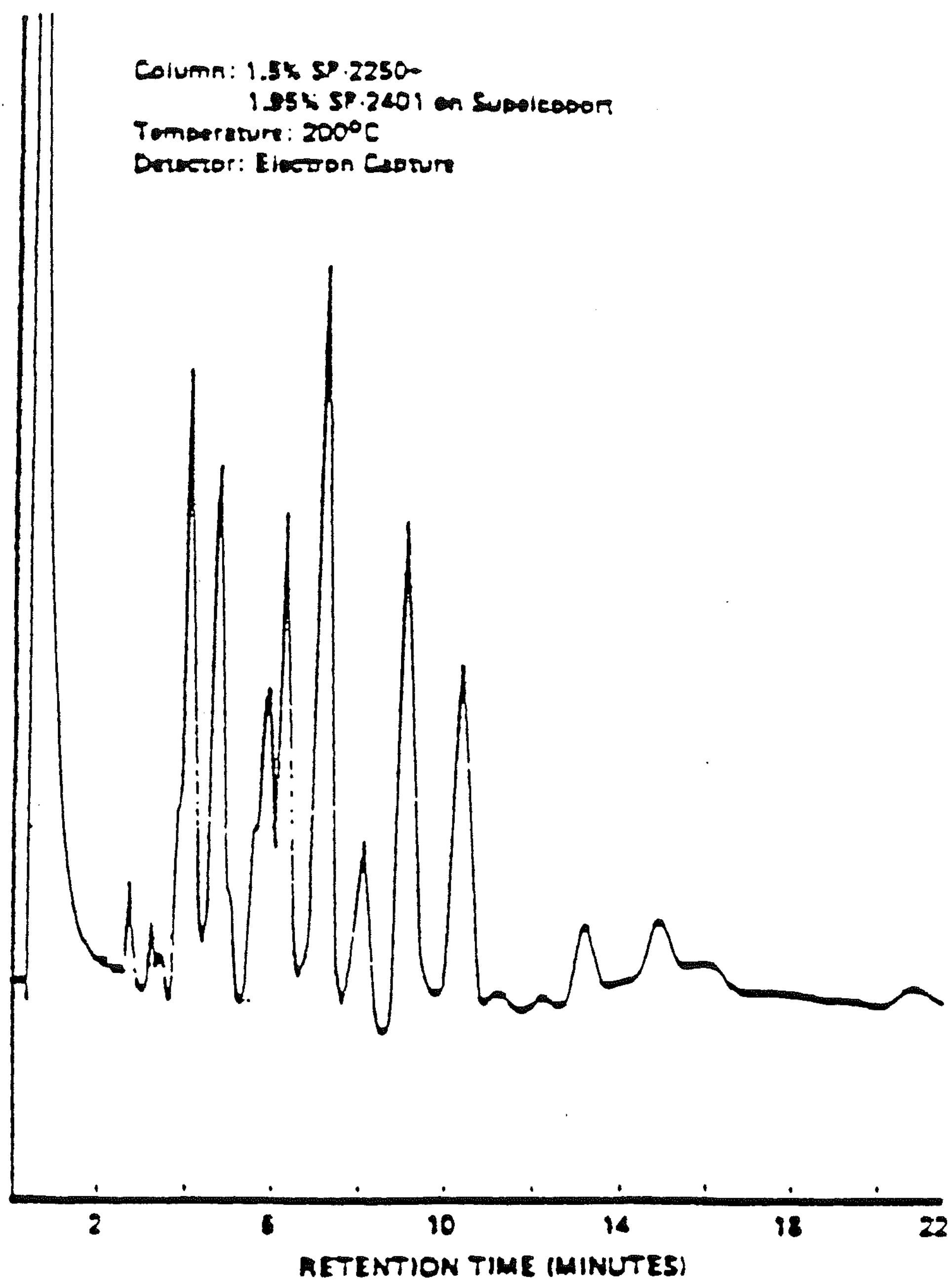


Figure 5
Gas Chromatogram of Aroclor 1260

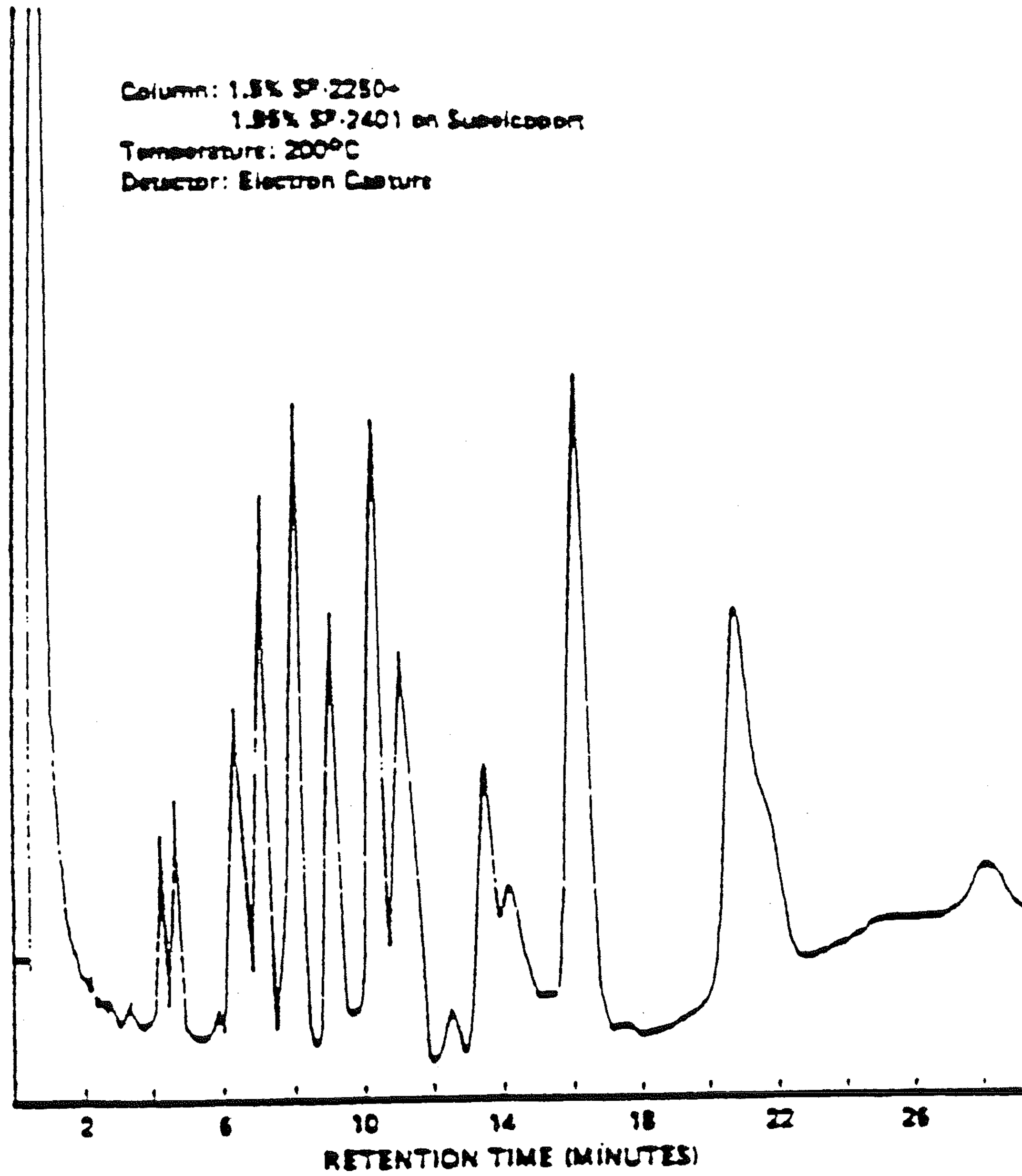


Figure 6

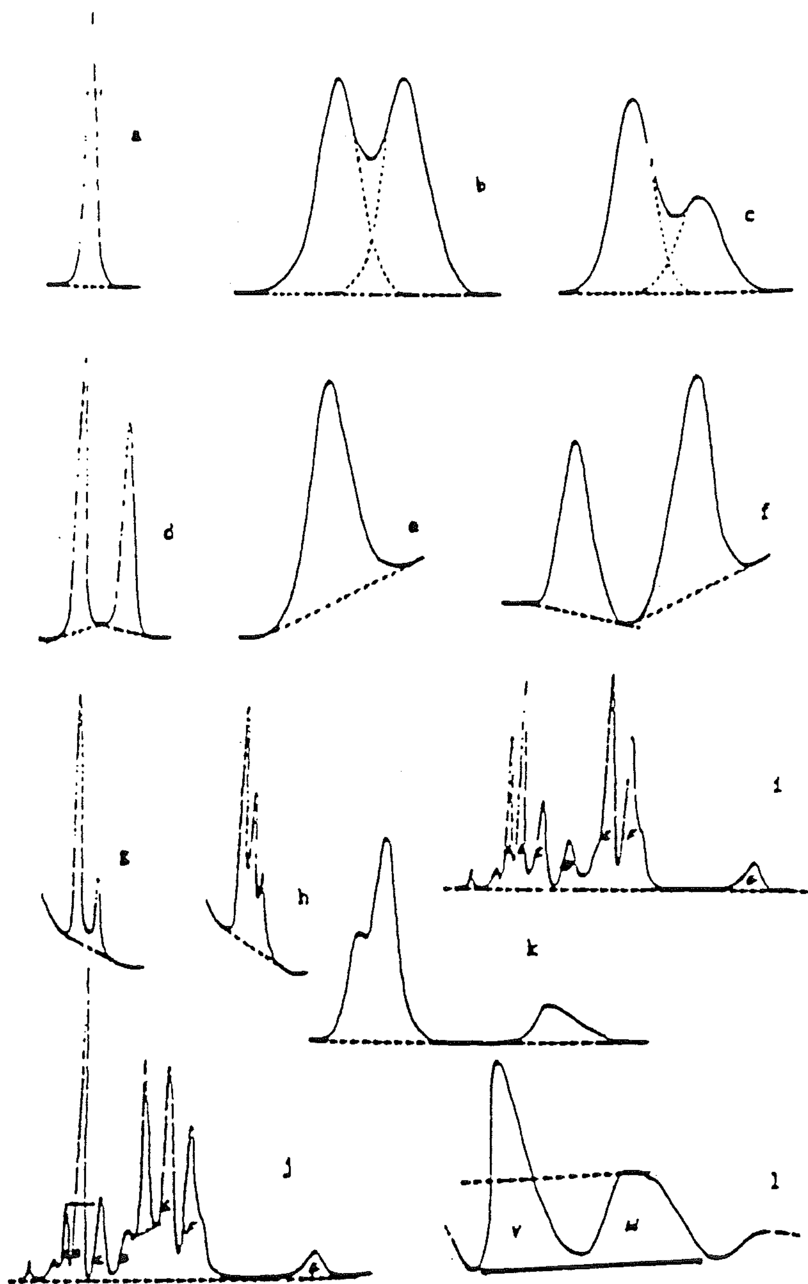


Fig. 6—Baseline construction for some typical gas chromatographic peaks. a, symmetrical separated flat baseline; b and c, overlapping flat baseline; d, separated (pen does not return to baseline between peaks); e, separated sloping baseline; f, separated (pen goes below baseline between peaks); g, α- and γ-BHC sloping baseline; h, α-, β-, and γ-BHC sloping baseline; i, chlordane flat baseline; j, heptachlor and heptachlor epoxide superimposed on chlordane; k, chair-shaped peaks, unsymmetrical peak; l, p,p'-DDT superimposed on toxaphene.

Figure 7

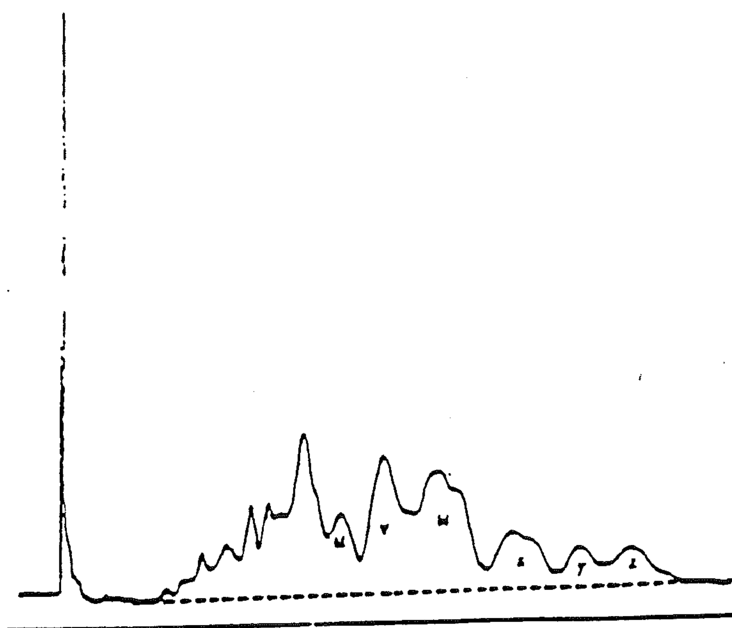


Fig. 7a—Baseline construction for multiple residues with standard toxaphene.

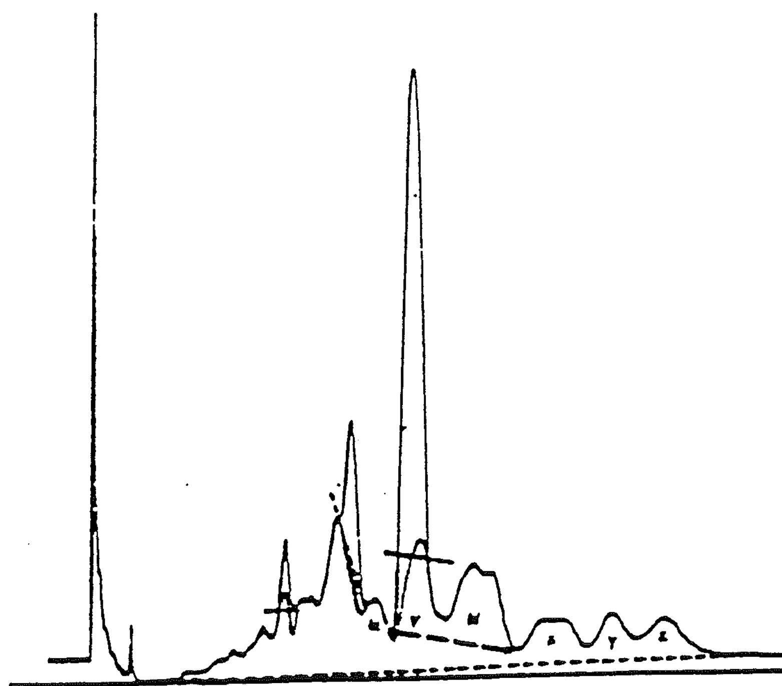


Fig. 7b—Baseline construction for multiple residues with toxaphene, DDE and o,p'-, and p,p'-DDT.

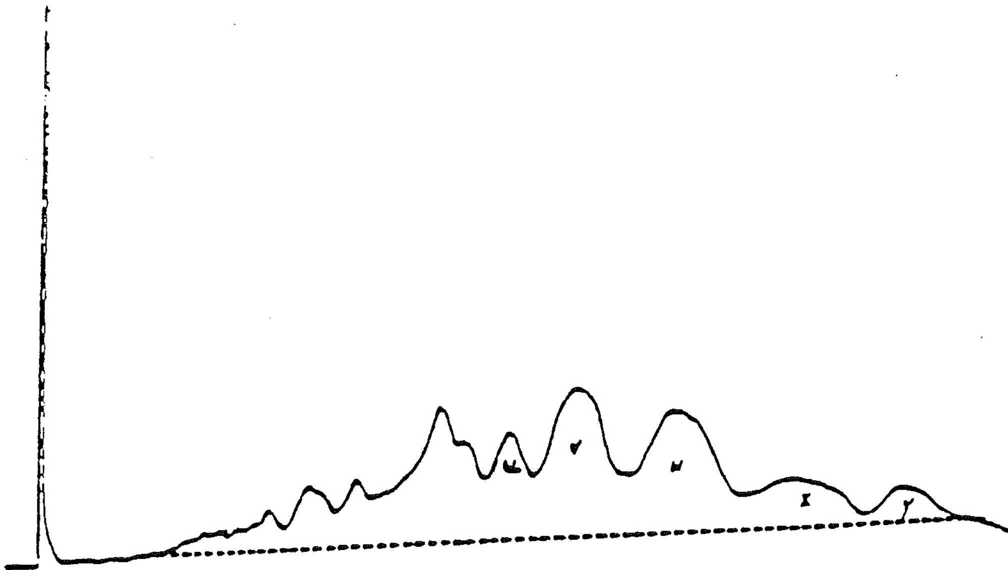


Fig. 8a—Baseline construction for multiple residues: standard toxaphene.

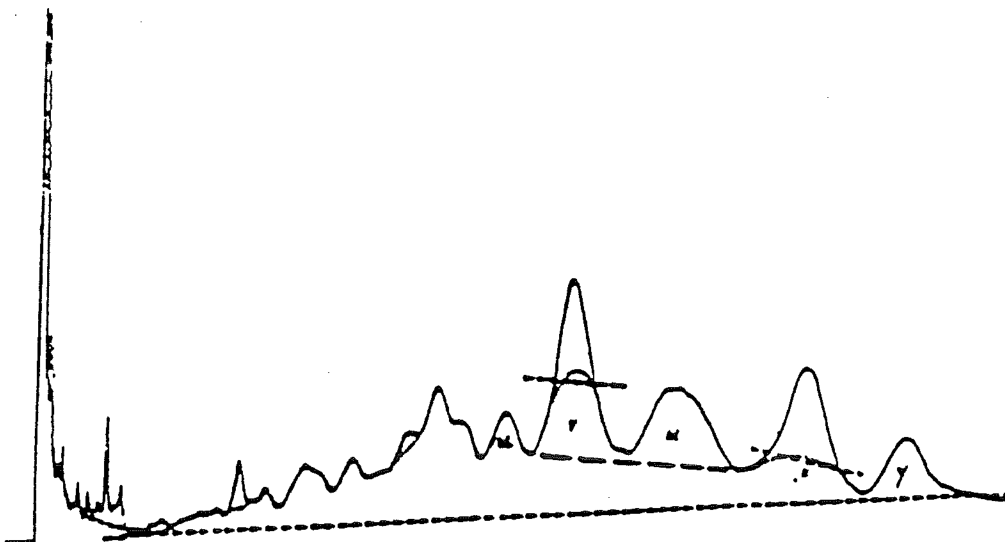


Fig. 8b—Baseline construction for multiple residues: rice bran with BHC, toxaphene, DDT, and methoxychlor.

Figure 9

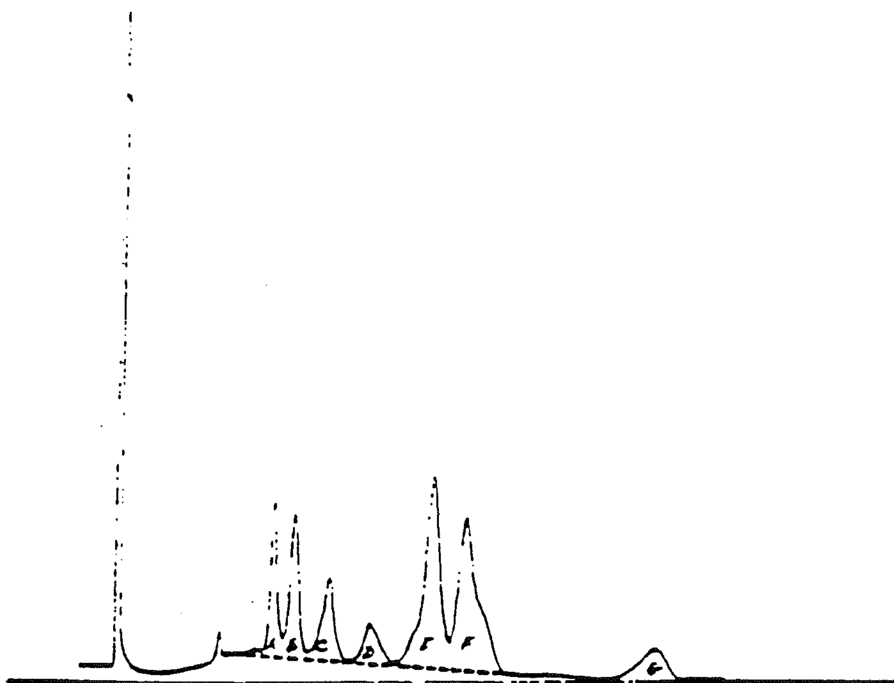


Fig. 9a—Baseline construction for multiple residues: standard chlordane.

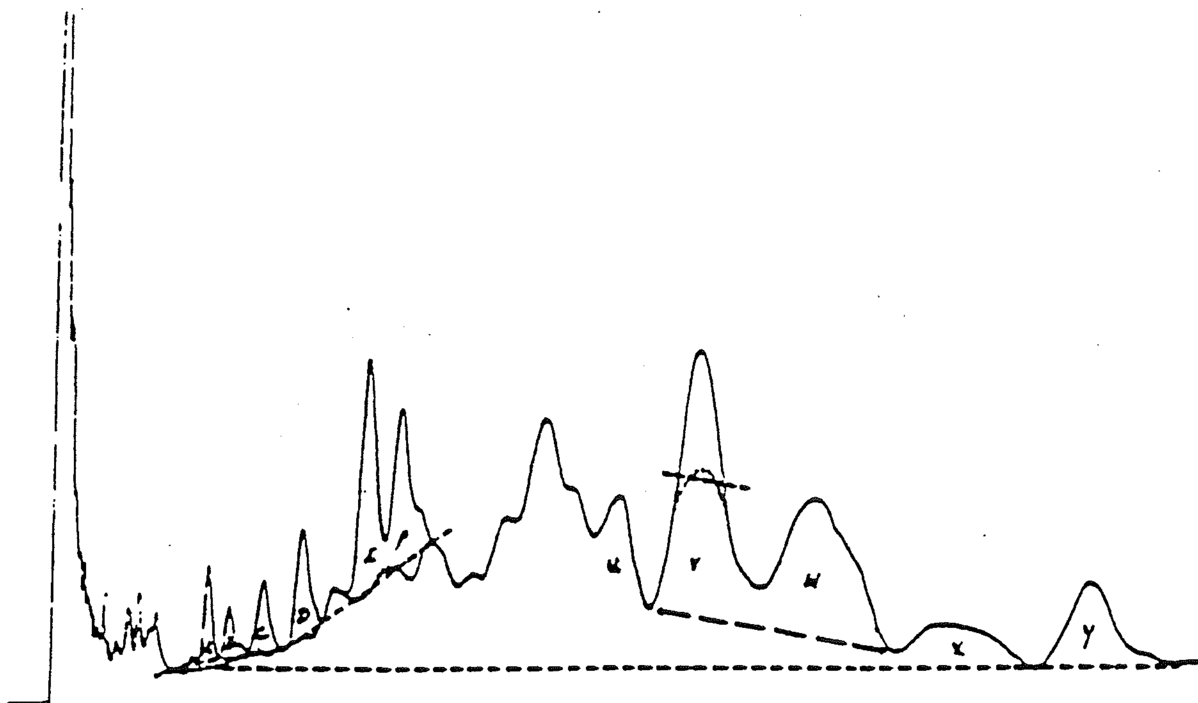
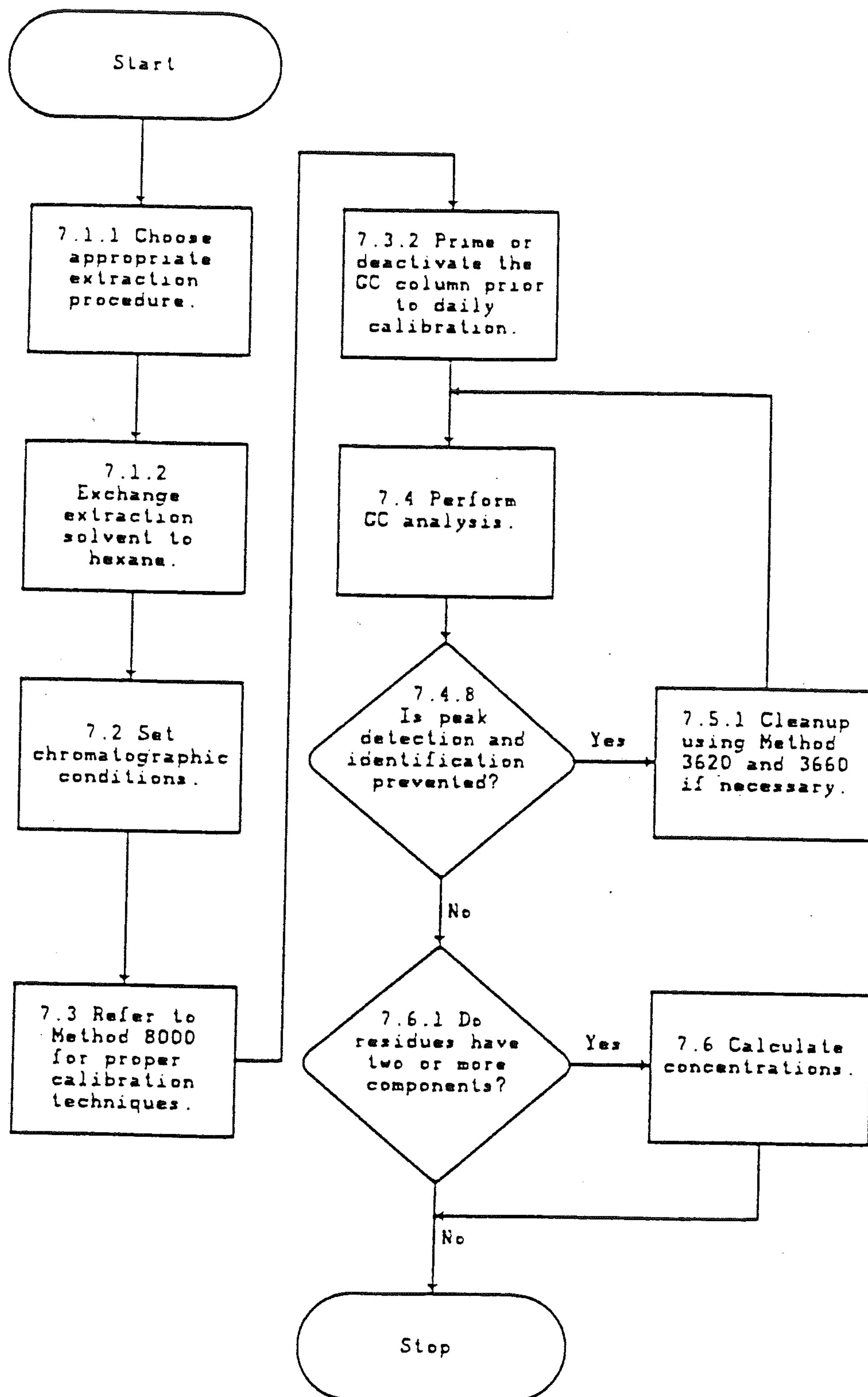


Fig. 9b—Baseline construction for multiple residues: rice bran with chlordane, toxaphene, and DDT.


Start
7.1.1 Choose appropriate extraction procedure.
7.1.2 Exchange extraction solvent to hexane.
7.2 Set chromatographic conditions.
7.3 Refer to Method 8000 for proper calibration techniques.
7.3.2 Prime or deactivate the GC column prior to daily calibration.
7.4 Perform GC analysis.
7.4.8 Is peak detection and identification prevented?
Yes
7.5.1 Cleanup using Method 3620 and 3660 if necessary.
No
7.6.1 Do residues have two or more components?
Yes
7.6 Calculate concentrations.
No
Stop

METHOD 8081

ORGANOCHLORINE PESTICIDES AND PCBs AS AROCLORS BY GAS CHROMATOGRAPHY: CAPILLARY COLUMN TECHNIQUE

1.0 SCOPE AND APPLICATION

1.1 Method 8081 is used to determine the concentrations of various organochlorine pesticides, and polychlorinated biphenyls (PCBs) as Aroclors, in extracts from solid and liquid matrices. A large number of compounds will give a response in the electron capture detector (ECD) using this method; performance data for the following compounds are provided as part of this method:

Compound Name	CAS No.[a]
Aldrin	309-00-2
alpha-BHC	319-84-6
beta-BHC	319-85-7
delta-BHC	319-86-8
gamma-BHC (Lindane)	58-89-9
gamma-Chlordane	57-74-9
4,4'-DDD	72-54-8
4,4'-DDE	72-55-9
4,4'-DDT	50-29-3
Dieldrin	60-57-1
Endosulfan I	959-98-8
Endosulfan II	33212-65-9
Endosulfan sulfate	1031-07-8
Endrin	72-20-8
Endrin aldehyde	7421-93-4
Heptachlor	76-44-8
Heptachlor epoxide	1024-57-3
4,4'-Methoxychlor	72-43-5
Toxaphene	8001-35-2
Aroclor-1016	12674-11-2
Aroclor-1221	1104-28-2
Aroclor-1232	11141-16-5
Aroclor-1242	53469-21-9
Aroclor-1248	12672-29-6
Aroclor-1254	11097-69-1
Aroclor-1260	11096-82-5

[a] Chemical Abstract Services Registry Number.

1.2 This capillary GC/ECD method allows the analyst the option of using 0.25-0.32 mm ID capillary columns (narrow bore) or 0.53 mm ID capillary columns (wide bore). Performance data are provided for both options.

1.3 The use of narrow bore columns are recommended when the analyst requires greater chromatographic resolution and is analyzing a relatively clean sample or an extract that has been prepared with one or more of the clean-up options referenced in the method. Wider bore columns (0.53 mm) are suitable for more complex environmental and waste matrices. The 0.53 mm ID columns can be mounted in 1/4 inch packed column injectors.

1.4 Table 1 lists average retention times and method detection limits (MDLs) for each compound of interest, in water and soil matrices, for the wide-bore capillary column version of this method. Table 2 lists average retention times and method detection limits (MDLs) for each compound of interest, in water and soil matrices, for the narrow-bore capillary column version of this method. The MDLs for the components of a specific sample may differ from those listed in Tables 1 and 2 because they are dependent upon the nature of interferences in the sample matrix. Retention time information given in Table 2 was obtained on two wide-bore, open tubular columns connected to the injector port of a gas chromatograph through an injection tee made of deactivated glass. Table 3 lists the Estimated Quantitation Limits (EQLs) for other matrices.

1.5 When this method is used to analyze for any or all of the target compounds, compound identification based on single column analysis should be confirmed on a second column, or should be supported by at least one other qualitative technique. This method describes analytical conditions for a second gas chromatographic column that can be used to confirm the measurements made with the primary column.

1.6 This method is restricted to use by or under the supervision of analysts experienced in the use of a gas chromatograph (GC) and in the interpretation of gas chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method.

1.7 Extracts suitable for analysis by this method may also be analyzed for organophosphorus pesticides (Method 8141) and triazine herbicides.

2.0 SUMMARY OF METHOD

2.1 A measured volume or weight of sample (approximately 1 L for liquids, 2 g to 30 g for solids) is extracted using the appropriate sample extraction technique specified in Methods 3510, 3520, 3540, 3541, 3550 and 3580. Liquid samples are extracted at neutral pH with methylene chloride using either a separatory funnel (Method 3510) or a continuous liquid-liquid extractor (Method 3520). Solid samples are extracted with hexane-acetone (1:1) or methylene chloride-acetone (1:1) using either Soxhlet extraction (Method 3540), Automated Soxhlet (Method 3541), or Ultrasonic Extraction (Method 3550). A variety of cleanup steps may be applied to the extract, depending on (1) the nature of the coextracted matrix interferences and (2) the target analytes. After cleanup, the extract is analyzed by injecting a 1 μL sample into a gas chromatograph with a narrow- or wide-bore fused silica capillary column and electron capture detector (GC/ECD).

2.2 The MDLs achievable in routine analyses of complex samples using Method 8081 will usually be dependent on the degree of interference associated

with the presence of coeluting compounds to which the ECD will respond, rather than on the inherent limitations in detector performance or the irreducible noise associated with instrument electronics. If interferences prevent identification and qualification of the analytes within quality control (QC) limits at relevant concentrations, Method 8081 may also be performed on samples that have undergone cleanup. Method 3630, Silica Gel Column Cleanup, by itself, or followed by Method 3660, Sulfur Cleanup, may be used to eliminate interferences in the analysis. Method 3640, Gel-Permeation Cleanup, is applicable for samples that contain high amounts of lipids, waxes and other high molecular weight co-extractables.

3.0 INTERFERENCES

3.1 Refer to Methods 3550 (Section 3.5, in particular), 3600, and 8000.

3.2 Sources of interference in this method can be grouped into three broad categories: contaminated solvents, reagents or sample processing hardware; contaminated GC carrier gas, parts, column surfaces or detector surfaces; and the presence of coeluting compounds in the sample matrix to which the ECD will respond. Knowledge of good laboratory practices is assumed, including steps to be followed in routine testing and cleanup of solvents, reagents and sample processing hardware, and instrument maintenance. The discussion that follows focuses on sources of interference associated with the sample matrix and compound classes that represent common sources of interference, particularly phthalate esters, organosulfur compounds, lipids, and waxes. Interferences coextracted from the samples will vary considerably from waste to waste. While general cleanup techniques are referenced or provided as part of this method, unique samples may require additional cleanup approaches to achieve desired degrees of discrimination and quantitation.

3.3 Interferences by phthalate esters introduced during sample preparation can pose a major problem in pesticide determinations. These materials may be removed prior to analysis using Gel Permeation Cleanup - pesticide option (Method 3640) or as Fraction III of the silica gel cleanup procedure (Method 3630). Common flexible plastics contain varying amounts of phthalate esters which 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 phthalate esters can best be minimized by avoiding contact with any plastic materials and checking all solvents and reagents for phthalate contamination. Exhaustive cleanup of solvents, reagents and glassware may be required to eliminate background phthalate ester contamination.

3.4 The presence of elemental sulfur will result in large peaks that interfere with the detection of later eluting organochlorine pesticides. Method 3660 is suggested for removal of sulfur. Since the recovery of endrin aldehyde (using the TBA procedure) is drastically reduced, this compound must be determined prior to sulfur cleanup.

3.5 Waxes, lipids other high molecular weight co-extractables can be removed by Gel-Permeation Cleanup (Method 3640).

3.6 Other pesticides may be interferences in this method. Table 4 lists the names and retention times of organophosphorus pesticides which co-elute with organochlorine pesticides on wide-bore capillary columns. Organophosphorus pesticides are eliminated by the Gel Permeation Chromatography cleanup - pesticide option (Method 3640).

3.7 It may be difficult to quantitate Aroclor patterns and single component pesticides together. Pesticides can be removed by sulfuric acid/permanganate cleanup (Method 3665) and silica fractionation (Method 3630). Guidance on the identification of PCBs is given in Section 7.6.4.

4.0 APPARATUS AND MATERIALS

4.1 Glassware (see Methods 3510, 3520, 3540, 3541, 3550, 3630, 3640, and 3660 for specifications).

4.2 Kuderna-Danish (K-D) apparatus.

4.2.1 Concentrator tube - 10 mL graduated (Kontes K-570050-1025 or equivalent). If extracts are stored in the concentrator tube, a ground glass stopper is used to prevent evaporation of concentrates.

4.2.2 Evaporation flask - 500 mL (Kontes K-570001-500 or equivalent). Attach to concentrator with springs.

4.2.3 Snyder column - Three ball macro (Kontes K-503000-0121 or equivalent).

4.2.4 Springs, clips and clamps - 1/2 inch springs (Kontes K-662750 or equivalent), or any other equivalent fastener, e.g., neck standard taper clips. Clamp (Kontes 675300 or equivalent).

4.2.5 Boiling chips - Approximately 10/40 mesh (silicon carbide or equivalent). Prior to use, heat to 400°C for 30 minutes or Soxhlet extract with methylene chloride.

4.3 Gas chromatograph - Analytical system complete with gas chromatograph suitable for on-column and split-splitless injection and all required accessories including syringes, analytical columns, gases, electron capture detector, and recorder/integrator or data system.

4.3.1 Narrow-bore columns

4.3.1.1 Column 1 - 30 m x 0.25 or 0.32 mm internal diameter (ID) fused silica capillary column chemically bonded with SE-54 (DB 5 or equivalent), 1 μm film thickness.

4.3.1.2 Column 2 - 30 m x 0.25 mm ID fused silica capillary column chemically bonded with 35 percent phenyl methylpolysiloxane (DB 608, SPB 608, or equivalent), 25 μm coating thickness, 1 μm film thickness.

4.3.1.3 Narrow bore columns should be installed in split/splitless (Grob-type) injectors.

4.3.2 Wide-bore columns

4.3.2.1 Column 1 - 30 m x 0.53 mm ID fused silica capillary column chemically bonded with 35 percent phenyl methylpolysiloxane (DB 608, SPB 608, RTx-35, or equivalent), 0.5 μm or 0.83 μm film thickness.

4.3.2.2 Column 2 - 30 m x 0.53 mm ID fused silica capillary column chemically bonded with 50 percent phenyl methylpolysiloxane (DB 1701, or equivalent), 1.0 μm film thickness.

4.3.2.3 Column 3 - 30 m x 0.53 mm ID fused silica capillary column chemically bonded with SE-54 (DB 5, SPB 5, RTx, or equivalent), 1.5 μm film thickness.

4.3.2.4 Wide-bore columns should be installed in 1/4 inch injectors with deactivated liners designed specifically for use with these columns.

4.4 GC injector ports can be of critical concern, especially in the analysis of DDT and Endrin. Injectors that are contaminated, chemically active, or too hot can cause the degradation ("breakdown") of the analytes. Endrin and DDT breakdown to endrin aldehyde, endrin ketone, DDD, or DDE. When such breakdown is observed, clean and deactivate the injector port, break off at least 0.5 M of the column and remount it. Check the injector temperature and lower it to 205°C, if required. Endrin and DDT breakdown is less of a problem when ambient on-column injectors are used.

5.0 REAGENTS

5.1 Reagent or pesticide grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Organic-free reagent water. All references to water in this method refer to organic-free reagent water as defined in Chapter One.

5.3 Solvents and reagents: As appropriate for Method 3510, 3520, 3540, 3541, 3550, 3630, 3640, or 3660: n-hexane, diethyl ether, methylene chloride, acetone, ethyl acetate, and isooctane (2,2,4-trimethylpentane). All solvents should be pesticide quality or equivalent, and each lot of solvent should be determined to be phthalate free.

5.4 Silica gel (optional) PR grade (100/200 mesh) - Before use, activate at least 16 hours at 130° to 140°C. Deactivate with water (3.3 percent, by

weight) and equilibrate for 1 hour. Disposable silica cartridges (LC-silica or equivalent), 1 g each, may be used in place of the deactivated silica gel.

5.5 Stock standard solutions:

5.5.1 Prepare stock standard solutions at a concentration of 1000 mg/L by dissolving 0.1000 ± 0.0010 g of assayed reference material in isooctane or hexane and diluting to volume in a 100 mL volumetric flask. When compound purity is assayed to be 96 percent or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards can be used at any concentration if they are certified by the manufacturer or by an independent source.

5.5.1.1 Beta-BHC and dieldrin are not adequately soluble in isooctane. Acetone, or toluene should be used for the preparation of the stock standard solutions of these compounds.

5.5.2 Transfer the stock standard solutions into bottles with Teflon-lined screw-caps. Store at 4°C and protect from light. Stock standards should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

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

5.6 Calibration standards:

5.6.1 Calibration standards, at a minimum of three concentrations for each parameter of interest, are prepared through dilution of the stock standards with isooctane. One of the concentrations should be at a concentration near, but above, the method detection limit. The remaining concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the GC.

5.6.2 Calibration solutions must be replaced after two months, or sooner, if comparison with check standards indicates a problem.

5.6.3 Although all single column analytes can be resolved on a new 35 percent phenyl methylpolysiloxane column, some analytes co-elute on the other columns or on older 35 percent phenyl methylpolysiloxane columns. Two calibration mixtures should be prepared for the single component analytes of this method to eliminate potential resolution and quantitation problems. Recommended low point mixtures are given in Table 9.

5.7 Internal standards (if internal standard calibration is used):

5.7.1 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. Pentachloronitrobenzene is suggested as an internal standard.

5.7.2 Prepare calibration standards at a minimum of three concentrations for each analyte of interest as described in Section 5.6.

5.7.3 To each calibration standard, add a known constant amount of one or more internal standards.

5.7.4 Analyze each calibration standard according to Section 7.0.

5.8 Surrogate standards: The analyst should monitor the performance of the extraction, cleanup (when used), and analytical system, and the effectiveness of the method in dealing with each sample matrix, by spiking each sample, standard, and organic-free reagent water blank with pesticide surrogates. Because GC/ECD analyses are more subject to interference than GC/MS analyses, a secondary surrogate is to be used when sample interference is apparent. Decachlorobiphenyl is the primary surrogate, and should be used whenever possible. However, if recovery is low, or compounds interfere with decachlorobiphenyl, then 2,4,5,6-tetrachloro-m-xylene should be evaluated for acceptance. Proceed with corrective action when both surrogates are out of limits for a sample (Section 8.3). Method 3500, Section 5.3.2, indicates the proper procedure for preparing these surrogates.

6.0 SAMPLE COLLECTION, PRESERVATION AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

6.2 Extracts must be stored under refrigeration and analyzed within 40 days of extraction.

7.0 PROCEDURE

7.1 Extraction:

7.1.1 Refer to Chapter Two for guidance in choosing the appropriate extraction procedure. In general, water samples are extracted at a neutral pH with methylene chloride as a solvent using a separatory funnel (Method 3510) or a continuous liquid-liquid extractor (Method 3520). Extract solid samples with hexane-acetone (1:1) using either of the Soxhlet extraction (Method 3540 or 3541) or ultrasonic extraction (Method 3550) procedures.

NOTE: Hexane/acetone (1:1) may be a more effective extraction solvent for organochlorine pesticide and PCBs in some environmental and waste matrices. The current solvent mixture recommended in Method 3550 is methylene chloride/acetone (1:1).

7.1.2 Spiked samples are used to verify the applicability of the chosen extraction technique to each new sample type. Each sample must be spiked with the compounds of interest to determine the percent recovery and the limit of detection for that sample.

7.1.2.1 Spiking of water samples should be performed by adding appropriate amounts of pesticide and PCB compounds, dissolved in

methanol, to the water sample immediately prior to extraction. After addition of the spike, mix the samples manually for 1 to 2 minutes. Typical spiking concentrations for water samples are 1 to 10 µg/L for samples in which pesticides and PCBs were not detected and 2 to 5 times the background concentration in those cases where pesticides and PCBs are present (use of mixtures of Aroclors other than 1016/1260 is not recommended with this method).

7.1.2.2 Spiking of soil samples should be performed by adding appropriate amounts of pesticide and PCB compounds, which are dissolved in methanol, to the solid samples. The solid sample should be wet prior to the addition of the spike (at least 20 percent moisture) and should be mixed thoroughly with a glass rod to homogenize the material. Allow the spike to equilibrate with the solid for 1 hour at room temperature prior to extraction. Transfer the entire spiked portion with the test compounds to the extraction thimble for Soxhlet extraction (Method 3540), Automated Soxhlet (Method 3541), or proceed with the ultrasonic extraction (Method 3550).

7.2 Cleanup/Fractionation

7.2.1 Cleanup procedures may not be necessary for a relatively clean sample matrix, but most extracts from environmental and waste samples will require additional preparation before analysis. The specific cleanup procedure used will depend on the nature of the sample to be analyzed and the data quality objectives for the measurements. General guidance for sample extract cleanup is provided in this section.

7.2.2 If a sample is of biological origin, or contains high molecular weight materials, the use of GPC cleanup/pesticide option (Method 3640) is recommended.

7.2.3 If only PCBs are to be measured in a sample, the sulfuric acid/permanganate cleanup (Method 3665), followed by silica gel fractionation (Method 3630) or Florisil cartridge cleanup (Method 3620), is recommended.

7.2.4 If both PCBs and pesticides are to be measured in the sample, isolation of the PCB fraction by silica gel fractionation (Method 3630) is recommended.

7.2.5 If only pesticides are to be measured, cleanup by Method 3620 or Method 3630 is recommended.

7.2.6 Elemental sulfur, which may appear in certain sediments and industrial wastes, interferes with the electron capture gas chromatography of certain pesticides. Sulfur should be removed by the technique described in Method 3660, Sulfur Cleanup.

7.3 Gas chromatography conditions (Recommended):

7.3.1 Narrow-bore columns:

7.3.1.1 Column 1:

Carrier gas (He) = 16 psi
Injector temperature = 225°C
Detector temperature = 300°C
Initial temeprature = 100°C, hold 2 minutes
Temperature program = 100°C to 160°C at 15°C/min, followed by; 160°C to 270°C at 5°C/min
Final temperature = 270°C.

7.3.1.2 Column 2:

Carrier gas (N_2) = 20 psi
Injector temperature = 225°C
Detector temperature = 300°C
Initial temeprature = 160°C, hold 2 minutes
Temperature program = 160°C to 290°C at 5°C/min
Final temperature = 290°C, hold 1 minute.

7.3.1.3 Table 1 gives the retention times and MDLs that can be achieved by this method for the organochlorine pesticides and PCBs. Examples of the separations achieved with the SE-54 fused silica capillary column are shown in Figures 1 through 6.

7.3.2 Wide-bore columns:

7.3.2.1 Column 1 and Column 2:

Carrier gas (He) = 5-7 mL/minute
Makeup gas (argon/methane (P-5 or P-10) or N_2) = 30 mL/min
Injector temperature = 250°C
Detector temperature = 290°C
Initial temeprature = 150°C, hold 0.5 minute
Temperature program = 150°C to 270°C at 5°C/min
Final temperature = 270°C, hold 10 minutes.

7.3.2.2 Column 3:

Carrier gas (He) = 6 mL/minute
Makeup gas (argon/methane (P-5 or P-10) or N_2) = 30 mL/min
Injector temperature = 205°C
Detector temperature = 290°C 310
Initial temeprature = 140°C, hold 2 minutes
Temperature program = 140°C to 240°C at 10°C/min, hold 5 minutes at 240°C, 240°C to 265°C at 5°C,
Final temperature = 265°C, hold 18 minutes.

7.3.3 Additional columns - The columns listed in this section were used to develop the method performance data; they are recommended for use in the analysis of organochlorine pesticides and PCBs. Their specification is not intended to prevent laboratories from using columns that are developed after promulgation of the method. Laboratories may use other capillary columns if they document method performance data (e.g.

chromatographic resolution, analyte breakdown, and MDL's) equal to or better than that provided with the method.

7.3.4 Table 2 gives the retention times and MDLs that can be achieved by this method for the organochlorine pesticides or PCBs. Examples of the separations achieved with the 35 percent phenyl methylpolysiloxane, 50 percent phenyl methylpolysiloxane and SE-54 fused-silica, wide-bore, open-tubular columns are shown in Figures 1 through 6.

7.4 Calibration:

7.4.1 Refer to Method 8000 for proper calibration techniques. Use Tables 1 and 2 for guidance on selecting the lowest point on the calibration curve.

7.4.2 The procedure for internal or external calibration may be used. Refer to Method 8000 for a description of each of these procedures.

7.4.3 Because several of the pesticides may co-elute on any single column, two calibration mixtures are provided that minimize the problem (Section 5.6.3). These calibration mixtures are also listed in Table 9, along with the low point concentration of each analyte in the mixture. The concentrations provided should be detectable on a GC/ECD suitable for use with this method. Mixtures of Aroclors other than 1016/1260 are not recommended for use with this method.

7.4.4 Because of the low concentration of pesticide standards injected on a GC/ECD, column adsorption may be a problem when the GC has not been used for a day. Therefore, the GC column should be primed or deactivated by injecting a PCB or pesticide standard mixture approximately 20 times more concentrated than the mid-concentration standard. Inject this standard mixture prior to beginning initial or daily calibration.

Caution: Several analytes, including Aldrin, may be observed in the injection just following this system priming. Always run an acceptable blank prior to running any standards or samples.

7.5 Gas chromatographic analysis:

7.5.1 Refer to Method 8000. If the internal standard calibration technique is used, add 10 µL of internal standard to the sample extract prior to injection.

7.5.2 Follow Method 8000 for instruction on the analysis sequence, appropriate dilutions, establishing daily retention time windows, and identification criteria. Analysis of a mid-concentration standard after each group of 20 samples is recommended (Section 8.3.4).

7.5.3 Examples of GC/ECD chromatograms generated by instruments with wide- or narrow-bore columns are presented in Figures 1 through 6.

7.5.4 Record the sample volume injected and the resulting peak sizes (in area units or peak heights).

7.5.5 If the peak response is less than 2.5 times the baseline noise level, the validity of the quantitative result may be questionable. The analyst should consult with the source of the sample to determine whether further concentration of the sample is warranted by the context in which the result is to be used.

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

7.5.7 Identification of mixtures (i.e. PCBs and toxaphene) is based on the characteristic "fingerprint" retention time and shape of the indicator peak(s); and quantitation is based on the area under the characteristic peaks as compared to the area under the corresponding calibration peak(s) of the same retention time and shape generated using either internal or external calibration procedures (Section 7.6).

7.5.8 Identify compounds in the sample by comparing the retention times of the peaks in the sample chromatogram with those of the peaks in standard chromatograms. The retention time window used to make identifications is based upon measurements of actual retention time variations over the course of 7 to 10 consecutive injections. (Tables 5 and 6). A suggested window size can be calculated by multiplying the standard deviation of a retention time window by three.

7.5.9 Quantitation of the compound(s) of interest is premised on: 1) a linear response of the ECD to the ranges of concentrations of the compound(s) of interest encountered in the sample extract and the corresponding calibration extract; and 2) a direct linear proportionality between the magnitude of response of the ECD over the width(s) of the retention window(s) (the area under the characteristic or "fingerprint" peak[s]) in the sample and calibration extracts. Proper quantitation requires the appropriate selection of a baseline from which the area under the characteristic peak(s) can be calculated.

7.5.10 If compound identification or quantitation are precluded due to interference (e.g., broad, rounded peaks or ill-defined baselines are present) cleanup of the extract or replacement of the capillary column or detector is warranted. Rerun sample on alternate instrumentation to determine if the problem is of instrument or sample origin. Refer to Section 7.2 for the procedures to be followed in sample cleanup.

7.6 <u>Quantitation of Multiple Component Analytes</u>:

7.6.1 Scope (excerpted from U.S. FDA, PAM): Residues which are mixtures of two or more components present problems in measurement. When they are found together, e.g., toxaphene and DDT, the problem of quantitation becomes even more difficult. Suggestions are offered in the following sections for handing toxaphene, chlordane, PCB, DDT, and BHC.

7.6.2 Toxaphene: Quantitative calculation of toxaphene or strobane is difficult, but reasonable accuracy can be obtained. To calculate toxaphene on GC/ECD: (a) adjust the sample size so that the major toxaphene peaks are 10-70% of full-scale deflection (FSD); (b) inject a toxaphene standard that is estimated to be within ±10 ng of the sample;

(c) quantitate using the five major peaks or the total area of the toxaphene pattern.

7.6.2.1 To measure total area, construct the baseline of standard toxaphene between its extremities; and construct the baseline under the sample, using the distances of the peak troughs to baseline on the standard as a guide. This procedure is made difficult by the fact that the relative heights and widths of the peaks in the sample will probably not be identical to the standard.

7.6.2.2 A series of toxaphene residues have been calculated using the total peak area for comparison to the standard and also using the area of the last four peaks only, in both sample and standard. The agreement between the results obtained by the two methods justifies the use of the latter method for calculating toxaphene in a sample where the early eluting portion of the toxaphene chromatogram shows interferences from other substances such as DDT.

7.6.3 Chlordane is a technical mixture of at least 11 major components and 30 or more minor components. Trans- and cis-chlordane (alpha and gamma), respectively, are the two major components of technical chlordane. However, the exact percentage of each in the technical material is not completely defined, and is not consistent from batch to batch.

7.6.3.1 The GC pattern of a chlordane residue may differ considerably from that of the technical standard. Depending on the sample substrate and its history, residues of chlordane can consist of almost any combination of: constituents from the technical chlordane, plant and/or animal metabolites, and products of degradation caused by exposure to environmental factors such as water and sunlight.

7.6.3.2 When the chlordane residue does not resemble technical chlordane, but instead consists primarily of individual, identifiable peaks, quantitate the peaks of alpha-chlordane, gamma-chlordane, and heptachlor separately against the appropriate reference materials, and report the individual residues.

7.6.3.3 When the GC pattern of the residue resembles that of technical chlordane, the analyst may quantitate chlordane residues by comparing the total area of the chlordane chromatogram using the five major peaks or the total area. If the heptachlor epoxide peak is relatively small, include it as part of the total chlordane area for calculation of the residue. If heptachlor and/or heptachlor epoxide are much out of proportion, calculate these separately and subtract their areas from the total area to give a corrected chlordane area. (Note that octachlor epoxide, a metabolite of chlordane, can easily be mistaken for heptachlor epoxide on a nonpolar GC column.)

7.6.3.4 To measure the total area of the chlordane chromatogram, proceed as in Section 7.6.2 on toxaphene. Inject an amount of technical chlordane standard which will produce a

chromatogram in which the major peaks are approximately the same size as those in the sample chromatograms.

7.6.4 Polychlorinated biphenyls (PCBs): Quantitation of residues of PCB involves problems similar to those encountered in the quantitation of toxaphene, strobane, and chlordane. In each case, the chemical is made up of numerous compounds which generate multi-peak chromatograms. Also, in each case, the chromatogram of the residue may not match that of the standard.

7.6.4.1 Mixtures of PCBs of various chlorine contents were sold for many years in the U.S. by the Monsanto Co. under the trade name Aroclor (1200 series and 1016). Although these Aroclors are no longer marketed, the PCBs remain in the environment and are sometimes found as residues in foods, especially fish.

7.6.4.2 Since standards are not generally available for all of the congeners of chlorinated biphenyl, PCB residues are quantitated by comparison to one or more of the Aroclor materials, depending on the chromatographic pattern of the residue. A choice must be made as to which Aroclor or mixture of Aroclors will produce a chromatogram most similar to that of the residue. This may also involve a judgement about what proportion of the different Aroclors to combine to produce the appropriate reference material.

7.6.4.3 PCB Quantitation option #1- Quantitate the PCB residues by comparing the total area of the chlorinated biphenyl peaks to the total area of peaks from the appropriate Aroclor(s) reference materials. Measure the total area or height response from the common baseline under all the peaks. Use only those peaks from the sample that can be attributed to chlorobiphenyls. These peaks must also be present in the chromatogram of the reference materials. A mixture of Aroclors may be required to provide the best match of the GC patterns of the sample and reference.

7.6.4.4 PCB Quantitation option #2- Quantitate the PCB residues by comparing the responses of 3 to 5 major peaks in each appropriate Aroclor standard with the peaks obtained from the chlorinated biphenyls in the sample extract. The amount of Aroclor is calculated using each of the major peaks, and the results of the 3 to 5 determinations are averaged. Major peaks are defined as those peaks in the Aroclor standards that are at least 30% of the height of the largest Aroclor peak. Later eluting Aroclor peaks are generally the most stable in the environment.

7.6.4.5 For samples where Aroclor patterns are not apparent, but appear to contain weathered PCBs, several diagnostic peaks have been identified in Table 10. Analysts should examine chromatographs containing these peaks carefully, as these samples may contain PCBs.

7.6.5 Hexachlorocyclohexane (BHC, from the former name, benzene hexachloride): Technical grade BHC is a cream-colored amorphous solid with a very characteristic musty odor; it consists of a mixture of six chemically distinct isomers and one or more heptachlorocyclohexanes and

octachlorocyclohexanes. Commercial BHC preparations may show a wide variance in the percentage of individual isomers present. Quantitate each isomer (α, β, γ, and δ) separately against a standard of the respective pure isomer.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control (QC) procedures. Quality control to validate sample extraction is covered in Method 3500 and in the extraction method utilized. If the extract cleanup was performed, follow the QC in Method 3600 and in the specific cleanup method.

8.2 DDT and endrin are easily degraded in the injection port, if the injection port or front of the column is contaminated with buildup of high boiling residue from sample injection. Check for degradation problems by injecting a mid-concentration standard containing only 4,4'-DDT and endrin. Look for the degradation products of 4,4'-DDT (4,4'-DDE and 4,4'-DDD) and endrin (endrin ketone and endrin aldehyde). If degradation of either DDT or endrin exceeds 20%, take corrective action before proceeding with calibration, (refer to Method 8000 and Section 4.4 of Method 8081). Calculate percent breakdown as follows:

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

$$\text{\% breakdown for Endrin} = \frac{\text{Total endrin degradation peak area (endrin aldehyde + endrin ketone)}}{\text{peak areas (endrin + aldehyde + ketone)}} \times 100$$

8.3 Mandatory quality control to evaluate the GC system operation is found in Method 8000. The following steps are recommended as additional method QC.

8.3.1 The quality control (QC) reference sample concentrate (Method 8000) should contain the organochlorine pesticides at 10 μg/L. If this method is to be used for analysis of PCBs, chlordane or toxaphene only, the QC reference sample concentrate should contain the most representative multi-component mixture at a concentration of 50 mg/L in acetone. The frequency of the QC reference sample analysis is equivalent to a minimum of 1 per 20 samples or 1 per batch if less than 20 samples. If the recovery of any compound found in the QC reference sample is less than 80 percent or greater than 120 percent of the certified value, the laboratory performance is judged to be out of control, and the problem must be corrected. A new set of calibration standards should be prepared and analyzed.

8.3.2 Calculate surrogate standard recovery on all samples, blanks, and spikes. Determine if the recovery is within limits (limits established by performing QC procedures outlined in Method 8000).

If recovery is not within limits, the following are required:

8.3.2.1 Check to be sure there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.

8.3.2.2 Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.

8.3.2.3 Reextract and reanalyze the sample if none of the above are a problem or flag the data as "estimated concentration."

8.3.3 The breakdown of DDT and endrin should be measured before samples are analyzed. Injector maintenance and recalibration should be completed if the breakdown is greater than 15% for either compound (Section 8.2).

8.3.4 Include a mid-concentration calibration standard after each group of 20 samples in the analysis sequence as a calibration check. The response factors for the mid-concentration calibration should be within 30 percent of the average values for the multiconcentration calibration. When this continuing calibration is out of this acceptance window, the laboratory should stop analyses, clean the injector, replace the septum and recalibrate the system.

8.3.5 Whenever quantitation is accomplished using an internal standard, internal standards must be evaluated for acceptance. The measured area of the internal standard must be no more than 50 percent different from the average area calculated during calibration. When the internal standard peak area is outside the limit, all samples that fall outside the QC criteria must be reanalyzed.

8.4 <u>GC/MS confirmation</u>: Any compounds confirmed by two columns should also be confirmed by GC/MS if the concentration is sufficient for detection by GC/MS as determined by the laboratory generated detection limits.

8.4.1 The GC/MS would normally require a minimum concentration of 10 ng/µL in the final extract for each single-component compound.

8.4.2 The pesticide extract and associated blank should be analyzed by GC/MS as per Section 7.0 of Method 8270.

8.4.3 The confirmation may be from the GC/MS analysis of the base/neutral-acid extracts (sample and blank). However, if the compounds are not detected in the base/neutral-acid extract even though the concentrations are high enough, a GC/MS analysis of the pesticide extract should be performed.

8.4.4 A QC reference sample of the compound must also be analyzed by GC/MS. The concentration of the QC reference standard must demonstrate the ability to confirm the pesticides/Aroclors identified by GC/ECD.

8.5 Whenever silica gel cleanup is used, demonstrate that the fractionation scheme is reproducible. Batch to batch variation in the composition of the silica gel material may cause a change in the distribution patterns of the organochlorine pesticides and PCBs as Aroclors. When compounds are found in more than one fraction, add the concentrations of the various fractions, making corrections for the final volume of the fractions. It is up to the analyst to decide whether the cut-off point should be 5 percent or less of the concentration in the fraction where the compound is expected to elute.

9.0 METHOD PERFORMANCE

9.1 The MDL is defined in Chapter One. The MDL concentrations listed in Tables 1 and 2 were obtained using organic-free reagent water and sandy loam soil. Details for determining MDLs are given in Chapter One. The MDL actually achievable in a given analysis will vary depending on detector response characteristics, irreducible noise from instrument electronics and matrix effects.

9.2 This method has been tested in a single laboratory by using clean hexane and liquid and solid waste extracts that were spiked with the test compounds at three concentrations. Single-operator precision, overall precision, and method accuracy were found to be related to the concentration of the compound and the type of matrix. Results of the single-laboratory method evaluation are given in Table 4.

9.3 The accuracy and precision obtainable following this method will be determined by the sample matrix, sample preparation technique, optional cleanup techniques, and calibration procedures used.

10.0 REFERENCES

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TABLE 1

GAS CHROMATOGRAPHIC RETENTION TIMES AND METHOD DETECTION LIMITS FOR THE ORGANOCHLORINE PESTICIDES AND PCBs AS AROCLORS[a] USING WIDE-BORE CAPILLARY COLUMNS

Compound	Retention DB 608[c]	Time (min) DB 1701[c]	MDL[b] Water (µg/L)	MDL[b] Soil (µg/Kg)
Aldrin	11.84	12.50	0.034	2.2
alpha-BHC	8.14	9.46	0.035	1.9
beta-BHC	9.86	13.58	0.023	3.3
delta-BHC	11.20	14.39	0.024	1.1
gamma-BHC (Lindane)	9.52	10.84	0.025	2.0
alpha-Chlordane	15.24	16.48	0.008	
gamma-Chlordane	14.63	16.20	0.037	1.5
4,4'-DDD	18.43	19.56	0.050	4.2
4,4'-DDE	16.34	16.76	0.058	2.5
4,4'-DDT	19.48	20.10	0.081	3.6
Dieldrin	16.41	17.32	0.044	NA
Endosulfan I	15.25	15.96	0.030	2.1
Endosulfan II	18.45	19.72	0.040	2.4
Endosulfan Sulfate	20.21	22.36	0.035	3.6
Endrin	17.80	18.06	0.039	3.6
Endrin aldehyde	19.72	21.18	0.050	1.6
Heptachlor	10.66	11.56	0.040	2.0
Heptachlor epoxide	13.97	15.03	0.032	2.1
4,4'-Methoxychlor	22.80	22.34	0.086	5.7
Toxaphene	MR	MR	NA	NA
Aroclor-1016	MR	MR	0.054	57.0
Aroclor-1221	MR	MR	NA	NA
Aroclor-1232	MR	MR	NA	NA
Aroclor-1242	MR	MR	NA	NA
Aroclor-1248	MR	MR	NA	NA
Aroclor-1254	MR	MR	NA	NA
Aroclor-1260	MR	MR	0.90	70.0

Water = Organic-free reagent water.
Soil = Sandy loam soil.
MR = Multiple peak responses.
NA = Data not available.

[a] U.S. EPA Method 8081. Organochlorine Pesticides and PCBs as Aroclors. Environmental Protection Agency. Office of Research and Development, Washington, DC 20460.

TABLE 1
(Continued)

[b] MDL is the method detection limit. MDL was determined from the analysis of seven replicate aliquots of each matrix processed through the entire analytical method (extraction, silica gel cleanup, and GC/ECD analysis). MDL = t(n-1, 0.99) x SD, where t(n-1, 0.99) is the student's t value appropriate for a 99% confidence interval and a standard deviation with n-1 degrees of freedom, and SD is the standard deviation of the seven replicate measurements.

[c] Temperature program: 150°C (hold 1/2 minutes) to 270°C at 5°C/min, helium head pressure at 10 psi.

TABLE 2

GAS CHROMATOGRAPHIC RETENTION TIMES AND METHOD DETECTION LIMITS FOR THE ORGANOCHLORINE PESTICIDES AND PCBs AS AROCLORS[a] USING NARROW-BORE CAPILLARY COLUMNS

Compound	Retention Col. 1[c]	Time (min) Col. 1[d]	MDL[b] Liquid (µg/L)	Solid (µg/Kg)
Aldrin	14.51	14.70	0.034	2.2
alpha-BHC	11.43	10.94	0.035	1.9
beta-BHC	12.59	11.51	0.023	3.3
delta-BHC	13.69	12.20	0.024	1.1
gamma-BHC (Lindane)	12.46	11.71	0.025	2.0
alpha-Chlordane				
gamma-Chlordane	17.34	17.02	0.037	1.5
4,4'-DDD	21.67	20.11	0.050	4.2
4,4'-DDE	19.09	18.30	0.058	2.5
4,4'-DDT	23.13	21.84	0.081	3.6
Dieldrin	19.67	18.74	0.044	NA
Endosulfan I	18.27	17.62	0.030	2.1
Endosulfan II	22.17	20.11	0.040	2.4
Endosulfan sulfate	24.45	21.84	0.035	3.6
Endrin	21.37	19.73	0.039	3.6
Endrin aldehyde	23.78	20.85	0.050	1.6
Heptachlor	13.41	13.59	0.040	2.0
Heptachlor epoxide	16.62	16.05	0.032	2.1
4,4'-Methoxychlor	28.65	24.43	NA	NA
Toxaphene	MR	MR	0.086	5.7
Aroclor-1016	MR	MR	NA	NA
Aroclor-1221	MR	MR	0.054	57.0
Aroclor-1232	MR	MR	NA	NA
Aroclor-1242	MR	MR	NA	NA
Aroclor-1248	MR	MR	NA	NA
Aroclor-1254	MR	MR	NA	NA
Aroclor-1260	MR	MR	0.90	70.0

Liquid = Organic-free reagent water.
Solid = Sandy loam soil.
MR = Multiple peak responses.
NA = Data not available.

TABLE 2
(Continued)

[a] U.S. EPA Method 8081. Organochlorine Pesticides and PCBs as Aroclors. Environmental Protection Agency. Office of Research and Development, Washington, DC 20460.

[b] MDL is the method detection limit. MDL was determined from the analysis of seven replicate aliquots of each matrix processed through the entire analytical method (extraction, cleanup, and GC/ECD analysis). MDL = t(n-1, 0.99) x SD, where t(n-1, 0.99) is the student's t value appropriate for a 99% confidence interval and a standard deviation with n-1 degrees of freedom, and SD is the standard deviation of the seven replicate measurements.

[c] 30 m x 0.25 mm ID DB 608 fused silica, open-tubular column (1 µm film thickness).

[d] 30 m x 0.25 mm ID DB 5 fused silica, open-tubular column (1 µm film thickness).

TABLE 3

ESTIMATED QUANTITATION LIMITS (EQL) FOR VARIOUS MATRICES[a]

Matrix	Factor[b]
Ground water	10
Low-concentration soil by sonication with GPC cleanup	670
High-concentration soil and sludges by sonication	10,000
Non-water miscible waste	100,000

a Sample EQLs are highly matrix-dependent. The EQLs listed herein are provided for guidance and may not always be achievable.

b EQL = [Method detection limit for water (Table 1) or (Table 2) wide bore or narrow bore options] x [Factor (Table 3)]. For nonaqueous samples, the factor is on a wet-weight basis.

TABLE 4

RETENTION TIMES OF OTHER PESTICIDES DETECTED USING METHOD 8081

Analyte	DB 608	DB 1701
Trifluralin	5.16	8.58
Diallate (isomer 1)	7.15	8.05
Diallate (isomer 2)	7.42	8.58
PCNB	9.03	9.91
Dichlone	10.80	decomp.
Isodrin	13.47	13.93
Dichlorvos		
Naled		
Prometon		
Propazine		
Atrazine		
Terbuthylazine		
Simazine		
Dichlorofenthion		
Methyl chlorphrophos		
Ronnel		
Captan	16.83	17.32
Chlorobenzilate	17.58	18.97
Prometryn		
Ametryn		
Metribuzin		
Terbutryn		
Chlorpyrophos		
Trichlorinate		
Chlorfenvinphos		
Tetrachlorovinphos		
Anilazine		
Cynazine		
Hexazinone		
Captafol	22.51	23.11
Mirex	22.75	23.11
Leptophos		
Coumaphos		

Temperature program: 150°C (hold 1/2 minutes) to 270°C at 5°C/min, helium head pressure at 10 psi.

TABLE 5

REPRODUCIBILITY OF RETENTION TIMES OF THE ORGANOCHLORINE PESTICIDES FOR TEN CONSECUTIVE INJECTIONS USING THE NARROW-BORE CAPILLARY COLUMNS

Compound	Retention Time Reproducibility SD (min)[a]
alpha-BHC	0.010
beta-BHC	0.009
gamma-BHC	0.011
delta-BHC	0.011
Heptachlor	0.008
Aldrin	0.009
Heptachlor epoxide	0.009
alpha-Chlordane	
gamma-Chlordane	0.012
Endosulfan I	0.010
4,4'-DDE	0.008
Dieldrin	0.008
Endrin	0.007
Endosulfan II	0.006
4,4'-DDD	0.008
Endrin aldehyde	0.007
Endosulfan sulfate	0.008
4,4'-DDT	0.008
4,4'-Methoxychlor	0.007
Toxaphene	0.004-0.006[b]
Aroclor-1016	0.042-0.104[b]
Aroclor-1260	0.035-0.040[b]

SD = Standard deviation.

[a] Number of determinations is 10.

[b] Value determined for 3 major peaks of each mixture.

TABLE 6

REPRODUCIBILITY OF RETENTION TIMES OF THE ORGANOCHLORINE PESTICIDES FOR TEN CONSECUTIVE INJECTIONS USING THE WIDE-BORE CAPILLARY COLUMNS

	Retention Time Reproducibility SD (min)[a]	
Compound	DB 5	DB 608
alpha-BHC	0.006	0.007
beta-BHC	0.007	0.008
gamma-BHC	0.007	0.008
delta-BHC	0.005	0.006
Heptachlor	0.007	0.008
Aldrin	0.007	0.008
Heptachlor epoxide	0.007	0.008
alpha-Chlordane		
gamma-Chlordane	0.007	0.009
Endosulfan I	0.007	0.009
4,4'-DDE	0.008	0.007
Dieldrin	0.007	0.009
Endrin	0.008	0.007
Endosulfan II	0.013	0.010
4,4'-DDD	0.013	0.010
Endrin aldehyde	0.010	0.010
Endosulfan sulfate	0.007	0.010
4,4'-DDT	0.007	0.007
4,4'-Methoxychlor	0.007	0.007

SD = Standard deviation.

[a] Number of determinations is 9.

[b,c] These compound pairs cannot be resolved on the DB 5 wide-bore open tubular column under the conditions listed in Section 7.3.

TABLE 7
ELUTION PATTERNS AND AVERAGE RECOVERIES OF THE ORGANOCHLORINE PESTICIDES AND AROCLOR BY METHOD 8081 WITH SILICA GEL FRACTIONATION (LIQUID WASTE NO. 1 EXTRACT)

Compound	Average Recovery ± SD (RSD)[a,b]			
	Fraction I hexane (80 mL)	Fraction II hexane (50 mL)	Fraction III methylene chloride (15 mL)	Total Recovery
alpha-BHC		57 ± 2.5(4.4)	22 ± 9.2(42)	79 ± 10(13)
beta-BHC			90 ± 3.1(3.4)	90 ± 3.1(3.4)
gamma-BHC			90 ± 4.0(4.4)	90 ± 4.0(4.4)
delta-BHC			90 ± 11(12)	90 ± 11(12)
Heptachlor	90 ± 11(12)			90 ± 11(12)
Aldrin	92 ± 9.2(10)			92 ± 9.2(10)
Heptachlor epoxide			89 ± 4.1(4.6)	89 ± 4.1(4.6)
alpha-Chlordane				
gamma-Chlordane	85 ± 7.2(8.5)	10 ± 9.2(92)		95 ± 8.0(8.4)
Endosulfan I			88 ± 3.8(4.3)	88 ± 3.8(4.3)
4,4'-DDE	95 ± 16(17)			95 ± 16(17)
Dieldrin			82 ± 4.3(5.3)	82 ± 4.3(5.3)
Endrin			65 ± 3.1(4.7)	65 ± 3.1(4.7)
Endosulfan II			79 ± 7.1(9.0)	79 ± 7.1(9.0)
4,4'-DDD		33 ± 4.0(15)	43 ± 16(37)	76 ± 16(21)
Endrin aldehyde			C	C
Endosulfan sulfate			83 ± 4.0(4.8)	83 ± 4.0(4.8)
4,4'-DDT	88 ± 18(21)			88 ± 18(21)
4,4'-Methoxychlor			75 ± 4.6(6.1)	75 ± 4.6(6.1)
Aroclor-1016	118 ± 9.8(8.3)			118 ± 9.8(8.3)
Aroclor-1260	100 ± 18(18)			100 ± 18(18)

TABLE 7
(continued)

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[a] The values given represent the average percent recoveries from three replicate determination ± one standard deviation. The numbers in parentheses are the relative standard deviations.

[b] The amounts spiked are 15,000 30,000, and 150,000 ng per 2 mL extract per column for the organochlorine pesticides and Aroclor-1016/Aroclor-1260, respectively.

[c] Unable to determine recovery because of interference.

TABLE 8
ELUTION PATTERNS AND AVERAGE RECOVERIES OF THE ORGANOCHLORINE PESTICIDES AND AROCLOR BY SILICA GEL CHROMATOGRAPHY

Compound	Average Recovery ± SD (RSD)[a,b]			
	Fraction I hexane (80 mL)	Fraction II hexane (50 mL)	Fraction III methylene chloride (15 mL)	Total Recovery
alpha-BHC		55 ± 6.1(11)	20 ± 1.7(8.7)	75 ± 6.0(8.0)
beta-BHC			94 ± 3.0(3.2)	94 ± 3.0(3.2)
gamma-BHC			89 ± 4.1(4.6)	89 ± 4.1(4.6)
delta-BHC			92 ± 5.2(5.6)	92 ± 5.2(5.6)
Heptachlor	70 ± 7.7(11)			70 ± 7.7(11)
Aldrin	65 ± 4.6(7.1)			65 ± 4.6(7.1)
Heptachlor epoxide			91 ± 5.7(6.3)	91 ± 5.7(6.3)
alpha-Chlordane				
gamma-Chlordane	71 ± 3.2(4.5)	10 ± 2.0(20)		81 ± 4.9(6.1)
Endosulfan I			88 ± 5.1(5.8)	88 ± 5.1(5.8)
4,4'-DDE	76 ± 7.1(9.3)			76 ± 7.1(9.3)
Dieldrin			85 ± 9.4(11)	85 ± 9.4(11)
Endrin			87 ± 6.4(7.3)	87 ± 6.4(7.3)
Endosulfan II			81 ± 4.5(5.5)	81 ± 4.5(5.5)
4,4'-DDD		36 ± 2.0(5.6)	49 ± 1.2(2.4)	85 ± 3.1(3.6)
Endrin aldehyde			71 ± 9.2(13)	71 ± 9.2(13)
Endosulfan sulfate			86 ± 5.0(5.8)	86 ± 5.0(5.8)
4,4'-DDT	61 ± 7.9(13)			61 ± 7.9(13)
4,4'-Methoxychlor			99 ± 17(17)	99 ± 17(17)
Aroclor-1016	104 ± 2.5(2.4)			104 ± 2.5(2.4)
Aroclor-1260	95 ± 7.5(7.9)			95 ± 7.5(7.9)

TABLE 8
(Continued)

[a] The values given represent the average percent recoveries from three replicate determinations ± one standard deviation. The numbers in parentheses are the relative standard deviations.

[b] The amounts spiked are 3,000, 6,000, and 30,000 ng per 2 mL extract per column for the organochlorine pesticides and Aroclor-1016/Aroclor-1260, respectively.

Table 9

Individual Standard Mixtures For Single Component Pesticides.

Individual Standard Mix A	Low Point Concentration (g/L)	Individual Standard Mix B	Low Point Concentration (g/L)
α-BHC	5.0	β-BHC	5.0
Heptachlor	5.0	δ-BHC	5.0
γ-BHC	5.0	Aldrin	5.0
Endosulfan I	5.0	Heptachlor epoxide	5.0
Dieldrin	10.0	α-Chlordane	5.0
Endrin	10.0	γ-Chlordane	5.0
p,p'-DDD	10.0	p,p'-DDE	10.0
p,p'-DDT	10.0	Endosulfan sulfate	10.0
Methoxychlor	50.0	Endrin aldehyde	10.0
Tetrachloro-m-xylene	20.0	Endrin ketone	10.0
Decachlorobiphenyl	20.0	Endosulfan II	10.0
		Tetrachloro-m-xylene	20.0
		Decachlorobiphenyl	20.0

TABLE 10
PEAKS DIAGNOSTIC OF PCBs OBSERVED IN 0.53 mm ID COLUMN ANALYSIS

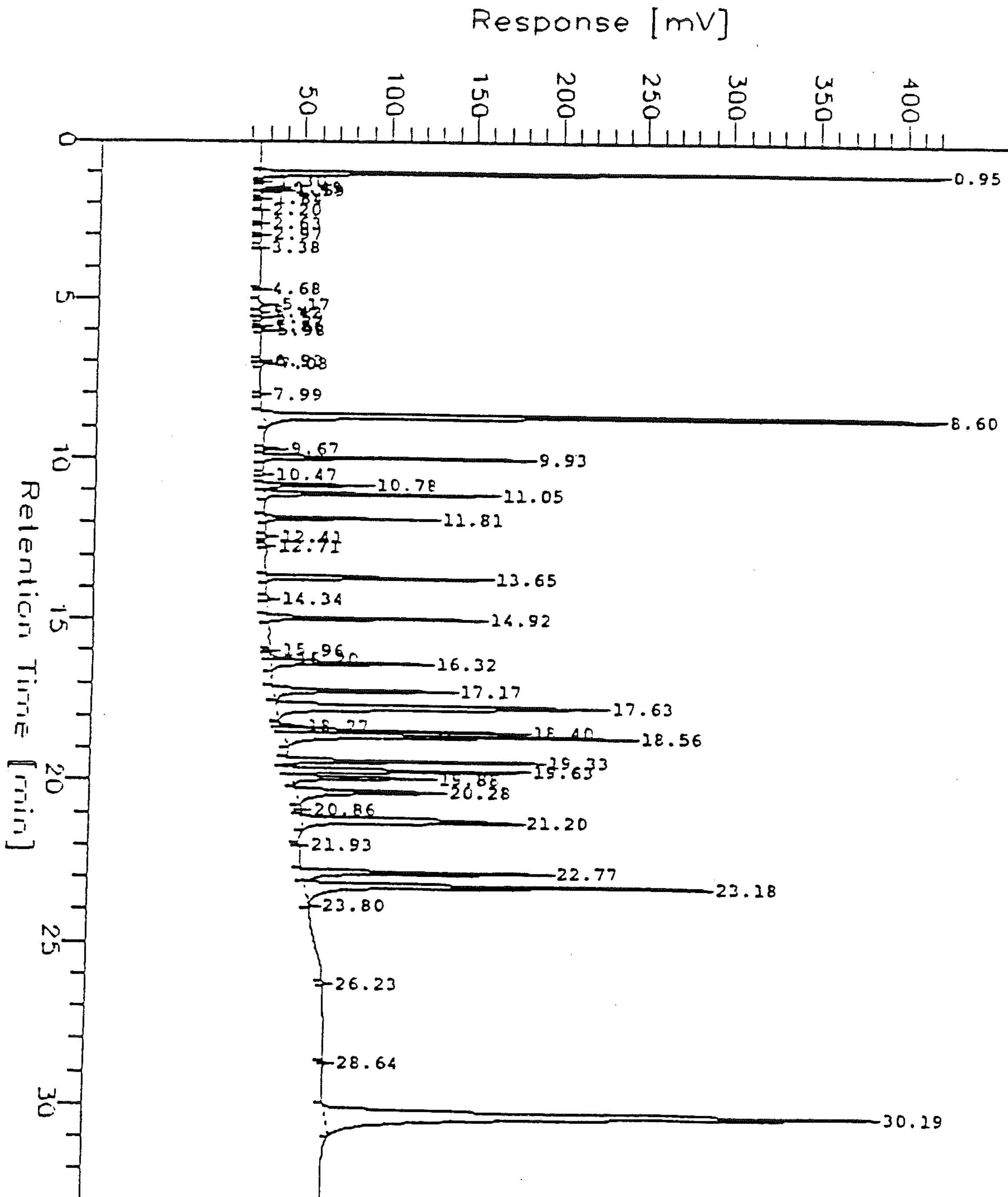
Peak No.	RT on DB 608[a]	RT on DB 1701[a]	Aroclor[b]	Pesticide Retention Window
I	4.90	4.66	1221	Before TCmX
II	7.15	6.96	1221, 1232, 1248	Before α-BHC
III	7.89	7.65	1061, <u>1221</u>, 1232, 1242,	Before α-BHC
IV	9.38	9.00	1016, 1232, 1242, 1248,	just after α-BHC on DB 1701;just before γ-BHC on DB 608
V	10.69	10.54	<u>1016, 1232, 1242</u>,	1248 α-BHC and heptachlor on DB 1701; just after heptachlor on DB 608
VI	14.24	14.12	<u>1248</u>, 1254	γ-BHC and heptachlor epoxide on DB 1701; heptachlor epoxide and γ-chlordane on DB 608
VII	14.81	14.77	1254	Heptachlor epoxide and γ-chlordane on DB 1701; α- and γ-chlordane on DB 608
VIII	16.71	16.38	<u>1254</u>	DDE and dieldrin on DB 1701; dieldrin and endrin on DB 608
IX	19.27	18.95	1254, 1260	Endosulfan II on DB 1701; DDT on DB 608
X	21.22	21.23	<u>1260</u>	Endrin aldehyde and endosulfan sulfate on DB 1701; endosulfan sulfate and methoxychlor on DB 608
XI	22.89	22.46	1260	Just before endrin ketone on DB 1701; after endrin ketone on DB 608

[a] Using oven temperature program: T_i = 150°C, hold 30 seconds; increase temperature at 5°C/minutes to 275°C.

[b] Underlined Aroclor indicates the largest peak in the pattern.

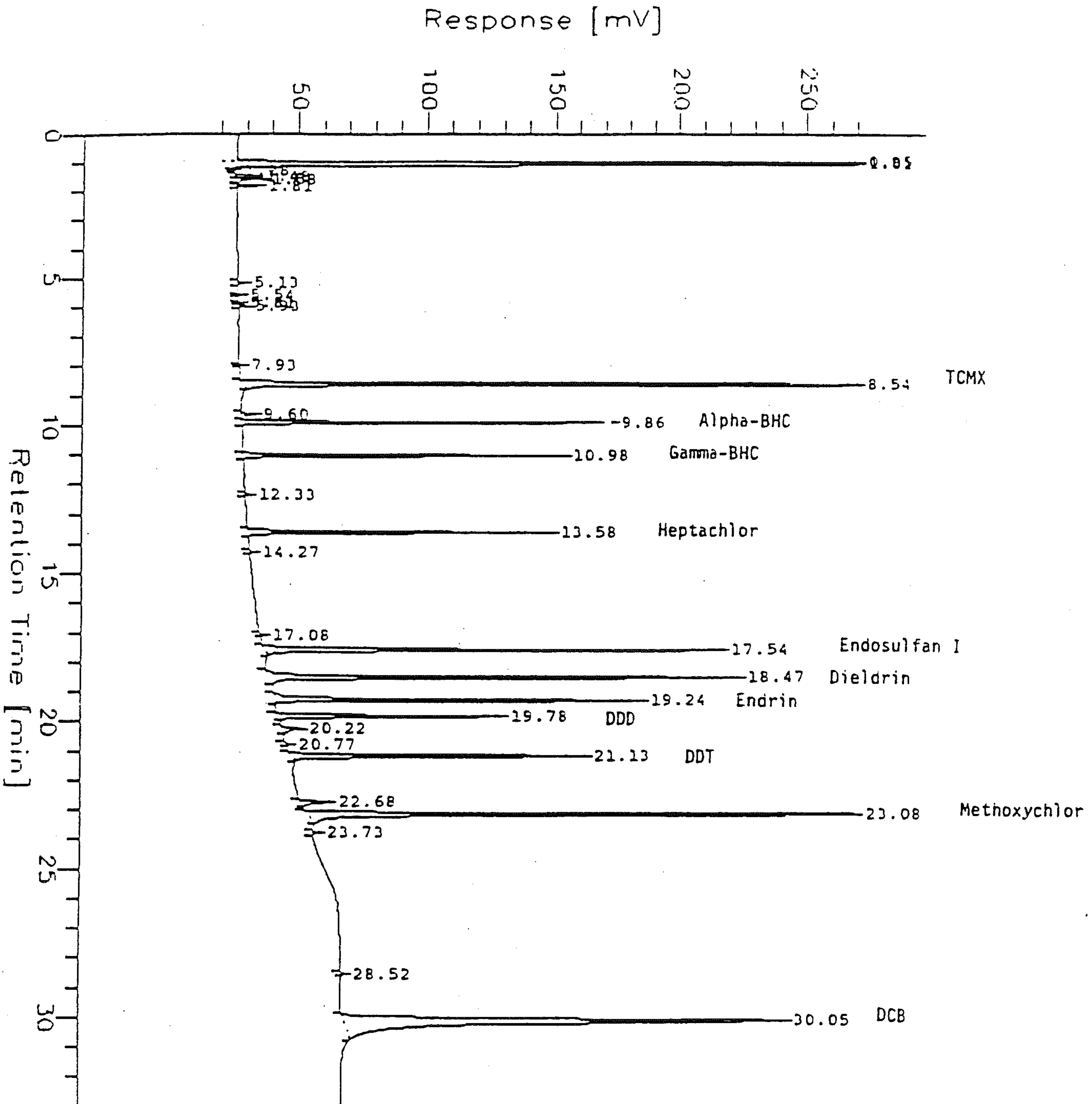
FIGURE 1.
GAS CHROMATOGRAM OF THE MIXED ORGANOCHLORINE PESTICIDE STANDARD

Start Time : 0.00 min End Time : 33.00 min Low Point : 20.00 mV High Point : 420.00 mV
Scale Factor: 0 Plot Offset: 20 mV Plot Scale: 400 mV



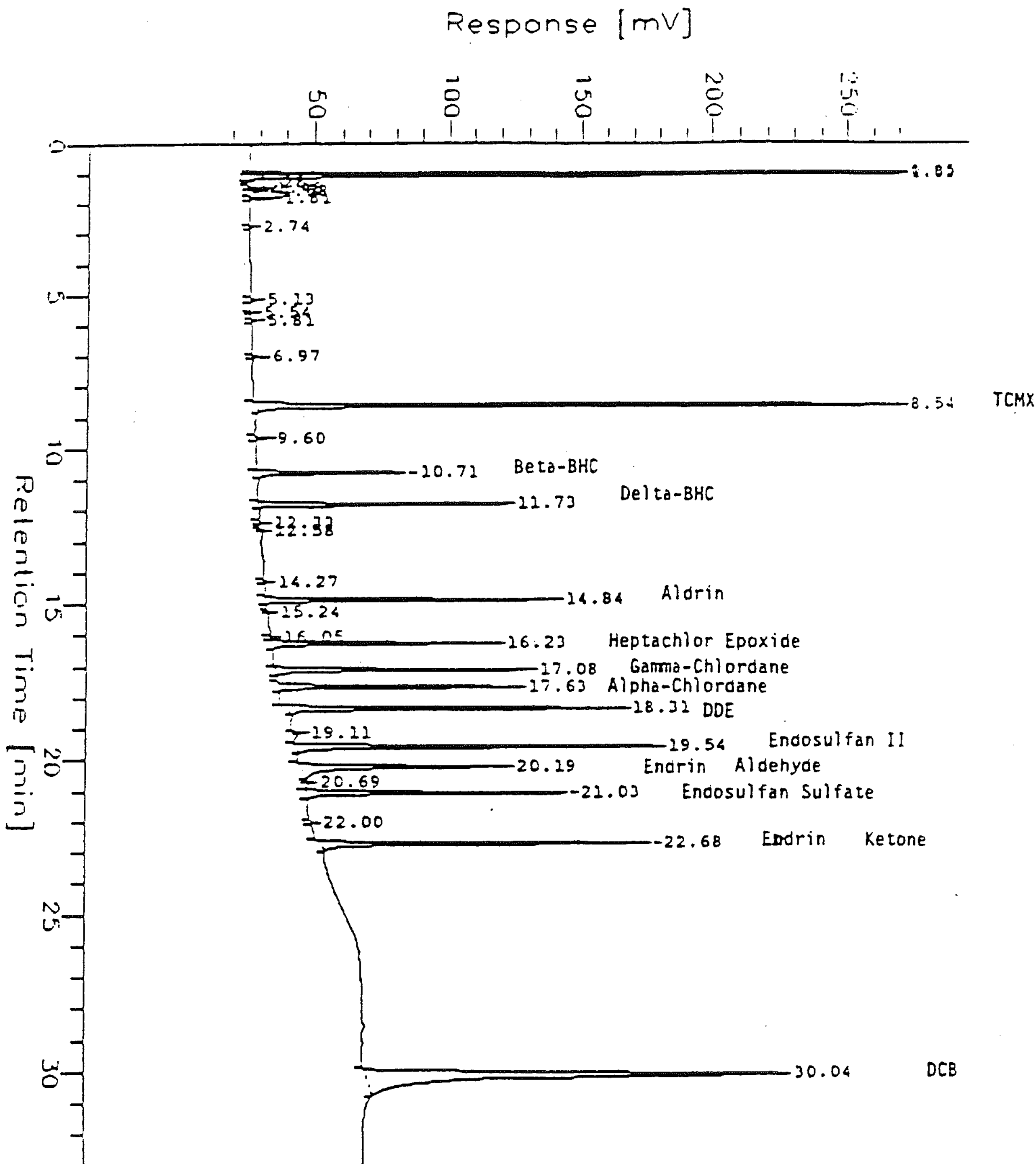
Column: 30 m x 0.25 mm ID, DB 5
Temperature program: 100°C (hold 2 minutes) to 160°C at 15°C/min, then at 5°C/min to 270°C; carrier He at 16 psi.

FIGURE 2.
GAS CHROMATOGRAM OF INDIVIDUAL ORGANOCHLORINE PESTICIDE STANDARD MIX A



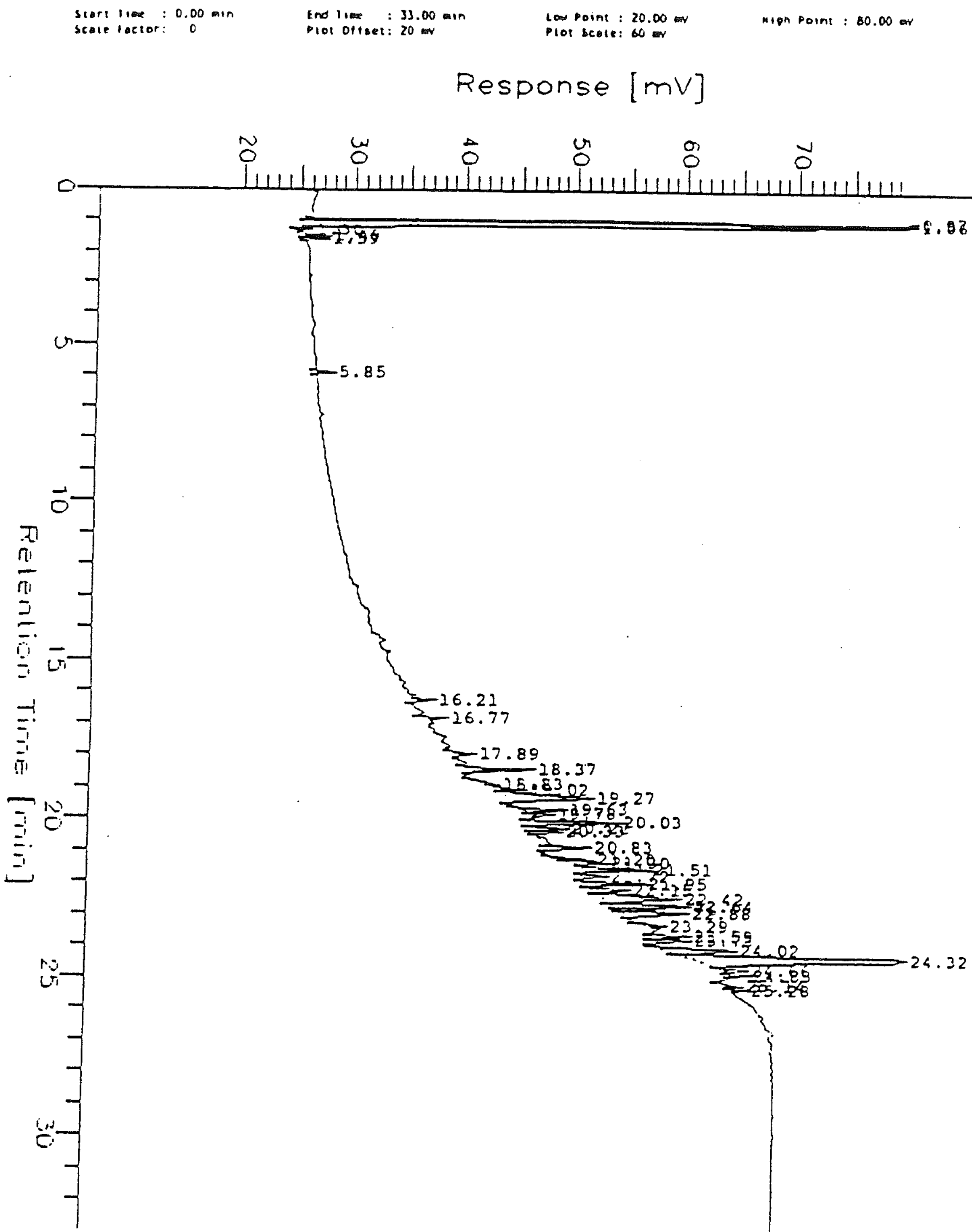
Column: 30 m x 0.25 mm ID, DB 5
Temperature program: 100°C (hold 2 minutes) to 160°C at 15°C/min, then at 5°C/min to 270°C; carrier He at 16 psi.

FIGURE 3.
GAS CHROMATOGRAM OF INDIVIDUAL ORGANOCHLORINE PESTICIDE STANDARD MIX B



Column: 30 m x 0.25 mm ID, DB 5
Temperature program: 100°C (hold 2 minutes) to 160°C at 15°C/min, then at 5°C/min to 270°C; carrier He at 16 psi.

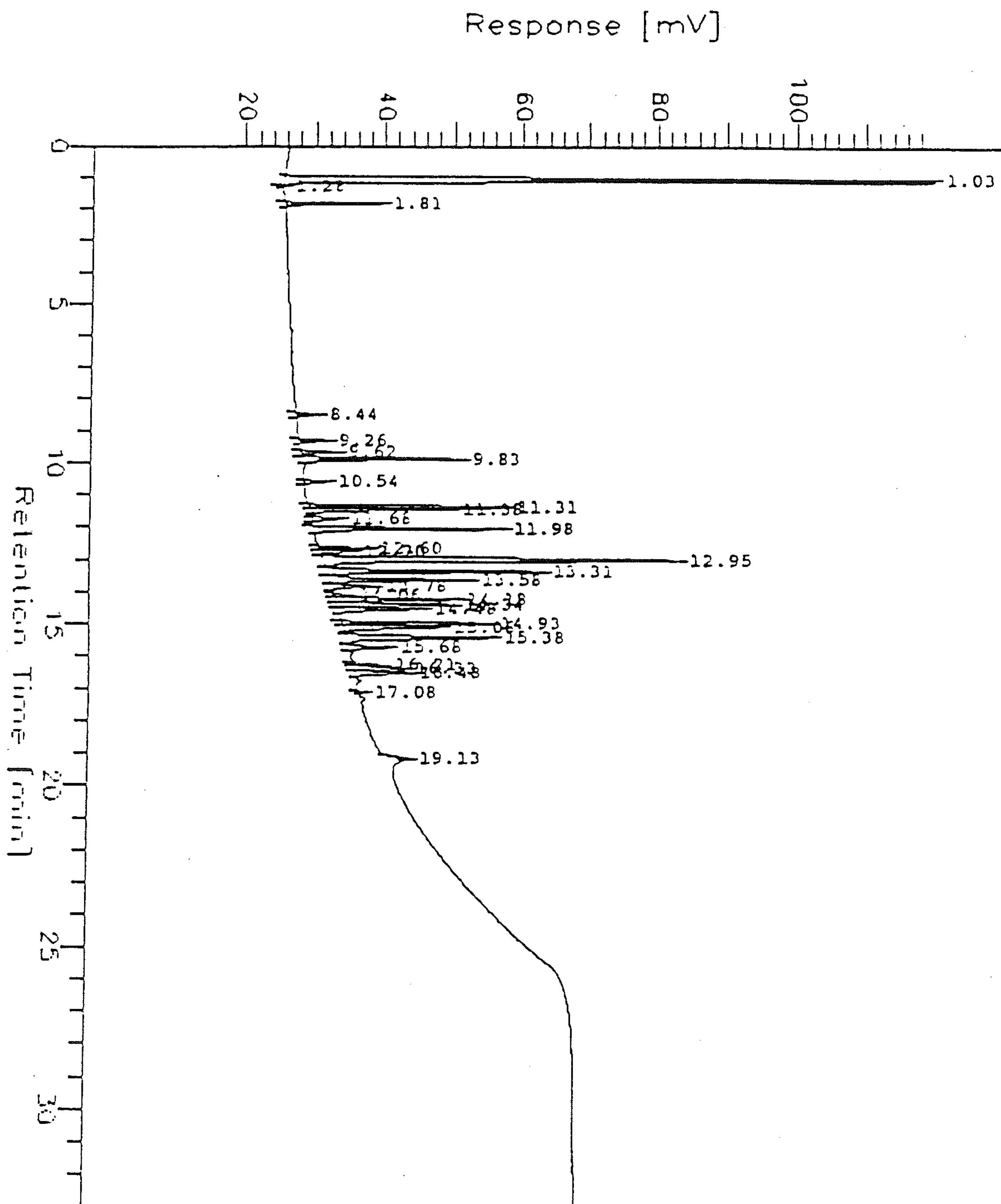
FIGURE 4.
GAS CHROMATOGRAM OF THE TOXAPHENE STANDARD



Column: 30 m x 0.25 mm ID, DB 5

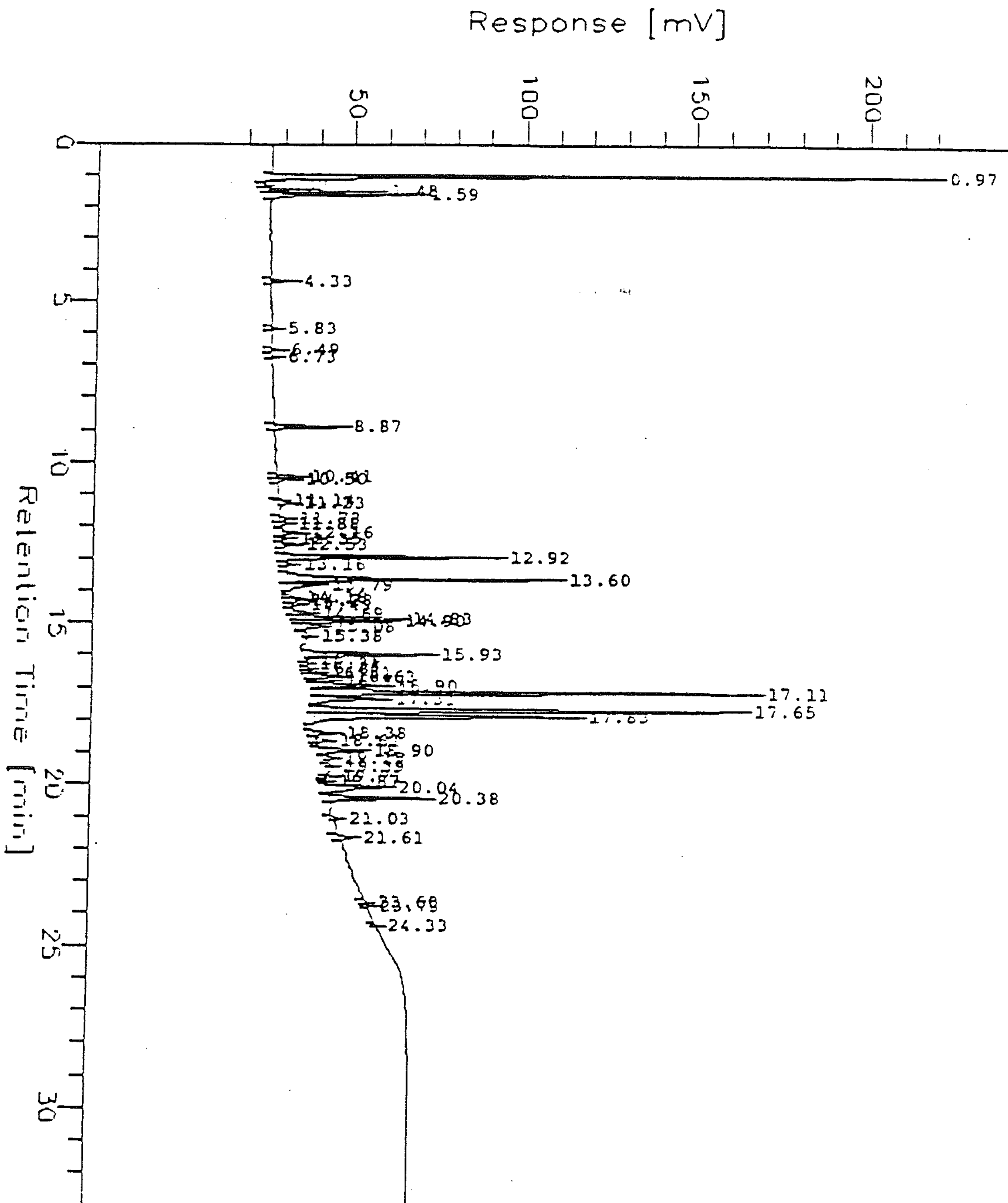
Temperature program: 100°C (hold 2 minutes) to 160°C at 15°C/min, then at 5°C/min to 270°C; carrier He at 16 psi.

FIGURE 5.
GAS CHROMATOGRAM OF THE AROCLOR-1016 STANDARD



Column: 30 m x 0.25 mm ID DB 5 fused silica capillary.
Temperature program: 100°C (hold 2 minutes) to 160°C at 15°C/min, then at 5°C/min to 270°C; carrier He at 16 psi.

FIGURE 6.
GAS CHROMATOGRAM OF THE TECHNICAL CHLORDANE STANDARD



Column: 30 m x 0.25 mm ID DB 5 fused silica capillary.
Temperature program: 100°C (hold 2 minutes) to 160°C at 15°C/min, then at 5°C/min to 270°C; carrier He at 16 psi.