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SINGLE-LABORATORY EVALUATION OF METHOD 8120 CHLORINATED HYDROCARBONS

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EPA Contracts 68-03-3226, 68-03-3511

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PREFACE

This is the final report for Work Assignments 2-13 and 3-15, EPA Contracts No. 68-03-3226 and 68-03-3511, entitled, "Single-Laboratory Evaluation of Method 8120 -- Chlorinated Hydrocarbons," conducted at Acurex Corporation, Project Nos. 8006 and 8008. These projects were directed by Dr. Viorica Lopez-Avila.

This report was written by Dr. Viorica Lopez-Avila. Technical support for both projects was provided by Mr. Nikhil Shah Dodhiwala and Mr. June Milanes.

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NOTICE

This document is a preliminary draft. It has not been formally released by the U.S. Environmental Protection Agency and should not at this stage be construed to represent Agency policy. It is being circulated for comments on its technical merit and policy implications. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

SECTION 1

INTRODUCTION

Regulation of hazardous waste activities under the Resource Conservation and Recovery Act (RCRA) of 1976 and its elements requires use of analytical methodologies that provide reliable data. The document "Test Methods for Evaluating Solid Waste," Office of Solid Waste Manual SW-846, revised recently (1), provides a compilation of methods for evaluating RCRA solid wastes for environmental and human health hazards. One of the methods in this document, Method 8120, addresses the determination of chlorinated hydrocarbons. This method provides sample extract cleanup and gas chromatographic conditions for the determination of 15 compounds in a variety of environmental samples including groundwater, liquids, and solids. Analyses are done on packed columns at various temperatures, and compounds are detected with an electron capture detector.

Problems with the current Method 8120 include the following:

- The primary column specified in the method is a 1.8 m x 2 mm ID glass column packed with 1 percent SP-1000 on Supelcoport (100/120 mesh) which needs to be operated at two temperatures (65°C and 150°C) in order to chromatograph 8 of the 15 compounds; no information is included in the method about the other 7 compounds.

- The confirmatory column specified in the method is a 1.8 m x 2 mm ID glass column packed with 1.5 percent OV-1/2.4 percent OV-225 on Supelcoport (80/100 mesh) which needs to be operated at three temperatures (75°C, 100°C, and 165°C) in order to chromatograph 9 of the 15 compounds.

- The current Method 8120 does not specify isomers for trichlorobenzenes, tetrachlorobenzenes, and BHCs.

- Method detection limits are given for only 9 of the 15 compounds listed in the method, and their values are given only for the water matrix.

- Surrogate compounds are required to be spiked in the sample matrix prior to extraction, yet no compounds are suggested for this purpose. Likewise, internal standards are required whenever internal standard calibration is used for quantification purposes, yet no internal standards are recommended.

- Extract cleanup is performed according to Method 3620, yet no recovery data are included in the method to indicate that the 15 compounds are recovered quantitatively from the Florisil column by elution with petroleum ether.

The purpose of this study was to conduct a single-laboratory evaluation of Method 8120. The range of compounds of interest was expanded to include all the trichlorobenzenes, tetrachlorobenzenes, and the BHC isomers. Twenty-two compounds shown in Table 1 were used in the evaluation studies. Since the analysis with packed column did not give satisfactory results, five fused-silica capillary columns were evaluated for their suitability for this type of compounds. The results of the fused-silica capillary columns evaluation were published in the journal of High-Resolution Chromatography and Chromatography Communications in February 1988. The gas chromatographic procedure selected for incorporation in the revised Method 8120 was subjected to ruggedness testing.

Florisil cartridges were evaluated for sample extract cleanup in order to simplify and standardize the Florisil cleanup procedure. Possible interferences from other chlorinated compunds such as chlorinated phenols, toluenes, xylenes, polynuclear aromatic hydrocarbons, and other compounds were investigated. Method detection limits were established and the modified method was tested on a variety of sample matrices which included reagent and San Francisco Bay water, two leachates, a sandy loam soil, five NBS Standard Reference Materials (SRM-1572, SRM-1575, SRM-1632a, SRM-1633a, and SRM-1645), sediments from the Detroit River and the Bloody Run Creek, a soil from the Love Canal area, a PCB-contaminated soil, and a standard reference material obtained from the Canada Centre for Inland Waters.

A revised protocol was prepared and is included as Appendix B. The final evaluation of the revised method was conducted at three concentrations, each in triplicate. The precision and accuracy results indicate that the revised Method 8120 could be reliably applied to the determination of chlorinated hydrocarbons in liquid and solid matrices.

TABLE 1. COMPOUNDS LISTED IN REVISED EPA METHOD 8120

Compound	CAS no.
Benzal chloride	98-87-3
Benzotrichloride	98-07-7
Benzyl chloride	100-44-7
2-Chloronaphthalene	91-58-7
1,2-Dichlorobenzene	95-50-1
1,3-Dichlorobenzene	541-73-1
1,4-Dichlorobenzene	106-46-1
Hexachlorobenzene	118-74-1
Hexachlorobutadiene	87-68-3
alpha-Hexachlorocyclohexane (alpha-BHC)	319-84-6
beta-Hexachlorocyclohexane (beta-BHC)	319-85-7
gamma-Hexachlorocyclohexane (gamma-BHC)	58-89-9
delta-Hexachlorocyclohexane (delta-BHC)	319-86-8
Hexachlorocyclopentadiene	77-47-4
Hexachloroethane	67-72-1
Pentachlorobenzene	608-93-5
1,2,3,4-Tetrachlorobenzene	634-66-2
1,2,4,5-Tetrachlorobenzene	95-94-2
1,2,3,5-Tetrachlorobenzene	634-90-2
1,2,4-Trichlorobenzene	120-82-1
1,2,3-Trichlorobenzene	87-61-6
1,3,5-Trichlorobenzene	108-70-3

SECTION 2

CONCLUSIONS

Based on the results presented in Section 6 of this report, the following conclusions were drawn concerning the determination of chlorinated hydrocarbons.

- EPA Method 8120, revised as presented in Appendix B, can be used for the determination of 22 chlorinated hydrocarbons in complex environmental matrices. Use of a megabore DB-210 fused-silica capillary column for primary analysis has been found to be advantageous over the packed column specified in the original Method 8120. A megabore DB-WAX fused-silica capillary column is recommended for confirmatory analysis since it can resolve the 1,2,3,5-and 1,2,4,5-tetrachlorobenzene isomers.

- The cleanup procedures recommended in the original Method 8120 have been evaluated. The use of gel permeation chromatography (Method 3640) and Method 3660 for elemental sulfur removal as options were found to be appropriate. When Florisil chromatography (Method 3620) is used with petroleum ether as the eluant as specified in the original method, not all compounds are recovered. Therefore, Method 3620 was modified to allow quantitative recovery of 20 compounds. At the same time, a procedure using 1-g Florisil disposable cartridges and hexane/acetone (9:1) as the eluant was developed. This procedure gave quantitative recoveries of all test compounds, regardless of the matrix used.

SECTION 3

RECOMMENDATIONS

The revised Method 8120 presented in this report has been evaluated in a single laboratory using a few relevant environmental samples. However, the method should be evaluted in a number of laboratories and with additional samples. This process could help to determine the range of applicability of the methods and would serve to define its interlaboratory performance.

SECTION 4

LITERATURE REVIEW

In the initial phase of this study, a literature review covering analytical methods for the determination of the chlorinated hydrocarbons in water, soil, and sediment samples was performed. For this review, the Computerized Chemical Abstracts search was used, as well as several reports dealing specifically with the analysis of organic compounds in water. Furthermore, recent issues of Analytical Chemistry, the Journal of Chromatography, the Journal of Chromatographic Science, the Association of the Official Analytical Chemists Journal, and the Environmental Science and Technology were searched to gather recent references that had not yet been entered in the computer database.

The computer searches were performed by using DIALOG. Chemical Abstracts files were searched back to 1977 for all references containing "chlorinated benzenes," "gas chromatography," "extraction," and "cleanup." Approximately 50 articles were judged to be scientifically relevant to the objectives of this study and were retrieved from the literature.

The literature review summary is included as Appendix A and presents the material in the following order:

- Sample preservation techniques
- Extraction techniques for water, sediment, and soil
- Cleanup techniques
- Gas chromatographic analysis (columns, retention time information, chromatographic problems)
- Compound confirmation.

SECTION 5

EXPERIMENTAL PROCEDURES

The method development tasks included evaluation of gas chromatographic procedures with fused-silica capillary columns and electron capture detection, sample extraction, extract cleanup, sample preservation, determination of method precision, accuracy, and detection limits , and confirmation of the chlorinated hydrocarbons by gas chromatography/mass spectrometry.

5.1 SAMPLE ACQUISITION

The following samples were used in this study:

San Francisco Bay water (pH 8.0), collected close to Leslie Salt Hill (off Seaport Blvd., South San Francisco). The sample was refrigerated at 4°C until analyzed.

Leachate samples prepared from the Detroit Sediment and the Bloody Run Creek sediment (specified below) as follows: 100 g (wet weight) of each sediment were mixed with 1,600 mL deionized water, adjusted to pH 5.2 with 0.5 N acetic acid, and shaken for 24 hours on a mechanical shaker. Details of the procedure are given in Method 1310 of the SW-846 Methods manual (1). Each leachate was filtered through an 0.45 µm Millipore filter (Fischer Scientific) prior to extraction with methylene chloride.

Sandy Loam soil (Matrix 1), obtained from Soils Incorporated, Puyallup, Washington, and characterized as follows: pH 5.9 to 6.0; 89 percent sand, 7 percent silt, 4 percent clay, cation exchange capacity 7 meq/100 g, and total organic carbon content 1290 ± 185 mg/kg.

Sediment sample (Matrix 2) of unknown origin, contaminated with petroleum hydrocarbons.

NBS Standard Reference Materials (Matrices 3 through 7) used in the methods development are identified in Table 2.

Detroit River sediment (Matrix 8), collected from the Detroit River at Station 30CR by Indiana University staff. It was reportedly highly contaminated with PCBs, chlorinated naphthalenes and terphenyls (1- to 3-ppm levels). Ed Furlong of Indiana University, who has been working on the organic chemical characterization of this sediment, will publish his findings at a later date in the Journal of Great Lakes Research (2).

TABLE 2. IDENTIFICATION OF THE NBS STANDARD REFERENCE MATERIALS USED IN THE METHOD EVALUATION

Material	Description
SRM-1575	Pine needles obtained from Manistee State Park (Muskegon, Michigan). The material was air-dried, ground, dried again at 85°C, mixed in a feed blender, and sterilized by irradiating with Cobalt 60.
SRM-1645	River sediment dredged from the bottom of Indiana Harbor Canal near Gary, Indiana. The material was freeze-dried, sieved through a 180-μm screen, mixed in a blender, and sterilized by irradiating. Total organic carbon content is 30,000 mg/kg.
SRM-1572	Citrus leaves from the Lake Alfred area of central Florida. The material was air-dried, ground to pass through a 425-μm screen, dried at 85°C, mixed in a feed blender, and sterilized by irradiating with Cobalt 60.
SRM-1632a	Coal obtained from the Humphrey No. 7 mine and coal preparation plant of the Consolidation Coal Co., Osage, West Virginia. Contains approximately 1.8 to 1.9 percent sulfur and was ground to pass through a 60-mesh sieve.
SRM-1633a	Coal flyash, obtained from a coal-fired power plant that uses Pennsylvania and West Virginia coals. The material was sieved to pass through a 90-μm screen.

Bloody Run Creek sediment (Matrix 9), a grab sample from the creek downstream of the 102nd-Street dump site in the Love Canal area. Jaffe and Hites reported ppm concentrations of dichloro(trifluoromethyl)benzophenone, dichloro(trifluoromethyl)difluorodiphenylmethane, and various chlorinated trifluoromethyl-substituted biphenyls (3).

Love Canal soil (Matrix 10), obtained from the Environmental Research Center of the University of Nevada in Las Vegas, Nevada.

PCB-contaminated soil sample (Matrix 11), obtained from Dr. William Budde of EPA-Cincinnati.

EC-2 Standard Reference Material obtained from Alfred S. Y. Chau of Canada Centre for Inland Waters, Ontario, Canada. This material was collected from Lake Ontario near Niagara River in 1980. It was freeze-dried in 25-kg lots, ground and sieved to give a 200- to 325-mesh dry sediment. The bulk sample was blended until homogeneous and then subsampled in 25-g amber bottles. The reference values for chlorobenzenes and hexachlorobutadiene present in EC-2 are given in Table 3. In addition, this sediment was found to contain polynuclear aromatic hydrocarbons: fluoranthene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-c,d]pyrene, benzo[g,h,i]perylene, and PCBs at 1 to 3 ppm (4).

Standards: High-purity benzyl chloride, 2-chloronaphthalene, 1,2-dichlorobenzene, 1,3-dichlorobenzene, 1,4-dichlorobenzene, hexachlorobenzene, hexachlorobutadiene, alpha-BHC, beta-BHC, gamma-BHC, and 1,2,4-trichlorobenzene were obtained from the U.S. EPA Pesticides and Industrial Chemicals Repository. Benzal chloride, 1,2,3,5-tetrachlorobenzene, and the brominated compounds were obtained from Aldrich Chemical Company, Inc. The remainder of the compounds listed in Table 1 and the other chlorinated compounds listed in other tables of this report were obtained from Ultrascientific Inc. Stock solutions of each test compound were prepared in isooctane (Burdick & Jackson Lab, Inc.) at concentrations of 1 mg/mL. Working calibration standards were prepared in isooctane by serial dilution of a composite stock solution prepared from the individual stock solutions.

5.2 EVALUATION OF GAS CHROMATOGRAPHY

Gas chromatography with electron capture detection was evaluated with both packed and capillary columns. The gas chromatographs used throughout these evaluations were a Varian 3400 gas chromatograph equipped with a constant current pulsed frequency electron capture detector (ECD) and interfaced to a Spectra Physics 4290 integrator and a Varian 6000 gas chromatograph also equipped with a constant current pulsed frequency ECD and interfaced to a Vista 402 data station. All injections were performed with an autosampler Varian Model 8000.

TABLE 3. REFERENCE VALUES FOR CHLOROBENZENES AND HEXACHLOROBUTADIENE IN EC-2[a]

Compound	Concentration (ng/g)
1,3,5-Trichlorobenzene	34.3 ± 2.6
1,2,4-Trichlorobenzene	80.7 ± 5.4
1,2,4,5-Tetrachlorobenzene	84.0 ± 4.9
1,2,3,4-Tetrachlorobenzene	36.5 ± 2.4
Pentachlorobenzene	48.6 ± 2.4
Hexachlorobenzene	200.6 ± 13.2
Hexachlorobutadiene	21.3 ± 1.6

[a]Data taken from Reference 4.

Packed Column Studies

For the packed column work, the instrumental parameters were as follows:

- Column dimensions -- 2 m x 2 mm ID glass column
- Liquid phase -- 1 percent SP-1000 on Supelcoport (100/120 mesh)
- Carrier gas -- nitrogen at 20.5 mL/min
- Injection volume -- 2 µL (on-column)
- Injector temperature -- 150°C
- Detector temperature -- 200°C
- Temperature -- 65°C isothermal
  -- 150°C isothermal
  -- 65°C to 175°C (28 min hold) at 5°C/min

Capillary Column Studies

For the capillary column work, the instrumental parameters are summarized in Table 4. Five fused-silica capillary columns coated with various liquid phases have been investigated.

5.3 EXTRACTION AND SPIKING TECHNIQUES

5.3.1 Sample Extraction

The extraction efficiencies for the Method 8120 compounds from reagent water at pH 2, 7, and 9, were determined by using separatory funnel extraction with methylene chloride (Method 3510). The compounds were spiked into each water sample at 0.1 to 20 µg/L or 1 to 200 µg/L; analysis of the extracts was performed by GC/ECD using the DB-210 fused-silica capillary column and external standard calibration.

Soil or sediment samples were extracted either with hexane/acetone (1:1) in a Soxhlet extractor (Method 3540) or with methylene chloride/acetone (1:1) by using a sonic probe (Heat Systems Ultrasonics, Inc., Model W-375) following the procedures specified in Method 3550.

5.3.2 Soil Spiking Studies

The following procedures were used for spiking soil samples:

Spiking and Blending was performed in a Waring laboratory blender (Waring Products Division, Dynamics Corporation of America, New Hartford, Connecticut). Five hundred grams sandy loam (Puyallup, Washington) were mixed with 200 mL deionized water and blended at full speed for 2 minutes. Twenty milliliters of an isooctane solution containing Method 8120 compounds at concentrations of 1 to 200 µg/mL were added and blending was continued for another 10 minutes, cooling intermittently, to obtain a smooth slurry. Immediately after blending, the slurry was separated into 35-g portions. Stirring was done for very short times (10 sec) after each portion was removed from the blender. The various portions were serially labeled in the order in which the removal was done. Only those carrying the even number were analyzed immediately. The portions carrying odd numbers were kept frozen for up to 6 months at -10°C.

Spiking and Tumbling was performed in a tumbler from Norton Chemical Products Division, Akron, Ohio. The amount of soil, deionized water, and the volume of the spiking solution were the same as for blending. Before the spiking solution was added, the soil was mixed with deionized water and equilibrated for 1 hour. Tumbling was maintained for 12 hours following spiking. The spiked soil was then split into 35-g portions.

Spiking and Overnight Equilibration: 500 g sandy loam soil (Puyallup, Washington) were mixed with 200 mL deionized water. The slurry was allowed to equilibrate for 1 hour and then the spiking solution was added. The spiked slurry was maintained at room temperature for 17 hours. Before splitting into 35-g portions and in between the removal of the 35-g portions, the slurry was mixed with a glass rod.

TABLE 4. GC OPERATING CONDITIONS FOR THE FUSED-SILICA CAPILLARY COLUMN ANALYSES

	Column 1	Column 2	Column 3	Column 4	Column 5
Instrument	Varian 6000 equipped with ECD	Varian 3400 equipped with ECD	Varian 3400 equipped with ECD	Varian 3400 equipped with ECD	Varian 6000 equipped with ECD
Column dimensions	15 m x 0.53 mm ID	30 m x 0.53 mm ID	30 m x 0.53 mm ID	30 m x 0.32 mm ID	30 m x 0.53 mm ID
Type of liquid phase	SPB-5 (methylphenyl silicone)	SPB-35 (phenyl methyl silicone)	DB-210 (trifluoropropyl methyl silicone)	DB-1301 (cyanopropyl methyl silicone)	DB-WAX (polyethylene glycol)[a]
Film thickness (μm)	1.5	1.0	1.0	1.5	1.0
Carrier gas	Helium	Helium	Helium	Helium	Helium
Carrier flow (mL/min)	10	10	10	1.5	10
Temperature program	50°C to 175°C (hold 20 min) at 4°C/min	50°C to 240°C (hold 10 min) at 4°C/min	65°C to 175°C (hold 20 min) at 4°C/min	100°C to 250°C (hold 20 min) at 5°C/min	60°C to 170°C (hold 30 min) at 4°C/min
Injector temperature (°C)	220	220	220	220	200
Detector temperature (°C)	300	250	250	250	230
Injection volume (μL)	1.5	1.5	1.5	1.5	1.5
Type of injection	On-column	On-column	On-column	Splitless (splitless time 60 sec; split flow 60 mL/min)	On-column

[a]Two DB-WAX fused silica capillary columns have been evaluated in this study. They are identified as columns No. 52861 and 130906.

5.4 EXTRACT CLEANUP TECHNIQUES

5.4.1 Gel Permeation Chromatography (GPC)

The GPC conditions were as follows:

- Instrument -- HPLC Perkin Elmer Series 4
- Column -- 25 mm ID x 650 mm glass, packed with Bio-Beads SX-3 (~70 g)
- Flowrate -- 5 mL/min
- Mobile phase -- methylene chloride
- Injection volume -- 5 mL
- Detector -- Perkin Elmer variable wavelength UV detector operated at 254 nm and 0.05/AUFS

The procedure given in Section 7.3.3 of the revised Method 8120 which is included in Appendix B of this report was followed.

5.4.2 Removal of Elemental Sulfur

Two milliliters of a working standard of known concentration (in hexane) were shaken with 1 mL 2-propanol and 1 mL tetrabutylammonium sulfite reagent for at least 1 min. Sodium sulfite crystals (100 mg) were then added. If the sodium sulfite crystals disappeared, more sodium sulfite was added in 100-mg portions until a solid residue remained after repeated shaking. Finally, 5 mL reagent water were added and the test tube was shaken for another minute. Centrifugation was employed to promote phase separation; following centrifugation, the hexane layer was separated for gas chromatographic analysis.

5.4.3 Florisil Chromatography

Florisil (J. T. Baker Chemical Co., 60/80 mesh size, lot no. 442707) was activated at 130°C for at least 16 hours before use. Calibration of the Florisil was performed by the lauric acid method (5). Glass columns (20 mm ID x 500 mm length) were packed with 12.3 g activated Florisil and prewashed with 200 mL petroleum ether (Matheson, Coleman & Bell) before use. The test compounds were eluted from the Florisil first with 200 mL petroleum ether and then with 200 mL petroleum ether/diethyl ether (1:1). The fractions were concentrated to 10 mL by Kuderna-Danish evaporation.

Florisil disposable cartridges (Supelco, Inc.) containing LC-Florisil (particle size 40 µm, pore size 60 Å) were prewashed with 4 mL pesticide-grade hexane prior to use. They were eluted in sets of 12 on a specially designed vacuum manifold (SPE vacuum manifold, Supelco Inc.) that provided increased sample throughput while the volume of the eluting solvent

was kept to a minimum. The eluting solvents evaluated with the Florisil disposable cartridges were hexane, hexane/diethyl ether (1:1), and hexane/acetone (9:1).

5.5 SAMPLE PRESERVATION

Sample preservation studies were carried out for both water and soil samples. Fourteen one-liter reagent water samples were spiked with the test compounds at one concentration and were stored at 4°C for up to 21 days. Two samples were extracted immediately; the other samples were removed at day 1, 3, 7, 10, 14, and 21 and analyzed for the 22 test compounds. Duplicate measurements were performed at each time event. In addition, six one-liter reagent water samples were spiked with the test compounds at one concentration, adjusted to pH 2 with 6N H_2SO_4 and stored at 4°C. Two samples were extracted immediately; the other samples were analyzed at day 7 and 14. This experiment was repeated at pH 9.

Spiked soils samples were kept frozen at -10°C for 5 months and 6 months.

5.6 GC/MS METHODOLOGY

A Finnigan 4510B GC/MS system interfaced to a Finnigan Nova 4X data system was used in this study. The GC was equipped with a split/splitless injector. The column was a 30 m x 0.25 mm ID DB-5 fused-silica capillary column (0.25 µm film thickness) supplied by J&W Scientific, Inc. The GC instrumental conditions were as follows:

- Temperature program -- 40°C to 300°C at 8°C/min
- Injector temperature -- 250°C
- Transfer line temperature -- 260°C
- Injection volume --1 µL
- Injection solvent -- methylene chloride
- Carrier gas -- helium at 10 psi at 40°C

The MS conditions were as follows:

- Ion source tuning -- as per EPA DFTPP requirement
- Ion source temperature -- 190°C
- Scanning mass range -- 45 to 450 amu
- Scan rate --1 sec/cycle

- Electron energy --70 eV
- Multiplier voltage --1,400 eV.

SECTION 6

RESULTS AND DISCUSSION

6.1 EVALUATION OF GAS CHROMATOGRAPHY

6.1.1 Packed Column Studies

Results of the analyses performed on packed columns are presented in Table 5. GC/ECD chromatograms of working standards and sample extracts are shown in Figures 1 through 6. Both isothermal and temperature-programmed conditions were evaluated. At 65°C, which is the temperature specified in the current Method 8120, only 11 compounds elute from the 1-percent SP-1000 column within 30 minutes. At 150°C, 6 compounds elute within 4 minutes, but hexachlorocyclopentadiene, beta-BHC, and delta-BHC still do not elute from the gas chromatographic column. Resolution is so poor at 150°C that the compounds cannot be identified. When temperature-programmed conditions were used, the separation of the early eluting peaks was acceptable, but the late eluting components give broad peaks, and the background from column bleed is excessive. A GC/ECD chromatogram of a composite standard containing the 22 test compounds and obtained under temperature-programmed conditions is presented in Figure 5. A GC/ECD chromatogram of the Bloody Run Creek sediment extract was obtained under the same temperature-programmed conditions (Figure 6). No peaks could be identified because of poor resolution. It is interesting to note that a hexane blank, analyzed immediately after the Bloody Run Creek sediment extract had been analyzed at 65°C isothermally, showed a very high background (Figure 7) because many of the compounds from the previous analysis had not eluted from the gas chromatographic column at 65°C (isothermal).

The following conclusion can be drawn from these data: when analyzing complex environmental samples by GC/ECD the sample column temperature must be programmed from a low temperature (e.g., 50°C to 65°C) to about 20°C below the maximum operating temperature of the column and maintained at that temperature for 15 to 30 minutes, depending on the complexity of the sample.

The isothermal analysis of environmental sample extracts on packed columns was ruled out, and no further effort was put into developing a temperature-programmed analysis for the packed column because of inadequate resolution.

TABLE 5. RETENTION TIMES (MIN) OF THE METHOD 8120 COMPOUNDS ON A 2 M X 2 MM ID GLASS COLUMN PACKED WITH 1 PERCENT SP-1000 ON SUPELCOPORT (100/120 MESH)

Compound	65°C Isothermal	150°C Isothermal
Benzyl chloride	6.60	[b]
Benzal chloride	22.00	[b]
1,2-Dichlorobenzene	5.42	[b]
1,3-Dichlorobenzene	3.64	[b]
1,4-Dichlorobenzene	4.31	[b]
1,2,4-Trichlorobenzene	12.90	[b]
1,2,3-Trichlorobenzene	20.26	[b]
1,3,5-Trichlorobenzene	6.30	[b]
1,2,3,4-Tetrachlorobenzene	[a]	1.47
1,2,4,5-Tetrachlorobenzene	[a]	1.03
1,2,3,5-Tetrachlorobenzene	[a]	1.00
Pentachlorobenzene	[a]	1.87
Hexachlorocyclopentadiene	[a]	[a]
Benzotrichloride	18.42	[b]
2-Chloronaphthalene	[a]	1.97
Hexachloroethane	3.93	[b]
Hexachlorobutadiene	6.15	[b]
alpha-BHC	[a]	10.05
beta-BHC	[a]	[a]
gamma-BHC	[a]	20.65
delta-BHC	[a]	[a]
Hexachlorobenzene	[a]	3.94

[a]Compound did not elute under the specified conditions.
[b]Not analyzed at that temperature.

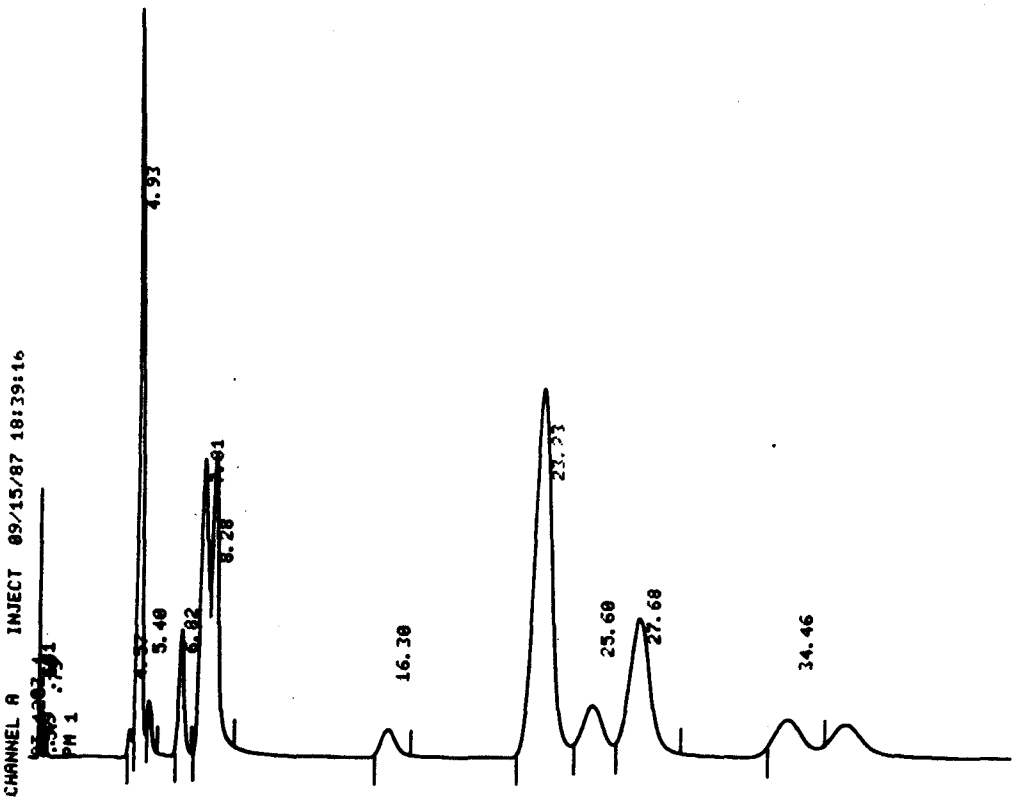

Figure 1. GC/ECD chromatogram of Method 8120 composite standard (concentration 0.1 to 20 ng/µL) analyzed on a 1-percent SP-1000 packed column, isothermal at 65°C.

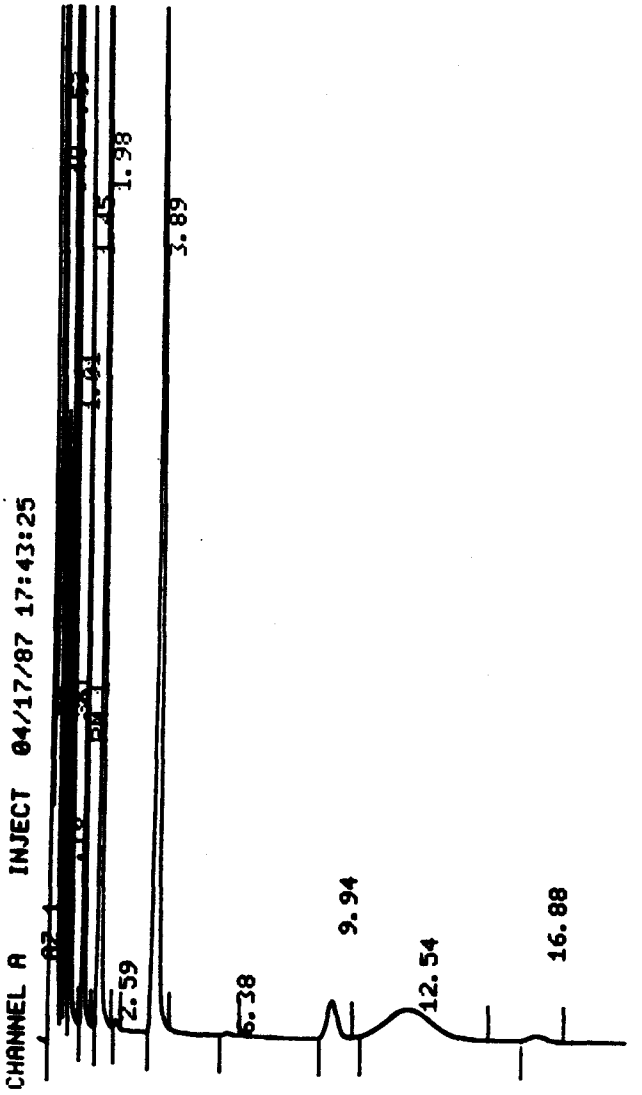

Figure 2. GC/ECD chromatogram of Method 8120 composite standard (concentration 0.1 to 20 ng/µL) analyzed on a 1-percent SP-1000 packed column, isothermal at 150°C.

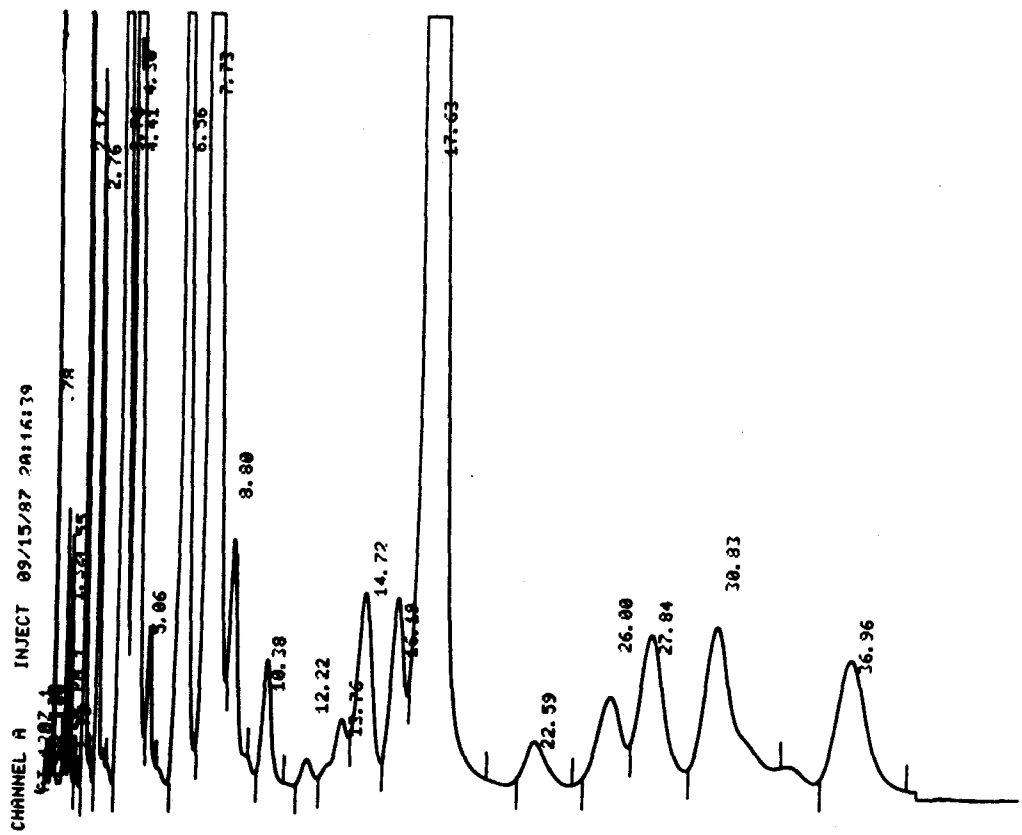

Figure 3. GC/ECD chromatogram of Bloody Run Creek sediment extract (10-fold dilution) analyzed on a 1-percent SP-1000 packed column, isothermal at 65°C.

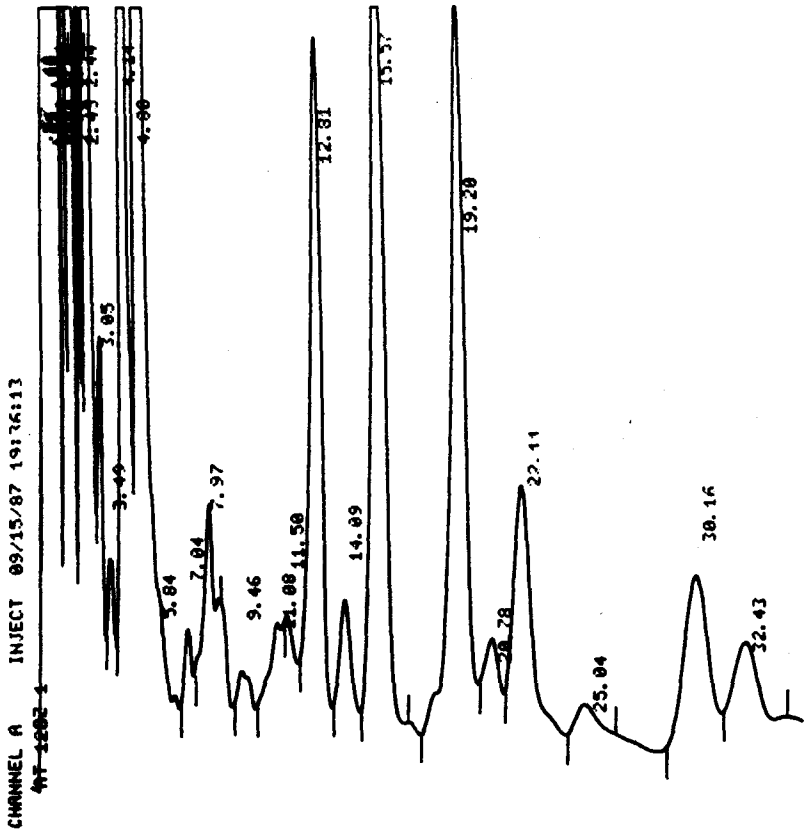

Figure 4. GC/ECD chromatogram of Bloody Run Creek sediment extract (10-fold dilution) analyzed on a 1-percent SP-1000 packed column, isothermal at 150°C.

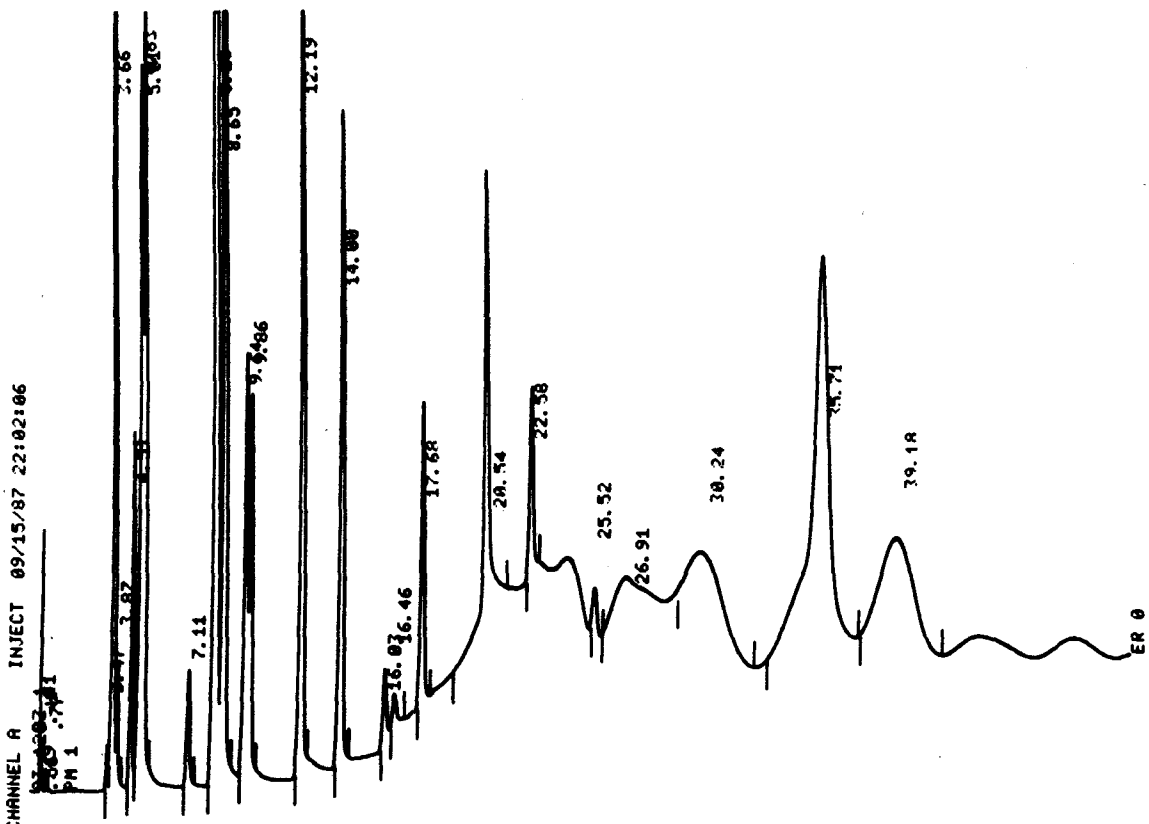

Figure 5. GC/ECD chromatogram of Method 8120 composite standard analyzed on a 1-percent SP-1000 packed column, temperature programmed from 65°C to 175°C (hold 28 min) at 5°C/min.

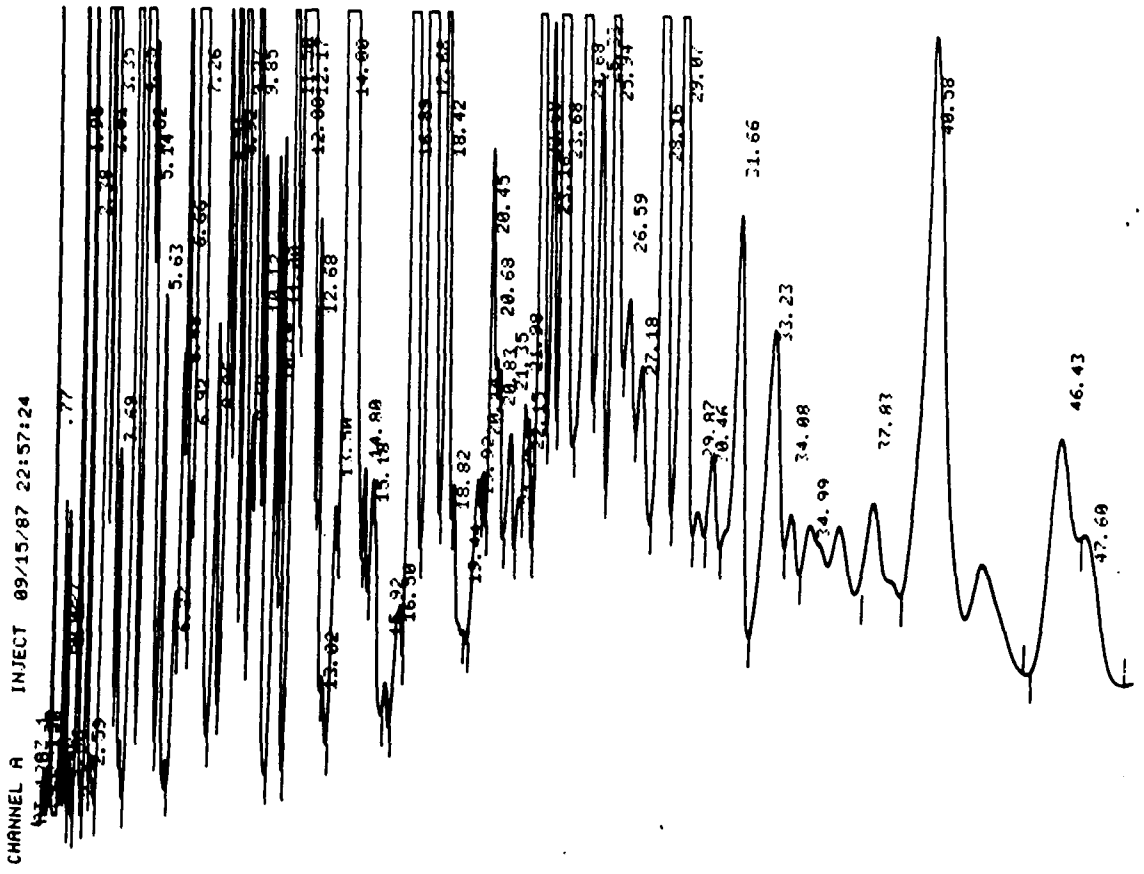

Figure 6. GC/ECD chromatogram of Bloody Run Creek sediment extract (10-fold dilution) analyzed on a 1-percent SP-1000 packed column, temperature programmed from 65°C to 175°C (hold 28 min) at 5°C/min.

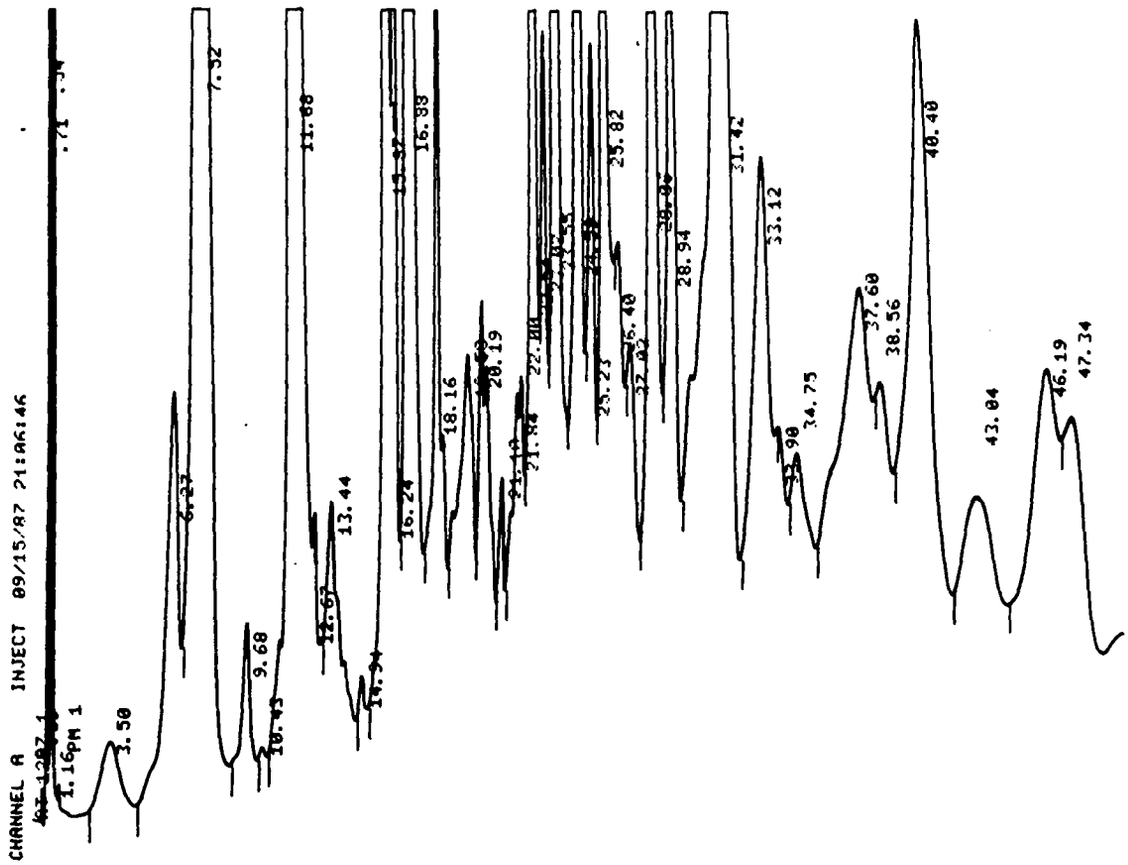

Figure 7. GC/ECD chromatogram of a hexane blank analyzed immediately after the Bloody Run Creek sediment extract was analyzed on a 1-percent SP-1000 packed column at 65°C, isothermal. The column was held at 65°C for 40 min, then clean hexane was injected and the temperature was programmed from 65°C to 175°C (hold 28 min) at 5°C/min.

6.1.2 Capillary Column Studies

GC/ECD chromatograms of a composite standard containing the 22 compounds analyzed on five fused-silica capillary columns are shown in Figures 8 through 15. Tables 6 through 10 summarize the retention times of the 22 test compounds for each fused-silica capillary column and Tables 11 through 14 summarize the retention times of other chlorinated compounds such as chlorinated toluenes, xylenes, naphthalenes, styrenes, etc. The coeluting compounds among the 22 test compounds are:

SPB-5: benzyl chloride/1,4-dichlorobenzene
benzotrichloride/hexachlorobutadiene
hexachlorocyclopentadiene/1,2,3,5-tetrachlorobenzene
2-chloronaphthalene/1,2,3,4-tetrachlorobenzene
beta-BHC/gamma-BHC

SPB-35: 2-chloronaphthalene/1,2,3,4-tetrachlorobenzene
1,2,3,5-/1,2,4,5-tetrachlorobenzene

DB-210: benzal chloride/1,2,4-trichlorobenzene
1,2,3,5-/1,2,4,5-tetrachlorobenzene

DB-1301: benzotrichloride/1,2,3-trichlorobenzene
hexachlorocyclopentadiene/1,2,3,5-/1,2,4,5-tetrachlorobenzene

DB-WAX: benzal chloride/1,2,3-trichlorobenzene
2-chloronaphthalene/pentachlorobenzene

Additional discussion of the fused-silica capillary column evaluation can be found in Reference 6.

Of six bromoaromatics tested for suitability as internal standards, α,α'-dibromo-m-xylene is best suited with retention times of 18.41 min for the DB-210 column and 35.94 min for the DB-WAX column. 1,3,5-Tribromobenzene (11.67 min on the DB-210 column and 22.60 min on the DB-WAX column) is also suitable, however, it coelutes with α,2,6-trichlorotoluene, and incomplete separation from 1,2,3,4-tetrachlorobenzene is found when the latter is present at >1 ng/µL. Of 35 chlorinated aromatics tested for suitability as surrogates, α,2,6-trichlorotoluene, 1,4-dichloronaphthalene and 2,3,4,5,6-pentachlorotoluene are recommended. Their retention times on the DB-210 column are 12.96, 17.43, and 18.96 min, respectively, and on the DB-WAX column 23.34, 26.33, and 27.66 min, respectively.

6.2 EXTRACTION TECHNIQUES

The results of the single-laboratory evaluation of the Methods 3510 and 3550 are summarized in this section. In the case of Method 3510, 800 mL to 1,000 mL of liquid sample (spiked with the three surrogate compounds α,2,6-trichloro-toluene, 1,4-dichloronaphthalene, and 2,3,4,5,6-pentachlorotoluene) was extracted at neutral pH in a separatory funnel with 60 mL methylene chloride. The extraction was repeated twice;

SPB-5 FSCC

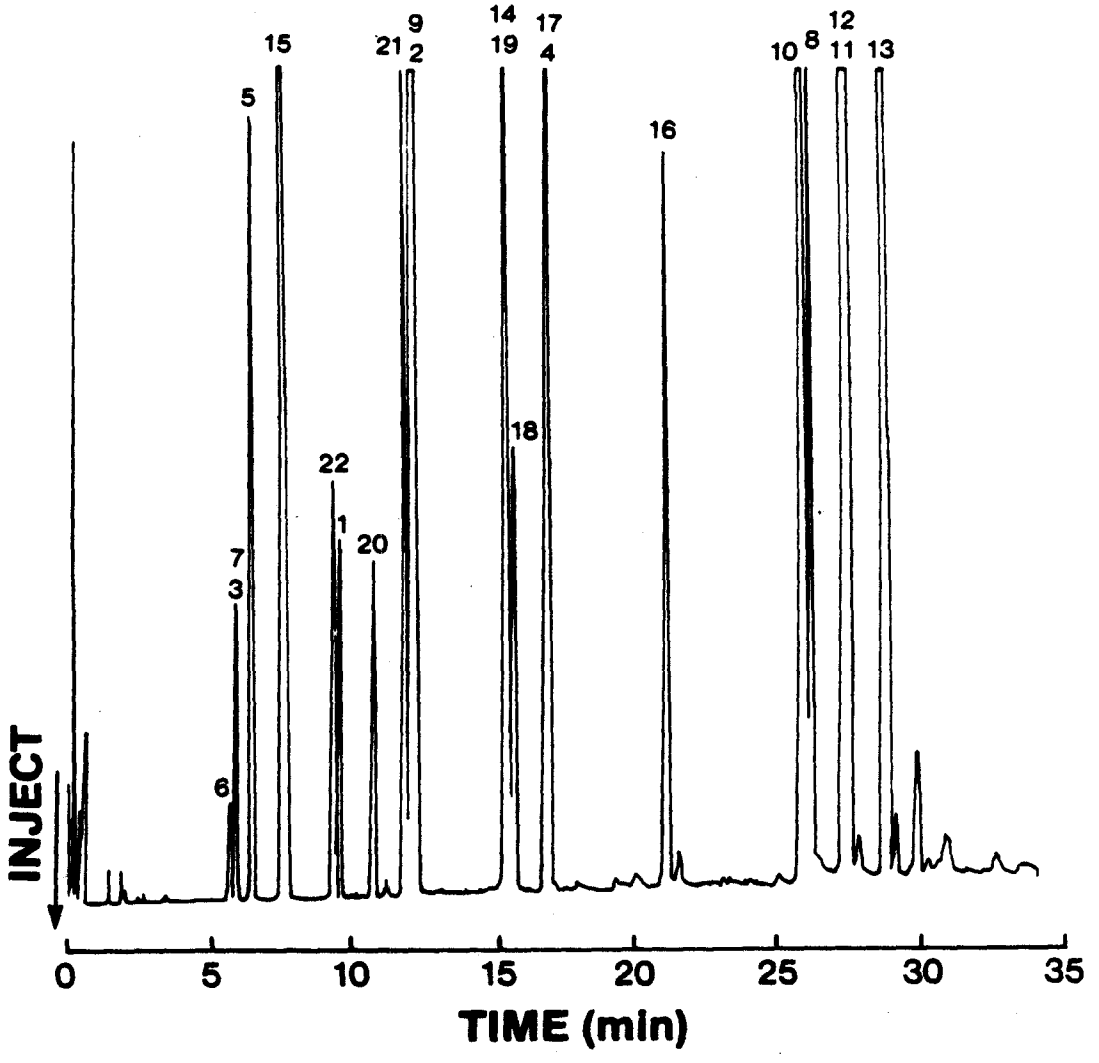

Figure 8. GC/ECD chromatogram of Method 8120 compounds analyzed on a SPB-5 fused-silica capillary column; the GC operating conditions are given in Table 4. For peak identification refer to Table 6. Standards in isooctane at concentrations between 0.05 and 10 ng/µL.

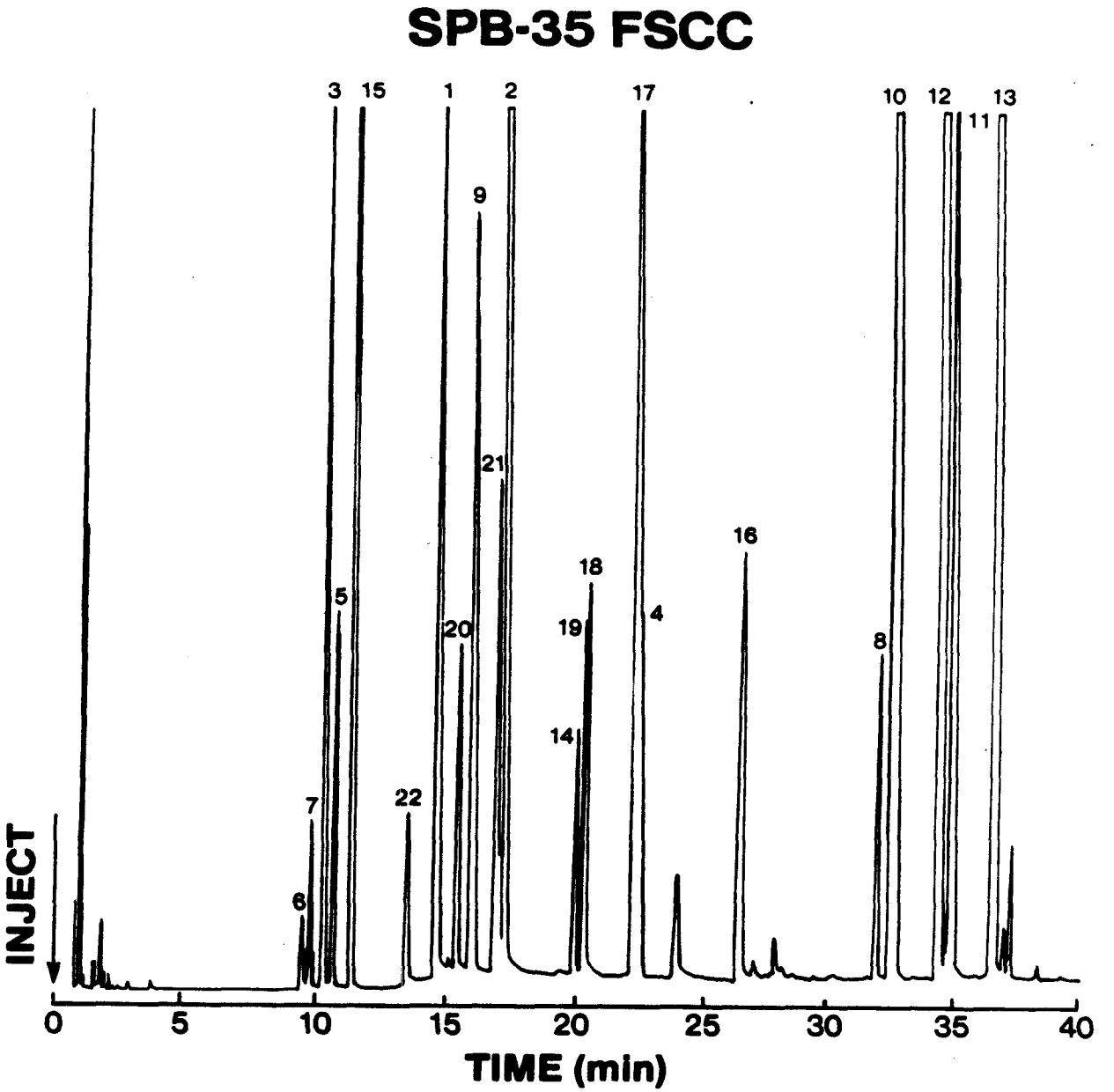

Figure 9. GC/ECD chromatogram of Method 8120 compounds analyzed on a SPB-35 fused-silica capillary column; the GC operating conditions are given in Table 4. For peak identification refer to Table 7. Standards in isooctane at concentrations between 0.05 and 10 ng/µL.

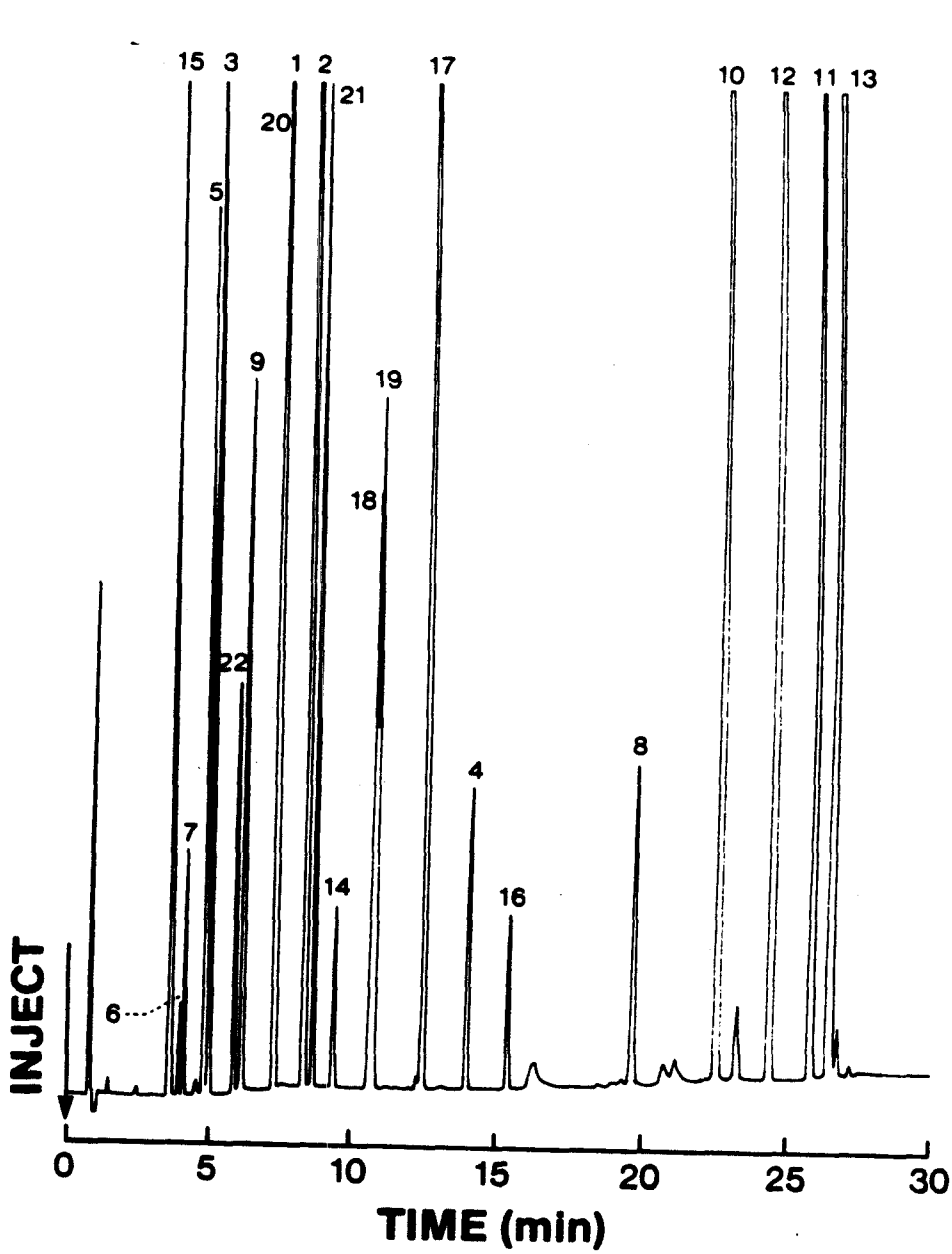

Figure 10. GC/ECD chromatogram of Method 8120 compounds analyzed on a DB-210 fused-silica capillary column; the GC operating conditions are given in Table 4. For peak identification, refer to Table 8. Standards in isooctane at concentrations between 0.05 and 10 ng/µL.

DB-210 FSCC

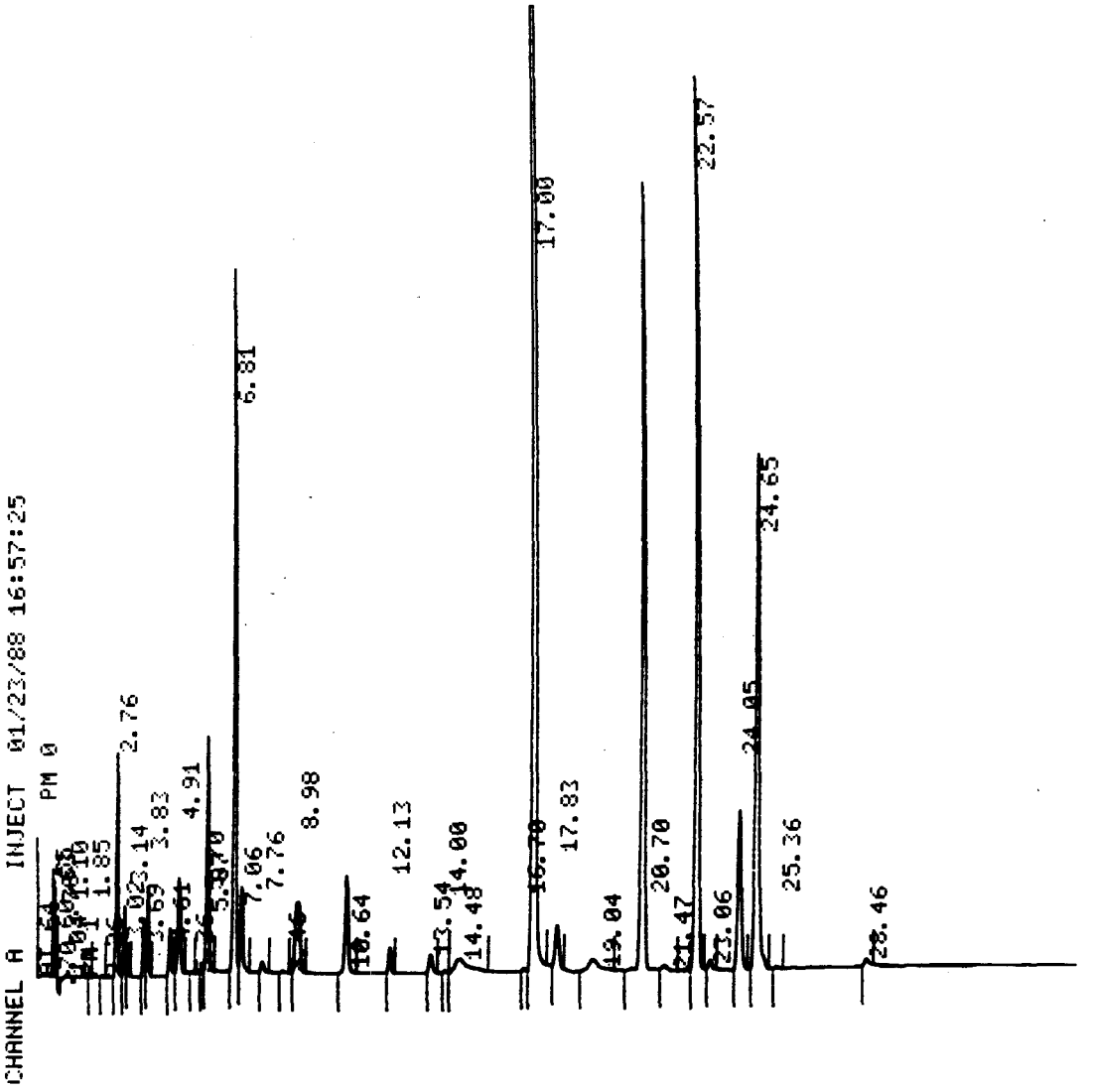

Figure 11. GC/ECD chromatogram of Method 8120 compounds analyzed on a DB-210 fused-silica capillary column; the GC operating conditions are given in Table 4. For peak identification, refer to Table 8. Standards in isooctane at concentrations between 0.01 and 2 ng/µL. Internal standard is α,α'-dibromo-m-xylene at 0.5 ng/µL (retention time 17:00 min).

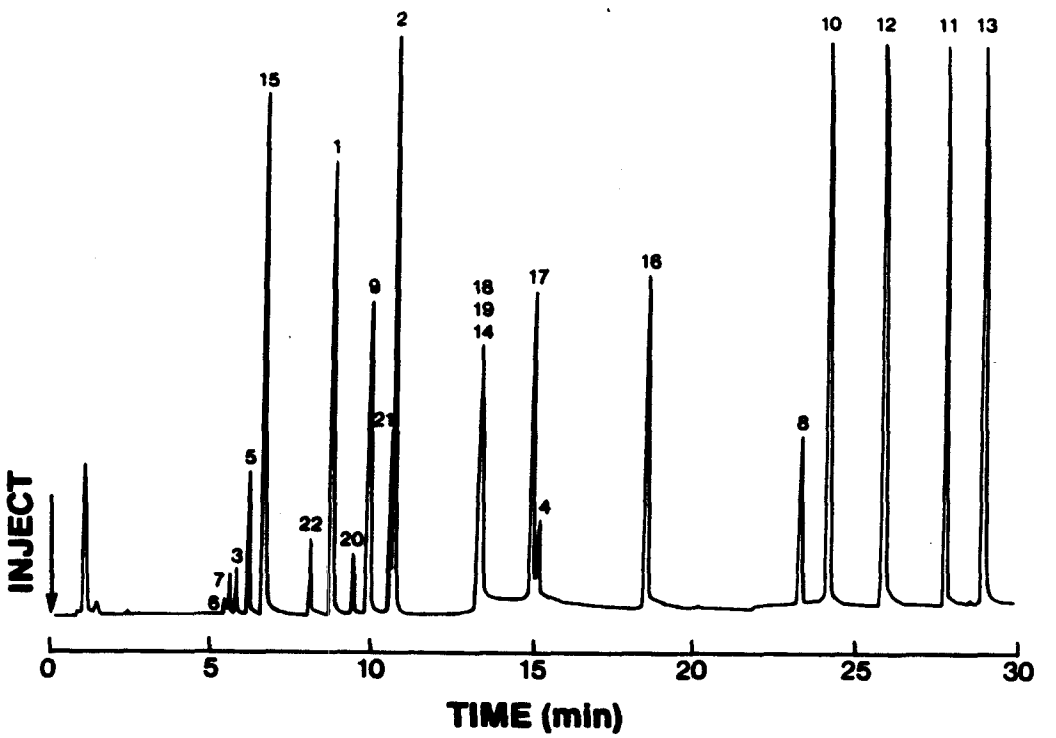

Figure 12. GC/ECD chromatogram of Method 8120 compounds analyzed on a DB-1301 fused-silica capillary column; the GC operating conditions are given in Table 4. For peak identification, refer to Table 9. Standards in isooctane at concentrations between 0.1 and 20 ng/µL.

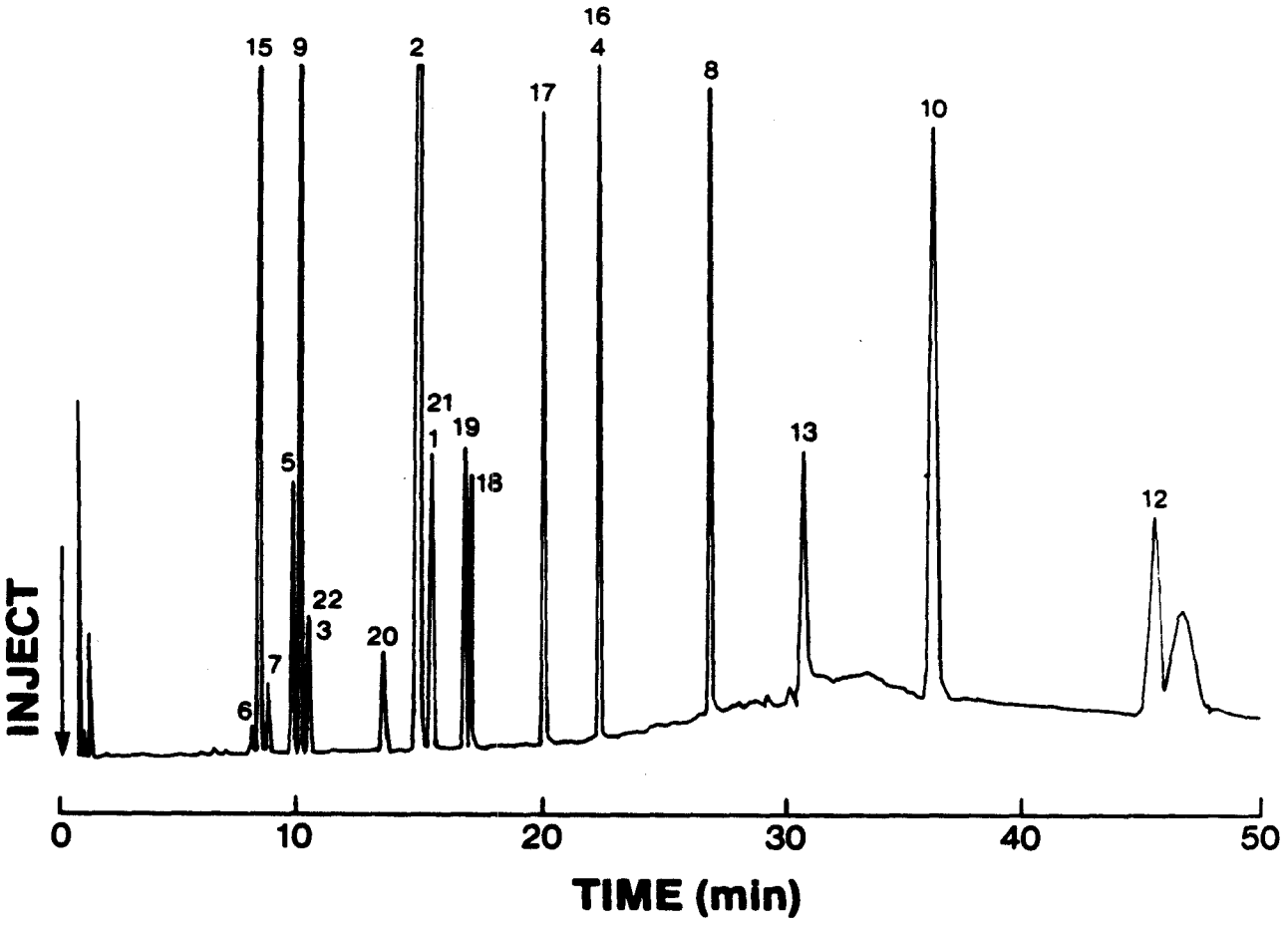

Figure 13. GC/ECD chromatogram of Method 8120 compounds analyzed on a DB-WAX fused-silica capillary column (No. 52861); the GC operating conditions are given in Table 4. For peak identification, refer to Table 10. Standards in isooctane at concentrations between 0.1 and 20 ng/µL.

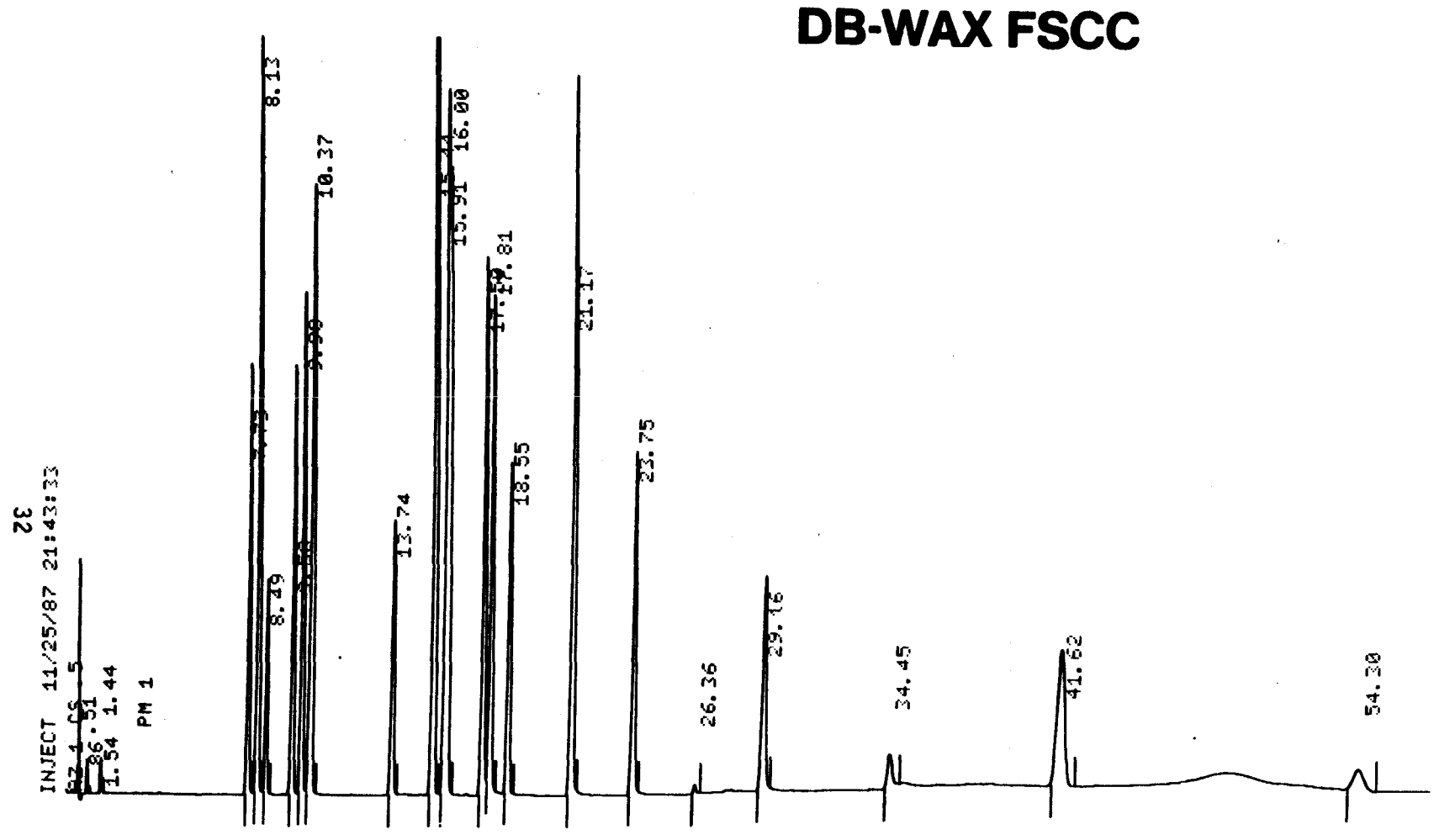

Figure 14. GC/ECD chromatogram of Method 8120 compounds analyzed on a DB-WAX fused-silica capillary column (No. 130906); the GC operating conditions are given in Table 4. For peak identification, refer to Table 10. Standards in isooctane at concentrations between 0.1 and 20 ng/µL.

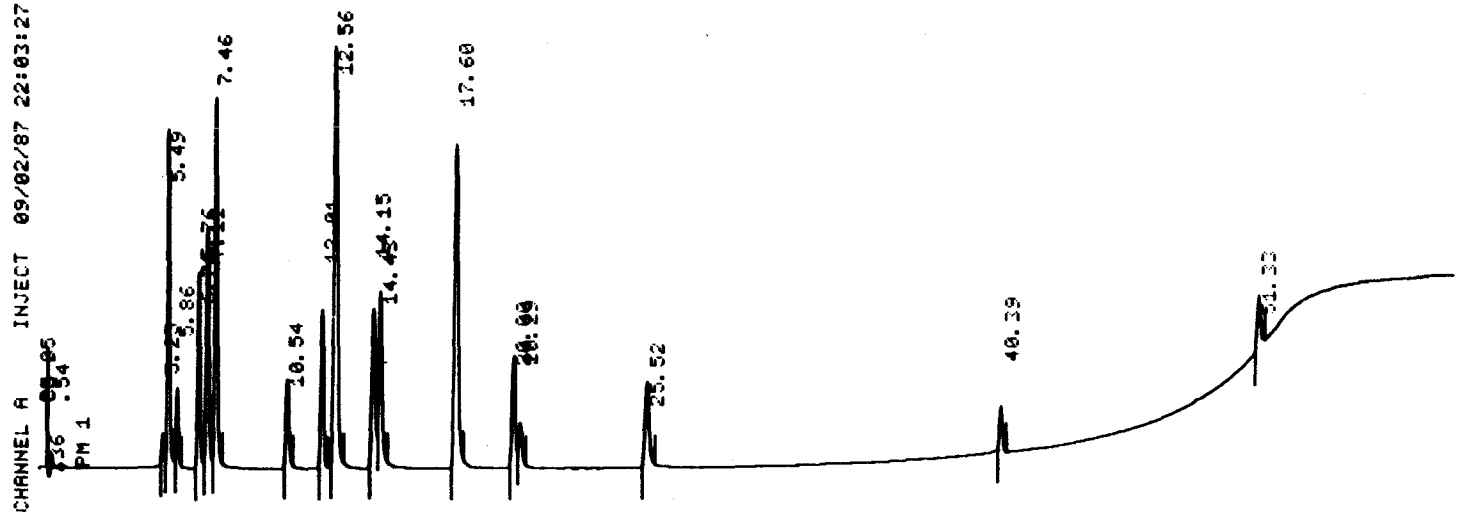

Figure 15. GC/ECD chromatogram of Method 8120 compounds analyzed on a Supelcowax 10 fused-silica capillary column; the GC operating conditions are given in Table 4. Standards in isooctane at concentrations between 0.1 and 20 ng/µL. The order of elution is the same as for the DB-WAX column.

TABLE 6. RETENTION TIMES (MIN) OF THE METHOD 8120 COMPOUNDS ON A 15 M X 0.53 MM ID SPB-5 FUSED-SILICA CAPILLARY COLUMN

Compound No.	Compound	Retention time (min)[a]						
		8°C/min[b]	8°C/min[c]		6°C/min	4°C/min	3°C/min	2°C/min
6	1,3-Dichlorobenzene	4.45	4.46	4.45	5.16	5.90	6.39	7.79
3	Benzyl chloride[d]	4.58	4.57	4.56	5.61	6.08	6.61	7.57
7	1,4-Dichlorobenzene[d]	4.60	4.57	4.56	5.61	6.08	6.61	7.57
5	1,2-Dichlorobenzene	4.91	4.93	4.92	6.41	6.66	7.30	8.46
15	Hexachloroethane	5.58	5.58	5.56	7.68	7.76	8.62	10.18
22	1,3,5-Trichlorobenzene	6.62	6.57	6.55	7.82	9.52	10.85	13.18
1	Benzal chloride	6.64	6.67	6.64	8.64	9.76	11.14	13.59
20	1,2,4-Trichlorobenzene	7.38	7.32	7.30	9.41	10.90	12.60	15.58
21	1,2,3-Trichlorobenzene	7.95	7.91	7.88	9.55	12.00	13.98	17.50
9	Hexachlorobutadiene[e]	7.98	8.09	8.06	9.66	12.36	14.44	18.19
2	Benzotrichloride[e]	8.00	8.09	8.06	9.66	12.36	14.44	18.19
19	1,2,3,5-Tetrachlorobenzene[f]	9.82	9.82	9.78	11.88	15.56	18.59	24.16
14	Hexachlorocyclopentadiene[f]	9.85	9.82	9.78	11.88	15.56	18.59	24.16
18	1,2,4,5-Tetrachlorobenzene	9.88	9.82	9.78	12.04	15.82	18.96	24.72
4	2-Chloronaphthalene[g]	10.40	10.57	10.56	12.89	17.04	20.52	26.92
17	1,2,3,4-Tetrachlorobenzene[g]	10.64	10.57	10.56	12.89	17.04	20.52	26.92
16	Pentachlorobenzene	12.69	12.73	12.67	15.68	21.15	25.89	34.81
10	alpha-BHC	15.18	15.20	15.15	18.91	25.96	32.26	44.25
8	Hexachlorobenzene	15.20	15.36	15.15	18.91	26.21	32.58	44.64
11	beta-BHC[h]	15.92	16.04	15.98	19.98	27.56	34.38	47.37
12	gamma-BHC[h]	16.06	16.04	15.98	19.98	27.56	34.38	47.37
13	delta-BHC	16.84	16.82	16.78	20.88	28.89	36.20	50.14

[a]Temperature program: 50°C to 175°C; hold 20 min at 175°C; injector temperature 220°C; detector temperature 300°C. Helium as carrier gas at 10 mL/min; nitrogen as makeup gas at 30 mL/min.
[b]Individual standards.
[c]Composite standard; duplicate determinations.
[d,e,f,g,h]These pairs cannot be resolved on the SPB-5 fused-silica capillary column.

TABLE 7. RETENTION TIMES (MIN) OF THE METHOD 8120 COMPOUNDS ON A 30 M X 0.53 MM ID SPB-35 FUSED-SILICA CAPILLARY COLUMN

Compound number	Compound	Retention time[a,b] (min)
6	1,3-Dichlorobenzene	9.85
7	1,4-Dichlorobenzene	10.16
3	Benzyl chloride	10.67
5	1,2-Dichlorobenzene	11.05
15	Hexachloroethane	11.80
22	1,3,5-Trichlorobenzene	14.00
1	Benzal chloride	15.15
20	1,2,4-Trichlorobenzene	15.96
9	Hexachlorobutadiene	16.53
21	1,2,3-Trichlorobenzene	17.43
2	Benzotrichloride	17.72
14	Hexachlorocyclopentadiene	20.60
19	1,2,3,5-Tetrachlorobenzene[c]	20.93
18	1,2,4,5-Tetrachlorobenzene[c]	21.01
17	1,2,3,4-Tetrachlorobenzene[d]	22.91
4	2-Chloronaphthalene[d]	23.00
16	Pentachlorobenzene	27.08
8	Hexachlorobenzene	32.48
10	alpha-BHC	33.06
12	gamma-BHC	34.97
11	beta-BHC	35.41
13	delta-BHC	37.11

[a]Temperature program: 50°C to 240°C (hold 10 min at 240°C) at 4°C/min; injector temperature 220°C; detector temperature 250°C. Helium as carrier gas at 10 mL/min; nitrogen as makeup gas at 30 mL/min.
[b]Composite standard.
[c,d]These pairs cannot be resolved on the SPB-35 fused-silica capillary column.

TABLE 8. RETENTION TIMES (MIN) OF THE METHOD 8120 COMPOUNDS ON A 30 M X 0.53 MM ID DB-210 FUSED-SILICA CAPILLARY COLUMN

Compound number	Compound	Retention time (min)									
				65°C to 175°C (hold 20 min) at 4°C/min							
		65°C to 175°C (hold 20 min) at 2°C/min[a]	65°C to 175°C (hold 15 min) at 3°C/min[a]	b	5-9 11:42[c]	5-10 11:44[c]	5-11 11:03[c]	5-12 13:03[c]	65°C to 175°C (hold 15 min) at 5°C/min[a]	75°C to 175°C (hold 20 min) at 5°C/min[a]	85°C to 175°C (hold 25 min) at 6°C/min[a]
15	Hexachloroethane	3.82	3.59	3.41	3.47	3.44	3.44	3.43	3.32	2.61	2.04
6	1,3-Dichlorobenzene	4.38	3.94	3.74	3.78	3.75	3.76	3.74	3.60	3.38	2.58
7	1,4-Dichlorobenzene	5.26	4.11	3.88	3.93	3.90	3.90	3.89	3.73	3.46	2.61
5	1,2-Dichlorobenzene	5.26	4.11	4.55	4.58	4.55	4.55	4.53	4.11	3.65	2.78
3	Benzyl chloride	5.26	4.83	4.70	4.74	4.71	4.70	4.68	4.32	4.18	3.09
22	1,3,5-Trichlorobenzene	6.71	5.02	5.57	5.61	5.58	5.58	5.55	5.22	4.30	3.21
9	Hexachlorobutadiene	5.50	5.02	5.86	5.93	5.90	5.90	5.87	5.49	4.30	3.21
20	1,2,4-Trichlorobenzene[d]	7.21	6.42	6.96	7.04	6.99	6.99	6.96	6.43	5.09	3.79
1	Benzal chloride[d]	7.21	6.42	6.98	7.04	6.99	6.99	6.96	6.43	5.09	3.79
2	Benzotrichloride	8.86	7.74	7.92	8.04	7.98	7.98	7.98	7.28	5.84	4.35
21	1,2,3-Trichlorobenzene	8.86	8.96	8.27	8.33	8.27	8.27	8.27	7.55	6.08	4.35
14	Hexachlorocyclopentadiene	10.14	10.22	8.94	9.06	8.99	8.99	8.99	8.13	6.58	5.70
19	1,2,3,5-Tetrachlorobenzene[e]	10.83	9.30	10.19	10.39	10.24	10.24	10.22	9.25	7.60	4.91
18	1,2,4,5-Tetrachlorobenzene[e]	10.43	8.96	10.31	10.29	10.24	10.24	10.22	9.25	7.55	4.55
17	1,2,3,4-Tetrachlorobenzene	14.31	11.75	12.07	12.11	12.07	12.06	12.06	10.67	8.94	6.75
4	2-Chloronaphthalene	17.32	14.03	13.57	13.66	13.62	13.60	13.60	13.10	11.80	8.60
16	Pentachlorobenzene	17.32	14.03	14.99	15.06	15.02	15.09	15.02	14.70	11.24	8.60
8	Hexachlorobenzene	31.00	23.58	19.36	19.45	19.42	19.39	19.40	19.02	17.08	11.43
10	alpha-BHC	36.84	27.52	22.37	22.42	22.40	22.38	22.38	20.54	18.58	13.38
12	gamma-BHC	40.43	29.98	24.22	24.30	24.28	24.24	24.26	21.71	19.72	14.64
11	beta-BHC	43.39	31.93	25.66	25.76	25.73	25.68	25.70	22.22	20.24	15.61
13	delta-BHC	44.51	32.73	26.30	26.38	26.36	26.32	26.32	22.70	20.47	16.12

[a]Composite standards, single determinations.
[b]Individual standards.
[c]Composite standards; replicate analyses done over four consecutive days.
[d,e]These pairs cannot be resolved on the DB-210 fused-silica capillary column.

TABLE 9. RETENTION TIMES OF THE METHOD 8120 COMPOUNDS ON A 30 M x 0.32 MM ID DB-1301 FUSED-SILICA CAPILLARY COLUMN[a]

Compound number	Compound	Retention time (min)[b]			
		Individual standard	Composite standard	Composite standard	Composite standard
6	1,3-Dichlorobenzene	5.61	5.58	5.59	5.61
7	1,4-Dichlorobenzene	5.74	5.58	5.73	5.74
3	Benzyl chloride	5.93	5.92	5.93	5.94
5	1,2-Dichlorobenzene	6.30	6.32	6.33	6.34
15	Hexachloroethane	6.78	6.78	6.78	6.80
22	1,3,5-Trichlorobenzene	8.24	8.22	8.23	8.24
1	Benzal chloride	8.91	8.91	8.91	8.93
20	1,2,4-Trichlorobenzene	9.55	9.55	9.56	9.58
9	Hexachlorobutadiene	10.04	10.03	10.04	10.05
2	Benzotrichloride[c]	10.80	10.78	10.80	10.81
21	1,2,3-Trichlorobenzene[c]	10.72	10.78	10.68	10.70
14	Hexachlorocyclopentadiene	13.37	13.40	13.39	13.40
18	1,2,4,5-Tetrachlorobenzene[d]	13.44	13.40	13.45	13.40
19	1,2,3,5-Tetrachlorobenzene[d]	13.44	13.40	13.45	13.40
17	1,2,3,4-Tetrachlorobenzene[d]	15.01	15.01	15.00	15.01
4	2-Chloronaphthalene	15.23	15.21	15.20	15.21
16	Pentachlorobenzene	18.51	18.54	18.54	18.53
8	Hexachlorobenzene	23.31	23.32	23.31	23.31
10	alpha-BHC	24.16	24.18	24.18	24.17
12	gamma-BHC	25.84	25.86	25.86	25.85
11	beta-BHC	27.79	27.79	27.79	27.78
13	delta-BHC	28.99	29.00	29.00	29.00

[a]Temperature program: 100°C to 250°C (hold 20 min) at 5°C/min; injector temperature 220°C; detector temperature, 250°C; helium as carrier gas at 1.5 mL/min; nitrogen as makeup gas at 40 mL/min.

[b]Single determination for individual standards. Three replicate determinations for composite standard.

[c,d]This pair/group cannot be resolved on the DB-1301 fused-silica capillary column.

TABLE 10. RETENTION TIMES (MIN) OF THE METHOD 8120 COMPOUNDS ON A 30 M X 0.53 MM ID DB-WAX FUSED-SILICA CAPILLARY COLUMN

Compound Number	Compound	Retention time (min)					
		60°C to 170°C (hold 30 min) at 4°C/min[a]	60°C to 170°C (hold 30 min) at 4°C/min[b]		70°C to 185°C (hold 10 min) at 3°C/min	70°C to 130°C (hold 2 min) at 3°C/min; 130°C to 185°C (hold 10 min) at 5°C/min	70°C to 130°C (hold ? min) at 3°C/min; 130°C to 185°C (hold 20 min) at 8°C/min
6	1,3-Dichlorobenzene	7.84	7.99	7.95	6.83	6.84	6.89
15	Hexachloroethane	8.26	8.37	8.33	7.23	7.22	7.27
7	1,4-Dichlorobenzene	8.53	8.71	8.68	7.58	7.59	7.64
5	1,2-Dichlorobenzene	9.60	9.75	9.72	8.73	8.71	8.77
9	Hexachlorobutadiene	9.98	10.11	10.08	9.12	9.10	9.15
22	1,3,5-Trichlorobenzene	10.41	10.45	10.41	9.50	9.48	9.54
3	Benzyl chloride	10.51	10.45	10.41	9.50	9.48	9.54
20	1,2,4-Trichlorobenzene	13.63	13.63	13.57	13.21	13.20	13.25
2	Benzotrichloride	15.10	15.20	15.12	15.14	15.12	15.17
1	Benzal chloride[d]	15.59	15.64	15.56	15.74	15.73	15.78
21	1,2,3-Trichlorobenzene[d]	15.70	15.64	15.62	15.74	15.73	15.78
19	1,2,3,5-Tetrachlorobenzene	17.07	17.07	17.00	17.48	17.48	17.53
18	1,2,4,5-Tetrachlorobenzene	17.20	17.36	17.28	17.84	17.84	17.89
17	1,2,3,4-Tetrachlorobenzene	20.40	20.43	20.33	21.74	21.90	21.95
4	2-Chloronaphthalene[e]	22.54	22.80	22.70	24.80	25.18	24.82
16	Pentachlorobenzene[e]	22.76	22.80	22.70	24.80	25.18	24.84
14	Hexachlorocyclopentadiene	[c]	[c]	[c]	[c]	[c]	[c]
8	Hexachlorobenzene	27.44	27.55	27.44	30.94	30.30	28.62
13	delta-BHC	30.54	30.96	30.82	35.22	33.22	30.88
10	alpha-BHC	36.43	37.10	36.86	38.94	36.48	34.04
12	gamma-BHC	45.52	46.59	46.24	44.10	41.56	[c]
11	beta-BHC	[c]	[c]	[c]	[c]	[c]	[c]

[a]Individual standards.
[b]Composite standard.
[c]Not able to determine.
[d,e]These pairs cannot be resolved on the DB-WAX fused-silica capillary column.

TABLE 11. RETENTION TIMES (MIN) OF OTHER CHLORINATED AROMATIC COMPOUNDS ON A 15 M X 0.53 MM ID SPB-5 FUSED-SILICA CAPILLARY COLUMN

Compound	Retention time (min)[a]
2-Chloro-p-xylene	8.00
α-Chloro-o-xylene	8.89
α-Chloro-m-xylene	8.97
α-Chloro-p-xylene	9.09
α,3-Dichlorotoluene	11.48
α,4-Dichlorotoluene	12.00
2,6-Dichlorostyrene	12.17
2,5-Dichlorostyrene	12.54
3,4-Dichlorostyrene	13.21
2,4,5-Trichlorotoluene	14.67
α,α'-Dichloro-o-xylene	15.36
α,2,4-Trichlorotoluene	15.80
α,2,6-Trichlorotoluene	15.95
α,α'-Dichloro-m-xylene	16.84
α,α'-Dichloro-p-xylene	16.96
α,3,4-Trichlorotoluene	17.38
α,α',2,6-Tetrachlorotoluene	19.48
1,4-Dichloronaphthalene	22.17
2,7-Dichloronaphthalene	22.36
1,5-Dichloronaphthalene	22.37 and 28.70
1,2-Dichloronaphthalene	22.86
2,4,5,6-Tetrachloro-m-xylene	23.36
2,3,4,5,6-Pentachlorotoluene	24.94
α,α,α,α',α',α'-Hexachloro-p-xylene	26.73
α,α,α,α',α',α'-Hexachloro-m-xylene	28.00
1,2,3,4-Tetrachloronaphthalene	31.97
α,α',2,3,5,6-Hexachloro-p-xylene	34.78
α,α',2,4,5,6-Hexachloro-m-xylene	34.81

(continued)

[a]Analysis was performed on a 15 m x 0.53 mm ID SPB-5 fused-silica capillary column; 50°C to 175°C (hold 20 min) at 4°C/min; injector temperature 220°C; detector temperature 300°C.

TABLE 11. (concluded)

Compound	Retention time (min)[a]
Octachloronaphthalene	b
4-Chloro-p-terphenyl	b
2,4-Dichloro-p-terphenyl	b
2,5-Dichloro-p-terphenyl	b
2,5-Dichloro-m-terphenyl	b
2,5-Dichloro-o-terphenyl	b

[a]Analysis was performed on a 15 m x 0.53 mm ID SPB-5 fused-silica capillary column; 50°C to 175°C (hold 20 min) at 4°C/min; injector temperature 220°C; detector temperature 300°C.

[b]No response; compound does not elute from the GC column under the conditions specified above.

TABLE 12. RETENTION TIMES (MIN) OF OTHER CHLORINATED AROMATIC COMPOUNDS ON A 30 M X 0.53 MM ID SPB-35 FUSED-SILICA CAPILLARY COLUMN

Compound	Retention time (min)[a]
α-Chloro-m-xylene	14.12
α-Chloro-p-xylene	14.25
α-Chloro-o-xylene	14.31
α,3-Dichlorotoluene	17.34
2,6-Dichlorostyrene	17.42
α,4-Dichlorotoluene	17.45
2,5-Dichlorostyrene	17.46
3,4-Dichlorostyrene	18.67
2,4,5-Trichlorotoluene	19.77
α,α'-Dichloro-o-xylene	21.98
α,2,4-Trichlorotoluene	22.29
α,2,6-Trichlorotoluene	22.47
α,α'-Dichloro-m-xylene	23.68
α,3,4-Trichlorotoluene	23.92
α,α'-Dichloro-p-xylene	23.93
1,4-Dichloronaphthalene	28.61
1,5-Dichloronaphthalene	28.81 and 35.82
2,7-Dichloronaphthalene	28.82
1,2-Dichloronaphthalene	29.37
2,4,5,6-Tetrachloro-m-xylene	29.63
2,3,4,5,6-Pentachlorotoluene	31.44
α,α,α,α',α',α'-Hexachloro-m-xylene	33.07
α,α,α,α',α',α'-Hexachloro-p-xylene	34.42
1,2,3,4-Tetrachloronaphthalene	39.37
α,α',2,3,5,6-Hexachloro-p-xylene	41.95
α,α',2,4,5,6-Hexachloro-m-xylene	41.95
α,α',2,6-Tetrachlorotoluene	12.46 and 15.04
2-Chloro-p-xylene	b

[a]Analysis was performed on a 30 m x 0.53 mm ID SPB-35 fused-silica capillary column; 50°C to 240°C (hold 10 min) at 4°C/min; injector temperature 220°C; detector temperature 250°C.
[b]Not analyzed.

TABLE 13. RETENTION TIMES (MIN) OF OTHER CHLORINATED AROMATIC COMPOUNDS ON A 30 M X 0.53 MM ID DB-210 FUSED-SILICA CAPILLARY COLUMN

Compound	Retention time (min)[a]
α-Chloro-p-xylene	6.66
α-Chloro-m-xylene	6.86
2,6-Dichlorostyrene	7.52
2,5-Dichlorostyrene	8.11
α,3-Dichlorotoluene	8.99
α,4-Dichlorotoluene	9.10
3,4-Dichlorostyrene	9.55
2-Chloro-p-xylene	9.71
2,4,5-Trichlorotoluene	9.90
α,2,4-Trichlorotoluene	12.14
α-Chloro-o-xylene	12.88
α,α'-Dichloro-o-xylene	12.94
α,2,6-Trichlorotoluene	12.96
α,3,4-Trichlorotoluene	14.22
α,α'-Dichloro-m-xylene	14.65
α,α'-Dichloro-p-xylene	14.86
α,α',2,6-Tetrachlorotoluene	15.04
2,4,5,6-Tetrachloro-m-xylene	17.26
1,4-Dichloronaphthalene	17.43
1,5-Dichloronaphthalene	17.62 and 23.72
2,7-Dichloronaphthalene	18.29
1,2-Dichloronaphthalene	18.62
2,3,4,5,6-Pentachlorotoluene	18.96
α,α,α,α',α',α'-Hexachloro-m-xylene	19.87
α,α,α,α',α',α'-Hexachloro-p-xylene	21.38
1,2,3,4-Tetrachloronaphthalene	26.32
α,α',2,4,5,6-Hexachloro-m-xylene	29.57
α,α',2,3,5,6-Hexachloro-p-xylene	29.58

[a]Analysis was performed on a 30 m X 0.53 mm ID DB-210 fused-silica capillary column; 1 μm film thickness; 65°C to 175°C (hold 20 min) at 4°C/min; injector temperature 220°C; detector temperature 250°C.

TABLE 14. RETENTION TIMES (MIN) OF OTHER CHLORINATED AROMATIC COMPOUNDS ON A 30 M X 0.53 MM ID DB-WAX FUSED-SILICA CAPILLARY COLUMN

Compound	Retention time (min)[a]
α-Chloro-m-xylene	12.09
α-Chloro-o-xylene	12.58
2,6-Dichlorostyrene	14.53
2,5-Dichlorostyrene	14.60
2,4,5-Trichlorotoluene	15.98
3,4-Dichlorostyrene	17.18
α,3-Dichlorotoluene	18.12
α,4-Dichlorotoluene	18.34
α,2,4-Trichlorotoluene	22.98
α,2,6-Trichlorotoluene	23.34
α,α'-Dichloro-o-xylene	25.09
2,4,5,6-Tetrachloro-m-xylene	25.79
α-Chloro-p-xylene	26.06
2-Chloro-p-xylene	26.08
α,α',2,6-Tetrachlorotoluene	26.11
α,3,4-Trichlorotoluene	26.26
2,7-Dichloronaphthalene	26.28
1,5-Dichloronaphthalene	26.32 and 28.57
1,4-Dichloronaphthalene	26.33
α,α'-Dichloro-m-xylene	27.07
α,α-Dichloro-p-xylene	27.26
2,3,4,5,6-Pentachlorotoluene	27.66
1,2-Dichloronaphthalene	29.28
α,α,α,α',α',α'-Hexachloro-m-xylene	29.63
α,α,α,α',α',α'-Hexachloro-p-xylene	31.41
α,α',2,4,5,6-Hexachloro-m-xylene	32.94
1,2,3,4,-Tetrachloronaphthalene	39.84
α,α',2,3,5,6-Hexachloro-p-xylene	b

[a]Analysis was performed on a 30 m x 0.53 mm ID DB-WAX fused-silica capillary column; 1 μm film thickness; 70°C to 130°C (hold 2 min) at 3°C/min; 130°C to 185°C (hold 20 min) at 8°C/min; injector temperature 220°C; detector temperature 250°C.

[b]No response; compound does not elute from the GC column under the conditions specified above.

the methylene chloride extracts were combined, exchanged to hexane and then analyzed by gas chromatography with electron capture detection. The results for Method 3510 for two sediment leachates, two reagent waters (identified in Table 15 as method blanks for leachates 1 or 2) and one surface water are presented in Table 15. All compounds were recovered quantitatively (recovery >75 percent) regardless of the matrix. Only in the case of the Bloody Run Creek sediment leachate, recoveries were either too low or too high because the target compounds were spiked at approximately 0.1 to 20 µg/L and some of the compounds were present in the sample at mg/L concentrations (Table 16).

All test compounds were recovered quantitatively from water by extraction with methylene chloride regardless of sample pH. Table 17 shows the recovery data at pH 7, 2, and 9 for each of the 22 compounds.

Evaluation of the extraction techniques for soil samples was performed with environmental samples, either unspiked or spiked with the 22 target compounds. The extraction was performed either with hexane/acetone (1:1) in a Soxhlet extractor (Method 3540) or with methylene chloride/acetone (1:1) using a sonicator probe (Method 3550). The amount of soil or sediment used for Soxhlet extraction was 10 g and for sonication extraction 30 g. In each case, the material was mixed with an equivalent amount of anhydrous sodium sulfate prior to extraction, and the extracts were cleaned up by Florisil chromatography (Method 3620). Tables 18 and 19 summarize the results for the Bloody Run Creek sediment and the Detroit River Sediment extracts, respectively. Although it is very difficult to draw a conclusion about the efficiency of the extraction technique from the individual measurements for the target analytes, the Soxhlet extraction seems to be more exhaustive than the sonication. Of course, two factors need to be taken into consideration when analyzing the data presented in Tables 18 and 19: the weight of sample and the extraction solvent.

Additional effort is needed to optimize the Soxhlet extraction technique. Although sediment samples are usually extracted for 8 to 16 hours by the Soxhlet method, Chau et al. (4) found no difference in the recoveries of chlorobenzenes and hexachlorobutadiene when using varying extraction times. However, Chau et al. (4) reported that recoveries of chlorobenzenes from standard reference material EC-2 by sonication with acetone/hexane (1:1) were about 80 percent for penta- and hexachlorobenzene, 70 percent for hexachlorobutadiene and tetrachlorobenzenes, and 50 percent for dichlorobenzenes. We have extracted this standard reference material using Method 3550 (sonication with 1:1 methylene chloride/acetone) and analyzed the extract following the conditions in the revised Method 8120. The results of our analyses are given in Table 20. The only two compounds for which the certified values agree with our measured values were 1,3,5-trichlorobenzene and hexachlorobenzene. For the remainder of compounds, our results were either lower (for 1,2,4-trichlorobenzene, 1,2,4,5-tetrachlorobenzene, and hexachlorobutadiene) or higher (for 1,2,3,4-tetrachlorobenzene and

TABLE 15. OVERALL PERCENT RECOVERIES FOR METHODS 3510 AND 8120

Compound	Amount spiked (µg)	Leachate 1 (Detroit sediment)	Method Blank for Leachate 1	Leachate 2 (Bloody Run Creek sediment)[f]	Method Blank for Leachate 2	San Francisco Bay water
Hexachloroethane	0.1	92	100	130	88	92
1,3-Dichlorobenzene	10	82	98	39	69	75
1,4-Dichlorobenzene	10	82	99	53	72	79
1,2-Dichlorobenzene	10	91	101	[d]	86	92
Benzyl chloride	10	150[a]	163[a]	[d]	144[a]	155[a]
1,3,5-Trichlorobenzene	1.0	83	98	30	79	92
Hexachlorobutadiene	0.1	91	100	[d]	89	97
Benzal chloride[b] 1,2,4-Trichlorobenzene[b]	2.0	96	104	110	94	99
Benzotrichloride	2.0	96	104	270	97	102
1,2,3-Trichlorobenzene	1.0	96	108	40	95	105
Hexachlorocyclopentadiene	0.1	100	107	200	93	100
1,2,4,5-Tetrachlorobenzene[c] 1,2,3,5-Tetrachlorobenzene[c]	2.0	93	102	150	107	100
1,2,3,4-Tetrachlorobenzene	1.0	98	105	130	96	103
2-Chloronaphthalene	20	92	103	149	84	97
Pentachlorobenzene	0.1	75	86	300	68	79
Hexachlorobenzene	0.1	98	110	160	93	110
alpha-BHC	1.0	97	108	510	107	105
gamma-BHC	1.0	100	105	240	96	104
beta-BHC	1.0	99	106	150	97	106
delta-BHC	1.0	100	107	170	96	104
Volume extracted (mL)[e]		800	800	800	800	1,000
Sample pH		5.14	5.10	5.12	5.10	8.03
Surrogate recovery (percent)						
α,2,6-Trichlorotoluene	1.0	81	94	101	77	97
1,4-Dichloronaphthalene	10	82	110	151	90	95
2,3,4,5,6-Pentachlorotoluene	1.0	80	90	55	75	89

[a]Unable to explain the high recovery. Spiking solution has been verified and found to contain 10 ng/µL.
[b,c]These pairs cannot be resolved on the DB-210 fused-silica capillary column.
[d]Not able to determine recovery because the spike level was below the background level.
[e]$V_{extract}$ is 10 mL for each sample.
[f]High recoveries are due to high concentrations of the Method 8120 compounds in the leachate (see Table 16).

TABLE 16. RESULTS OF METHOD 8120 ANALYSES FOR BLOODY RUN CREEK LEACHATE (UNSPIKED)

Compound	Concentration[a] (µg/L)
Hexachloroethane	1.3
1,3-Dichlorobenzene	340
1,4-Dichlorobenzene	340
1,2-Dichlorobenzene	2,600
Benzyl chloride	3,600
1,3,5-Trichlorobenzene	120
Hexachlorobutadiene	11
Benzal chloride[b]	160
1,2,4-Trichlorobenzene[b]	
Benzotrichloride	6.2
1,2,3-Trichlorobenzene	69
Hexachlorocyclopentadiene	2.5
1,2,4,5-Tetrachlorobenzene[c]	110
1,2,3,5-Tetrachlorobenzene[c]	
1,2,3,4-Tetrachlorobenzene	140
2-Chloronaphthalene	1,100
Pentachlorobenzene	14
Hexachlorobenzene	1.8
alpha-BHC	250
gamma-BHC	26
beta-BHC	18
delta-BHC	44

[a]Final volume of extract is 10 mL. Volume of leachate extracted by Method 3510 is 800 mL (pH 5.12). Extract was diluted 10-fold prior to GC/ECD analysis.

[b,c]These pairs cannot be resolved on the DB-210 fused-silica capillary column.

TABLE 17. RECOVERIES OF THE METHOD 8120 COMPOUNDS AS A FUNCTION OF pH

Compound	Spike level (µg/L)	Percent Recovery[a]					
		pH 7		pH 2		pH 9	
Hexachloroethane	1.0	108	93	105	107	106	105
1,3-Dichlorobenzene	100	106	85	101	105	104	101
1,4-Dichlorobenzene	100	118	82	109	114	113	109
1,2-Dichlorobenzene	100	113	87	107	111	109	107
Benzyl chloride	100	111	89	105	109	108	106
1,3,5-Trichlorobenzene	10	117	89	109	116	112	109
Hexachlorobutadiene	1.0	113	87	107	112	109	108
Benzalchloride[b] 1,2,4-Trichlorobenzene[b]	20	108	96	105	105	107	106
Benzotrichloride	10	109	100	108	107	109	108
1,2,3-Trichlorobenzene	10	113	93	109	114	111	109
Hexachlorocyclopentadiene	1.0	81	66	80	87	82	81
1,2,4,5-Tetrachlorobenzene[c] 1,2,3,5-Tetrachlorobenzene[c]	20	117	94	112	118	114	112
1,2,3,4-Tetrachlorobenzene	10	114	95	109	115	111	110
2-Chloronaphthalene	200	119	95	113	120	114	112
Pentachlorobenzene	1.0	118	98	113	117	114	112
Hexachlorobenzene	1.0	121	100	116	121	116	115
alpha-BHC	10	108	99	106	108	106	106
gamma-BHC	10	108	99	106	108	107	106
beta-BHC	10	109	93	106	109	108	107
delta-BHC	10	105	95	103	105	104	103

[a]Duplicate experiments were performed at each pH.
[b,c]These pairs cannot be resolved on the DB-210 fused-silica capillary column.

TABLE 18. CONCENTRATIONS (ng/μL EXTRACT) OF THE METHOD 8120 COMPOUNDS IDENTIFIED IN THE BLOODY RUN CREEK SEDIMENT[a]

Compound	t_R (min)	Method 3540 (Soxhlet extraction) A	B	C	Method 3550 (Sonication extraction) A	B	C
Hexachloroethane	3.39	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
1,3-Dichlorobenzene	3.70	116	6.3	24.7	<0.5	<0.5	<0.5
1,4-Dichlorobenzene	3.85	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
1,2-Dichlorobenzene	4.49	0.08	0.40	0.53	2.08	2.69	0.92
Benzyl chloride	4.64	0.09	0.07	0.08	1.28	1.76	0.65
1,3,5-Trichlorobenzene	5.51	0.43	c	0.28	0.04	0.05	0.02
Hexachlorobutadiene	5.83	<0.01	0.01	0.01	0.05	0.07	0.02
Benzal chloride[d] 1,2,4-Trichlorobenzene[d]	6.92	0.01	0.02	0.02	0.04	0.06	0.03
Benzotrichloride	7.91	0.01	0.004	0.002	0.01	0.03	0.01
1,2,3-Trichlorobenzene	8.20	<0.01	0.01	0.01	0.02	<0.01	<0.01
Hexachlorocyclopentadiene	8.92	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
1,2,3,5-Tetrachlorobenzene[e] 1,2,4,5-Tetrachlorobenzene[e]	10.24	<0.01	0.05	0.05	0.08	0.08	0.07
1,2,3,4-Tetrachlorobenzene	11.96	0.05	0.03	0.04	0.18	0.34	0.02
2-Chloronaphthalene	13.50	0.40	0.73	1.09	2.70	5.88	1.00
Pentachlorobenzene	14.92	0.005	0.02	0.03	0.14	0.27	0.04
Hexachlorobenzene	19.29	0.01	0.02	0.03	0.09	0.15	0.03
alpha-BHC[b]	22.24	0.017	0.014	0.031	0.06	0.14	0.02
gamma-BHC[b]	24.14	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
beta-BHC[b]	25.60	0.004	0.011	0.020	0.02	0.04	0.013
delta-BHC[b]	26.22	0.004	0.005	0.009	0.007	0.012	0.006

[a]Each extract was subjected to Forisil chromatography (Method 3620) prior to GC/ECD analysis on the DB-210 fused-silica capillary column. Fraction 1 was eluted with 200 mL petroleum ether; Fraction 2 with 200 mL petroleum ether/diethyl ether (1:1). Final volume of Fraction 1 or Fraction 2 is 10 mL. Weight of sediment sample is 10 g for Soxhlet extraction and 30 g for sonication. To convert to concentrations in ng/g of sediment, multiply the values given in ng/μL extract by 1,000 for Soxhlet extraction and 333 for sonication extraction.

[b]Determined in Fractions 1 and 2 (Florisil chromatography).

[c]Not resolved from hexachlorobutadiene.

[d,e]These pairs cannot be resolved on the DB-210 fused-silica capillary column.

TABLE 19. CONCENTRATIONS (ng/μL EXTRACT) OF THE METHOD 8120 COMPOUNDS IDENTIFIED IN THE DETROIT RIVER SEDIMENT[a]

Compound	t_R (min)	Method 3540 (Soxhlet extraction) A	B	C	Method 3550 (Sonication extraction) A	B	C
Hexachloroethane	3.39	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
1,3-Dichlorobenzene	3.70	0.35	0.33	<0.1	0.91	<0.1	<0.1
1,4-Dichlorobenzene	3.85	3.88	6.07	0.04	<0.01	0.04	0.05
1,2-Dichlorobenzene	4.49	0.02	0.02	0.05	0.03	0.03	0.05
Benzyl chloride	4.64	1.64	1.82	0.04	2.2	<0.01	0.03
1,3,5-Trichlorobenzene	5.51	0.012	0.036	0.004	0.007	0.005	0.007
Hexachlorobutadiene	5.83	0.002	0.002	0.001	0.002	0.001	0.002
Benzal chloride[c] 1,2,4-Trichlorobenzene[c]	6.92	0.009	0.019	0.011	0.012	0.009	0.016
Benzotrichloride	7.91	0.012	0.031	0.005	0.005	0.007	0.006
1,2,3-Trichlorobenzene	8.20	0.008	0.005	0.005	0.003	0.005	0.004
Hexachlorocyclopentadiene	8.92	0.002	0.003	0.001	0.001	<0.001	0.001
1,2,3,5-Tetrachlorobenzene[d] 1,2,4,5-Tetrachlorobenzene[d]	10.24	<0.01	0.017	0.002	0.006	0.012	0.016
1,2,3,4-Tetrachlorobenzene	11.96	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
2-Chloronaphthalene	13.50	0.10	0.11	0.14	0.40	0.72	1.14
Pentachlorobenzene	14.92	0.002	0.002	0.004	0.004	0.001	0.002
Hexachlorobenzene	19.29	0.003	0.003	0.004	0.007	0.004	0.005
alpha-BHC[b]	22.24	0.003	0.010	0.012	0.009	0.008	0.012
gamma-BHC[b]	24.14	<0.005	<0.005	0.005	0.007	0.007	0.008
beta-BHC[b]	25.60	0.005	0.038	0.009	0.008	0.013	0.013
delta-BHC[b]	26.22	0.007	0.028	0.029	0.015	0.018	0.021

[a]Each extract was subjected to Florisil chromatography (Method 3620) prior to GC/ECD analysis on the DB-210 fused-silica capillary column. Fraction 1 was eluted with 200 mL petroleum ether; Fraction 2 with 200 mL petroleum ether/diethyl ether (1:1). Final volume of Fraction 1 or Fraction 2 is 10 mL. Each fraction was diluted 1,000-fold prior to analysis. Weight of sediment sample is 10 g for Soxhlet extraction and 30 g for sonication. To convert to concentrations in ng/g of sediment, multiply the values given in ng/μL extract by 1,000 for Soxhlet extraction and 333 for sonication extraction.

[b]Found in Fractions 1 and 2 (Florisil chromatography).

[c,d]These pairs cannot be resolved on the DB-210 fused-silica capillary column.

TABLE 20. RESULTS OF THE METHOD 8120 ANALYSIS FOR EC-2

Compound	Certified value[a] (ng/g)	Value determined by revised Method 8120[b]
1,3,5-Trichlorobenzene	34.3 ± 2.6	32.7
1,2,4-Trichlorobenzene	80.7 ± 5.4	7.1
1,2,4,5-Tetrachlorobenzene	84.0 ± 4.9	29.8
1,2,3,4-Tetrachlorobenzene	36.5 ± 2.4	78.0
Pentachlorobenzene	48.6 ± 2.4	92.6
Hexachlorobenzene	200.6 ± 13.2	167.9
Hexachlorobutadiene	21.3 ± 1.6	11.8

[a]Data taken from Reference 4.
[b]Weight of sample is 10 g. Extraction was performed by Method 3550. The extract was cleaned up by Florisil chromatography. 1-g Florisil disposable cartridges and elution with hexane/acetone (9:1) were employed.

pentachlorobenzene) than the certified values. No other experiments were attempted to solve the discrepancy.

A method to prepare reference materials from soils is described in Appendix C.

6.3 EXTRACT CLEANUP TECHNIQUES

Fractionation or cleanup of sample extracts prior to instrumental analysis (e.g., gas chromatography) is used to remove coextracted materials that often interfere with the determination of target analytes. Such fractionations are usually accomplished by column chromatography (e.g., on Florisil, alumina, silica gel), gel permeation chromatography, or acid/base partitioning. More elaborate fractionation schemes that involve a combination of such cleanup procedures can be quite tedious, and experienced analysts are required for their successful application.

Standardized cleanup procedures such as Methods 3610 and 3620 published in EPA SW-846(1) specify amounts of alumina and Florisil in excess of 10 g and large volumes of eluting solvents (e.g., a 12-g Florisil column and 200 mL of petroleum ether are recommended for cleanup of sample extracts containing chlorinated hydrocarbons). Such large volumes of solvents increase the likelihood of sample contamination by impurities in solvents. Furthermore, the adsorbent materials and the solvents are not recycled, and although such materials are not overly expensive, the time required for the preparation of the adsorbent, for the packing of the chromatographic columns, and the evaporation of solvents contributes to the overall cost of analysis.

Use of disposable Florisil cartridges known as Supelclean™, Quick-Sep™, Sep-Pak™, and Bond-Elut™ for sample extract cleanup has been investigated. When using disposable cartridges, the elution conditions are typically chosen to retain the target analytes on the adsorbent while the coextracted materials are washed from the cartridge with the eluant. Alternatively, the coextracted materials are retained while the target analytes are eluted from the cartridge.

This section presents the results of the gel permeation chromatography experiments, sulfur cleanup experiments, and the Florisil cleanup experiments.

6.3.1 Gel Permeation Chromatography (GPC)

Due to time and budgetary constraints, it was not possible to develop and then evaluate a GPC procedure for Method 8120. Instead, the current GPC procedure given in Method 3640 was chosen and evaluated with the target analytes.

A Bio-Beads SX-3 GPC column and methylene chloride were used to separate the target compounds from corn oil interferents. To determine the elution profile of corn oil (which is representative of lipid materials), a solution of corn oil in methylene chloride was injected into the GPC column and 10-mL fractions were collected at 2-min intervals for 36 min. Each fraction was

evaporated to dryness and the residue was determined gravimetrically. Table 21 presents the results of the gravimetric analyses. It can be seen that the elution of corn oil begins with Fraction 9 and over 94 percent of the corn oil is removed in the first 150 mL of solvent (Table 21). The GPC elution volumes of the chlorinated hydrocarbons are greater than 150 mL, thus complete separation of these compounds from lipid materials is achieved by GPC.

To establish the elution profiles of the chlorinated hydrocarbons, a composite solution of the 22 chlorinated hydrocarbons (in isooctane) was injected onto the Bio-Beads SX-3 column which was subsequently eluted with methylene chloride at 5 mL/min. Fifteen 20-mL fractions were collected over 60 minutes. Methylene chloride was exchanged to hexane following Kuderna-Danish evaporation, and each fraction was analyzed by GC/ECD on the DB-210 fused-silica capillary column. Table 22 shows the amounts of various chlorinated hydrocarbons that were recovered in fractions F-10 through F-13. The elution profiles are reproducible for the two duplicate experiments, however, the overall recoveries of the chlorinated hydrocarbons are somewhat low. Additional experimental work is needed to determine why the recoveries are low and what can be done to improve them.

6.3.2 Sulfur Removal

Presence of elemental sulfur in sample extracts is undesirable especially when chlorinated hydrocarbons need to be determined because sulfur gives large peaks that interfere with the analysis of half of the target compounds (Figure 16 as compared to Figure 10). Method 3660 is recommended by EPA for cleanup of sample extracts containing elemental sulfur; however, the current procedure does not specify how well the procedure works for the chlorinated hydrocarbons.

We have used the procedure by Jensen et al. (7), which is the procedure from which Method 3660 was derived, and determined the recoveries of the target compounds when subjected to the TBA reagent. All recoveries were quantitative and removal of sulfur is complete (Table 23). Thus, Method 3660 is adequate for incorporation in Method 8120.

6.3.3 Florisil Cleanup

Cleanup of the sample extracts was performed initially according to the procedure given in EPA Method 3620 (1). In this procedures, Florisil (60/80 mesh), activated (prior to use) at 130°C for at least 16 hours, is used, and the target compounds are eluted with 200 mL petroleum ether. Under these conditions, most of the chlorinated hydrocarbons listed in Table 24 were recovered quantitatively (recovery >78 percent), except for the BHC isomers, benzal chloride, and benzotrichloride. When a second fraction was collected by eluting the Florisil column with 200 mL petroleum ether/diethyl ether (1:1), the BHC isomers were recovered quantitatively; however, benzal chloride and benzotrichloride were not recovered at all (Table 25). It was then concluded that the Florisil procedure given in Method 3620 needs to be modified by requiring collection of an additional fraction in order to

TABLE 21. GPC ELUTION PROFILE FOR CORN OIL

Fraction No.	Weight of residue[a] (mg)
F-1	<0.0001
F-2	<0.0001
F-3	<0.0001
F-4	<0.0001
F-5	<0.0001
F-6	<0.0001
F-7	<0.0001
F-8	<0.0001
F-9	0.0013
F-10	0.0059
F-11	0.0564
F-12	0.2458
F-13	0.3392
F-14	0.2328
F-15	0.0590
F-16	0.0028
F-17	0.0026
F-18	0.0021
Total	0.9479 g (95 percent recovery)

[a]5 mL of a 200-mg/mL corn oil solution in methylene chloride were loaded to a Bio-Beads SX-3 column; 18 fractions, 10-mL each, were collected over 36 min. The procedure is given in Section 7.3.3 of the revised Method 8120 which is included in Appendix B of this report.

TABLE 22. GPC ELUTION PROFILES FOR THE METHOD 8120 COMPOUNDS[a]

Compound	Amount spiked (µg)	Amount recovered (µg)					Recovery (percent)	Amount recovered (µg)					Recovery (percent)
		F-10	F-11	F-12	F-13	Total		F-10	F-11	F-12	F-13	Total	
Hexachloroethane	5	<0.1	0.5	1.7	0.6	2.8	56	<0.1	0.4	1.7	0.8	2.9	58
1,3-Dichlorobenzene	500	<0.5	108	190	9.7	308	62	<0.5	70	192	18	280	56
1,4-Dichlorobenzene	500	6.2	135	334	16	491	98	<0.5	91	331	29.1	451	90
1,2-Dichlorobenzene	500	15.4	108	185	9.1	318	64	1.6	77	187	17.6	283	57
Benzyl chloride	500	<0.1	154	28	0.4	182	36	4	153	49	0.7	207	41
1,3,5-Trichlorobenzene	50	0.7	12.7	29.7	1.9	45	90	<0.1	7.9	29	3.2	40.1	80
Hexachlorobutadiene	5	<0.1	2.1	1.6	<0.1	3.7	75	<0.1	1.7	1.8	0.1	3.6	72
Benzal chloride[b] 1,2,4-Trichlorobenzene[b]	100	1.4	34.0	21.5	0.9	58	116	0.6	32	25	1.6	59.2	118
Benzotrichloride	50	0.5	15.0	12.6	0.5	28.6	57	0.2	13	13.3	1.0	27.5	55
1,2,3-Trichlorobenzene	50	<0.1	10.4	21.0	1.9	33.3	67	<0.1	7.7	21.0	3.4	32.1	64
Hexachlorocyclopentadiene	5	<0.1	3.5	1.9	0.04	5.4	109	<0.1	2.5	2.3	0.06	4.9	98
1,2,4,5-Tetrachlorobenzene[c] 1,2,3,5-Tetrachlorobenzene[c]	50	<0.1	8.5	20.1	1.9	30.5	61	<0.1	5.9	20.7	3.4	30.0	60
1,2,3,4-Tetrachlorobenzene	50	<0.1	11.0	24.4	4.9	40.3	81	<0.1	8.8	25.1	8.2	42.1	84
2-Chloronaphthalene	1000	<1.0	242	431	19.8	693	69	<1.0	147	402	34	583	58
Pentachlorobenzene	5	<0.1	0.6	3.2	0.4	4.2	84	<0.1	0.4	2.4	0.4	3.2	64
Hexachlorobenzene	5	<0.1	0.5	5.0	0.8	6.3	126	<0.1	0.4	5.1	1.2	6.7	134
alpha-BHC	50	9.3	17.3	1.7	<0.05	28.3	57	6.7	18.1	2.5	0.05	27.4	55
gamma-BHC	50	7.8	17.0	2.4	<0.05	27.2	54	5.5	17.6	3.9	0.07	27.1	54
beta-BHC	50	<0.1	8.6	18.0	2.3	28.9	58	<0.1	7.2	19.6	5.3	32.1	64
delta-BHC	50	<0.1	15.6	13.9	0.6	30.1	60	<0.1	13.7	15.1	14.5	43.3	87

[a]Duplicate determinations. 5 mL of a composite stock solution of the test compounds (in isooctane) were loaded to a Bio-Beads SX-3 column; fifteen 20-mL fractions were collected; methylene chloride was exchanged to hexane and the fractions were analyzed by GC/ECD using the DB-210 fused-silica capillary column. No compounds were detected in Fractions F-1 through F-9, F-14, and F-15.

[b,c]These pairs cannot be resolved on the DB-210 fused-silica capillary column.

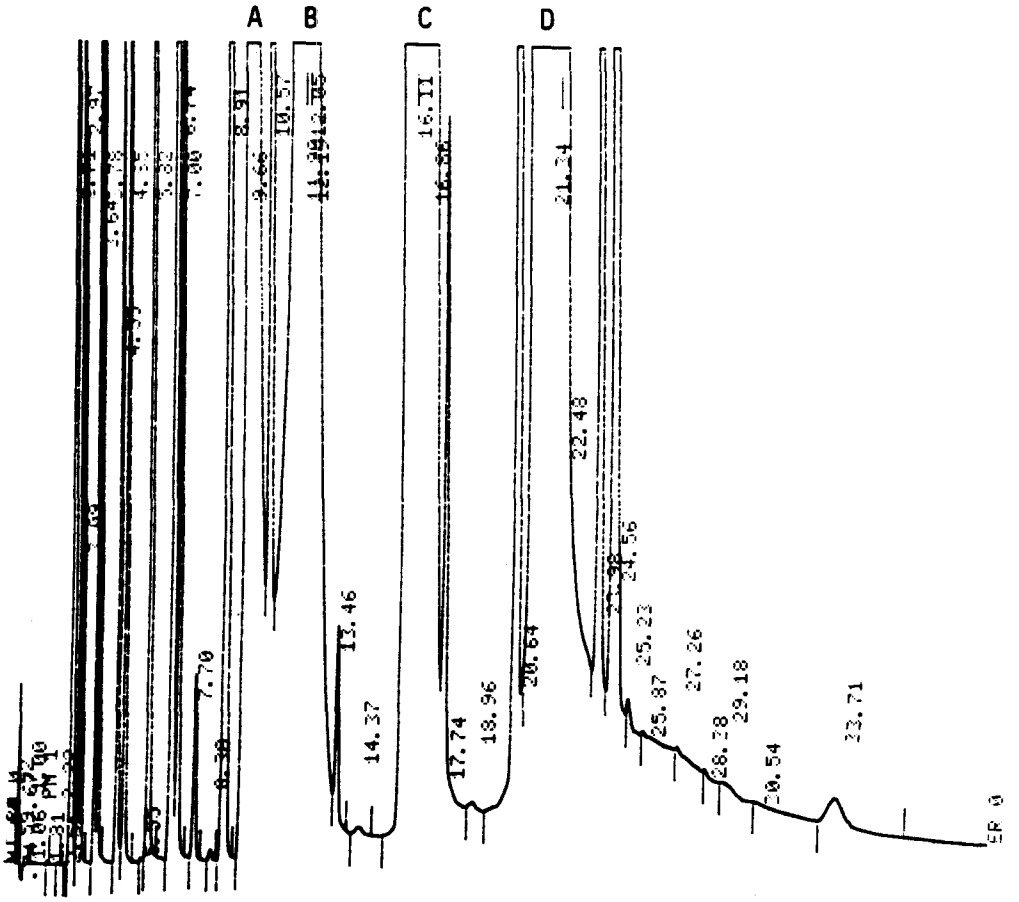

Figure 16. GC/ECD chromatogram of a Method 8120 composite standard containing elemental sulfur. Analysis was done on a 30 m x 0.53 mm ID DB-210 fused-silica capillary column. The GC operating conditions are given in Table 4. Peaks labeled A, B, C, D represent elemental sulfur (S_n- where n is 2,4,6,8).

TABLE 23. RECOVERY OF THE METHOD 8120 COMPOUNDS USING THE TBA PROCEDURE FOR REMOVAL OF ELEMENTAL SULFUR[a]

Compound	Amount spiked (µg)	Percent recovery			
		1[b]	2[b]	3[c]	4[c]
Hexachloroethane	0.1	101	100	101	100
1,3-Dichlorobenzene	10	106	105	104	106
1,4-Dichlorobenzene	10	105	104	104	105
1,2-Dichlorobenzene	10	106	104	103	105
Benzyl chloride	10	103	101	102	102
1,3,5-Trichlorobenzene	1	106	103	103	104
Hexachlorobutadiene	0.1	104	102	102	102
Benzal chloride[d] 1,2,4-Trichlorobenzene[d]	1	103	103	103	103
Benzotrichloride	1	103	103	104	104
1,2,3-Trichlorobenzene	1	106	105	105	106
Hexachlorocyclopentadiene	0.1	110	108	110	110
1,2,4,5-Tetrachlorobenzene[e] 1,2,3,5-Tetrachlorobenzene[e]	1	106	102	102	104
1,2,3,4-Tetrachlorobenzene	1	105	104	105	105
2-Chloronaphthalene	20	104	102	103	103
Pentachlorobenzene	0.1	88	86	87	86
Hexachlorobenzene	0.1	107	106	106	106
alpha-BHC	1	104	104	104	105
gamma-BHC	1	103	104	104	105
beta-BHC	1	104	102	102	102
delta-BHC	1	104	104	105	106

[a]Procedure by S. Jensen et al. (Reference 7).
[b]Duplicate determinations with standards only.
[c]Duplicate determinations with standards spiked with sulfur (300 µg/mL).
[d,e]These pairs cannot be resolved on the DB-210 fused-silica capillary column.

TABLE 24. ELUTION PATTERNS OF THE METHOD 8120 COMPOUNDS FROM THE FLORISIL COLUMN BY ELUTION WITH PETROLEUM ETHER

Compound	Amount (µg)	Recovery (percent)
Hexachloroethane	1.0	95
1,3-Dichlorobenzene	100	84
1,4-Dichlorobenzene	100	83
1,2-Dichlorobenzene	100	89
Benzyl chloride	100	62
1,3,5-Trichlorobenzene	10	88
Hexachlorobutadiene	1.0	91
Benzal chloride[a,c]	10	0
1,2,4-Trichlorobenzene[a]	10	17
Benzotrichloride[c]	10	0
1,2,3-Trichlorobenzene	10	90
Hexachlorocyclopentadiene	1.0	85
1,2,4,5-Tetrachlorobenzene[b]	10	89
1,2,3,5-Tetrachlorobenzene[b]		
1,2,3,4-Tetrachlorobenzene	10	93
2-Chloronaphthalene	200	84
Pentachlorobenzene	1.0	90
Hexachlorobenzene	1.0	86
alpha-BHC	10	3
gamma-BHC	10	0
beta-BHC	10	2
delta-BHC	10	1

[a,b]These pairs cannot be resolved on the DB-210 fused-silica capillary column.

[c]Separate experiments were performed with benzal chloride and benzotrichloride to verify that these compounds are not recovered from Florisil by elution with petroleum ether.

TABLE 25. ELUTION PATTERNS OF THE METHOD 8120 COMPOUNDS FROM THE FLORISIL COLUMN BY ELUTION WITH PETROLEUM ETHER (FRACTION 1) AND PETROLEUM ETHER/DIETHYL ETHER 1:1 (FRACTION 2)

Compound	Amount (µg)	Recovery (percent)			
		Fraction 1		Fraction 2	
Hexachloroethane	1.0	99	102	0	0
1,3-Dichlorobenzene	100	101	106	0	0
1,4-Dichlorobenzene	100	101	108	0	0
1,2-Dichlorobenzene	100	100	105	0	0
Benzyl chloride	100	78	86	21	12
1,3,5-Trichlorbenzene	10	99	106	0	0
Hexachlorobutadiene	1.0	98	104	0	0
Benzal chloride[a,c]	10	0	0	0	0
1,2,4-Trichlorobenzene[a]	10	59	60	0	0
Benzotrichloride[c]	10	0	0	0	0
1,2,3-Trichlorobenzene	10	95	98	0	0
Hexachlorocyclopentadiene	1.0	93	94	0	0
1,2,4,5-Tetrachlorobenzene[b] 1,2,3,5-Tetrachlorobenzene[b]	10	100	106	0	0
1,2,3,4-Tetrachlorobenzene	10	96	112	0	0
2-Chloronaphthalene	200	111	119	0	0
Pentachlorobenzene	1.0	126	132	0	0
Hexachlorobenzene	1.0	113	120	0	0
alpha-BHC	10	0	0	93	97
gamma-BHC	10	0	0	106	105
beta-BHC	10	0	0	108	109
delta-BHC	10	0	0	70	73

[a,b]These pairs cannot be resolved on the DB-210 fused-silica capillary column.

[c]Separate experiments were performed with benzal chloride and benzotrichloride to verify that these compounds are not recovered from Florisil in either fraction.

recover quantitatively 20 of the 22 target analytes. An additional 8 chlorinated hydrocarbons that were subjected to this Florisil procedure were found to behave similarly (Table 26).

Table 27 summarizes the recoveries of the 22 target compounds and their distribution profiles in the absence of interferents (Samples 2 and 3) and in the presence of interferents such as corn oil material (Samples 4 and 5), diesel fuel type hydrocarbons (Samples 6 and 7), and phthalate esters (Samples 8 and 9). The data shown in Table 27 indicate that 18 compounds are recovered quantitatively from the Florisil column with 5 mL hexane. The BHC isomers cannot be recovered with hexane only; therefore, a more polar solvent (e.g., diethyl ether) is needed to elute the analytes from the Florisil column. However, the distribution profiles of the BHC isomers are not reproducible when hexane and hexane/diethyl ether (1:1) are used as the eluants. It is interesting to note that when the solution that was applied to the Florisil cartridge contained 10 percent acetone, then the BHC isomers were eluted quantitatively with 5 mL hexane.

To verify that all compounds can be recovered quantitatively from the Florisil cartridge by elution with 5 mL hexane followed by 10 mL of hexane/diethyl ether (1:1), we conducted an experiment in which the Florisil cartridges were loaded with the target compounds at three different levels. The amounts of the analytes were ranging from 0.02 µg to 2.0 µg for those compounds that give large signals on the electron capture detector (e.g., hexachloroethane, hexachlorobenzene) and from 4 µg to 400 µg for 2-chloronaphthalene. Two and five replicates were performed, depending on concentration (Tables 28 and 29). Improved reproducibilities and excellent recoveries were achieved when the eluting solvent was a mixture of hexane/acetone (9:1). Although hexane/acetone (9:1) elutes the test compounds from the Florisil cartridge very efficiently (Table 30), at the same time it also removes the corn oil materials (Table 31). In contrast to hexane, this solvent mixture is somewhat less desirable; nonetheless, it proved to give reproducible and quantitative recoveries for the 22 target analytes.

The Florisil procedure was tested with nine environmental materials including relatively clean matrices such as a sandy loam soil, and highly contaminated samples, such as the Detroit River Sediment and the Bloody Run Creek sediment. With very few exceptions, all of the target compounds were recovered satisfactorily when spiked into sample extracts at known concentrations. These results are presented in a subsequent section that addresses method performance.

Use of disposable cartridges reduces solvent usage and labor cost in sample preparation. Because cartridges are prepackaged and ready for use, there is no need for adsorbent calibration, activation, or deactivation. Furthermore, sets of 12 or 24 extracts, depending on the capacity of the vacuum manifold, can be cleaned up simultaneously with no danger of sample contamination, thus sample throughput is increased significantly. In addition, a significant error factor resulting from operator and material variables that may affect the quality of the results can be eliminated.

TABLE 26. ELUTION PATTERNS OF OTHER CHLORINATED AROMATIC COMPOUNDS FROM THE FLORISIL COLUMN BY ELUTION WITH PETROLEUM ETHER (FRACTION 1) AND PETROLEUM ETHER/DIETHYL ETHER 1:1 (FRACTION 2)

Compound	Amount (µg)	Recovery (percent)			
		Fraction 1		Fraction 2	
α-Chloro-o-xylene	10	88	96	0	0
α,α,4-Trichlorotoluene	10	96	112	0	0
α,α'-Dichloro-m-xylene	10	0	0	94	96
1,2,3,4-Tetrachloronaphthalene	10	80	77	0	0
2,7-Dichloronaphthalene	10	91	96	0	0
α,3-Dichlorotoluene	10	93	94	0	0
α,α',2,4,5,6-Hexachloro-m-xylene	10	100	100	0	0
α,2,6-Trichlorotoluene	10	57	54	31	38

TABLE 27. RECOVERIES OF THE METHOD 8120 COMPOUNDS FROM FLORISIL[a,b]

Compound	Amount spiked (µg)	Fraction 1 (5 mL hexane)								Fraction 2 (5 mL hexane)								Fraction 3 (5 mL diethyl ether/hexane 1:1)							
		2A	3A	4A	5A	6A	7A	8A[c]	9A[c]	2B	3B	4B	5B	6B	7B	8B	9B	2C	3C	4C	5C	6C	7C	8C	9C
Hexachloroethane	0.1	90	80	90	90	80	75	87	89	2	1	2	3	3	2	2	3	0	0	0	0	0	0	0	0
1,3-Dichlorobenzene	10	77	75	80	81	62	61	78	81	2	1	2	3	3	1	2	0	0	0	0	0	0	0	0	0
1,4-Dichlorobenzene	10	91	88	95	96	80	78	93	97	3	2	2	3	4	1	2	0	0	0	0	0	0	0	0	0
1,2-Dichlorobenzene	10	74	73	77	78	62	62	76	79	3	2	2	3	3	1	2	0	0	0	0	0	0	0	0	0
Benzyl chloride	10	62	55	63	64	52	53	64	66	3	5	3	4	4	2	2	4	0	0	0	0	0	0	0	0
1,3,5-Trichlorobenzene	1	91	86	96	97	260[d]	270[d]	89	94	3	2	3	4	13	5	2	0	0	0	0	0	0	0	0	0
Hexachlorobutadiene	0.1	89	84	90	93	60	70	80	90	2	1	1	2	3	1	2	0	0	0	0	0	0	0	0	0
Benzal chloride[e]	1	93	90	96	96	76	76	84	96	4	3	3	4	5	2	3	0	0	0	0	0	0	0	0	0
1,2,4-Trichlorobenzene[e]																									
Benzotrichloride	1	92	82	94	94	80	82	95	98	3	1	2	3	3	1	3	2	3	0	0	0	0	0	0	3
1,2,3-Trichlorobenzene	1	93	89	97	97	65	67	92	95	3	2	2	3	4	1	2	3	0	0	0	0	0	0	0	0
Hexachlorocyclopentadiene	0.1	87	80	90	90	70	70	87	93	2	0	2	2	3	0	2	0	0	0	0	0	0	0	0	0
1,2,4,5-Tetrachlorobenzene[f]	1	81	76	85	85	54	57	78	83	3	0	3	4	2	2	3	0	0	0	0	0	0	0	0	0
1,2,3,5-Tetrachlorobenzene[f]																									
1,2,3,4-Tetrachlorobenzene	1	126	122	130	131	93	97	125	129	3	2	3	4	4	2	3	0	0	0	0	0	0	0	0	0
2-Chloronaphthalene	20	67	63	70	69	62	65	66	69	4	3	3	5	9	5	3	9	9	11	4	4	14	15	5	3
Pentachlorobenzene	0.1	80	80	90	90	70	70	85	86	5	4	4	5	6	4	4	0	8	8	9	2	929	789	459	4
Hexachlorobenzene	0.1	110	97	110	110	70	76	100	110	4	3	3	5	4	2	3	0	2	3	1	11	3	1	2	2
alpha-BHC	1	95	56	93	94	77	82	99	102	18	63	35	30	14	4	4	0.9	0	7	2	2	0	0	0	2
gamma-BHC	1	60	3	50	53	53	68	88	89	64	45	66	63	55	26	5	0.3	8	80	37	37	5	2	1	3
beta-BHC	1	0	1	8	9	2	3	87	94	40	4	33	35	40	53	3	0.4	62	95	45	41	42	25	0	2
delta-BHC	1	0	0	1	1	2	3	85	92	2	0.5	2	2	2	2	4	6	100	100	95	104	109	108	13	3

[a]Florisil disposable cartridges (1 g) were used. Fraction 1 was eluted with 5 mL hexane, Fraction 2 with 5 mL hexane, and Fraction 3 with 5 mL diethyl ether/hexane (1:1).
[b]Samples 2,3 are standards in hexane. Samples 4,5 are standards in hexane containing corn oil at 20 mg/mL. Samples 6,7 are standard in hexane containing diesel fuel at 20 mg/mL. Samples 8,9 are standards in hexane containing the Method 8060 phthalate esters at 20 µg/mL.
[c]Solution applied to the Florisil cartridge contained 10 percent acetone. It is very likely that this caused the elution of beta-BHC and delta-BHC in Fraction 1.
[d]High recovery due to matrix interference.
[e,f]These pairs cannot be resolved on the DB-210 fused-silica capillary column.
[g]High recovery of pentachlorobenzene in Fraction 3 is likely due to matrix interference since pentachlorobenzene elutes in Fraction 1.

TABLE 28. RECOVERIES OF THE METHOD 8120 COMPOUNDS USING FLORISIL DISPOSABLE CARTRIDGES (ELUTION WITH HEXANE AND HEXANE/DIETHYL ETHER 1:1)

Compound	Amount spiked (µg)	Percent recovery[a]										Average recovery (percent)	RSD (percent)
		Rep.1 Fr.1	Rep.1 Fr.2	Rep.2 Fr.1	Rep.2 Fr.2	Rep.3 Fr.1	Rep.3 Fr.2	Rep.4 Fr.1	Rep.4 Fr.2	Rep.5 Fr.1	Rep.5 Fr.2		
Hexachloroethane	0.1	76	0	65	0	88	0	92	0	89	0	82	14
1,3-Dichlorobenzene	10	68	0	55	0	83	0	87	0	84	0	75	18
1,4-Dichlorobenzene	10	68	0	57	0	82	0	87	0	82	0	75	16
1,2-Dichlorobenzene	10	69	0	59	0	84	0	89	0	85	0	77	16
Benzyl chloride	10	69	11	65	9	85	9	88	16	77	24	91	14
1,3,5-Trichlorobenzene	1	73	0	61	0	87	0	94	0	88	0	81	17
Hexachlorobutadiene	0.1	71	0	57	0	87	0	94	0	89	0	80	19
Benzal chloride[b] 1,2,4-Trichlorobenzene[b]	1.0	70	0	67	0	80	0	83	0	78	0	76	9.0
Benzotrichloride	1.0	70	0	67	0	89	0	92	0	69	0	77	16
1,2,3-Trichlorobenzene	1.0	73	0	66	0	89	0	95	0	84	0	81	15
Hexachlorocyclopentadiene	0.1	72	0	59	0	87	0	94	0	78	0	78	17
1,2,4,5-Tetrachlorobenzene[c] 1,2,3,5-Tetrachlorobenzene[c]	1.0	73	0	62	0	90	0	97	0	86	3	82	18
1,2,3,4-Tetrachlorobenzene	1.0	80	0	73	0	93	0	98	0	89	4	87	12
2-Chloronaphthalene	20	65	0	61	0	77	0	82	5	81	6	75	16
Pentachlorobenzene	0.1	61	0	54	0	71	6	76	0	65	0	67	15
Hexachlorobenzene	0.1	110	0	102	0	129	0	140	0	123	0	121	13
alpha-BHC	1.0	46	60	57	46	94	0	97	9	41	72	104	6.6
gamma-BHC	1.0	0	97	0	95	78	33	81	49	0	102	107	13
beta-BHC	1.0	0	86	0	86	0	81	0	119	0	94	93	16
delta-BHC	1.0	0	89	0	88	0	85	0	114	0	93	94	12

[a]Florisil disposable cartridges (1 g) were used. Fraction 1 was eluted with 5 mL hexane, Fraction 2 with 10 mL hexane/diethyl ether (1:1). Final volume of each fraction is 2 mL.

[b,c]These pairs cannot be resolved on the DB-210 fused-silica capillary column.

TABLE 29. RECOVERIES OF THE METHOD 8120 COMPOUNDS USING FLORISIL DISPOSABLE CARTRIDGES AS A FUNCTION OF ANALYTE CONCENTRATIONS[a]

Compound	Amount spiked (µg)	Percent recovery				Amount spiked (µg)	Percent recovery			
		Rep.1 Fr.1	Rep.1 Fr.2	Rep.2 Fr.1	Rep.2 Fr.2		Rep.1 Fr.1	Rep.1 Fr.2	Rep.2 Fr.1	Rep.2 Fr.2
Hexachloroethane	2.0	80	0	80	0	0.02	70	0	60	0
1,3-Dichlorobenzene	200	98	0	100	0	2.0	63	0	54	0
1,4-Dichlorobenzene	200	129	0	133	0	2.0	81	0	70	0
1,2-Dichlorobenzene	200	100	0	103	0	2.0	67	0	57	0
Benzyl chloride	200	88	0	90	0	2.0	62	0	52	0
1,3,5-Trichlorobenzene	20	120	0	124	0	0.2	85	0	74	0
Hexachlorobutadiene	2.0	100	0	103	0	0.02	70	0	60	0
Benzal chloride[b] 1,2,4-Trichlorobenzene[b]	20	80	0	79	0	0.2	89	0	75	0
Benzotrichloride	20	70	0	70	0	0.2	121	0	98	0
1,2,3-Trichlorobenzene	20	93	0	95	0	0.2	58	0	57	0
Hexachlorocyclopentadiene	2.0	135	0	140	0	0.02	80	0	80	0
1,2,4,5-Tetrachlorobenzene[c] 1,2,3,5-Tetrachlorobenzene[c]	20	103	0	105	0	0.2	78	0	67	0
1,2,3,4-Tetrachlorobenzene	20	86	0	88	0	0.2	74	0	64	0
2-Chloronaphthalene	400	109	0	116	0	4.0	98	0	83	0
Pentachlorobenzene	2.0	90	0	92	0	0.02	80	0	70	0
Hexachlorobenzene	2.0	110	0	115	0	0.02	120	0	100	0
alpha-BHC	20	76	6	75	13	0.2	97	2.0	82	0
gamma-BHC	20	63	37	40	63	0.2	53	24	58	14
beta-BHC	20	2.0	100	0	110	0.2	2.0	43	0	41
delta-BHC	20	0	88	0	94	0.2	0	58	0	55

[a]Florisil disposable cartridges (1 g) were used. Fraction 1 was eluted with 5 mL hexane, Fraction 2 with 10 mL hexane/diethyl ether (1:1).
[b,c]These pairs cannot be resolved on the DB-210 fused-silica capillary column.

TABLE 30. RECOVERIES OF THE METHOD 8120 COMPOUNDS USING FLORISIL DISPOSABLE CARTRIDGES (ELUTION WITH HEXANE/ACETONE 9:1)

Compound	Amount spiked (µg)	Percent recovery[a]										Average recovery (percent)	RSD (percent)
		Rep.1 Fr.1	Rep.1 Fr.2	Rep.2 Fr.1	Rep.2 Fr.2	Rep.3 Fr.1	Rep.3 Fr.2	Rep.4 Fr.1	Rep.4 Fr.2	Rep.5 Fr.1	Rep.5 Fr.2		
Hexachloroethane	1.0	92	0	96	0	96	0	97	0	96	0	95	2.0
1,3-Dichlorobenzene	100	99	0	102	0	103	0	104	0	99	0	101	2.3
1,4-Dichlorobenzene	100	98	0	101	0	103	0	102	0	98	0	100	2.3
1,2-Dichlorobenzene	100	100	0	102	0	103	0	104	0	101	0	102	1.6
Benzyl chloride	100	100	0	101	0	101	0	103	0	99	0	101	1.5
1,3,5-Trichlorobenzene	10	95	0	99	0	99	0	101	0	98	0	98	2.2
Hexachlorobutadiene	1.0	92	0	95	0	96	0	97	0	94	0	95	2.0
Benzal chloride[b] 1,2,4-Trichlorobenzene[b]	10	99	0	99	0	100	0	100	0	98	0	99	0.8
Benzotrichloride	10	91	0	88	0	94	0	96	0	81	0	90	6.5
1,2,3-Trichlorobenzene	10	96	0	97	0	98	0	100	0	95	0	97	2.0
Hexachlorocyclopentadiene	1.0	100	0	104	0	105	0	108	0	100	0	103	3.3
1,2,4,5-Tetrachlorobenzene[c] 1,2,3,5-Tetrachlorobenzene[c]	10	95	0	98	0	99	0	101	0	97	0	98	2.2
1,2,3,4-Tetrachlorobenzene	10	98	0	99	0	100	0	101	0	98	0	99	1.3
2-Chloronaphthalene	200	94	0	95	0	94	0	97	0	94	0	95	1.4
Pentachlorobenzene	1.0	102	0	105	0	105	0	106	0	104	0	104	1.5
Hexachlorobenzene	1.0	77	0	79	0	79	0	79	0	78	0	78	1.1
alpha-BHC	10	100	3.0	100	3.0	100	4.0	100	0	99	0	100	0.4
gamma-BHC	10	99	3.0	99	3.0	99	4.0	100	0	98	0	99	0.7
beta-BHC	10	95	0	96	3.0	94	3.0	98	0	94	0	95	1.8
delta-BHC	10	95	0	99	3.0	94	3.0	100	0	96	0	97	2.7

[a]Florisil disposable cartridges (1 g) were used. Fraction 1 was eluted with 5 mL of hexane/acetone 9:1, Fraction 2 with an additional 5 mL of hexane/acetone 9:1. Final volume of each fraction is 10 mL.

[b,c]These pairs cannot be resolved on the DB-210 fused-silica capillary column.

TABLE 31. ELUTION PROFILES OF CORN OIL FROM FLORISIL DISPOSABLE CARTRIDGES

Percent recovery[a]				Percent recovery[a]		
Amount spiked (mg)	Fraction 1 (5 mL hexane)	Fraction 2 (5 mL hexane)	Fraction 3 (5 mL hexane/ diethyl ether (1:1))	Amount spiked (mg)	Fraction 1 (5 mL hexane/ acetone (9:1))	Fraction 2 (5 mL hexane/ acetone (9:1))
10	0	0	102	10	101	0
200	63	4.8	32	20	91	0.8
500	72	2.7	20	500	91	0.9

[a]Florisil disposable cartridges (1 g) were used; 1 mL of a corn oil solution in hexane (concentration 10 mg/mL, 200 mg/mL, 500 mg/mL) was used in each case.

An additional advantage of the Florisil procedure is the complete removal of phenolic compounds by the Florisil material. If chlorinated hydrocarbons are to be determined in the presence of the phenolic compounds, then this Florisil cleanup is a must, because the 12 chlorinated hydrocarbons elute in the retention window of the phenolic compounds when the gas chromatographic analysis is performed on the DB-210 fused-silica capillary column.

6.4 PRESERVATION STUDY

Tables 32 through 34 summarize the results of the preservation experiments for water samples. The same results are presented in Figures 17 through 28. Tables 35 and 36 summarize the results for spiked soil samples that were kept frozen at -10°C for 5 and 6 months, respectively. At pH 7, recoveries were ≥80 percent at day 1 for all compounds when spiked in reagent water. BHCs appeared to be stable for up to 21 days while compounds such as benzyl chloride, benzal chloride, and benzotrichloride were found to degrade rapidly. Recovery of benzal chloride at day 21 was slightly above 10 percent and the recoveries of benzyl chloride and benzotrichloride were about 20 percent. Hexachlorobutadiene and hexachlorocyclopentadiene also degraded quite rapidly. The latter was reported to be very photosensitive to sunlight or long wave UV light (8). Its half-life is less than 3.5 min in aqueous solution and less than 1.6 min and 2.5 min in hexane and methanol, respectively (8). At pH 2 benzyl chloride, benzotrichloride, hexachlorobutadiene, and hexachlorocyclopentadiene appeared to be slightly more stable. Recoveries of the rest of the compounds were not much different from those obtained at pH 7.

At pH 9, benzal chloride disappeared much faster than benzyl chloride or benzotrichloride, and delta BHC was the only BHC compound that degraded. It is interesting to note that at pH 9 recovery of pentachlorobenzene was about 250 percent at day 7 and about 230 percent at day 14. Additional work is needed in order to determine whether the apparent increase in the concentration of pentachlorobenzene is due to pentachlorobenzene being formed in the sample from other chlorinated benzenes or to an interferent that might be coeluting with pentachlorobenzene on the DB-210 fused-silica capillary column.

Data on the preservation of soil samples by freezing at -10°C indicate that only half of the compounds can be preserved (e.g., tetrachlorobenzenes, 2-chloronaphthalene, pentachlorobenzene, hexachlorobenzene, and the four BHC isomers) since the other compounds have either disappeared completely (e.g., benzotrichloride and hexachlorocyclopentadiene) or only small percentages were recovered after 5 and 6 months (e.g., recovery of benzal chloride is 4.3 percent and recovery of benzyl chloride is 10 percent).

TABLE 32. CONCENTRATION (ng/μL OF EXTRACT) AS A FUNCTION OF TIME AT pH 7[a]

Compound	Spike Level (ng/μL)	Day 0		Day 1		Day 3		Day 7		Day 10	Day 14		Day 21	
Hexachloroethane	0.1	0.108	0.093	0.088	0.082	0.073	0.045	0.074	0.066	0.024	0.035	0.043	0.066	0.051
1,3-Dichlorobenzene	10.0	10.6	8.51	7.08	6.27	5.51	3.06	5.57	4.71	2.02	2.86	2.90	5.47	4.91
1,4-Dichlorobenzene	10.0	11.8	8.82	8.24	7.35	6.70	4.21	6.08	5.29	2.98	3.90	3.85	5.64	5.31
1,2-Dichlorobenzene	10.0	11.3	8.69	8.40	7.41	6.60	3.88	6.39	5.50	2.65	3.77	3.79	5.72	5.48
Benzyl chloride	10.0	11.1	8.90	9.05	8.18	7.73	4.96	6.26	5.85	3.99	3.43	2.91	2.19	2.32
1,3,5-Trichlorobenzene	1.0	1.17	0.890	0.847	0.799	0.702	0.432	0.622	0.557	0.240	0.302	0.378	0.538	0.447
Hexachlorobutadiene	0.1	0.113	0.087	0.080	0.075	0.065	0.037	0.059	0.053	0.019	0.022	0.033	0.050	0.031
Benzal chloride[b] 1,2,4-Tetrachlorobenzene[b]	2.0	2.17	1.92	1.67	1.58	1.37	0.871	1.08	0.943	0.362	0.271	0.326	0.351	0.300
Benzotrichloride	1.0	1.09	1.00	0.888	0.840	0.779	0.585	0.693	0.626	0.265	0.118	0.305	0.380	0.094
1,2,3-Tetrachlorobenzene	1.0	1.13	0.926	0.872	0.829	0.732	0.397	0.695	0.631	0.247	0.326	0.424	0.612	0.548
Hexachlorocyclopentadiene	0.1	0.162	0.132	0.104	0.103	0.096	0.058	0.062	0.057	0.032	0.038	0.055	0.055	0.038
1,2,4,5-Tetrachlorobenzene[c] 1,2,3,5-Tetrachlorobenzene[c]	2.0	2.35	1.89	1.82	1.74	1.56	0.87	1.38	1.25	0.475	0.578	0.491	1.185	0.998
1,2,3,4-Tetrachlorobenzene	1.0	1.14	0.949	0.903	0.874	0.795	0.435	0.727	0.671	0.251	0.306	0.452	0.645	0.575
2-Chloronapnthalene	20.0	23.8	19.1	18.1	17.7	16.3	10.3	13.9	13.2	6.47	7.88	10.1	12.8	12.5
Pentachlorobenzene	0.1	0.118	0.098	0.096	0.094	0.087	0.059	0.073	0.069	0.041	0.043	0.056	0.065	0.058
Hexachlorobenzene	0.1	0.121	0.100	0.101	0.100	0.093	0.061	0.076	0.070	0.041	0.042	0.050	0.066	0.060
alpha-BHC	1.0	1.08	0.990	1.02	1.02	1.01	0.783	0.901	0.892	0.683	0.761	0.772	0.881	0.899
gamma-BHC	1.0	1.08	0.989	1.02	1.03	1.02	0.807	0.902	0.884	0.732	0.799	0.795	0.883	0.905
beta-BHC	1.0	1.09	0.933	1.09	1.10	1.14	0.775	0.895	0.895	0.870	0.852	0.767	0.820	0.894
delta-BHC	1.0	1.05	0.945	1.02	1.02	1.04	0.800	0.900	0.890	0.850	0.862	0.809	0.868	0.913
Surrogate recovery (percent)														
α,2,6-Trichlorotoluene	0.1	89	75	83	85	88	68	86	84	96	94	79	72	78
1,4-Dichloronaphthalene	1.0	98	87	87	90	91	72	76	74	86	86	73	66	71
2,3,4,5,6-Pentachlorobenzene	0.1	95	83	92	91	97	77	86	85	92	90	77	75	80

[a]To convert to μg/L of water, multiply the values given by a factor of 2.
[b],[c]These pairs cannot be resolved on the DB-210 fused-silica capillary column.

TABLE 33. CONCENTRATION (ng/μL OF EXTRACT) AS A FUNCTION OF TIME AT pH 2[a]

Compound	Spike Level (ng/μL)	Day 0		Day 7		Day 14	
Hexachloroethane	0.1	0.105	0.107	0.088	0.071	0.089	0.084
1,3-Dichlorobenzene	10.0	10.1	10.5	7.18	5.24	7.12	6.55
1,4-Dichlorobenzene	10.0	10.9	11.4	7.61	5.72	8.09	7.47
1,2-Dichlorobenzene	10.0	10.7	11.1	8.23	5.98	8.51	7.84
Benzyl chloride	10.0	10.5	10.9	7.81	5.60	4.41	4.18
1,3,5-Trichlorobenzene	1.0	1.09	1.16	0.778	0.581	0.818	0.739
Hexachlorobutadiene	0.1	0.107	0.112	0.079	0.056	0.079	0.072
Benzal chloride[b] 1,2,4-Trichlorobenzene[b]	2.0	2.10	2.10	1.48	1.09	0.459	0.452
Benzotrichloride	1.0	1.08	1.07	0.837	0.674	0.605	0.597
1,2,3-Trichlorobenzene	1.0	1.09	1.14	0.860	0.658	0.926	0.852
Hexachlorocyclopentadiene	2.0	0.160	0.173	0.081	0.062	0.103	0.102
1,2,4,5-Tetrachlorobenzene[c] 1,2,3,5-Tetrachlorobenzene[c]	2.0	2.24	2.36	1.77	1.32	1.74	1.67
1,2,3,4-Tetrachlorobenzene	1.0	1.09	1.15	0.892	0.698	0.878	0.846
2-Chloronaphthalene	20.1	22.6	23.9	16.9	13.5	17.7	16.9
Pentachlorobenzene	0.1	0.113	0.117	0.086	0.071	0.094	0.091
Hexachlorobenzene	0.1	0.116	0.121	0.087	0.072	0.087	0.084
alpha-BHC	1.0	1.06	1.08	0.962	0.898	0.969	0.954
gamma-BHC	1.0	1.06	1.08	0.957	0.897	0.981	0.965
beta-BHC	1.0	1.06	1.09	0.987	0.907	0.969	0.944
delta-BHC	1.0	1.03	1.05	0.962	0.905	0.967	0.954
Surrogate recovery (percent)							
α,2,6-Trichlorotoluene		91	93	96	86	99	96
1,4-Dichloronaphthalene		95	100	82	75	100	98
2,3,4,5,6-Pentachlorobenzene		94	98	94	86	102	99

[a]To convert to μg/L of water, multiply the values given by a factor of 2.
[c,d]These pairs cannot be resolved on the DB-210 fused-silica capillary column.

TABLE 34. CONCENTRATION (ng/μL OF EXTRACT) AS A FUNCTION OF TIME AT pH 9[a]

Compound	Spike Level (ng/μL)	Day 0		Day 7		Day 14	
Hexachloroethane	0.1	0.106	0.105	0.099	0.089	0.081	0.086
1,3-Dichlorobenzene	10.0	10.4	10.1	9.25	8.09	6.38	6.53
1,4-Dichlorobenzene	10.0	11.3	10.9	9.36	8.07	7.02	7.15
1,2-Dichlorobenzene	10.0	10.9	10.7	9.99	8.62	7.64	7.91
Benzyl chloride	10.0	10.8	10.6	7.44	6.83	4.14	4.18
1,3,5-Tricnlorobenzene	1.0	1.12	1.09	0.994	0.819	0.706	0.792
Hexachlorobutadiene	0.1	0.109	0.108	0.096	0.079	0.067	0.079
Benzal chloride[a] 1,2,4-Trichlorobenzene[a]	2.0	2.15	2.13	0.958	0.793	0.452	0.438
Benzotrichloride	1.0	1.09	1.08	0.809	0.754	0.578	0.606
1,2,3-Trichlorobenzene	1.0	1.11	1.09	1.05	0.895	0.823	0.914
Hexachlorocyclopentadiene	0.1	0.164	0.161	0.158	0.137	0.100	0.116
1,2,4,5-Tetrachlorobenzene[b] 1,2,3,5-Tetrachlorobenzene[b]	2.0	2.28	2.24	2.15	1.79	1.59	1.84
1,2,3,4-Tetrachlorobenzene	1.0	1.11	1.10	1.09	0.939	0.835	0.941
2-Chloronaphthalene	20.0	22.9	22.4	22.4	18.8	16.3	18.1
Pentachlorobenzene	0.1	0.114	0.112	0.278	0.234	0.213	0.255
Hexachlorobenzene	1.0	0.116	0.115	0.113	0.094	0.086	0.096
alpha-BHC	1.0	1.06	1.06	1.04	0.961	0.934	0.958
gamma-BHC	1.0	1.07	1.06	1.03	0.957	0.940	0.959
beta-BHC	1.0	1.08	1.07	1.09	1.02	0.981	0.988
delta-BHC	1.0	1.04	1.03	0.710	0.644	0.684	0.642
Surrogate recovery (percent)							
α,2,6-Trichlorotoluene		90	85	96	90	99	100
1,4-Dichloronaphthalene		93	94	101	97	98	99
2,3,4,5,6-Pentachlorobenzene		93	91	100	96	103	104

[a]To convert to μg/L of water, multiply the values given by a factor of 2.
[c,d]These pairs cannot be resolved on the DB-210 fused-silica capillary column.

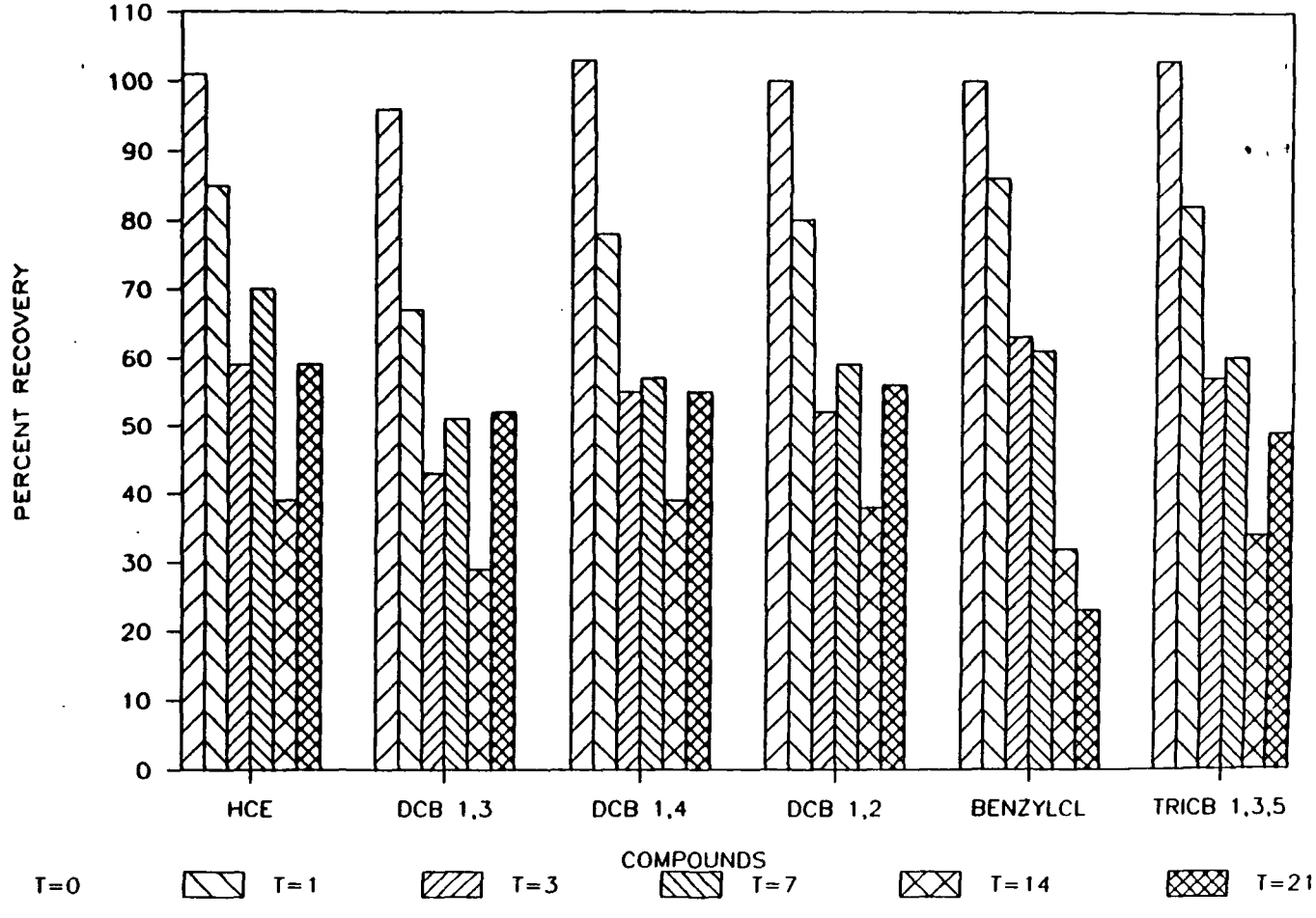

Figure 17. Recovery as a function of time at pH 7 for: hexachloroethane, 1,3-dichlorobenzene, 1,4-dichlorobenzene, 1,2-dichlorobenzene, benzyl chloride, and 1,3,5-trichlorobenzene.

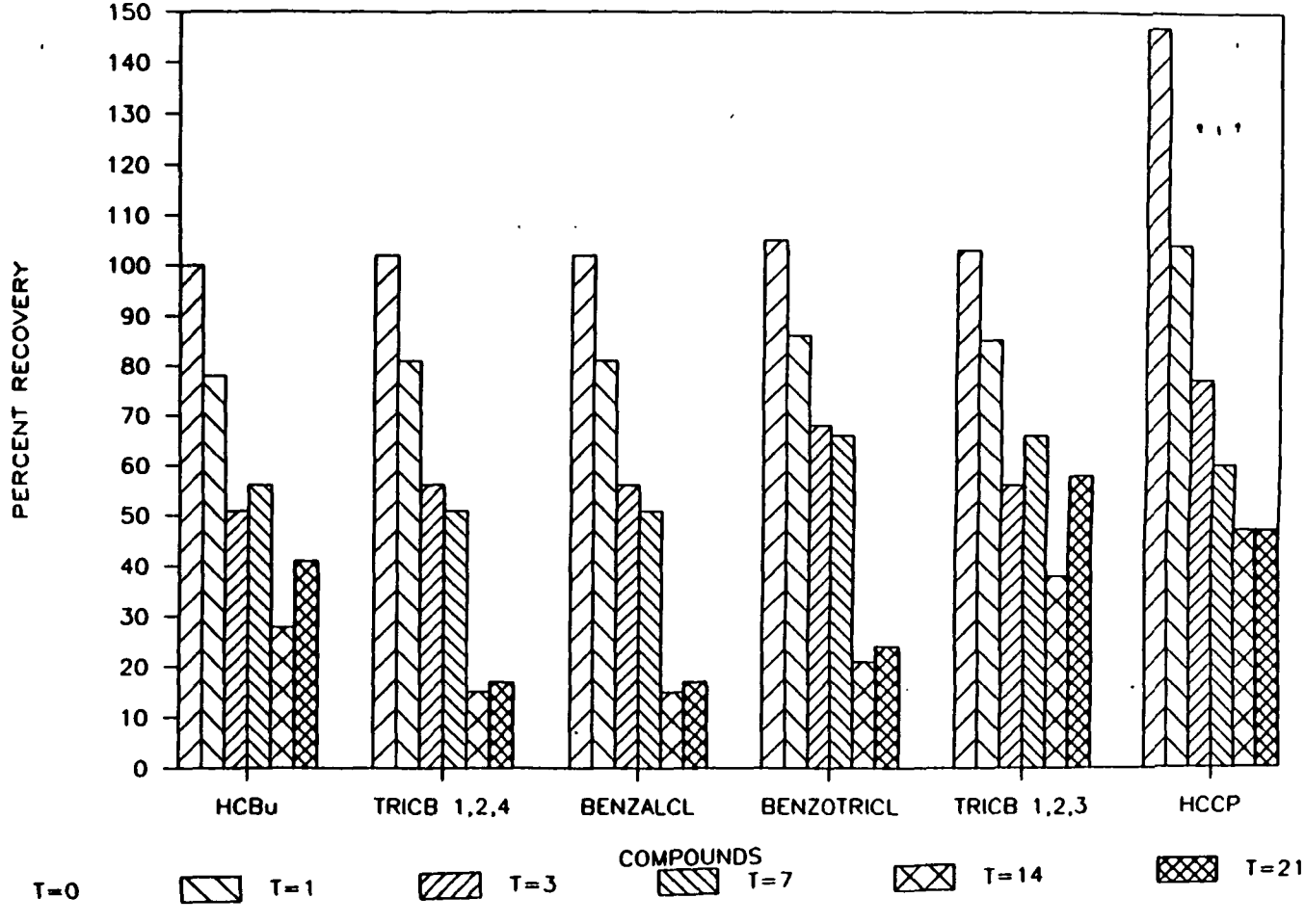

Figure 18. Recovery as a function of time at pH 7 for: hexachlorobutadiene, 1,2,4-trichlorobenzene, benzal chloride, benzotrichloride, 1,2,3-trichlorobenzene, and hexachlorocyclopentadiene.

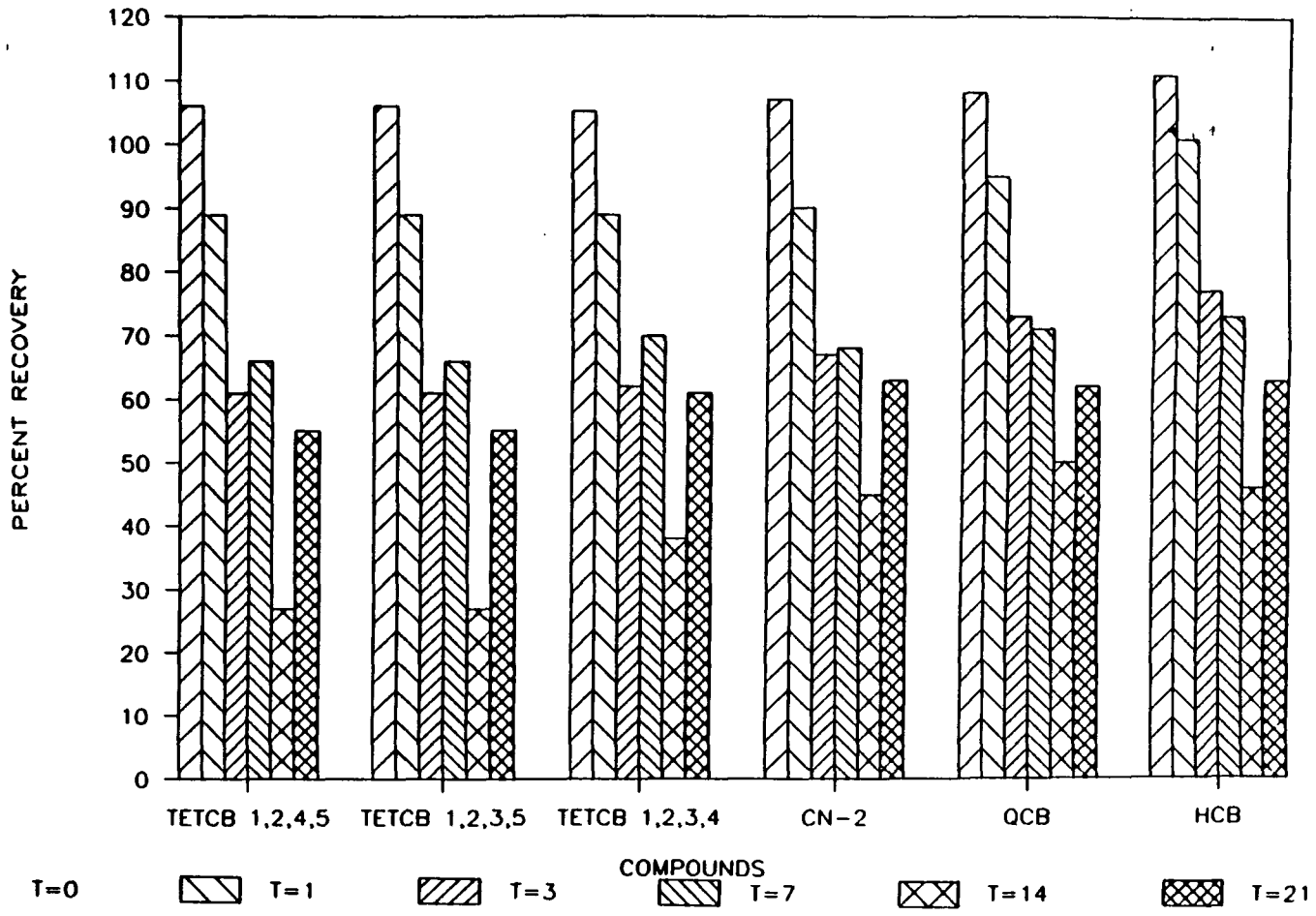

Figure 19. Recovery as a function of time at pH 7 for: 1,2,4,5-tetrachlorobenzene, 1,2,3,5-tetrachlorobenzene, 1,2,3,4-tetrachlorobenzene, 2-chloronaphthalene, pentachlorobenzene, and hexachlorobenzene.

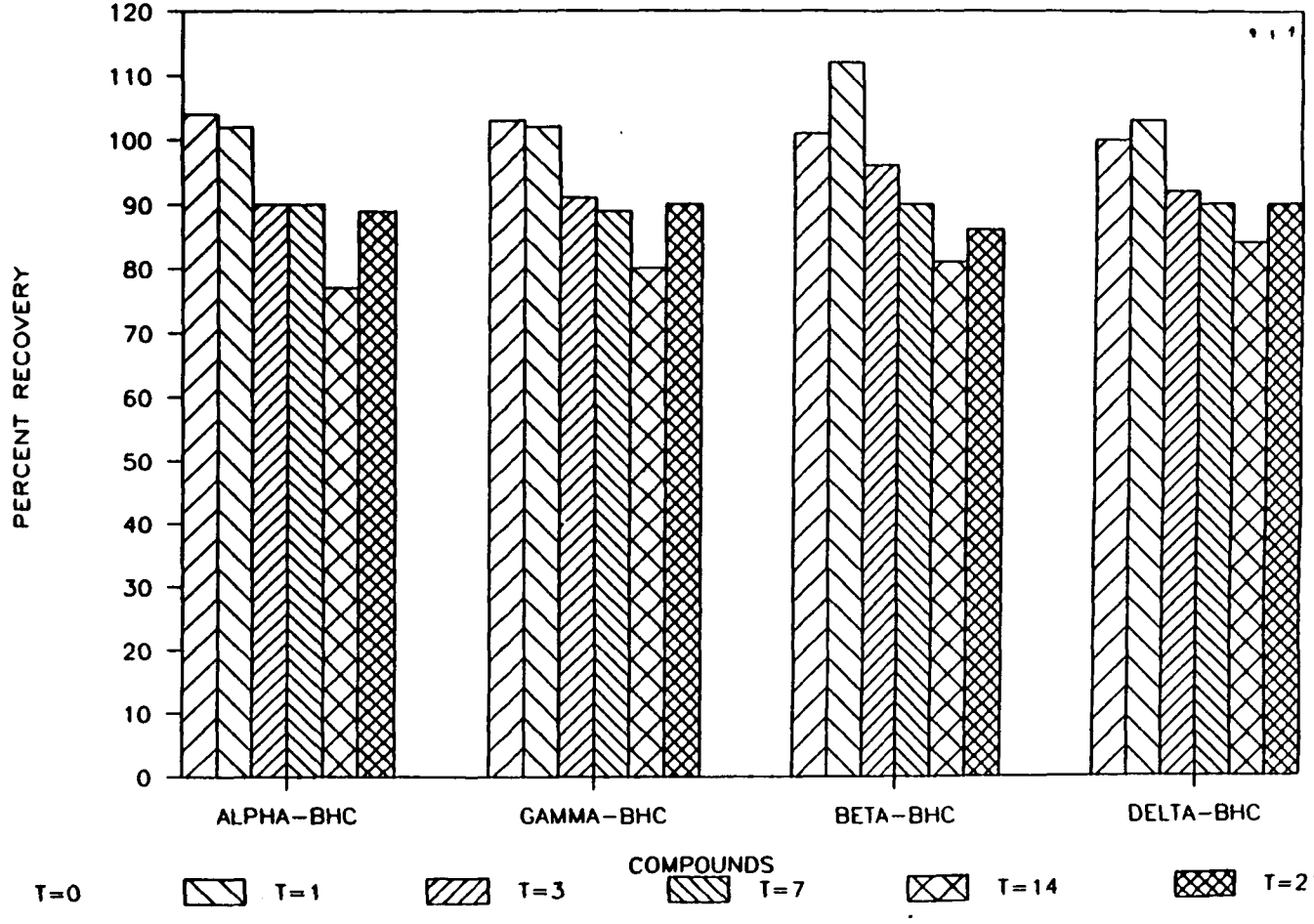

Figure 20. Recovery as a function of time at pH 7 for: alpha-BHC, gamma-BHC, beta-BHC, and delta-BHC.

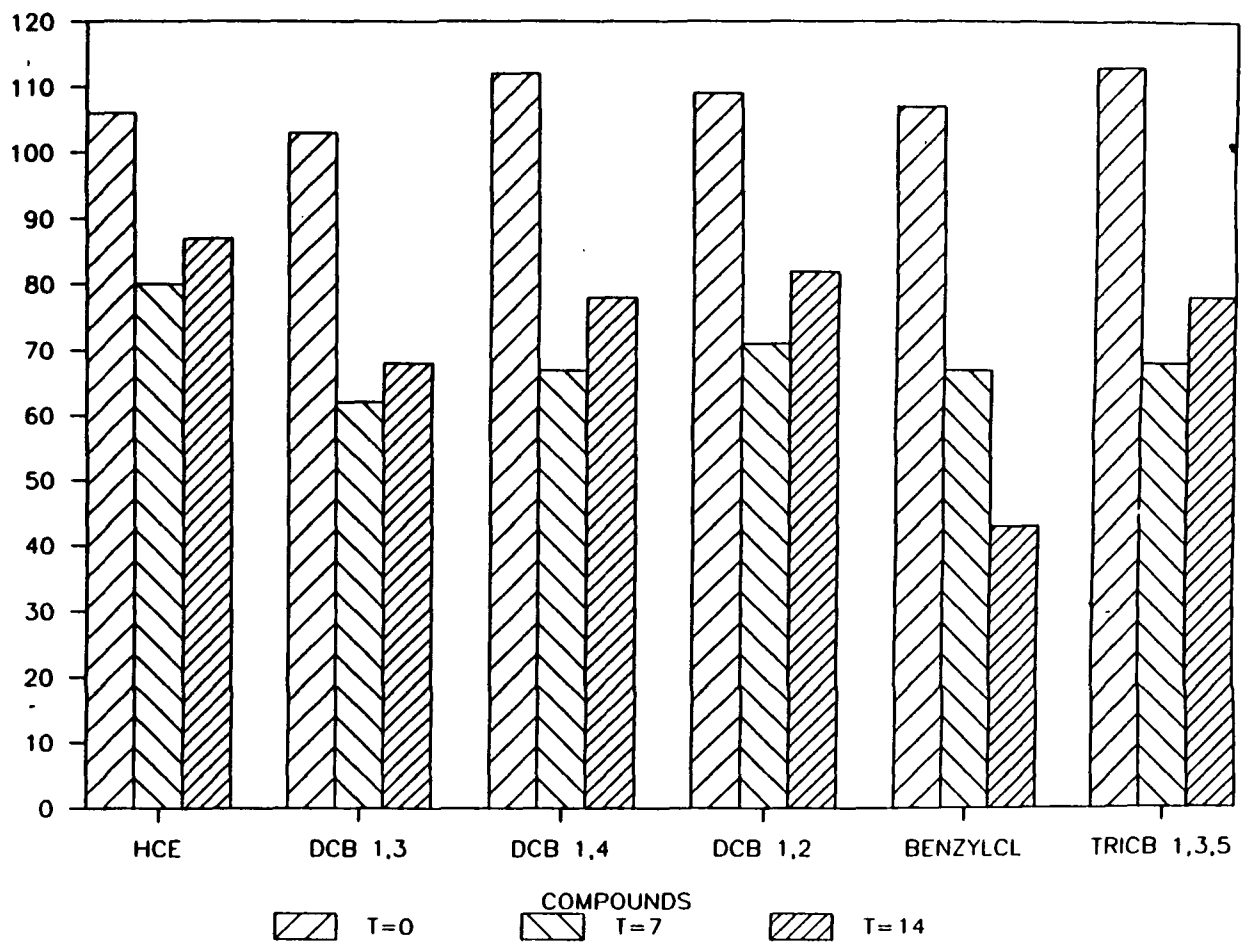

Figure 21. Recovery as a function of time at pH 2 for: hexachloroethane, 1,3-dichlorobenzene, 1,2-dichlorobenzene, 1,4-dichlorobenzene, benzyl chloride, and 1,3,5-trichlorobenzene.

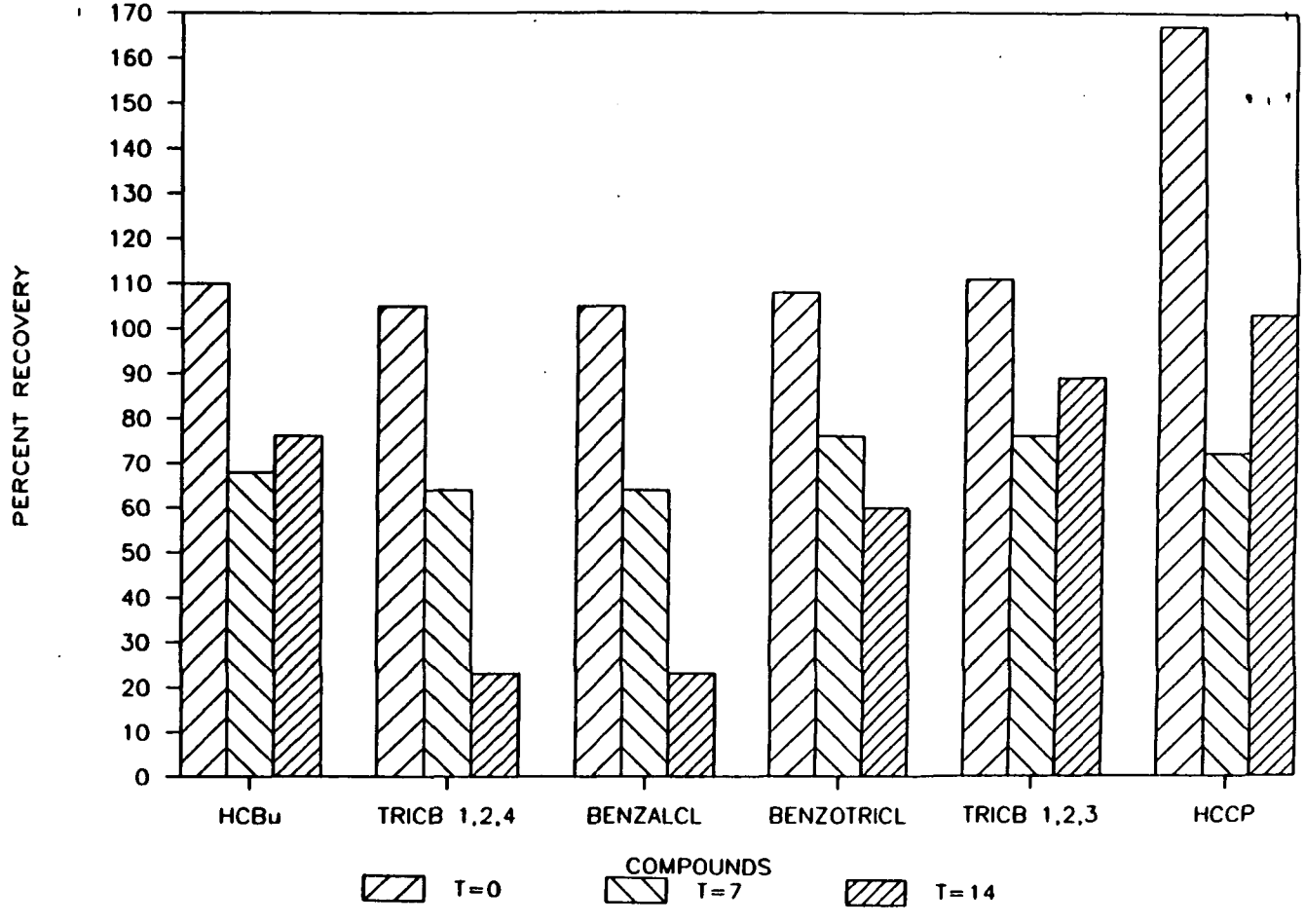

Figure 22. Recovery as a function of time at pH 2 for: hexachlorobutadiene, 1,2,4-trichlorobenzene, benzal chloride, benzotrichloride, 1,2,3-trichlorobenzene, and hexachlorocyclopentadiene.

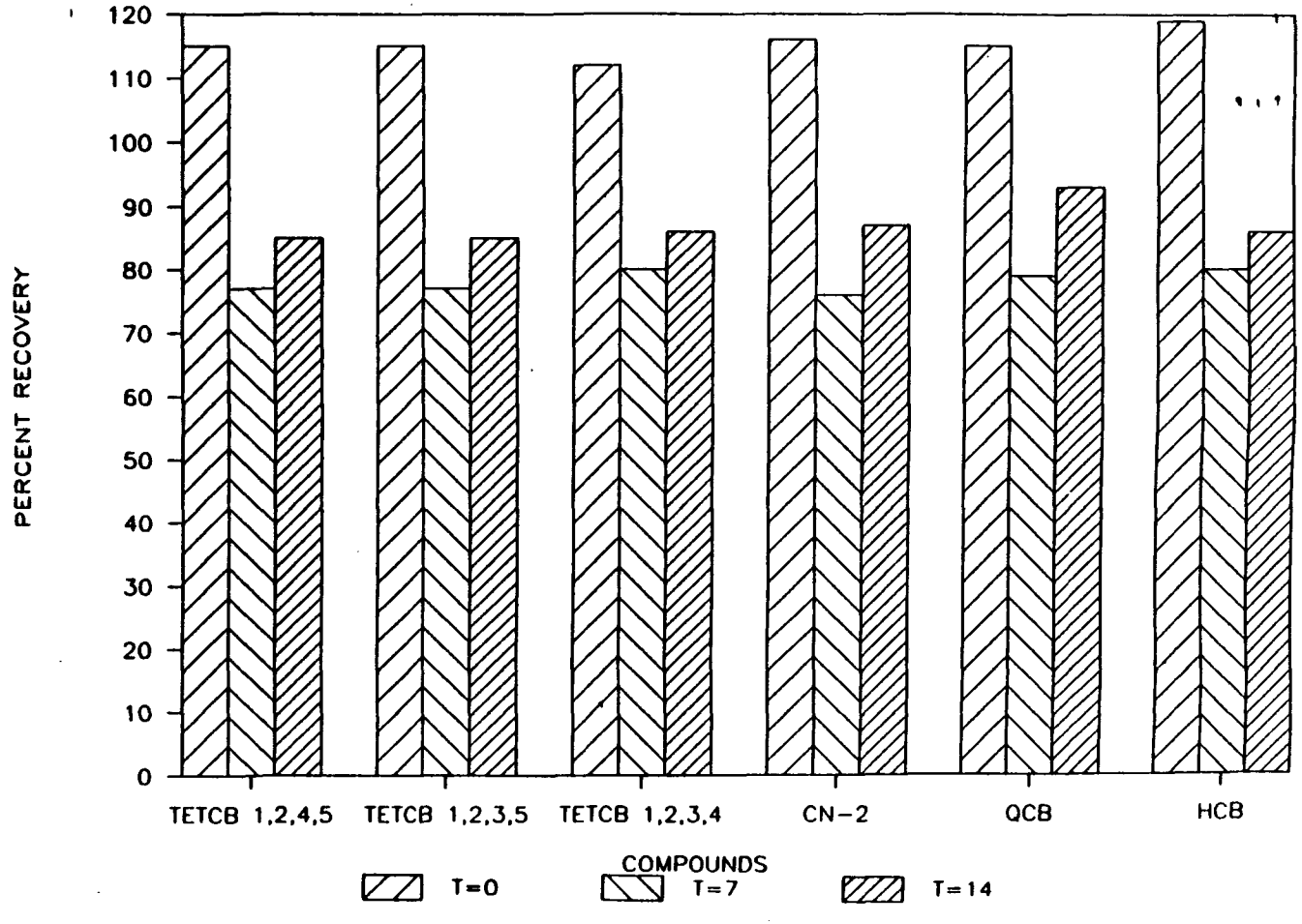

Figure 23. Recovery as a function of time at pH 2 for: 1,2,4,5-tetrachlorobenzene, 1,2,3,5-tetrachlorobenzene, 1,2,3,4-tetrachlorobenzene, 2-chloronaphthalene, pentachlorobenzene, and hexachlorobenzene.

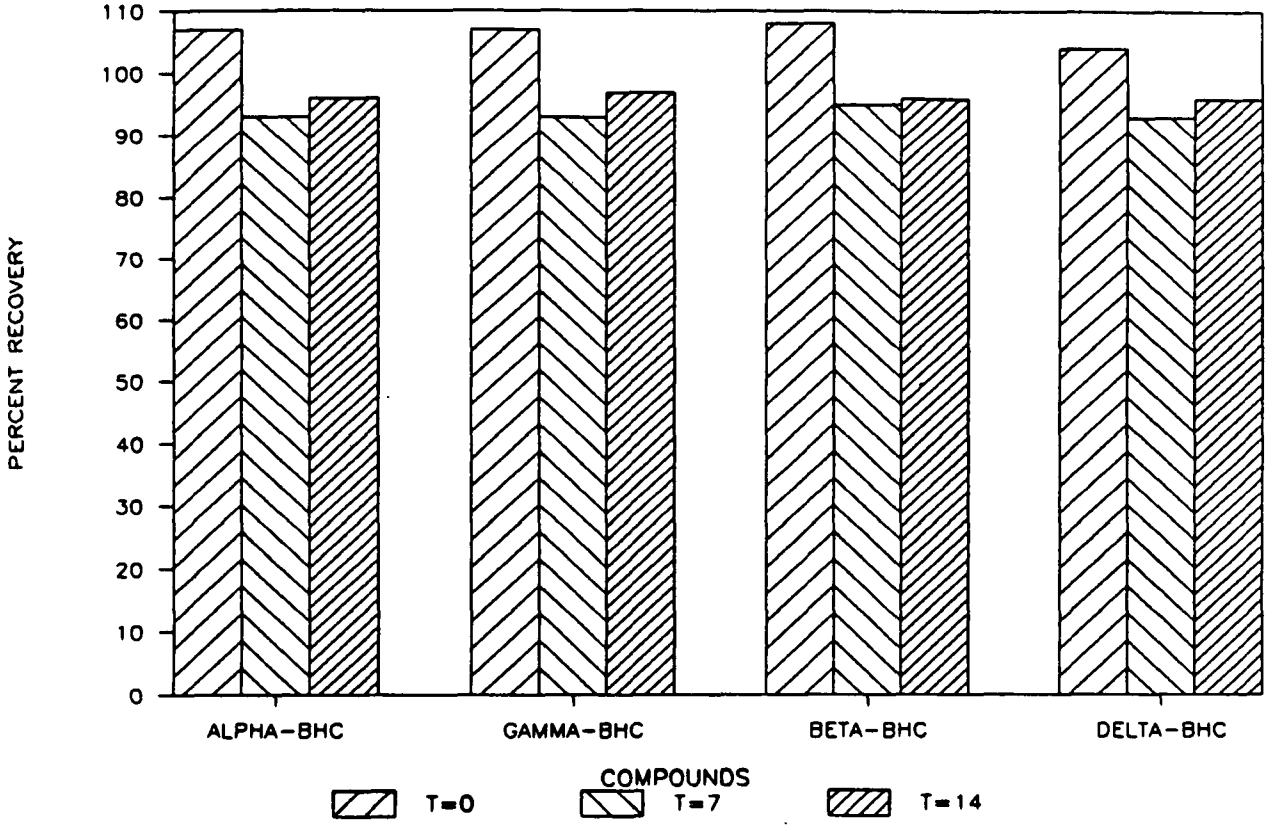

Figure 24. Recovery as a function of time at pH 2 for: alpha-BHC, gamma-BHC, beta-BHC, and delta-BHC.

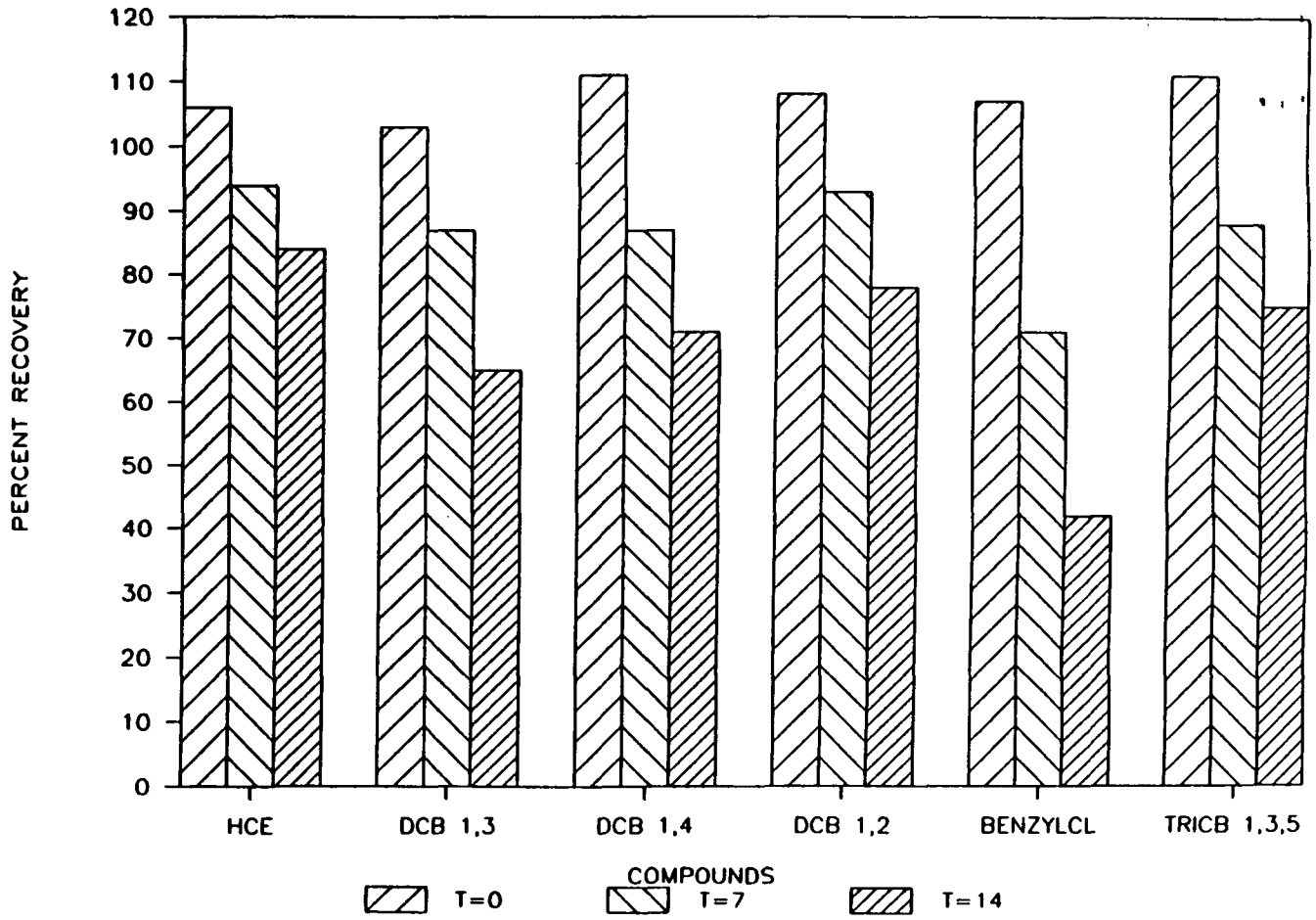

Figure 25. Recovery as a function of time at pH 9 for: hexachloroethane, 1,3-dichlorobenzene, 1,4-dichlorobenzene, 1,2-dichlorobenzene, benzyl chloride, and 1,3,5-trichlorobenzene.

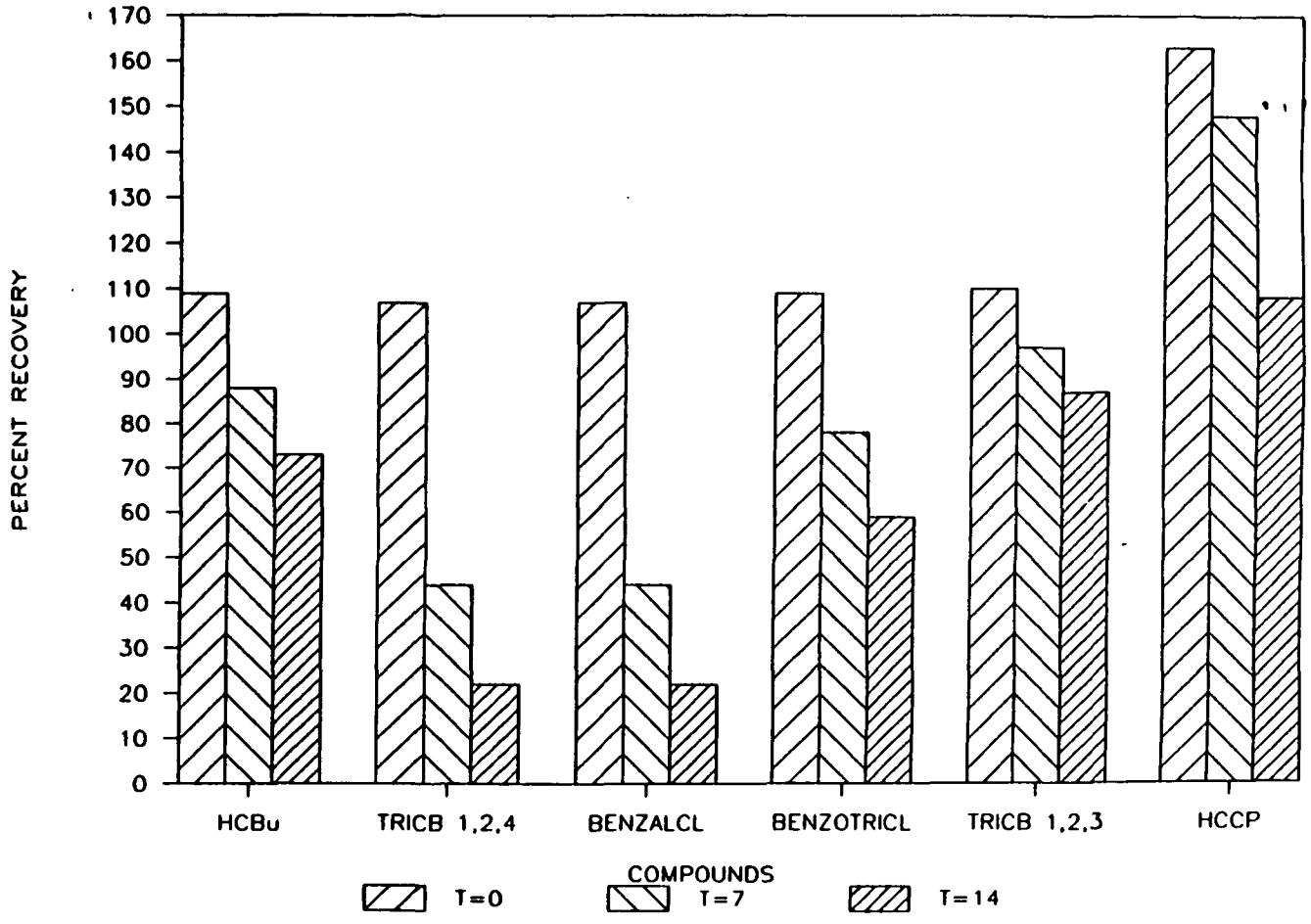

Figure 26. Recovery as a function of time at pH 9 for: hexachlorobutadiene, 1,2,4-trichlorobenzene, benzal chloride, benzotrichloride, 1,2,3-trichlorobenzene, and hexachlorocyclopentadiene.

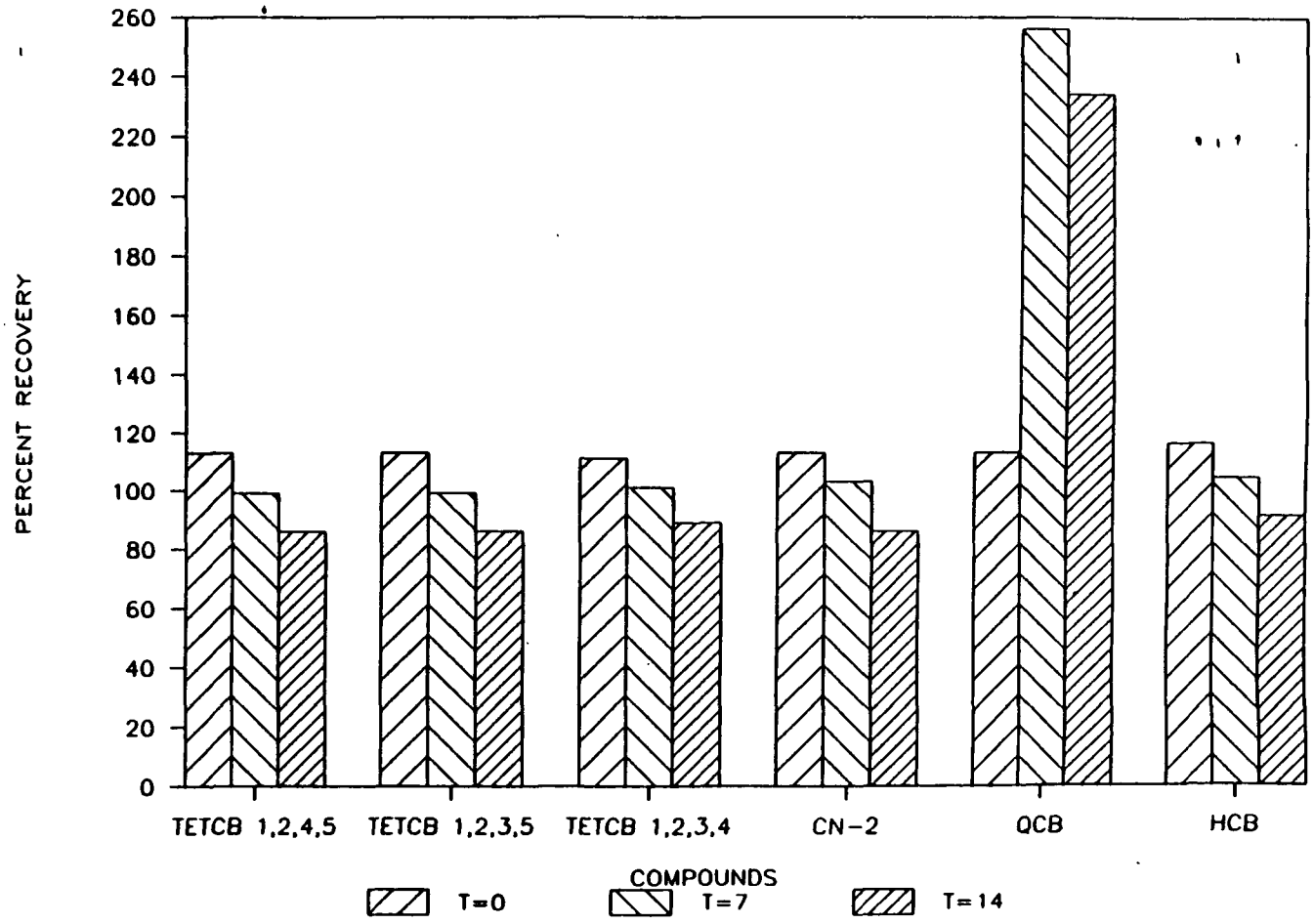

Figure 27. Recovery as a function of time at pH 9 for: 1,2,4,5-tetrachlorobenzene, 1,2,3,5-tetrachlorobenzene, 1,2,3,4-tetrachlorobenzene, 2-chloronaphthalene, pentachlorobenzene, and hexachlorobenzene.

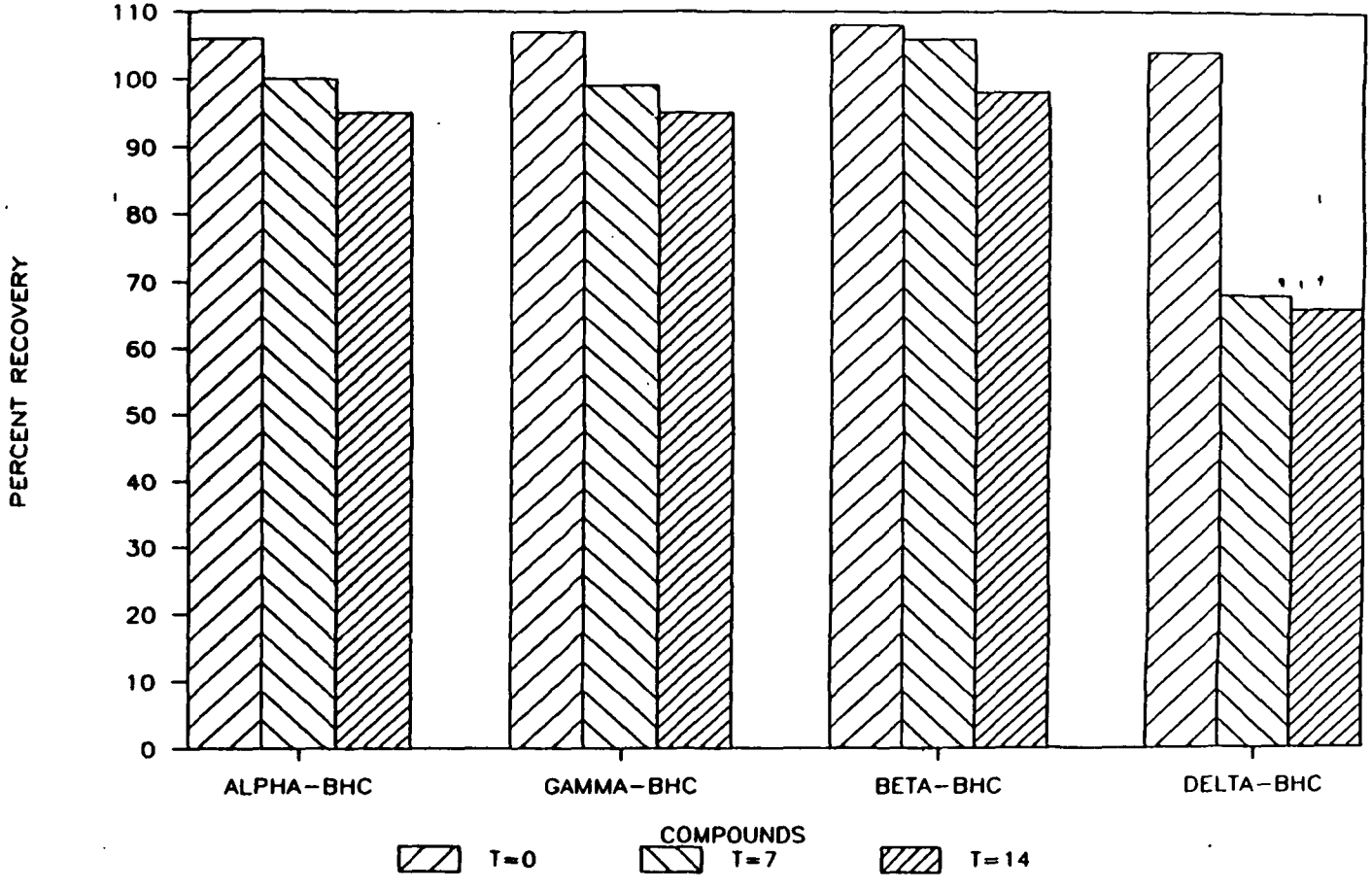

Figure 28. Recovery as a function of time at pH 9 for: alpha-BHC, gamma-BHC, beta-BHC, and delta-BHC.

TABLE 35. HOMOGENEITY OF SPIKED SOIL SAMPLES PREPARED BY BLENDING AND KEPT FROZEN FOR 5 MONTHS

Compound	Spike Level (ng/µL)	Concentration (ng/µL extract)[a] -1	-2	-3	-4	-5	Average	Percent RSD
Hexachloroethane	0.1	0.02	0.02	0.02	0.02	0.02	0.02	0
1,3-Dichlorobenzene	10.0	0.27	0.19	0.18	0.07	0.06	0.15	59.0
1,4-Dichlorobenzene	10.0	3.68	2.34	2.74	2.74	2.93	2.89	17.1
1,2-Dichlorobenzene	10.0	1.54	1.59	1.37	1.61	1.44	1.51	6.8
Benzyl chloride	10.0	1.16	1.30	0.93	1.00	0.90	1.06	15.9
1,3,5-Trichlorobenzene	1.0	0.41	0.38	0.39	0.36	0.37	0.38	5.1
Hexachlorobutadiene	0.1	0.025	0.026	0.029	0.027	0.031	0.028	8.6
Benzal chloride[b] 1,2,4-Trichlorobenzene[b]	2.0	0.075	0.086	0.090	0.091	0.094	0.087	8.5
Benzotrichloride	1.0	0	0	0	0	0	0	--
1,2,3-Trichlorobenzene	1.0	0.22	0.29	0.32	0.30	0.36	0.30	17.1
Hexachlorocyclopentadiene	0.1	0	0	0	0	0	0	--
1,2,4,5-Tetrachlorobenzene[c] 1,2,3,5-Tetrachlorobenzene[c]	2.0	0.51	0.69	0.84	0.81	0.89	0.75	20.3
1,2,3,4-Tetrachlorobenzene	1.0	0.43	0.61	0.72	0.69	0.79	0.65	21.2
2-Chloronaphthalene	20.0	12.8	15.0	16.8	16.0	17.5	15.6	11.7
Pentachlorobenzene	0.1	0.042	0.052	0.058	0.058	0.063	0.055	14.6
Hexachlorobenzene	0.1	0.033	0.041	0.047	0.052	0.051	0.044	16.4
alpha-BHC	1.0	0.64	0.73	0.79	0.78	0.82	0.75	9.4
gamma-BHC	1.0	0.71	0.82	0.88	0.86	0.91	0.84	9.2
beta-BHC	1.0	0.37	0.57	0.74	0.69	0.80	0.63	27.0
delta-BHC	1.0	0.60	0.78	0.88	0.85	0.92	0.81	15.6
Surrogate recovery (percent)								
α,2,6-Trichlorotoluene	0.1	104	114	100	105	110	107	4.7
1,4-Dichloronaphthalene	1.0	100	104	91	96	104	99	5.1
2,3,4,5,6-Pentachlorotoluene	0.1	100	103	92	109	107	104	7.4

[a]To convert to ng/g of soil, multiply the values given in ng/µL extract by 400.
[b,c]These pairs cannot be resolved on the DB-210 fused-silica capillary column.

TABLE 36. HOMOGENEITY OF SPIKED SOIL SAMPLES PREPARED BY BLENDING AND KEPT FROZEN FOR 6 MONTHS

Compound	Spike level (ng/µL)	Concentration (ng/µL extract)[a] -6	-7	-8	-9	Average	Percent RSD
Hexachloroethane	0.1	0.01	0.008	0.012	0.016	0.012	28.5
1,3-Dichlorobenzene	10.0	0.12	0.10	0.17	0.10	0.12	26.9
1,4-Dichlorobenzene	10.0	2.36	1.05	2.97	2.16	2.14	37.5
1,2-Dichlorobenzene	10.0	1.13	0.80	1.09	0.87	0.97	16.7
Benzyl chloride	10.0	0.53	0.40	0.52	0.42	0.47	14.3
1,3,5-Trichlorobenzene	1.0	0.34	0.21	0.28	0.26	0.27	19.7
Hexachlorobutadiene	0.1	0.021	0.011	0.016	0.018	0.017	24.7
Benzal chloride[b] 1,2,4-Trichlorobenzene[b]	2.0	0.09	0.05	0.06	0.07	0.07	24.4
Benzotrichloride	1.0	0	0	0	0	0	--
1,2,3-Trichlorobenzene	1.0	0.31	0.15	0.20	0.18	0.21	33.2
Hexachlorocyclopentadiene	0.1	0.011	0.006	0.006	0.01	0.008	32.9
1,2,4,5-Tetrachlorobenzene[c] 1,2,3,5-Tetrachlorobenzene[c]	2.0	0.96	0.37	0.51	0.51	0.59	43.7
1,2,3,4-Tetrachlorobenzene	1.0	0.80	0.31	0.45	0.43	0.50	42.4
2-Chloronaphthalene	20.0	20.75	8.14	11.02	14.24	13.54	40.0
Pentachlorobenzene	0.1	0.07	0.039	0.048	0.047	0.051	26.0
Hexachlorobenzene	0.1	0.044	0.025	0.029	0.035	0.033	25.0
alpha-BHC	1.0	0.81	0.58	0.69	0.68	0.69	13.7
gamma-BHC	1.0	0.86	0.63	0.73	0.73	0.74	12.8
beta-BHC	1.0	0.75	0.34	0.51	0.48	0.52	32.8
delta-BHC	1.0	0.84	0.57	0.70	0.69	0.70	15.8
Surrogate recovery (percent)							
α,2,6-Trichlorotoluene	0.1	98	91	90	90	92	3.6
1,4-Dichloronaphthalene	1.0	91	91	100	95	94	3.9
2,3,4,5,6-Pentachlorotoluene	0.1	78	96	79	95	88	9.8

[a]To convert to ng/g of soil, multiply the values given in ng/µL extract by 400.
[b,c]These pairs cannot be resolved on the OB-210 fused-silica capillary column.

6.5 REVISED METHOD 8120 PROTOCOL

The revised Method 8120 was evaluated in terms of the reproducibility of the injection technique, the linearity of response over several orders of magnitude in concentration, the precision of the identification and measurement of the gas chromatographic technique, and the minimum detectable levels for the target analytes were established. Subsequent subsections address the reproducibility of the injection technique, the instrument calibration, and the method detection limit. Furthermore, a ruggedness test of the gas chromatographic procedure was performed and is described in this section.

6.5.1 Reproducibility of the GC Technique

To establish the reproducibility of the GC technique, 10 consecutive injections of isooctane blanks, spiked with 10 µL of a 1,3,5-tribromobenzene solution at 100 ng/µL (nominal concentration of 1,3,5-tribromobenzene that was analyzed is 1 ng/µL), were performed with an autosampler.

The results are presented in Table 37 as the retention time (minutes) and the absolute response of the 1,3,5-tribromobenzene, the average values of the two parameters, and their corresponding standard deviations (SD) and relative standard deviations (RSD). The reproducibility of the retention time and detector response for the 10 consecutive injections are 0.67 percent and 0.8 percent, respectively. When actual samples were analyzed over a 24-hour period (Table 38), the reproducibility of retention time on three different days for 9 to 25 injections ranged from 0.066 to 0.13 percent. Similarly, the reproducibility of detector response ranged from 14 to 28 percent. The internal standard that was tested in this case was α,α'-dibromo-m-xylene.

Tables 39 and 40 present the retention times of the Method 8120 compounds relative to α,α'-dibromo-m-xylene and 2,5-dibromotoluene, respectively. Table 41 shows the reproducibility of the detector response for each target analyte over a period of five days for six injections. With the exception of 1,4-dichlorobenzene, the target analytes exhibited percent RSDs better than 15 percent, with 72 percent of the values under 10 percent.

6.5.2 Instrument Calibration

Quantification of the target analytes is typically performed using two types of calibration: external standard calibration and internal standard calibration. In the former case, working solutions containing the target analytes are analyzed prior to samples to determine the linear dynamic range of the detector. Quantification of compounds in an unknown sample is performed by comparing the detector responses obtained for the unknown sample to that measured for a calibration standard that is within the linear range of the instrument. In the latter case, the linear dynamic range of the instrument needs to be established the same way. In addition, an internal standard is spiked into every calibration standard and unknown sample. After the sample is analyzed, the ratio of detector responses of each test compound

TABLE 37. REPRODUCIBILITY OF RETENTION TIME AND ABSOLUTE PEAK AREA FOR 1,3,5-TRIBROMOBENZENE SPIKED AS INTERNAL STANDARD IN ISOOCTANE BLANKS[a]

Injection number	Retention time (min)	Detector response
1	11.70	5093338
2	11.69	4982222
3	11.70	4978096
4	11.68	5013383
5	11.70	4996981
6	11.69	5052108
7	11.70	5000252
8	11.69	5033607
9	11.69	5074277
10	11.68	5025909
Average	11.69	5025017
SD	0.0079	38687
RSD (percent)	0.067	0.8

[a]Analyses were performed using an autosampler, the DB-210 column, and the operating conditions given in Table 4. Each isooctane blank was spiked with 10 µL of a 1,3,5-tribromobenzene solution in isooctane (concentration 100 ng/µL).

TABLE 38. REPRODUCIBILITY OF ABSOLUTE RESPONSE AND RETENTION TIME FOR α,α'-DIBROMO-M-XYLENE[a]

Date	Retention time (min)				Detector response			
	Average value	SD	RSD (percent)	n[b]	Average value	SD	RSD (percent)	n[b]
November 13, 1987	16.601	0.011	0.066	25	283,621	38,746	14	25
November 17, 1987	16.65	0.020	0.102	11	284,484	68,100	24	11
November 20, 1987	16.70	0.020	0.130	9	305,529	86,467	28	9

[a]Analyses were performed using an autosampler, the DB-210 column, and the operating conditions given in Table 4. Each standard or sample extract was spiked with 10 µL of a α,α'-dibromo-m-xylene solution in isooctane (concentration 100 ng/µL).
[b]Number of determinations.

TABLE 39. RELATIVE RETENTION TIMES (RRT) OF THE METHOD 8120 COMPOUNDS ON THE DB-210 FUSED-SILICA CAPILLARY COLUMN[a]

Compound	RRT			Average RRT	Percent RSD
	Std. 1	Std. 2	Std. 3		
Hexachloroethane	0.1574	0.1565	0.1564	0.1568	0.35
1,3-Dichlorobenzene	0.1723	0.1720	0.1719	0.1721	0.12
1,4-Dichlorobenzene	0.1795	0.1792	0.1791	0.1793	0.12
1,2-Dichlorobenzene	0.2117	0.2115	0.2113	0.2115	0.09
Benzyl chloride	0.2206	0.2198	0.2197	0.2200	0.22
1,3,5-Trichlorobenzene	0.2648	0.2640	0.2645	0.2644	0.15
Hexachlorobutadiene	0.2826	0.2820	0.2818	0.2821	0.15
Benzal chloride[b]	0.3399	0.3393	0.3391	0.3394	0.12
1,2,4-Trichlorobenzene[b]	0.3399	0.3393	0.3391	0.3394	0.12
Benzotrichloride	0.3942	0.3931	0.3928	0.3934	0.19
1,2,3-Trichlorobenzene	0.4091	0.4086	0.4084	0.4087	0.09
Hexachlorocyclopentadiene	0.4502	0.4498	0.4484	0.4495	0.21
1,2,4,5-Tetrachlorobenzene[c]	0.5224	0.5221	0.5224	0.5223	0.03
1,2,3,5-Tetrachlorobenzene[c]	0.5224	0.5221	0.5224	0.5223	0.03
1,2,3,4-Tetrachlorobenzene	0.6208	0.6207	0.6203	0.6206	0.04
2-Chloronaphthalene	0.7090	0.7091	0.7087	0.7089	0.03
Pentachlorobenzene	0.7913	0.7921	0.7916	0.7917	0.05
Hexachlorobenzene	1.0459	1.0478	1.0460	1.0466	0.10
alpha-BHC	1.2200	1.2204	1.2215	1.2206	0.06
gamma-BHC	1.3298	1.3321	1.3313	1.3311	0.09
beta-BHC	1.4186	1.4194	1.4203	1.4194	0.06
delta-BHC	1.4538	1.4546	1.4555	1.4546	0.06

[a]Internal standard is α,α'-dibromo-m-xylene; analyses were performed on December 4, 1987.

[b,c]These pairs cannot be resolved on the DB-210 fused-silica capillary column.

TABLE 40. RELATIVE RETENTION TIMES (RRT) OF THE METHOD 8120 COMPOUNDS ON THE DB-WAX FUSED-SILICA CAPILLARY COLUMN[a]

Compound	RRT						Average RRT	Percent RSD
	Std. 1	Std. 2	Std. 3	Std. 4	Std. 5	Std. 6		
Hexachloroethane	0.4383	0.4377	0.4377	0.4377	0.4377	0.4380	0.4379	0.06
1,3-Dichlorobenzene	0.4167	0.4167	0.4167	0.4167	0.4167	0.4169	0.4167	0.02
1,4-Dichlorobenzene	0.4577	0.4571	0.4577	0.4577	0.4577	0.4579	0.4576	0.06
1,2-Dichlorobenzene	0.5164	0.5164	0.5164	0.5164	0.5164	0.5162	0.5164	0.02
Benzyl chloride[c]	0.5590	0.5585	0.5580	0.5590	0.5585	0.5593	0.5587	0.08
1,3,5-Trichlorobenzene[c]	0.5590	0.5585	0.5580	0.5590	0.5585	0.5593	0.5587	0.08
Hexachlorobutadiene	0.5380	0.5375	0.5375	0.5375	0.5375	0.5378	0.5376	0.04
Benzal chloride	0.8577	0.8577	0.8577	0.8577	0.8571	0.8581	0.8577	0.04
1,2,4-Trichlorobenzene	0.7407	0.7396	0.7407	0.7407	0.7407	0.7411	0.7406	0.07
Benzotrichloride	0.8318	0.8323	0.8323	0.8318	0.8318	0.8323	0.8321	0.03
1,2,3-Trichlorobenzene	0.8625	0.8631	0.8625	0.8620	0.8625	0.8630	0.8626	0.05
Hexachlorocyclopentadiene	0.5380	0.5375	0.5375	0.5375	0.5375	0.5378	0.5376	0.04
1,2,4,5-Tetrachlorobenzene	0.9601	0.9590	0.9596	0.9596	0.9596	0.9601	0.9597	0.04
1,2,3,5-Tetrachlorobenzene	0.9434	0.9429	0.9429	0.9429	0.9429	0.9439	0.9432	0.04
1,2,3,4-Tetrachlorobenzene	1.1412	1.1412	1.1407	1.1407	1.1407	1.1419	1.1411	0.04
2-Chloronaphthalene[d]	1.2803	1.2798	1.2803	1.2803	1.2803	1.2816	1.2804	0.05
Pentachlorobenzene[d]	1.2803	1.2798	1.2803	1.2803	1.2803	1.2816	1.2804	0.05
Hexachlorobenzene	1.5720	1.5720	1.5714	1.5709	1.5720	1.5728	1.5719	0.04
alpha-BHC	b	b	b	b	b	b	b	b
gamma-BHC	b	b	b	b	b	b	b	b
beta-BHC	b	b	b	b	b	b	b	b
delta-BHC	b	b	b	b	b	b	b	b

[a]Internal standard is 2,5-dibromotoluene; analyses were performed on November 25, 1987.
[b]Not able to chromatograph the BHCs on the DB-WAX fused-silica capillary column.
[c,d]These pairs cannot be resolved on the DB-WAX fused-silica capillary column.

TABLE 41. RESPONSE FACTORS FOR THE SINGLE-LEVEL CALIBRATION DATA FOR THE METHOD 8120 COMPOUNDS ANALYZED ON THE DB-210 FUSED-SILICA CAPILLARY COLUMN

Compound	Concentration (ng/µL)	11-13-87 06:55 pm	11-14-87 01:04 am	11-14-87 09:22 am	11-14-87 05:40 pm	11-17-87 10:35 pm	11-18-87 06:08 am	RSD (percent)
Hexachloroethane	0.001	14.2×10^7	14.1×10^7	14.2×10^7	14.1×10^7	12.2×10^7	13.4×10^7	5.8
1,3-Dichlorobenzene	0.1	4.1×10^5	4.1×10^5	4.1×10^5	4.1×10^5	3.5×10^5	3.8×10^5	6.4
1,4-Dichlorobenzene	0.2	1.9×10^5	1.9×10^5	1.9×10^5	2.0×10^5	3.4×10^5	3.7×10^5	34.3
1,2-Dichlorobenzene	0.1	4.6×10^5	4.6×10^5	4.6×10^5	4.6×10^5	4.1×10^5	4.4×10^5	4.6
Benzyl chloride	0.1	7.6×10^5	7.6×10^5	7.5×10^5	7.6×10^5	6.8×10^5	7.3×10^5	4.3
1,3,5-Trichlorobenzene	0.01	4.3×10^6	4.3×10^6	4.3×10^6	4.3×10^6	3.8×10^6	4.1×10^6	4.9
Hexachlorobutadiene	0.001	10.3×10^7	10.1×10^7	10.3×10^7	10.3×10^7	9.0×10^7	9.4×10^7	5.7
Benzal chloride[a]	0.001	3.1×10^6	3.1×10^6	3.0×10^6	3.1×10^6	2.8×10^6	2.9×10^6	4.2
1,2,4-Trichlorobenzene[a]	0.05	3.1×10^6	3.1×10^6	3.0×10^6	3.1×10^6	2.8×10^6	2.9×10^6	4.2
Benzotrichloride	0.005	3.4×10^7	3.4×10^7	3.5×10^7	3.6×10^7	3.9×10^7	4.4×10^7	10.5
1,2,3-Trichlorobenzene	0.1	7.4×10^6	7.4×10^6	7.4×10^6	7.4×10^6	6.7×10^6	7.3×10^6	3.9
Hexachlorocyclopentadiene	0.1	9.3×10^5	9.2×10^5	9.6×10^5	10.2×10^5	9.9×10^5	9.3×10^5	4.1
1,2,4,5-Tetrachlorobenzene[b]	0.01	8.0×10^6	8.0×10^6	8.1×10^6	8.0×10^6	8.8×10^6	9.5×10^6	7.4
1,2,3,5-Tetrachlorobenzene[b]	0.01	8.0×10^6	8.0×10^6	8.1×10^6	8.0×10^6	8.8×10^6	9.5×10^6	7.4
1,2,3,4-Tetrachlorobenzene	0.01	11.7×10^6	12.2×10^6	12.4×10^6	12.5×10^6	11.4×10^6	11.4×10^6	4.2
2-Chloronaphthalene	0.5	12.1×10^4	12.6×10^4	12.7×10^4	12.1×10^4	11.9×10^4	11.7×10^4	3.2
Pentachlorobenzene	0.01	19.9×10^6	19.9×10^6	19.9×10^6	19.9×10^6	18.4×10^6	19.9×10^6	3.1
Hexachlorobenzene	0.005	6.5×10^7	6.7×10^7	6.6×10^7	6.5×10^7	6.0×10^7	7.2×10^7	5.9
alpha-BHC	0.01	7.3×10^7	7.3×10^7	7.3×10^7	7.2×10^7	5.5×10^7	6.2×10^7	11.3
gamma-BHC	0.01	7.2×10^7	7.2×10^7	7.2×10^7	7.2×10^7	5.3×10^7	6.4×10^7	11.5
beta-BHC	0.01	2.5×10^7	2.5×10^7	2.5×10^7	2.5×10^7	1.7×10^7	2.1×10^7	14.6
delta-BHC	0.01	5.8×10^7	5.8×10^7	5.8×10^7	5.8×10^7	3.9×10^7	4.6×10^7	15.7

[a,b]These pairs cannot be resolved on the DB-210 fused-silica capillary column.

to the internal standard is compared to that in the calibration standard to determine the concentration of the target analyte.

During the course of this project, we performed four sets of multilevel calibrations for the DB-210 fused-silica capillary column and one set for the DB-WAX fused-silica capillary column. Initially, we analyzed standards ranging from 0.01 ng/μL to 0.5 ng/μL for compounds such as hexachloroethane, hexachlorobenzene, and from 1.0 ng/μL to 100 ng/μL for 2-chloronaphthalene. The remainder of the compounds were at concentrations in between those values. From the data in Table 42, we concluded that the linear range extends only from 0.01 ng to 0.1 ng for hexachloroethane and correspondingly for the remainder of compounds. The data presented in Tables 43 through 46 give the individual response factors, the average response factors, and the percent RSDs for four sets of multilevel calibrations.

6.5.3 Method Accuracy and Precision

To establish method accuracy and precision, we spiked reagent water samples, sandy loam samples, and highly contaminated river sediment samples with the target analytes at concentrations ranging from 1.0 to 200 μg/L (for water), 330 to 66,000 ng/g (for sandy loam soil), and 1.3 to 260 ng/g and 5.4 to 1,080 ng/g (for Love Canal and PCB-contaminated soil), and processed them according to the analytical scheme. Furthermore, extracts of nine environmental matrices (including some of the samples listed above) and NBS standard reference materials were spiked with the target analytes and processed according to the method. Table 47 presents the recovery and precision data for water samples and Table 48 presents recovery and precision data for a sandy loam soil. Tables 49 and 50 present the results from two (contaminated) soil samples spiked at four concentrations, each in triplicate or quadruplicate. Tables 51 through 59 present recovery data (using the DB-210 and the DB-WAX columns) for the nine environmental sample extracts that were spiked with the target compounds and processed according to the method. Figures 29 through 46 show how recovery of each target compound varies with matrix.

In the case of the water samples, method precision was better than 9 percent and compound recoveries (method accuracy) were greater than 87 percent (Table 47).

In the case of the contaminated soil samples, method precision was better than 22 percent (except for 1,4-dichlorobenzene, 1,2-dichlorobenzene, and hexachlorocyclopentadiene), and for most compounds, the recoveries were greater than 70 percent. Furthermore, method recovery does not seem to be a function of analyte concentration or matrix.

In addition to the spiked samples and extracts , we have also analyzed a series of EPA performance evaluation samples to determine if the target analytes can be identified and quantified accurately in the presence of other organic compounds of environmental significance. Tables 60 through 69 summarize the results of these analyses.

TABLE 42. MULTILEVEL CALIBRATION DATA FOR STANDARDS ANALYZED ON 5/27/87

Compound	Response factor						Average	Percent RSD
	0.01 to 2.0 ng/µL	0.02 to 4.0 ng/µL	0.05 to 10.0 ng/µL	0.1 to 20.0 ng/µL	0.2 to 40.0 ng/µL	0.5 to 100.0 ng/µL		
Hexachloroethane	26.20×10^6	30.70×10^6	28.60×10^6	22.70×10^6	15.84×10^6	9.15×10^6	22.20×10^6	37.2
1,3-Dichlorobenzene	9.75×10^3	9.50×10^3	9.50×10^3	10.90×10^3	12.40×10^3	14.30×10^3	11.06×10^3	17.6
1,4-Dichlorobenzene	2.33×10^4	2.33×10^4	2.53×10^4	3.12×10^4	3.45×10^4	2.80×10^4	2.76×10^4	16.4
1,2-Dichlorobenzene	7.19×10^4	7.83×10^4	9.54×10^4	10.20×10^4	8.30×10^4	5.27×10^4	8.06×10^4	21.8
Benzyl chloride	6.50×10^4	6.97×10^4	8.30×10^4	9.27×10^4	10.70×10^4	6.40×10^4	8.02×10^4	21.5
1,3,5-Trichlorobenzene	4.93×10^5	5.02×10^5	5.41×10^5	6.56×10^5	6.13×10^5	4.30×10^5	5.39×10^5	15.4
Hexachlorobutadiene	14.48×10^6	15.43×10^6	18.42×10^6	17.70×10^6	13.50×10^6	8.30×10^6	14.60×10^6	24.8
Benzal chloride[a]	17.14×10^5	19.40×10^5	16.96×10^5	13.20×10^5	9.13×10^5	5.18×10^5	13.50×10^5	40.4
1,2,4-Trichlorobenzene[a]	17.14×10^5	19.40×10^5	16.96×10^5	13.20×10^5	9.13×10^5	5.18×10^5	13.50×10^5	40.4
Benzotrichloride	11.55×10^6	9.88×10^6	6.55×10^6	4.60×10^6	2.93×10^6	1.52×10^6	6.17×10^6	63.8
1,2,3-Trichlorobenzene	11.94×10^5	12.82×10^5	15.33×10^5	15.30×10^5	11.80×10^5	7.34×10^5	12.42×10^5	23.7
Hexachlorocyclopentadiene	4.99×10^6	5.45×10^6	6.27×10^6	8.50×10^6	8.31×10^6	6.14×10^6	6.61×10^6	22.2
1,2,4,5-Tetrachlorobenzene[b]	8.95×10^5	9.07×10^5	10.40×10^5	11.85×10^5	9.50×10^5	5.69×10^5	9.24×10^5	22.1
1,2,3,5-Tetrachlorobenzene[b]	8.95×10^5	9.07×10^5	10.40×10^5	11.85×10^5	9.50×10^5	5.69×10^5	9.24×10^5	22.1
1,2,3,4-Tetrachlorobenzene	23.50×10^5	25.99×10^5	27.98×10^5	23.60×10^5	16.90×10^5	9.97×10^5	21.32×10^5	31.4
2-Chloronaphthalene	2.05×10^4	2.18×10^4	2.19×10^4	2.78×10^4	2.88×10^4	2.26×10^4	2.39×10^4	14.6
Pentachlorobenzene	4.34×10^6	4.26×10^6	4.38×10^6	5.26×10^6	6.10×10^6	5.04×10^6	4.90×10^6	14.7
Hexachlorobenzene	8.33×10^6	8.81×10^6	9.21×10^6	13.30×10^6	12.40×10^6	8.56×10^6	10.10×10^6	21.5
alpha-BHC	11.43×10^6	11.06×10^6	7.91×10^6	5.74×10^6	3.90×10^6	2.10×10^6	7.02×10^6	54.1
gamma-BHC	10.25×10^6	10.06×10^6	7.55×10^6	5.60×10^6	3.78×10^6	2.09×10^6	6.56×10^6	50.8
beta-BHC	2.97×10^6	3.40×10^6	4.00×10^6	3.50×10^6	2.58×10^6	1.58×10^6	3.01×10^6	28.2
delta-BHC	9.95×10^6	10.40×10^6	7.90×10^6	5.95×10^6	4.05×10^6	2.43×10^6	6.78×10^6	47.3

[a,b] These pairs cannot be resolved on the DB-210 fused-silica capillary column.

TABLE 43. MULTILEVEL CALIBRATION DATA FOR STANDARDS ANALYZED ON 6/4/87

Compound	Response factor							Average	Percent RSD
	0.01 to 2.0 ng/µL	0.02 to 4.0 ng/µL	0.04 to 8.0 ng/µL	0.05 to 10.0 ng/µL	0.07 to 14.0 ng/µL	0.08 to 16.0 ng/µL	0.1 to 20.0 ng/µL		
Hexachloroethane	24.1×10^6	28.7×10^6	29.2×10^6	28.0×10^6	25.1×10^6	23.9×10^6	22.4×10^6	26.5×10^6	9.1
1,3-Dichlorobenzene	9.9×10^3	9.4×10^3	9.3×10^3	9.4×10^3	9.6×10^3	9.8×10^3	10.6×10^3	9.6×10^3	2.5
1,4-Dichlorobenzene	2.3×10^4	2.3×10^4	2.4×10^4	2.5×10^4	2.6×10^4	2.7×10^4	3.0×10^4	2.5×10^4	6.5
1,2-Dichlorobenzene	6.8×10^4	7.5×10^4	8.7×10^4	9.2×10^4	9.6×10^4	9.7×10^4	9.9×10^4	8.8×10^4	13.5
Benzyl chloride	6.2×10^4	6.8×10^4	7.7×10^4	8.1×10^4	8.5×10^4	8.7×10^4	9.0×10^4	7.9×10^4	13.1
1,3,5-Trichlorobenzene	4.1×10^5	4.4×10^5	4.6×10^5	4.7×10^5	4.8×10^5	4.9×10^5	5.5×10^5	4.7×10^5	9.3
Hexachlorobutadiene	12.2×10^6	12.9×10^6	14.1×10^6	14.7×10^6	15.1×10^6	15.2×10^6	15.4×10^6	14.2×10^6	8.7
Benzal chloride[a]	14.8×10^5	17.1×10^5	17.3×10^5	16.2×10^5	14.5×10^5	13.8×10^5	12.9×10^5	15.2×10^5	11.0
1,2,4-Trichlorobenzene[a]	14.8×10^5	17.1×10^5	17.3×10^5	16.2×10^5	14.5×10^5	13.8×10^5	12.9×10^5	15.2×10^5	11.0
Benzotrichloride	10.2×10^6	9.4×10^6	7.2×10^6	6.4×10^6	5.4×10^6	5.1×10^6	4.5×10^6	6.9×10^6	31.7
1,2,3-Trichlorobenzene	10.7×10^5	11.4×10^5	12.5×10^5	13.1×10^5	13.6×10^5	13.6×10^5	13.8×10^5	12.7×10^5	9.5
Hexachlorocyclopentadiene	5.2×10^6	5.6×10^6	5.9×10^6	6.2×10^6	6.6×10^6	6.8×10^6	7.7×10^6	6.3×10^6	13.2
1,2,4,5-Tetrachlorobenzene[b]	6.8×10^5	7.1×10^5	7.0×10^5	7.1×10^5	7.3×10^5	7.4×10^5	7.7×10^5	7.2×10^5	4.1
1,2,3,5-Tetrachlorobenzene[b]	6.8×10^5	7.1×10^5	7.0×10^5	7.1×10^5	7.3×10^5	7.4×10^5	7.7×10^5	7.2×10^5	4.1
1,2,3,4-Tetrachlorobenzene	18.8×10^5	20.1×10^5	21.9×10^5	22.3×10^5	21.7×10^5	21.2×10^5	20.6×10^5	20.9×10^5	5.8
2-Chloronaphthalene	2.3×10^4	2.3×10^4	2.4×10^4	2.4×10^4	2.5×10^4	2.6×10^4	2.7×10^4	2.5×10^4	6.0
Pentachlorobenzene	4.1×10^6	4.1×10^6	4.1×10^6	4.1×10^6	4.2×10^6	4.2×10^6	4.5×10^6	4.2×10^6	3.5
Hexachlorobenzene	7.9×10^6	7.9×10^6	8.3×10^6	8.6×10^6	9.2×10^6	9.7×10^6	10.9×10^6	8.9×10^6	12.2
alpha-BHC	9.2×10^6	9.6×10^6	7.8×10^6	7.1×10^6	6.2×10^6	5.7×10^6	5.3×10^6	7.3×10^6	23.1
gamma-BHC	14.5×10^6	12.7×10^6	9.9×10^6	8.8×10^6	7.4×10^6	7.0×10^6	6.3×10^6	9.5×10^6	32.0
beta-BHC	4.3×10^6	4.0×10^6	4.9×10^6	4.3×10^6	3.9×10^6	3.8×10^6	3.7×10^6	4.1×10^6	10.0
delta-BHC	12.8×10^6	12.0×10^6	9.8×10^6	8.7×10^6	7.4×10^6	6.9×10^6	6.4×10^6	9.1×10^6	27.4

[a,b]These pairs cannot be resolved on the DB-210 fused-silica capillary column.

TABLE 44. MULTILEVEL CALIBRATION DATA FOR STANDARDS ANALYZED ON 6/18/87

Compound	Response factor							Average	% RSD
	0.01 to 2.0 ng/µL	0.02 to 4.0 ng/µL	0.04 to 8.0 ng/µL	0.05 to 10.0 ng/µL	0.07 to 14.0 ng/µL	0.08 to 16.0 ng/µL	0.1 to 20.0 ng/µL		
Hexachloroethane	24.8×10^6	29.9×10^6	30.5×10^6	29.0×10^6	25.9×10^6	24.8×10^6	22.8×10^6	26.8×10^6	11.1
1,3-Dichlorobenzene	9.8×10^3	9.8×10^3	10.0×10^3	9.9×10^3	10.2×10^3	10.4×10^3	10.9×10^3	10.1×10^3	4.0
1,4-Dichlorobenzene	2.4×10^4	2.4×10^4	2.6×10^4	2.6×10^4	2.8×10^4	2.9×10^4	3.1×10^4	2.7×10^4	9.7
1,2-Dichlorobenzene	7.0×10^4	7.7×10^4	9.2×10^4	9.7×10^4	10.1×10^4	10.2×10^4	10.2×10^4	9.2×10^4	14.1
Benzyl chloride	6.2×10^4	6.7×10^4	7.9×10^4	8.3×10^4	8.8×10^4	10.2×10^4	9.1×10^4	8.2×10^4	16.9
1,3,5-Trichlorobenzene	5.4×10^5	5.5×10^5	5.9×10^5	5.8×10^5	6.3×10^5	6.4×10^5	6.8×10^5	6.0×10^5	8.5
Hexachlorobutadiene	14.9×10^6	15.9×10^6	18.4×10^6	18.8×10^6	18.8×10^6	18.9×10^6	17.8×10^6	17.6×10^6	9.1
Benzal chloride[a]	17.5×10^5	20.3×10^5	19.1×10^5	17.6×10^5	15.8×10^5	14.8×10^5	13.4×10^5	16.9×10^5	14.3
1,2,4-Trichlorobenzene[a]	17.5×10^5	20.3×10^5	19.1×10^5	17.6×10^5	15.8×10^5	14.8×10^5	13.4×10^5	16.9×10^5	14.3
Benzotrichloride	11.6×10^6	10.1×10^6	7.6×10^6	6.8×10^6	5.7×10^6	5.3×10^6	4.7×10^6	7.4×10^6	34.9
1,2,3-Trichlorobenzene	18.3×10^5	14.8×10^5	16.1×10^5	16.1×10^5	16.8×10^5	16.6×10^5	15.6×10^5	16.3×10^5	6.7
Hexachlorocyclopentadiene	5.6×10^6	7.6×10^6	7.5×10^6	7.4×10^6	8.1×10^6	7.9×10^6	8.7×10^6	7.5×10^6	12.9
1,2,4,5-Tetrachlorobenzene[b]	8.4×10^5	9.5×10^5	10.3×10^5	10.1×10^5	11.8×10^5	11.4×10^5	11.8×10^5	10.5×10^5	12.2
1,2,3,5-Tetrachlorobenzene[b]	8.4×10^5	9.5×10^5	10.3×10^5	10.1×10^5	11.8×10^5	11.4×10^5	11.8×10^5	10.5×10^5	12.2
1,2,3,4-Tetrachlorobenzene	23.0×10^5	26.2×10^5	29.7×10^5	29.3×10^5	27.5×10^5	26.7×10^5	24.8×10^5	26.7×10^5	8.9
2-Chloronaphthalene	2.1×10^4	2.5×10^4	2.5×10^4	2.5×10^4	2.7×10^4	2.7×10^4	$5.6^c \times 10^4$	2.9×10^4	40.4
Pentachlorobenzene	4.2×10^6	4.3×10^6	4.4×10^6	4.4×10^6	4.8×10^6	4.6×10^6	5.0×10^6	4.5×10^6	6.4
Hexachlorobenzene	12.7×10^6	8.9×10^6	9.1×10^6	8.8×10^6	10.2×10^6	10.9×10^6	12.1×10^6	10.4×10^6	15.2
alpha-BHC	8.3×10^6	9.4×10^6	8.2×10^6	7.5×10^6	6.5×10^6	6.2×10^6	5.7×10^6	7.4×10^6	17.9
gamma-BHC	11.0×10^6	11.1×10^6	9.2×10^6	8.4×10^6	7.3×10^6	6.9×10^6	6.2×10^6	8.6×10^6	22.6
beta-BHC	3.3×10^6	3.5×10^6	4.2×10^6	4.2×10^6	4.0×10^6	3.9×10^6	3.6×10^6	3.8×10^6	9.3
delta-BHC	9.8×10^6	10.7×10^6	9.1×10^6	8.3×10^6	7.2×10^6	6.9×10^6	6.2×10^6	9.7×10^6	37.6

[a,b]These pairs cannot be resolved on the DB-210 fused-silica capillary column.
[c]Peak not integrated correctly.

TABLE 45. MULTILEVEL CALIBRATION DATA FOR STANDARDS ANALYZED ON 6/30/87 AND 7/1/87

Compound	Response factor							Average	Percent RSD
	0.01 to 2.0 ng/µL	0.02 to 4.0 ng/µL	0.04 to 8.0 ng/µL	0.05 to 10.0 ng/µL	0.07 to 14.0 ng/µL	0.08 to 16.0 ng/µL	0.1 to 20.0 ng/µL		
Hexachloroethane	29.7×10^6	36.3×10^6	34.4×10^6	32.6×10^6	28.6×10^6	27.1×10^6	26.5×10^6	30.7×10^6	12.2
1,3-Dichlorobenzene	9.9×10^3	10.1×10^3	10.1×10^3	10.5×10^3	11.4×10^3	11.8×10^3	12.8×10^3	10.9×10^3	9.9
1,4-Dichlorobenzene	2.4×10^4	2.5×10^4	2.7×10^4	2.9×10^4	3.2×10^4	3.4×10^4	3.9×10^4	3.0×10^4	17.8
1,2-Dichlorobenzene	7.5×10^4	8.9×10^4	10.8×10^4	11.6×10^4	11.6×10^4	11.5×10^4	12.3×10^4	10.6×10^4	16.4
Benzyl chloride	7.1×10^4	8.2×10^4	9.84×10^4	10.6×10^4	10.8×10^4	10.7×10^4	11.7×10^4	9.8×10^4	16.6
1,3,5-Trichlorobenzene	4.6×10^5	4.9×10^5	5.2×10^5	5.5×10^5	5.8×10^5	6.0×10^5	6.7×10^5	5.5×10^5	12.9
Hexachlorobutadiene	13.7×10^6	15.4×10^6	17.4×10^6	18.3×10^6	18.4×10^6	18.3×10^6	19.2×10^6	17.2×10^6	11.5
Benzal chloride[a]	18.4×10^5	21.0×10^5	19.8×10^5	18.4×10^5	16.3×10^5	15.4×10^5	15.0×10^5	17.8×10^5	12.7
1,2,4-Trichlorobenzene[a]	18.4×10^5	21.0×10^5	19.8×10^5	18.4×10^5	16.3×10^5	15.4×10^5	15.0×10^5	17.8×10^5	12.7
Benzotrichloride	13.3×10^6	10.7×10^6	7.9×10^6	7.1×10^6	5.9×10^6	5.5×10^6	5.1×10^6	7.9×10^6	38.4
1,2,3-Trichlorobenzene	13.3×10^5	14.0×10^5	15.5×10^5	16.5×10^5	16.3×10^5	16.1×10^5	17.4×10^5	15.6×10^5	9.3
Hexachlorocyclopentadiene	8.2×10^6	7.6×10^6	7.6×10^6	8.0×10^6	8.7×10^6	9.1×10^6	10.3×10^6	8.5×10^6	9.1
1,2,4,5-Tetrachlorobenzene[b]	8.1×10^5	8.2×10^5	8.4×10^5	8.9×10^5	9.1×10^5	9.2×10^5	10.1×10^5	8.9×10^5	7.9
1,2,3,5-Tetrachlorobenzene[b]	8.1×10^5	8.2×10^5	8.4×10^5	8.9×10^5	9.1×10^5	9.2×10^5	10.1×10^5	8.9×10^5	7.9
1,2,3,4-Tetrachlorobenzene	21.1×10^5	23.9×10^5	25.9×10^5	26.2×10^5	24.8×10^5	24.0×10^5	24.6×10^5	24.4×10^5	6.9
2-Chloronaphthalene	2.3×10^4	2.4×10^4	2.6×10^4	2.8×10^4	2.9×10^4	3.0×10^4	3.4×10^4	2.8×10^4	13.5
Pentachlorobenzene	4.6×10^6	4.7×10^6	4.8×10^6	5.0×10^6	5.2×10^6	5.3×10^6	5.6×10^6	5.1×10^6	7.0
Hexachlorobenzene	15.1×10^6	10.4×10^6	11.1×10^6	10.5×10^6	12.1×10^6	12.1×10^6	14.1×10^6	12.2×10^6	14.7
alpha-BHC	12.0×10^6	10.6×10^6	8.6×10^6	8.6×10^6	6.7×10^6	7.1×10^6	6.5×10^6	8.6×10^6	24.1
beta-BHC	6.2×10^6	5.3×10^6	5.6×10^6	5.3×10^6	4.9×10^6	4.9×10^6	4.5×10^6	5.2×10^6	10.6
gamma-BHC	16.8×10^6	14.0×10^6	10.9×10^6	9.7×10^6	8.3×10^6	7.9×10^6	7.1×10^6	10.7×10^6	33.2
delta-BHC	13.3×10^6	12.7×10^6	10.4×10^6	9.6×10^6	8.4×10^6	8.3×10^6	7.5×10^6	10.0×10^6	22.4

[a,b]These pairs cannot be resolved on the DB-210 fused-silica capillary column.

TABLE 46. MULTILEVEL CALIBRATION DATA FOR THE METHOD 8120 COMPOUNDS ANALYZED ON THE DB-WAX FUSED-SILICA CAPILLARY COLUMN

Compound	RRT						Average RRT	Percent RSD
	Std. 1	Std. 2	Std. 3	Std. 4	Std. 5	Std. 6		
Hexachloroethane	0.4383	0.4377	0.4377	0.4377	0.4377	0.4380	0.4379	0.06
1,3-Dichlorobenzene	0.4167	0.4167	0.4167	0.4167	0.4167	0.4169	0.4167	0.02
1,4-Dichlorobenzene	0.4577	0.4571	0.4577	0.4577	0.4577	0.4579	0.4576	0.06
1,2-Dichlorobenzene	0.5164	0.5164	0.5164	0.5164	0.5164	0.5162	0.5164	0.02
Benzyl chloride[c]	0.5590	0.5585	0.5580	0.5590	0.5585	0.5593	0.5587	0.08
1,3,5-Trichlorobenzene[c]	0.5590	0.5585	0.5580	0.5590	0.5585	0.5593	0.5587	0.08
Hexachlorobutadiene	0.5380	0.5375	0.5375	0.5375	0.5375	0.5378	0.5376	0.04
Benzal chloride	0.8577	0.8577	0.8577	0.8577	0.8571	0.8581	0.8577	0.04
1,2,4-Trichlorobenzene	0.7407	0.7396	0.7407	0.7407	0.7407	0.7411	0.7406	0.07
Benzotrichloride	0.8318	0.8323	0.8323	0.8318	0.8318	0.8323	0.8321	0.03
1,2,3-Trichlorobenzene	0.8625	0.8631	0.8625	0.8620	0.8625	0.8630	0.8626	0.05
Hexachlorocyclopentadiene	0.5380	0.5375	0.5375	0.5375	0.5375	0.5378	0.5376	0.04
1,2,4,5-Tetrachlorobenzene	0.9601	0.9590	0.9596	0.9596	0.9596	0.9601	0.9597	0.04
1,2,3,5-Tetrachlorobenzene	0.9434	0.9429	0.9429	0.9429	0.9429	0.9439	0.9432	0.04
1,2,3,4-Tetrachlorobenzene	1.1412	1.1412	1.1407	1.1407	1.1407	1.1419	1.1411	0.04
2-Chloronaphthalene[d]	1.2803	1.2798	1.2803	1.2803	1.2803	1.2816	1.2804	0.05
Pentachlorobenzene[d]	1.2803	1.2798	1.2803	1.2803	1.2803	1.2816	1.2804	0.05
Hexachlorobenzene	1.5720	1.5720	1.5714	1.5709	1.5720	1.5728	1.5719	0.04
alpha-BHC	b	b	b	b	b	b	b	b
gamma-BHC	b	b	b	b	b	b	b	b
beta-BHC	b	b	b	b	b	b	b	b
delta-BHC	b	b	b	b	b	b	b	b

[a]Internal standard is 2,5-dibromotoluene; analyses were performed on November 25, 1987.
[b]Not able to chromatograph the BHCs on the DB-WAX fused-silica capillary column.
[c,d]These pairs cannot be resolved on the DB-WAX fused-silica capillary column.

TABLE 47. ACCURACY AND PRECISION DATA FOR METHODS 3510 AND 8120 (WITHOUT CLEANUP) USING SPIKED REAGENT WATER

Compound	Spike level (µg/L)	Average recovery[a,b] (percent)	Precision (percent RSD)
Hexachloroethane	1.0	96	4.0
1,3-Dichlorobenzene	100	87	8.7
1,4-Dichlorobenzene	100	89	8.9
1,2-Dichlorobenzene	100	92	5.7
Benzyl chloride	100	90	6.2
1,3,5-Trichlorobenzene	10	93	6.2
Hexachlorobutadiene	1.0	95	3.6
Benzal chloride[c] 1,2,4-Trichlorobenzene[c]	10	95	3.0
Benzotrichloride	1.0	97	2.1
1,2,3-Trichlorobenzene	10	95	4.4
Hexachlorocyclopentadiene	10	97	5.1
1,2,4,5-Tetrachlorobenzene[d] 1,2,3,5-Tetrachlorobenzene[d]	10	94	6.0
1,2,3,4-Tetrachlorobenzene	10	96	3.4
2-Chloronaphthalene	200	91	6.5
Pentachlorobenzene	1.0	89	6.5
Hexachlorobenzene	1.0	92	7.1
alpha-BHC	10	96	2.6
gamma-BHC	10	96	2.8
beta-BHC	10	103	3.6
delta-BHC	10	103	2.7
Surrogate recovery (percent)			
α,2,6-Trichlorotoluene	1.0	85	6.5
1,4-Dichloronaphthalene	10	78	6.1
2,3,4,5,6-Pentachlorotoluene	1.0	80	5.9

[a]Number of determinations is 5.
[b]Final volume of extract is 10 mL.
[c,d]These pairs cannot be resolved on the DB-210 fused-silica capillary column.

TABLE 48. ACCURACY AND PRECISION DATA FOR METHODS 3550 AND 8120 (WITHOUT CLEANUP) USING SPIKED SANDY LOAM SOIL

Compound	Spike level (ng/g)	Average recovery[a,b] (percent)	Precision (percent RSD)
Hexachloroethane	330	83	4.6
1,3-Dichlorobenzene	33,000	81	12.6
1,4-Dichlorobenzene	33,000	89	11.0
1,2-Dichlorobenzene	33,000	84	7.1
Benzyl chloride	33,000	121	5.9
1,3,5-Trichlorobenzene	3,000	75	5.3
Hexachlorobutadiene	330	83	4.7
Benzal chloride[c]	3,300	89	2.7
1,2,4-Trichlorobenzene[c]			
Benzotrichloride	3,300	90	2.9
1,2,3-Trichlorobenzene	3,300	79	4.3
Hexachlorocyclopentadiene	330	44	25.9
1,2,4,5-Tetrachlorobenzene[d]	3,300	80	4.4
1,2,3,5-Tetrachlorobenzene[d]			
1,2,3,4-Tetrachlorobenzene	3,300	88	2.9
2-Chloronaphthalene	66,000	100	6.4
Pentachlorobenzene	330	81	3.5
Hexachlorobenzene	330	81	3.2
alpha-BHC	3,300	100	2.9
gamma-BHC	3,300	99	4.1
beta-BHC	3,300	92	2.4
delta-BHC	3,300	97	1.5
Surrogate recovery (percent)			
α,2,6-Trichlorotoluene	330	86	2.7
1,4-Dichloronaphthalene	3,300	88	4.5
2,3,4,5,6-Pentachlorotoluene	330	98	11.7

[a]Number of determinations is 5.
[b]Final volume of extract is 10 mL.
[c,d]These pairs cannot be resolved on the DB-210 fused-silica capillary column.

TABLE 49. METHOD PRECISION AND ACCURACY FOR THE LOVE CANAL SOIL (MATRIX 10)

Compound	Spike level[a] (ng/g)	Average[b]	RSD (percent)	Spike level[a] (ng/g)	Average[b]	RSD (percent)	Spike level[a] (ng/g)	Average[b]	RSD (percent)	Spike level[a] (ng/g)	Average[c]	RSD (percent)
Hexachloroethane	5.4	93.0	3.9	27	57.3	1.0	54	47.0	4.3	110	71.3	14
1,3-Dichlorobenzene	540	75.0	4.8	2,700	50.7	1.0	5,400	37.3	5.6	10,800	49.3	20
1,4-Dichlorobenzene	540	202[d]	61	2,700	69.3	22	5,400	65.7	17.0	10,800	100	21
1,2-Dichlorobenzene	540	87.7	36	2,700	62.7	4.9	5,400	58.0	4.6	10,800	63.8	17
Benzylchloride	540	61.0	2.8	2,700	68.3	14	5,400	63.3	11	10,800	62.8	21
1,3,5-Trichlorobenzene	54	123	6.6	270	67.3	12	540	56.0	1.8	1,080	67.0	16
Hexachlorobutadiene	5.4	97.0	3.6	27	62.7	6.0	54	55.7	7.3	110	62.5	18
Benzal chloride[e] 1,2,4-Trichlorobenzene[e]	54	97.3	6.8	270	77.0	6.7	540	62.0	3.2	1,080	62.8	11
Benzotrichloride	54	68.7	3.0	270	67.3	9.6	540	60.0	4.4	1,080	69.5	10
1,2,3-Trichlorobenzene	54	132	22	270	84.7	11	540	47.0	4.3	1,080	59.0	20
Hexachlorocyclopentadiene	5.4	94.3	11	27	74.3	4.1	54	63.7	7.4	110	62.0	11
1,2,4,5-Tetrachlorobenzene[f] 1,2,3,5-Tetrachlorobenzene[f]	54	89.3	9.3	270	76.0	5.3	540	42.3	5.5	1,080	70.5	15
1,2,3,4-Tetrachlorobenzene	54	88.7	5.6	270	79.0	5.8	540	72.3	3.2	1,080	74.3	19
2-Chloronaphthalene	1,080	72.3	0.8	5,400	73.0	4.1	10,800	70.3	0.8	21,600	63.8	9.0
Pentachlorobenzene	5.4	119	10	27	88.3	5.7	54	81.0	3.7	110	61.0	6.3
Hexachlorobenzene	5.4	68.7	15	27	86.7	15	54	82.0	2.4	110	80.8	8.1
alpha-BHC	54	87.7	5.7	270	74.3	8.9	540	87.0	3.0	1,080	90.5	8.7
gamma-BHC	54	87.0	8.1	270	81.7	10	540	83.7	2.5	1,080	92.5	5.6
beta-BHC	54	86.7	6.4	270	82.0	6.3	540	74.0	16	1,080	83.5	10
delta-BHC	54	104	10	270	75.0	8.7	540	71.0	9.9	1,080	90.3	10
Surrogate recovery (percent)												
o,2,6-Trichlorotoluene	54	82.0	3.2	54	79.7	5.7	54	80.7	1.4			
1,4-Dichloronaphthalene	540	76.3	5.5	540	81.7	9.9	540	81.7	4.9			
2,3,4,5,6-Pentachlorotoluene	54	79.7	10.2	54	87.7	5.9	54	87.7	0.6			

[a]Concentrations are given on a dry weight basis.
[b]Thirty grams of wet soil (moisture content is 38.4 percent) were spiked individually with 100 µL, 500 µL, or 1,000 µL or a solution containing 1 to 200 µg/mL of the Method 8120 compounds. Three replicates were performed at each concentration. Each extract was cleaned up by Florisil with hexane/acetone (9:1).
[c]Number of replicates is four. Two replicates were done with 30 g wet soil, the other two replicates were done with 15 g wet soil; the final volumes of the Florisil fractions were 20 mL and 10 mL, respectively, to compensate for the fact that the concentrations of Method 8120 compounds in the extracts were different.
[d]High recovery because 1,4-dichlorobenzene was present in the sample at 1,900 ng/g.
[e]These pairs cannot be resolved on the DB-210 fused-silica capillary column.

TABLE 50. METHOD PRECISION AND ACCURACY FOR THE PCB-CONTAMINATED SOIL (MATRIX 11)

Compound	Spike level[a] (ng/g)	Average[b]	RSD (percent)	Spike level[a] (ng/g)	Average[b]	RSD (percent)	Spike level[a] (ng/g)	Average[b]	RSD (percent)
Hexachloroethane	1.3	60.0	17	6.5	59.7	5.4	13	97.0	6.3
1,3-Dichlorobenzene	130	60.0	22	650	56.7	5.4	1,300	65.7	19
1,4-Dichlorobenzene	130			650	107	72	1,300	90.0	8.4
1,2-Dichlorobenzene	130	79.3	23	650	79.3	4.4	1,300	100	17
Benzyl chloride	130	86.3	21	650	77.0	5.7	1,300	106	20
1,3,5-Trichlorobenzene	13	70.0	22	65	73.3	3.4	130	81.7	8.0
Hexachlorobutadiene	1.3	62.0	19	6.5	65.7	3.2	13	76.0	11
1,2,4-Trichlorobenzene[d] Benzal chloride[d]	13	71.0	16	65	78.3	6.4	130	119	6.6
Benzotrichloride	13	58.0	17	65	81.0	12	130	113	19
1,2,3-Trichlorobenzene	13	72.3	11	65	80.7	6.8	130	103	15
Hexachlorocyclopentadiene	1.3	48.7	34	6.5	70.3	4.6	13	71.7	15
1,2,4,5-Tetrachlorobenzene[e] 1,2,3,5-Tetrachlorobenzene[e]	13	71.0	8.5	65	69.0	5.0	130	99.3	14
1,2,3,4-Tetrachlorobenzene	13	80.7	8.4	65	77.3	2.7	130	104	11
2-Chloronaphthalene	260	70.7	9.6	1,300	76.3	0.76	2,600	88.3	0.7
Pentachlorobenzene	1.3	95.3	8.2	6.5	81.3	3.6	13	96.0	8.3
Hexachlorobenzene	1.3	72.3	13	6.5	78.3	3.2	13	99.7	7.8
alpha-BHC	13	c							
gamma-BHC	13	c							
beta-BHC	13	c							
delta-BHC	13	c							
Surrogate recovery (percent)									
o,2,6-Trichlorotoluene	13	79.3	13.5	13	76.7	3.3	13	95.3	0.6
1,4-Dichloronaphthalene	130	79.3	9.6	130	69.7	3.3	130	90.0	11.1
2,3,4,5,6-Pentachlorotoluene	13	85	10.5	13	78.3	3.2	13	98.3	6.5

[a]Concentrations are given on a dry weight basis.
[b]Thirty grams of wet soil (moisture content is 38.4 percent) were spiked individually with 100 µL, 500 µL, or 1,000 µL or a solution containing 1 to 200 µg/mL of the Method 8120 compounds. Three replicates were performed at each concentration. Each extract was cleaned up by Florisil with hexane/acetone (9:1).
[c]BHC isomers could not be determined because Matrix 11 was highly contaminated with PCBs which overlap with the BHC isomers on the DB-210 fused-silica capillary column.
[d,e]These pairs cannot be resolved on the DB-210 fused silica capillary column.

TABLE 51. RECOVERIES OF THE METHOD 8120 COMPOUNDS FOUND IN THE SPIKED LOAM SOIL EXTRACT AFTER FLORISIL CARTRIDGE CLEANUP (MATRIX 1)

Compound	Spike level (ng/µL of extract)[b]	Recovery (percent)[a] DB-210	DB-WAX
Hexachloroethane	0.1	88	77
1,3-Dichlorobenzene	10	86	79
1,4-Dichlorobenzene	10	93	78
1,2-Dichlorobenzene	10	98	79
Benzyl chloride	10	96	74
1,3,5-Trichlorobenzene	1	92	74
Hexachlorobutadiene	0.1	83	74
Benzal chloride[c] 1,2,4-Trichlorobenzene[c]	1	140	82
Benzotrichloride	1	88	76
1,2,3-Trichlorobenzene	1	103	96
Hexachlorocyclopentadiene	0.1	36	74
1,2,4,5-Tetrachlorobenzene[d] 1,2,3,5-Tetrachlorobenzene[d]	1	86	83
1,2,3,4-Tetrachlorobenzene	1	104	84
2-Chloronaphthalene	20	90	87
Pentachlorobenzene	0.1	90	87
Hexachlorobenzene	0.1	99	89
alpha-BHC	1	102	a
gamma-BHC	1	105	a
beta-BHC	1	95	a
delta-BHC	1	110	a
Surrogate recovery (percent)			
α,2,6-Trichlorotoluene	0.1	106	80
1,4-Dichloronaphthalene	1	e	74
2,3,4,5,6-Pentachlorotoluene	0.1	87	66

[a]Not able to chromatograph the BHC isomers on the DB-WAX column.
[b]The sandy loam soil sample was first extracted with methylene chloride/acetone (1:1) using Method 3550. A portion of the extract, after solvent exchange, was spiked with the Method 8120 compounds and the surrogates and subjected to Florisil cartridge cleanup.
[c,d]These pairs cannot be resolved on the DB-210 fused-silica capillary column.
[e]Recovery not determined because of matrix interference.

TABLE 52. RECOVERIES OF THE METHOD 8120 COMPOUNDS FOUND IN THE SPIKED PGN-1B SHELL SAMPLE EXTRACT AFTER FLORISIL CARTRIDGE CLEANUP (MATRIX 2)

Compound	Spike level (ng/µL of extract)[b]	Recovery (percent)[a] DB-210	DB-WAX
Hexachloroethane	0.1	79	70
1,3-Dichlorobenzene	10	71	71
1,4-Dichlorobenzene	10	78	70
1,2-Dichlorobenzene	10	84	72
Benzyl chloride	10	96	70
1,3,5-Trichlorobenzene	1	75	70
Hexachlorobutadiene	0.1	65	66
Benzal chloride[c] 1,2,4-Trichlorobenzene[c]	1	102	78
Benzotrichloride	1	84	70
1,2,3-Trichlorobenzene	1	89	82
Hexachlorocyclopentadiene	0.1	31	66
1,2,4,5-Tetrachlorobenzene[d] 1,2,3,5-Tetrachlorobenzene[d]	1	70	74
1,2,3,4-Tetrachlorobenzene	1	80	75
2-Chloronaphthalene	20	78	82
Pentachlorobenzene	0.1	76	82
Hexachlorobenzene	0.1	76	83
alpha-BHC	1	98	a
gamma-BHC	1	98	a
beta-BHC	1	85	a
delta-BHC	1	114	a
Surrogate recovery (percent)			
α,2,6-Trichlorotoluene	0.1	82	73
1,4-Dichloronaphthalene	1	e	67
2,3,4,5,6-Pentachlorotoluene	0.1	70	62

[a]Not able to chromatograph the BHC isomers on the DB-WAX column.
[b]The PGN-1B Shell sample was first extracted with methylene chloride/acetone (1:1) using Method 3550. A portion of the extract, after solvent exchange, was spiked with the Method 8120 compounds and the surrogates and subjected to Florisil cartridge cleanup.
[c,d]These pairs cannot be resolved on the DB-210 fused-silica capillary column.
[e]Recovery not determined because of matrix interference.

TABLE 53. RECOVERIES OF THE METHOD 8120 COMPOUNDS FOUND IN THE SPIKED PINE NEEDLE NBS SRM-1575 SAMPLE EXTRACT AFTER FLORISIL CARTRIDGE CLEANUP (MATRIX 3)

Compound	Spike level (ng/µL of extract)[b]	Recovery (percent)[a] DB-210	DB-WAX
Hexachloroethane	0.1	72	73
1,3-Dichlorobenzene	10	68	81
1,4-Dichlorobenzene	10	65	80
1,2-Dichlorobenzene	10	79	84
Benzyl chloride	10	83	77
1,3,5-Trichlorobenzene	1	67	77
Hexachlorobutadiene	0.1	59	71
Benzal chloride[c]			
1,2,4-Trichlorobenzene[c]	1	95	109
Benzotrichloride	1	76	68
1,2,3-Trichlorobenzene	1	81	64
Hexachlorocyclopentadiene	0.1	46	71
1,2,4,5-Tetrachlorobenzene[d]			
1,2,3,5-Tetrachlorobenzene[d]	1	76	85
1,2,3,4-Tetrachlorobenzene	1	78	88
2-Chloronaphthalene	20	100	94
Pentachlorobenzene	0.1	85	94
Hexachlorobenzene	0.1	78	92
alpha-BHC	1	93	a
gamma-BHC	1	91	a
beta-BHC	1	65	a
delta-BHC	1	114	a
Surrogate recovery (percent)			
α,2,6-Trichlorotoluene	0.1	98	85
1,4-Dichloronaphthalene	1	e	85
2,3,4,5,6-Pentachlorotoluene	0.1	86	81

[a]Not able to chromatograph the BHC isomers on the DB-WAX column.
[b]The pine needle NBS SRM-1575 sample was first extracted with methylene chloride/acetone (1:1) using Method 3550. A portion of the extract, after solvent exchange, was spiked with the Method 8120 compounds and the surrogates and subjected to Florisil cartridge cleanup.
[c,d]These pairs cannot be resolved on the DB-210 fused-silica capillary column.
[e]Recovery not determined because of matrix interference.

TABLE 54. RECOVERIES OF THE METHOD 8120 COMPOUNDS FOUND IN THE SPIKED RIVER SEDIMENT NBS SRM-1645 SAMPLE EXTRACT AFTER FLORISIL CARTRIDGE CLEANUP (MATRIX 4)

Compound	Spike level (ng/μL of extract)[b]	Recovery (percent)[a] DB-210	DB-WAX
Hexachloroethane	0.1	70	60
1,3-Dichlorobenzene	10	57	66
1,4-Dichlorobenzene	10	59	65
1,2-Dichlorobenzene	10	67	67
Benzyl chloride	10	84	68
1,3,5-Trichlorobenzene	1	63	68
Hexachlorobutadiene	0.1	60	64
Benzal chloride[c]	1	85	73
1,2,4-Trichlorobenzene[c]			
Benzotrichloride	1	80	67
1,2,3-Trichlorobenzene	1	74	75
Hexachlorocyclopentadiene	0.1	23	64
1,2,4,5-Tetrachlorobenzene[d]	1	59	70
1,2,3,5-Tetrachlorobenzene[d]			
1,2,3,4-Tetrachlorobenzene	1	b	71
2-Chloronaphthalene	20	b	81
Pentachlorobenzene	0.1	70	81
Hexachlorobenzene	0.1	190	136
alpha-BHC	1	99	a
gamma-BHC	1	107	a
beta-BHC	1	105	a
delta-BHC	1	73	a
Surrogate recovery (percent)			
α,2,6-Trichlorotoluene	0.1	e	76
1,4-Dichloronaphthalene	1	e	86
2,3,4,5,6-Pentachlorotoluene	0.1	e	66

[a]Not able to chromatograph the BHC isomers on the DB-WAX column.
[b]The river sediment NBS SRM-1645 sample was first extracted with methylene chloride/acetone (1:1) using Method 3550. A portion of the extract, after solvent exchange, was spiked with the Method 8120 compounds and the surrogates and subjected to Florisil cartridge cleanup.
[c,d]These pairs cannot be resolved on the DB-210 fused-silica capillary column.
[e]Recovery not determined because of matrix interference.

TABLE 55. RECOVERIES OF THE METHOD 8120 COMPOUNDS FOUND IN THE SPIKED CITRUS LEAVES NBS SRM-1572 SAMPLE EXTRACT AFTER FLORISIL CARTRIDGE CLEANUP (MATRIX 5)

Compound	Spike level (ng/µL of extract)[b]	Recovery (percent)[a] DB-210	DB-WAX
Hexachloroethane	0.1	78	129
1,3-Dichlorobenzene	10	67	142
1,4-Dichlorobenzene	10	120	139
1,2-Dichlorobenzene	10	80	148
Benzyl chloride	10	112	140
1,3,5-Trichlorobenzene	1	46	140
Hexachlorobutadiene	0.1	57	128
Benzal chloride[c] 1,2,4-Trichlorobenzene[c]	1	96	133
Benzotrichloride	1	90	117
1,2,3-Trichlorobenzene	1	70	169
Hexachlorocyclopentadiene	0.1	123	128
1,2,4,5-Tetrachlorobenzene[d] 1,2,3,5-Tetrachlorobenzene[d]	1	50	134
1,2,3,4-Tetrachlorobenzene	1	69	135
2-Chloronaphthalene	20	84	156
Pentachlorobenzene	0.1	58	156
Hexachlorobenzene	0.1	61	165
alpha-BHC	1	99	a
gamma-BHC	1	101	a
beta-BHC	1	85	a
delta-BHC	1	98	a
Surrogate recovery (percent)			
α,2,6-Trichlorotoluene	0.1	88	76
1,4-Dichloronaphthalene	1	78	71
2,3,4,5,6-Pentachlorotoluene	0.1	88	103

[a]Not able to chromatograph the BHC isomers on the DB-WAX column.
[b]The citrus leaves NBS SRM-1572 sample was first extracted with methylene chloride/acetone (1:1) using Method 3550. A portion of the extract, after solvent exchange, was spiked with the Method 8120 compounds and the surrogates and subjected to Florisil cartridge cleanup.
[c,d]These pairs cannot be resolved on the DB-210 fused-silica capillary column.

TABLE 56. RECOVERY OF METHOD 8120 COMPOUNDS FOUND IN THE SPIKED COAL NBS SRM-1632a SAMPLE EXTRACT AFTER FLORISIL CLEANUP (MATRIX 6)

Compound	Spike level (ng/μL of extract)[b]	Recovery (percent)[a] DB-210	DB-WAX
Hexachloroethane	0.1	70	58
1,3-Dichlorobenzene	10	58	67
1,4-Dichlorobenzene	10	59	60
1,2-Dichlorobenzene	10	73	71
Benzyl chloride	10	85	68
1,3,5-Trichlorobenzene	1	59	68
Hexachlorobutadiene	0.1	54	59
Benzal chloride[c]	1	94	101
1,2,4-Trichlorobenzene[c]			
Benzotrichloride	1	75	55
1,2,3-Trichlorobenzene	1	73	86
Hexachlorocyclopentadiene	0.1	28	59
1,2,4,5-Tetrachlorobenzene[d]	1	63	70
1,2,3,5-Tetrachlorobenzene[d]			
1,2,3,4-Tetrachlorobenzene	1	75	85
2-Chloronaphthalene	20	80	80
Pentachlorobenzene	0.1	74	80
Hexachlorobenzene	0.1	67	76
alpha-BHC	1	98	a
gamma-BHC	1	100	a
beta-BHC	1	90	a
delta-BHC	1	75	a
Surrogate recovery (percent)			
α,2,6-Trichlorotoluene	0.1	104	71
1,4-Dichloronaphthalene	1	48	67
2,3,4,5,6-Pentachlorotoluene	0.1	75	65

[a]Not able to chromatograph the BHC isomers on the DB-WAX column.
[b]The coal NBS SRM-1632a sample was first extracted with methylene chloride/acetone (1:1) using Method 3550. A portion of the extract, after solvent exchange, was spiked with the Method 8120 compounds and the surrogates and subjected to Florisil cartridge cleanup.
[c,d]These pairs cannot be resolved on the DB-210 fused-silica capillary column.

TABLE 57. RECOVERIES OF THE METHOD 8120 COMPOUNDS FOUND IN THE SPIKED COAL FLYASH NBS SRM-1633a SAMPLE EXTRACT AFTER FLORISIL CARTRIDGE CLEANUP (MATRIX 7)

Compound	Spike level (ng/μL of extract)[b]	Recovery (percent)[a] DB-210	DB-WAX
Hexachloroethane	0.1	76	65
1,3-Dichlorobenzene	10	69	72
1,4-Dichlorobenzene	10	39	69
1,2-Dichlorobenzene	10	83	73
Benzyl chloride	10	96	74
1,3,5-Trichlorobenzene	1	68	74
Hexachlorobutadiene	1	65	66
Benzal chloride[c]			
1,2,4-Trichlorobenzene[c]	1	103	75
Benzotrichloride	1	82	61
1,2,3-Trichlorobenzene	1	91	79
Hexachlorocyclopentadiene	0.1	35	66
1,2,4,5-Tetrachlorobenzene[d]			
1,2,3,5-Tetrachlorobenzene[d]	1	61	70
1,2,3,4-Tetrachlorobenzene	1	83	72
2-Chloronaphthalene	20	78	77
Pentachlorobenzene	0.1	71	77
Hexachlorobenzene	0.1	78	82
alpha-BHC	1	101	a
gamma-BHC	1	102	a
beta-BHC	1	97	a
delta-BHC	1	100	a
Surrogate recovery (percent)			
α,2,6-Trichlorotoluene	0.1	89	70
1,4-Dichloronaphthalene	1	e	62
2,3,4,5,6-Pentachlorotoluene	0.1	65	60

[a]Not able to chromatograph the BHC isomers on the DB-WAX column.
[b]The coal flyash NBS SRM-1633a samples was first extracted with methylene chloride/acetone (1:1) using Method 3550. A portion of the extract, after solvent exchange, was spiked with the Method 8120 compounds and the surrogates and subjected to Florisil cartridge cleanup.
[c,d]These pairs cannot be resolved on the DB-210 fused-silica capillary column.
[e]Recovery not determined because of matrix interference.

TABLE 58. RECOVERIES OF THE METHOD 8120 COMPOUNDS FOUND IN THE SPIKED DETROIT RIVER SEDIMENT SAMPLE EXTRACT AFTER FLORISIL CARTRIDGE CLEANUP (MATRIX 8)

Compound	Spike level (ng/μL of extract)[b]	Recovery (percent)[a] DB-210	DB-WAX
Hexachloroethane	10	93	70
1,3-Dichlorobenzene	1,000	122	79
1,4-Dichlorobenzene	1,000	111	80
1,2-Dichlorobenzene	1,000	97	78
Benzyl chloride	1,000	97	77
1,3,5-Trichlorobenzene	100	152	77
Hexachlorobutadiene	10	80	69
Benzal chloride[c]			
1,2,4-Trichlorobenzene[c]	100	113	114
Benzotrichloride	100	100	86
1,2,3-Trichlorobenzene	100	113	91
Hexachlorocyclopentadiene	10	272	69
1,2,4,5-Tetrachlorobenzene[d]			
1,2,3,5-Tetrachlorobenzene[d]	100	125	89
1,2,3,4-Tetrachlorobenzene	100	65	87
2-Chloronaphthalene	2,000	94	88
Pentachlorobenzene	10	115	88
Hexachlorobenzene	10	90	87
alpha-BHC	100	98	a
gamma-BHC	100	98	a
beta-BHC	100	92	a
delta-BHC	100	125	a
Surrogate recovery (percent)			
α,2,6-Trichlorotoluene	10	101	83
1,4-Dichloronaphthalene	100	e	74
2,3,4,5,6-Pentachlorotoluene	10	92	69

[a]Not able to chromatograph the BHC isomers on the DB-WAX column.
[b]The Detroit River sediment sample was first extracted with methylene chloride/acetone (1:1) using Method 3550. A portion of the extract, after solvent exchange, was spiked with the Method 8120 compounds and the surrogates and subjected to Florisil cartridge cleanup.
[c,d]These pairs cannot be resolved on the DB-210 fused-silica capillary columns.
[e]Recovery not determined because of matrix interference.

TABLE 59. RECOVERIES OF THE METHOD 8120 COMPOUNDS FOUND IN THE SPIKED BLOODY RUN CREEK SEDIMENT SAMPLE EXTRACT AFTER FLORISIL CARTRIDGE CLEANUP (MATRIX 9)

Compound	Spike level (ng/µL of extract)[b]	Recovery (percent)[a] DB-210	DB-WAX
Hexachloroethane	100	82	66
1,3-Dichlorobenzene	10,000	57	74
1,4-Dichlorobenzene	10,000	87	76
1,2-Dichlorobenzene	10,000	100	77
Benzyl chloride	10,000	91	78
1,3,5-Trichlorobenzene	1,000	59	78
Hexachlorobutadiene	100	85	85
Benzal chloride[c]			
1,2,4-Trichlorobenzene[c]	1,000	104	73
Benzotrichloride	1,000	94	80
1,2,3-Trichlorobenzene	1,000	110	89
Hexachlorocyclopentadiene	100	83	85
1,2,4,5-Tetrachlorobenzene[d]			
1,2,3,5-Tetrachlorobenzene[d]	1,000	77	82
1,2,3,4-Tetrachlorobenzene	1,000	115	69
2-Chloronaphthalene	20,000	85	63
Pentachlorobenzene	100	107	63
Hexachlorobenzene	100	181	78
alpha-BHC	1,000	99	a
gamma-BHC	1,000	99	a
beta-BHC	1,000	96	a
delta-BHC	1,000	99	a
Surrogate recovery (percent)			
α,2,6-Trichlorotoluene	100	106	78
1,4-Dichloronaphthalene	1,000	176	103
2,3,4,5,6-Pentachlorotoluene	100	126	57

[a]Not able to chromatograph the BHC isomers on the DB-WAX column.
[b]The Bloody Run Creek sediment sample was first extracted with methylene chloride/acetone (1:1) using Method 3550. A portion of the extract, after solvent exchange, was spiked with the Method 8120 compounds and the surrogates and subjected to Florisil cartridge cleanup.
[c,d]These pairs cannot be resolved on the DB-210 fused-silica capillary columns.

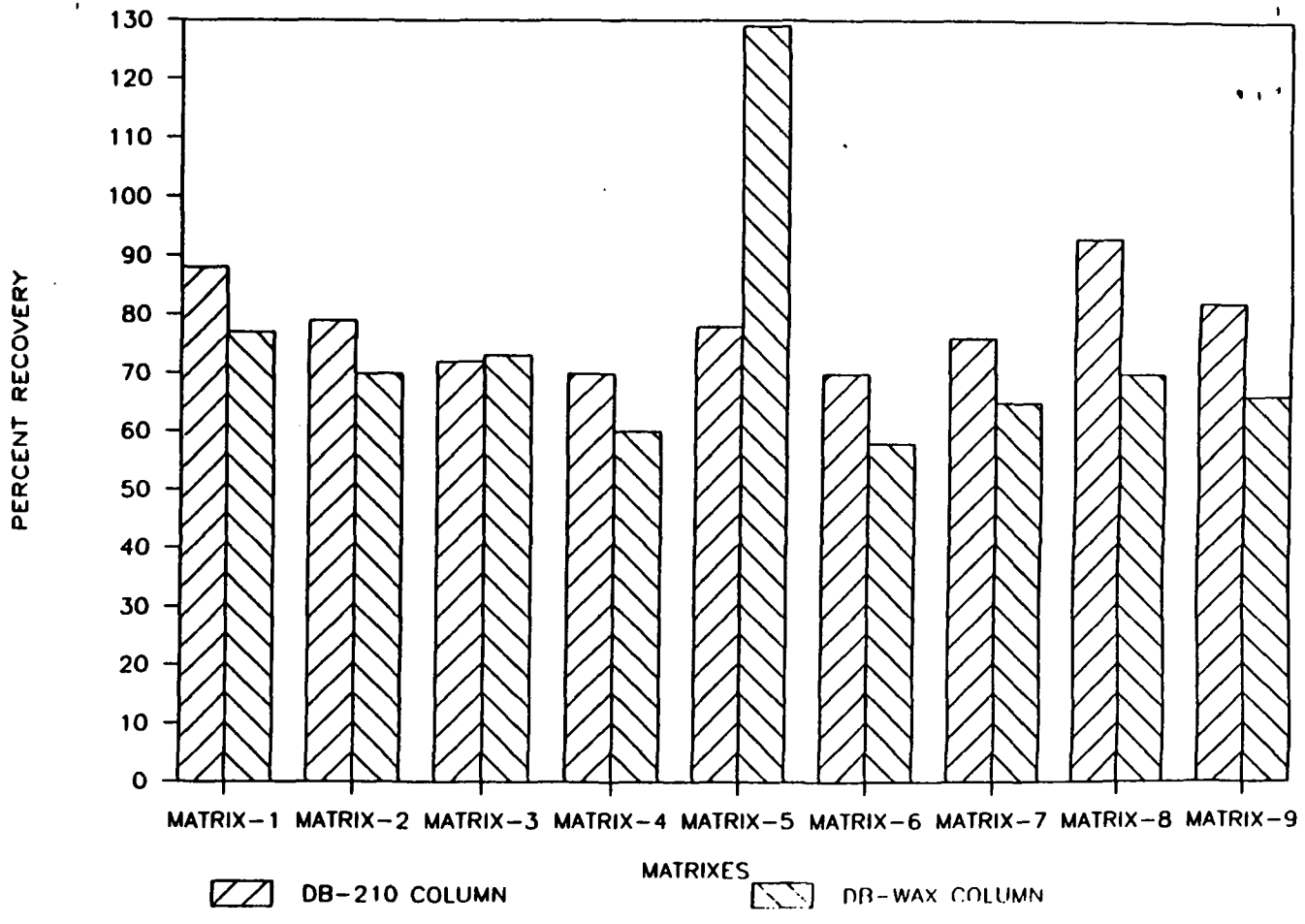

Figure 29. Recovery as a function of matrix for hexachloroethane

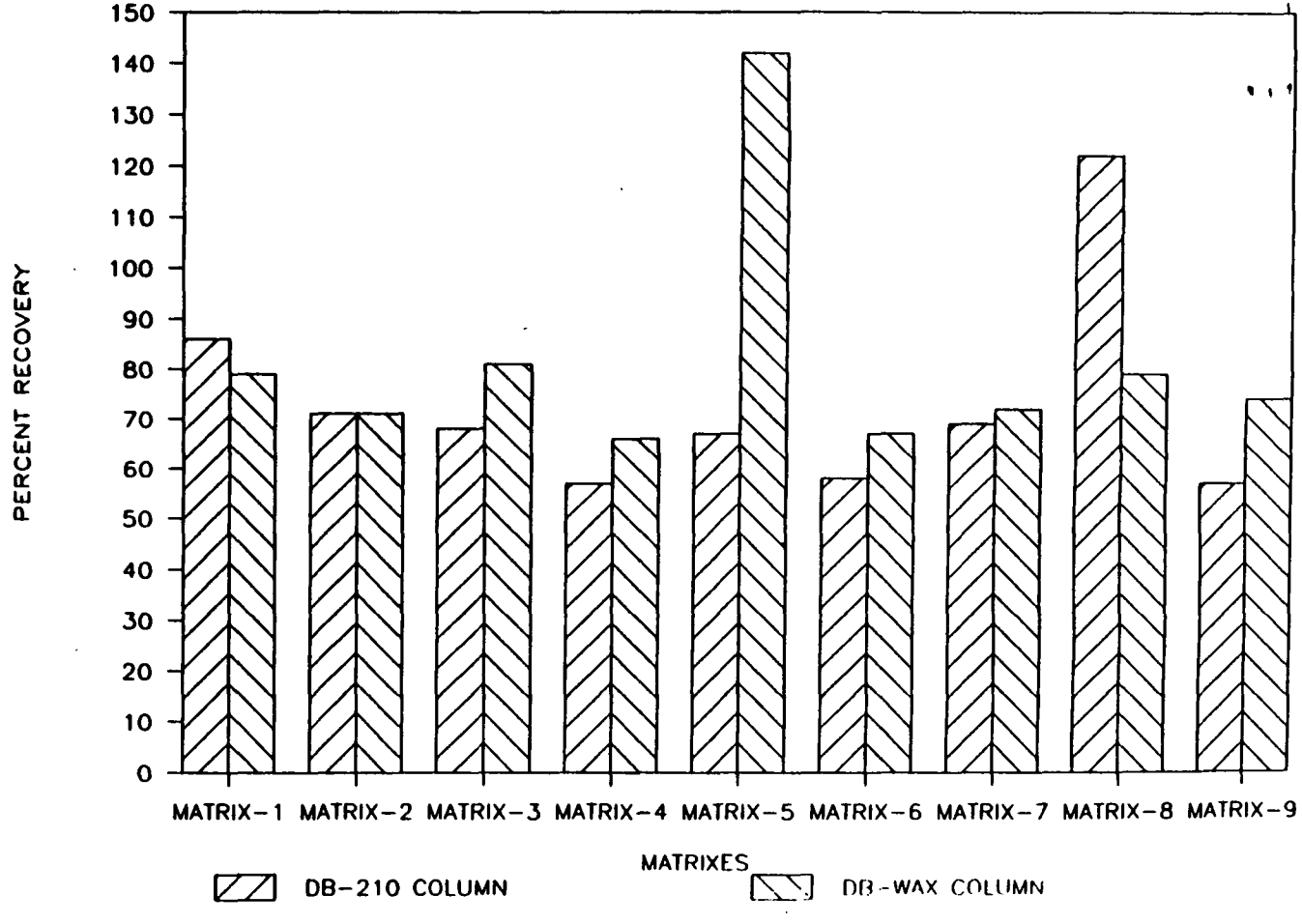

Figure 30. Recovery as a function of matrix for 1,3-dichlorobenzene.

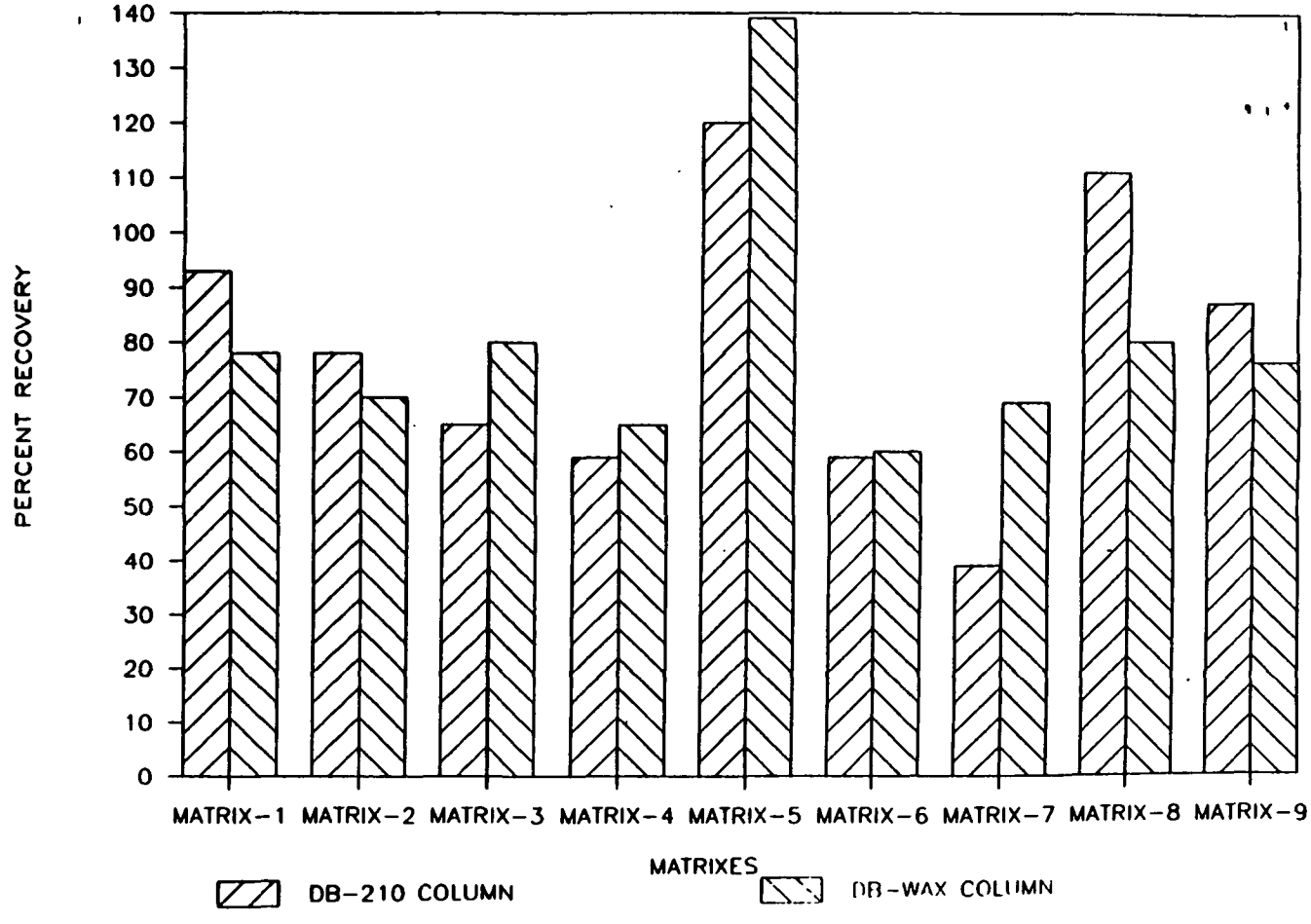

Figure 31. Recovery as a function of matrix for 1,4-dichlorobenzene.

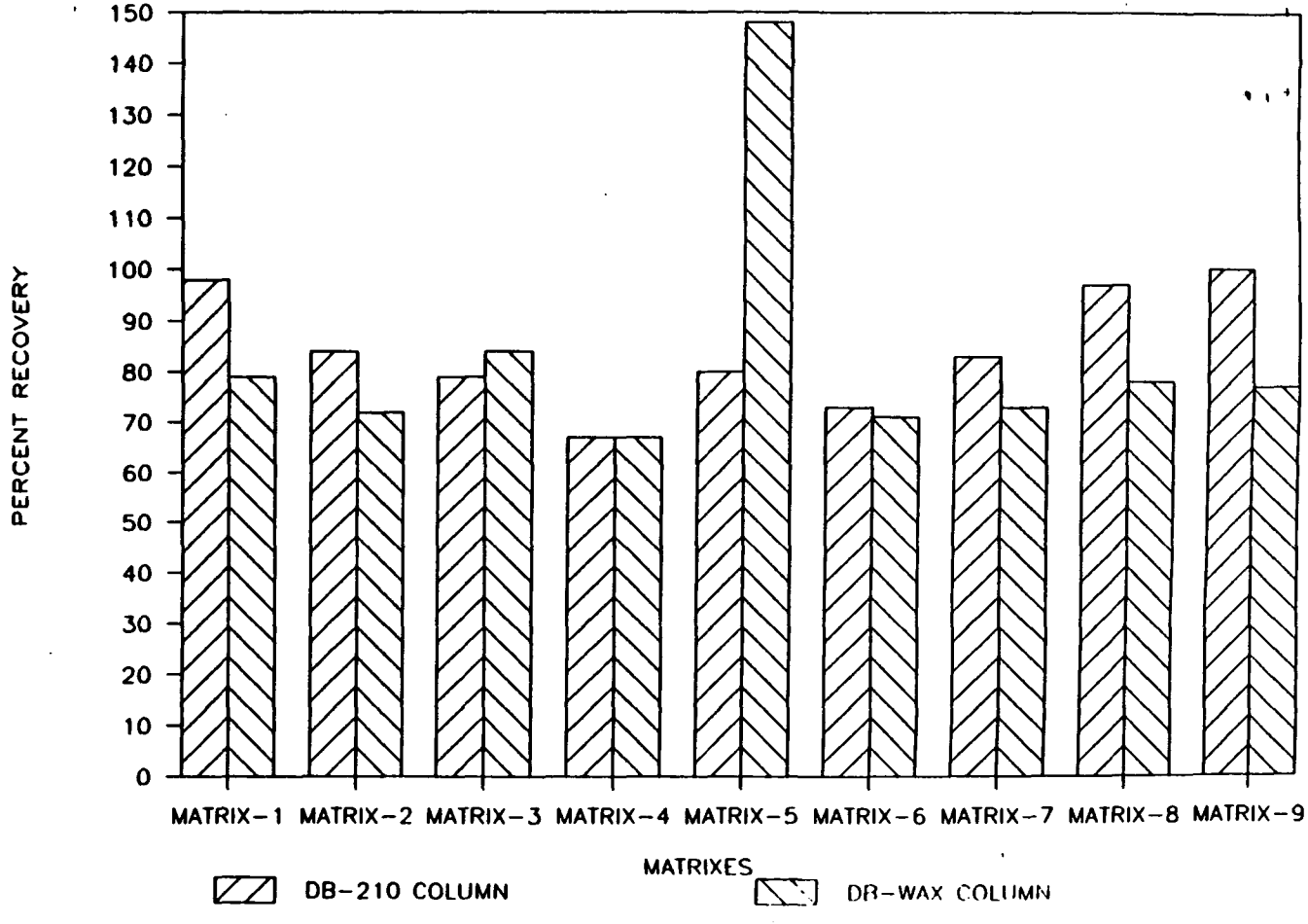

Figure 32. Recovery as a function of matrix for 1,2-dichlorobenzene.

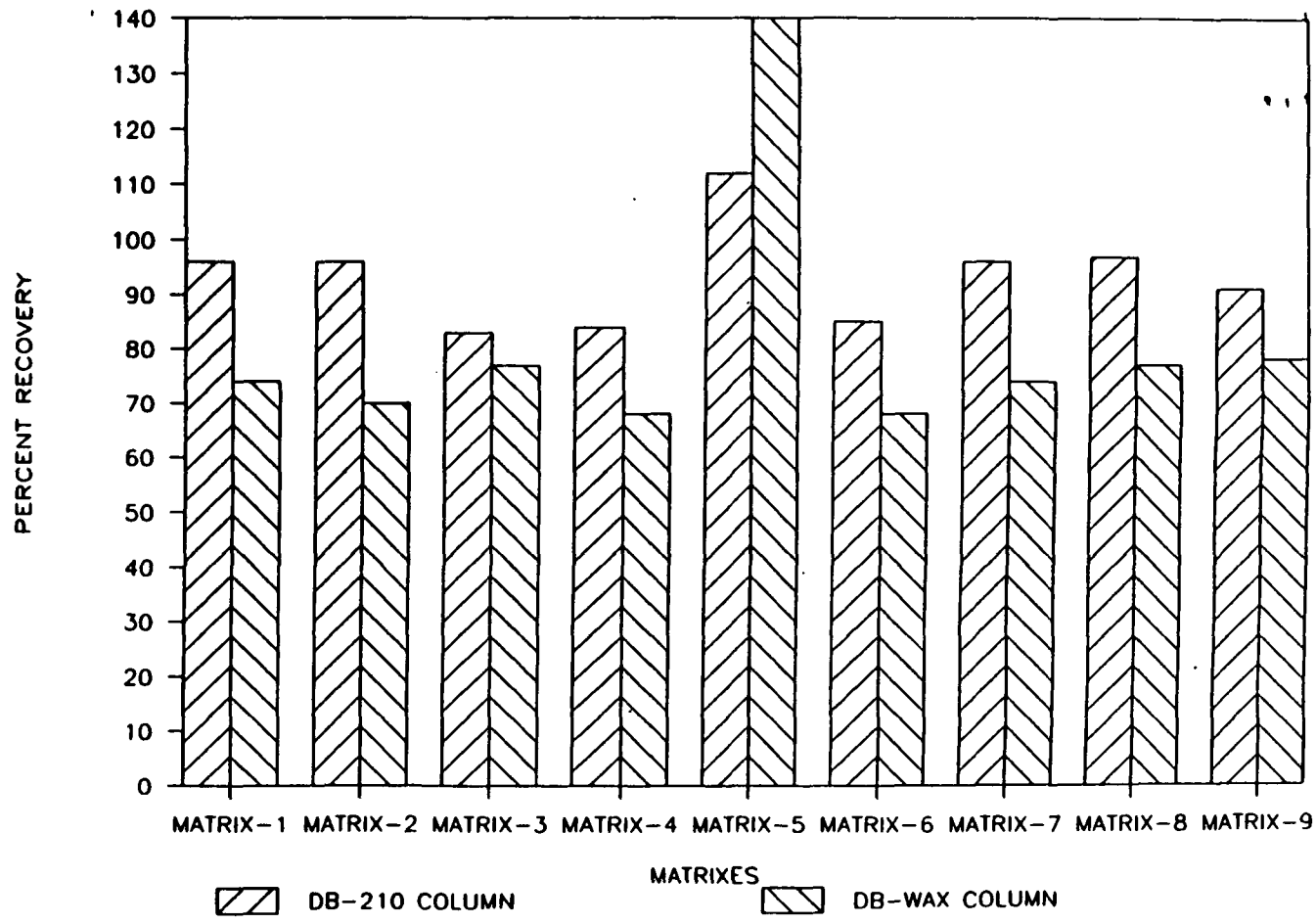

Figure 33. Recovery as a function of matrix for benzyl chloride.

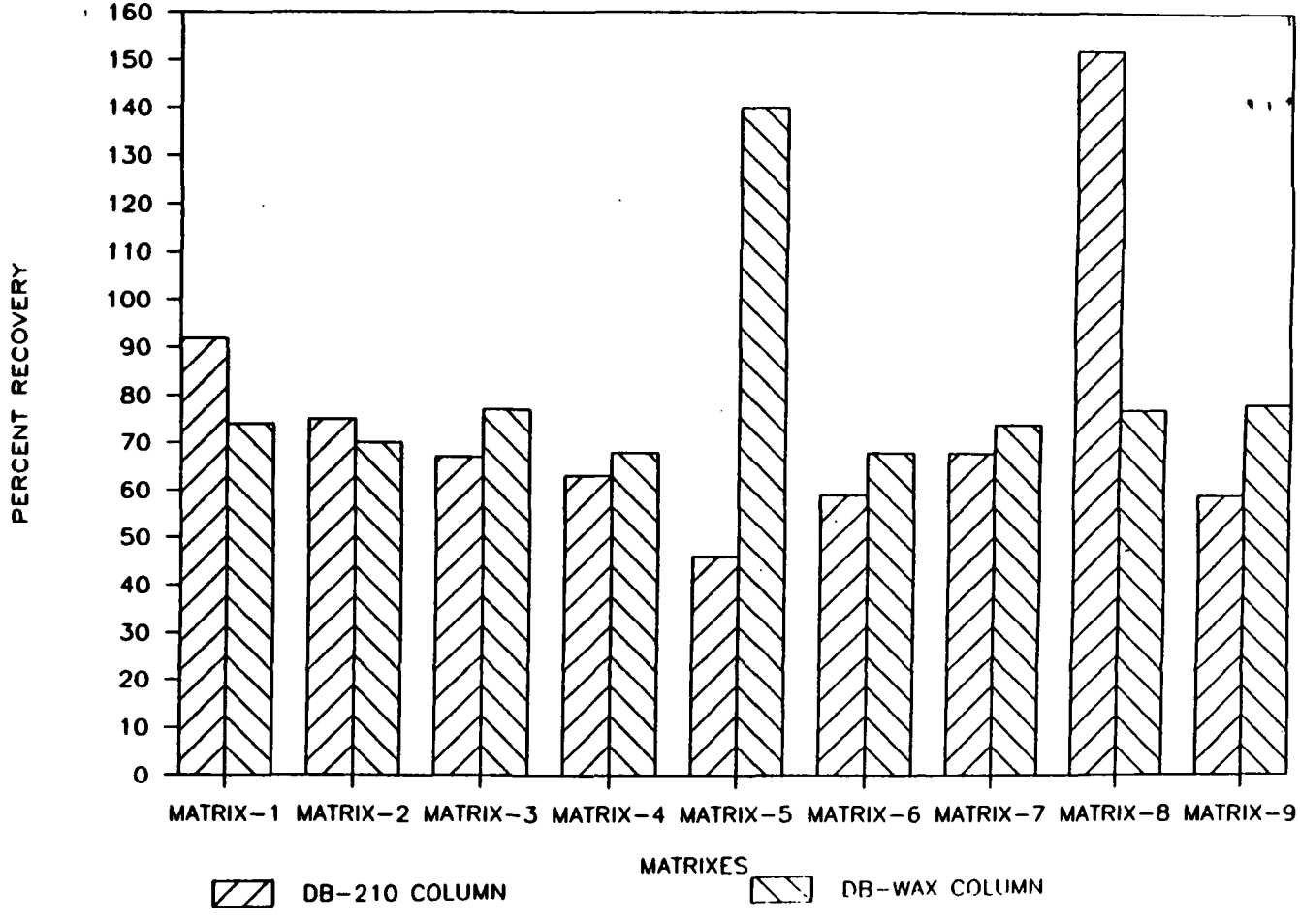

Figure 34. Recovery as a function of matrix for 1,3,5-trichlorobenzene.

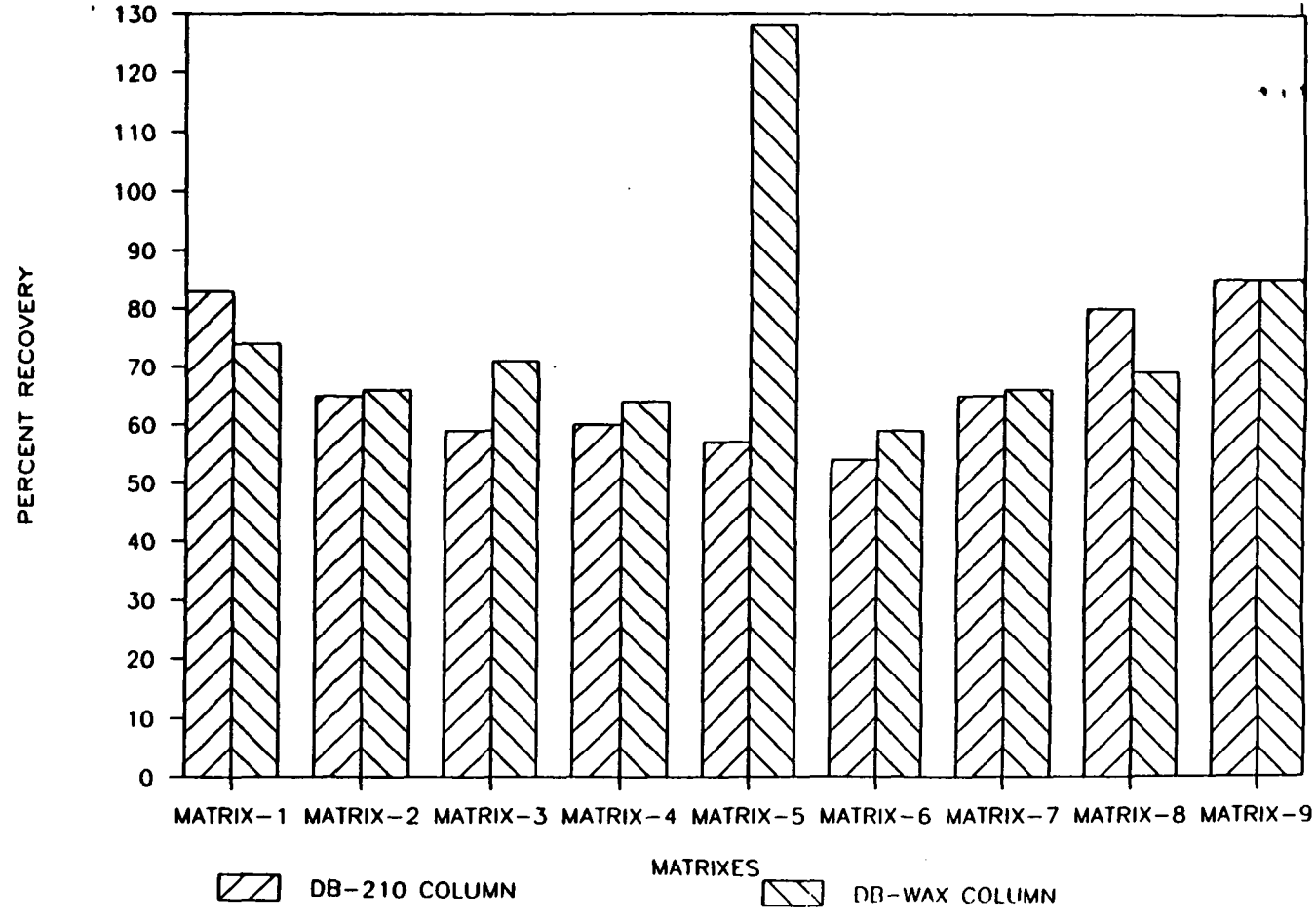

Figure 35. Recovery as a function of matrix for hexachlorobutadiene.

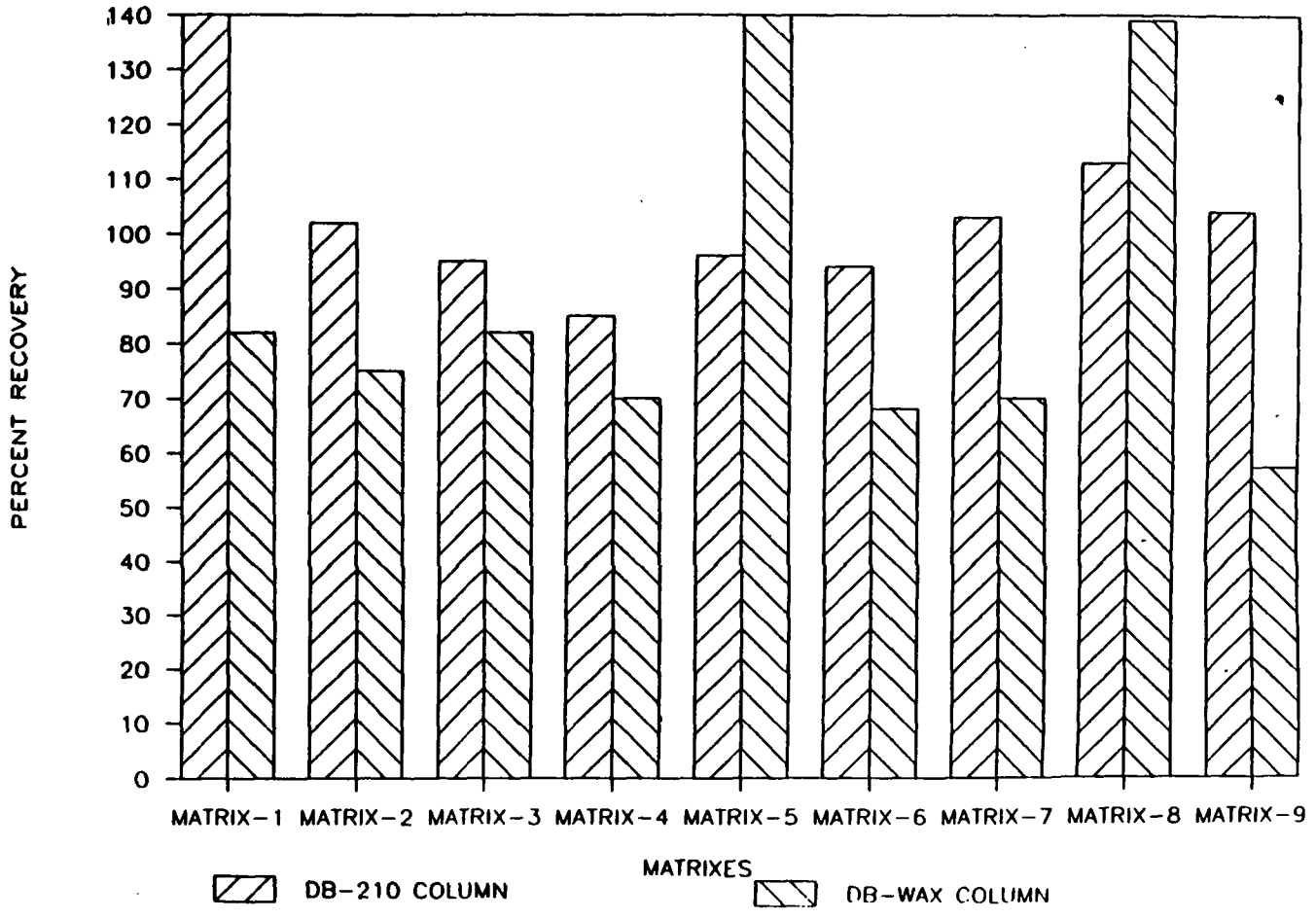

Figure 36. Recovery as a function of matrix for 1,2,4-trichlorobenzene.

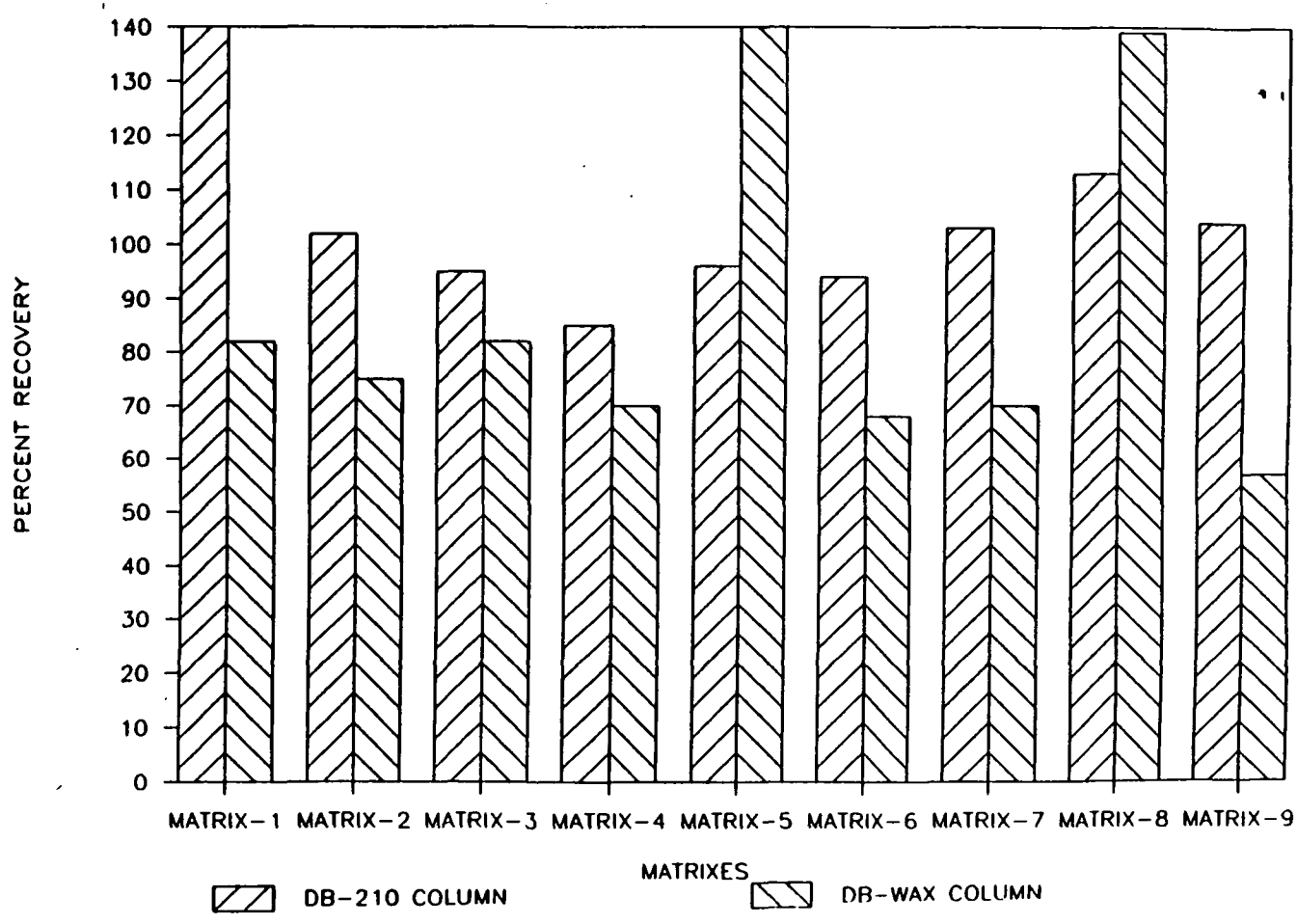

Figure 37. Recovery as a function of matrix for benzal chloride.

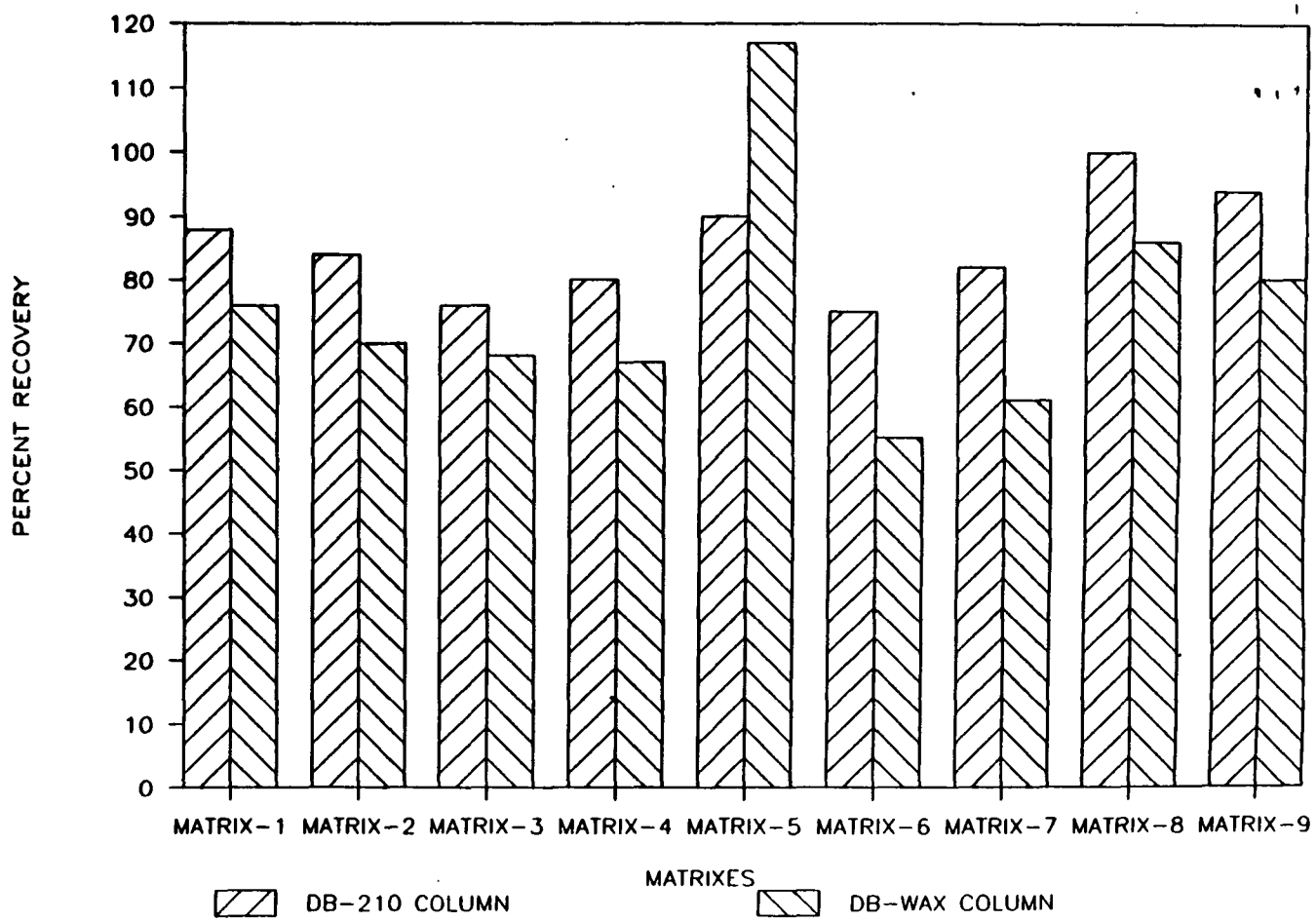

Figure 38. Recovery as a function of matrix for benzotrichloride.

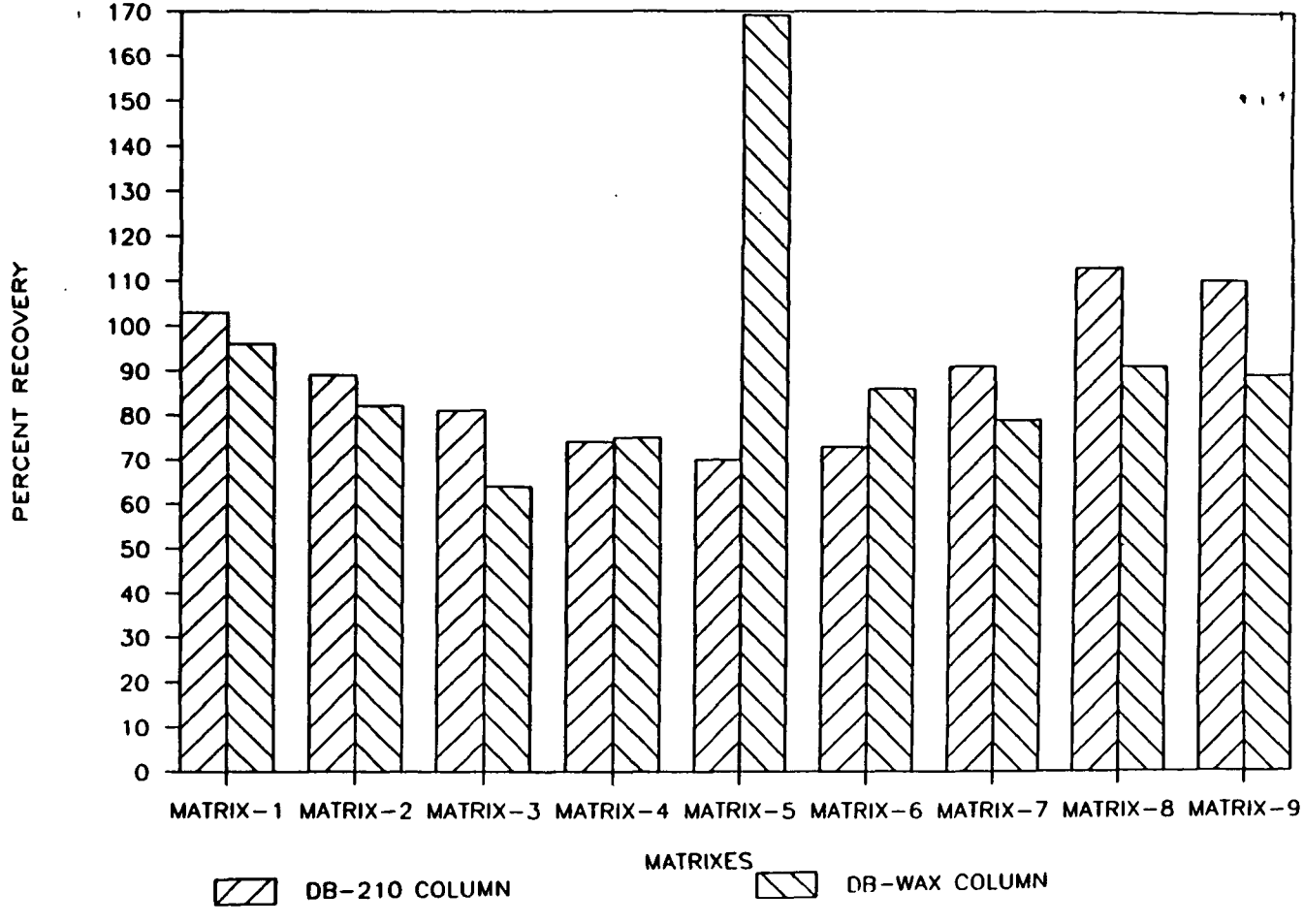

Figure 39. Recovery as a function of matrix for 1,2,3-trichlorobenzene.

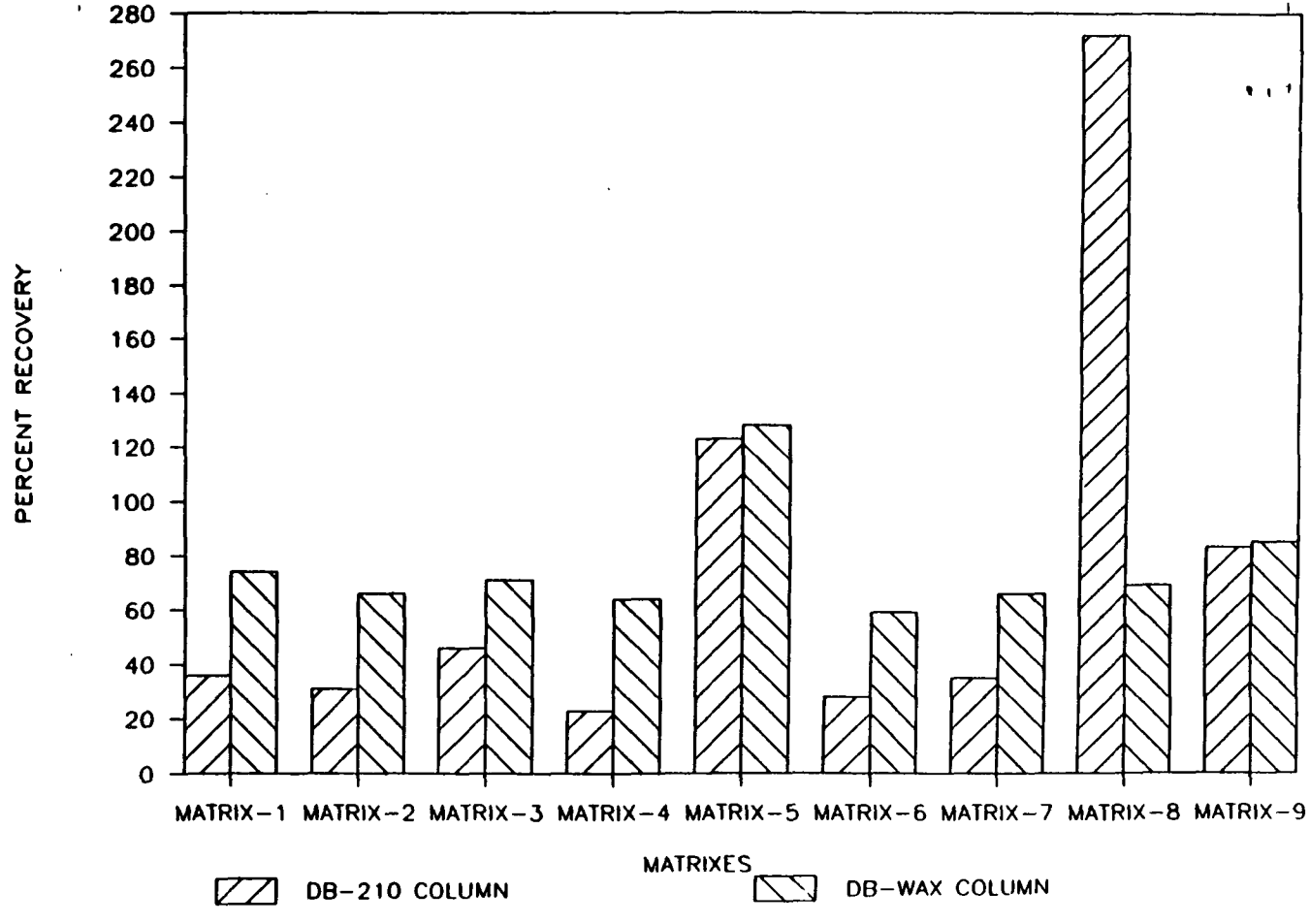

Figure 40. Recovery as a function of matrix for hexachlorocyclopentadiene.

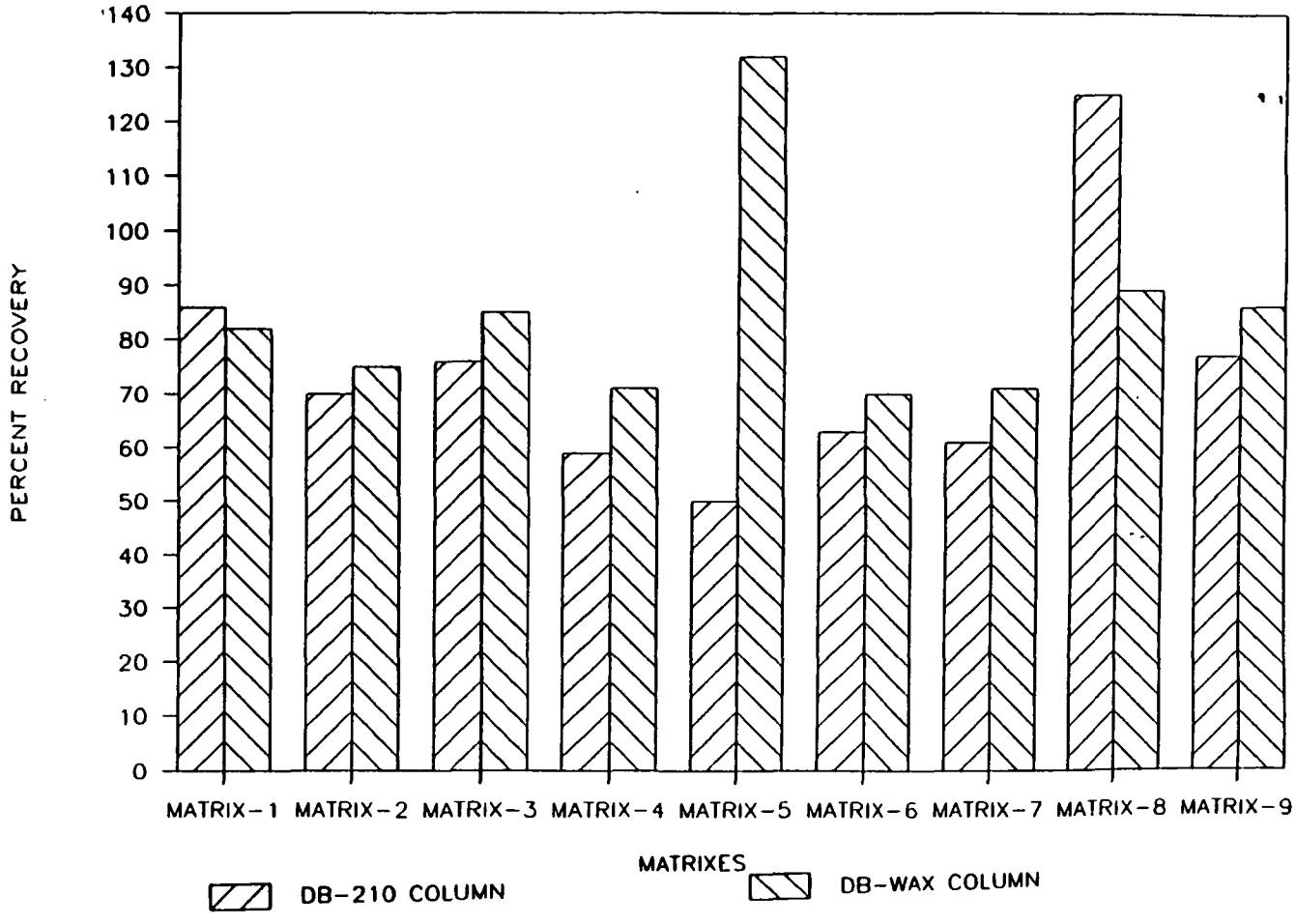

Figure 41. Recovery as a function of matrix for 1,2,4,5-tetrachlorobenzene.

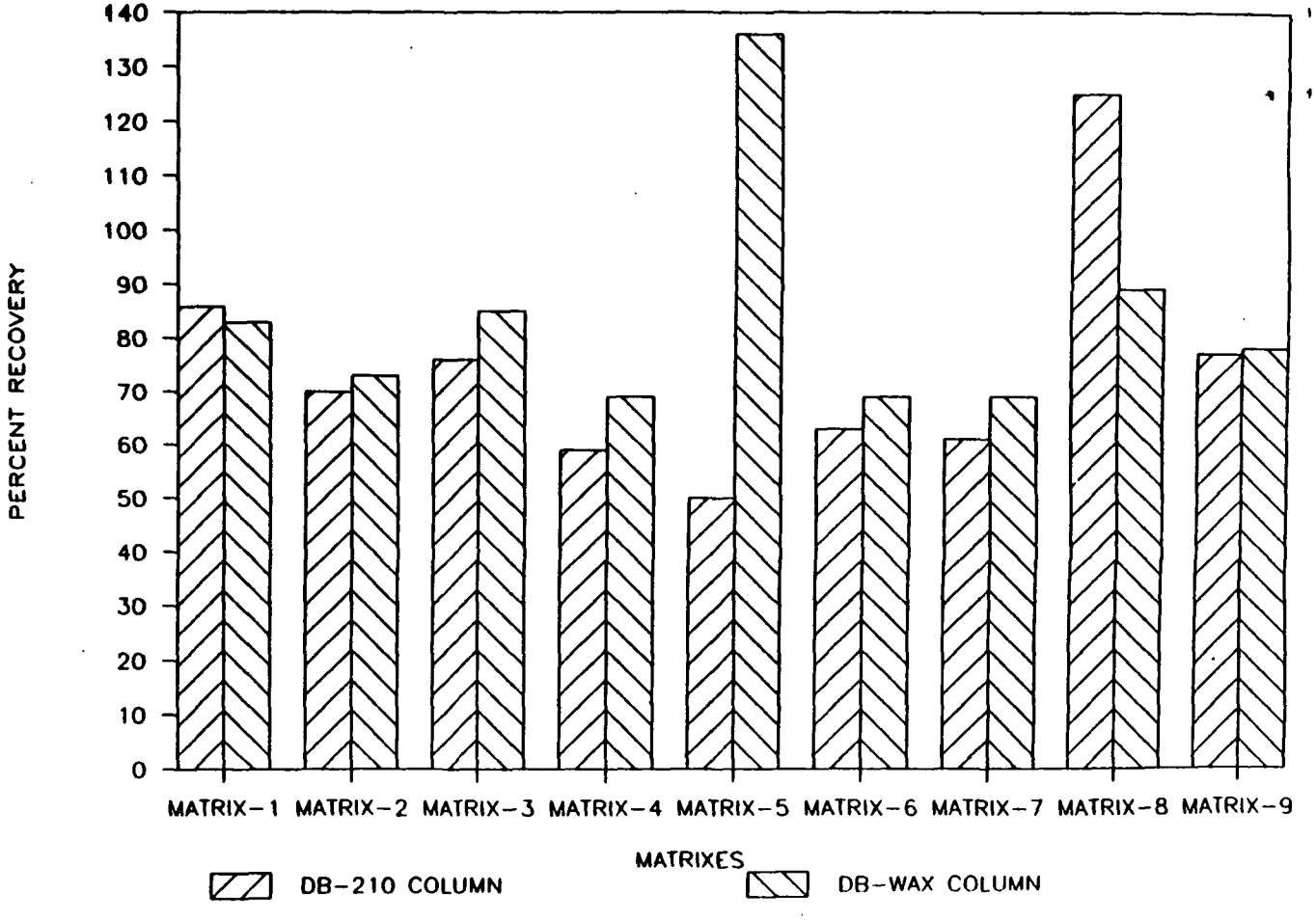

Figure 42. Recovery as a function of matrix for 1,2,3,5-tetrachlorobenzene.

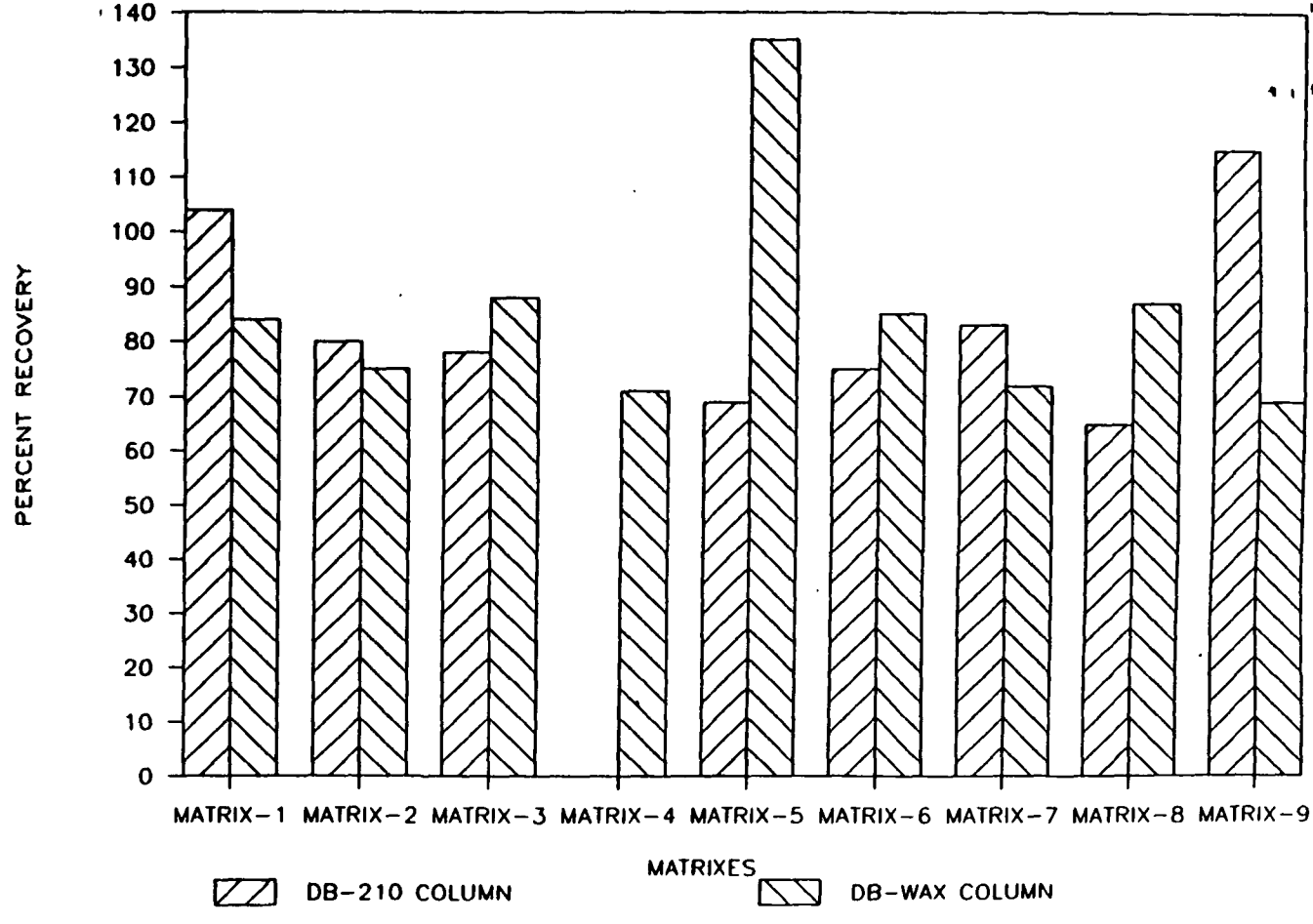

Figure 43. Recovery as a function of matrix for 1,2,3,4-tetrachlorobenzene.

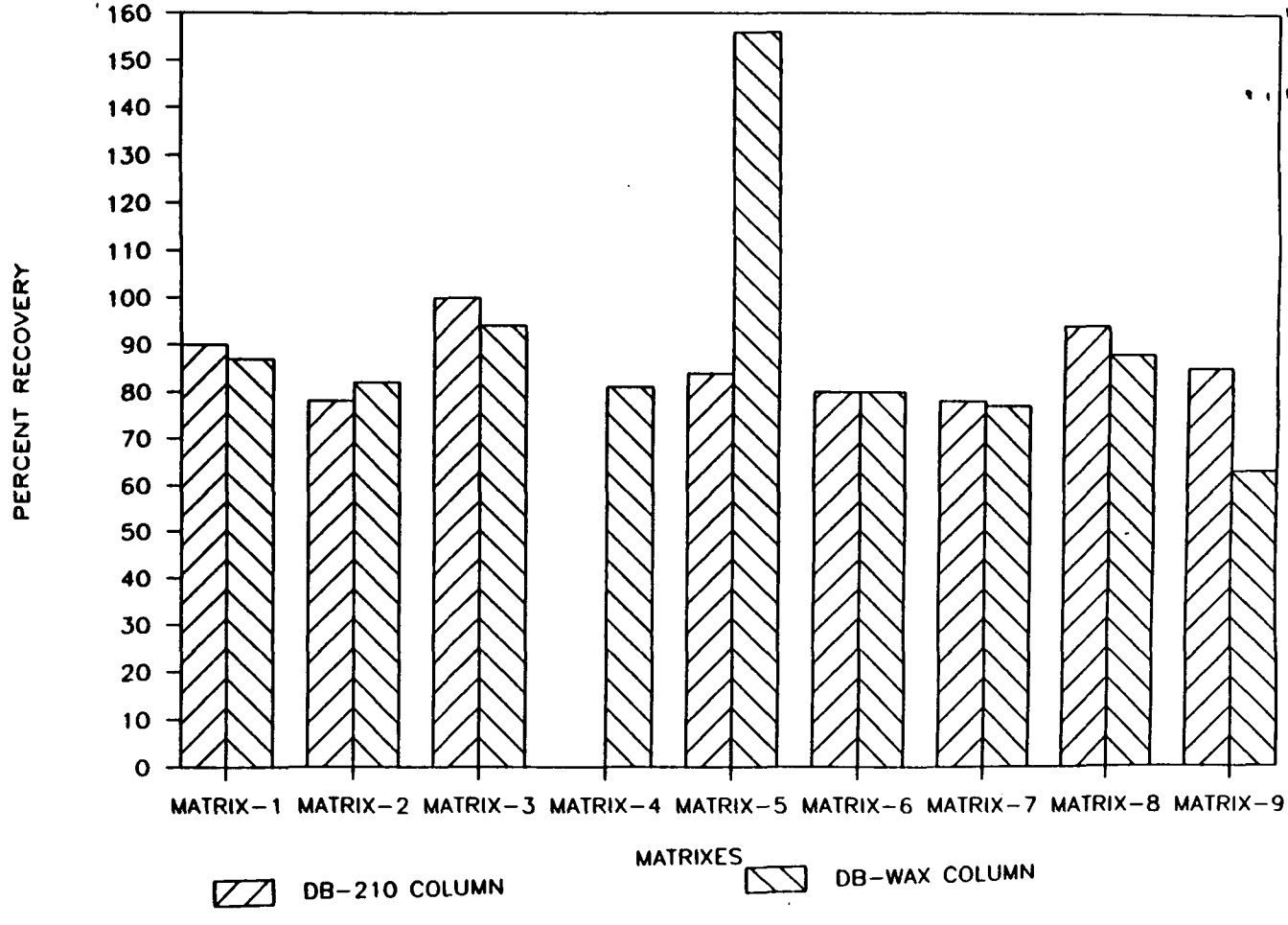

Figure 44. Recovery as a function of matrix for 2-chloronaphthalene.

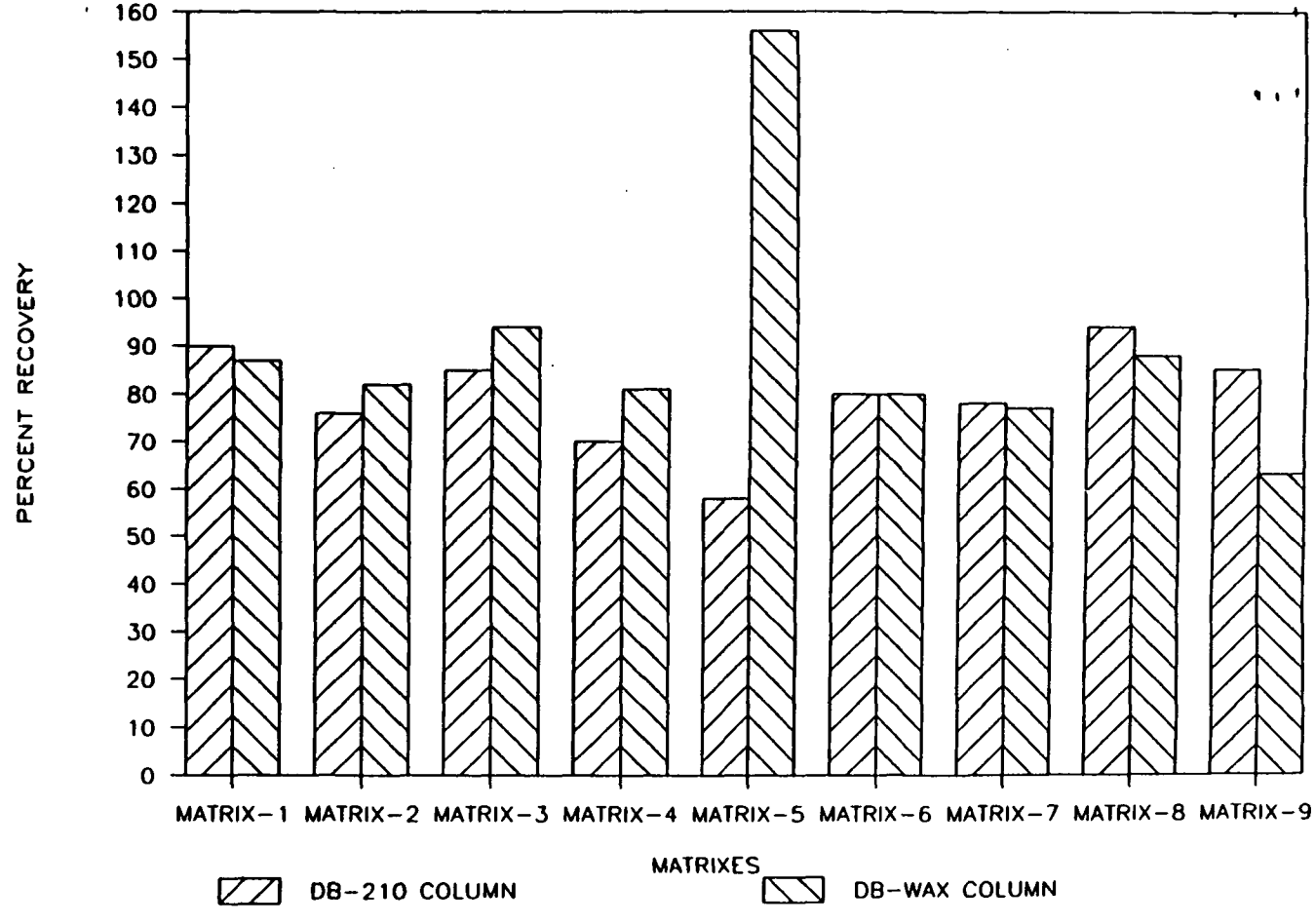

Figure 45. Recovery as a function of matrix for pentachlorobenzene.

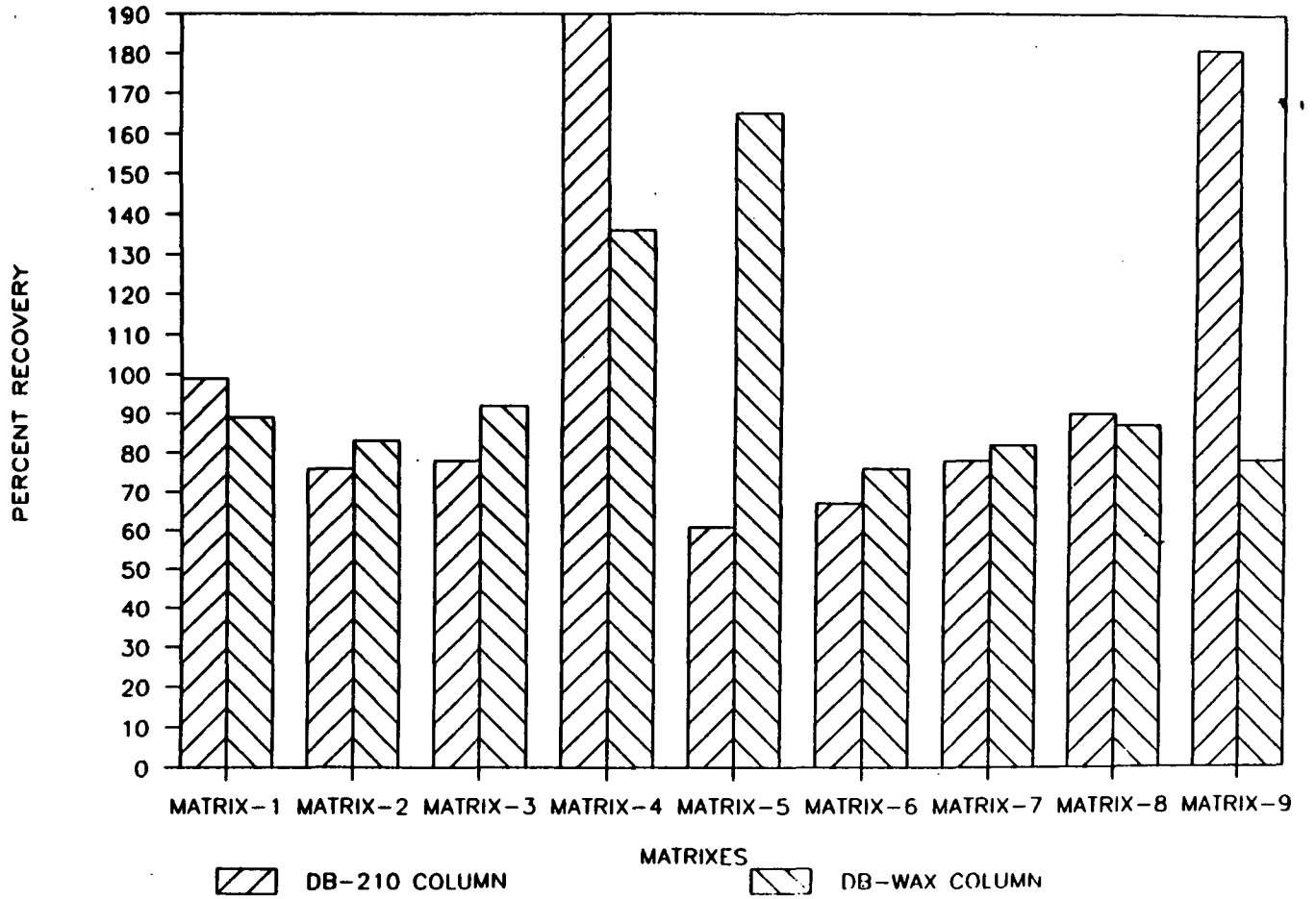

Figure 46. Recovery as a function of matrix for hexachlorobenzene.

TABLE 60. COMPOUNDS IDENTIFIED IN EPA SAMPLE WP-485 -- POLYNUCLEAR AROMATICS II

Compounds known to be present in the sample at µg/L		Compounds found by Method 8120 at µg/L	
Acenaphthylene	100	Hexachlorobutadiene	0.034
Phenanthrene	100		
Fluoranthene	10.0		
Benzo(a)anthracene	10.0		
Benzo(a)pyrene	10.0		
Benzo(b)fluoranthene	10.0		
Dibenzo(a,h)anthracene	10.0		
Benzo(g,h,i)perylene	10.0		

TABLE 61. COMPOUNDS IDENTIFIED IN EPA SAMPLE WP-281 SAMPLE 2

Compounds known to be present in the sample at µg/L		Compounds found by Method 8120 at µg/L
Phenol	15.0	None
2,4-Dimethylphenol	12.5	
2-Chlorophenol	8.3	
4-Chloro-3-methylphenol	20.0	
2,4-Dichlorophenol	10.0	
2,4,6-Trichlorophenol	12.5	
Pentachlorophenol	10.0	
2-Nitrophenol	20.0	
4-Nitrophenol	15.0	

TABLE 62. COMPOUNDS IDENTIFIED IN EPA SAMPLE WP-281 SAMPLE 4[a]

Compounds known to be present in the sample at µg/L		Compounds found by Method 8120 at µg/L
Phenol	100	None
2,4-Dimethylphenol	83.3	
2,Chlorophenol	110	
4-Chloro-3-Methylphenol	175	
2,4-Dichlorophenol	70	
2,4,6-Trichlorophenol	125	
Pentachlorophenol	90	
2-Nitrophenol	175	
4-Nitrophenol	130	

[a]GC/ECD chromatograms of the EPA WP-281 Sample 4 before and after Florisil cartridge chromatography are shown in Figures 47 and 48, respectively.

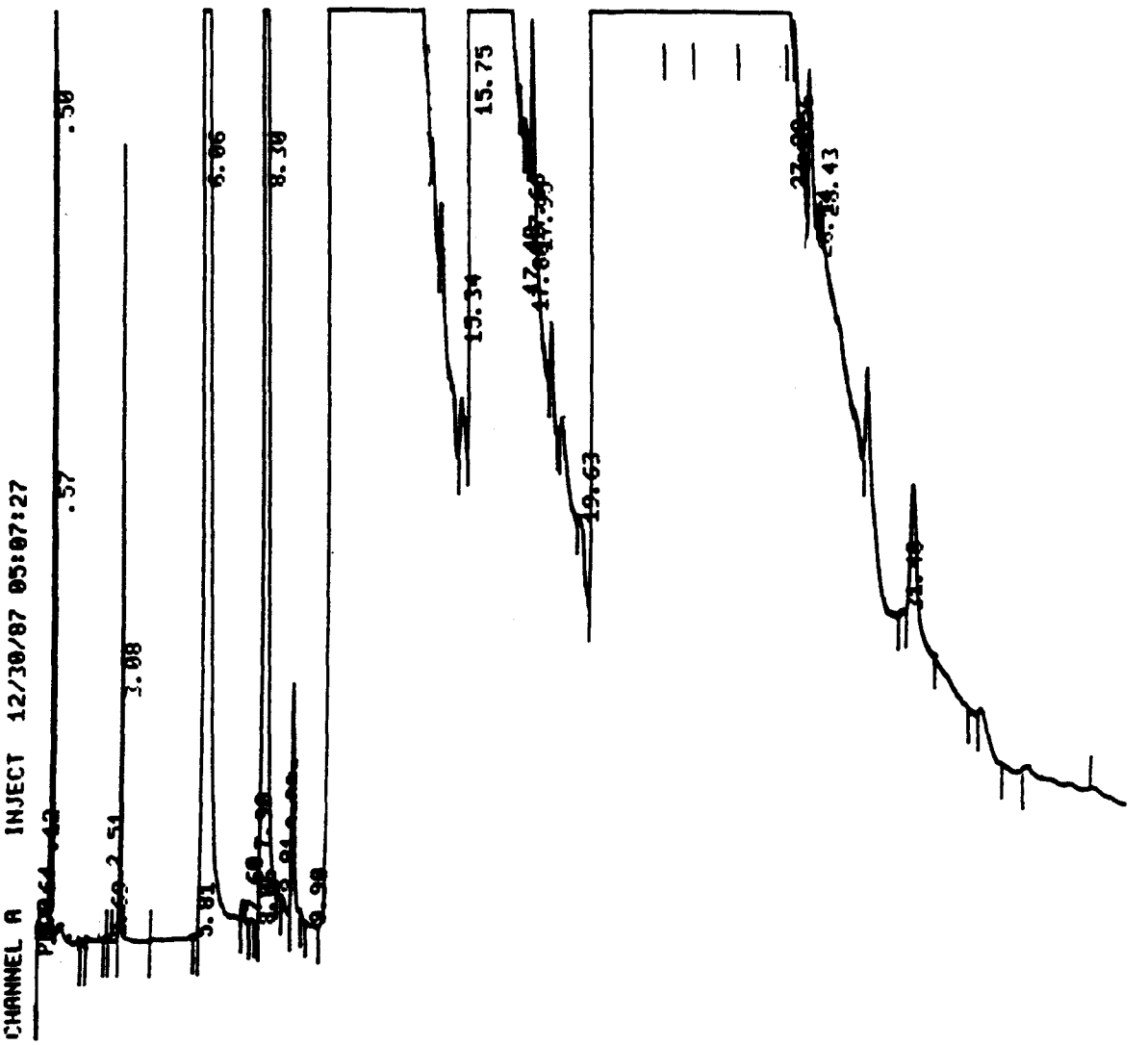

Figure 47. GC/ECD chromatogram of EPA WP-281 Sample 4 before Florisil cartridge chromatography.

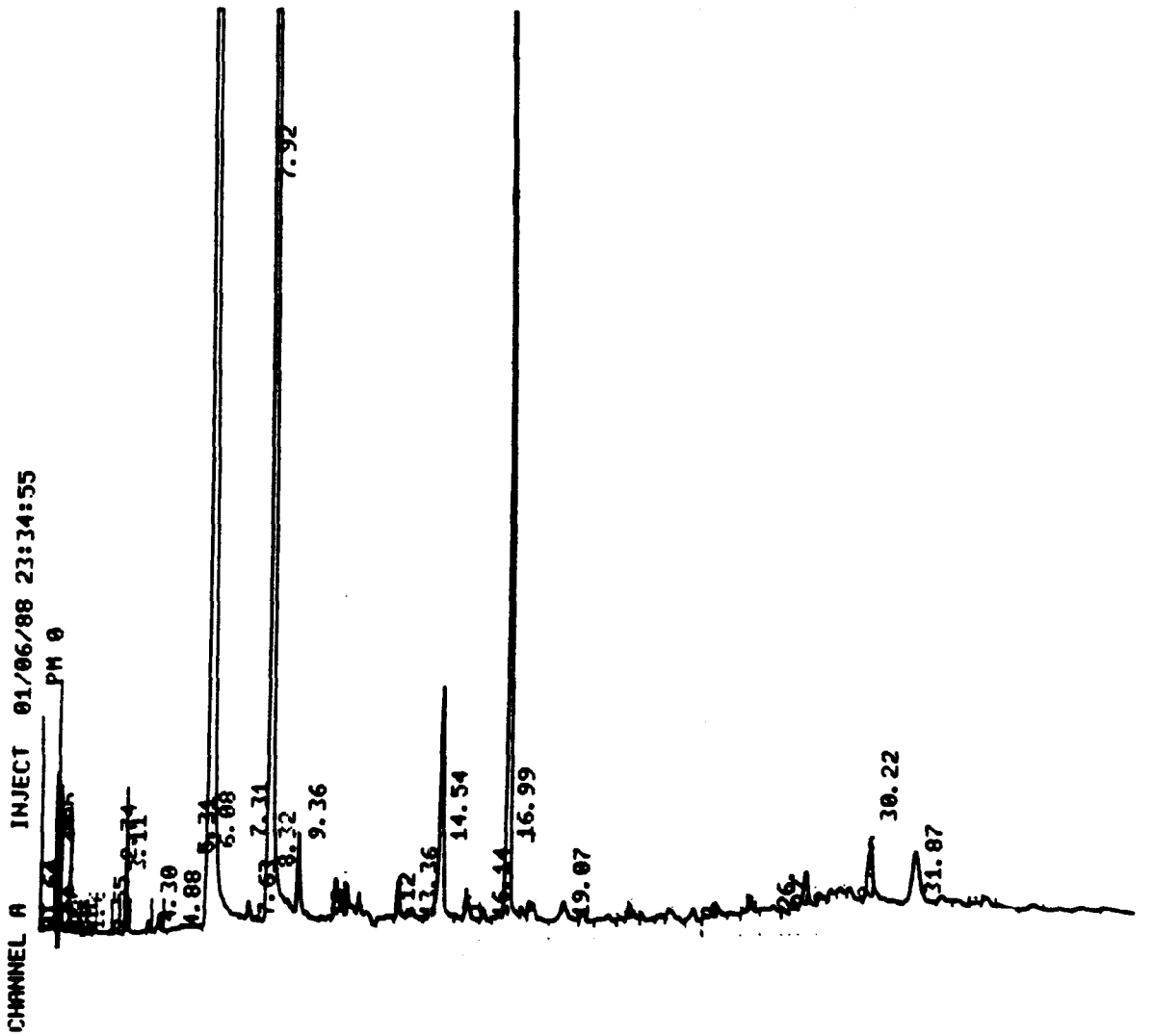

Figure 48. GC/ECD chromatogram of EPA WP-281 Sample 4 after Florisil cartridge chromatography.

TABLE 63. RESULTS OF GC/ECD ANALYSES FOR EPA CHECK SAMPLE WP-685

Compound	True value (µg/mL)	Found value (µg/mL)	Bias (percent)
alpha-BHC	100	117	+17
gamma-BHC	100	85	-15

[a]Analyses were performed on the DB-210 capillary column; the GC operating conditions are listed in Table 4; the solution provided by EPA was not spiked into water but it was diluted 100X and analyzed directly. Other compounds present in the sample include: heptachlor, heptachlor epoxide, dieldrin, endrin, and 4,4'-DDD.

TABLE 64. RESULTS OF GC/ECD ANALYSES FOR EPA CHECK SAMPLE WP-186[a]

Compound	True value (µg/mL)	Found value (µg/mL)	Bias (percent)
1,3,5-Trichlorobenzene	100	107	+7
1,2,3-Trichlorobenzene	100	85	-15
1,2,4,5-Tetrachlorobenzene	100	105	+5
1,2,3,4-Tetrachlorobenzene	100	96	-4

[a]Analyses were performed on the DB-210 capillary column; the GC operating conditions are listed in Table 4; the solution provided by EPA was not spiked into water but it was diluted 100X and analyzed directly. Other compounds present in the sample include: 4-chlorobenzotrifluoride, m-chlorotoluene, 2,4-dichlorotoluene, 2,4,5-trichloroaniline, pentachloronitrobenzene.

TABLE 65. COMPOUNDS IDENTIFIED IN EPA WP-1082 SAMPLE 1[a]

Compounds known to be present in the sample (µg/L)		Compounds found by EPA Method 8120	Concentration (µg/L)		Bias (percent)	
			Before Florisil Cartridge	After Florisil Cartridge	Before Florisil Cartridge	After Florisil Cartridge
4-Chlorobenzotrifluoride	62.4					
m-Chlorotoluene	38.3					
2,4-Dichlorotoluene	49.8					
1,3,5-Trichlorobenzene	62.5	1,3,5-Trichlorobenzene	36.2	26.5	-42	-58
1,2,3-Trichlorobenzene	75.5	1,2,3-Trichlorobenzene	24.9	24.6	-67	-67
1,2,4,5-Tetrachlorobenzene	50.7	1,2,4,5-Tetrachlorobenzene	12.1	13.3	-76	-74
1,2,3,4-Tetrachlorobenzene	70.3	1,2,3,4-Tetrachlorobenzene	49.1	37.2	-30	-47
2,4,6-Trichloroaniline	59.4					
Pentachloronitrobenzene	74.5					

[a]Dilution factor for extract is 100. 1 mL sample provided by EPA was spiked into 1 L water; $V_{extract}$ 10 mL; additional 10-fold dilution prior to GC/ECD.

TABLE 66. COMPOUNDS IDENTIFIED IN EPA WP-1082 SAMPLE 2

Compounds known to be present in the sample (µg/L)		Compounds found by EPA Method 8120	Concentration (µg/L)		Bias (percent)	
			Before Florisil Cartridge[a]	After Florisil Cartridge[b]	Before Florisil Cartridge	After Florisil Cartridge
4-Chlorobenzotrifluoride	249					
m-Chlorotoluene	201					
2,4-Dichlorotoluene	177					
1,3,5-Trichlorobenzene	250	1,3,5-Trichlorobenzene	198	134	-21	-46
1,2,3-Trichlorobenzene	205	1,2,3-Trichlorobenzene	78.5	88.5	-62	-57
1,2,4,5-Tetrachlorobenzene	231	1,2,4,5-Tetrachlorobenzene	72.5	73.5	-69	-68
1,2,3,4-Tetrachlorobenzene	200	1,2,3,4-Tetrachlorobenzene	145	136	-28	-32
2,4,6-Trichloroaniline	301					
Pentachloronitrobenzene	351					

[a]Dilution factor is 500.
[b]Values given are the average determinations at dilutions of 10 and 100 fold.

TABLE 67. COMPOUNDS IDENTIFIED IN EPA WP-482 SAMPLE 3

Compounds known to be present in the sample (µg/L)		Compounds found by EPA Method 8120	Concentration (µg/L)		Bias (percent)	
			Before Florisil Cartridge	After Florisil Cartridge	Before Florisil Cartridge	After Florisil Cartridge
1,4-Dichlorobenzene	24.8	1,4-Dichlorobenzene	68.3[a]	26.1	+175	+5.2
Bis(2-chloroisopropyl)ether	38.8					
Hexachloroethane	30.0	Hexachloroethane	15.0[b]	9.0	-50	-70
Nitrobenzene	76.5					
Naphthalene	24.8					
Dimethyl phthalate	40.0					
Acenaphthene	19.5					
Fluorene	51.2					
4-Chlorophenyl phenyl ether	76.7					
4-Bromophenyl phenyl ether	41.5					
Anthracene	40.0					
Fluoranthene	29.8					
Butyl benzyl phthalate	51.3					
Chrysene	69.9					
Ethyl hexyl phthalate	29.1					
Benzo(b)fluoranthene	40.0					
Benzo(a)pyrene	24.9					
Dibenzo(a,h)anthracene	40.7					
Benzo(g,h,i)perylene	80.4					

[a]Dilution factor is 10.
[b]Dilution factor is 100.

TABLE 68. COMPOUNDS IDENTIFIED IN EPA WP-482 SAMPLE 4

Compounds known to be present in the sample (µg/L)		Compounds found by EPA Method 8120	Concentration (µg/L)		Bias (percent)	
			Before Florisil Cartridge	After Florisil Cartridge	Before Florisil Cartridge	After Florisil Cartridge
1,4-Dichlorobenzene	251	1,4-Dichlorobenzene	ND	195[a]	--	-22
Bis(2-chloroisopropyl) ether	204					
Hexachloroethane	303	Hexachloroethane	168[b]	70[b]	-45	-77
Nitrobenzene	373					
Naphthalene	250					
Dimethyl phthalate	404					
Acenaphthene	197					
Fluorene	250					
4-Chlorophenyl phenyl ether	374					
4-Bromophenyl phenyl ether	373					
Anthracene	200					
Fluoranthene	301					
Butyl benzyl phthalate	250					
Chrysene	209					
Ethyl hexyl phthalate	153					
Benzo(b)fluoranthene	203					
Benzo(a)pyrene	224					
Dibenzo(a,h)anthracene	204					
Benzo(g,h,i)perylene	300					

[a]Dilution factor is 100.
[b]Dilution factor is 1,000.
ND -- Not detected because the sample was diluted too much.

TABLE 69. COMPOUNDS IDENTIFIED IN EPA WP-482 SAMPLE 1

Compounds known to be present in the sample (µg/L)		Compounds found by EPA Method 8120	Concentration (µg/L)		Bias (percent)	
			Before Florisil Cartridge	After Florisil Cartridge	Before Florisil Cartridge	After Florisil Cartridge
Bis-2-chloroethyl ether	48.2					
1,3-Dichlorobenzene	52.0	1,3-Dichlorobenzene	32.6[a]	16.2[a]	-37	-69
1,2-Dichlorobenzene	24.7	1,2-Dichlorobenzene	9.8[a]	10.8	-60	-56
Nitrosodipropylamine	34.8					
Isophorone	76.7					
Bis(2-chloroethoxy)methane	48.6					
1,2,4-Trichlorobenzene	25.3	1,2,4-Trichlorobenzene	6.2[a]	2.9[a]	-75	-89
Hexachlorobetadiene	49.6	Hexachlorobutadiene	23.0[b]	20.5[b]	-54	-59
2-Chloronaphthalene	25.4	2-Chloronaphthalene	19.9[a]	20.7[a]	-22	-19
2,6-Dinitrotoluene	76.5					
2,4-Dinitrotoluene	73.8					
Diethyl phthalate	25.1					
Hexachlorobenzene	35.7	Hexachlorobenzene	45.7[b]	49.4[b]	+28	+38
Phenanthrene	40.2					
Dibutyl phthalate	24.9					
Pyrene	60.2					
Benzo(a)anthracene	73.9					
Dioctylphthalate	43.9					
Benzo(k)fluoranthene	45.7					

[a]Dilution factor is 10.
[b]Dilution factor is 100.

The data in Tables 63 and 64 indicate biases of -15 to +17 percent for alpha-BHC, gamma-BHC, 1,3,5- and 1,2,3-trichlorobenzene, and 1,2,4,5- and 1,2,3,4-tetrachlorobenzene when no other compounds were present in the sample. Biases as high as -76 percent for 1,2,4,5-tetrachlorobenzene were encountered when other chlorinated compounds were present (Tables 65 and 66). Fractionation of samples extracts by Florisil cartridge chromatography did not help. Much higher biases (e.g., +175 percent) were encountered when 1,4-dichlorobenzene and hexachloroethane were present in the sample, at the same concentration, because the two compounds give such different detector signals. Consequently, the sample extract had to be diluted to get the signal within the detector's linear range (Table 67). Nonetheless, all Method 8120 compounds can be determined in the presence of other EPA base/neutral compounds and organochlorine pesticides (Tables 68 and 69). If the EPA's priority pollutant acidic compounds are present, the Florisil procedure that utilizes a 1-g disposable cartridge and hexane/acetone (9:1) as the eluting solvent may be used to separate the Method 8120 compounds from the EPA's priority pollutant phenols.

6.5.4 Method Detection Limits

The method detection limits (MDL) are presented in Tables 70 and 71. They were determined by spiking seven or eight reagent-grade water samples with the 22 chlorinated hydrocarbons and subjecting them to the entire analytical process. Blank measurements were performed in triplicate (Table 72). MDLs were determined from the standard deviations of the seven or eight replicates and the Student's t value for a one-tailed test at the 99 percent confidence level (6 degrees of freedom). For water samples that were subjected to Florisil, MDLs ranged from 1.4 to 1,300 ng/L. When a 1.5 µL aliquot of a 2-mL extract (after Florisil cleanup) obtained from 1 L of water containing the test compounds was used, the amounts injected onto the GC column ranged from about 1 pg to 1,000 pg. These amounts are sufficient for identifying the compounds, since our lowest-level calibration standard used for quantifying the samples contained 1 to 500 pg/µL, and we normally inject 1.5-µL aliquots. Detection limits lower than those given in Tables 70 and 71 may be achievable by using larger samples and by concentrating the extracts to 0.5 mL instead of 2 mL. However, a minimum extract volume of 2 mL is suggested for Method 8120 as 1 mL is needed for the primary analysis and another 1-mL aliquot is saved for the confirmatory analysis.

6.5.5 Ruggedness Test for Method 8120

A ruggedness test was performed for Method 8120 to determine how sensitive the method is to changes of seven specified conditions. The seven variables are listed in Table 73 and include: injector temperature, detector temperature, injection volume, type of response factors used in calibration, solvent, and presence or absence of two matrix interferents (diesel hydrocarbons and organochlorine pesticides). The seven variables are assigned the letters A,a through G,g (Table 74). For example, the injector temperature is 230°C in experiments 1 through 4 and 210°C in experiments 5 through 8.

TABLE 70. CONCENTRATIONS OF THE METHOD 8120 COMPOUNDS IN WATER SAMPLES FOR THE MDL STUDY (SUBJECTED TO FLORISIL CARTRIDGE CLEANUP)

Compound	Spike level (ppt)	Concentration (ppt) Rep.1	Rep.2	Rep.3	Rep.4	Rep.5	Rep.6	Rep.7	Rep.8	Average (ppt)	SD (ppt)	MDL[b] (ppt)
Hexachloroethane	2	2.4	1.9	1.3	0.8	1.3	0.9	1.2	1.8	1.26	0.54	1.6
1,3-Dichlorobenzene	200	296	312	146	124	130	210	80	142	180	84.5	250
1,4-Dichlorobenzene	400	999	1,240	648	384	712	784	572	376	714	295	890
1,2-Dichlorobenzene	200	244	466	262	192	188	258	204	236	250	90	270
Benzyl chloride	200	166	308	229	130	168	158	122	166	180	61	180
1,3,5-Trichlorobenzene	20	9.8	22.4	13.4	16.6	14.8	14.2	10.0	16.4	14.7	4.0	12
Hexachlorobutadiene	2	1.2	2.6	2.2	2.0	1.9	2.2	1.4	2.0	1.94	0.45	1.4
Benzal chloride	2	a	a	a	a	a	a	a	a	--	--	--
1,2,4-Trichlorobenzene	100	89.2	72.8	91.6	90.0	119	200	54.0	73.0	98.7	45.1	140
Benzotrichloride	10	6.6	3.9	8.8	6.0	1.1	5.6	3.7	8.4	4.64	2.0	6.0
1,2,3-Trichlorobenzene	200	139	134	142	118	138	140	126	162	137	12.8	39
Hexachlorocyclopentadiene	200	299	271	362	216	118	262	136	226	236	81	240
1,2,4,5-Tetrachlorobenzene[c] 1,2,3,5-Tetrachlorobenzene[c]	20	24.0	18.6	23.4	15.8	19.0	19.8	19.2	15.0	19.4	3.2	9.5
1,2,3,4-Tetrachlorobenzene	20	14.2	14.2	14.6	9.2	21.8	13.8	14.6	17.0	14.9	3.5	11
2-Chloronaphthalene	1,000	398	262	380	720	1,550	830	1,240	840	780	450	1,300
Pentachlorobenzene	20	20.0	18.8	31.8	14.4	52.4	14.6	18.6	22.8	24.2	12.7	38
Hexachlorobenzene	10	11.8	8.8	12.6	12.6	13.4	11.2	10.8	15.0	12.0	1.85	5.6
alpha-BHC	20	18.2	19.6	22.4	10.2	18.2	14.8	14.4	16.2	16.8	3.72	11
gamma-BHC	20	25.0	30.4	32.0	12.2	23.4	15.0	14.6	17.2	20.2	7.56	23
beta-BHC	20	27.6	31.8	41.8	12.8	21.8	14.6	15.2	16.8	21.3	10.2	31
delta-BHC	20	29.0	26.6	31.6	12.2	21.0	16.4	17.4	19.6	21.7	6.73	20
Surrogate recovery (percent)												
α,2,6-Trichlorotoluene	200	62	61	63	41	63	49	56	71			
1,4-Dichloronaphthalene	2,000	66	57	90	45	85	50	60	75			
2,3,4,5,6-Pentachlorotoluene	200	58	51	69	36	45	31	52	68			

[a]No concentration given because benzal chloride coelutes with 1,2,4-trichlorobenzene. Estimated MDL is 2-5 ppt.
[b]MDL is the method detection limit was determined from the analysis of eight replicate aliquots processed through the entire analytical method (extraction, Florisil cleanup, and GC/ECD analysis). MDL = $t_{(n-1,0.99)} \times SD$ where $t_{(n-1,0.99)}$ is the Student's value appropriate for a 99 percent confidence interval and a standard deviation with n-1 degrees of freedom, and SD is the standard deviation of the eight replicate measurements.
[c]This pair cannot be resolved on the DB-210 fused-silica capillary column.

TABLE 71. CONCENTRATIONS OF THE METHOD 8120 COMPOUNDS IN WATER SAMPLES FOR THE MDL STUDY (NO FLORISIL CARTRIDGE CLEANUP)

Compound	Spike level (ppt)	Concentration (ppt)							Average (ppt)	SD (ppt)	MDL[b] (ppt)
		Rep.1	Rep.2	Rep.3	Rep.4	Rep.5	Rep.6	Rep.7			
Hexachloroethane	2	1.8	1.2	1.6	1.4	1.4	1.2	2.3	1.4	0.39	1.3
1,3-Dichlorobenzene	200	162	202	164	236	124	174	312	196	61.8	190
1,4-Dichlorobenzene	400	344	370	358	296	324	332	372	342	27.3	86
1,2-Dichlorobenzene	200	262	256	274	172	192	208	170	219	44.2	140
Benzyl chloride	200	186	188	204	110	150	176	130	163	34.3	110
1,3,5-Trichlorobenzene	20	14.2	12	15.8	9.8	13.2	14.6	12.6	13.2	1.96	6.2
Hexachlorobutadiene	2	2.2	1.8	2.4	2.1	1.7	1.8	1.8	1.9	0.26	0.8
Benzal chloride	2	[a]	[a]	[a]	[a]	[a]	[a]	[a]	--	--	--
1,2,4-Trichlorobenzene	100	102	84	100	74	81	77	64	83	13.7	43
Benzotrichloride	10	8.6	5.2	10.6	6.0	9.8	9.0	7.1	5.0	2.0	6.3
1,2,3-Trichlorobenzene	200	156	146	170	126	150	162	138	150	14.8	46
Hexachlorocyclopentadiene	200	277	218	348	230	142	190	160	224	71.0	220
1,2,4,5-Tetrachlorobenzene[c] 1,2,3,5-Tetrachlorobenzene[c]	20	18.2	17.8	20.0	22.8	23.0	28.4	19.2	21.3	3.73	12
1,2,3,4-Tetrachlorobenzene	20	17.2	20.0	22.0	18.4	20.8	20.0	19.4	19.7	1.57	4.9
2-Chloronaphthalene	1,000	624	742	732	1,270	920	760	1,080	875	229	720
Pentachlorobenzene	20	18.0	17.8	19.2	10.4	14.6	17.2	14.4	15.9	3.0	9.4
Hexachlorobenzene	10	9.0	9.4	10.4	10.3	11.9	10.5	12.2	9.5	1.18	3.7
alpha-BHC	20	17.4	16.4	17.2	13.4	18.4	19.2	15.0	16.7	2.0	6.3
gamma-BHC	20	18.2	18.0	18.0	13.6	19.8	17.4	16.0	17.3	2.0	6.3
beta-BHC	20	15.8	15.2	15.8	15.4	18.6	18.0	14.6	16.2	1.5	4.7
delta-BHC	20	13.4	14.4	14.6	15.0	18.4	18.0	14.8	15.5	1.9	6.0
Surrogate recovery (percent)											
α,2,6-Trichlorotoluene	200	73	69	71	52	74	75	60			
1,4-Dichloronaphthalene	2,000	87	68	84	58	79	86	69			
2,3,4,5,6-Pentachlorotoluene	200	71	57	77	44	65	80	62			

[a]No concentration given because benzal chloride coelutes with 1,2,4-trichlorobenzene.
[b]MDL is the method detection limit. MDL was determined from the analysis of seven replicate aliquots processed through the entire analytical method (extraction and GC/ECD analysis). MDL = $t_{(n-1,0.99)} \times SD$, where $t_{(n-1,0.99)}$ is the Student's t value appropriate for a 99 percent confidence interval and a standard deviation with n-1 degrees of freedom, and SD is the standard deviation of seven replicate measurements.
[c]This pair cannot be resolved on the DB-210 fused-silica capillary column.

TABLE 72. CONCENTRATIONS OF THE METHOD 8120 COMPOUNDS DETECTED IN METHOD BLANKS

Compound	Concentration (ppt)							
	Without Florisil Cleanup				With Florisil Cleanup			
	Rep.1	Rep.2	Rep.3	Rep.4	Rep.1	Rep.2	Rep.3	Rep.4
Hexachloroethane	0.14	0.16	0.15	0.17	0.15	0.20	0.20	0.21
1,3-Dichlorobenzene								
1,4-Dichlorobenzene								
1,2-Dichlorobenzene								
Benzyl chloride								
1,3,5-Trichlorobenzene								
Hexachlorobutadiene								
Benzal chloride								
1,2,4-Trichlorobenzene								
Benzotrichloride	2	4		3		1		2
1,2,3-Trichlorobenzene								
Hexachlorocyclopentadiene								
1,2,4,5-Tetrachlorobenzene								
1,2,3,5-Tetrachlorobenzene								
1,2,3,4-Tetrachlorobenzene								
2-Chloronaphthalene								
Pentachlorobenzene								
Hexachlorobenzene			1	1				
alpha-BHC								
gamma-BHC						1	1	1
beta-BHC						2	1	
delta-BHC								
Surrogate recovery (percent)								
α,2,6-Trichlorotoluene	76	80	80	84	76	68	72	68
1,4-Dichloronaphthalene	75	77	81	81	130	70	78	72
2,3,4,5,6-Pentachlorotoluene	70	72	81	74	77	66	77	62

TABLE 73. LIST OF CONDITIONS ALTERED AND ASSIGNED VALUES FOR GAS CHROMATOGRAPHIC ANALYSIS (METHOD 8120)

Condition	No.	Letter	Value for capital letter	Value for lower case letter
Injector temperature (°C)	1	A,a	230	210
Detector temperature (°C)	2	B,b	260	240
Injection volume (µL)	3	C,c	3	1
Calibration	4	D,d	Using average RF	Using single RF
Solvent	5	E,e	Hexane	Hexane-acetone (50:50)
Interferences from matrix (diesel hydrocarbons)	6	F,f	With diesel hydrocarbons	Without
Interferences from matrix (chlorinated pesticides)	7	G,g	With organo-chlorine pesticides	Without

TABLE 74. DESIGN FOR TEST OF EXPERIMENTAL CONDITIONS

Experimental condition	Values of conditions in determination No. 1	2	3	4	5	6	7	8
1	A	A	A	A	a	a	a	a
2	B	B	b	b	B	B	b	b
3	C	c	C	c	C	c	C	c
4	D	D	d	d	d	d	D	D
5	E	e	E	e	e	E	e	E
6	F	f	f	F	F	f	f	F
7	G	g	g	G	g	G	G	g

The analytical results are presented as percent recovery of each test compound in each of the eight experiments (Table 75). Table 76 shows the group differences V_A through V_G which were calculated from equations 1 through 7.

$$V_A = 1/4(s + t + u + v) - 1/4(w + x + y + z) = A-a \quad (1)$$
$$V_B = 1/4(s + t + w + x) - 1/4(u + v + y + z) = B-b \quad (2)$$
$$V_C = 1/4(s + u + w + y) - 1/4(t + v + x + z) = C-c \quad (3)$$
$$V_D = 1/4(s + t + y + z) - 1/4(u + v + w + x) = D-d \quad (4)$$
$$V_E = 1/4(s + u + x + z) - 1/4(t + v + w + y) = E-e \quad (5)$$
$$V_F = 1/4(s + v + w + z) - 1/4(t + u + x + y) = F-f \quad (6)$$
$$V_G = 1/4(s + v + x + y) - 1/4(t + u + w + z) = G-g \quad (7)$$

For example, V_A for hexachloroethane represents the average for the A determinations minus the average for the a determinations (e.g., $V_A = 1/4\ (93 + 114 + 78 + 89) - 1/4\ (68 + 101 + 85 + 119) = 0.25$ which means that an injection temperature of 230°C gave a slightly higher response than at 210°C.

The results showed that the GC method is reasonably rugged. Of course, the results for individual compounds vary, but overall it was found that:

- Raising the injector temperature from 210°C to 230°C had essentially no effect.
- Raising the detector temperature had a clear positive effect.
- Increasing the injection volume had a clear negative effect, mainly because of column overloading.
- Use of the average RF in calibration is significantly more advantageous than use of single RF.
- There was essentially no difference between hexane and hexane/acetone (1:1) as solvents.
- The presence of diesel fuel hydrocarbons resulted in lower responses.
- In the presence of chlorinated pesticides, the BHCs went off scale although they could still be identified, whereas the determination of the other 18 compounds was essentially not affected.

6.5.6 Confirmation by GC/MS

Table 77 gives the retention times (as scan numbers) and the three most intense ions in the mass spectra of the 22 target compounds, the three internal standards, and the three surrogate compounds proposed in the revised Method 8120. GC/MS chromatograms of a composite standard containing the 22 target compounds at 1 ng/µL and 5 ng/µL (in methylene chloride) are given in

TABLE 75. RUGGEDNESS TEST FOR METHOD 8120 -- RECOVERY DATA FOR THE 22 TEST COMPOUNDS

Compound	Percent recovery							
	1 (s)	2 (t)	3 (u)	4 (v)	5 (w)	6 (x)	7 (y)	8 (z)
Hexachloroethane	93	114	78	89	68	101	85	119
1,3-Dichlorobenzene	132	116	108	78	117	134	97	82
1,4-Dichlorobenzene	149	115	99	82	126	128	84	82
1,2-Dichlorobenzene	143	119	115	83	132	130	96	80
Benzyl chloride	128	121	109	89	111	122	101	94
1,3,5-Trichlorobenzene	140	118	94	83	119	122	78	83
Hexachlorobutadiene	115	103	119	94	106	107	101	97
Benzal chloride[b]	94	138	73	93	70	113	83	119
1,2,4-Trichlorobenzene[b]	94	138	73	93	70	113	83	119
Benzotrichloride	78	139	60	99	56	105	73	130
1,2,3-Trichlorobenzene	118	125	103	79	110	132	89	81
Hexachlorocyclopentadiene	125	119	108	100	93	117	111	119
1,2,4,5-Tetrachlorobenzene[c]	124	131	99	78	117	136	88	80
1,2,3,5-Tetrachlorobenzene[c]	124	131	99	78	117	136	88	80
1,2,3,4-Tetrachlorobenzene	112	136	98	80	105	135	87	81
2-Chloronaphthalene	129	146	82	92	128	127	90	86
Pentachlorobenzene	120	128	82	121	92	146	102	97
Hexachlorobenzene	76	96	104	100	86	101	90	94
alpha-BHC	a	137	59	a	56	a	a	126
gamma-BHC	a	137	58	a	56	a	a	127
beta-BHC	a	126	109	a	108	a	a	107
delta-BHC	a	158	69	a	66	a	a	128

[a]Not able to quantify compound because of interference from the other organochlorine pesticides.

[b,c]These pairs cannot be resolved on the DB-210 fused-silica capillary column.

TABLE 76. RUGGEDNESS TEST FOR METHOD 8120 -- GROUP DIFFERENCES FOR THE 22 TEST COMPOUNDS

Compound	Group differences						
	V_A	V_B	V_C	V_D	V_E	V_F	V_G
Hexachloroethane	0.2	1.2	-24.7	18.7	8.7	-2.2	-2.7
1,3-Dichlorobenzene	1.0	33.5	11.0	-2.5	12.0	-11.5	4.5
1,4-Dichlorobenzene	6.2	42.7	12.7	-1.2	12.7	3.2	5.2
1,2-Dichlorobenzene	5.5	37.5	18.5	-5.5	9.5	-5.5	1.5
Benzyl chloride	4.7	22.2	5.7	3.2	7.7	-7.7	1.2
1,3,5-Trichlorobenzene	8.2	40.2	6.2	0.2	10.2	3.2	2.2
Hexachlorobutadiene	5.0	5.0	10.0	-2.5	8.5	-4.5	-2.0
Benzal chloride[a]	3.2	11.7	-35.7	21.2	3.7	-7.7	-4.2
1,2,4-Trichlorobenzene[a]	3.2	11.7	-35.7	21.2	3.7	-7.7	-4.2
Benzotrichloride	3.0	4.0	-51.5	25.0	1.5	-3.5	-7.5
1,2,3-Trichlorobenzene	3.2	33.2	0.7	-2.7	7.7	-15.2	-0.2
Hexachlorocyclopentadiene	3.0	4.0	-4.5	14.0	11.5	-4.5	3.5
1,2,4,5-Tetrachlorobenzene[b]	2.7	40.7	0.7	-1.7	6.2	-13.7	-0.2
1,2,3,5-Tetrachlorobenzene[b]	2.7	40.7	0.7	-1.7	6.2	-13.7	-0.2
1,2,3,4-Tetrachlorobenzene	4.5	35.5	-7.5	-0.5	4.5	-19.5	-1.5
2-Chloronaphthalene	4.5	45.0	-5.5	5.5	-8.0	-2.5	-1.0
Pentachlorobenzene	3.5	21.0	-24.0	1.5	0.5	-7.0	22.5
Hexachlorobenzene	1.2	-7.2	-8.7	-8.7	0.7	-8.7	-3.2
alpha-BHC[c]	3.5	2.0	-37.0	37.0	-2.0	-3.5	-94.5
gamma-BHC[c]	3.0	2.0	-37.5	37.5	-2.0	-3.0	-94.5
beta-BHC[c]	5.0	4.5	-4.0	4.0	-4.5	-5.0	-112.5
delta-BHC[c]	8.2	6.7	-37.7	37.7	-6.7	-8.2	-105.2
Statistics[d]							
Mean	3.6	23.5	-7.3	4.6	6.0	-7.1	0.8
Standard deviation	1.9	17.3	19.4	10.5	5.1	6.0	6.3
Standard error	0.5	4.1	4.6	2.5	1.2	1.4	1.5
Lower limit of mean	2.7	14.9	-17.0	-0.6	3.4	-10.1	-2.4
Upper limit of mean	4.6	32.1	2.3	9.8	8.5	-4.2	3.9

[a,b]These pairs cannot be resolved on the DB-210 fused-silica capillary column.
[c]To calculate group differences for these compounds, values of 0 were used for the missing data in Table 75.
[d]Student t value is 2.11. The BHC isomers were excluded from the statistics.

TABLE 77. RETENTION TIMES (SCAN NUMBERS) AND THREE MOST INTENSE IONS OF THE METHOD 8120 COMPOUNDS ANALYZED BY GC/MS USING A 30 M X 0.25 MM ID (0.25 µm FILM THICKNESS) DB-5 FUSED-SILICA CAPILLARY COLUMN[a]

Compound	Scan No.	Ions at m/z (relative intensity)
1,3-Dichlorobenzene	598	146 (100), 148 (63), 111 (38)
1,4-Dichlorobenzene	606	146 (100), 148 (62), 111 (36)
Benzyl chloride	612	91 (100), 126 (25), 65 (12)
1,2-Dichlorobenzene	644	146 (100), 148 (62), 111 (41)
Hexachloroethane	703	117 (100), 119 (96), 201 (76)
1,3,5-Trichlorobenzene	786	180 (100), 182 (95), 184 (30)
Benzal chloride	794	125 (100), 127 (31), 63 (17)
1,2,4-Trichlorobenzene	845	180 (100), 182 (95), 184 (30)
1,2,3-Trichlorobenzene	891	180 (100), 182 (96), 145 (31)
Hexachlorobutadiene	897	225 (100), 227 (66), 190 (41)
Benzotrichloride	904	159 (100), 161 (63), 89 (18)
1,2,4,5-Tetrachlorobenzene	1031	216 (100), 214 (76), 218 (46)
1,2,3,5-Tetrachlorobenzene	1029	216 (100), 214 (76), 218 (46)
Hexachlorocyclopentadiene	1035	237 (100), 239 (67), 235 (62)
2-Chloronaphthalene	1078	162 (100), 127 (36), 164 (32)
1,2,3,4-Tetrachlorobenzene	1081	216 (100), 214 (78), 218 (47)
Pentachlorobenzene	1229	250 (100), 252 (61), 248 (61)
alpha-BHC	1393	183 (100), 181 (98), 219 (85)
Hexachlorobenzene	1407	284 (100), 286 (81), 282 (51)
beta-BHC	1436	109 (100), 181 (83), 111 (80)
gamma-BHC	1448	181 (100), 183 (97), 219 (82)
delta-BHC	1486	109 (100), 181 (97), 183 (97)
2,5-Dibromotoluene (IS)	968	250 (100), 169 (68), 89 (66)
1,3,5-Tribromobenzene (IS)	1129	314 (100), 316 (100), 74 (96)
α,α'-Dibromo-m-xylene (IS)	1228	183 (100), 104 (99), 185 (96)
α,2,6-Trichlorotoluene (SU-1)	1050	159 (100), 161 (64), 194 (18)
1,4-Dichloronaphthalene (SU-2)	1265	196 (100), 198 (63), 126 (31)
2,3,4,5,6-Pentachlorotoluene (SU-3)	1376	229 (100), 227 (81), 264 (67)

[a]The GC/MS operating conditions are as follows: 40°C to 300°C at 8°C/min; injector temperature 250°C; transfer line temperature: 260°C; ion source temperature: 190°C; scanning mass range, 45 to 450 amu; electron energy, 70 eV; multiplier voltage, 1,400 eV; scan rate, 1 sec.

IS -- internal standards.

SU -- surrogate compound.

Figures 49 and 50, respectively. The sensitivity of the GC/MS instrument is estimated to be approximately 0.5 to 1 ng per compound.

6.5.7 Changes Suggested for Incorporation in Method 8120 Protocol

The following items were incorporated in a proposed revision of Method 8120 which is included in Appendix B.

- The list of target compounds was expanded to include 22 target compounds.
- Extract cleanup using Florisil cartridges was included as an option.
- A GPC step for removal of waxes and lipids from municipal sludges and other high-lipid matrixes was included.
- Spiking levels for each individual analyte were suggested.
- A procedure for spiking soil samples was included.
- Internal standards and surrogates were specified.
- The use of fused-silica open tubular columns in place of the packed columns was specified.
- The GC retention times of the 22 compounds, the surrogates and the internal standards on the specified columns and at the specified conditions were included.
- A table suggesting the five concentration levels for multi level calibration (Method 8000) was included.
- Tables with MDLs and precision and accuracy data for a water and a soil matrix were included.

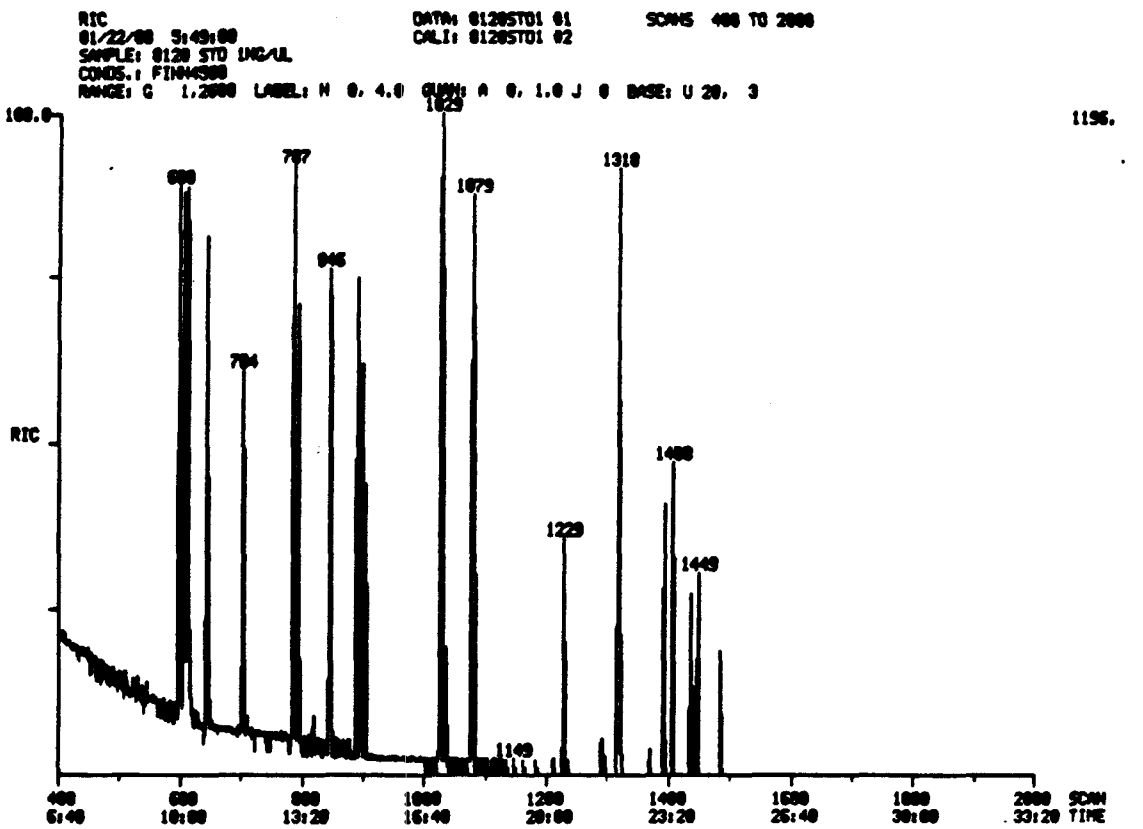

Figure 49. GC/MS chromatogram of 1 ng of Method 8120 composite standard injected on column. GC/MS conditions are given in Table 77, Footnote a.

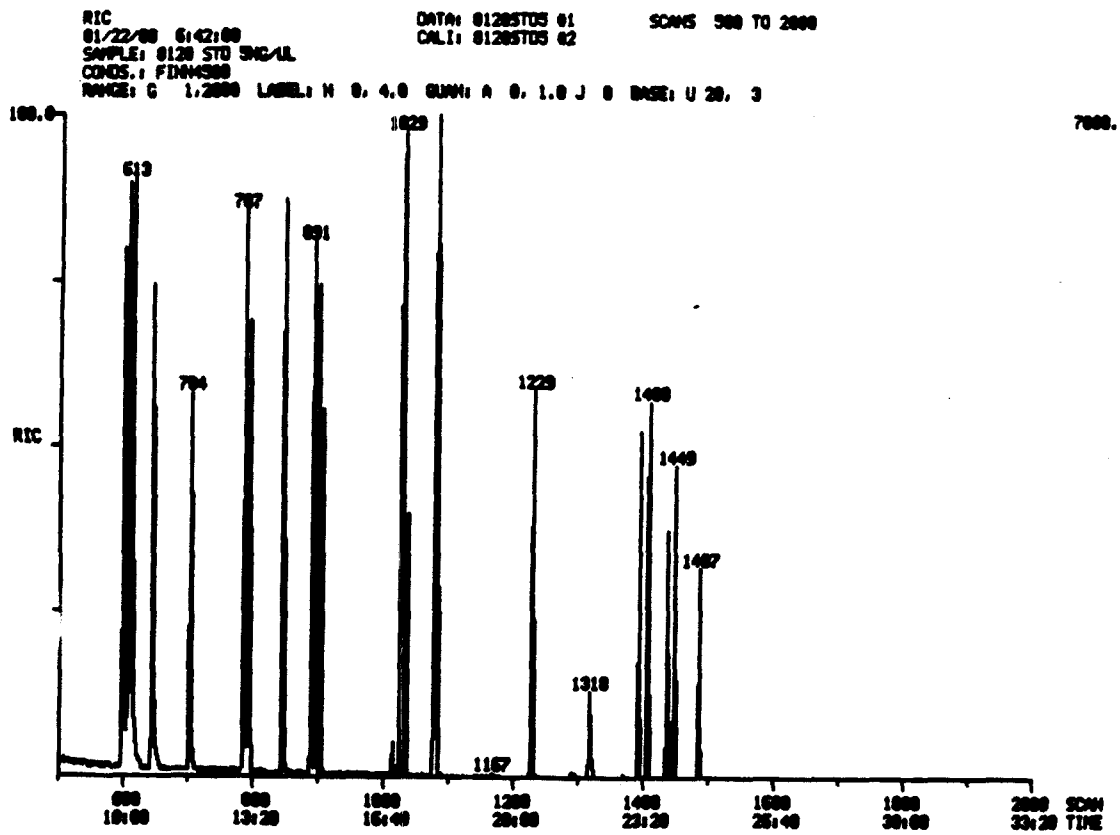

Figure 50. GC/MS chromatogram of 5 ng of Method 8120 composite standard injected on column. GC/MS conditions are given in Table 77, Footnote a.

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7. Jensen, S. L., L. Renberg, and L. Reutergardh, "Residue Analysis of Sediment and Sewage Sludge for Organochlorines in the Presence of Elemental Sulfur," Anal. Chem. 49:316-318, 1977.

8. Chou, S-F. J., R. A. Griffin, and M-I. M. Chou, "Effect of Soluble Salts and Caustic Soda on Solubility and Adsorption of Hexachlorocyclopentadiene," in: Land Disposal of Hazardous Waste, Proceedings of the 8th Annual Research Symposium, Fort Mitchell, Kentucky, PB 82-173022, 137-149, 1982.

APPENDIX A

LITERATURE REVIEW

CONTENTS

FIGURES

TABLES

TABLES (CONTINUED)

TABLES (CONCLUDED)

LIST OF COMPOUND ABBREVIATIONS USED IN THIS REPORT

Abreviation	Complete Name
CBs	Chlorobenzenes
2-CN	2-Chloronaphthalene
DCB	Dichlorobenzene
HCB	Hexachlorobenzene
HCE	Hexachloroethane
HCBu	Hexachlorobutadiene
BHC	Hexachlorocyclohexane
HCCP	Hexachlorocyclopentadiene
OCPs	Organochlorine Pesticides
OPPs	Organophosphorus Pesticides
QCB	Pentachlorobenzene
PCBs	Polychlorinated Biphenyls
PCDPEs	Polychlorinated Diphenyl Ethers
PCDBFs	Polychlorinated Dibenzofurans
PCDBDs	Polychlorinated Dibenzodioxins
PCNs	Polychlorinated Naphthalenes
PCTs	Polychlorinated Terphenyls
TeCB	Tetrachlorobenzene
TCB	Trichlorobenzene

SECTION 1

INTRODUCTION

The Resource Conservation and Recovery Act (RCRA) of 1976 and its elements require the Environmental Protection Agency (EPA) to regulate hazardous waste activities. Implementation and enforcement of RCRA requires analytical methodologies that will provide reliable data. The document "Test Methods for Evaluating Solid Waste," Office of Solid Waste Manual SW-846, revised recently, provides a compilation of methods for evaluating RCRA solid wastes for environmental and human health hazards. SW-846 Method 8120 for chlorinated hydrocarbons requires evaluation as part of an ongoing program of EPA-Las Vegas. To assist EPA-Las Vegas in this evaluation, Acurex was asked to perform a literature review and recommend approaches for sample extraction, cleanup, analysis, and compound confirmation.

This report presents the literature review pertinent to this study. This literature review was performed using the computerized Chemical Abstracts search and several EPA reports dealing with the analysis of organic compounds in water. Furthermore, recent issues of Analytical Chemistry, the Journal of Chromatography, the Journal of Chromatographic Science, the Journal of the Association of Official Analytical Chemists, and Environmental Science and Technology were searched to gather recent references that were not in the computer data base.

The computer searches were done using DIALOG. Chemical Abstracts files were searched back to 1977, for all references containing "chlorinated hydrocarbons," "gas chromatography," "extraction," and "cleanup." Approximately fifty articles that were judged to be scientifically relevant to the objectives of this study were retrieved from the literature.

The literature review summary that is presented in this report addresses the following:

- Sample preservation techniques
- Extraction techniques for water, sediment, and soil
- Cleanup techniques
- Gas chromatographic analysis (columns, retention time information, chromatographic problems)
- Compound confirmation.

SECTION 2

CHEMICAL STRUCTURES, PHYSICO-CHEMICAL PROPERTIES, MANUFACTURE, AND INDUSTRIAL USES

2.1 CHEMICAL STRUCTURES AND PHYSICO-CHEMICAL PROPERTIES

The Chemical Abstracts Registry (CAS) numbers, chemical structures, molecular formulae, and the nomenclatures for 22 chlorinated hydrocarbons that are proposed for evaluation in this study are given in Table 1. Their physico-chemical properties are listed in Table 2.

2.2 MANUFACTURE AND INDUSTRIAL USES

Benzyl Chloride, Benzal Chloride, and Benzotrichloride

Benzyl chloride, benzal chloride, and benzotrichloride are manufactured by the chlorination of toluene and are converted to various chemical intermediates or products. Benzyl chloride is utilized in the manufacture of butyl-benzyl phthalate; benzal chloride is hydrolyzed to benzaldehyde, and benzotrichloride is converted to benzoyl chloride (1). Small amounts of benzotrichloride are used in the manufacture of benzotrifluoride, an intermediate in the manufacture of dyes, and in the synthesis of hydroxybenzophenone ultraviolet light stabilizers (1).

Chlorinated Benzenes

Chlorinated benzenes, with the exception of 1,3-dichlorobenzene, 1,3,5-trichlorobenzene and 1,2,3,5-tetrachlorobenzene, are produced by chlorinating benzene in the presence of a Friedel-Crafts catalyst (ferric chloride) (1). Each compound, except hexachlorobenzene, can be further chlorinated to produce various higher-chlorinated benzenes. Pure compounds are obtained by distillation and crystallization.

1,2-Dichlorobenzene is used in the manufacture of toluene diisocyanates and 3,4-dichloroaniline, and it has found some limited use as a heat transfer fluid. 1,4-Dichlorobenzene is used in mothballs and room deodorant blocks. 1,2,4-Trichlorobenzene has limited uses as a solvent and as a dye carrier in the textile industry. 1,2,4,5-Tetrachlorobenzene is used exclusively as the raw material for 2,4,5-triacid and its esters, and for hexachlorophene. The other chlorinated benzenes have no significant industrial applications.

TABLE 1. CAS NUMBERS, CHEMICAL STRUCTURES, MOLECULAR FORMULAE, AND NOMENCLATURES OF 22 CHLORINATED HYDROCARBONS PROPOSED FOR EVALUATION OF METHOD 8120

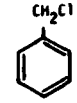
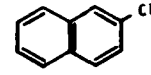
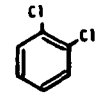
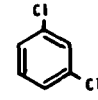
Common name	Chemical Abstracts Registry No.	Chemical structure	Molecular formula (molecular weight)	Nomenclature
1. Benzal chloride	98-87-3		$C_7H_6Cl_2$ (160)	(Dichloromethyl)benzene or alpha,alpha-Dichlorotoluene
2. Benzotrichloride	98-07-7		$C_7H_5Cl_3$ (194)	(Trichloromethyl)benzene or alpha,alpha,alpha-Trichlorotoluene
3. Benzyl chloride	100-44-7		C_7H_7Cl (126)	alpha-Chlorotoluene or (Chloromethyl) benzene
4. 2-Chloronaphthalene	91-58-7		$C_{10}H_7Cl$ (162)	2-Chloronaphthalene
5. 1,2-Dichlorobenzene	95-50-1		$C_6H_4Cl_2$ (146)	1,2-Dichlorobenzene
6. 1,3-Dichlorobenzene	541-73-1		$C_6H_4Cl_2$ (146)	1,3-Dichlorobenzene

TABLE 1. (continued)

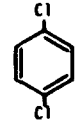
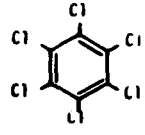
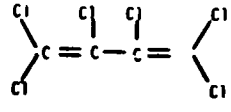
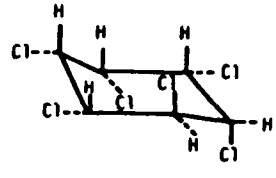
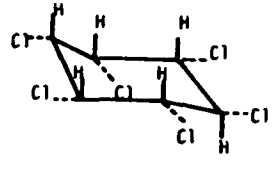
Common name	Chemical Abstracts Registry No.	Chemical structure	Molecular formula (molecular weight)	Nomenclature
7. 1,4-Dichlorobenzene	106-46-7		$C_6H_4Cl_2$ (146)	1,4-Dichlorobenzene
8. Hexachlorobenzene	118-74-1		C_6Cl_6 (282)	Hexachlorobenzene
9. Hexachlorobutadiene	87-68-3		C_4Cl_6 (258)	Hexachlorobutadiene
10. alpha-BHC	319-84-6		$C_6H_6Cl_6$ (288)	alpha-1,2,3,4,5,6-Hexachlorocyclohexane
11. beta-BHC	319-85-7		$C_6H_6Cl_6$ (288)	beta-1,2,3,4,5,6-Hexachlorocyclohexane

TABLE 1. (continued)

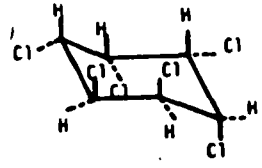
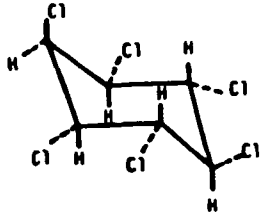
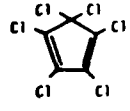
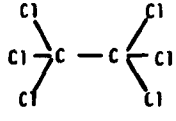
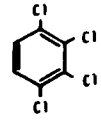
	Common name	Chemical Abstracts Registry No.	Chemical structure	Molecular formula (molecular weight)	Nomenclature
12.	gamma-BHC (lindane)	58-89-9		$C_6H_6Cl_6$ (288)	gamma-1,2,3,4,5,6-Hexachlorocyclohexane
13.	delta-BHC	319-86-8		$C_6H_6Cl_6$ (288)	delta-1,2,3,4,5,6-Hexachlorocyclohexane
14.	Hexachlorocyclopentadiene	77-47-4		C_5Cl_6 (270)	Hexachlorocyclopentadiene
15.	Hexachloroethane	67-72-1		C_2Cl_6 (234)	Hexachloroethane
16.	1,2,3,4-Tetrachlorobenzene	634-66-2		$C_6H_2Cl_4$ (214)	1,2,3,4-Tetrachlorobenzene

TABLE 1. (concluded)

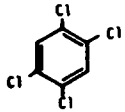
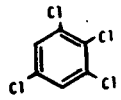
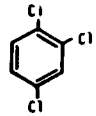
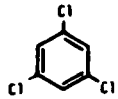
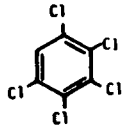
	Common name	Chemical Abstracts Registry No.	Chemical structure	Molecular formula (molecular weight)	Nomenclature
17.	1,2,4,5-Tetrachlorobenzene	95-94-2		$C_6H_2Cl_4$ (214)	1,2,4,5-Tetrachlorobenzene
18.	1,2,3,5-Tetrachlorobenzene	634-90-2		$C_6H_2Cl_4$ (214)	1,2,3,5-Tetrachlorobenzene
19.	1,2,4-Trichlorobenzene	120-82-1		$C_6H_3Cl_3$ (180)	1,2,4-Trichlorobenzene
20.	1,2,3-Trichlorobenzene	87-61-6		$C_6H_3Cl_3$ (180)	1,2,3-Trichlorobenzene
21.	1,3,5-Trichlorobenzene	108-70-3		$C_6H_3Cl_3$ (180)	1,3,5-Trichlorobenzene
22.	Pentachlorobenzene	608-93-5		C_6HCl_5 (248)	Pentachlorobenzene

TABLE 2. PHYSICO-CHEMICAL PROPERTIES OF THE METHOD 8120 COMPOUNDS

Compound name	Melting point[a] (°C)	Boiling point[a] (°C)	Density[a] (Kg/L)	Water solubility at 25°C (mg/L)	log K_{ow}[c]
Benzal chloride	-16.4	205.2	1.2560	h	h
Benzotrichloride	-4.75	220.6	1.3740	h	h
Benzyl chloride	-39.2	179.4	1.1135	h	h
2-Chloronaphthalene	61.0[f]	259.0	1.2656	6.74[f]	h
1,2-Dichlorobenzene	-16.97	180.4	1.3022	45[f]	3.59[g]
1,3-Dichlorobenzene	-24.76	173.0	1.2828	123[f]	3.59[g]
1,4-Dichlorobenzene	53.04	174.1	1.2475	90[b], 79[f]	3.4[b]; 3.59[g]
Hexachlorobenzene	228.7	319.3	1.5960	0.005[b]	5.5[b]; 6.53[g]
Hexachlorobutadiene	-21.0[e]	215.0[e]	1.5542[e]	2[f]	3.4[b]
alpha-BHC	159.2	288.0[e]	h	1.63[d];1.21 to 2.03[f]	h
beta-BHC	311.7	$60.0^{0.5}$[e]	h	0.70[d];0.13 to 0.7[f]	h
gamma-BHC	112.9	323.4[e]	h	7.3 to 10.0[d];8.6 to 31.4[f]	h
delta-BHC	140.8	$600^{0.36}$[e]	h	h	h
Hexachlorocyclopentadiene	11.34	239.0	1.7100	1.8[f]	h
Hexachloroethane	185.0	186.0	2.0940	5.0;50[f]	h
1,2,3,4-Tetrachlorobenzene	47[g]; 46.0	254.9	1.7000	4.3[b];4.27[g]	4.5[b]; 5.05[g]
1,2,4,5-Tetrachlorobenzene	140[g];139.5	248.0	1.8330	0.59[g]	5.05[g]
1,2,3,5-Tetrachlorobenzene	54[g];51.0	246.0	h	3.47[g]	5.05[g]
1,2,4-Trichlorobenzene	25[g];17.15	213.8	1.4483	30[b];34[g]	4.0[b]; 4.27[g]
1,2,3-Trichlorobenzene	53[g];53.5	218.5	h	31[g]	4.27[g]
1,3,5-Trichlorobenzene	63[g];63.5	208.5	h	6.5[g]	4.27[g]
Pentachlorobenzene	86[g];85.0	276.0	$1.8342^{16.5}$[e]	0.56[b]	4.9[b]; 5.79[g]

[a]Data taken from Reference 1.
[b]Data taken from Reference 2.
[c]K_{ow} is the octanol/water partition coefficient.
[d]Data taken from Reference 3.
[e]Data taken from Reference 4.
[f]Data taken from Reference 5.
[g]Data taken from Reference 6.
[h]Information is not available.

BHCs

Benzene hexachloride (BHC) or hexachlorocyclohexane is the fully saturated product formed by light-catalyzed addition of chlorine to benzene. The reaction produces a number of stereo-isomeric compounds of the composition $C_6H_6Cl_6$. The composition of the various isomers in benzene hexachloride depends on the conditions of manufacture but is commonly as follows:

- alpha (65 percent)
- beta (7 percent)
- gamma (14 percent)
- all others (14 percent)

The physico-chemical properties of the four major isomers are included in Table 2.

Lindane is one of the oldest chlorinated insecticides. It is used on field crops, vegetable crops, fruit crops, viticulture, etc.

Hexachlorocyclopentadiene

Hexachlorocyclopentadiene is obtained by chlorination of cyclopentadiene with alkaline hypochlorite solution at 40°C; the reaction product is recovered by fractional distillation. Preparation of hexachloro-cyclopentadiene by thermal dechlorination of octachlorocyclopentene at 470°C to 480°C was also reported (1).

2-Chloronaphthalene

Ferric chloride-catalyzed chlorination of molten naphthalene at 100°C to 110°C gives a crude product which, distilled at 259°C to 260°C, gives a fraction containing 91 percent 1-chloronaphthalene and 9 percent 2-chloronaphthalene (1). Pure 2-chloronaphthalene can be prepared from 2-naphthylamine via the diazonium salt by the Sandmeyer reaction (1).

Hexachloroethane

Hexachloroethane is obtained by chlorination of tetrachloroethylene, in the presence of ferric chloride, at 100°C to 140°C (1). Minor amounts of hexachloroethane are formed in many industrial chlorination processes of saturated and unsaturated C_2 hydrocarbons. Hexachloroethane is used in the formulations of high-pressure lubricants, as a degasifier in the manufacture of aluminum and magnesium metals, and also as a chain transfer agent in the radiochemical emulsion preparation of propylene-tetrafluoroethylene copolymer (1).

2.3 OCCURRENCE

Table 3 summarizes the median concentrations of chlorinated hydrocarbons or industrial effluents, ambient water, sediments, and biota for stations collectively maintained by EPA regions and other government agencies (e.g., U. S. Geological Survey) in a computerized water quality database called STORET (STOrage and RETrieval) (7). Only two of the chlorinated hydrocarbons listed in Table 3 were detected in water samples in more than 10 percent of the samples (7). Because not all of the STORET stations had measured sediment and biota concentration, there are fewer values for these matrices.

The occurrence of the chlorinated benzenes in the environment seems to be related to their high production (approximately 200,000 metric tons in the U.S. in 1978) as well as to their uses which were described in Section 2.2 (8). Those compounds that may have entered the environment are not readily biodegraded, photolyzed, or hydrolyzed (5). Table 4 identifies the wastes dumped at Hyde Park, the S and N areas, and Love Canal in New York State from 1953 until 1979. Leachates from the disposal sites have contaminated the Niagara River and, subsequently, Lake Ontario. Chlorobenzene concentrations in the Niagara River were reported by Oliver and Nicol (10) and are given in Table 5. Chlorobenzene and chlorotoluene concentrations in the Niagara River watershed were reported by Elder et al. (11) and are presented in Table 6. A series of unexpected compounds which were related to benzyl chloride and benzoyl chloride wastes were found at the 102nd Street bay and in the Bloody Run Creek (11). The benzyl derivatives detected in samples collected from the 102nd Street area were attributed to migration of organics from the Love Canal area because the 102nd Street dump is not known to contain any benzyl chloride wastes and because the highest concentration of benzyl derivatives in the bay was directly in front of the storm sewer outfall from the Love Canal area (11). Elder et al. (11) attributed the presence of various chlorinated benzyl alcohols, benzaldehydes, and benzoic acids to reaction of labile chlorine attached to the carbon adjacent to the benzene ring. Thus, benzyl alcohol formed from benzyl chloride and benzoic acid formed from benzotrichloride (11). Oliver and Nicol (10) reported that the concentrations of all chlorinated benzenes (except 1,4-and 1,2-dichlorobenzenes) were below 1 ppt in Lakes Ontario and Huron. The mean concentrations for 1,4-dichlorobenzene were 45 ppt for Lake Ontario and 4 ppt for Lake Huron. 1,2-Dichlorobenzene was detected only in Lake Ontario at a mean concentration of 5 ppt. Drinking water samples collected from three cities in the Lake Ontario vicinity contained mean concentrations of 13 ppt for 1,4-dichlorobenzene, 3 ppt for 1,2-dichlorobenzene, and 2 ppt for 1,2,4-trichlorobenzene (10).

Chlorobenzene concentrations in the Great Lakes were also investigated (10). Concentrations are lowest in Lake Superior (~ 10 ppb), somewhat higher in Lakes Huron and Erie (~ 26 ppb for Lake Huron and ~ 38 ppb for Lake Erie) and much higher in Lake Ontario (~ 560 ppb). The values given represent the sum of the dichloro- through hexachlorobenzenes. Because about 50 percent of the sediments in Lake Ontario come from the Niagara River, the contamination of Lake Ontario was attributed to the chemical manufacturing effluents and the waste disposal site leachates (10).

TABLE 3. MEDIAN CONCENTRATIONS OF THE CHLORINATED HYDROCARBONS FOR INDUSTRIAL EFFLUENTS (µg/L), AMBIENT WATER (µg/L), SEDIMENTS (µg/Kg), AND BIOTA (µg/Kg) FOR THE UNITED STATES FROM ALL STORET STATIONS[a,b]

Compound	Effluents			Water			Sediment			Biota		
	Median (µg/L)	n[c]	Percent detectable	Median (µg/L)	n	Percent detectable	Median (µg/Kg)	n	Percent detectable	Median (µg/Kg)	n	Percent detectable
alpha-BHC	<0.007	630	4.1	<0.018	1,470	8.0	<3.0	416	6.0	0.006	320	17
beta-BHC	<0.007	633	2.0	<0.050	1,010	1.3	d	d	d	d	d	d
gamma-BHC	<0.007	628	1.4	<0.100	880	0.8	<10.0	331	0.3	<0.050	127	1.6
delta-BHC	<0.050	62	d	0.020	4,505	27.0	<2.0	596	0.5	d	d	d
Chloronaphthalene	<10.000	1,255	1.4	<10.000	863	0.2	<500	340	0.3	<2.000	108	0
Hexachloroethane	<10.000	1,253	2.0	<10.000	882	0.1	<500	356	0	<2.000	116	0
Hexachlorobutadiene	<6.000	1,190	1.6	<10.000	593	0.2	<500	196	0	<2.500	51	0
Hexachlorocyclopentadiene	<10.000	1,228	0.9	<10.000	854	0.1	<500	344	0	<2.500	116	0
1,2-Dichlorobenzene	<10.000	1,311	2.5	<10.000	1,077	0.6	<500	352	0.9	<2.000	115	0
1,3-Dichlorobenzene	<10.000	1,301	1.5	<10.000	986	0.3	<500	357	0.3	<2.000	115	0
1,4-Dichlorobenzene	<10.000	1,306	1.7	<0.100	8,576	3.0	<500	357	2.0	<2.000	117	0
Trichlorobenzene	<10.000	1,256	2.1	<10.000	882	0.3	<500	353	0.6	<2.000	114	0
Hexachlorobenzene	<10.000	1,267	2.2	0.020	1,786	26.0	<200	448	1.0	<2.500	136	0

[a] If less than 10 percent of the values contained in the median are detectable, the median is reported as "less than".
[b] Data taken from Reference 7.
[c] n is the number of stations.
[d] Information is not available.

TABLE 4. WASTES DUMPED AT HYDE PARK, THE S AND N AREAS, AND LOVE CANAL[a]

Type of Waste	Loading (tons)		
	Hyde Park[b]	S and N areas	Love Canal
Chlorobenzene	16,500	18,900	2,000
Benzyl chloride	3,400	1,600	2,400
BHCs	2,000		6,900
Benzotrichlorides	1,700		
Chlorotoluenes	1,700		
Hexachlorocyclopentadiene	1,100	17,400	

[a]Data taken from Reference 9.
[b]The Hyde Park area was used by Hooker Chemical Company as a dump for approximately 160 million pounds of toxic wastes from 1953 to 1979.

TABLE 5. CHLOROBENZENE CONCENTRATIONS IN THE NIAGARA RIVER (ppt)[a]

Compound	Site[b] 1	2	3	4
1,3-Dichlorobenzene	<1	18	8	6
1,4-Dichlorobenzene	1	52	94	19
1,2-Dichlorobenzene	<1	9	56	12
1,3,5-Trichlorobenzene	<0.1	1	8	2
1,2,4-Trichlorobenzene	0.1	12	107	7
1,2,3-Trichlorobenzene	<0.1	2	38	2
1,2,3,5-Tetrachlorobenzene	<0.05	1	3	0.2
1,2,4,5-Tetrachlorobenzene	<0.05	4	31	2
1,2,3,4-Tetrachlorobenzene	0.06	6	126	3
Pentachlorobenzene	0.05	2	22	0.7
Hexachlorobenzene	0.02	17	1	0.2

[a]Data taken from Reference 10.

[b]Sampling sites: 1, upstream of Grand Island and the city of Niagara Falls, NY, mean of five samples collected in upper Niagara River; 2, at Niagara Falls, NY, just below waste disposal dump; 3, at Niagara Falls, NY, just below chemical manufacturing company effluent discharge; 4, near Niagara-on-the-Lake at the mouth of the river; mean of six samples, three collected in the spring and three in the fall of 1980.

TABLE 6. ORGANIC COMPOUNDS IDENTIFIED IN THE NIAGARA RIVER WATERSHED (ppm)[a]

Compound	102nd Street	Bloody Run Creek	Gill Creek
Chlorobenzenes			
Chlorobenzene	b	c	c
Dichlorobenzenes	c	c	c
Trichlorobenzenes	40	8	c
Tetrachlorobenzenes	200	25	c
Pentachlorobenzene	100	10	d
Hexachlorobenzene	8	10	30
Chlorotoluenes			
Dichlorotoluenes	20	90	d
Trichlorotoluenes	100	50	d
Tetrachlorotoluenes	40	10	d
Pentachlorotoluenes	40	5	d
Hexachlorotoluenes	40	d	d
Heptachlorotoluenes	20	d	d
BHCs	10	c	d

[a]Data taken from Reference 11.
[b]Sample was not analyzed for this compound.
[c]Compound was detected in water at a level of 0.1 to 1 ppb or in sediment at a level of 0.5 to 2 ppm but was not quantitated.
[d]Compound was not detected in water or in sediment; lower limits of sensitivity are about 0.1 ppb in water and 0.5 ppm in sediment.

Amounts of chlorobenzenes in Lake Ontario compartments reported by Oliver (2) are presented in Table 7. The detection of chlorobenzenes in lake trout at levels as high as 130 ppb for hexachlorobenzene is striking. This indicates that such compounds are quite persistent in the environment, and the fact that they were detected in fish samples shows that chlorinated benzenes are bioconcentrated.

TABLE 7. AMOUNTS (Kg) OF CHLOROBENZENES IN LAKE ONTARIO COMPARTMENTS[a]

Compartment	1,2,4-TCB	1,2,3,4-TeCB	QCB	HCB
Bottom sediments	11,000	3,300	4,100	8,500
Lake water	700	210	90	90
Suspended sediments	10	4	4	9
Biota	2	2	2	8

[a]Data taken from Reference 2.

SECTION 3

ANALYTICAL METHODOLOGIES FOR CHLORINATED HYDROCARBONS

A summary of published methods for the determination of chlorinated hydrocarbons in water, wastewater, soils, etc., is presented in Table 8. Examination of this table shows a wide range of detection methods (e.g., gas chromatography with electron capture detection, Hall electrolytic conductivity or photoionization detection, and gas chromatography/mass spectrometry) that vary in sensitivity, selectivity, complexity, ease of operation, etc. A detailed discussion of each of these techniques follows. Sample preservation and the isolation of the chlorinated hydrocarbons from water, soil, and sediments are discussed first. The sample extract cleanup and the analysis techniques are discussed next and are followed by a discussion of the compound confirmation techniques that were reported in the literature.

3.1 SAMPLE PRESERVATION

The importance of proper sample preservation cannot be overemphasized. The choice of the preservation method depends on the type of sample, the compound(s) to be determined in the sample, the duration of sample storage prior to analysis, and the analytical procedure to be used (21). The method chosen must not impair the analytical procedure to be used. Amber glass bottles are the container of choice because of the protection from photodegradation. The bottle must not be prerinsed with sample before collection (12). Composite samples should be collected in glass containers and refrigerated. When automatic sampling equipment is to be used, then it must be free of any tygon tubing (12). Most investigators report that water samples should be refrigerated at 4°C while soils and sediments should be frozen until analysis. Oliver and Nicol (10) stored water samples in bottles without headspace and with aluminum foil caps at 4°C until extraction (<48 hrs).

Weil and Quentin (22) investigated the effect of container, temperature, and light on the storage of water samples containing lindane at 10 µg/L and reported substantial loss during a 2-week storage period for polyethylene containers. In another study, Millar et al. (23) investigated the effects of pH, temperature, and residual chlorine on the preservation of spiked water samples containing BHCs and other organochlorine pesticides in glass bottles sealed with aluminum-foil-lined caps, for a period of 7 days. The results of Millar's study are summarized in Table 9. It is evident from the data that, at pH 10 and 24°C the losses were significant for alpha-, gamma-, and

TABLE 8. SUMMARY OF ANALYTICAL METHODOLOGIES FOR CHLORINATED HYDROCARBONS

Method	Matrix	Compounds	Extraction procedure	Cleanup procedure	Analysis procedure	MDL (µg/L or µg/Kg)	Reference
EPA Method 612	Water	1,2-DCB 1,3-DCB 1,4-TCB 1,2,4-TCB 2-CN HCB HCE HCBu	Separatory funnel methylene chloride (no pH adjustment)	12 g Florisil; 20 mL petroleum ether	GC/ECD 1.8 m x 2 mm ID glass column packed with 1 percent SP-1000 on Supelcoport (100/120 mesh) 1.8 m x 2 mm ID glass column packed with 1.5 percent OV-1/2.4 percent OV-225 on Supelcoport (80/100 mesh)	0.03 - 1.34	12
EPA Method 625	Water	1,2-DCB 1,3-DCB 1,4-DCB 1,2,4-TCB HCB alpha-BHC beta-BHC gamma-BHC delta-BHC HCE HCCP HCBu 2-CN	Separatory funnel continuous liquid-liquid extractor methylene chloride (pH > 11 and then pH < 2)	None	GC/MS 1.8 m x 2 mm ID glass column packed with 3 percent SP-2250 on Supelcoport (100/120 mesh)	0.9 - 4.4	13
EPA Method 1625	Water	1,2-DCB 1,3-DCB 1,4-DCB 1,2,3-TCB 1,2,4-TCB HCE 2-CN HCB HCCP HCBu	Separatory funnel continuous liquid-liquid extractor methylene chloride (pH 12-13 and then pH < 2)	None	Isotope dilution GC/MS 30 m x 0.25 mm ID DB-5 fused-silica capillary column or equivalent	10	14
EPA Method 8120	Liquids Solids	1,2-DCB 1,3-DCB 1,4-DCB HCB HCBu BHCs HCCP HCE TeCB 1,2,4-TCB QCB Benzal chloride Benzotrichloride Benzyl chloride	EPA Method 3510 EPA Method 3520 EPA Method 3540 EPA Method 3550	EPA Method 3620	GC/ECD 1.8 m x 2 mm ID glass column packed with 1 percent SP-1000 on Supelcoport (100/120 mesh) 1.8 m x 2 mm ID glass column packed with 1.5 percent OV-1/2.4 percent OV-225 on Supelcoport (80/100 mesh)	0.03 - 1.34	15

MDL - Method detection limit.

TABLE 8. (concluded)

Method	Matrix	Compounds	Extraction procedure	Cleanup procedure	Analysis procedure	MDL (µg/L or µg/Kg)	Reference
EPA Method 8010	Liquids Solids	1,2-DCB 1,3-DCB 1,4-DCB	EPA Method 5030	None	GC/Hall 8 ft x 0.1 in ID glass column packed with 1 percent SP-1000 on Carbopak-B (60/80 mesh) 6 ft x 0.1 in ID glass column packed with n-octane on Porasil C	0.15 - 0.32	16
EPA Method 8020	Liquids Solids	1,2-DCB 1,3-DCB 1,4-DCB	EPA Method 5030	None	GC/PID 6 ft x 0.08 in ID glass column packed with 5 percent SP-1200/1.75 percent Bentone on Supelcoport (100/120 mesh) 8 ft x 0.1 in ID glass column packed with 5 percent 1,2,3-Tris(2-cyanoethoxy)-propane on Chromosorb W-AW (60/80 mesh)	0.3 - 0.4	17
EPA Method 8080	Liquids Solids	alpha-BHC beta-BHC gamma-BHC delta-BHC	EPA 3510 EPA 3520 EPA 3540 EPA 3550	EPA Method 3620	GC/ECD 1.8 m x 4 mm ID glass column packed with 1.5 percent SP-2250/1.95 percent SP-2401 on Supelcoport 1.8 m x 4 mm ID glass column packed with 3 percent OV-1 on Supelcoport	0.003-0.009[a]	18
EPA Method 8250 8270	Liquids Solids	alpha-BHC beta-BHC gamma-BHC delta-BHC 2-CN 1,2-DCB 1,3-DCB 1,4-DCB HCB HCBu HCCP HCE QCB 1,2,4,5-TeCB 1,2,4-TCB	EPA 3510 EPA 3520 EPA 3540 EPA 3550	None	GC/MS 2 m x 2 mm ID glass column packed with 3 percent SP-2250 DB on Supelcoport (100/120 mesh) (8250) 30 m x 0.25 mm ID DB-5 fused-silica capillary column (8270)	10[b]; 660[c]	19 20

MDL - Method detection limit.
[a]These values were reported for reagent water.
[b]This value was reported for ground water.
[c]Ths value was reported for low-level soil/sediment.

TABLE 9. PRESERVATION OF WATER SAMPLES CONTAINING BHCs AT 4°C AND 24°C

Compound	Recovery[a] (percent) pH 2	pH 7	pH 10
t = 4°C			
alpha-BHC	64	60	82
beta-BHC	86	98	81
gamma-BHC	100	100	84
delta-BHC	80	108	74
t = 24°C			
alpha-BHC	65	68[b] (25)[c]	19
beta-BHC	84	87	95
gamma-BHC	94	93	15
delta-BHC	100[b] (64)[c]	101[b] (77)[c]	36[b] (26)[c]

[a]Data taken from Reference 23. Average of four replicates unless accompanied by parenthetical values.
[b]Average of two replicates.
[c]When residual chlorine was present; average of two replicates.

delta-BHC. Residual chlorine also contributes to the decrease in compound concentration, expecially for delta-BHC (23).

Stability of the chlorinated hydrocarbons in soils has not been systematically investigated. Storage of soil samples at room temperature should be avoided since degradation of some chlorinated compounds does occur (24). Losses of delta-BHC after incubation of soil samples at 25°C, under aerobic conditions, were observed 7 days after initiation of experiment, and only 35 to 40 percent of it was found at day 30 of the experiment (24). Storage of freeze-dried sediment samples at 4°C, in the dark, indicated no evidence of degradation or volatilization for some chlorinated benzenes and hexachlorobutadiene (Table 10).

Deep freezing at -20°C appears to be the most suitable method for storage of solid matrices since it has the widest range of application, causes the least changes in the samples, and makes the addition of preservatives unnecessary.

3.2 EXTRACTION

A number of methods have been reported for isolation of chlorinated hydrocarbons from water, soil, and sediment. The extraction techniques that have been used on water samples include liquid-liquid extraction by stirring, separatory funnel extraction, and extraction in a continuous liquid-liquid extractor, and adsorption onto polymeric materials such as XAD resins and other liquid-chromatographic bonded stationary phases. The methods used for extraction of soil and sediment samples with organic solvents include Soxhlet extraction and sonication. Each of these techniques will be reviewed below.

3.2.1 Extraction of Water Samples

Table 11 is a summary of extraction methods for water samples published in the literature for chlorinated hydrocarbons. The following describes in detail some of these procedures.

3.2.1.1 Liquid-Liquid Extraction

Liquid-liquid extraction is the simplest and most widely used technique for extraction of organic compunds from water. This technique consists of mixing the sample with a water-immiscible solvent in the original sample container, a separatory funnel, or a continuous liquid-liquid extractor. An important parameter for the liquid-liquid extraction is the solvent. It must be immiscible with water, it must extract the organics of interest from the sample, and it must not interfere with the analysis procedure.

In the case of the separatory funnel technique, up to 1 liter of an aqueous sample is extracted in a separatory funnel by shaking it with an organic solvent. The layers are allowed to separate and the organic solvent is drawn off. Solvents with a density greater than that of water are preferred since the organic layer can be removed more easily.

TABLE 10. EFFECT OF LONG-TERM COLD STORAGE ON LEVELS OF CHLOROBENZENES AND HEXACHLOROBUTADIENE IN FREEZE-DRIED SEDIMENT SAMPLES[a]

Compound	Reference value ± SD (ng/g)[b]	Residue level after storage (ng/g)		
		12 months	24 months	48 months
1,3,5-Trichlorobenzene	34.3 ± 2.6	29	37	32
1,2,4-Trichlorobenzene	80.7 ± 5.4	79	71	88
1,2,4,5-Tetrachlorobenzene	84.0 ± 4.9	91	106	91
1,2,3,4-Tetrachlorobenzene	36.5 ± 2.4	37	32	34
Pentachlorobenzene	48.6 ± 2.4	49	44	48
Hexachlorobenzene	200.6 ± 13.2	207	188	190
Hexachlorobutadiene	21.3 ± 1.6	c	21	18

[a]Data taken from Reference 25.
[b]Triplicate analyses.
[c]Information is not available.
SD -- Standard deviation.

TABLE 11. SUMMARY OF EXTRACTION TECHNIQUES FOR WATER SAMPLES

Method	Solvent	Compound	Recovery (percent)	Spiking level (ppb)	Reference
Solvent extraction (bottle/stirbar)	Pentane	DCBs, TCBs, TeCBs, QCB, HCB	80 to 96 80 to 91	0.0001 to 0.011 0.001 to 0.1	10, 26, 27
Solvent extraction (separatory funnel, continuous liquid-liquid extractor)	Methylene chloride	DCBs, 1,2,4-TCB, HCB, HCCP, HCBu, HCE, 2-CN	<160	10 to 100	12
Solvent extraction (separatory funnel, continuous liquid-liquid extractor)	Methylene chloride	DCBs, 1,2,4-TCB, HCB, HCCP, HCBu, HCE, 2-CN, BHCs	<172	100	13, 14[a]
Solvent extraction (separatory funnel)	Methylene chloride	BHCs	92 to 109	0.02 to 0.04	23
	15 percent methylene chloride in hexane	BHCs	86 to 106	0.02 to 0.04	23
Solvent extraction (separatory funnel)	Methylene chloride	DCBs, TcBs, TeCBs, QCB, HCB	Table 12[b]		28
Solvent extraction (separatory funnel)	Methylene chloride	DCBs, TCBs, TeCBs, QCB, HCB, BHCs	c		11
Solvent extraction (bottle/stirbar)	Cyclohexane	HCB PCBs	c		29
Solvent extraction (turbo-stirring)	Hexane	BHCs HCB	quantitative	ppt	30
Adsorption onto Chromosorb 102 (100 mm x 1.5 mm ID; 60 mg)	Pentane	DCBs, TCBs, TeCBs, QCB, HCB	86 to 97 80 to 91	0.0001 to 0.011 0.001 to 01	25

[a]Refer to EPA Method 1625 for compound recovery data.
[b]For EPA Method 625, first partition was at pH 11, the second at pH 2. For EPA Method 625.1, first partition was at pH 7, the second at pH 2.
[c]Information is not available.

Disadvantages of the separatory funnel extraction are:

- Limited sample size
- Emulsion formation during extraction of wastewaters.

To break emulsions, it has been recommended that the extract be passed through a 25-mm-thick glass wool pad (31).

Several reports dealing with the determination of chlorinated hydrocarbons in water samples involve liquid-liquid extraction; however, there appears to be little consensus as to the best organic solvent, the extraction conditions (e.g., solvent-to-liquid ratios, time, degree of agitation, pH), or the use of salts to enhance partitioning into the organic layer. Table 11 lists the various systems used and the percent recoveries reported. Among the solvents reported we found: pentane (10, 26, 27), methylene chloride (11,12,13,14,23,28), 15 percent methylene chloride in hexane (23), cyclohexane (29), and hexane (30). Most literature reports indicate that extraction at neutral pH gives quantitative recoveries for the chlorinated hydrocarbons.

Eichelberger et al. (28) assessed the performance of the EPA Methods 625 and 625.1 for a series of organic compounds including those of interest to our study. The basic difference in the two EPA methods is in the extraction step. In EPA Method 625, the water sample is first adjusted to pH>11 and extracted with methylene chloride to recover the neutral and the basic compounds; the acidic compounds are then extracted at pH <1. In EPA Method 625.1, the extraction with methylene chloride is first performed at pH 7 followed by acidification and extraction of the acidic compounds at pH 2. The pH 7 extraction minimizes the risk of base-catalyzed reactions of analytes (28). Qualitatively, there appears to be no difference between the two methods, except for alpha-BHC and gamma-BHC (Table 12). This was attributed to the base-sensitivity of the two compounds since each of them chromatographs well on the packed column recommended in EPA Method 625. The alpha- and gamma-isomers of BHC have two chlorines in a transaxial configuration with hydrogen which is a favorable arrangement for base-catalyzed dehydrochlorination (28). The delta-isomer has a similar configuration but apparently reacts much more slowly with the base (28).

Dichlorobenzenes had somewhat low and variable recoveries when analyzed by EPA Method 625; this was attributed partly to their volatility which leads to losses during the extract concentration and partly to imprecise peak area measurements caused by poor resolution from the solvent on the fused-silica capillary column (28).

The low recovery of hexachlorocyclopentadiene was attributed to degradation during sample storage and processing (28). Hexachlorocyclopentadiene was found to be highly photoreactive, exhibiting a half-life of less than 10 min in water (5); tetrachlorocyclopentadiene was

TABLE 12. ACCURACY AND PRECISION MEASUREMENTS OF SUBSTITUTED BENZENES WITH EPA METHODS 625 AND 625.1

Compound	EPA Method 625[a]			EPA Method 625.1[a]		
	Spike level (µg/L)	Mean recovery (percent)	SD (percent)	Spike level (µg/L)	Mean recovery (percent)	SD (percent)
1,2-Dichlorobenzene	3.8	105	122	10	61	10
1,3-Dichlorobenzene	3.8	50	31	10	58	6.1
1,4-Dichlorobenzene	13.8	37	4.6	10	68	11
1,2,4-Trichlorobenzene	3.8	86	23	10	76	11
1,2,3-Trichlorobenzene	4	58	9.9	b		
1,3,5-Trichlorobenzene	4	40	5.8	b		
1,2,3,4-Tetrachlorobenzene	4	59	12	b		
1,2,3,5-Tetrachlorobenzene	4	50	9.1	b		
Pentachlorobenzene	4	55	9.8	b		
Hexachlorobenzene	3.8	73	18	10	98	24
alpha-BHC	5	0		10	90	18
beta-BHC	6	91	23	10	95	7.3
gamma-BHC	7	0		10	87	12
delta-BHC	6	72	27	10	92	4.9
Hexachloroethane	3.8	76	23	10	55	6.2
Hexachlorobutadiene	3.8	74	18	10	64	15
Hexachlorocyclopentadiene		b		10	38	7.1
2-Chloronaphthalene	3.8	78	23	10	75	9.1

[a]The number of determinations is 5 to 10 for the EPA Method 625 and 7 for the EPA Method 625.1. Data taken from Reference 28.
[b]Not measured.
SD -- Standard deviation.

reported to be the primary photolysis product (5). Hydrolysis of hexachlorocyclopentadiene is also relatively fast (half-life is 14 days at 25°C) and is independent of pH in the range of pH 5 to pH 9 (5).

One of the more recent devices introduced specifically for liquid-liquid extractions is the Mixxor (Xydex Corp., Bedford, Massachusetts). This device utilizes a piston-cylinder principle for extraction. It comes in various sizes and can handle sample volumes up to 50 mL. The mixing is accomplished by moving a piston up and down in the mixing chamber five or six times (equivalent to 40 or more shakes in a separatory funnel). The system is fast, precise, and safe (32). The main disadvantage is the ease with which emulsions are generated (32) and maybe the volume limitation.

3.2.1.2 Adsorption

Preconcentration of the chlorinated hydrocarbons from water onto a macroreticular resin was reported by Oliver and Bothen (27). Approximately 60 mg of Chromosorb 102 resin, packed into a borosilicate glass tube (100 mm long x 1.5 mm ID) was used for a 500-mL water sample, and the chlorobenzenes were recovered quantitatively (recovery 95 percent) from the resin using 300 µL pentane. The recovery efficiency of the preconcentration technique on the Chromosorb 102 resin was compared with that of the pentane extraction technique at two concentrations in the ppt range (27). The authors concluded that both techniques recover more than 80 percent of the amounts spiked, and excellent agreement between the resin column and the pentane extraction technique was reported for two river water samples (27).

3.2.2 Extraction of Sediment and Soil Samples

This section summarizes the extraction techniques reported in the literature for soil and sediment samples. Examples of solvent and solvent mixtures used for extraction, type of extraction, compounds investigated, and recovery data are presented in Table 13.

Lee et al. (25) concluded that the Soxhlet extraction is the most exhaustive method for the extraction of organics from solid samples. No difference in the recoveries of chlorobenzenes and hexachlorobutadiene was reported with Soxhlet extraction times ranging from 3 hrs to 16 hrs. When using ultrasonication, recoveries of chlorobenzenes from a standard reference material were approximately 80 percent for penta- and hexachlorobenzenes, 70 percent for hexachlorobutadiene and tetrachlorobenzenes, 50 to 70 percent for trichlorobenzenes, and 50 percent for dichlorobenzenes.

The Soxhlet extraction technique is also recommended by EPA and has been standardized as EPA Method 3540. A validation study of the Soxhlet procedure was done by Michael et al. (33). Recoveries of 2-chloronaphthalene and 1,4-dichlorobenzene ranged from 87.1 to 93.4 and from 58.5 to 78.7, respectively, for spike levels in the percent range.

Warner et al. (34) developed a solvent extraction method for solid wastes that is applicable to a wide range of compounds, gives acceptable

TABLE 13. SUMMARY OF THE EXTRACTION TECHNIQUES FOR SOILS AND SEDIMENTS

Solvent	Type of extraction	Compound	Recovery (percent)	Spiking level (ppb)	Reference
Hexane-acetone (41:59)	Soxhlet	1,3-DCB 1,4-DBC 1,2-DCB 1,3,5-TCB 1,2,3-TCB 1,2,3,5-TeCB 1,2,4,5-TeCB 1,2,3,4-TeCB QCB HCB HCE HCBu	100	ppb[a]	25
Methylene chloride	Soxhlet	2-CN 1,4-DCB	87.1 to 93.4 58.5 to 78.7	$1x10^6$; $5x10^6$; $1x10^7$ $1x10^7$; $5x10^7$; $1x10^8$	33
Hexane-acetone (1:1)	Soxhlet	1,2-DCB 1,3-DCB 1,4-DCB 1,3,5-TCB 1,2,4-TCB 1,2,3-TCB 1,2,3,5-TeCB 1,2,4,5-TeCB 1,2,3,4-TeCB QCB HCB	b	b	10
Hexane-acetone (1:1)	Ultrasonication	1,3-DCB 1,4-DCB 1,2-DCB 1,3,5-TCB 1,2,3-TCB 1,2,3,5-TeCB 1,2,4,5-TeCB QCB HCB HCE HCBu	50 for DCBs 50 to 70 for TCBs 70 for HCBu and TeCB 80 for QCB and HCB	ppb[a]	25
Methylene chloride	Ultrasonication	HCE 1,4-DCB QCB HCB 1-CN	57 to 70 51 to 60	50,000 250,000	34

[a]Not specified.
[b]Information is not available.

recoveries and reproducibility, and is easily performed at a reasonable cost. The waste matrices include: aqueous sludges, dry solids, soils, tars, oils, and oily sludges. This method is a dry neutral extraction procedure with methylene chloride (one extraction only) and with anhydrous sodium sulfate which is added to remove any water present. Ultrasonication is used to promote the interaction of the solvent and the waste. Screening steps are incorporated in the method to determine the neutralization requirement of the waste matrix, the residue weight of the extract, and the optimum concentration of the extract for subsequent gas chromatographic analysis (34).

3.3 CLEANUP

Several types of cleanup techniques are available for removal of coextractants from a sample matrix. They are:

- Liquid-solid chromatography (Florisil, alumina, silica gel)
- Gel permeation chromatography
- Sulfur removal

3.3.1 Liquid-Solid Chromatography

In the following discussions, the application of Florisil, alumina, and silica gel to the cleanup of sample extracts prior to gas chromatographic analysis is addressed. Table 14 is a summary of the cleanup procedures reported in the literature.

3.3.1.1 Florisil

Florisil is a synthetic magnesium silicate manufactured by Floridin company from magnesium sulfate and sodium silicate; magnesium silicate is filtered, dried, and calcinated at 650°C. Examples of cleanup methods using Florisil are listed in Table 14.

Jan and Malnersic (35) used Florisil to clean up fish extracts that were contaminated with chlorinated benzenes. The hexane extract of a fish sample was passed through a Florisil column and eluted with 20 mL of 6 percent diethyl ether in hexane. Additional cleanup of the collected fraction with 2-percent ethanolic KOH allowed detection of low ppb levels of chlorinated benzenes in fish and mussel tissue (35).

The elution patterns of BHCs, penta- and hexachlorobenzenes, hexachlorobutadiene, and hexachlorocyclopentadiene from Florisil using hexane and 20 percent methylene chloride in hexane were reported by Mes (36) and are shown in Table 15. It is interesting to note the different behavior of the BHC isomers: alpha-BHC elutes in Fraction I (35 mL hexane) while beta-, delta-, and gamma-BHCs elute in Fraction II (40 mL of 20 percent methylene chloride in hexane).

TABLE 14. SUMMARY OF CLEANUP PROCEDURES

Adsorbent	Eluting solvent	Compound	Recovery (percent)	Reference
Florisil, activated at 130 to 140°C	6 percent, 15 percent, 50 percent diethyl ether in hexane	BHCs	97 to 100	23
Florisil (7 cm x 1 cm ID) and 0.5 cm Na_2SO_4 on top	6 percent diethyl ether in hexane	1,4-DCB; 1,2-DCB; 1,3,5-TCB; 1,2,4-TCB; 1,2,3-TCB; 1,2,4,5-TeCB; 1,2,3,4-TeCB; QCB; HCB	a	35
Florisil, activated at 130°C, 20 g	20 percent methylene chloride in hexane; 50 percent methylene chloride, 0.35 percent acetonitrile, 49.65 percent hexane; 50 percent methylene chloride, 1.5 percent acetonitrile, 48.5 percent hexane	BHCs HCB OCPs OPPs	> 90	37
Florisil, activated at 130°C	6 percent diethyl ether in hexane	HCCP gamma-BHC	100 90	38
Florisil	6 percent diethyl ether in petroleum ether	BHCs, DCBs, HCB, HCBu, HCCP, HCE, TeCB, TCB	> 80	39
Florisil and silicic acid	Hexane; 20 to 80 percent methylene chloride in hexane; 20 percent ethyl acetate in methylene chloride	Tables 15, 16, 17	Table 15, 16, 17	36, 40
Alumina (deactivated with 10 percent water)	Hexane; 50 percent diethyl ether in hexane	BHCs	a	23
A-540 basic alumina (5 g per mg of halogenated material)	Heptane	CBs, PCBs, PCTs, PCNs, PCDFEs, PCDBDs	a	41
Neutral alumina activity grade I deactivated with 5 percent water	Hexane	HCCP gamma-BHC	100 100	38
Silica gel (100/200 mesh) activated at 300°C	Hexane; 15 percent benzene in hexane	HCCP gamma-BHC	99 100	38
Silica gel	Hexane; 10 percent methylene chloride in hexane; methylene chloride, methanol	DCBs, TCBs, TeCBs, QCB, HCB, BHCs	a	11
GPC SX-3 (200/400 mesh), 60 g, 60 x 2.5 cm ID column (48 cm bed)	Methylene chloride-cyclohexane (1:1)	b	a	19

[a]Information is not available.
[b]GPC is recommended for the elimination of lipids, polymers, copolymers, proteins, natural resins, steroids, and other high-molecular-weight compounds present in the sample extracts (19).

TABLE 15. ELUTION PATTERNS OF SOME CHLORINATED HYDROCARBONS FROM A SEMIMICRO FLORISIL COLUMN

Compound (2.5 µg each)	Recovery[a,b] (percent)		
	Fraction I	Fraction II	Total
Hexachlorobenzene	85	0	85
Hexachloro-1,3-butadiene	86	0	86
alpha-BHC	85	0	85
Hexachloropentadiene	85	0	85
Pentachlorobenzene	80	0	80
beta-BHC	0	103	103
gamma-BHC	0	99	99
delta-BHC	0	102	102

[a]Data taken from Reference 40.
[b]Fraction I was eluted with 35 mL hexane. Fraction II was eluted with 40 mL 20 percent methylene chloride in hexane.

Mills et al. (37) also used 20 percent methylene chloride in hexane to recover various pesticides including alpha-, beta-, and delta-BHCs, and hexachlorobenzene from fat extracts and reported that approximately 85 to 90 percent of the butterfat and 70 to 80 percent of the corn oil are retained by Florisil during elution with 20 percent methylene chloride in hexane, while only 25 to 35 percent of the butterfat and 20 to 30 percent of the corn oil are retained during elution with 6 percent and 15 percent di ethyl ether in petroleum ether.

McMahon and Burke (39) reported recoveries of >80 percent for the BHCs, 1,3-dichlorobenzene, 1,4-dichlorobenzene, hexachlorobenzene, hexachlorobutadiene, hexachlorocyclopentadiene, hexachloroethane, tetra- and trichlorobenzenes when elution of the Florisil is done with 6 percent diethyl ether in petroleum ether.

A combined Florisil-silicic acid column was used to separate chlorinated hydrocarbons into several fractions (36, 40). The elution patterns and percent recoveries are shown in Table 16. Florisil retains the lipids and prefractionates the chlorinated hydrocarbons while the silicic acid provides partial separation of chlorinated hydrocarbons from PCBs and organochlorine pesticides. Florisil and silica gel were first activated to 300°C (7 hours) and 130°C (overnight), respectively. Florisil was then deactivated with 2 percent water (v/w) and shaken for 2 to 3 hours, and the silicic acid was deactivated with 5 percent water (v/w), shaken for 15 min and then allowed to equilibrate for 24 hours. The deactivated silicic acid is prepared fresh every 5 days. Compounds are eluted from the Florisil-silicic acid column as follows: Fraction I, 35 mL hexane; Fractions II through V, 40 mL of 20, 40, 60, and 80 percent methylene chloride in hexane, respectively; Fraction VI, 40 mL of 20 percent ethyl acetate in methylene chloride. The effect of increasing the polarity of the eluent on the elution pattern of the chlorinated hydrocarbons from the combined Florisil-silica gel column is shown in Table 17.

If PCBs are not expected to be present in the matrix, then a Florisil column alone can be used for the cleanup of chlorinated hydrocarbon residues. However, it should be noted, that if toxaphene is present, 25 percent of the toxaphene present is recovered in Fraction I, and this may cause problems in identifying the other compounds (40).

3.3.1.2 Alumina

Use of basic alumina to fractionate complex mixtures of chlorinated aromatic compounds was reported by Albro and Parker (41). The fractionation scheme involving A-540 basic alumina is shown in Figure 1. The solvent required to fractionate the compounds depends upon the composition of the sample. In most cases, aliphatic hydrocarbons and chlorobenzenes are eluted with heptane (3 to 4 mL heptane per gram of alumina); PCBs, PCNs, PCTs, and PCDPEs are eluted with 2 percent methylene chloride in hexane, and PCDBDs and PCDBFs are eluted with 20 percent methylene chloride in hexane (10 mL per gram of alumina). Under these conditions, the phthalate esters are retained

TABLE 16. ELUTION PATTERNS OF SOME CHLORINATED HYDROCARBONS FROM A COMBINED FLORISIL-SILICIC ACID COLUMN

Compound (2.5 µg each)	Recovery[a,b,c] (percent)				
	Fraction I	Fraction II	Fraction IV	Fraction VI	Total
Pentachlorobenzene	107	1	0	0	108
Hexachlorobenzene	95	0	0	0	95
alpha-BHC	0	96	0	0	96
beta-BHC	0	26	74	0	100
gamma-BHC	0	93	7	0	100

[a]Data taken from Reference 40.
[b]4.5 g Deactivated Florisil (2 percent); 4.5 g silicic acid.
Fraction I was eluted with 35 mL hexane.
Fraction II was eluted with 40 mL 20 percent methylene chloride in hexane.
Fraction IV was eluted with 40 mL 60 percent methylene chloride in hexane.
Fraction VI was eluted with 40 mL 20 percent ethyl acetate in methylene chloride.
[c]Fractions III and V were eluted with 40 mL 40 percent and 80 percent methylene chloride in hexane, respectively. No results were reported for Fractions III and V.

TABLE 17. EFFECT OF INCREASED SOLVENT POLARITY ON SEPARATION OF CHLORINATED HYDROCARBONS FROM A COMBINED FLORISIL-SILICIC ACID COLUMN

Compound (2.5 µg each)	Recovery[a,b] (percent)			
	Fraction I	Fraction II	Fraction III	Total
Hexachlorobenzene	92	0	0	92+
Hexachloro-1,3-butadiene	95	0	0	95
Pentachlorobenzene	80	0	0	80
1,2,4-Trichlorobenzene	78	0	0	78
alpha-BHC	0	97	1	98
beta-BHC	1	40	57	97
gamma-BHC	0	88	0	88
delta-BHC	0	2	101	103

[a]Data taken from Reference 36.
[b]4.5 g Deactivated Florisil (2 percent); 4.5 g silicic acid.
Fraction I was eluted with 2 percent methylene chloride in hexane.
Fraction II was eluted with 20 percent methylene chloride in hexane.
Fraction III was eluted with 60 percent methylene chloride in hexane.

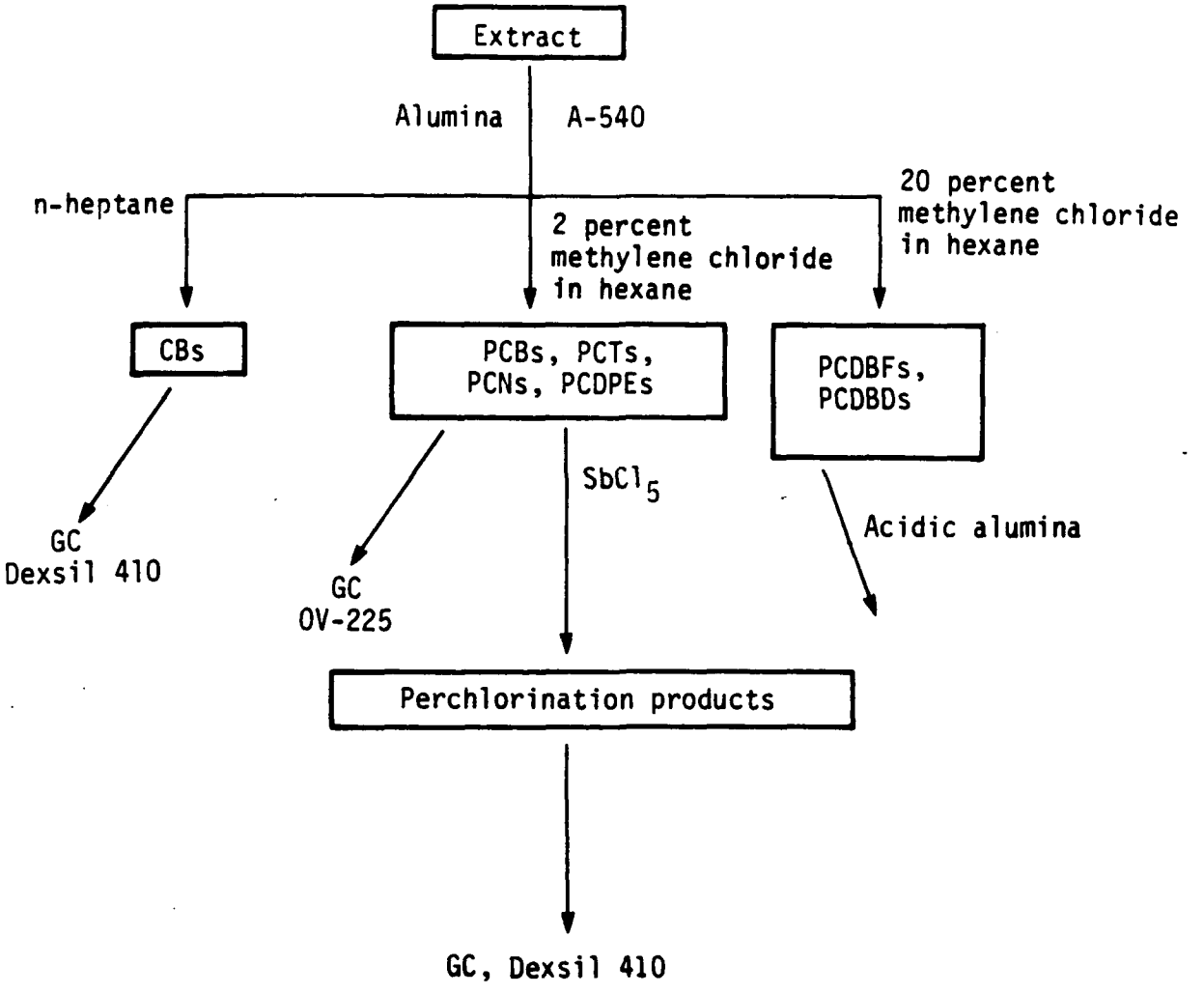


Figure 1. Fractionation scheme for chlorinated benzenes, PCBs, PCTs, PCDPEs, PCNs using alumina chromatography (41).

on the alumina column. They can be eluted with 50 percent methylene chloride in hexane using 10 mL of solvent per gram of alumina (41).

Law and Goerlitz (38) and Millar et al. (23) used neutral alumina to clean up water sample extracts containing hexachlorocyclopentadiene and BHCs as well as other organochlorine pesticides. It was found that alumina was more efficient than Florisil and silica gel for the removal of naturally occuring organic acids and pigments (38).

3.3.1.3 Silica Gel

Silica gel used in combination with Florisil was reported by Mes (36, 40). Law and Goerlitz (38) and Elder et al. (11) used silica gel alone for cleanup of environmental sample extracts suspected to contain chlorinated hydrocarbons. Elution of hexachlorocyclopentadiene from the silica gel column with hexane was quantitative (38). A more polar solvent mixture (15 percent benzene in hexane) was required to elute gamma-BHC from the silica gel column (38).

Oliver and Nicol (10) used silica gel in combination with alumina and Florisil to clean up fish extracts. The cleanup was performed in two steps: the hexane extract was first applied to a large column of Na_2SO_4/alumina/ silica gel/Florisil; the eluate was then concentrated and applied to a small column of 40 percent H_2SO_4 on silica gel.

3.3.2 Gel Permeation Chromatography (GPC)

In gel permeation chromatography the separation mechanism is based on differences in molecular size. Large molecules cannot diffuse into the pores of the gel and elute first whereas the smaller molecules are retained longer and elute later.

The use of GPC (Biobeads SX-3) with methylene chloride-cyclohexane (1:1) allows separation of the chlorinated hydrocarbons from adipose tissue (42). Table 18 gives the GPC elution volumes for the chlorinated benzenes and other organochlorine pesticides of environmental significance. Under the conditions indicated in Table 18, 99.98 percent of the fat is removed by GPC.

Recovery studies were carried out on GPC-cleaned fat fortified prior to extraction at concentrations of 10, 100, and 500 ng/g on extracted fat basis. The overall recoveries of the chlorinated benzenes and BHCs were quantitative, except for trichlorobenzenes and hexachlorobutadiene (Table 19).

3.3.3 Sulfur Removal

Sulfur and organosulfur compounds, if present, may give large peaks which could mask the region from the solvent peak to the earliest eluting chlorinated benzene if packed columns are used for the gas chromatographic analysis.

TABLE 18. GPC ELUTION VOLUMES FOR SOME CHLORINATED BENZENES AND ORGANOCHLORINE PESTICIDES[a]

Compound	GPC elution volume[b] (mL)
1,4-Dichlorobenzene	200 to 220
1,3-Dichlorobenzene	210 to 220
1,2-Dichlorobenzene	210 to 220
1,3,5-Trichlorobenzene	200 to 220
Hexachlorobutadiene	170 to 210
1,2,3-Trichlorobenzene	210 to 230
2,4,5-Trichlorotoluene	200 to 220
1,2,3,5-Tetrachlorobenzene	200 to 220
1,2,3,4-Tetrachlorobenzene	200 to 230
Pentachlorobenzene	200 to 230
Hexachlorobenzene	200 to 230
alpha-BHC	190 to 230
Chlordene	170 to 210
gamma-BHC	200 to 230
beta-BHC	240 to 280
Heptachlor	170 to 210
Aldrin	170 to 210
Octachlorostyrene	170 to 210
Oxychlordane	170 to 200
Heptachlor epoxide	170 to 210
gamma-Chlordane	180 to 210
trans-Nonachlor	170 to 210
alpha-Chlordane	170 to 220
alpha-Endosulfan	170 to 220
2,4'-DDE	170 to 210
4,4'-DDE	180 to 210
Dieldrin	180 to 210
Endrin	170 to 210
cis-Nonachlor	180 to 230
4,4'-DDD	190 to 220
4,4'-DDT	180 to 210
Photomirex	180 to 210
Mirex	180 to 210
Methoxychlor	190 to 210
Decachlorobiphenyl	170 to 210
Hexabromobiphenyl	200 to 220
Aroclor 1260	180 to 220

[a]Data taken from Reference 42.
[b]236 mL bed volume SX-3 gel with methylene chloride-cyclohexane (1 + 1, v/v) eluant.

TABLE 19. RECOVERIES (PERCENT ± SD, DUPLICATE DETERMINATIONS) OF ORGANOCHLORINE CONTAMINANTS[a]

Compound	Fortification level (ng/g)		
	10	100	500
1,3,5-Trichlorobenzene	63.1 ± 1.2	64.2 ± 3.9	57.7 ± 16
Hexachlorobutadiene	43.3 ± 1.6	60.1 ± 10.7	62.1 ± 5.1
1,2,3-Trichlorobenzene	62.1 ± 1.7	68.9 ± 2.9	65.7 ± 0.8
2,4,5-Trichlorotoluene	94.5 ± 4.6	79.9 ± 3.2	76.0 ± 0.7
1,2,3,4-Tetrachlorobenzene	82.6 ± 1.4	84.4 ± 0.5	83.9 ± 1.9
Pentachlorobenzene	110.5 ± 2.9	91.2 ± 1.6	90.5 ± 1.2
Hexachlorobenzene	102.3 ± 3.1	87.3 ± 1.8	92.5 ± 0.4
alpha-BHC	111.5 ± 4.9	89.2 ± 3.7	90.5 ± 2.4
gamma-BHC	88.4 ± 2.9	96.2 ± 7.8	125.6 ± 0.4
beta-BHC	120.1 ± 4.7	91.6 ± 11.2	92.7 ± 4.6

[a]Data taken from Reference 42.

Sulfur may be removed as a discrete fraction by GPC (43). Alternatively, several chemical methods are available for removal of sulfur: reaction with metallic mercury (44), activated copper (45), Raney nickel (46), tetrabutylammonium sulfite (47), and potassium cyanide (48). Lopez-Avila et al. (49) reported quantitative recoveries for BHCs using the tetrabutylammonium sulfite procedure, and Jensen et al. (47) reported for the same procedure recoveries of 94 and 79 percent for hexachlorobenzene and gamma-lindane, respectively.

3.4 SOLVENT CONCENTRATION

Because of the volatility of chlorinated benzenes, procedures for the concentration of solutions containing nanogram levels of these compounds were reported. Lee et al. (25) investigated rotary evaporation and the use of a three-stage macro-Snyder column. In both cases, 200 mL hexane-acetone (41:59) spiked with known amounts of chlorinated benzenes were evaporated in the presence of 3 mL isooctane as keeper. Recoveries were lower for the rotary evaporation (e.g., 50 to 70 percent for dichlorobenzenes and 70 to 85 percent for tri-, tetra, penta-, and hexachlorobenzenes) than for the macro-Snyder column. In the latter case, recoveries were always >90 percent. Experiments with Kuderna-Danish evaporation techniques and equipment conducted by Burke et al. (50) have shown that losses do occur when solutions are concentrated to volumes of less than 0.5 mL by a stream of air. Use of a micro-Snyder column with two bubbles allows concentration of a 10-mL solution to 0.1 to 0.3 mL without loss of pesticides (50). The three-bubble micro-Snyder column did not permit a great reduction in volume while the one-bubble micro-Snyder column showed significant losses of pesticides during solvent evaporation.

Kuderna-Danish, rotary evaporation, hot-plate evaporation, and nitrogen blowdown were also evaluated by Erickson et al. (51). Mean recoveries of 1,3-dichlorobenzene for the macro-evaporation techniques were 85 percent for Kuderna-Danish evaporation, 78 percent for rotary evaporation, 77 percent for hot-plate evaporation, and 83 percent for nitrogen blowdown with methylene chloride as solvent. Use of 15 percent methylene chloride in hexane did not affect the mean recoveries. However, when the micro-evaporation techniques were investigated, problems were encountered in micro-Kuderna-Danish concentrations. The solvent volume could not be reduced to a 0.2-mL volume even after 25 to 30 min. The nitrogen blowdown with column was superior to the nitrogen blowdown without column or to the micro-Kuderna-Danish technique (51).

3.5 GC ANALYSIS

This section addresses the gas chromatographic analysis techniques including gas chromatography/mass spectrometry. Basically, the chlorinated hydrocarbons are separated on the packed or capillary column at elevated temperatures, and the compounds are detected with an electron capture detector (ECD), photoionization detector (PID), Hall electrolytic conductivity detector (HECD) or a mass spectrometer. Section 3.5.1 addresses the separation of the chlorinated benzenes, toluenes, BHCs, etc., on gas chromatographic columns (capillary and packed) and Section 3.5.2 addresses

their identification using various gas chromatographic detectors. A brief summary of compound confirmation techniques is presented in Section 3.5.3.

3.5.1 Gas Chromatographic Columns

Open tubular glass and fused-silica capillary columns have been reported in the literature for the separation of chlorinated benzenes, toluenes, BHCs, etc. Table 20 summarizes the GC columns, conditions, and the detectors reported in the literature. Representative chromatograms of chlorinated hydrocarbons obtained on various open tubular capillary columns and packed columns are shown in Figures 2 through 6. None of the literature reports that we were able to retrieve addressed all compounds listed in Table 1. Most reports addressed the chlorinated benzenes and the chlorinated BHCs.

Figures 2 and 3 show chromatograms of a mixture of 12 chlorinated benzenes that were separated on a Carbowax 20M capillary column and a SP-2100 capillary column. The analytical conditions and the retention times of the 12 compounds are given in Table 21. The Carbowax 20M column separates all compounds; the SP-2100 column separates all but the 1,2,3,5- and 1,2,4,5-tetrachlorobenzenes. Use of a DB-17 and DB-5 fused-silica capillary columns was reported by LeBel and Williams (42). In addition to the chlorinated benzenes and hexachlorobutadiene, LeBel and Williams (42) also reported retention times for other chlorinated pesticides which are included in Table 22. The DB-17 column was chosen as the primary column because most of the organochlorine pesticides could be resolved using a relatively short column. Thirteen chlorinated hydrocarbons of interest to our study were resolved on the DB-17 fused-silica capillary column. Furthermore, it appears that the organochlorine pesticides do not interfere with the analysis of the 13 chlorinated hydrocarbons. The DB-5 fused-silica capillary column resolves fewer compounds than the DB-17 column. 1,4-Dichlorobenzene coelutes with 1,3-dichlorobenzene and hexachlorobutadiene coelutes with 1,2,3-trichlorobenzene (Table 22).

Separation of 12 chlorinated benzenes and 7 brominated benzenes on a 15 m SE-52 capillary column was reported by Crow et al. (52). 1,3-Dichlorobenzene coelutes with 1,4-dichlorobenzene and 1,2,3,5-tetrachlorobenzene coelutes with 1,2,4,5-tetrachlorobenzene on the SE-52 capillary column (Table 23). Furthermore, 1,2,3-trichlorobenzene coelutes with 1,2-dibromobenzene (52).

The effect of increasing chlorine substitution on retention time was reported by Haken and Korhonen (53). The retention indices of the chlorobenzene isomers on a 25 m x 0.22 mm ID SE-30 fused-silica capillary column and a 22 m x 0.30 mm ID Carbowax 20M glass capillary column were determined at 120, 140, 160, and 180°C, and are shown in Tables 24 and 25.

The elution order is similar to that reported for the SP-2100 (26) and SE-52 (52) columns, the various isomers eluting in the order of their boiling points. The 1,2,3,5- and 1,2,4,5-tetrachlorobenzenes were not resolved on the SE-30 column (Table 24). The 1,3- and 1,4-dichlorobenzenes were resolved

TABLE 20. GC COLUMNS AND CONDITIONS REPORTED FOR THE ANALYSIS OF CHLORINATED HYDROCARBONS

Column	GC conditions	Detector	Detection limit	Reference
30 m x 0.25 mm ID glass capillary column coated with Carbowax 20M (0.08 μm film thickness)	33°C (3 min hold) to 180°C at at 10°C/min	ECD	0.01 ppt for QCB, HCB 0.05 ppt for TeCB 0.1 ppt for TCB 1.0 ppt for DCB (concentration factors 1,000 to 2,500)	27
30 m x 0.25 mm ID glass capillary column coated with SP-2100 (0.20 μm film thickness)	33°C (3 min hold) to 180°C at at 10°C/min	ECD	a	27
15 m x 0.25 mm ID DB-17 fused-silica capillary column	80°C (2 min hold) to 220°C (1 min hold) at 20°C/min then to 280°C (6 min hold) at 5°C/min	ECD	c	42
15 m x 0.25 mm ID DB-5 fused-silica capillary column	80°C (2 min hold) to 220°C (1 min hold) then to 275°C (5 min hold) at 5°C/min	ECD	c	42
15 m x 0.25 mm ID DB-17 fused-silica capillary column	116°C (1 min hold) to 276°C (9 min hold) at 16°C/min	GC/MS (SIM)	Table 22	42
15 m SE-52 glass capillary column	60°C to 280°C at 4°C/min	GC/MS (methane CI)	5 ng for positive CI; DCBs not detected in negative CI; TCBs and TeCB 5 to 50 times less sensitive in negative CI than positive CI. QCB and HCB 5 to 20 times more sensitive in negative CI than positive CI	52
22 m x 0.3 mm ID glass capillary column coated with Carbowax 20M	Isothermal at 120°C, 140°C, 160°C, 180°C	b	c	53
25 m x 0.22 mm ID vitreous silica coated with SE-30	Isothermal at 130°C, 140°C, 160°C, 180°C	b	c	53
50 m x 0.35 mm ID glass capillary column coated with SE-54	100°C to 250°C at 3°C/min	ECD	c	29

[a]Same detection limits as for the Carbowax 20M column.
[b]Detector not specified.
[c]Not specified.
[d]Detection limits are given for air and biological samples.

TABLE 20. (continued)

Column	GC conditions	Detector	Detection limit	Reference
50 m x 0.26 mm ID glass capillary column coated with SE-54 (0.25 μm film thickness)	40°C to 250°C (programming rate not specified)	ECD	c	30
60 m x 0.32 mm ID fused-silica capillary column chemically bonded with DB-1 (1 μm film thickness)	60°C to 200°C at 2°C/min	ECD	0.9 pg for 1,2-DCB	54
30 m x 0.25 mm ID fused-silica capillary column bonded with Supelcowax-10 (0.25 μm film thickness)	105°C (7 min hold) to 245°C at 5°C/min	FID	8-17 μg/g	55
30 m x 0.32 mm ID fused-silica capillary column coated with DB-1301 (1 μm film thickness)	70°C to 200°C at 20°C/min, then to 240°C at 3°C/min	ECD	c	56
30 m x 0.25 mm ID fused-silica capillary column bonded with DB-519 (0.25 μm film thickness)	60°C (5 min hold) to 170°C (20 min hold) at 5°C/min	FID	c	57
30 m x 0.53 mm ID fused-silica capillary column bonded with SPB-35 (0.5 μm film thickness)	50°C (1 min hold) to 220°C at 8°C/min; 50°C (1 min/hold) to 240°C at 4°C/min or 6°C/min; 70°C (1 min hold) to 220°C at 8°C/min; 70°C (1 min hold) to 240°C at 4°C/min or 6°C/min	ECD	c	58
1.8 m x 0.2 mm ID glass column packed with OV-1 on Gas-Chrom Q (100/120 mesh)	105°C (4 min hold) to 140°C (8 min hold) at 16°C/min	ECD	Table 31	25
12 m x 0.2 mm ID fused-silica capillary column coated with Carbowax 20M and cross-linked with OV-1	40°C (0.5 min hold) to 80°C (5 min hold) at 30°C/min, then to 140°C (5 min hold) at 8°C/min	ECD	Table 31	25
10 ft x 1/8 in silanized glass column packed with (A) 0.5 percent Carbowax E-20M over bonded E-20M on 80/100 mesh Chromosorb W-AW and 5 percent Synerg C; (B) 0.2 percent Carbowax E-40M and 0.5 percent Synerg C on GLC-110 (130/140 mesh)	50°C (2 min hold) to 200°C (6 min hold) at 10°C/min 60°C (2 min hold) to 190°C at 12°C/min	PID (10.2 eV)	d	59

[a]Same detection limits as for the Carbowax 20M column.
[b]Detector not specified.
[c]Not specified.
[d]Detection limits are given for air and biological samples.

TABLE 20. (concluded)

Column	GC conditions	Detector	Detection limit	Reference
2 m x 2 mm ID glass column packed with 3 percent Dexsil 410 on Anakrom AS (90/100 mesh)	80°C (3 min hold) to 150°C at 2°C/min	FID ECD	c	41
1.8 m x 4 mm ID glass column packed with 10 percent OV-101 on Chromosorb W (80/100 mesh)	Isothermal at 130°C	ECD (^{3}H) ECD (^{63}Ni)	29	60
3 m x 2 mm ID glass column packed with 0.5 percent Silar 10C Chromosorb WAW (80/100 mesh)	100°C to 200°C at 8°C/min	ECD	c	61

[a]Same detection limits as for the Carbowax 20M column.
[b]Detector not specified.
[c]Not specified.
[d]Detection limits are given for air and biological samples.

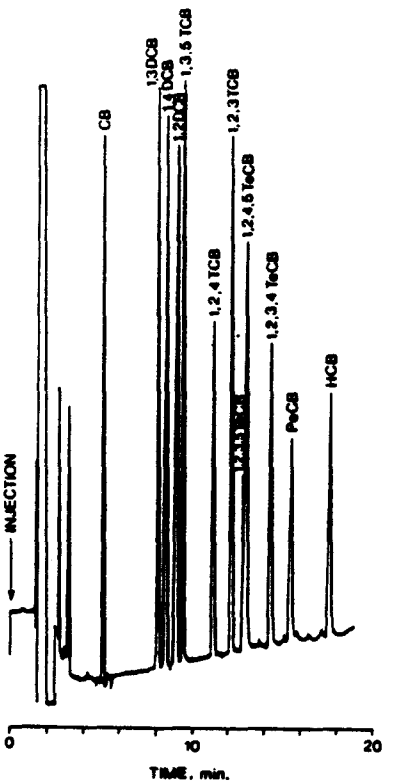


Figure 2. Chromatogram of chlorobenzene mixture in pentane on Carbowax 20M capillary column. Chlorobenzene concentration in µg/L; CB (30,000); 1,3-DCB (74); 1,4-DCB (132); 1,2-DCB (72); 1,3,5-TCB (13); 1,2,4-TCB (8.1); 1,2,3-TCB (7.4); 1,2,3,5-TeCB (1.3); 1,2,4,5-TeCB (8.9); 1,2,3,4-TeCB (2.9); QCB (1.4); HCB (1.2). Refer to Table 21 for gas chromatographic conditions (Reference 26).

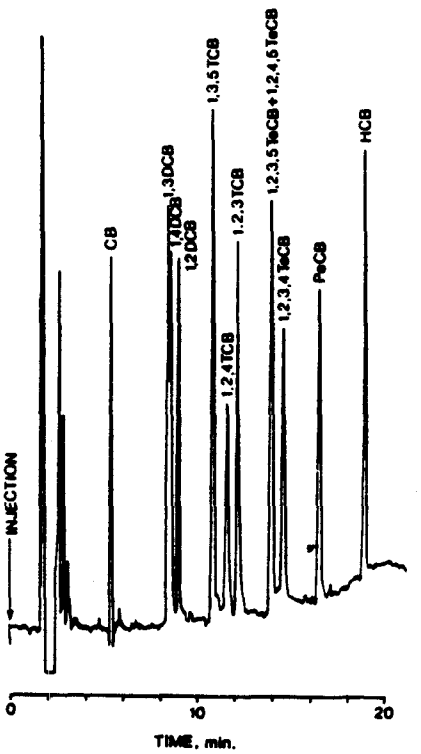


Figure 3. Chromatogram of chlorobenzene mixture in pentane on SP-2100 capillary column (chlorobenzene concentrations are the same as for Figure 2). Refer to Table 21 for gas chromatographic conditions (Reference 26).

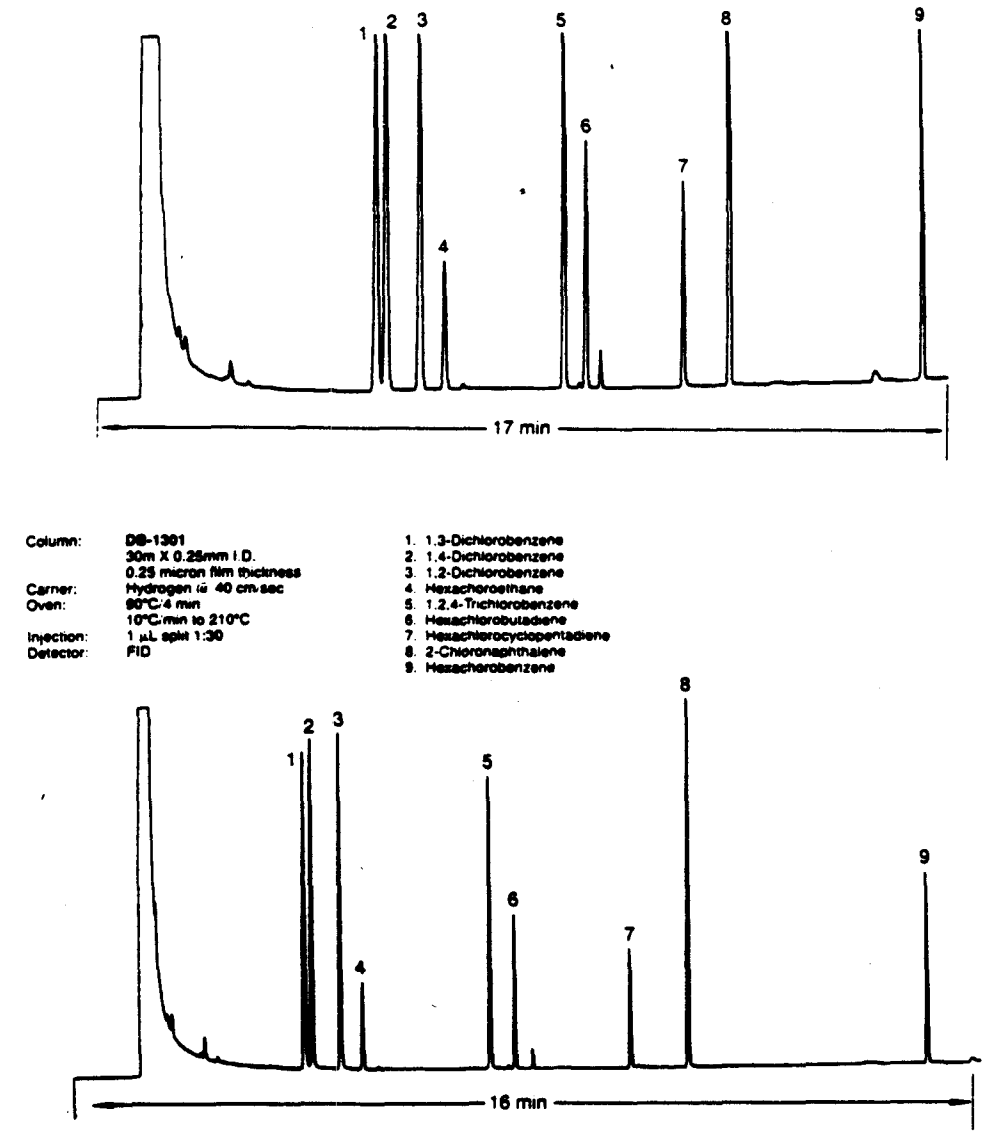


Figure 4. GC/FID chromatograms of chlorinated hydrocarbons analyzed on a DB-1301 fused-silica capillary column (Reference 62).

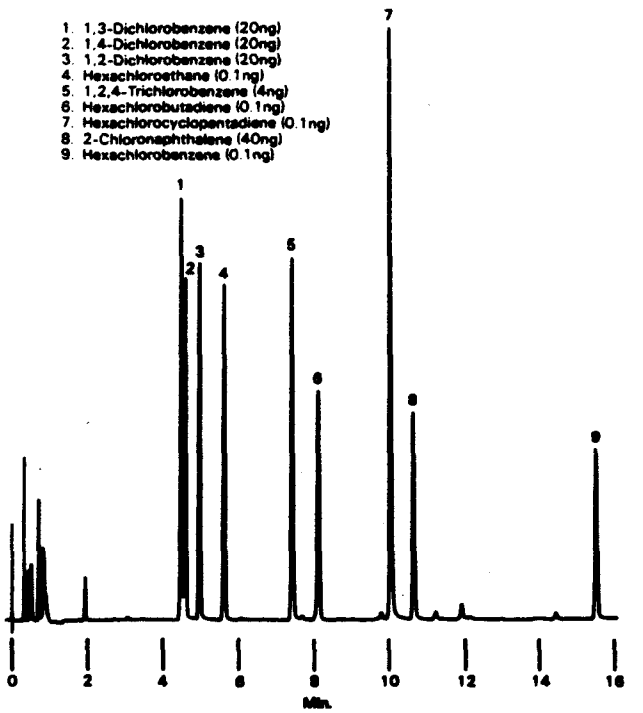


Figure 5. GC/ECD chromatogram of chlorinated hydrocarbons on a SPB-5 15 m x 0.53 mm ID fused-silica capillary column (1.5 µm film thickness). Column temperature: 50°C to 175°C at 8°C/min. and hold; injector temperature: 220°C; detector temperature: 250°C; flowrate: 10 mL/min, helium; makeup gas flow: 20 mL/min, nitrogen;detection: ECD, sens.: 128 x 10^{-11} AFS, sample: 1 µL chlorinated hydrocarbons standard in isooctane, amounts (0.1-40 ng) (Reference 63).

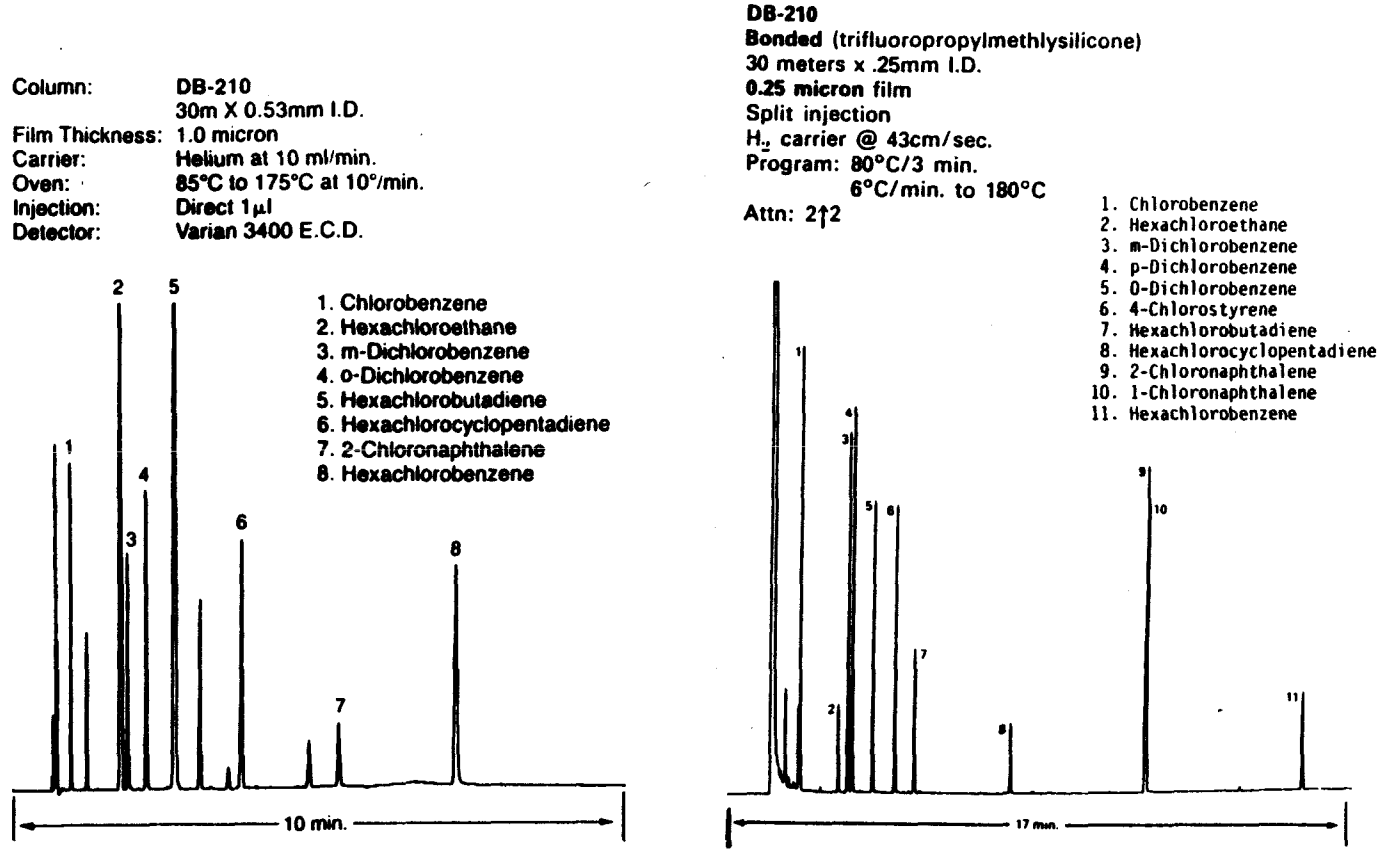


Figure 6. GC/ECD chromatograms of chlorinated hydrocarbons on a DB-210 30 m x 0.53 mm ID fused-silica capillary column (left) and DB-210 30 m x 0.25 mm ID fused-silica capillary column (right) (Reference 62).

TABLE 21. RETENTION TIMES AND RESPONSE FACTORS FOR CHLOROBENZENES[a]

Compound	Retention time (sec)		Response factor[e] (counts/pg)
	Carbowax 20M[b,c]	SP-2100[c,d]	
Chlorobenzene	311	303	0.17
1,3-Dichlorobenzene	493	486	103
1,4-Dichlorobenzene	519	496	48
1,2-Dichlorobenzene	550	521	94
1,3,5-Trichlorobenzene	576	625	770
1,2,4-Trichlorobenzene	675	670	680
1,2,3-Trichlorobenzene	737	704	1,220
1,2,3,5-Tetrachlorobenzene	777	813	1,720
1,2,4,5-Tetrachlorobenzene	785	814	980
1,2,3,4-Tetrachlorobenzene	867	853	2,040
Pentachlorobenzene	934	967	3,920
Hexachlorobenzene	1,059	1,111	5,150

[a]Data taken from Reference 26.
[b]30 m x 0.25 mm ID Carbowax 20M coated glass capillary column (~0.08 μm film thickness).
[c]Temperature program: 33°C (hold 3 min) to 180°C at 10°C/min; nitrogen flow rate at 1.3 mL/min; splitless injection: 5 μL (pentane). Detector and injector temperatures 275°C.
[d]30 m x 0.25 mm ID SP-2100 coated glass capillary column (0.2 μm film thickness).
[e]The authors did not specify the capillary column. It appears that response factors were determined on the Carbowax 20M column because only this column can resolve 1,2,3,5- and 1,2,4,5-tetrachlorobenzene.

TABLE 22. RETENTION TIMES OF CHLORINATED BENZENES, ORGANOCHLORINE PESTICIDES AND PCBs ON DB-17 AND DB-5 FUSED-SILICA CAPILLARY COLUMNS

Compound	Retention time[a]		
	DB-17[b]	DB-5[c]	MDL[d]
1,4-Dichlorobenzene	2.55	2.79	e
1,3-Dichlorobenzene	2.69	2.80	e
1,2-Dichlorobenzene	3.05	3.12	e
1,3,5-Trichlorobenzene	3.73	4.10	11.0
Hexachlorobutadiene	4.38	4.84	1.2
1,2,3-Trichlorobenzene	4.86	4.82	5.9
2,4,5-Trichlorotoluene	5.32	5.49	14.3
1,2,3,5-Tetrachlorobenzene	5.36	5.74	13.1
1,2,3,4-Tetrachlorobenzene	6.18	6.12	4.8
Pentachlorobenzene	7.09	7.09	1.9
Hexachlorobenzene	8.30	8.26	1.4
alpha-BHC	8.54	8.17	1.2
Chlordene	8.85	8.79	e
gamma-BHC	9.04	8.56	1.4
beta-BHC	9.16	8.50	3.0
Heptachlor	9.49	9.50	e
Aldrin	10.00	10.00	e
Octachlorostyrene	10.52	10.55	e
Oxychlordane	10.73	10.65	e
Heptachlor epoxide	11.00	10.65	e
gamma-Chlordane	11.32	11.06	e

[a]Relative to aldrin (RRT = 10.00): retention time 10.41 min (DB-17); 10.90 min (DB-5). Data taken from Reference 42.

[b]15 m x 0.25 mm ID DB-17 fused-silica column (J&W Scientific); oven temperature: 80°C (2 min hold) at 20°C/min to 220°C (1 min hold) then program at 5°C/min to 280°C (6 min hold). Helium gas at 1.5 mL/min with nitrogen makeup at 30 mL/min; injector temperature 260°C; detector temperature 325°C.

[c]15 m x 0.25 mm ID DB-5 fused-silica capillary column (J&W Scientific); oven temperature: 80°C (2 min hold) at 20°C/min to 220°C (1 min hold) then program at 5°C/min to 275°C (5 min hold). Helium carrier gas at 1 mL/min with nitrogen makeup gas at 30 mL/min; injector temperature 260°C; detector temperature 325°C.

[d]Minimum detection limit (ng/g) based on area reject of 3,000 counts per 1 g sample in 2 mL extract.

[e]Information is not available.

TABLE 22. (concluded)

Compound	Retention time[a]	
	DB-17[b]	DB-5[c]
trans-Nonachlor	11.38	11.44
alpha-Chlordane	11.64	11.29
alpha-Endosulfan	11.69	11.33
2,4'-DDE	11.70	11.15
4,4'-DDE	12.24	11.73
Dieldrin	12.34	11.79
Endrin	13.18	12.26
cis-Nonachlor	13.26	12.72
4,4'-DDD	13.56	12.63
2,4'-DDT	13.56	12.68
4,4'-DDT	14.32	13.45
Photomirex	14.80	14.18
Mirex	16.73	15.85
Methoxychlor	16.94	14.90
Decachlorobiphenyl	20.55	19.60
Hexabromobiphenyl	23.20	20.50

[a]Relative to aldrin (RRT = 10.00): retention time 10.41 min (DB-17); 10.90 min (DB-5). Data taken from Reference 42.

[b]15 m x 0.25 mm ID DB-17 fused-silica column (J&W Scientific); oven temperature: 80°C (2 min hold) at 20°C/min to 220°C (1 min hold) then program at 5°C/min to 280°C (6 min hold). Helium gas at 1.5 mL/min with nitrogen makeup at 30 mL/min; injector temperature 260°C; detector temperature 325°C.

[c]15 m x 0.25 mm ID DB-5 fused-silica capillary column (J&W Scientific); oven temperature: 80°C (2 min hold) at 20°C/min to 220°C (1 min hold) then program at 5°C/min to 275°C (5 min hold). Helium carrier gas at 1 mL/min with nitrogen makeup gas at 30 mL/min; injector temperature 260°C; detector temperature 325°C.

TABLE 23. RETENTION TIMES OF HALOGENATED BENZENES ON A 15 M SE-52 CAPILLARY COLUMN[a,b]

Compound	Retention time (min)
Chlorobenzene	2.38
Bromobenzene	2.53
1,4-Dichlorobenzene	3.38
1,3-Dichlorobenzene	3.43
1,2-Dichlorobenzene	4.02
1,3,4-Trichlorobenzene	5.42
1,2,4-Trichlorobenzene	6.41
1,4-Dibromobenzene	6.51
1,3-Dibromobenzene	6.52
1,2-Dibromobenzene	7.27
1,2,3-Trichlorobenzene	7.30
1,2,3,5-Tetrachlorobenzene	10.23
1,2,4,5-Tetrachlorobenzene	10.23
1,2,3,4-Tetrachlorobenzene	11.43
1,3,5-Tribromobenzene	12.50
Pentachlorobenzene	15.30
Hexachlorobenzene	20.31
Tetrabromobenzene	21.06
Hexabromobenzene	36.31

[a]GC conditions were as follows: injector temperature, 280°C; transfer line temperature, 280°C; GC carrier gas, methane; split ratio, 10/1; column temperature, 60 to 280°C at 4°C/min; flow rate, 25 cm/s. Methane was employed as a carrier gas because it was found that helium or hydrogen tended to disturb the CI reagent ion plasma.

[b]Data taken from Reference 52.

TABLE 24. RETENTION INDICES OF CHLOROBENZENE ISOMERS ON A 25 M x 0.22 MM ID SE-30 FUSED-SILICA CAPILLARY COLUMN[a]

Compound	Temperature (°C)			
	120	140	160	180
1,3-Dichlorobenzene	964	1,013	1,016	1,021
1,4-Dichlorobenzene	970	1,015	1,016	1,021
1,2-Dichlorobenzene	1,005	1,038	1,050	1,057
1,3,5-Trichlorobenzene	1,131	1,144	1,150	1,159
1,2,5-Trichlorobenzene	1,177	1,183	1,193	1,207
1,2,3-Trichlorobenzene	1,211	1,217	1,228	1,247
1,2,3,5-Tetrachlorobenzene	1,326	1,329	1,344	1,367
1,2,4,5-Tetrachlorobenzene	1,326	1,329	1,344	1,367
1,2,3,4-Tetrachlorobenzene	1,366	1,371	1,388	1,412
Pentachlorobenzene	1,496	1,505	1,525	1,552
Hexachlorobenzene	1,656	1,673	1,695	1,723

[a]Data taken from Reference 53.

TABLE 25. RETENTION INDICES OF CHLOROBENZENE ISOMERS ON A 22 M x 0.30 MM ID CARBOWAX 20M GLASS CAPILLARY COLUMN[a]

Compound	Temperature (°C)			$\frac{I_{CW\ 20M}}{I_{SE-30}}$[b]
	140	160	180	
1,3-Dichlorobenzene	1,415	1,434	1,509	1.41
1,4-Dichlorobenzene	1,438	1,471	1,529	1.44
1,2-Dichlorobenzene	1,447	1,514	1,575	1.44
1,3,5-Trichlorobenzene	1,515	1,545	1,590	1.34
1,2,5-Trichlorobenzene	1,630	1,653	1,698	1.39
1,2,3-Trichlorobenzene	1,705	1,735	1,775	1.41
1,2,3,5-Tetrachlorobenzene	1,754	1,786	1,824	1.33
1,2,4,5-Tetrachlorobenzene	1,764	1,793	1,830	1.33
1,2,3,4-Tetrachlorobenzene	1,871	1,908	1,941	1.37
Pentachlorobenzene	1,956	1,999	2,027	1.31
Hexachlorobenzene	2,124	2,178	2,204	1.28

[a]Data taken from Reference 53.
[b]Ratio determined at 160°C; for values on SE-30 column see Table 24.

at 120°C; higher temperatures caused the two compounds to overlap. The retention on the more polar Carbowax 20M is increased, as expected, although the elution order is not altered. Complete separation of the 1,2,3,5- and 1,2,4,5-tetrachlorobenzenes was achieved on the Carbowax 20M column at 120 and 140°C (Table 25).

The incremental effect of chlorine addition is shown in Tables 26 and 27. For both stationary phases the incremental differences increase with temperature. Furthermore, the effect is dependent upon the position of the chlorines (53). For example, in the case of the 1,3-dichlorobenzene, 1,3,5-trichlorobenzene, and 1,2,3,5-tetrachlorobenzene, which are the lowest retention isomers at 160°C on the SE-30 column, the retention index increases were 88, 103, and 126 index units, whereas in the case of 1,2-dichlorobenzene, 1,2,3-trichlorobenzene, and 1,2,3,4-tetrachlorobenzene, which are the highest retention isomers at 160°C on the SE-30 column, the retention index increases were 105, 129, and 137, respectively. The same trend is observed on the Carbowax 20M column (Table 27). However, in the case of the Carbowax 20M column, the highest retention isomers exhibit significantly larger retention increases. The relative polar and steric effects are indicated by increments shown in Tables 26 and 27, and by retention index ratios on the two columns determined at 160°C (Table 25). It appears that the polar effects are maximized with the 1,2,3,4-tetrachlorobenzene (53), and with further substitution the polar effects are reduced due to steric constraints.

Other open-tubular capillary columns reported for the analysis of chlorinated benzenes include: OV-1 (25), DX-4 (25), SE-54 (29,30), DB-1 (54), Supelcowax-10 (55), DB-1301 (56), DB-519 (57), SPB-35 (58), and Carbowax 20M cross-linked with OV-1 (25).

Packed column analysis of the chlorinated benzenes and other chlorinated hydrocarbons was reported by Langhorst and Nestrick (59) on some specially prepared column packings. Chromatograms are shown in Figure 7.

Three gas chromatographic column packings were employed for these analyses. Column packing A, consisting of 0.50 percent Carbowax E-20M over bonded E-20M on 80/100 mesh Chromosorb W-AW and 5 percent Synerg C, is a specially prepared packing available from HNU Systems, Inc. Its design provides high efficiency, high solvent capacity, isomer resolution characteristics, and minimum liquid phase bleed (59).

Column packing B consists of 0.20 percent Carbowax E-40M and 0.50 percent Synerg C on 130/140 mesh GLC-110. Its design characteristics are essentially the same as those described for column packing A, and it is also available from HNU Systems. However, this packing is a surface-coated glass bead packing and provides certain unique performance characteristics; it is especially useful for high-sensitivity determinations using the photoionization detector. In particular, the optimum carrier velocity (v_{opt}) for this packing, as determined from the Van Deemter plot for hydrocarbon elution, is unusually low for 2-mm ID columns. This particular packing demonstrates a v_{opt} of approximately 8 cm^3/min for helium carrier when tested in a 2 mm ID x 180 cm glass column. This combination of high capacity, high

TABLE 26. INCREMENTAL EFFECT OF CHLORINE SUBSTITUTION AND TEMPERATURE ON RETENTION INDICES ON A 25 M x 0.22 MM ID SE-30 FUSED-SILICA CAPILLARY COLUMN[a]

Compound	Temperature (°C)							
	120		140		160		180	
	$\sum\Delta I^b$	ΔI^c	$\sum\Delta I^b$	ΔI^c	$\sum\Delta I^b$	ΔI^c	$\sum\Delta I^b$	ΔI^c
1,3-Dichlorobenzene	132	66	177	89	176	88	174	87
1,4-Dichlorobenzene	138	69	179	90	176	88	174	87
1,2-Dichlorobenzene	173	87	202	101	210	105	215	108
1,3,5-Trichlorobenzene	299	100	308	103	310	103	317	106
1,2,4-Trichlorobenzene	345	115	347	116	353	118	365	122
1,2,3-Trichlorobenzene	379	126	381	127	388	129	405	135
1,2,3,5-Tetrachlorobenzene	494	124	493	123	504	126	525	131
1,2,4,5-Tetrachlorobenzene	494	124	493	123	504	126	525	131
1,2,3,4-Tetrachlorobenzene	534	134	535	134	548	137	570	143
Pentachlorobenzene	664	133	559	134	685	137	710	142
Hexachlorobenzene	824	137	837	140	855	143	881	147

[a]Data taken from Reference 53.
[b]Total retention index increase.
[c]Retention index increase per chlorine atom.

TABLE 27. INCREMENTAL EFFECT OF CHLORINE SUBSTITUTION AND TEMPERATURE ON RETENTION INDICES ON A 22 M x 0.30 MM ID CARBOWAX 20M GLASS CAPILLARY COLUMN[a]

Compound	Temperature (°C)					
	140		160		180	
	$\sum\Delta I^b$	ΔI^b	$\sum\Delta I^b$	ΔI^b	$\sum\Delta I^b$	ΔI^b
1,3-Dichlorobenzene	158	79	164	82	220	110
1,4-Dichlorobenzene	181	91	201	101	240	120
1,2-Dichlorobenzene	190	95	244	122	286	143
1,3,5-Trichlorobenzene	258	86	275	92	301	100
1,2,4-Trichlorobenzene	373	124	383	128	409	136
1,2,3-Trichlorobenzene	448	149	465	155	486	162
1,2,3,5-Tetrachlorobenzene	497	124	516	129	535	134
1,2,4,5-Tetrachlorobenzene	507	127	523	131	541	135
1,2,3,4-Tetrachlorobenzene	614	154	638	160	652	163
Pentachlorobenzene	699	140	729	146	738	148
Hexachlorobenzene	867	145	908	151	915	153

[a]Data taken from Reference 53.
[b]Total retention index increase.

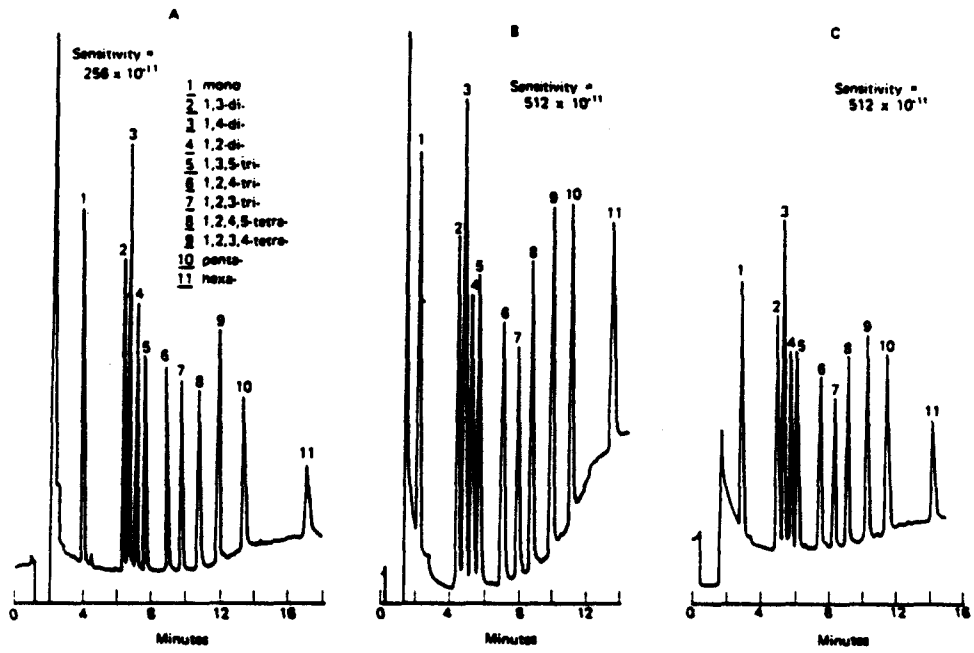


Figure 7. Comparison of high-performance column packings for the separation of chlorobenzenes (Reference 59).

efficiency, short retention times, and low carrier gas flow rates gave improved sensitivity when used with the photoionization detector.

Column packing C in Figure 7 was a combination of the first two column packings. The first 9 in. of column B described above were unpacked and replaced with the packing described for column A. This front end packing moved the monochlorobenzene peak away from the solvent front and protected the packing B from stripping of the liquid phase during injection.

Eleven chlorinated benzenes were completely resolved on any of the three packing materials. No data were reported for the 1,2,3,5-tetrachloro-benzene isomer; therefore, we cannot conclude whether or not all the chlorinated benzenes can be resolved.

Chromatography of various chlorinated benzenes on Dexsil 410 (41), OV-101 (60,64), OV-101/OV-210 (60), OV-225 mixed (64), OV-105 (64), and Silar 10C (61) are presented in Tables 28, 29, and 30. A GC/ECD chromatogram of eight chlorinated hydrocarbons analyzed on a glass column packed with 1 percent SP-1000 is shown in Figure 8 (65).

3.5.2 Gas Chromatographic Detectors

Gas chromatographic detectors reported in the literature for the analysis of chlorinated hydrocarbons include the electron capture detector, the photoionization detector, the electrochemical detector, the Hall electrolytic conductivity detector, and the mass spectrometer. Lee et al. (25) used a mass-selective detector in the selected ion monitoring mode to improve the detector sensitivity. Table 31 summarizes the sensitivities to various chlorinated benzenes relative to hexachlorobenzene of both the electron capture detector and the mass spectrometer. The characteristic ions for each chlorinated benzene are also shown. Quantitation by mass spectrometry was performed using anthracene-d_{10} as internal standard (25). Since dichlorobenzenes were approximately 50 times less sensitive to the electron capture detector than hexachlorobenzene, the levels reported for dichlorobenzenes using the electron capture detector are less reliable than those reported for higher chlorinated benzenes. It can be seen in Table 31 that the much higher relative sensitivity of the mass spectrometer detector for the dichlorobenzene make such a detector more desirable for the analysis of environmental samples.

To increase the sensitivity of the electron capture detector for those chlorinated hydrocarbons that have few chlorine atoms, Miller and Grimsrud (66) proposed the doping of the carrier gas with oxygen (up to 3.5 parts per thousand). The dichlorobenzene isomers show small, but measurable, differences in their enhancements in the order 1,2-, 1,4-, and 1,3-dichlorobenzene having enhancement values of 1.5, 2.0, and 2.4, respectively, at 300°C.

A new electrochemical detector for gas chromatography that uses the same pyrolysis furnace as the Hall electrolytic conductivity detector, but where the analysis is based on the potentiometric determination of the chloride,

TABLE 28. GC OF CHLOROBENZENES ON A DEXSIL 410 PACKED COLUMN[a]

Compound	Retention time (min)[b]
Chlorobenzene	0.86
1,3- + 1,4-Dichlorobenzene	2.44
1,2-Dichlorobenzene	3.20
1,3,5-Trichlorobenzene	6.32
1,2,4-Trichlorobenzene	7.10
1,2,3-Trichlorobenzene	8.60
1,2,3,5-Tetrachlorobenzene	11.82
1,2,3,4-Tetrachlorobenzene	12.90
Pentachlorobenzene	17.80
Hexachlorobenzene	23.68

[a]Data taken from Reference 41.
[b]Column 2 m x 2 mm ID glass column packed with 3 percent Dexsil 410 on Anakrom AS 90/100 mesh. Initial temperature 80°C, 3 min hold, to 150°C at 2°C/min. Helium flow rate is 35 mL/min.

TABLE 29. RELATIVE RETENTION TIMES OF CHLORINATED BENZENES ON AN OV-101 AND AN OV-101/OV-210 COLUMN, BOTH OPERATED AT 130°C[a]

Compound	Relative retention time		Sensitivity (ng)[d]
	OV-101[b]	Mixed[c]	
1,3-Dichlorobenzene	0.08	0.08	60
1,4-Dichlorobenzene	0.08	0.08	110
1,2-Dichlorobenzene	0.09	0.10	65
Hexachloroethane	0.10	0.12	0.3
1,3,5-Trichlorobenzene	0.15	0.16	15
3,5-Dichlorotoluene	0.16	0.13	30
2,6-Dichlorotoluene	0.16	0.14	20
2,4-Dichlorotoluene	0.16	0.13	25
2,5-Dichlorotoluene	0.16	0.13	30
1,2,4-Trichlorobenzene	0.18	0.21	24
α,4-Dichlorotoluene	0.19	0.26	1.2
2,3-Dichlorotoluene	0.19	0.16	25
3,4-Dichlorotoluene	0.20	0.16	30
1,4-Dibromobenzene	0.20	0.21	5
1,3-Dibromobenzene	0.20	0.21	25
1,2,3-Trichlorobenzene	0.22	0.25	9
Benzotrichloride	0.23	0.25	0.8
1,2-Dibromobenzene	0.23	0.25	2
Hexachlorobutadiene	0.24	0.22	0.5
2,4,5-Trichlorotoluene	0.34	0.37	35
1,2,3,5-Tetrachlorobenzene	0.40	0.41	7
1,2,4,5-Tetrachlorobenzene	0.40	0.42	7
α,2,4-Trichlorotoluene	0.42	0.48	1
α,2,6-Trichlorotoluene	0.42	0.50	1.6
Hexachlorocyclopentadiene	0.43	e	1.5
α,3,4-Trichlorotoluene	0.50	0.63	1.3
1,2,3,4-Tetrachlorobenzene	0.50	0.54	7
1,3,5-Tribromobenzene	0.61	0.60	1.5
2-Chlorobiphenyl	0.90	e	400
Pentachlorobenzene	1.00	1.00	1.5
2,4-Dichlorobenzotrichloride	1.31	1.33	3
2,3,4,5,6-Pentachlorotoluene	2.07	2.04	1
Hexachlorobenzene	2.40	2.27	4
Tribromobenzene	2.54	2.37	6.5
1,2,4,5-Tetrabromobenzene	2.55	2.37	5
gamma-BHC	2.76	e	5
delta-BHC	2.92	4.42	6
4,4'-Dichlorobiphenyl	3.47	e	300

[a]Data taken from Reference 60.
[b]OV-101 column parameters are given in Table 20.
[c]Mixed OV-101 + OV-210 column; operating parameters are given in Table 20.
[d]For 50 percent full-scale deflection of the recorder pen (electrometer sensitivity is 1×10^{-9} A for full-scale deflection).
[e]Information is not available.

TABLE 30. RETENTION TIMES RELATIVE TO PENTACHLOROBENZENE (RR) FOR VARIOUS COLUMNS AT 130°C AND 150°C[a]

Compound	RR at 130°C				RR at 150°C
	OV-225 Mixed	OV-101	OV-105	OV-210 Mixed	OV-225 Mixed
1,3,5-Trichlorobenzene	0.14	0.15	0.18	0.16	0.18
1,2,3-Trichlorobenzene	0.24	0.22	0.29	0.25	0.27
1,2,4-Trichlorobenzene	0.19	0.18	0.22	0.21	0.23
1,2,3,5-Tetrachlorobenzene	0.40	0.40	0.44	0.41	0.43
1,2,3,4-Tetrachlorobenzene	0.52	0.50	0.57	0.54	0.56
1,2,4,5-Tetrachlorobenzene	0.40	0.40	0.42	0.42	0.44
Hexachlorobutadiene	0.20	0.24	0.25	0.22	0.24
Pentachlorobenzene	1.00	1.00	1.00	1.00	1.00
Hexachlorobenzene	2.42	2.40	2.32	2.27	2.27
alpha-BHC	3.38	2.05	2.74	2.57	3.05
gamma-BHC	5.08	2.76	3.73	3.50	4.42

[a]Data taken from Reference 64.

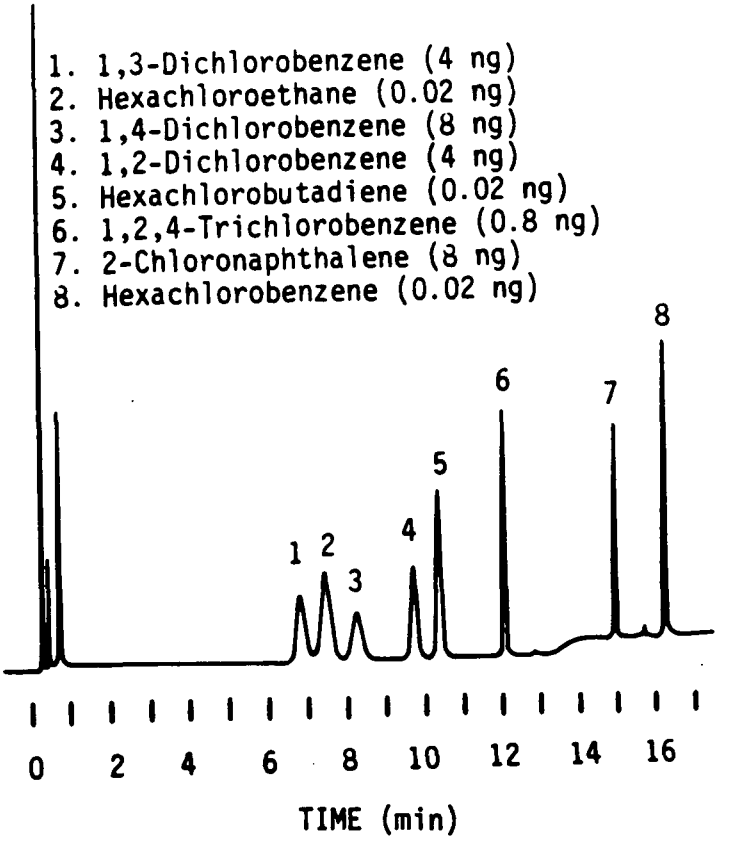


Figure 8. GC/ECD chromatogram of chlorinated hydrocarbons analyzed on a 2 m x 2 mm ID glass column packed with 1 percent SP-1000 on Supelcoport (100/120 mesh) (Reference 65).

TABLE 31. RELATIVE SENSITIVITIES (HCB = 10.0) AND CHARACTERISTIC IONS OF CHLOROBENZENES AND HEXACHLOROBUTADIENE

Compound	Relative sensitivity[a]		Characteristic ion at m/z
	ECD[b]	MSD[c]	
1,3-Dichlorobenzene	0.26	5.55	146
1,4-Dichlorobenzene	0.19	5.17	146
1,2-Dichlorobenzene	0.27	4.97	146
1,3,5-Trichlorobenzene	2.02	5.06	180
1,2,4-Trichlorobenzene	1.65	4.79	180
1,2,3-Trichlorobenzene	2.49	5.05	180
1,2,3,5-Tetrachlorobenzene	4.40	d	216
1,2,4,5-Tetrachlorobenzene	2.34	d	216
1,2,3,4-Tetrachlorobenzene	3.88	4.64	216
Pentachlorobenzene	6.22	8.52	250
Hexachlorobenzene	10.0	10.0	284
Hexachlorobutadiene	12.1	4.46	225

[a]Relative sensitivity for hexachlorobenzene was arbitrarily set at 10.0. Data taken from Reference 25.
[b]Relative sensitivity of each compound on the electron-capture detector was determined with a Carbowax 20M capillary column.
[c]Relative sensitivity of each compound on the mass-selective detector was determined with an OV-1 capillary column using the SIM technique.
[d]Information is not available.

was reported by Driscoll et al. (67). This detector has been tested with chlorinated benzenes and was found to be sensitive in the 6- to 26-ng range (Table 32). While the Coulson detector has a detection limit of a few ng, the electrochemical detector seems to be nearly 1,000 times more sensitive.

3.5.3 Confirmation of Compound Identity

Several techniques are available for the confirmation of compounds detected with the gas chromatographic detectors. These include the multi-column confirmation technique, the chemical derivatization followed by extract reanalysis, and confirmation by gas chromatography/mass spectrometry.

The multi-column technique has been and still is a widely practiced procedure, although there have been reports that misinterpretation of compound identity occurred when the retention times were the only criteria used for identification. Two or three columns are routinely used to confirm compounds when GC is used for analysis.

Chemical derivatization techniques have been used intensively for confirmation in pesticide residue work but will be addressed only briefly here since these techniques are beyond the scope of this project. Table 33 identifies some of the chemical derivatization techniques reported for BHC (3).

Confirmation of compound identity by mass spectrometry has been reported (25); this technique can only be applied to those samples in which the compound concentration is above approximately 5 µg/L for water and 50 ng/g for soil samples. Alternatively, use of gas chromatography/mass spectrometry in the selected ion monitoring mode was found to give sensitivities comparable to those achieved with the electron capture detector.

In selecting the most appropriate method(s) for routine work, consideration should be given to those procedures that allow unambiguous confirmation of compound identity and that circumvent interference(s) in the quantitative analysis. Furthermore, the method should use routine instrumentation, should be easy to standardize, and should not include fractionation (the fractionation of an extract is not desirable since it increases the number of analyses).

TABLE 32. COMPARISON OF DETECTION LIMITS FOR CHLOROBENZENES

Compound	Detection limits[a]	
	HNU electrochemical detector (pg)	Coulson detector (ng)
Chlorobenzene	26	23
1,2-Dichlorobenzene	15	2
1,2,4-Trichlorobenzene	12	2
1,2,3,4-Tetrachlorobenzene	6	1
Pentachlorobenzene	10	2

[a]Data taken from Reference 67.

TABLE 33. CHEMICAL CONFIRMATION OF BHC ISOMERS[a]

Compounds	Reagents	Reaction conditions	Known interference
BHC isomers (all)	2 percent KOH in ethanol	100°C, 15 min, GC column: 200°C	BHC isomers mutually interfere
BHC isomers (alpha, beta, gamma)	0.1 g NaOMe in MeOH (2 mL)	50°C, 15 min, GC column: 200°C	BHC isomers mutually interfere
BHC isomers (alpha, gamma, delta)	1 mL concentrated H_2SO_4 (2 mL)	Room temperature	

[a]Data taken from Reference 3.

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APPENDIX B

METHOD 8120 -- CHLORINATED HYDROCARBONS (REVISED)

METHOD 8120

CHLORINATED HYDROCARBONS

1.0 SCOPE AND APPLICATION

1.1 This method provides procedures for the determination of certain chlorinated hydrocarbons in liquid and solid sample matrices. Table 1 indicates compounds that may be determined by this method and lists CAS Registry numbers and method detection limits (MDL) for each compound in a water matrix. The MDLs for the compounds of a specific sample may differ from those listed in Table 1 because they are dependent upon the nature of interferences in the sample matrix. Table 2 lists the practical quantitation limits (PQL) for other matrices.

1.2 When this method is used to analyze for any or all of the compounds listed in Table 1, compound identification should be supported by at least one additional qualitative technique. This method describes analytical conditions for a second gas chromatographic column that can be used to confirm the measurements made with the primary column. Retention time information obtained on two gas chromatographic columns is given in Table 3. Alternatively, gas chromatography/mass spectrometry could be used for compound confirmation.

1.3 This method is restricted to use by or under the supervision of analysts experienced in the use of a gas chromatograph and in the interpretation of gas chromatograms.

2.0 SUMMARY OF METHOD

2.1 A measured volume or weight of sample (100 mL to 1 L for liquids, 10 to 35 g for solids) is extracted by using one of the appropriate sample extraction techniques specified in Methods 3510, 3520, 3540, and 3550. Liquid samples are extracted at neutral pH with methylene chloride by using either a separatory funnel (Method 3510) or a continuous liquid-liquid extractor (Method 3520). Solid samples are extracted with hexane/acetone (1:1) by using a Soxhlet extractor (Method 3540) or with methylene chloride/acetone (1:1) by using a sonicator (Method 3550). After cleanup, the extract is analyzed by gas chromatography with electron capture detection (GC/ECD).

2.2 The sensitivity of Method 8120 usually depends on the level of interferences rather than on instrumental limitations. If interferences prevent detection of the analytes, Method 8120 may also be performed on samples that have undergone cleanup. This method provides a Florisil column fractionation, an elemental sulfur removal procedure, and a gel permeation chromatography cleanup procedure to aid in the elimination of interferences.

3.0 INTERFERENCES

3.1 Refer to Method 3500, 3600, and 8000.

3.2 Solvents, reagents, glassware, and other hardware used in sample processing may introduce artifacts which may result in elevated baselines causing misinterpretation of gas chromatograms. These materials must therefore be demonstrated to be free from interferents 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. Pesticide-grade or distilled-in-glass solvents are suitable for trace analysis without further purification. Each new batch of solvent should be checked for possible interferents as follows: concentrate to 1 mL the amount of solvent equivalent to the total volume to be used in the analysis. Inject 1 to 2 µL of the concentrate into a gas chromatograph equipped with an electron capture detector set at the lowest attenuation. If extraneous peaks are detected that are greater than 10 pg on-column, the solvent must be purified either by redistillation or by passing it through a column of highly activated alumina (acidic or basic alumina, activated at 300°C to 400°C) or Florisil.

3.3 Interferents coextracted from the samples will vary considerably from waste to waste. While general cleanup techniques are provided as part of this method, specific samples may require additional cleanup steps to achieve desired sensitivities.

3.4 Glassware must be scrupulously clean. Clean all glassware as soon as possible after use by rinsing with the last solvent used followed by thorough washing of the glassware in hot, detergent-containing water. Rinse with tap water, distilled water, acetone, and finally pesticide-quality hexane. Heavily contaminated glassware may require treatment in a muffle furnace at 400°C for 2 to 4 hours. Some high-boiling materials, such as PCBs, may not be eliminated by this treatment. Volumetric glassware should not be heated in a muffle furnace. Glassware should be sealed and stored in a clean environment immediately after drying and cooling to prevent any accumulation of dust or other contaminants. Store the glassware by inverting or after capping with aluminum foil.

3.5 Phthalate esters, if present in a sample, will interfere only with the BHC isomers because they elute in Fraction 2 of the Florisil procedure described in Method 3620. In the case of the Florisil cartridge procedure, the phthalate esters elute in the same fraction as the chlorinated hydrocarbons. However, they interfere only with the BHC isomers because the retention times of the phthalate esters are longer than those of the chlorinated hydrocarbons. The presence of phthalate esters can usually be minimized by avoiding contact with any plastic materials.

3.6 The presence of elemental sulfur will result in large peaks and often mask the region of compounds eluting after 1,2,4,5-tetrachlorobenzene (Compound No. 18 in the gas chromatogram shown in Figure 1). The tetrabutylammonium (TBA)-sulfite procedure (Method 3660) works well for the removal of elemental sulfur.

3.7 Waxes and lipids can be removed by gel permeation chromatography (Method 3640). Extracts containing high amounts of lipids are viscous and may even solidify at room temperature.

4.0 APPARATUS AND MATERIALS

4.1 Glassware: See Methods 3510, 3520, 3540, 3550, 3620, 3640, and 3660 for specifications.

4.2 Kuderna-Danish (K-D) apparatus, standard taper 19/22 ground glass joints (Kontes K-570025-0500 or equivalent):

4.2.1 Concentrator tube, 10 mL graduated (Kontes K-570050-1025 or equivalent). A ground-glass stopper is used to minimize evaporation of solvent after removal of the concentrator tube from the concentration apparatus.

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

4.2.3 Snyder column, three-ball macro (Kontes K-503000-0121 or equivalent).

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

4.2.5 Boiling chips, approximately 10/40 mesh. Heat to 400°C for 30 min or Soxhlet-extract with methylene chloride prior to use.

4.3 Gel permeation chromatograph (GPC):

4.3.1 Automated system:

4.3.1.1 Gel permeation chromatograph; Analytical Biochemical Labs, Inc.; GPC Autoprep 1002, or equivalent, including:

4.3.1.2 25-mm ID by 600- to 700-mm heavy-wall glass column packed with 70 g Bio-Beads SX-3, 200/400 mesh, Bio-Rad Laboratories, or equivalent.

4.3.1.3 Syringe, 10 mL with Luer Lock fitting

4.3.1.4 Syringe filter holder and filters, stainless steel and TFE, Gelman 4310, or equivalent.

4.3.2 Manual system assembly from parts:

4.3.2.1 24-mm ID by 600- to 700-mm heavy-wall glass column packed with 70 g Bio-Beads SX-3, 200/400 mesh, Bio-Rad Laboratories, or equivalent.

4.3.2.2 Pump, Altex Scientific, Model No. 1001A, semipreparative, solvent-metering system or equivalent. Pump capacity: 28 mL/min.

4.3.2.3 Detector, Altex Scientific, Model No. 153 or equivalent, with 254-nm UV source and 8-µL semipreparative flowcell (2 mm pathlengths).

4.3.2.4 Microprocessor/controller, Altex Scientific, Model No. 420 or equivalent, Microprocessor System Controller, with extended memory.

4.3.2.5 Injector, Altex Scientific, Catalog No. 201-56, sample injection valve, Teflon, with 10-mL sample loop, or equivalent.

4.3.2.6 Recorder

4.3.2.7 Effluent switching valve, Teflon slider valve, 3-way with 0.060-inch ports.

4.3.2.8 Supplemental pressure gauge with connecting tee, U.S. gauge, 0 to 200 psi, stainless steel installed as a "downstream" monitoring device between column and detector. Flowrate is typically 5 mL/min of methylene chloride.

4.4 Vacuum system for eluting disposable solid-phase cartridges.

4.4.1 Vacuum manifold consisting of individually adjustable, easily accessible flow control valves for up to 24 cartridges, sample rack, chemically resistant cover and seals, heavy-duty glass basin, removable stainless steel solvent guides, built-in vacuum gauge and valve.

4.4.2 Vacuum trap made of 500-mL side arm flask fitted with a one-hole stopper and glass tubing.

4.4.3 6-mL, 1-g solid-phase cartridges, LC-Florisil or equivalent, prepackaged, ready to use.

4.5 Gas chromatograph: An analytical system complete with gas chromatograph suitable for on-column injection, and all required accessories including syringes, analytical columns, gases, electron capture detector, and recorder/integrator or data system.

4.5.1 Column 1: 30 m x 0.53 mm ID fused-silica capillary column chemically bonded with trifluoropropyl methyl siloxane (DB-210 or equivalent).

4.5.2 Column 2: 30 m x 0.53 mm ID fused-silica capillary column chemically bonded with polyethylene glycol (DB-WAX or equivalent).

4.6 Chromatographic column for Florisil: 200-mm x 11-mm ID glass column.

5.0 REAGENTS

5.1 Reagent water: Water in which an interferent is not observed at the MDL of the parameters of interest.

5.2 Preservatives:

5.2.1 Sodium hydroxide (ACS certified), 10N in distilled water.

5.2.2 Sulfuric acid (ACS certified), mix equal volumes of concentrated sulfuric acid and distilled water.

5.3 Acetone, hexane, isooctane, diethyl ether, methylene chloride, petroleum ether: pesticide quality or equivalent.

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

5.5 Florisil pesticide grade (60/100 mesh): Before use, activate for at least 16 hours at 130°C. Alternatively, store Florisil in an oven at 130°C. Cool Florisil before use.

5.6 Tetrabutylammonium-sulfite reagent: A solution of 3.39 g (0.01 mol) tetrabutylammonium hydrogen sulfate in 100 mL of water is extracted with three 20-mL portions of hexane (to remove impurities); this solution is split into 1-mL portions to which 250 mg anhydrous sodium sulfite (ACS grade) are added.

5.7 Corn oil: 200 mg/mL in methylene chloride.

5.8 Stock standard solutions (1.0 µg/µL): Can be prepared from pure standard materials or can be purchased as certified solutions.

5.8.1 Prepare stock standard solutions by accurately weighing about 0.0100 g of pure compound. Dissolve the compound in isooctane and dilute to volume in a 10-mL volumetric flask. If compound purity is 96 percent or greater, the weight can be used without correction to calculate the concentration of the stock standard.

5.8.2 Transfer the stock standard solutions into sealed screw-cap bottles or ground-glass-stoppered reagent bottles. Store at 4°C and protect from light.

5.9 Calibration standards should be prepared at a minimum of five concentrations by dilution of the stock standards with isooctane. The suggested levels are listed in Table 4. However, the concentration levels should correspond to the expected range of concentrations found in real samples and should define the working range of the GC. Calibration solutions must be replaced after six months, or sooner if ongoing QC (Section 8) indicates a problem.

5.10 Internal standards: 2,5-dibromotoluene, 1,3,5-tribromobenzene, and α,α'-dibromo-m-xylene. The analyst can use any of the three compounds provided that they are resolved from matrix interferences.

5.10.1 Prepare an internal standard spiking solution which contains 50 µg/mL of any of the compounds listed above. Addition of 10 µL of this solution to 1 mL of sample extract is recommended. The spiking level of the internal standard should be kept constant for all samples and calibration standards. Store the internal standard spiking solutions at 4°C in Teflon-sealed containers. Standard solution should be replaced when ongoing QC (Section 8) indicates a problem.

5.11 Surrogate standard spiking solution:

5.11.1 The performance of the method should be monitored using surrogate compounds. Three surrogate compounds are recommended: α,2,6-trichlorotoluene, 1,4-dichloronaphthalene, and 2,3,4,5,6-pentachlorotoluene. Surrogate standards are added to all samples, method blanks, matrix spikes, and calibration standards.

5.11.2 Prepare a surrogate standard spiking solution which contains 1 µg/mL of α,2,6-trichlorotoluene and 2,3,4,5,6-pentachlorotoluene and 10 µg/mL of 1,4-dichloronaphthalene. Addition of 1 mL of this solution to 1 L of water sample or 10 g of solid sample is equivalent to 1 µg/L or 100 ng/g of α,2,6-trichlorotoluene and 2,3,4,5,6-pentachlorotoluene and 10 µg/L or 1,000 ng/g of 1,4-dichloronaphthalene. The spiking level of the surrogate standards may be adjusted accordingly if the final volume of extract is reduced below 10 mL. Store the spiking solutions at 4°C in Teflon-sealed containers. The solutions must be replaced after 6 months or sooner if onging QC (Section 8) indicates problems.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

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

6.2 The stability of the chlorinated hydrocarbons in soil has not been systematically investigated. Storage of soil samples at room temperature should be avoided since degradation of some chlorinated hydrocarbons has been reported to occur. Deep-freezing at -10°C or -20°C appears to be the most suitable method for storage of solid matrices since it has the widest range of application, causes the least changes in the samples, and makes the addition of preservatives unnecessary.

6.3 All aqueous samples must be extracted within 3 days of sample collection; all soil and sediment samples must be extracted within 30 days of sample collection. Extracts must be stored at <4°C and must be analyzed within 30 days of extraction.

7.0 PROCEDURES

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 pH with methylene chloride by using a separatory funnel (Method 3510) or a continuous liquid-liquid extractor (Method 3520). Solid samples are extracted with hexane/acetone (1:1) by using a Soxhlet extractor (Method 3540) or with methylene chloride/acetone (1:1) by using a sonicator (Method 3550).

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. Spiking of water samples should be performed by adding appropriate amounts of the Method 8120 compounds, dissolved in methanol or acetone, to the water samples immediately prior to extraction. After addition of the spike, mix the samples manually for 1 to 2 minutes. Typical spiking levels for water samples are 0.1 to 20 µg/L for samples in which the Method 8120 compounds were not detected and 2 to 5 times the background level in those cases where compounds are present. Spiking of solid samples should be performed by adding appropriate amounts of Method 8120 compounds, dissolved in methanol or acetone, to a soil slurry in water. The solid sample should be wet prior to the addition of the spike (typical moisture levels are 35 to 40 percent) and should be mixed thoroughly with a blender. Transfer the whole portion that was spiked with the test compounds to the extraction thimble for Soxhlet extraction (Method 3540) or proceed with the sonication in the case of Method 3550.

7.2 Solvent exchange: Prior to Florisil cleanup or gas chromatographic analysis, the extraction solvent must be exchanged to hexane. Sample extracts that will be subjected to gel permeation chromatography do not need solvent exchange. The exchange is performed during the K-D procedures listed in all of the extraction methods. The exchange is performed as follows:

7.2.1 Following K-D concentration of the methylene chloride extracts to 1 mL using the macro-Snyder column, allow the apparatus to cool and drain for at least 10 minutes.

7.2.2 Increase the temperature of the hot water bath to about 90°C. Momentarily remove the Snyder column, add 50 mL of hexane, a new glass bead, and attach the macro-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 to 10 minutes. 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 minutes.

7.2.3 Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 to 2 mL of hexane. A 5-mL syringe is recommended for this operation. Adjust the extract volume to 10 mL. Stopper the concentrator tube and store at 4°C if further processing will be performed immediately. If the extract will be stored longer than two days, it should be transferred to a Teflon-lined screw-cap vial. Proceed with cleanup or gas chromatographic analysis.

7.3 Cleanup/Fractionation:

7.3.1 Cleanup procedures may not be necessary for a relatively clean matrix. If removal of interferences such as chlorinated phenols, phthalate esters, etc., is required, proceed with the procedure outlined in Method 3620. Collect Fraction 1 by eluting with 200 mL petroleum ether and Fraction 2 by eluting with 200 mL of diethyl ether/petroleum ether (1:1). Note that, under these conditions, benzal chloride and benzotrichloride are not recovered from the Florisil column. The elution patterns and compound recoveries are given in Table 5.

7.3.2 As an alternative to Method 3620, the following Florisil cartridge procedure can be used for extract cleanup. With this method, benzal chloride and benzotrichloride are also recovered quantitatively.

7.3.2.1 Every lot of Florisil cartridges must be checked prior to use as follows. Install 1-g cartridges in the vacuum manifold. Wash each cartridge with 4 mL pesticide-grade hexane and discard the eluate. Add to each cartridge 2 mL of a composite standard containing the test compounds at 0.05 to 10 µg/mL and elute each cartridge with 5 mL hexane/acetone (9:1 v/v). Adjust the final volumes to 10 mL and analyze the eluates by GC/ECD. The lot of Florisil cartridges is acceptable if all 22 target compound recoveries are between 80 and 120 percent and if no other interferences are detected.

7.3.2.2 Prior to cleanup of sample extracts, the cartridges must be washed with hexane. This is accomplished by placing 10, 12, or 24 cartridges in the vacuum manifold (the number depends on the type of vacuum manifold; for example, Vac Elut SPS24 from Analytichem International can accommodate 24 cartridges) and passing at least 4 mL pesticide-grade hexane through each cartridge. While washing the cartridges, adjust the vacuum applied to each cartridge so that the flows through the cartridges are approximately equal. Do not allow the cartridges to go dry after they have been washed.

7.3.2.3 After the cartridges have been washed, release the vacuum and replace the collecting vials with 5-mL volumetric flasks. Care must be taken to ensure that the solvent line from each cartridge is placed inside the correct volumetric flask.

7.3.2.4 After the volumetric flasks have been set in the vacuum manifold, the vacuum is restored and the sample extracts are

added to the appropriate cartridges. Use a syringe or a volumetric pipet for transferring the extracts.

7.3.2.5 Elute each cartridge with 5 mL hexane/acetone (9:1 v/v) and collect the eluate in the 5-mL volumetric flask held inside the vacuum manifold. Adjust to the 5-mL mark if not all solvent is recovered. Transfer the eluates to clean sample vials for further concentration using nitrogen blow-down evaporation with a gentle stream of pure nitrogen. The elution patterns and compound recoveries are given in Table 6.

7.3.3 Removal of waxes and lipids by gel permeation chromatography (optional):

7.3.3.1 Packing the column: Place 70 g of Bio-Beads SX-3 in a 400-mL beaker, cover the beads with methylene chloride, and allow them to swell overnight (before packing the column). Transfer the swelled beads to the column and pump methylene chloride through the column from bottom to top at 5.0 mL/min. After approximately 1 hour, adjust the pressure to 7 to 10 psi and pump solvent for an additional 4 hours to remove all air from the column. Adjust the column pressure periodically, as required, to maintain 7 to 10 psi.

7.3.3.2 Calibration of the column: Load 5 mL of the corn-oil solution into sample loop No. 1 and 5 mL of the chlorinated hydrocarbons standard into sample loop No. 2. Inject the corn oil and collect 10-mL fractions (i.e., change fractions at 2-minute intervals) for 36 minutes. Inject the chlorinated hydrocarbons standard and collect 15-mL fractions for 60 minutes. Determine the corn-oil elution pattern by evaporating each fraction to dryness and determining the residue gravimetrically. Analyze the chlorinated hydrocarbons by gas chromatography and plot the concentration of each component in each fraction versus the total eluant volume (or time) from the injection points. Choose a "dump time" which allows >85 percent removal of the corn oil and >85 percent recovery of the chlorinated hydrocarbons. Choose the "collect time" that will extend at least 10 minutes past the elution of chlorinated hydrocarbons. Wash the column for at least 15 minutes between samples. Typical parameters selected are a dump time of 30 minutes (180 mL), and a wash time of 15 minutes (75 mL). The column can also be calibrated by the use of a 254-nm UV detector in place of gravimetric and GC analysis of the fractions. Measure the peak areas at various elution times to determine appropriate fractions. The SX-3 Bio-Beads column may be used for several months even if discoloration occurs. System calibration usually remains constant over this period of time if the column flowrate remains constant.

7.3.3.3 Prefilter the extracts or load all extracts via the filter holder to retain particulates that might cause flow stoppage. Load one 5.0-mL aliquot of the extract onto the GPC column. Use sufficient clean solvent after the extract loading to transfer the entire aliquot into the loop. Between extracts, purge

the sample loading tubing thoroughly with clean solvent. Process the extracts by using the dump, collect, and wash parameters determined from the calibration and collect the cleaned extracts in 250-mL amber bottles. Concentrate the extracts as described in Section 7.2.

7.3.4 Elemental Sulfur Removal (optional) -- Add 1 mL 2-propanol and 1 mL TBA-sulfite reagent to the hexane extract (2 mL) and shake for at least 1 minute. Add approximately 100 mg sodium sulfite crystals. If the sodium sulfite disappears, more sodium sulfite is added in 100-mg portions until a solid residue remains after repeated shaking. Water (5 mL) is added, and the test tube is shaken for another minute; this process is followed by centrifugation. Finally, the hexane layer is transferred to another vial for gas chromatographic analysis. Additional details of this procedure can be found in Reference 1.

7.4 Gas chromatography conditions (recommended):

7.4.1 Column 1: 30 m x 0.53 mm ID DB-210 fused-silica capillary column, 1-µm film thickness; carrier gas is helium at 10 mL/min; makeup gas is nitrogen at 40 mL/min; temperature program from 65°C to 175°C (hold 20 minutes) at 4°C/min; injector temperature 220°C; detector temperature 250°C.

7.4.2 Column 2: 30 m x 0.53 mm ID DB-WAX fused-silica capillary column; 1-µm film thickness; carrier gas is helium at 10 mL/min; makeup gas is nitrogen at 40 mL/min.; temperature program from 60°C to 170°C (hold 30 minutes) at 4°C/min; injector temperature 200°C; detector temperature 230°C.

7.4.3 Tables 1 and 3 give the MDLs and the retention times for 22 chlorinated hydrocarbons. Examples of the separations achieved with the DB-210 and DB-WAX fused-silica capillary columns are shown in Figures 1 and 2, respectively.

7.5 Calibration:

7.5.1 Refer to Method 8000 for proper calibration techniques. Use Table 4 for guidance.

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

7.6 Gas chromatographic analysis:

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

7.6.2 Follow step 7.6 in Method 8000 for instructions on analysis sequence, appropriate dilutions, daily retention time windows, and identification criteria.

7.6.3 Record the sample volume injected and the resulting peak areas.

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

7.6.5 If the response of a peak exceeds the working range of the system, dilute the extract and reanalyze.

7.6.6 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 obtained on the two columns specified in Section 7.4. The retention time window used to make identifications should be based upon measurements of actual retention time variations over the course of 10 consecutive injections. Three times the standard deviation of a retention time window can be used to calculate a suggested window size.

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 individual extraction method protocols. If extract cleanup is required, follow the QC presented in Method 3600 and in the specific cleanup method protocols.

8.2 Mandatory quality control to evaluate the GC system operation is found in Method 8000, Section 8.6.

8.2.1 Analyze a quality control check standard to demonstrate that the operation of the gas chromatograph is in control. The frequency of the check standard analysis is equivalent to 10 percent of the samples analyzed. If the recovery of any compound found in the check standard is less than 80 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 must be prepared and analyzed.

8.3 Calculate surrogate standard recoveries for all samples, blanks, and spikes. Determine if the recovery is within limits (limits established by performing QC procedures outlined in Method 8000, step 8.10).

8.3.1 If the recoveries are not within limits, the following are required:

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

- Recalculate the data or reanalyze the extract if any of the above checks reveals a problem.

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

8.4 An internal standard peak area check must be performed on all samples. The internal standard must be evaluated for acceptance by determining whether the measured area for the internal standard deviates by more than 50 percent from the average area for the internal standard in the calibration standards. When the internal standard peak area is outside that limit, all samples that fall outside the QC criteria must be reanalyzed.

8.5 GC/MS confirmation: Any compound 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.

8.5.1 The GC/MS would normally require a minimum concentration of 1 ng/μL in the final extract for each compound.

8.5.2 The sample extract and the associated blank should be analyzed by GC/MS as per Section 7.0 of Method 8270.

8.5.3 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 compounds identified by GC/ECD.

8.6 Include a mid-level calibration standard after each group of 20 samples in the analysis sequence. The response factors for the mid-level calibration must be within >30 percent of the average values for the multilevel calibration.

8.7 Demonstrate through the analyses of standards that the Florisil fractionation scheme is reproducible. When using the fractionation scheme given in Method 3620, batch-to-batch variations in the composition of the Florisil material may cause a change in the distribution patterns of the chlorinated hydrocarbons.

8.7.1 Whenever compounds are found in more than one fraction, add up the amounts of the various 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 as the minimum concentration of the test compound that can be measured and reported with 99 percent confidence that the value is

above zero. The MDLs listed in Table 1 were obtained by using reagent water. Details on how to determine MDLs are given in Reference 2. The MDLs actually achieved in a given analysis will vary since they depend on instrument sensitivity and matrix effects.

9.2 This method has been tested in a single laboratory by using reagent water and sandy loam samples and extracts which were spiked with the test compounds at one concentration. Single-operator precision and method accuracy were found to be related to the concentration of compound and the type of matrix. For exemplification, results of the single-laboratory method evaluation are given in Tables 7 and 8.

9.3 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

1.0 Jensen, S., L. Renberg, and L. Reutergardh, "Residue Analysis of Sediment and Sewage Sludge for Organochlorines in the Presence of Elemental Sulfur," Anal. Chem. 49: 316-318, 1977.

2.0 Glazer, J. A., G. D., Foerst, G. D., McKee, S. A., Quave, and W. L. Budde, "Trace Analyses for Wastewaters," Environ. Sci. and Technol. 15:1426-1431, 1981.

Table 1.
CHLORINATED HYDROCARBONS THAT CAN BE DETERMINED BY METHOD 8120 AND THEIR METHOD DETECTION LIMITS

Compound name	CAS no.	MDL[a] (ng/L)
Benzalchloride	98-87-3	2-5[b]
Benzotrichloride	98-07-7	6.0
Benzylchloride	100-44-7	180
2-Chloronaphthalene	91-58-7	1,300
1,2-Dichlorobenzene	95-50-1	270
1,3-Dichlorobenzene	541-73-1	250
1,4-Dichlorobenzene	106-46-1	890
Hexachlorobenzene	118-74-1	5.6
Hexachlorobutadiene	87-68-3	1.4
alpha-Hexachlorocyclohexane (alpha-BHC)	319-84-6	11
beta-Hexachlorocyclohexane (beta-BHC)	319-85-7	31
gamma-Hexachlorocyclohexane (gamma-BHC)	58-89-9	23
delta-Hexachlorocyclohexane (delta-BHC)	319-86-8	20
Hexachlorocyclopentadiene	77-47-4	240
Hexachloroethane	67-72-1	1.6
Pentachlorobenzene	608-93-5	38
1,2,3,4-Tetrachlorobenzene	634-66-2	11
1,2,4,5-Tetrachlorobenzene	95-94-2	9.5
1,2,3,5-Tetrachlorobenzene	634-90-2	8.1
1,2,4-Trichlorobenzene	120-82-1	130
1,2,3-Trichlorobenzene	87-61-6	39
1,3,5-Trichlorobenzene	108-70-3	12

[a]MDL is the method detection limit for reagent water. MDL was determined from the analysis of eight replicate aliquots processed through the entire analytical method (extraction, Florisil cartridge cleanup, and GC/EC analysis). MDL = $t_{(n-1,0.99)}$xSD where $t_{(n-1,0.99)}$ is the student's t value appropriate for a 99 percent confidence interval and a standard deviation with n-1 degrees of freedom, and SD is the standard deviation of the eight replicate measurements.
[b]Estimated from the instrument detection limit.

Table 2.
PRACTICAL QUANTITATION LIMIT (PQL) FACTORS FOR VARIOUS MATRICES[a]

Matrix	Factor[b]
Ground water	10
Low-level soil by sonication with GPC cleanup	670
High-level soil and sludges by sonication	10,000
Waste not miscible with water	100,000

[a]Sample PQLs are highly matrix-dependent. The PQLs listed herein are provided for guidance and may not always be achievable.
[b]PQL = [Method detection limit (Table 1)] x [Factor (Table 2)]. For nonaqueous samples, the factor is on a wet-weight basis.

Table 3.
GAS CHROMATOGRAPHIC RETENTION TIMES FOR THE CHLORINATED HYDROCARBONS

Compound no.	Compound name	Retention time (min) DB-210[a]	DB-WAX[b]
1	Benzal chloride	6.86	15.91
2	Benzotrichloride	7.85	15.44
3	Benzyl chloride	4.59	10.37
4	2-Chloronaphthalene	13.45	23.75
5	1,2-Dichlorobenzene	4.44	9.58
6	1,3-Dichlorobenzene	3.66	7.73
7	1,4-Dichlorobenzene	3.80	8.49
8	Hexachlorobenzene	19.23	29.16
9	Hexachlorobutadiene	5.77	9.98
10	alpha-BHC	22.21	41.62
11	beta-BHC	25.54	33.84
12	gamma-BHC	24.07	54.30
13	delta-BHC	26.16	33.79
14	Hexachlorocyclopentadiene	8.86	c
15	Hexachloroethane	3.35	8.13
16	Pentachlorobenzene	14.86	23.75
17	1,2,3,4-Tetrachlorobenzene	11.90	21.17
18	1,2,4,5-Tetrachlorobenzene	10.18	17.81
19	1,2,3,5-Tetrachlorobenzene	10.18	17.50
20	1,2,4-Trichlorobenzene	6.86	13.74
21	1,2,3-Trichlorobenzene	8.14	16.00
22	1,3,5-Trichlorobenzene	5.45	10.37

(continued)

[a]GC operating conditions: 30 m x 0.53 mm ID DB-210 fused-silica capillary column; 1-µm film thickness; carrier gas is helium at 10 mL/min; makeup gas is nitrogen at 40 mL/min; temperature program from 65°C to 175°C (hold 20 minutes) at 4°C/min; injector temperature 220°C; detector temperature 250°C.

[b]GC operating conditions: 30 m x 0.53 mm ID DB-WAX fused-silica capillary column; 1-µm film thickness; carrier gas is helium at 10 mL/min; makeup gas is nitrogen at 40 mL/min; temperature program from 60°C to 170°C (hold 30 minutes) at 4°C/min; injector temperature 200°C; detector temperature 230°C.

[c]Compound decomposes on-column.

Table 3.
(CONCLUDED)

Compound no.	Compound name	Retention time (min) DB-210[a]	Retention time (min) DB-WAX[b]
	Internal standards		
	2,5-Dibromotoluene	9.55	18.55
	1,3,5-Tribromobenzene	11.68	22.60
	α,α'-Dibromo-meta-xylene	18.43	35.94
	Surrogates		
	α,2,6-Trichlorotoluene	12.96	22.53
	1,4-Dichloronaphthalene	17.43	26.83
	2,3,4,5,6-Pentachlorotoluene	18.96	27.91

[a]GC operating conditions: 30 m x 0.53 mm ID DB-210 fused-silica capillary column; 1-μm film thickness; carrier gas is helium at 10 mL/min; makeup gas is nitrogen at 40 mL/min; temperature program from 65°C to 175°C (hold 20 minutes) at 4°C/min; injector temperature 220°C; detector temperature 250°C.

[b]GC operating conditions: 30 m x 0.53 mm ID DB-WAX fused-silica capillary column; 1-μm film thickness; carrier gas is helium at 10 mL/min; makeup gas is nitrogen at 40 mL/min; temperature program from 60°C to 170°C (hold 30 minutes) at 4°C/min; injector temperature 200°C; detector temperature 230°C.

[c]Compound decomposes on-column.

Table 4.
SUGGESTED CONCENTRATIONS FOR THE CALIBRATION SOLUTIONS[a]

Compound	Concentration (ng/µL)				
Benzal chloride	0.1	0.2	0.5	0.8	1.0
Benzotrichloride	0.1	0.2	0.5	0.8	1.0
Benzyl chloride	0.1	0.2	0.5	0.8	1.0
2-Chloronaphthalene	2.0	4.0	10	16	20
1,2-Dichlorobenzene	1.0	2.0	5.0	8.0	10
1,3-Dichlorobenzene	1.0	2.0	5.0	8.0	10
1,4-Dichlorobenzene	1.0	2.0	5.0	8.0	10
Hexachlorobenzene	0.01	0.02	0.05	0.08	0.1
Hexachlorobutadiene	0.01	0.02	0.05	0.08	0.1
alpha-BHC	0.1	0.2	0.5	0.8	1.0
beta-BHC	0.1	0.2	0.5	0.8	1.0
gamma-BHC	0.1	0.2	0.5	0.8	1.0
delta-BHC	0.1	0.2	0.5	0.8	1.0
Hexachlorocyclopentadiene	0.01	0.02	0.05	0.08	0.1
Hexachloroethane	0.01	0.02	0.05	0.08	0.1
Pentachlorobenzene	0.01	0.02	0.05	0.08	0.1
1,2,3,4-Tetrachlorobenzene	0.1	0.2	0.5	0.8	1.0
1,2,4,5-Tetrachlorobenzene	0.1	0.2	0.5	0.8	1.0
1,2,3,5-Tetrachlorobenzene	0.1	0.2	0.5	0.8	1.0
1,2,4-Trichlorobenzene	0.1	0.2	0.5	0.8	1.0
1,2,3-Trichlorobenzene	0.1	0.2	0.5	0.8	1.0
1,3,5-Trichlorobenzene	0.1	0.2	0.5	0.8	1.0
Surrogates					
α,2,6-Trichlorotoluene	0.02	0.05	0.1	0.15	0.2
1,4-Dichloronaphthalene	0.2	0.5	1.0	1.5	2.0
2,3,4,5,6-Pentachlorotoluene	0.02	0.05	0.1	0.15	0.2

[a]One or more internal standards should be spiked prior to GC/ECD analysis into all calibration solutions. The spike level of the internal standards should be kept constant for all calibration solutions.

Table 5.
ELUTION PATTERNS OF THE METHOD 8120 COMPOUNDS FROM THE FLORISIL COLUMN BY ELUTION WITH PETROLEUM ETHER (FRACTION 1) AND 1:1 PETROLEUM ETHER/DIETHYL ETHER (FRACTION 2)

Compound	Amount (µg)	Recovery (percent)[a]	
		Fraction 1[b]	Fraction 2[c]
Benzal chloride[d]	10	0	0
Benzotrichloride	10	0	0
Benzyl chloride	100	82	16
2-Chloronaphthalene	200	115	
1,2-Dichlorobenzene	100	102	
1,3-Dichlorobenzene	100	103	
1,4-Dichlorobenzene	100	104	
Hexachlorobenzene	1.0	116	
Hexachlorobutadiene	1.0	101	
alpha-BHC	10		95
beta-BHC	10		108
gamma-BHC	10		105
delta-BHC	10		71
Hexachlorocyclopentadiene	1.0	93	
Hexachloroethane	1.0	100	
Pentachlorobenzene	1.0	129	
1,2,3,4-Tetrachlorobenzene	10	104	
1,2,4,5-Tetrachlorobenzene[e]	10	102	
1,2,3,5-Tetrachlorobenzene[e]	10	102	
1,2,4-Trichlorobenzene	10	59	
1,2,3-Trichlorobenzene	10	96	
1,3,5-Trichlorobenzene	10	102	

[a]Values given represent average values of duplicate experiments.
[b]Fraction 1 was eluted with 200 mL petroleum ether.
[c]Fraction 2 was eluted with 200 mL petroleum ether/diethyl ether (1:1).
[d]This compound coelutes with 1,2,4-trichlorobenzene; separate experiments were performed with benzal chloride to verify that this compound is not recovered from the Florisil cleanup in either fraction.
[e]This pair cannot be resolved on the DB-210 fused-silica capillary columns.

Table 6.
RECOVERY OF THE METHOD 8120 COMPOUNDS FROM THE FLORISIL CARTRIDGE BY ELUTION WITH HEXANE/ACETONE (9:1 v/v)

Compounds	Amount (µg)	Average recovery[a] (percent)	Precision (percent RSD)
Benzal chloride[b]	10	99	0.8
Benzotrichloride	10	90	6.5
Benzyl chloride	100	101	1.5
2-Chloronaphthalene	200	95	1.4
1,2-Dichlorobenzene	100	102	1.6
1,3-Dichlorobenzene	100	101	2.3
1,4-Dichlorobenzene	100	100	2.3
Hexachlorobenzene	1.0	78	1.1
Hexachlorobutadiene	1.0	95	2.0
alpha-BHC	10	100	0.4
beta-BHC	10	95	1.8
delta-BHC	10	97	2.7
gamma-BHC	10	99	0.7
Hexachlorocyclopentadiene	1.0	103	3.3
Hexachloroethane	1.0	95	2.0
Pentachlorobenzene	1.0	104	1.5
1,2,3,4-Tetrachlorobenzene	10	99	1.3
1,2,4,5-Tetrachlorobenzene[c]	10	98	3.1
1,2,3,5-Tetrachlorobenzene[c]	10	98	3.1
1,2,4-Trichlorobenzene[b]	10	99	0.8
1,2,3-Trichlorobenzene	10	97	2.0
1,3,5-Trichlorobenzene	10	98	2.2

[a]The number of determinations is 5.
[b,c]These pairs cannot be resolved on the DB-210 fused-silica capillary column.

Table 7.
ACCURACY AND PRECISION DATA FOR METHOD 3510 AND METHOD 8120

Compound	Spike level (µg/L)	Average recovery[a,b] (percent)	Precision (percent RSD)
Benzal chloride[c]	10	95	3.0
Benzotrichloride	1.0	97	2.1
Benzyl chloride	100	90	6.2
2-Chloronaphthalene	200	91	6.5
1,2-Dichlorobenzene	100	92	5.7
1,3-Dichlorobenzene	100	87	8.7
1,4-Dichlorobenzene	100	89	8.9
Hexachlorobenzene	1.0	92	7.1
Hexachlorobutadiene	1.0	95	3.6
alpha-BHC	10	96	2.6
beta-BHC	10	103	3.6
gamma-BHC	10	96	2.8
delta-BHC	10	103	2.7
Hexachlorocyclopentadiene	10	97	5.1
Hexachloroethane	1.0	96	4.0
Pentachlorobenzene	1.0	89	6.5
1,2,3,4-Tetrachlorobenzene	10	96	3.4
1,2,4,5-Tetrachlorobenzene[d]	10	93	4.6
1,2,3,5-Tetrachlorobenzene[d]	10	93	4.6
1,2,4-Trichlorobenzene[c]	10	95	3.0
1,2,3-Trichlorobenzene	10	95	4.4
1,3,5-Trichlorobenzene	10	93	6.2
Surrogates			
α,2,6-Trichlorotoluene	1.0	85	6.5
1,4-Dichloronaphthalene	10	78	6.1
2,3,4,5,6-Pentachlorotoluene	1.0	80	5.9

[a]The number of determinations was 5.
[b]Final volume of extract was 10 mL. Florisil cleanup was not performed on any of the samples.
[c,d]These pairs cannot be resolved on the DB-210 fused-silica capillary column.

Table 8.
ACCURACY AND PRECISION DATA FOR METHOD 3550 AND METHOD 8120

Compound	Spike level (ng/g)	Average recovery[a,b] (percent)	Precision (percent RSD)
Benzal chloride[c]	3,300	89	2.7
Benzotrichloride	3,300	90	2.0
Benzyl chloride	33,000	121	5.9
2-Chloronaphthalene	66,000	100	6.4
1,2-Dichlorobenzene	33,000	84	7.1
1,3-Dichlorobenzene	33,000	81	12.6
1,4-Dichlorobenzene	33,000	89	11.0
Hexachlorobenzene	330	81	3.2
Hexachlorobutadiene	330	83	4.7
alpha-BHC	3,300	100	2.9
beta-BHC	3,300	92	2.4
gamma-BHC	3,300	99	4.1
delta-BHC	3,300	97	1.5
Hexachlorocyclopentadiene	330	44	25.9
Hexachloroethane	330	83	4.6
Pentachlorobenzene	330	81	3.5
1,2,3,4-Tetrachlorobenzene	3,300	88	2.9
1,2,4,5-Tetrachlorobenzene[d]	3,300	80	4.4
1,2,3,5-Tetrachlorobenzene[d]	3,300	80	4.4
1,2,4-Trichlorobenzene[c]	3,300	89	2.7
1,2,3-Trichlorobenzene	3,300	79	4.3
1,3,5-Trichlorobenzene	3,300	75	5.3
Surrogates			
α,2,6-Trichlorotoluene	330	86	2.7
1,4-Dichloronaphthalene	3,300	88	4.5
2,3,4,5,6-Pentachlorotoluene	330	98	11.7

[a]The number of determinations was 5.
[b]Final volume of extract was 10 mL. Florisil cleanup was not performed on any of the samples.
[c,d]These pairs cannot be resolved on the DB-210 fused-silica capillary column.

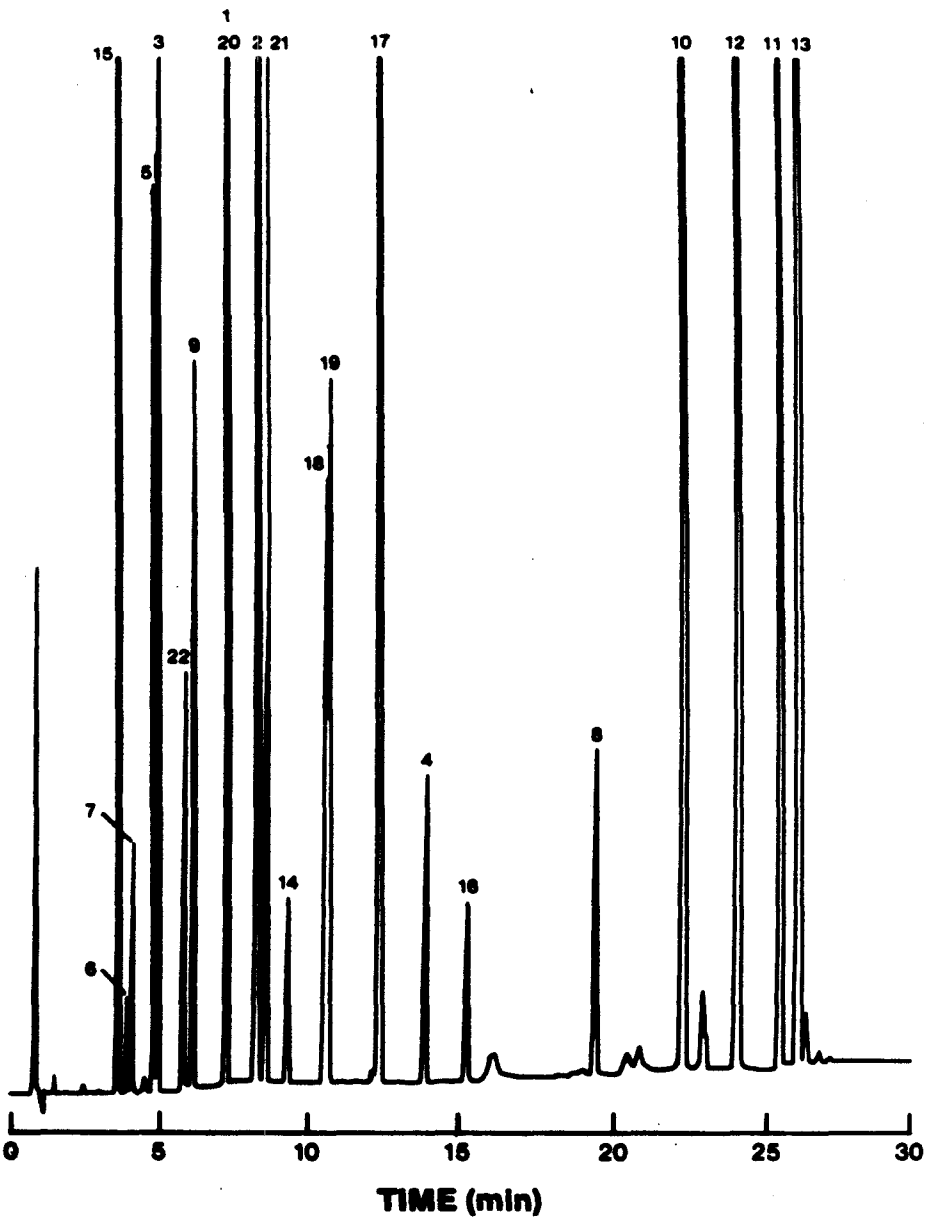


Figure 1. GC/EC chromatogram of Method 8120 composite standard analyzed on a 30 m x 0.53 mm ID DB-210 fused-silica capillary column. GC operating conditions are given in Section 7.4.

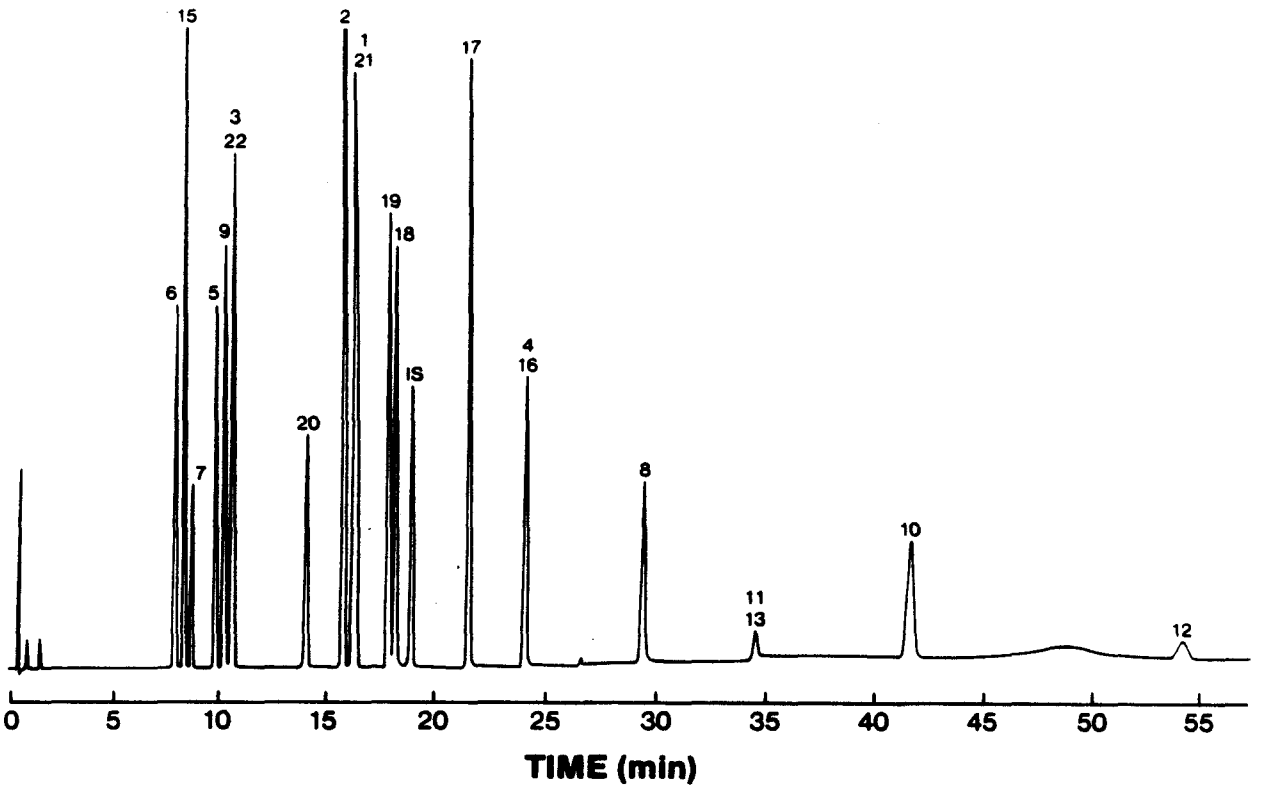
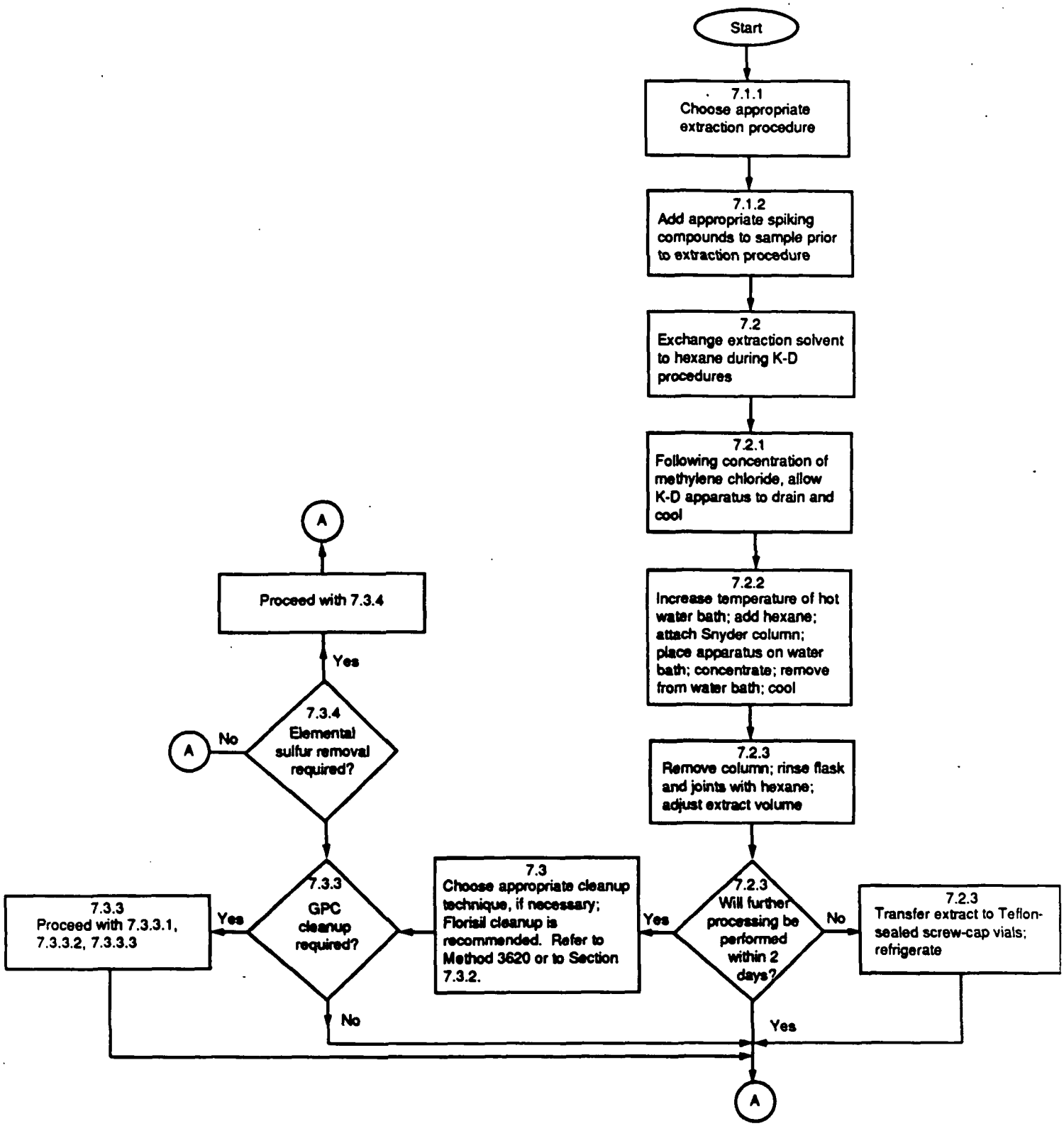
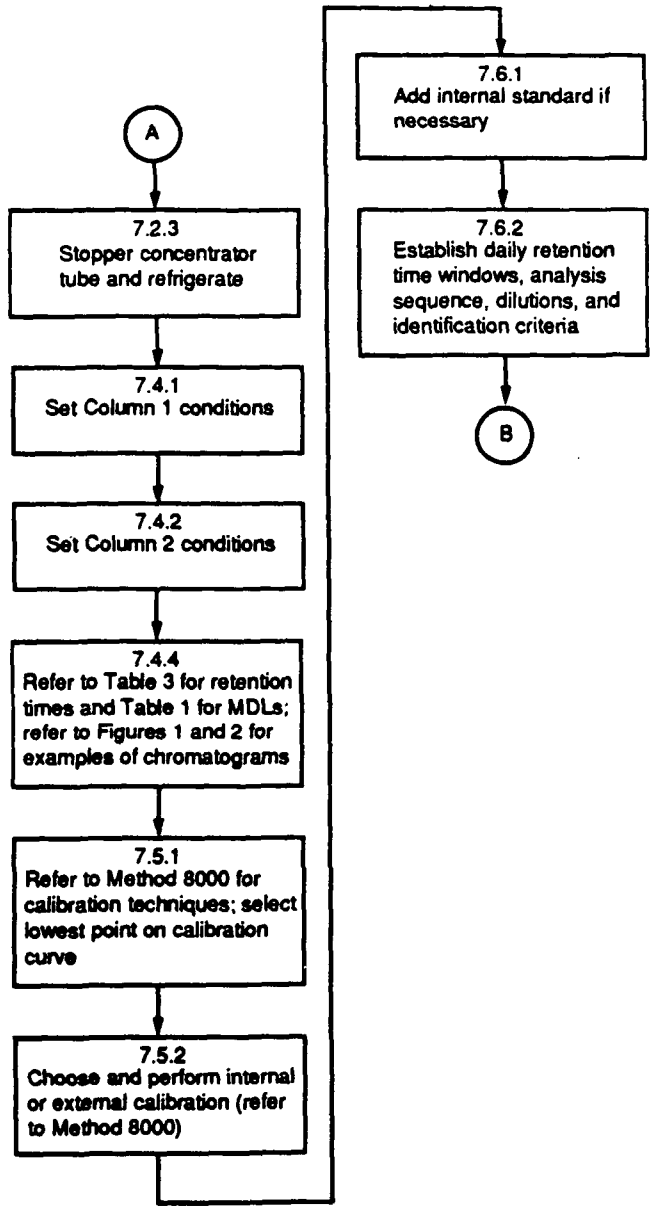


Figure 2. GC/EC chromatogram of Method 8120 composite standard analyzed on a 30 m x 0.53 mm ID DB-WAX fused-silica capillary column. GC operating conditions are given in Section 7.4.

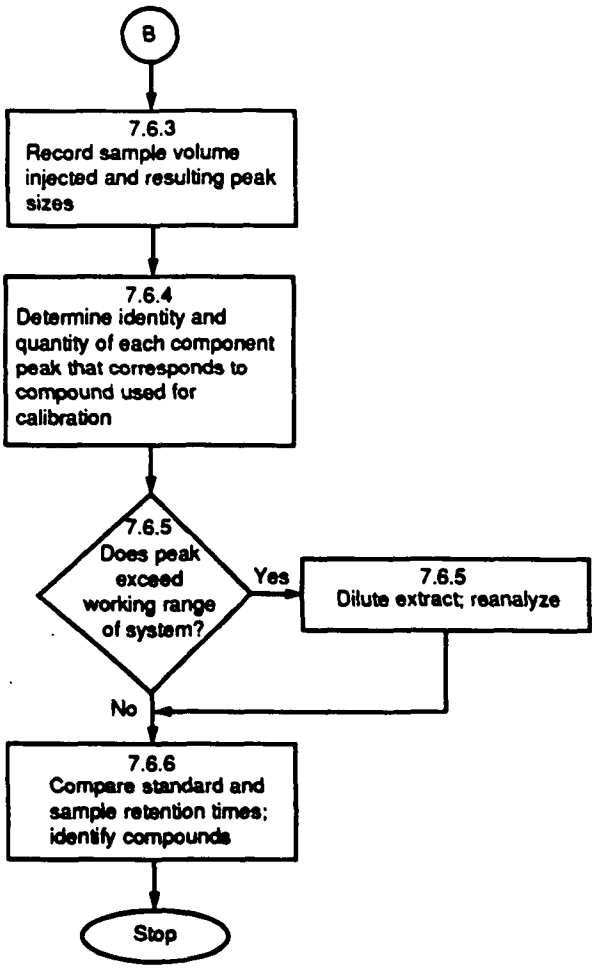
**** DRAFT September 30, 1988 ****

Method 8120 -- Chlorinated Hydrocarbons (Flowchart)




A
7.2.3
Stopper concentrator tube and refrigerate
7.4.1
Set Column 1 conditions
7.4.2
Set Column 2 conditions
7.4.4
Refer to Table 3 for retention times and Table 1 for MDLs; refer to Figures 1 and 2 for examples of chromatograms
7.5.1
Refer to Method 8000 for calibration techniques; select lowest point on calibration curve
7.5.2
Choose and perform internal or external calibration (refer to Method 8000)
7.6.1
Add internal standard if necessary
7.6.2
Establish daily retention time windows, analysis sequence, dilutions, and identification criteria
B

METHOD 8120 -- CHLORINATED HYDROCARBONS (FLOWCHART)
(concluded)



APPENDIX C

PREPARATION OF SPIKED SOIL SAMPLES

Preparation of reference materials is an area that needs attention, and some effort has been devoted in this study to the development of such materials. We prepared a wet reference material in which a slurry of sandy loam soil in water (approximately 60 to 70 percent moisture) was spiked with a concentrated stock solution of the target compounds in isooctane and mixed thoroughly in a blender. Blending resulted in a smooth slurry. Subsampling was done immediately to avoid setting. The material was split into 35-g portions, and individual portions were extracted and analyzed. In addition, we evaluated overnight tumbling and overnight equilibration of the wet soil with the spike to establish which preparation technique is most efficient. Tables 1, 2, and 3 summarize the results of the even-numbered aliquots from those experiments that were analyzed immediately. The results indicate that the blending technique gave better reproducibilities and higher recoveries than the other two techniques. Additional effort is needed to develop a technique for the preparation of reference materials.

Soil/sediment reference materials can be prepared using actual samples that contain the compounds of interest at known levels. This is very important since spiking the test compounds into a soil/sediment matrix could result in misleading information and generate false results. The following approach is recommended.

1. Identify possible sources based on the target compounds (e.g., Great Lakes sediments have been reported to contain chlorinated benzenes).

2. Collect a sufficient amount of sample and prepare reference materials (freeze-dry sediment, grind, sieve, homogenize).

3. Perform a gross characterization of the material (density, size, mineralogical composition, pH, TOC, TOX, etc.).

4. Subject the material to various extraction procedures (e.g., Soxhlet extraction, sonication, rotary shaker) and several solvents (such as hexane/acetone (1:1) and toluene/methanol (1:1)). Compare the extraction procedures by determining the total extractable material for each extraction/solvent combination.

TABLE 1. HOMOGENEITY OF SPIKED SOIL SAMPLES OBTAINED BY BLENDING

Compound	Concentration (ng/μL extract)									
	-2[a]	-6[a]	-8[a]	-10[a]	-12[a]	-14[a]	-16[a]	-18[a]	Average	Percent RSD
Hexachloroethane	0.08	0.06	0.06	0.07	0.05	0.04	0.05	0.05	0.06	22.1
1,3-Dichlorobenzene	4.40	2.86	2.79	3.66	2.07	2.04	2.04	9.21	3.63	66.2
1,4-Dichlorobenzene	8.60	3.58	2.77	5.96	3.50	6.02	6.62	4.04	5.14	38.6
1,2-Dichlorobenzene	6.20	4.11	3.89	5.68	2.82	2.64	2.58	3.44	3.92	35.0
Benzyl chloride	5.80	3.95	3.68	5.03	2.57	2.61	2.49	2.58	3.59	35.4
1,3,5-Trichlorobenzene	0.51	0.35	0.35	0.52	0.30	0.29	0.30	0.38	0.37	24.5
Hexachlorobutadiene	0.07	0.05	0.05	0.07	0.04	0.04	0.04	0.06	0.05	24.2
Benzal chloride[b] 1,2,4-Trichlorobenzene[b]	1.24	0.88	0.86	1.06	0.69	0.61	0.64	0.80	0.85	25.5
Benzotrichloride	0.44	0.22	0.15	0.11	0.04	0.04	0.05	0.11	0.14	92.6
1,2,3-Trichlorobenzene	0.63	0.49	0.46	0.66	0.44	0.42	0.45	0.52	0.51	17.6
Hexachlorocyclopentadiene	0.03	0.03	0.02	0.05	0.03	0.04	0.04	0.01	0.03	40.2
1,2,4,5-Tetrachlorobenzene[c] 1,2,3,5-Tetrachlorobenzene[c]	0.60	0.44	0.44	0.69	0.45	0.43	0.47	0.56	0.51	18.8
1,2,3,4-Tetrachlorobenzene	0.80	0.64	0.64	0.87	0.65	0.64	0.70	0.75	0.71	12.3
2-Chloronaphthalene	18.9	17.04	14.89	19.77	14.40	16.76	18.82	20.00	17.57	12.2
Pentachlorobenzene	0.07	0.06	0.05	0.08	0.06	0.06	0.07	0.07	0.06	14.2
Hexachlorobenzene	0.06	0.05	0.04	0.08	0.05	0.05	0.07	0.07	0.06	23.0
alpha-BHC	0.93	0.94	0.84	1.04	0.88	0.89	0.95	0.97	0.93	6.6
gamma-BHC	0.83	0.76	0.75	0.94	0.80	0.84	0.87	0.89	0.83	7.8
beta-BHC	0.73	0.66	0.65	0.89	0.72	0.76	0.80	0.82	0.75	10.8
delta-BHC	0.75	0.72	0.69	0.90	0.72	0.79	0.81	0.81	0.77	8.8
Surrogates recovery (percent)										
α,2,6-Trichlorotoluene	70	80	66	75	55	51	64	51	64	17.1
1,4-Dichloronaphthalene	79	100	70	91	64	69	73	62	76	17.5
2,3,4,5,6-Pentachlorotoluene	74	79	67	78	56	55	69	57	67	14.8

[a]The numbers given represent the various 35-g portions that were serially labeled in the order in which they were removed from blender; -4 was lost during sample preparation.
[b,c]These pairs cannot be resolved on the DB-210 fused-silica capillary column.

TABLE 2. HOMOGENEITY OF SPIKED SOIL SAMPLES OBTAINED BY TUMBLING

Compound	Concentration (ng/μL extract)										Percent RSD
	-2[a]	-4[a]	-6[a]	-8[a]	-10[a]	-12[a]	-14[a]	-16[a]	-18[a]	Average	
Hexachloroethane	0.004	0.004	0.003	0.003	0.003	0.003	0.004	0.005	0.006	0.004	26.7
1,3-Dichlorobenzene	0.05	0.79	0.59	0.68	0.49	0.53	0.51	0.88	0.82	0.64	23.9
1,4-Dichlorobenzene	2.0	4.70	2.41	2.38	1.91	1.98	3.02	3.23	2.43	2.67	33.2
1,2-Dichlorobenzene	0.19	0.13	0.10	0.22	0.17	0.15	0.27	0.28	0.24	0.19	32.9
Benzyl chloride	1.07	1.13	0.68	0.71	0.73	0.75	1.12	1.06	1.39	0.96	26.0
1,3,5-Trichlorobenzene	0.04	0.03	0.02	0.03	0.03	0.03	0.05	0.04	0.09	0.04	51.5
Hexachlorobutadiene	0.004	0.003	0.002	0.002	0.003	0.003	0.003	0.004	0.006	0.003	37.1
Benzal chloride[b] 1,2,4-Trichlorobenzene[b]	0.15	0.09	0.08	0.09	0.08	0.08	0.11	0.11	0.30	0.12	59.0
Benzotrichloride	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.012	36.7
1,2,3-Trichlorobenzene	0.09	0.06	0.05	0.06	0.05	0.06	0.07	0.08	0.07	0.066	20.2
Hexachlorocyclopentadiene	0.03	0.03	0.02	0.03	0.03	0.03	0.04	0.03	0.04	0.03	19.4
1,2,4,5-Tetrachlorobenzene[c] 1,2,3,5-Tetrachlorobenzene[c]	0.09	0.06	0.04	0.05	0.04	0.04	0.05	0.07	0.14	0.06	51.3
1,2,3,4-Tetrachlorobenzene	0.22	0.11	0.09	0.11	0.08	0.10	0.12	0.13	0.28	0.14	47.9
2-Chloronaphthalene	13.69	12.46	10.97	10.10	10.95	d	14.24	d	15.80	12.60	16.4
Pentachlorobenzene	0.02	0.01	0.01	0.01	0.01	0.02	0.01	0.02	0.03	0.016	45.4
Hexachlorobenzene	0.03	0.01	0.01	0.01	0.01	0.02	0.01	0.01	0.02	0.014	51.9
alpha-BHC	0.74	0.58	0.50	0.54	0.44	0.49	0.55	0.56	0.77	0.57	19.5
gamma-BHC	0.62	0.48	0.40	0.46	0.36	0.42	0.47	0.48	0.65	0.48	19.9
beta-BHC	0.73	0.66	0.63	0.68	0.61	0.66	0.78	0.71	0.80	0.70	9.3
delta-BHC	0.69	0.64	0.62	0.67	0.60	0.71	0.73	0.69	0.76	0.68	7.7
Surrogates recovery (percent)											
α,2,6-Trichlorotoluene	75	74	78	82	73	74	102	86	85	82	11.5
1,4-Dichloronaphthalene	99	89	78	114	73	95	98	100	111	95	14.3
2,3,4,5,6-Pentachlorotoluene	80	81	117	91	83	85	113	91	90	92	14.7

[a]The numbers given represent the various 35-g portions that were serially labeled in the order in which they were removed from blender. Dichlorobenzene isomers were not included in the spiking solution because they were present in the sample.
[b,c]These pairs cannot be resolved on the DB-210 fused-silica capillary column.
[d]Not able to quantitate due to improper peak integration.

TABLE 3. HOMOGENEITY OF SPIKED SOIL SAMPLES OBTAINED BY OVERNIGHT EQUILIBRATION WITH OCCASIONAL STIRRING

Compound	Concentration (ng/μL extract)									Percent RSD
	-2[a]	-4[a]	-6[a]	-8[a]	-10[a]	-12[a]	-14[a]	-18[a]	Average	
Hexachloroethane	0.004	0.005	0.005	0.006	0.005	0.003	0.004	0.003	0.004	26.5
1,3-Dichlorobenzene	0.94	1.55	1.59	2.54	2.87	1.57	0.82	1.74	1.70	41.4
1,4-Dichlorobenzene	2.29	5.84	6.87	7.67	7.23	5.20	2.71	5.22	5.38	37.1
1,2-Dichlorobenzene	0.12	0.79	0.77	0.48	0.44	0.57	0.19	0.57	0.49	49.4
Benzyl chloride	0.39	0.09	0.13	0.18	0.19	0.17	0.43	0.10	0.21	61.5
1,3,5-Trichlorobenzene	0.07	0.06	0.08	0.09	0.13	0.04	0.05	0.04	0.07	43.2
Hexachlorobutadiene	0.005	0.005	0.006	0.007	0.007	0.003	0.005	0.002	0.005	35.5
Benzal chloride[b] 1,2,4-Trichlorobenzene[b]	0.31	0.29	0.23	0.30	0.32	0.15	0.27	0.14	0.25	28.5
Benzotrichloride	0.20	0.15	0.08	0.13	0.13	0.06	0.14	0.03	0.12	45.6
1,2,3-Trichlorobenzene	0.13	0.13	0.08	0.12	0.14	0.06	0.11	0.06	0.10	32.5
Hexachlorocyclopentadiene	0.01	0.01	0.005	0.006	0.01	0.003	0.004	0.003	0.006	52.7
1,2,4,5-Tetrachlorobenzene[c] 1,2,3,5-Tetrachlorobenzene[c]	0.29	0.29	0.18	0.24	0.26	0.14	0.22	0.14	0.22	27.8
1,2,3,4-Tetrachlorobenzene	0.30	0.31	0.19	0.28	0.27	0.15	0.29	0.16	0.24	27.5
2-Chloronaphthalene	10.70	10.99	10.24	14.30	16.01	13.49	15.49	11.61	12.85	17.6
Pentachlorobenzene	0.04	0.04	0.03	0.04	0.03	0.02	0.04	0.03	0.034	21.9
Hexachlorobenzene	0.05	0.05	0.04	0.05	0.05	0.03	0.05	0.03	0.044	20.0
alpha-BHC	0.89	0.94	0.80	0.99	0.92	0.71	1.04	0.75	0.88	13.3
gamma-BHC	0.76	0.80	0.68	0.85	0.79	0.60	0.91	0.64	0.75	14.2
beta-BHC	0.66	0.73	0.66	0.83	0.76	0.65	0.88	0.80	0.75	11.5
delta-BHC	0.71	0.77	0.70	0.87	0.77	0.67	0.88	0.74	0.76	10.1
Surrogates recovery (percent)										
α,2,6-Trichlorotoluene	64	88	91	95	91	93	92	93	88	11.4
1,4-Dichloronaphthalene	79	82	86	103	122	83	117	115	98	18.2
2,3,4,5,6-Pentachlorotoluene	68	84	89	90	88	90	86	91	86	8.8

[a]The numbers given represent the various 35-g portions that were serially labeled in the order in which they were removed from blender. Dichlorobenzenes were not included in the spiking solution because they were present in the sample; -16 was lost during sample preparation.

[b,c]These pairs cannot be resolved on the DB-210 fused-silica capillary column.

5. Set up a study to investigate the effect of long-term storage on the level of the compounds of interest in the freeze-dried sediment (2 years, 24 time events, triplicate analyses).

6. Establish the homogeneity of the reference material (take 6 aliquots, 30 g each, 2 from the top, 2 from the middle, and 2 from the bottom; analyze each in triplicate). Two-way analysis of variance (ANOVA) should be performed to test the homogeneity of the material. Should the analysis of variance show the material to be not yet homogenous, then blending and homogeneity shall be continued.

7. Analyze the material by at least two methods (e.g., GC/ECD with two-column confirmation and gas chromatography/mass spectrometry). Compare results. Establish which extraction procedure gives the highest concentration for the compounds of interest and the lowest background.

8. Have an independent laboratory verify results using the same methods that were used in certifying the material.

The following are some of the difficulties that may be encountered when using actual samples for the preparation of the reference materials.

- Identifying sites for collection of material may be difficult.

- The target compound concentration will not be known unless analyses are carried out by at least two different methods and two laboratories (preferable).

- Target compound concentration may not be suitable for quality control studies.

- Matrix interferences could severely affect the determination of the target compound.