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Evaluation of Sample Extract Cleanup Using Solid-Phase Extraction Cartridges

Project Report

EVALUATION OF SAMPLE EXTRACT CLEANUP USING SOLID-PHASE EXTRACTION CARTRIDGES

by

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PREFACE

This is the final report for Work Assignment 0-11, EPA Contract No. 68-03-3511, "Evaluation of Sample Extract Cleanup Using Solid-Phase Extraction Cartridges," conducted at Acurex Corporation, Project No. 8110. The project was directed by Dr. Viorica Lopez-Avila.

The report was written by Dr. Viorica Lopez-Avila. Technical support for this project was provided by Ms. Janet Benedicto and Mr. June Milanes.

ABSTRACT

Fractionation and cleanup of sample extracts prior to instrumental analysis is used to remove coextracted materials that interfere with the determination of target analytes. Such fractionations and cleanups are usually accomplished by column chromatography, gel permeation chromatography, or acid-base partitioning. The purpose of this project was to evaluate the application of solid-phase extraction cartridges containing Florisil, alumina, silica, and diol to the fractionation and cleanup of sample extracts containing organochlorine pesticides and polychlorinated biphenyls listed in SW-846 Methods 8080/8081, phthalate esters listed in Method 8061, and phenolic compounds listed in Method 8040. Cartridge loading and the effects of matrix interferents such as those present in corn oil and diesel hydrocarbons, and elemental sulfur were investigated. Such interferents were selected because they mimic typical background contamination in the presence of which the target compounds may need to be determined. In addition to these synthetic matrices, several extracts of environmental samples were spiked with the target analytes at known concentrations and were then fractionated using the solid-phase extraction procedures. A draft protocol for the use of solid-phase extraction cartridges was prepared and was tested with spiked synthetic matrices and spiked extracts of real samples.

The results of this study indicate that the use of solid-phase extraction cartridges for the cleanup of sample extracts is feasible for a variety of matrices and target compounds. The use of cartridges simplifies the cleanup procedure, especially when automated (robotic) systems are used, reduces solvent and adsorbent usage and decreases labor cost in sample preparation. Also included in this report as an appendix is a literature review covering the state-of-the-art technology on the solid-phase extraction cartridges and their use in extract cleanup/fractionation.

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SECTION 1

INTRODUCTION

Fractionation or cleanup of sample extracts prior to instrumental analysis for organic compounds (e.g., gas chromatography) is used to remove coextracted materials that 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 the Office of Solid Waste Manual SW-846, revised recently (1), specify amounts of alumina and Florisil in excess of 10 g and large volumes of eluting solvents. For example, a 10-g Florisil column and 100 mL of 20 percent diethyl ether in hexane are recommended for cleanup of sample extracts containing phthalate esters. Such large volumes of solvents increase the likelihood of sample contamination by impurities present 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, for the elution of the target analytes from the columns, and for the evaporation of solvents contributes to the overall cost of analysis.

The purpose of this study was to evaluate the application of solid-phase extraction cartridges containing Florisil, alumina, silica, and diol to the fractionation/cleanup of sample extracts containing organochlorine pesticides and polychlorinated biphenyls listed in SW-846 Methods 8080/8081, phthalate esters listed in Method 8060, and phenolic compounds listed in Method 8040. Cartridge loading and the effects of matrix interferents such as those present in corn oil and diesel hydrocarbons, and elemental sulfur were investigated. Such interferents were selected because they mimic typical background contamination in the presence of which the target compounds may have to be determined. For example, corn oil is representative of the fatty acid triglycerides, and diesel hydrocarbons are representative of petroleum hydrocarbons. Elemental sulfur was chosen because this compound is extracted from soils or sediments along with target analytes and interferes with their gas chromatographic determination, especially when an electron capture detector is used for compound identification and quantification. In addition to these synthetic matrices, we have also used extracts of real samples which were spiked with the target analytes at known concentrations and were then fractionated using the solid-phase extraction cartridge procedure.

Subsequent sections of this report present the conclusions and recommendations of this study, details of the experimental procedures, and the results and discussion. Appendix A contains the literature review summary, and the protocol for sample extract cleanup is included as Appendix B.

SECTION 2

CONCLUSIONS

Currently, there are no EPA-approved sample extract cleanup procedures that specify the use of solid-phase extraction (SPE) cartridges. The only methods specifying SPE cartridges are Test Method No. SPE-500, Methods for Organochlorine Pesticides and Chlorophenoxy Acid Herbicides in Drinking Water and Raw Source Water for Endrin, Lindane, Methoxychlor, and Toxaphene, and Method 525, Determination of Organic Compounds in Drinking Water by Liquid-Solid Extraction and Capillary Column Gas Chromatography/Mass Spectrometry. Both methods use such cartridges for sample preconcentration and not for cleaning or fractionating the sample extract. Work presented in this report involves the development of such simplified extract cleanup procedures for use with methods presented in the EPA's SW-846 procedures manual.

Use of SPE cartridges reduces solvent and adsorbent 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, when commercially available automated systems are used, sets of 12 or 24 extracts, depending on the capacity of the vacuum manifold, can be cleaned up simultaneously with no danger of sample crosscontamination; thus, sample throughput can be increased significantly. In addition, errors resulting from operator and material variables that may affect the quality of the results can be minimized.

SECTION 3

RECOMMENDATIONS

- The protocol for extract cleanup using SPE cartridges which is presented in this report has been evaluated in a single laboratory only with a few relevant sample extracts. To establish the applicability range of the cartridge method and to define the interlaboratory method performance, the protocol should be evaluated by other laboratories and with additional samples.

- Use of SPE cartridges helps increase sample throughput, and reduces solvent and adsorbent usage and labor cost in sample preparation. To take full advantage of these benefits, automation of the sample extract step should be explored. Several robotics systems which are available commercially should be evaluated.

- Bonded-phase silicas and polymeric materials such as those available from Interaction Chemicals of Mountain View, California, should be evaluated for removal of matrix interferents present in extracts of soils, sediments, and other environmental matrices, and for fractionation of analytes of environmental significance.

SECTION 4

EXPERIMENTAL

Apparatus

a. Vacuum manifold -- VacElute manifold SPS24 (Analytichem International) or Visiprep (Supelco Inc.) or equivalent, consisting of glass vacuum basin, collection rack and funnel, collection vials, replaceable stainless steel delivery tips, built-in vacuum bleed valve and gauge; the system was connected to a vacuum pump or water aspirator through a vacuum trap made from a 500-mL side arm flask fitted with a one-hole stopper and glass tubing.

b. ASPEC robotic system (Gilson Medical Electronics, Inc) consisting of a sample processor and injector module and the Gilson fluid transfer unit (Model 401 Dilutor).

c. Gas chromatographs -- Varian 6000 with constant current/pulsed frequency dual electron capture detector (ECD) and interfaced to a Varian Vista 402 data system; Varian 6500 with constant current/pulsed frequency dual ECD and interfaced to a Varian Vista 604 data system.

d. Autosampler -- Varian, Model 8000

e. GC columns -- DB-608 and DB-1701, 30-m x 0.53-mm ID fused-silica open tubular columns for Method 8060 phthalate ester analysis and Method 8080 organochlorine pesticide/polychlorinated biphenyls analysis; DB-5 and DB-1701, 30-m x 0.53-mm ID fused-silica open tubular columns for Method 8040 phenol analysis. The GC operating conditions are given in Tables 1 through 3.

Materials

a. Cartridges -- Florisil, alumina, silica gel, or diol (40-µm particles, 60-Å pores) of 0.5 g, 1 g, and 2 g in size. The cartridges consist of serological-grade polypropylene tubes, 3 mL or 6 mL in volume; the adsorbent material is held between two polyethylene frits (30-µm pores).

b. Standards -- Analytical reference standards of the test compounds were obtained from the U.S. Environmental Protection Agency, Pesticides and Industrial Chemical Repository, Aldrich Chemical, Ultra Scientific Inc., Chem Service, and Scientific Polymer Products. Purities were stated to be greater than 98 percent. Stock solutions of each test compound were prepared by serial dilutions of a composite stock solution prepared from the industrial stock solutions.

c. Corn oil -- Stock solution was prepared in hexane at 1.1 mg/mL.

TABLE 1. RETENTION TIMES AND RELATIVE RETENTION TIMES OF ORGANOCHLORINE PESTICIDES ANALYZED ON THE DB-608/DB-1701 COLUMN PAIR[a]

Compound No.	Compound name	DB-608		DB-1701	
		t_r (min)	RRT	t_r (min)	RRT
1	alpha-BHC	9.79	0.912	10.22	0.953
2	gamma-BHC	11.28	1.051	11.64	1.086
3	beta-BHC	11.59	1.080	14.18	1.323
4	Heptachlor	12.47	1.162	12.41	1.158
5	delta-BHC	12.97	1.209	15.02	1.401
6	Aldrin	13.69	1.276	13.37	1.247
7	Heptachlor epoxide	15.84	1.476	15.79	1.473
8	Endosulfan I	17.13	1.596	16.73	1.561
9	4,4′-DDE	18.06	1.683	17.41	1.624
10	Dieldrin	18.28	1.704	17.99	1.678
11	Endrin	19.63	1.829	18.72	1.746
12	4,4′-DDD	20.14	1.877	20.07	1.872
13	Endosulfan II	20.32	1.894	20.32	1.896
14	4,4′-DDT	21.22	1.978	20.68	1.929
15	Endrin aldehyde	21.54	2.007	21.71	2.025
16	Endosulfan sulfate	21.99	2.049	22.81	2.128
17	4,4′-Methoxychlor	24.48	2.281	22.81	2.128
	Pentachloronitrobenzene (IS)[b]	10.73	1.000	10.72	1.000

[a]The GC operating conditions were as follows: 30-m x 0.53-mm ID DB-608 (0.83-μm film) and 30-m x 0.53-mm ID DB-1701 (1.0-μm film) connected to an 8-in injection tee (Supelco, Inc.). Temperature program: 150°C (0.5-min hold) to 275°C (15-min hold) at 5°C; injector temperature 250°C; detector temperature 320°C; helium carrier gas 6 mL/min; nitrogen makeup gas 20 mL/min.
[b]Internal standard.

TABLE 2. RETENTION TIMES AND RELATIVE RETENTION TIMES OF PHTHALATE ESTERS ANALYZED ON THE DB-608/DB-1701 COLUMN PAIR[a]

Compound no.	Compound name	DB-608		DB-1701	
		t_r (min)	RRT	t_r (min)	RRT
1	Dimethyl phthalate (DMP)	6.72	0.554	6.73	0.585
2	Diethyl phthalate (DEP)	8.69	0.716	8.85	0.770
3	Diisobutyl phthalate (DIBP)	12.74	1.050	13.36	1.162
4	Di-n-butyl phthalate (DBP)	14.68	1.210	15.13	1.316
5	Bis(4-methyl-2-pentyl) phthalate (BMPP)	15.76	1.299	16.73	1.455
6	Bis(2-methoxyethyl) phthalate (BMEP)	17.24	1.421	16.96	1.475
7	Diamyl phthalate (DAP)	17.94	1.479	18.64	1.621
8	Bis(2-ethoxyethyl) phthalate (BEEP)	18.93	1.561	18.80	1.635
9	Dihexyl phthalate (DHP)	19.70	1.624	19.56	1.701
10	Hexyl 2-ethylhexyl phthalate (HEHP)	21.50	1.772	22.48	1.955
11	Butyl benzyl phthalate (BBP)	24.64	2.031	23.76	2.066
12	Bis(2-n-butoxyethyl) phthalate (BBEP)	25.71	2.120	25.96	2.257
13	Bis(2-ethylhexyl) phthalate (DEHP)	24.94	2.056	26.35	2.291
14	Dicyclohexyl phthalate (DCP)	28.33	2.336	27.06	2.353
15	Di-n-octyl phthalate (DOP)	29.14	2.402	30.57	2.658
16	Dinonyl phthalate (DNP)	32.97	2.718	34.71	3.018
	Benzyl benzoate (IS)[b]	12.13	1.000	11.50	1.000

[a] GC operating conditions were as follows: 30-m x 0.53-mm ID DB-608 (0.83-μm film) and 30-m x 0.53-m ID DB-1701 (1.0-μm film) connected to an 8-in injection tee (Supelco, Inc.). Temperature program: 150°C (0.5-min hold) to 220°C at 5°C/min, then to 275°C (18-min hold) at 3°C/min; injector temperature 250°C; detector temperature 320°C; helium carrier gas 6 mL/min; nitrogen makeup gas 20 mL/min.

[b] Internal standard.

TABLE 3. RETENTION TIMES AND RELATIVE RETENTION TIMES OF THE PFB DERIVATIVES OF PHENOLIC COMPOUNDS ANALYZED ON THE DB-1701/DB-5 COLUMN PAIR[a,b,c]

Compound no.	Compound name	DB-1701		DB-5	
		t_r (min)	RRT	t_r (min)	RRT
1	Phenol	7.76	0.518	5.40	0.446
2	2-Methylphenol	9.03	0.603	6.73	0.556
3	3-Methylphenol	9.62	0.643	7.20	0.595
4	4-Methylphenol	9.76	0.652	7.38	0.610
5	2,4-Dimethylphenol	10.83	0.723	8.62	0.712
6	2-Chlorophenol	11.76	0.786	8.67	0.717
7	2,6-Dichlorophenol	13.70	0.915	10.98	0.907
8	4-Chloro-3-methylphenol	14.33	0.957	11.42	0.944
9	2,4-Dichlorophenol	15.56	1.039	12.22	1.010
10	2,4,6-Trichlorophenol	16.20	1.082	13.66	1.129
11	2,3,6-Trichlorophenol	17.38	1.161	14.51	1.199
12	2-Nitrophenol	18.59	1.242	13.38	1.106
13	2,4,5-Trichlorophenol	18.72	1.251	15.29	1.264
14	2,3,5-Trichlorophenol	18.75	1.253	15.36	1.269
15	2,3,5,6-Tetrachlorophenol	19.98	1.335	17.23	1.424
16	2,3,4,6-Tetrachlorophenol	20.21	1.350	17.45	1.442
17	2,3,4-Trichlorophenol	20.34	1.359	16.57	1.369
18	2,3,4,5-Tetrachlorophenol	22.79	1.522	19.12	1.580
19	Pentachlorophenol	23.64	1.579	20.76	1.716
20	2,4-Dinitrophenol	28.07	1.875	20.78	1.717
	Pentachloronitrobenzene (IS)[d]	14.97	1.000	12.10	1.000

[a] Not able to obtain a detector response from 4-nitrophenol, dinoseb, or 4,6-dinitro-o-cresol PFB derivatives.
[b] GC operating conditions were as follows: 30-m x 0.53-mm ID DB-5 (0.83-μm film) and 30-m x 0.53-mm ID DB-1701 (1.0-μm film) connected to an 8-inch injection tee (Supelco, Inc.). Temperature program: 150°C (5 min hold) to 275°C (15 min hold) at 5°C/min; injector temperature 250°C; detector temperature 320°C; helium carrier gas 6 mL/min; nitrogen makeup gas 20 mL/min.
[c] Phenols were derivatized with pentafluorobenzyl bromide (PFBBr) following the procedure by Lee et al. (2).
[d] Internal standard.

d. Diesel hydrocarbons -- Stock solution was prepared in hexane at 1 mg/mL.

e. Elemental sulfur -- Stock solution was prepared in hexane at 0.28 mg/mL.

f. Samples -- Those used in the method development are identified in Table 4.

Cartridge Cleanup Procedure

Florisil cartridges were conditioned with 4 mL hexane prior to use. Diol cartridges were conditioned with hexane with 10 percent acetone. Silica cartridges were conditioned with 4 mL hexane. Aliquots of 2 mL of standards or sample extracts in hexane were loaded onto SPE cartridges using a micropipette and were eluted with the solvents indicated in the tables summarizing the data. A Supelclean Visiprep vacuum manifold (Supelco, Inc.) and a VacElute SPS24 (Analytichem International) were used to simultaneously prepare as many as 12 samples (for the Visiprep system) or 24 samples (for the VacElute SPS24 system). When using the Visiprep system, the vacuum for each cartridge was adjusted manually using chemically inert screw-type valves. Additional details of the cartridge cleanup procedure can be found in the protocol included in Appendix B of this report.

Gas Chromatographic Analysis

All fractions were analyzed by gas chromatography with ECD using the dual-column approach. The retention times and the relative retention times of the target compounds are presented in Tables 1 through 3. Figures 1 through 3 show GC/ECD chromatograms obtained for each group of target compounds. Quantification of compounds was performed using internal standard calibrations.

TABLE 4. SAMPLES USED IN METHOD DEVELOPMENT

Material	Description
Sandy loam soil	Mixture of 20 percent organic soil and 80 percent sand
Sediment of undefined origin	Sediment sample contaminated with petroleum hydrocarbons
SRM-1572	Citrus leaves from 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 with cobalt-60 radiation.
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.
Sample 1	Soil sample taken from a greenhouse, identified as S-2A greenhouse south; known to contain 4,4'-DDE at 460 μg/Kg
Sample 2	Soil sample known to contain ppm levels of polynuclear aromatic hydrocarbons
Sample 3	Soil sample known to contain 4,4′-DDE at 4000 μg/Kg and 4,4′-DDD at 34,000 μg/Kg
Samples SS-2, SS-5, SS-7 and SS-8	Soil samples taken from a farm in Northern California, which was known to have used organochlorine pesticides, diazinon, ethion, ziram, carbaryl, benomyl, carbophenothion, and malathion.

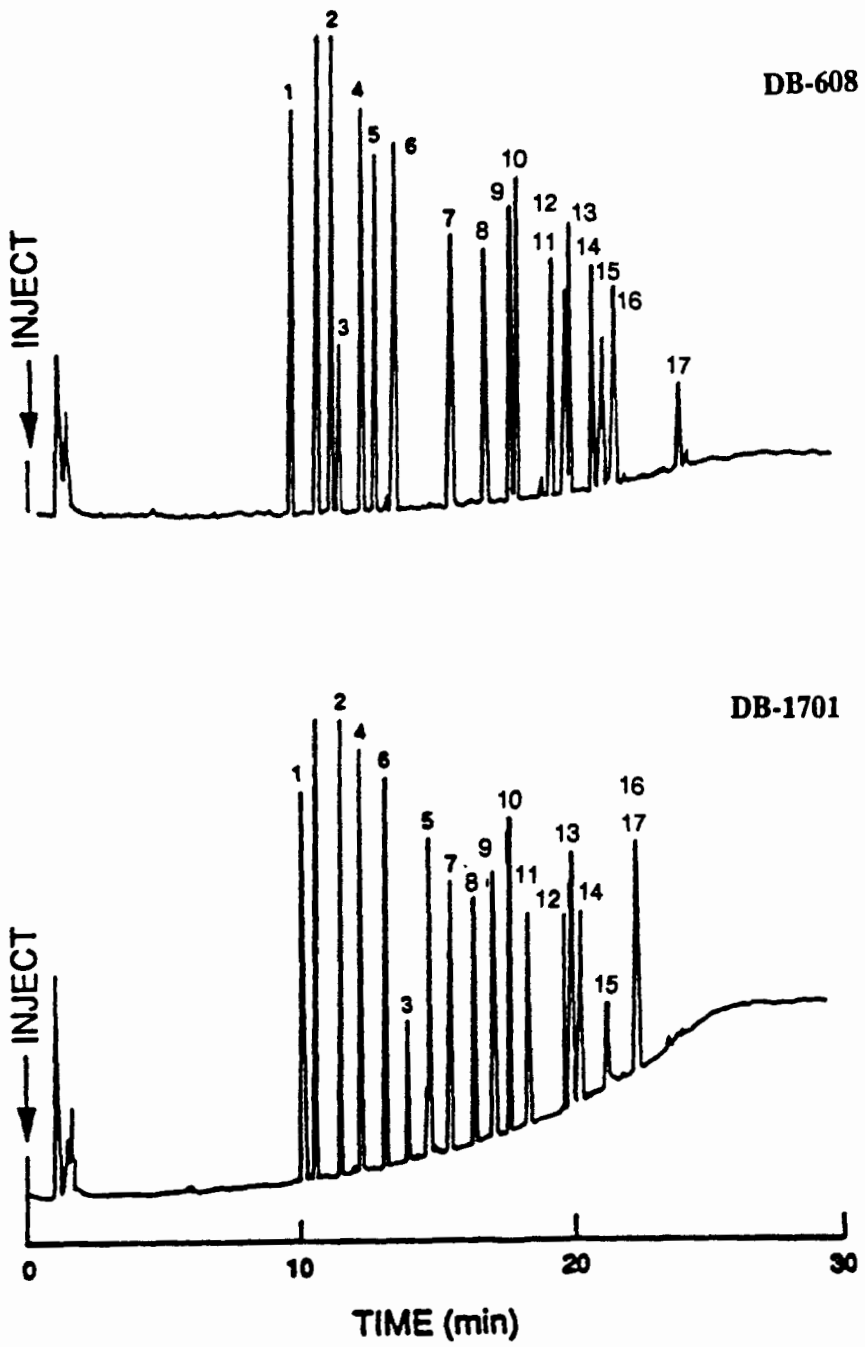

Figure 1. GC/ECD chromatograms of Method 8081 organochlorine pesticides analyzed on a DB-608/DB-1701 column pair. The GC operating conditions are given in Table 1.

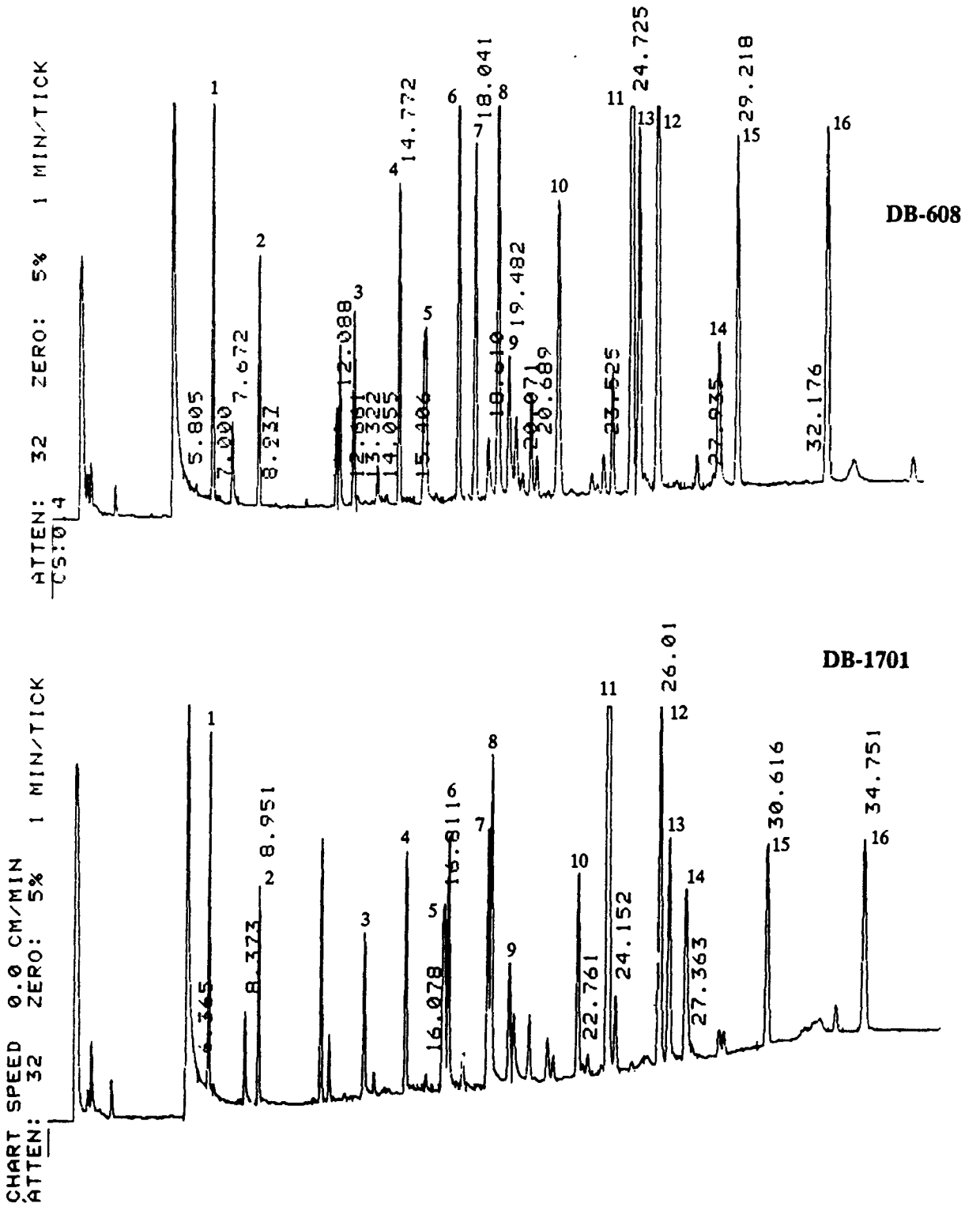

Figure 2. GC/ECD chromatograms of a phthalate esters standard analyzed on the DB-608/DB-1701 column pair. The GC operating conditions and peak assignments are given in Table 2.

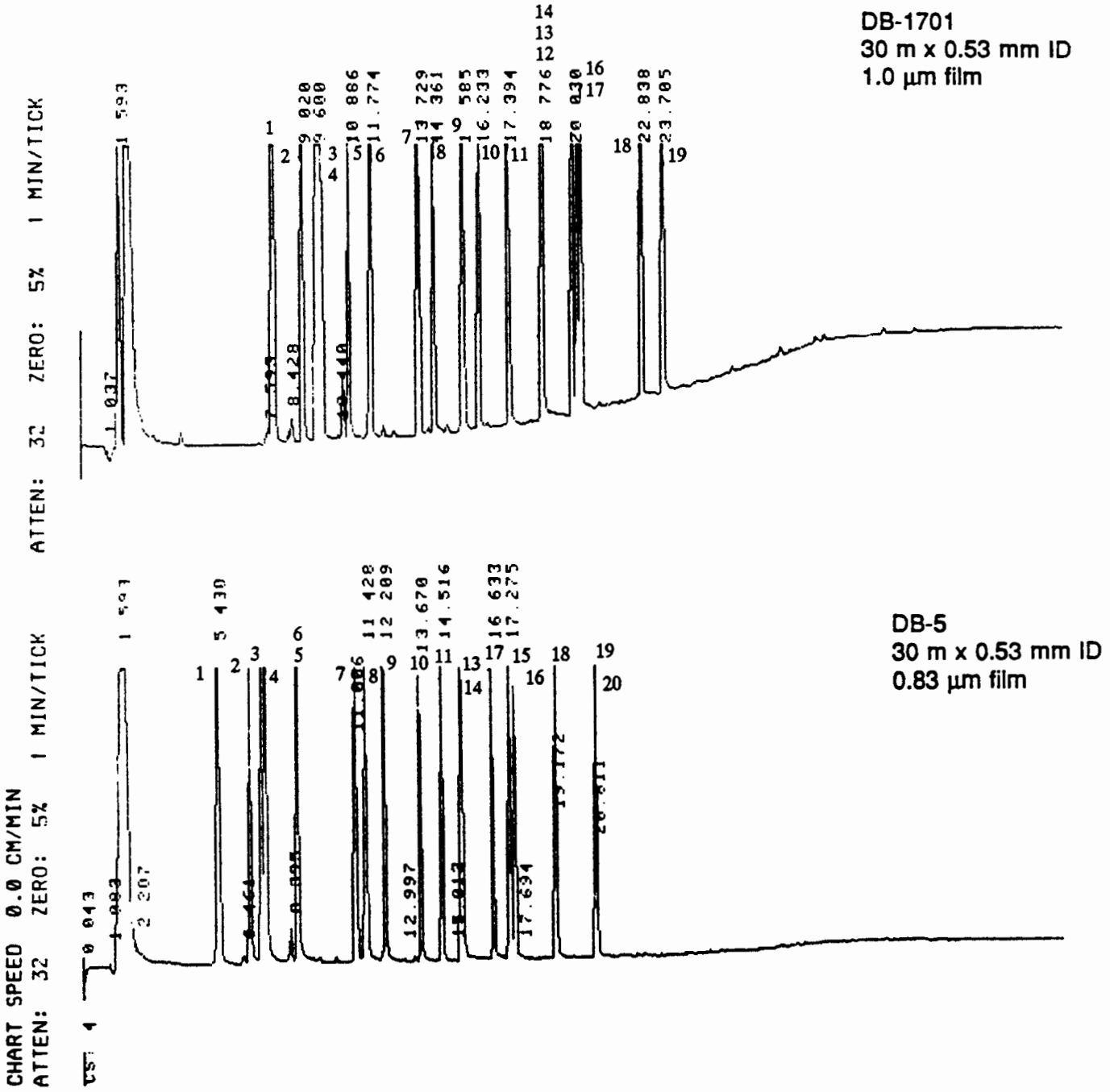

Figure 3. GC/ECD chromatograms of the PFB derivatives of phenolic compounds analyzed on the DB-1701/DB-5 column pair. The GC operating conditions and peak assignments are given in Table 3.

SECTION 5

RESULTS AND DISCUSSION

5.1 ORGANOCHLORINE PESTICIDES AND POLYCHLORINATED BIPHENYLS

The current SW-846 Methods 8080/8081 for organochlorine pesticides and polychlorinated biphenyls (PCBs) determination recommend use of either Florisil (Method 3620) or silica gel for cleanup of sample extracts containing organochlorine pesticides and PCBs. In Method 3620, Florisil (60/80 mesh) is activated for 16 hrs at 130°C. The charged Florisil column (10 g) is eluted with 200 mL of 6 percent diethyl ether in hexane (Fraction 1), 200 mL of 15 percent diethyl ether in hexane (Fraction 2), and 200 mL of 50 percent diethyl ether in hexane (Fraction 3). Compounds recovered in Fraction 1 include aldrin, the four BHC isomers, chlordane, 4,4′-DDD, 4,4′-DDE, 4,4′-DDT, endosulfan I, heptachlor, heptachlor epoxide, toxaphene, and the PCBs. Compounds recovered in Fraction 2 include dieldrin, endosulfan I, endrin, and endrin aldehyde. Endosulfan II, endosulfan sulfate, and some endrin aldehyde are recovered in Fraction 3. We evaluated Method 3620 and reported that, although compound recoveries were quantitative, the Florisil fractionation method is not suitable for samples that contain both organochlorine pesticides and PCBs (3) since the PCBs are eluted in the same fraction as the bulk of the organochlorine pesticides. We undertook the evaluation of the Florisil cartridges specifically for samples that contain only the organochlorine pesticides. The silica cartridges were considered since Method 8081 describes a procedure in which PCBs can be separated from the bulk of the organochlorine pesticides using silica gel deactivated with 3 percent water. Finally, diol cartridges were evaluated since at the time our study was conducted, EPA was considering the use of diol cartridges for incorporation into the Contract Laboratory Program protocols. This section describes the results of the Florisil, silica, and diol cartridge evaluation studies.

Two elution schemes were attempted initially. In Scheme A, the charged Florisil and silica cartridges were eluted with 3 mL hexane (Fraction 1) followed by 5 mL hexane with 26 percent methylene chloride (Fraction 2) and 5 mL hexane with 10 percent acetone (Fraction 3); in Scheme B, the charged Florisil and silica cartridges were eluted with 3 mL hexane (Fraction 1), 5 mL hexane with 4 percent diethyl ether (Fraction 2), and 5 mL hexane with 56 percent diethyl ether (Fraction 3). Hexane with 26 percent methylene chloride has approximately the same solvent strength as hexane with 4 percent diethyl ether, and hexane with 10 percent acetone has approximately the same solvent strength as hexane with 56 percent diethyl ether. Under the Scheme A conditions, silica gel proved superior to Florisil because it allowed complete separation of the PCBs from all but four organochlorine pesticides, quantitative recovery of all compounds, and almost complete separation of the Method 8081 organochlorine pesticides from the Method 8060 phthalate esters. The four organochlorine pesticides that eluted with the 16 phthalate esters could be identified and quantified without any difficulty because they were resolved from the phthalate esters on a 30-m x 0.25-mm ID DB-5 fused-silica capillary column.

The solvents used in Scheme B gave almost identical elution patterns for the Florisil and silica gel procedure with quite a few organochlorine pesticides spread among the three fractions. Because of this, no further work was undertaken using Scheme B.

The procedure given in Scheme A was tested at 2 organochlorine pesticide concentrations in quadruplicate. The results presented in Tables 5 and 6 show elution patterns, compound recoveries, and method precision for the 17-organochlorine pesticides listed in Table 1 and gamma-chlordane. The silica gel cartridges seemed to perform better than the Florisil cartridges (Table 5). Three organochlorine pesticides (heptachlor, aldrin, and 4,4′-DDE) were eluted only in Fraction 1. Nine organochlorine pesticides (the four BHC isomers, heptachlor epoxide, gamma-chlordane, endosulfan I, dieldrin, and 4,4′-DDD) were eluted only in Fraction 2. Endosulfan II was eluted in Fraction 3. Endrin aldehyde, 4,4′-DDT, endosulfan sulfate and 4,4′-methoxychlor were eluted in more than one fraction. Compound recoveries were quantitative and method precision (%RSD) was better than 11 percent for 14 of the 18 target compounds. Since endosulfan sulfate was not resolved from 4,4′-DDT on the 30-m x 0.25-mm ID DB-5 column, it is difficult to specify in which fraction this compound was recovered. Based on the other data presented in this section, it is expected that endosulfan sulfate would elute in Fraction 3 from either the silica cartridge (Table 5) or the Florisil cartridge (Table 6).

Table 6 presents the results for the Florisil SPE cartridge procedure. Eight pesticides (alpha-BHC, gamma-BHC, heptachlor, aldrin, gamma-chlordane, 4,4′-DDE, 4,4′-DDD, and 4,4′-DDT) were eluted in Fraction 1. All pesticides except heptachlor, aldrin, and 4,4′-DDE were also recovered in Fraction 2. Endosulfan II, endrin aldehyde, possibly endosulfan sulfate and 4,4′-methoxychlor were also eluted in Fraction 3.

Seven Aroclor mixtures were tested individually on the silica and the Florisil cartridges. In each case, the cartridges were loaded with 10 µg of the corresponding Aroclor and were eluted with 3 mL hexane. The recovery data given in Table 7 indicate that the Aroclors were recovered quantitatively from either cartridge with 3 mL hexane. Larger cartridges may require additional solvent to ensure complete removal of PCBs.

Other solvent mixtures used in eluting the organochlorine pesticides from 1-g Florisil and silica cartridges included hexane, hexane with 6 percent diethyl ether, hexane with 15 percent diethyl ether, and hexane with 50 percent diethyl ether (Tables 8 and 9). The Florisil cartridge is somewhat less polar than the silica cartridge, and more organochlorine pesticides were eluted from the Florisil cartridge with hexane.

To reduce the number of fractions that have to be collected in order to recover all 18 organochlorine pesticides, we eluted the silica cartridges with two 3-mL hexane portions and 5 mL of hexane with 50 percent diethyl ether. At least 3 mL hexane need to be passed through the silica cartridge to elute any PCBs that would interfere with the gas chromatographic analysis of the organochlorine pesticides. The second 3-mL hexane portion was used to verify the complete removal of PCBs from the cartridge (Table 10). Elution of silica cartridges with 5 mL hexane with 50 percent diethyl ether resulted in quantitative recovery of all organochlorine pesticides retained on the cartridge.

This elution scheme was further tested with silica cartridges of 0.5-g, 1-g, and 2-g size, each charged with 17 organochlorine compounds at 0.2 µg, 1.0 µg, and 2.0 µg per cartridge. Gamma-chlordane was not included among the target compounds because it was not available in pure form at the time the study began. Two fractions were collected from the 0.5-g and 1-g

TABLE 6. ELUTION PATTERNS AND PERCENT RECOVERIES OF THE ORGANOCHLORINE PESTICIDES FROM FLORISIL CARTRIDGES[a]

	Spiked at 0.5 µg per compound						Spiked at 5.0 µg per compound					
	Fraction 1 (3 mL hexane)		Fraction 2 (5 mL hexane with 26 percent methylene chloride)		Fraction 3 (5 mL hexane with 10 percent acetone)		Fraction 1 (3 mL hexane)		Fraction 2 (5 mL hexane with 26 percent methylene chloride)		Fraction 3 (5 mL hexane with 10 percent acetone	
Compound	Avg.	%RSD	Avg.	%RSD	Avg.	%RSD	Avg.	%RSD	Avg.	%RSD	Avg.	%RSD
alpha-BHC	82.6	3.4	26.3	10.7	0		79.0	13.7	34.1	5.6	0	
gamma-BHC	35.8	13.3	77.5	3.1	0		32.0	20.9	82.8	3.8	0	
beta-BHC	0		102	2.3	0		0		104	3.6	0	
Heptachlor	94.4	2.3	0		0		94.8	14.8	0		0	
delta-BHC	0		99.6	1.4	0		0		103	2.3	0	
Aldrin	93.1	2.0	0		0		94.6	14.2	0		0	
Heptachlor epoxide	0		102	2.4	0		0		104	3.9	0	
gamma-Chlordane	47.6	9.8	65.6	3.5	0		44.2	18.0	73.2	5.4	0	
Endosulfan I	0		101	2.7	0		0		104	4.3	0	
4,4′-DDE	94.5	1.7	0		0		96.8	14.9	0		0	
Dieldrin	0		101	2.9	0		0		105	4.4	0	
Endrin	0		57.2	7.5	0		[b]		[b]		[b]	
4,4′-DDD	38.5	12.3	68.8	2.9	0		37.7	19.9	77.3	4.9	0	
Endosulfan II	0		58.2	13.3	61.1	9.9	0		60.3	5.2	58.3	10.8
Endrin aldehyde	0		36.3	7.2	78.7	2.6	0		47.5	2.7	72.7	6.7
4,4′-DDT[c]	49.6	1.9	11.2	16.4	59.4	3.1	51.6	15.0	12.2	13.7	56.8	9.8
Endosulfan sulfate[c]												
4,4′-Methoxychlor	0		96.0	3.4	11.7	3.0	0		105	5.5	11.2	15.0

[a] 1-g LC-Florisil cartridges (Supelco Inc.) were used. The amount of compound loaded to the cartridge is 0.5 µg or 5.0 µg per compound (or 2 mL of a 0.25-µg/mL or 2.5-µg/mL solution in hexane). Fraction 1 was eluted with 3 mL hexane, Fraction 2 with 5 mL hexane with 26 percent methylene chloride, and Fraction 3 with 5 mL hexane with 10 percent acetone. Number of replicates was 4.

[b] Data not available due to poor chromatography on the 30-m x 0.25-mm ID DB-5 fused-silica capillary column.

[c] These compounds coelute on the 30-m x 0.25 mm ID DB-5 fused-silica capillary column.

TABLE 5. ELUTION PATTERNS AND PERCENT RECOVERIES OF THE ORGANOCHLORINE PESTICIDES FROM SILICA CARTRIDGES[a]

	Spiked at 0.5 μg per compound						Spiked at 5.0 μg per compound					
	Fraction 1 (3 mL hexane)		Fraction 2 (5 mL hexane with 26 percent methylene chloride)		Fraction 3 (5 mL hexane in 10 percent acetone)		Fraction 1 (3 mL hexane)		Fraction 2 (5 mL hexane with 26 percent methylene chloride)		Fraction 3 (5 mL hexane in 10 percent acetone)	
Compound	Avg.	%RSD	Avg.	%RSD	Avg.	%RSD	Avg.	%RSD	Avg.	%RSD	Avg.	%RSD
alpha-BHC	0		111	8.3	0		0		111	2.4	0	
gamma-BHC	0		110	8.5	0		0		111	2.3	0	
beta-BHC	0		109	7.8	0		0		111	2.7	0	
Heptachlor	98.4	10.8	0		0		105	1.0	0		0	
delta-BHC	0		106	9.3	0		0		110	3.5	0	
Aldrin	96.6	9.9	0		0		108	0.9	0		0	
Heptachlor epoxide	0		109	7.9	0		0		112	2.8	0	
gamma-Chlordane	0		105	3.5	0		0		108	6.5	0	
Endosulfan I	0		111	6.2	0		0		114	2.6	0	
4,4′-DDE	104	5.7	0		0		109	1.1	0		0	
Dieldrin	0		110	7.8	0		0		114	2.4	0	
Endrin[b]	b		b		b		b		b		b	
4,4′-DDD	0		111	6.2	0		0		114	3.3	0	
Endosulfan II	0		0		111	2.3	0		0		110	3.0
4,4′-DDT[c]	40.1	25.5	16.7	24.3	63.4	3.2	44.6	10.3	19.4	25.9	63.3	4.1
Endrin aldehyde	0		48.9	14.0	47.7	12.4	0		52.4	3.1	41.9	9.9
Endosulfan sulfate[c]												
4,4′-Methoxychlor	0		84.5	22.2	33.6	29.0	0		94.3	10.4	26.1	10.2

[a]1-g LC-silica cartridges (Supelco Inc.) were used. The amount of compound loaded to the cartridge is 0.5 or 5.0 μg per compound (or 2 mL of a 0.25-μg/mL or 2.5-μg/mL solution in hexane). Fraction 1 was eluted with 3 mL hexane, Fraction 2 with 5 mL hexane with 26 percent methylene chloride, and Fraction 3 with 5 mL hexane with 10 percent acetone. Number of replicates was 4.
[b]Data not available due to poor chromatography on the 30-m x 0.25-mm ID DB-5 fused-silica capillary column.
[c]These compounds coelute on the 30-m x 0.25-mm ID DB-5 fused-silica capillary column.

TABLE 7. PERCENT RECOVERIES OF THE AROCLORS FROM FLORISIL AND SILICA CARTRIDGES

	Percent recovery[a]	
Compound	LC-Florisil (1 g)	LC-Silica (1 g)
Aroclor 1016	105	124
Aroclor 1221	76.5	93.5
Aroclor 1232	90.1	118
Aroclor 1242	93.6	116
Aroclor 1248	97.2	114
Aroclor 1254	95.4	108
Aroclor 1260	89.7	112

[a] 1-g LC-Florisil or LC-silica solid-phase extraction cartridges (Supelco Inc.) were used. The amount of Aroclor loaded to each cartride is 10 μg (or 2 mL of 5-μg/mL solution in hexane). Hexane (3 mL) was used as eluent.

TABLE 8. ELUTION PATTERNS AND PERCENT RECOVERIES OF THE ORGANOCHLORINE PESTICIDES FROM FLORISIL CARTRIDGES[a]

Compound	Fraction 1 (3 mL hexane)	Fraction 2 (5 mL hexane with 6 percent diethyl ether)	Fraction 3 (5 mL hexane with 15 percent diethyl ether)	Fraction 4 (5 mL hexane with 50 percent diethyl ether)
alpha-BHC	88.7	24.4	0	0
gamma-BHC	60.0	66.1	0	0
beta-BHC	0	87.0	0	0
Heptachlor	88.8	3.6	0	0
delta-BHC	0	27.3	81.4	0
Aldrin	90.7	4.2	0	0
Heptachlor epoxide	0	94.5	0	0
Endosulfan I	0	94.9	0	0
gamma-Chlordane	70.5	0	0	0
4,4′-DDE	0	79.2	0	0
Dieldrin	0	105	0	0
Endrin	0	0	62.8	81.7
4,4′-DDD	0	0	0	84.0
Endosulfan II	76.0	70.4	0	0
4,4′-DDT	87.8	0	0	0
Endrin aldehyde	0	0	0	117
Endosulfan sulfate	0	113	0	0
4,4′-Methoxychlor	0	94.4	0	0

[a]Single determination; 1-g LC-Florisil cartridges were used. The amount loaded to each cartridge was 10 μg per compound.

TABLE 9. ELUTION PATTERNS AND PERCENT RECOVERIES OF THE ORGANOCHLORINE PESTICIDES FROM SILICA CARTRIDGES[a]

Compound	Fraction 1 (3 mL hexane)	Fraction 2 (5 mL 6 percent diethyl ether in hexane)	Fraction 3 (5 mL 15 percent diethyl ether in hexane)	Fraction 4 (5 mL 50 percent diethyl ether in hexane)
alpha-BHC	0	98.0	0	0
gamma-BHC	0	99.4	0	0
beta-BHC	0	85.0	0	0
Heptachlor	93.5	0	0	0
delta-BHC	0	0	89.0	0
Aldrin	96.2	0	0	0
Heptachlor epoxide	0	95.1	0	0
Endosulfan I	0	93.1	0	0
gamma-Chlordane	107	0	0	0
4,4′-DDE	0	79.1	0	0
Dieldrin	0	102	0	0
Endrin	0	0	45.2	54.8
4,4′-DDD	0	0	0	81.0
Endosulfan II	0	94.2	0	0
4,4′-DDT	108	0	0	0
Endrin aldehyde	0	0	0	108
Endosulfan sulfate	0	105	0	0
4,4′-Methoxychlor	0	80.8	36.0	0

[a]Single determination; 1-g LC-silica cartridges were used. The amount loaded to each cartridge was 10 μg per compound.

TABLE 10. ELUTION PATTERNS AND PERCENT RECOVERIES OF THE ORGANOCHLORINE PESTICIDES AND AROCLOR 1260 FROM SILICA CARTRIDGES[a]

Compound	Fraction 1 (3 mL hexane)	Fraction 2 (3 mL hexane)	Fraction 3 (5 mL hexane with 50 percent diethyl ether)
Aroclor 1260	101	0	0
alpha-BHC	0	59.5	61.1
gamma-BHC	0	0	101
beta-BHC	0	0	101
Heptachlor	101	8.1	0
delta-BHC	0	0	95.1
Aldrin	102	7.4	0
Heptachlor epoxide	0	0	103
gamma-Chlordane	75.1	8.1	0
Endosulfan I	0	0	103
4,4′-DDE	0	0	82.1
Dieldrin	0	0	117
Endrin	0	0	107
4,4′-DDD	0	0	68.4
Endosulfan II	0	59.8	40.2
4,4′-DDT	85.9	0	0
Endrin aldehyde	0	0	112
Endosulfan sulfate	0	90.4	0
4,4′-Methoxychlor	0	0	103

[a]Aroclor 1260 was spiked separately from the organochlorine pesticides. Single determination. The amount loaded to the cartridge was 10 μg per compound.

cartridges. An additional 5 mL of hexane with 50 percent diethyl ether were passed through the 2.0-g cartridges to collect Fraction 3. The results are summarized in Tables 11 through 13. All compounds, except endrin aldehyde, were recovered quantitatively (recovery >75 percent) in the two or three fractions combined. The elution patterns seem to vary with the size of the cartridge; however, they are very consistent within one cartridge size. For example, in the case of the 0.5-g cartridges, 7 compounds, namely alpha-BHC, gamma-BHC, heptachlor, aldrin, 4,4′-DDE, 4,4′-DDD, and 4,4′-DDT, were recovered in Fraction 1, and 13 compounds were recovered in Fraction 2, demonstrating that some compounds are present in both fractions. The number of compounds recovered in Fraction 1 from the 2-g cartridges decreased to three (heptachlor, aldrin, and 4,4′-DDE), and an additional 5 mL of hexane with 50 percent diethyl ether were needed to recover delta-BHC, endosulfan II, endrin aldehyde, and endosulfan sulfate from the 2-g silica cartridge (Table 13).

At the time we were evaluating the Florisil and silica cartridges for their applicability to the cleanup of sample extracts containing organochlorine pesticides, we came across a protocol using diol cartridges (4). The diol procedure specifies use of 0.5-g and 1-g cartridges, and elution of the organochlorine pesticides with hexane with 10 percent acetone. We evaluated this procedure using 0.5-g, 1-g, and 2-g cartridges charged with the target organochlorine pesticides at 0.2 µg, 1.0 µg, and 2.0 µg per cartridge. Two fractions were collected from the 0.5-g and 1-g cartridges, and four fractions were collected from the 2-g cartridges. For the 1-g cartridges charged at 2.0 µg per compound, we collected an additional fraction to verify that the compounds were eluted quantitatively from the cartridge.

The data are summarized in Tables 14 through 16. At the 0.2-µg spike level, sixteen compounds eluted in Fraction 1 from the 0.5-g cartridges, and only two compounds (endrin aldehyde and endosulfan sulfate) eluted in Fraction 2. Small amounts (recovery <6 percent) of delta-BHC and endosulfan II were found in Fraction 2 from the cartridges spiked at 2.0 µg per cartridge. As the cartridge size was increased, more compounds were found in Fraction 2. For example, in addition to delta-BHC and endosulfan II, endrin aldehyde and endosulfan sulfate were detected in Fraction 2 from the 1-g cartridges spiked at 0.5 µg and 2.0 µg per cartridge. In addition, beta-BHC and small amounts of gamma-BHC and 4,4′-methoxychlor were detected in Fraction 2 from the 1-g cartridges spiked with 2.0 µg. Finally, the elution patterns for the 2-g cartridges were quite different from those of the 0.5-g and 1-g cartridges, and they also varied with the amounts spiked on the cartridges (Table 16).

The diol procedure gave quantitative recoveries of the 17 organochlorine pesticides when hexane with 10 percent acetone was used to elute the analytes; however, PCBs also eluted in Fraction 1. An experiment was performed in which diol cartridges were eluted, first with 3 mL hexane (Fraction 1), then with two 5-mL portions of hexane with 10 percent acetone (Fractions 2 and 3). Under those conditions, PCBs and heptachlor, aldrin, endosulfan I, 4,4′-DDE, and 4,4′-DDT were recovered in Fraction 1, and the remainder of the pesticides eluted in Fraction 2, with most of the endrin aldehyde and endosulfan sulfate eluting in Fraction 3 (Table 17).

Matrix interferents such as corn oil, diesel hydrocarbons, and elemental sulfur, were added to hexane solutions containing the target analytes at known concentrations, and the

TABLE 11. PERCENT RECOVERIES AND ELUTION PATTERNS OF 17 ORGANOCHLORINE PESTICIDES FROM 0.5-g SILICA CARTRIDGES[a]

Compound	Spiked at 0.2 µg per cartridge				Spiked at 1.0 µg per cartridge				Spiked at 2.0 µg per cartridge			
	Fraction 1		Fraction 2		Fraction 1		Fraction 2		Fraction 1		Fraction 2	
alpha-BHC	86.3	101	35.3	20.8	76.7	72.1	34.3	38.3	87.1	85.8	35.3	36.4
gamma-BHC	0	16.0	105	101	9.2	12.1	93.9	90.1	15.4	16.9	93.8	92.1
beta-BHC	0	0	113	113	0	0	98.9	95.6	0	0	104	103
Heptachlor	104	103	0	0	85.6	86.4	0	0	95.1	93.9	0	0
delta-BHC	0	0	106	107	0	0	96.4	91.6	0	0	94.6	94.1
Aldrin	91.8	90.8	0	0	78.1	78.1	0	0	85.4	84.4	0	0
Heptachlor epoxide	0	0	112	113	0	0	101	97.3	0	0	103	100
Endosulfan I	0	0	112	116	0	0	103	97.7	0	0	105	104
4,4'-DDE	96.8	99.5	0	0	89.5	84.5	0	0	92.4	91.7	0	0
Dieldrin	0	0	109	111	0	0	96.3	92.3	0	0	93.5	92.4
Endrin	0	0	148	151	0	0	152	142	0	0	110	106
4,4'-DDD	92.5	110	0	0	88.8	82.5	20.1	23.9	92.8	91.6	19.5	22.1
Endosulfan II	0	0	107	108	0	0	95.4	92.8	0	0	99.4	97.0
4,4'-DDT	101	107	0	0	93.3	89.6	0	0	94.2	91.8	0	0
Endrin aldehyde	0	0	82.8	90.0	0	0	74.9	72.9	0	0	82.9	83.2
Endosulfan sulfate	0	0	111	118	0	0	122	94.7	0	0	101	100
4,4'-Methoxychlor	0	0	113	119	0	0	108	98.3	0	0	101	99.8

[a] Silica cartridges (Supelco lot SP0161) were used; each cartridge was conditioned with 4 mL hexane prior to use. Each experiment was performed in duplicate. Each cartridge was spiked with 2 mL of a hexane solution containing the organochlorine pesticides at the concentrations stated above. Fraction 1 was eluted with 5 mL hexane, Fraction 2 with 5 mL hexane with 50 percent diethyl ether. Vacuum manifold used was the Analytichem SPS24.

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TABLE 12. PERCENT RECOVERIES AND ELUTION PATTERNS FOR 17 ORGANOCHLORINE PESTICIDES FROM 1-g SILICA CARTRIDGES[a]

Compound	Spiked at 0.2 µg per cartridge				Spiked at 1.0 µg per cartridge				Spiked at 2.0 µg per cartridge			
	Fraction 1		Fraction 2		Fraction 1		Fraction 2		Fraction 1		Fraction 2	
alpha-BHC	0	0	92.8	96.3	0	0	99.6	96.4	3.9	8.5	102	105
gamma-BHC	0	0	91.5	94.5	0	0	97.2	94.2	0	0	95.0	96.3
beta-BHC	0	0	79.3	81.5	0	0	101	95.9	0	0	102	106
Heptachlor	89.8	89.0	0	0	99.1	98.6	0	0	102	105	3.5	4.3
delta-BHC	0	0	82.5	84.8	0	0	96.8	93.5	0	0	91.7	95.4
Aldrin	89.5	88.8	0	0	97.9	97.1	0	0	100	102	2.3	2.9
Heptachlor epoxide	0	0	92.5	94.8	0	0	101	97.2	0	0	99.7	102
Endosulfan I	0	0	101	104	0	0	101	97.3	0	0	102	105
4,4'-DDE	91.0	90.3	0	0	102	102	0	0	105	109	0	0
Dieldrin	0	0	89.3	92.5	0	0	95.5	92.6	0	0	91.2	92.5
Endrin	0	0	94.8	98.0	0	0	151	145	0	0	104	107
4,4'-DDD	0	0	84.8	92.0	13.4	11.6	95.6	94.1	14.2	24.8	94.7	93.2
Endosulfan II	0	0	88.5	91.5	0	0	98.8	95.6	0	0	99.4	102
4,4'-DDT	87.5	84.5	0	0	100	99.4	0	0	94.7	98.2	7.5	5.5
Endrin aldehyde	0	0	50.0	51.5	0	0	59.3	59.2	0	0	67.4	70.9
Endosulfan sulfate	0	0	94.5	97.5	0	0	98.2	95.3	0	0	99.1	102
4,4'-Methoxychlor	0	0	91.8	95.0	0	0	104	100	0	0	97.4	100

[a] Silica cartridges (Supelco lot SP0161) were used; each cartridge was conditioned with 4 mL hexane prior to use. Each experiment was performed in duplicate. Each cartridge was spiked with 2 mL of a hexane solution containing the organochlorine pesticides at the concentrations stated above. Fraction 1 was eluted with 5 mL hexane, Fraction 2 with 5 mL hexane with 50 percent diethyl ether. Vacuum manifold used was the Analytichem SPS24.

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TABLE 13. PERCENT RECOVERIES AND ELUTION PATTERNS OF 17 ORGANOCHLORINE PESTICIDES FROM 2-g SILICA CARTRIDGES[a]

Compound	Spiked at 0.2 µg per cartridge						Spiked at 1.0 µg per cartridge						Spiked at 2.0 µg per cartridge					
	Fraction 1		Fraction 2		Fraction 3		Fraction 1		Fraction 2		Fraction 3		Fraction 1		Fraction 2		Fraction 3	
alpha-BHC	0	0	93.3	91.5	0	0	0	0	98.2	93.6	0	0	0	0	103	104	0	0
gamma-BHC	0	0	92.5	89.8	0	0	0	0	98.2	93.9	0	0	0	0	98.3	99.3	0	3.4
beta-BHC	0	0	94.3	92.8	0	0	0	0	103	91.2	0	0	0	0	108	110	0	0
Heptachlor	21.3	33.0	85.8	75.3	0	0	22.0	25.4	90.7	88.5	0	0	11.8	36.7	97.4	96.3	0	0
delta-BHC	0	0	59.3	64.8	32.0	25.5	0	0	92.0	83.9	6.7	14.1	0	0	89.6	81.6	14.0	30.9
Aldrin	76.5	82.8	31.0	22.8	0	0	66.4	76.1	36.4	43.0	0	0	39.0	88.2	48.9	39.3	0	0
Heptachlor epoxide	0	0	95.5	94.8	0	0	0	0	104	97.7	0	0	0	0	105	106	0	0
Endosulfan I	0	0	96.3	96.0	0	0	0	0	105	98.8	0	0	0	0	107	110	0	0
4,4'-DDE	49.8	64.0	56.5	43.3	0	0	48.7	55.0	62.4	66.0	0	0	2.6	68.3	78.8	72.5	0	0
Dieldrin	0	0	93.0	92.8	0	0	0	0	99.4	95.1	0	0	0	0	98.6	99.8	0	0
Endrin	0	0	113	114	0	0	0	0	139	136	0	0	0	0	105	106	0	0
4,4'-DDD	0	0	97.3	98.8	0	0	0	0	105	100	0	0	0	0	108	109	0	0
Endosulfan II	0	0	0	0	83.0	82.8	0	0	22.5	20.5	77.4	81.6	0	0	15.5	11.9	88.7	96.4
4,4'-DDT	0	0	95.0	95.5	0	0	0	0	103	97.2	0	0	0	0	103	105	0	0
Endrin aldehyde	0	0	0	0	0	0	0	0	37.2	34.6	29.0	29.6	0	0	39.4	35.2	37.9	44.6
Endosulfan sulfate	0	0	0	0	74.5	76.3	0	0	0	0	88.1	90.2	0	0	0	0	97.2	104
4,4'-Methoxychlor	0	0	87.5	90.3	0	0	0	0	104	96.7	0	0	0	0	103	99.9	0	11.8

[a] Silica cartridges (Supelco lot SP0204) were used; each cartridge was conditioned with 4 mL hexane prior to use. Each experiment was performed in duplicate. Each cartridge was spiked with 2 mL of a hexane solution containing the organochlorine pesticides at the concentrations stated above. Fraction 1 was eluted with 5 mL hexane, Fraction 2 with 5 mL hexane with 50 percent diethyl ether, and Fraction 3 with 5 mL hexane with 50 percent diethyl ether. Vacuum manifold used was the Analytichem SPS24.

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TABLE 14. ELUTION PATTERNS AND PERCENT RECOVERIES OF 17 ORGANOCHLORINE PESTICIDES FROM 0.5-g DIOL CARTRIDGES[a]

Compound	Spiked at 0.2 µg per cartridge				Spiked at 1.0 µg per cartridge				Spiked at 2.0 µg per cartridge			
	Fraction 1		Fraction 2		Fraction 1		Fraction 2		Fraction 1		Fraction 2	
alpha-BHC	83.3	83.0	0	0	115	117	0	0	105	106	0	0
gamma-BHC	79.8	79.8	0	0	115	113	0	0	105	99.0	0	0
beta-BHC	84.0	84.5	0	0	122	120	0	0	105	101	0	0
Heptachlor	58.8	58.3	0	0	84.8	80.9	0	0	76.2	81.8	0	0
delta-BHC	77.5	77.0	0	0	112	111	0	0	102	94.5	4.8	5.4
Aldrin	53.0	52.8	0	0	82.5	79.2	0	0	72.2	76.9	0	0
Heptachlor epoxide	81.7	80.8	0	0	114	109	0	0	101	100	0	0
Endosulfan I	70.3	70.0	0	0	103	96.0	0	0	90.2	92.9	0	0
4,4'-DDE	55.8	55.0	0	0	87.4	82.6	0	0	74.0	78.9	0	0
Dieldrin	79.8	79.0	0	0	113	109	0	0	102	97.9	0	0
Endrin	77.0	76.3	0	0	113	107	0	0	98.0	97.4	0	0
4,4'-DDD	81.8	82.3	0	0	122	117	0	0	101	101	0	0
Endosulfan II	80.5	80.3	0	0	115	114	0	0	102	97.8	0	3.3
4,4'-DDT	72.0	70.8	0	0	106	101	0	0	93.9	94.7	0	0
Endrin aldehyde	0	0	38.8	36.8	84.1	78.2	24.2	24.3	12.4	15.4	65.8	67.3
Endosulfan sulfate	39.8	39.5	58.3	53.3	111	117	12.6	8.6	4.9	5.8	96.6	92.6
4,4'-Methoxychlor	82.5	82.3	0	0	118	117	0	0	100	97.7	0	0

[a] Diol cartridges (Supelco lot SP0155) were used; each cartridge was conditioned with 4 mL hexane with 10 percent acetone prior to use. Each experiment was performed in duplicate. Each cartridge was spiked with 2 mL of a hexane solution at the concentrations stated above. Fractions 1 and 2 were each eluted with 5 mL hexane with 10 percent acetone. Vacuum manifold used was the Analytichem SPS24.

ESD T0271

TABLE 15. ELUTION PATTERNS AND PERCENT RECOVERIES OF 17 ORGANOCHLORINE PESTICIDES FROM 1-g DIOL CARTRIDGES[a]

Compound	Spiked at 0.2 µg per cartridge				Spiked at 1.0 µg per cartridge				Spiked at 2.0 µg per cartridge					
	Fraction 1		Fraction 2		Fraction 1		Fraction 2		Fraction 1		Fraction 2		Fraction 3	
alpha-BHC	86.3	97.5	0	0	113	95.8	0	0	107	107	0	0	0	0
gamma-BHC	80.3	89.8	0	0	107	90.0	4.8	4.7	102	101	4.1	4.6	0	0
beta-BHC	60.5	62.3	0	0	112	94.5	0	0	97.8	93.5	15.4	20.2	0	0
Heptachlor	80.5	92.0	0	0	107	90.9	0	0	103	104	0	0	0	0
delta-BHC	52.8	51.8	32.7	41.5	101	87.1	8.9	8.0	84.5	78.1	26.1	5.4	0	0
Aldrin	77.3	88.5	0	0	104	89.3	0	0	99.7	102	0	0	0	0
Heptachlor epoxide	81.8	94.0	0	0	110	93.6	0	0	105	104	0	0	0	0
Endosulfan I	85.3	98.0	0	0	114	96.1	0	0	104	103	0	0	0	0
4,4'-DDE	82.5	94.0	0	0	111	95.0	0	0	100	101	0	0	0	0
Dieldrin	80.5	92.0	0	0	106	90.7	0	0	102	100	0	0	0	0
Endrin	81.3	94.0	0	0	111	94.2	0	0	97.2	97.6	0	0	0	0
4,4'-DDD	80.3	92.0	0	0	113	95.3	0	0	104	102	0	0	0	0
Endosulfan II	65.5	66.3	20.8	30.3	108	91.6	0	0	94.9	89.7	17.5	23.8	0	0
4,4'-DDT	81.0	92.8	0	0	110	94.4	0	0	102	100	0	0	0	0
Endrin aldehyde	0	0	50.3	46.5	50.8	41.3	54.0	55.9	15.8	11.7	75.0	71.7	20.9	21.1
Endosulfan sulfate	0	0	66.8	61.3	26.7	23.0	91.0	93.0	0	0	86.8	81.8	21.4	24.4
4,4'-Methoxychlor	73.8	80.5	0	0	108	91.6	0	0	97.1	93.1	0	10.9	0	0

[a] Diol cartridges (Supelco lot SP0216) were used; each cartridge was conditioned with 4 mL hexane with 10 percent acetone prior to use. Each experiment was performed in duplicate. Each cartridge was spiked with 2 mL of a hexane solution at the concentrations stated above. Fraction 1, 2, and 3 were each eluted with 5 mL hexane with 10 percent acetone. Vacuum manifold used was the Analytichem SPS24.

ESD T0272

TABLE 16. ELUTION PATTERNS AND PERCENT RECOVERIES OF 17 ORGANOCHLORINE PESTICIDES FROM 2-g DIOL CARTRIDGES[a]

Compound	Spiked at 0.2 µg per cartridge								Spiked at 1.0 µg per cartridge			
	Fraction 1		Fraction 2		Fraction 3		Fraction 4		Fraction 1		Fraction 2	
alpha-BHC	0	0	97.5	97.5	0	0	0	0	93.1	81.4	30.1	30.7
gamma-BHC	0	0	88.5	87.0	0	15.0	0	0	31.1	29.3	88.0	70.6
beta-BHC	0	0	0	0	75.0	58.5	0	0	0	0	105	81.3
Heptachlor	96.0	99.8	0	0	0	0	0	0	107	99.7	0	0
delta-BHC	0	0	0	0	0	0	73.5	61.5	0	0	96.6	76.2
Aldrin	96.0	82.8	0	0	0	0	0	0	108	100	0	0
Heptachlor epoxide	0	0	88.5	91.5	0	0	0	0	99.4	90.0	16.6	15.3
Endosulfan I	60.0	49.0	40.5	48.0	0	0	0	0	105	99.3	7.2	0
4,4'-DDE	97.5	83.0	0	0	0	0	0	0	110	104	0	0
Dieldrin	0	0	90.0	91.5	0	0	0	0	95.6	84.9	15.6	15.5
Endrin	0	0	85.5	90.0	0	0	0	0	103	94.0	9.7	8.5
4,4'-DDD	0	0	93.0	93.0	0	0	0	0	65.5	55.0	60.9	51.0
Endosulfan II	0	0	0	0	70.5	45.0	27.0	49.5	0	0	102	78.8
4,4'-DDT	30.0	0	67.5	73.5	0	0	0	0	103	95.4	8.6	7.6
Endrin aldehyde	0	0	0	0	0	0	0	0	0	0	20.4	11.6
Endosulfan sulfate	0	0	0	0	0	0	0	0	0	0	8.1	0
4,4'-Methoxychlor	0	0	0	0	77.0	78.0	0	0	0	0	102	76.7

(continued)

[a] Diol cartridges (Supelco lot SP0216) were used; each cartridge was conditioned with 4 mL hexane with 10 percent acetone prior to use. Each experiment was performed in duplicate. Each cartridge was spiked with 2 mL of a hexane solution at the concentrations stated above. Fractions 1, 2, 3, and 4 were each eluted with 5 mL hexane with 10 percent acetone. Vacuum manifold used was the Analytichem SPS24.

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TABLE 16. (Concluded)[a]

Compound	Spiked at 1.0 µg per cartridge				Spiked at 2.0 µg per cartridge							
	Fraction 3		Fraction 4		Fraction 1		Fraction 2		Fraction 3		Fraction 4	
alpha-BHC	0	0	0	0	11.5	9.2	101	102	0	0	0	0
gamma-BHC	0	0	0	0	0	0	98.8	99.9	4.0	5.2	0	0
beta-BHC	0	0	0	0	0	0	43.4	28.1	68.7	83.0	0	0
Heptachlor	0	0	0	0	105	108	5.8	5.6	0	0	0	0
delta-BHC	0	0	0	0	0	0	8.2	3.8	82.9	77.6	15.2	30.0
Aldrin	0	0	0	0	104	108	3.4	3.6	0	0	0	0
Heptachlor epoxide	0	0	0	0	37.8	30.3	85.4	91.8	0	0	0	0
Endosulfan I	0	0	0	0	84.0	84.1	39.6	44.4	0	0	0	0
4,4'-DDE	0	0	0	0	103	106	4.7	4.4	0	0	0	0
Dieldrin	0	0	0	0	25.7	18.4	86.8	91.2	0	0	0	0
Endrin	0	0	0	0	45.8	37.4	73.1	80.3	0	0	0	0
4,4'-DDD	0	0	0	0	0	0	99.1	99.4	0	0	0	7.5
Endosulfan II	0	0	0	0	0	0	36.1	19.5	75.3	86.6	4.0	0
4,4'-DDT	0	0	0	0	62.6	59.3	61.6	67.3	0	0	0	0
Endrin aldehyde	64.3	61.4	12.8	17.4	0	0	7.5	7.9	0	0	0	0
Endosulfan sulfate	88.9	84.8	10.8	18.6	4.2	0	0	0	0	0	0	0
4,4'-Methoxychlor	0	0	0	0	0	0	84.1	77.2	19.9	29.5	0	0

[a] Diol cartridges (Supelco lot SP0216) were used; each cartridge was conditioned with 4 mL hexane with 10 percent acetone prior to use. Each experiment was performed in duplicate. Each cartridge was spiked with 2 mL of a hexane solution at the concentrations stated above. Fractions 1, 2, 3, and 4 were each eluted with 5 mL hexane with 10 percent acetone. Vacuum manifold used was the Analytichem SPS24.

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TABLE 17. ELUTION PATTERNS AND PERCENT RECOVERIES OF 17 ORGANOCHLORINE PESTICIDES AND AROCLOR 1260 FROM 1-g DIOL CARTRIDGES

Compound	Spiked with organochlorine pesticides at 0.2 µg and Aroclor 1260 at 80 µg per cartridge			Spiked with organochlorine pesticides at 0.2 µg and Aroclor 1260 at 2 µg per cartridge		
	Fraction 1 (3 mL hexane)	Fraction 2 (5 mL hexane with 10 percent acetone)	Fraction 3 (5 mL hexane with 10 percent acetone)	Fraction 1 (3 mL hexane)	Fraction 2 (5 mL hexane with 10 percent acetone)	Fraction 3 (5 mL hexane with 10 percent acetone)
Aroclor 1260	90	10	0	100	0	0
alpha-BHC	0	93	0	0	106	0
gamma-BHC	0	105	0	0	96	0
beta-BHC	0	103	0	0	100	0
Heptachlor	112	0	0	102	0	0
delta-BHC	0	97.3	0	0	113	0
Aldrin	116	0	0	110	0	0
Heptachlor epoxide	0	97.3	0	0	112	0
Endosulfan I	58.5	71.5	0	59.2	93.2	0
4,4'-DDE	124	0	0	123	0	0
Dieldrin	0	108	0	0	112	0
Endrin	0	>100[a]	0	0	100	0
4,4'-DDD	0	99.5	0	0	100	0
Endosulfan II	0	>100[a]	0	0	100	0
4,4'-DDT	>100[a]	0	0	100	0	0
Endrin aldehyde	0	39.5	60.5	0	35.0	65.0
Endosulfan sulfate	0	29.2	70.8	0	14.0	86.0
4,4'-Methoxychlor	0	>100[a]	0	0	100	0

[a]Cannot be quantitated accurately because of interference from Aroclor 1260.

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solutions were then subjected to the silica or the diol cartridge cleanup procedure to establish if any changes occurred in the target compound elution pattern and in their recoveries caused by matrix interferents (Tables 18 and 19). These interferents were selected because they mimic typical background contamination in certain environmental sample matrices that could also be contaminated with the target compounds. For example, corn oil would be representative of fatty acid triglycerides, and diesel hydrocarbons of petroleum hydrocarbons. The data presented in Tables 18 and 19 indicate that neither the corn oil nor the diesel hydrocarbons affected the elution patterns of the 17 organochlorine pesticides. Elemental sulfur, if present, is eluted from the silica cartridge with 5 mL hexane and will interfere only with the gas chromatographic analysis of heptachlor and aldrin on the DB-1701 column (Figure 4). 4,4′-DDE and 4,4′-DDT also elute in Fraction 1, however, they can be quantified without any difficulty on any of the two columns. The remainder of the 17 organochlorine pesticides are retained on the silica cartridge and then eluted with hexane with 50 percent diethyl ether. The diol cartridge procedure was also evaluated to determine whether elemental sulfur, if present, can be separated from the organochlorine pesticides. We found that when the cartridge is eluted with hexane with 10 percent acetone, the elemental sulfur elutes from the cartridge together with the organochlorine pesticides and will interfere with the gas chromatographic analysis on the DB-1701 column of compounds 1 through 6 in Table 1 (Figure 5). It is possible that elemental sulfur could be removed as in the case of the silica cartridge, however, we have not tested this yet.

5.2 PHTHALATE ESTERS

Florisil and alumina SPE cartridges were evaluated for their use in phthalate ester analysis. These cartridges were chosen because the current SW-846 Method 8060 recommends use of either Florisil (Method 3620) or alumina (Method 3610) for cleanup of sample extracts containing phthalate esters. In Method 3620, Florisil (60/80 mesh) is activated for 16 hours at 140°C and then deactivated with water (3 percent by weight). The charged Florisil column is eluted with hexane (40 mL) to remove interfering compounds; phthalate esters are then recovered with 100 mL hexane with 20 percent diethyl ether. In Method 3610, neutral alumina, activity Super I, W206 series, is activated for 16 hours at 400°C and the phthalate esters are recovered with 140 mL of hexane with 20 percent diethyl ether.

We have evaluated both methods with hexane solutions containing the 16 phthalate esters listed in Table 2. The percent recoveries of the 16 compounds are presented elsewhere (5). Alumina cleanup is preferred over the Florisil cleanup since it allows recovery of all target compounds by elution with hexane with 20 percent diethyl ether. When Florisil cleanup was used, BMEP, BEEP, and BBEP could not be recovered at all, and DMP and DEP gave recoveries of only 40 and 57 percent, respectively.

To improve the recoveries of the five phthalate esters mentioned above, we have taken Florisil and alumina SPE cartridges of 0.5-g, 1.0-g, and 2-g size, charged them with the target compounds and interferents, and eluted them with hexane with 10 percent acetone (for Florisil) or hexane with 20 percent acetone (for alumina). We had at first attempted to elute the phthalate esters from the alumina cartridge with hexane with 20 percent diethyl ether. Since none of the phthalate esters was recovered after 10 mL solvent passed through the cartridge, we changed the eluting solvent to hexane with 10 percent acetone and later to hexane with 20 percent acetone to improve the recovery of BMEP, BEEP and BBEP. The results of these experiments are summarized in Tables 20, 21, and 22.

TABLE 18. PERCENT RECOVERIES AND ELUTION PATTERNS OF 17 ORGANOCHLORINE PESTICIDES FROM 1-g SILICA CARTRIDGES IN THE PRESENCE OF CORN OIL AND DIESEL HYDROCARBONS[a]

Compound	Corn oil as interferents						Diesel hydrocarbons as interferents					
	Fraction 1		Fraction 2		Fraction 3		Fraction 1		Fraction 2		Fraction 3	
alpha-BHC	0	0	121	119	0	0	0	0	115	116	0	0
gamma-BHC	0	0	124	122	0	0	0	0	118	120	0	0
beta-BHC	0	0	114	111	0	0	0	0	106	108	0	0
Heptachlor	119	123	0	0	0	0	115	113	0	0	0	0
delta-BHC	0	0	115	112	0	0	0	0	108	111	0	0
Aldrin	119	120	0	0	0	0	112	110	0	0	0	0
Heptachlor epoxide	0	0	123	121	0	0	0	0	118	120	0	0
Endosulfan I	0	0	121	118	0	0	0	0	117	119	0	0
4,4'-DDE	113	120	0	0	0	0	120	118	0	0	0	0
Dieldrin	0	0	117	114	0	0	0	0	111	114	0	0
Endrin	0	0	143	142	0	0	0	0	150	156	0	0
4,4'-DDD	0	13.3	109	106	0	0	14.2	16.5	106	108	0	0
Endosulfan II	0	0	113	110	0	0	0	0	109	111	0	0
4,4'-DDT	103	114	0	0	0	0	115	109	0	0	0	0
Endrin aldehyde	0	0	66.7	64.7	26.9	31.8	0	0	55.4	62.5	31.0	31.6
Endosulfan sulfate	0	0	108	105	0	0	0	0	98.2	103	0	0
4,4'-Methoxychlor	0	0	110	107	0	0	0	0	105	107	0	0

[a] Silica cartridges (Supelco lot SP0161) were used; each cartridge was conditioned with 4 mL hexane prior to use. Each experiment was performed in duplicate. Each cartridge was spiked with 2 mL of a hexane solution containing the organochlorine pesticides at 0.5 µg/mL, the corn oil at 500 µg/mL, and the diesel hydrocarbons at 1000 µg/mL. Fraction 1 was eluted with 5 mL hexane, Fraction 2 with 5 mL hexane with 50 percent diethyl ether, and Fraction 3 with 5 mL hexane with 50 percent diethyl ether. Vacuum manifold used was the Analytichem SPS24.

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TABLE 19. PERCENT RECOVERIES AND ELUTION PATTERNS OF 17 ORGANOCHLORINE PESTICIDES FROM 1-g DIOL CARTRIDGES IN THE PRESENCE OF CORN OIL AND DIESEL HYDROCARBONS[a]

Compound	Corn oil as interferents						Diesel hydrocarbons as interferents					
	Fraction 1		Fraction 2		Fraction 3		Fraction 1		Fraction 2		Fraction 3	
alpha-BHC	121	119	0	0	0	0	115	116	0	0	0	0
gamma-BHC	120	118	0	0	0	0	116	118	0	0	0	0
beta-BHC	108	106	0	0	0	0	102	104	0	0	0	0
Heptachlor	120	119	0	0	0	0	117	119	0	0	0	0
delta-BHC	108	107	0	0	0	0	108	110	0	0	0	0
Aldrin	115	113	0	0	0	0	111	117	0	0	0	0
Heptachlor epoxide	120	116	0	0	0	0	120	122	0	0	0	0
Endosulfan I	121	120	0	0	0	0	120	124	0	0	0	0
4,4'-DDE	115	115	0	0	0	0	116	122	0	0	0	0
Dieldrin	118	116	0	0	0	0	118	120	0	0	0	0
Endrin	111	111	0	0	0	0	116	120	0	0	0	0
4,4'-DDD	112	110	0	0	0	0	115	118	0	0	0	0
Endosulfan II	111	108	0	0	0	0	114	115	0	0	0	0
4,4'-DDT	110	110	0	0	0	0	114	117	0	0	0	0
Endrin aldehyde	28.6	26.8	73.0	76.8	0	0	22.8	0	69.8	42.6	0	0
Endosulfan sulfate	0	0	102	108	0	0	0	0	111	107	0	0
4,4'-Methoxychlor	100	99.0	0	0	0	0	98.6	100	0	0	0	0

[a] Diol cartridges (Supelco lot SP0206) were used; each cartridge was conditioned with 4 mL hexane with 10 percent acetone prior to use. Each experiment was performed in duplicate. Each cartridge was spiked with 2 mL of a hexane solution containing the organochlorine pesticides at 0.5 µg/mL, the corn oil at 500 µg/mL, and the diesel hydrocarbons at 1000 µg/mL. Fractions 1, 2, and 3 were each eluted with 5 mL hexane with 10 percent acetone in hexane. Vacuum manifold used was the Analytichem SPS24.

ESD T0274

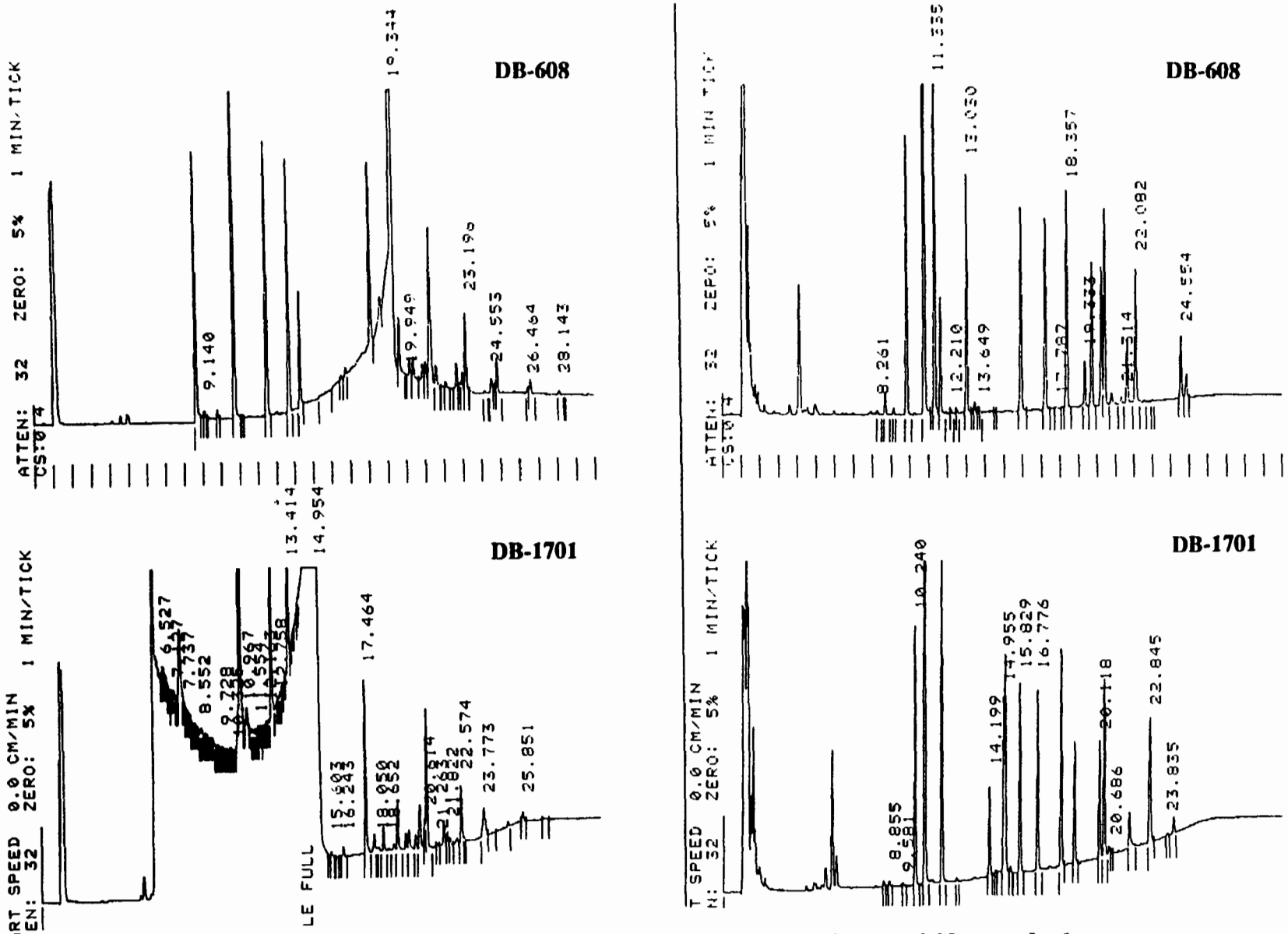

Figure 4. GC/ECD chromatograms of a Method 8081 organochlorine pesticide standard containing elemental sulfur, passed through a silica cartridge; Fraction 1 (left), Fraction 2 (right). The GC operating conditions are given in Table 1

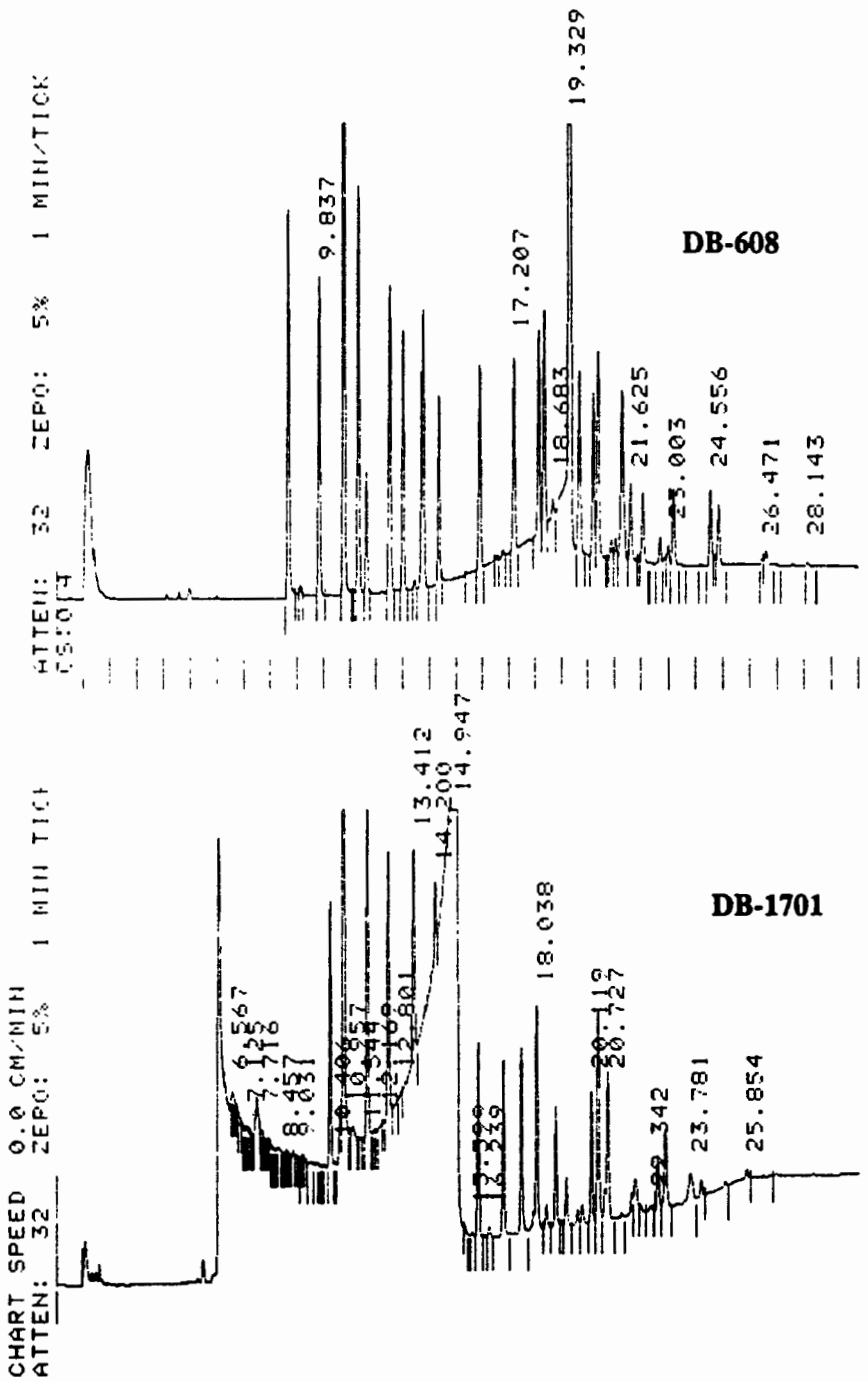

Figure 5. GC/ECD chromatograms of a Method 8081 organochlorine pesticide standard containing elemental sulfur, passed through a diol cartridge. Hexane with 10 percent acetone was used as eluant.

TABLE 20. ELUTION PATTERNS AND PERCENT RECOVERIES OF THE PHTHALATE ESTERS FROM THE FLORISIL CARTRIDGES USING HEXANE WITH 10 PERCENT ACETONE[a]

	0.5-g cartridge						1-g cartridge						2-g cartridge					
Compound	40-µg spike Fraction 1		80-µg spike Fraction 1		120-µg spike Fraction 1		40-µg spike Fraction 1		80-µg spike Fraction 1		120-µg spike Fraction 1		40-µg spike Fraction 1		80-µg spike Fraction 1		120-µg spike Fraction 1	
DMP	98.9	101	81.2	80.8	73.9	76.4	91.1	87.6	42.1	57.7	28.5	35.7	70.9	95.3	37.1	39.5	63.6	72.9
DEP	108	113	91.3	93.1	83.7	85.3	99.5	95.1	81.2	87.3	78.6	76.5	111	94.0	100	101	107	107
DIBP	109	106	92.8	91.7	87.8	91.8	94.9	88.6	88.7	92.1	90.6	88.1	114	103	92.2	92.8	86.9	86.0
DBP	104	107	87.4	88.5	80.1	83.1	100	105	89.1	87.4	87.9	85.8	108	108	91.4	92.4	82.5	80.9
BMPP	106	114	98.2	95.9	86.4	90.2	112	99.1	95.4	94.1	92.5	89.2	115	116	94.8	95.8	105	98.5
BMEP[b]	16.0	15.6	11.9	14.8	10.7	15.9	[c]	[c]	[c]	[c]	[c]	[c]	[c]	[c]	[c]	[c]	[c]	[c]
DAP	107	111	94.8	91.5	82.7	87.9	96.8	92.1	89.4	92.5	88.1	85.6	113	106	91.8	92.3	83.4	82.6
BEEP	96.6	97.6	74.7	69.3	65.8	71.6	96.0	91.1	[d]	[d]	[d]	[d]	[d]	[d]	[d]	[d]	[d]	[d]
HEHP	99.6	98.4	75.6	75.9	65.3	68.9	101	90.8	70.6	70.2	66.1	63.9	83.9	93.8	68.9	84.3	77.8	77.5
DHP	105	109	91.0	87.6	78.6	86.0	99.4	94.1	88.6	87.9	85.1	82.5	106	103	86.4	90.9	80.6	78.3
BBP	108	109	84.1	82.3	67.5	71.3	99.8	97.3	80.4	82.8	70.1	69.5	109	104	83.2	93.9	101	97.2
BBEP	113	117	98.5	94.3	83.2	91.4	105	89.9	95.3	102	97.4	93.5	118	112	98.3	95.9	94.1	87.0
DEHP	111	111	92.1	87.6	76.5	84.5	95.6	87.4	68.0	74.7	47.1	50.2	111	65.8	82.9	84.4	81.5	77.6
DCP	91.4	81.6	62.9	61.7	53.5	57.0	97.0	84.1	62.0	53.7	59.0	48.0	69.6	72.0	59.9	57.3	72.2	59.9
DOP	120	114	102	93.2	83.3	95.4	99.9	94.3	98.1	97.9	98.5	93.0	114	115	103	99.4	97.3	86.9
DNP	118	118	103	92.2	83.1	95.9	111	98.8	98.1	100	98.3	94.8	118	115	101	99.3	92.8	88.5

[a] Each cartridge was preconditioned with 4 mL hexane prior to use. Each experiment was performed in duplicate. Fraction 1 was eluted with 5 mL hexane with 10 percent acetone; Fraction 2 with 5 mL hexane with 10 percent acetone. A third fraction was collected from the 2-g cartridge by elution with 5 mL hexane with 10 percent acetone.

[b] Additional BMEP was recovered from the 0.5-g Florisil cartridge by eluting the cartridge with an additional 5 mL hexane with 10 percent acetone (Fraction 2). The recoveries in Fraction 2 were 70.3 and 71.3 percent for the 40-µg spike, 55.4 and 54.3 percent for the 80-µg spike, 53.4 and 54.1 percent for the 120-µg spike.

[c] Compound not recovered in any of the three fractions.

[d] BEEP phthalate was recovered by eluting the cartridge with an additional 5 mL hexane with of 10 percent acetone. Total recoveries were 75.1 and 79.3 percent for the 80-µg spike (1-g cartridge), 57.3 and 56.5 percent for the 120-µg spike (1-g cartridge), 94.6 percent for the 40-µg spike (2-g cartridge), 55.4 and 62.0 percent for the 80-µg spike (2-g cartridge), 70.2 and 79.0 percent for the 120-µg spike (2-g cartridge).

TABLE 21. ELUTION PATTERNS AND PERCENT RECOVERIES OF THE PHTHALATE ESTERS FROM ALUMINA CARTRIDGES USING HEXANE WITH 10 PERCENT AND 20 PERCENT ACETONE[a]

Compound	Hexane with 10 percent acetone				Hexane with 20 percent acetone			
	Fraction 1 (5 mL)		Fraction 2 (5 mL)		Fraction 1 (5 mL)		Fraction 2 (5 mL)	
DMP	78.6	65.6	47.9	28.8	101	102	0	0
DEP	101	84.5	0	0	103	103	0	0
DIBP	94.0	75.8	0	0	105	104	0	0
DBP	101	88.1	0	0	109	107	0	0
BMPP	86.4	37.0	0	0	104	102	0	0
BMEP	0	0	31.5	40.3	66.6	61.6	38.8	34.8
DAP	63.6	57.3	0	0	106	100	0	0
BEEP	16.6	19.6	109	102	121	102	0	0
HEHP	68.5	56.9	0	0	103	99.3	0	0
DHP	99.9	89.3	0	0	112	105	0	0
BBP	93.8	89.6	10.3	5.4	106	100	0	0
BBEP	75.4	66.3	50.2	47.6	114	103	0	0
DEHP	99.1	88.3	0	0	102	83.1	0	0
DCP	73.3	67.0	0	0	99.0	90.5	0	0
DOP	97.9	120	0	0	118	107	0	0
DNP	89.5	113	0	0	93.5	101	0	0

[a] 1-g alumina cartridges (Supelco lot SP 0214) were used; each cartridge was preconditioned with 4 mL hexane prior to use. Each experiment was performed in duplicate; the amount spiked was 40 μg per component per cartridge (2 mL of 20 μg/mL in hexane).

TABLE 22. ELUTION PATTERNS AND PERCENT RECOVERIES OF THE PHTHALATE ESTERS FROM THE ALUMINA CARTRIDGES OF VARIOUS SIZES USING HEXANE WITH 20 PERCENT ACETONE[a]

	0.5-g cartridge						1.0-g cartridge						2.0-g cartridge					
Compound	40-µg spike Fraction 1		80-µg spike Fraction 1		120-µg spike Fraction 1		40-µg spike Fraction 1		80-µg spike Fraction 1		120-µg spike Fraction 1		40-µg spike Fraction 1		80-µg spike Fraction 1		120-µg spike Fraction 1	
DMP	106	108	67.8	72.6	69.5	71.3	108	117	100	92.1	115	113	98.6	93.8	92.3	73.2	84.1	93.0
DEP	111	112	76.2	78.9	73.1	75.3	139	148	106	125	126	127	106	108	105	102	112	104
DIBP	92.5	94.3	79.8	80.6	116	115	77.5	85.4	93.8	108	96.9	94.0	84.6	86.5	119	110	99.8	100
DBP	101	103	83.8	86.7	91.3	89.6	101	109	109	121	103	101	95.4	94.6	108	103	98.2	92.8
BMPP	98	96.4	81.4	82.6	100	109	75.1	90.4	92.3	107	83.3	81.5	81.8	80.3	101	98.1	81.5	78.8
BMEP	98.8	104	76.0	79.4	87.7	88.8	87.1	93.8	92.2	101	90.3	88.5	[b]	[b]	[b]	[b]	[b]	[b]
DAP	103	104	83.6	83.2	99.3	98.7	92.4	101	103	116	95.0	93.0	82.4	84.4	98.6	94.9	87.7	83.3
BEEP	107	110	80.9	84.6	95.2	94.5	96.5	105	97.7	109	103	96.6	81.6[c]	67.9[c]	76.9[c]	55.8[c]	45.6[c]	70.3[c]
HEHP	102	104	68.3	72.0	78.1	69.8	81.1	104	90.3	110	87.4	86.2	74.9	78.8	94.1	87.9	78.5	74.2
DHP	101	100	81.5	87.4	101	85.4	116	126	94.9	106	118	116	95.5	97.8	87.8	81.6	101	93.7
BBP	113	116	59.2	61.9	62.0	60.5	103	110	99.1	106	104	103	89.3	91.0	96.8	92.8	94.5	88.4
BBEP	86.4	78.5	83.0	91.1	117	113	88.1	92.5	99.4	110	104	103	73.3	73.9	101	96.5	87.3	79.5
DEHP	112	112	77.3	87.8	96.6	91.3	99.4	107	100	113	93.5	92.0	85.6	87.0	99.1	93.1	90.2	85.6
DCP	100	102	63.9	62.3	73.5	72.6	99.3	105	92.4	106	90.5	89.9	57.4	59.1	82.1	71.1	60.7	57.5
DOP	84.3	74.3	79.6	90.5	103	101	93.3	108	101	113	103	102	85.6	86.5	101	97.1	93.1	85.9
DNP	77.1	66.2	80.7	89.5	96.4	94.7	106	114	103	114	113	110	88.9	91.5	100	96.1	102	92.9

[a] J. T. Baker alumina cartridges: Lot B41714 for 0.5-g size, Lot B12505 for 1-g size, and Lot B41714 for 2-g size. Each cartridge was preconditioned with 4 mL hexane prior to use. Each experiment was performed in duplicate. Fraction 1 was eluted with 5 mL hexane with 20 percent acetone; Fraction 2 with 5 mL hexane with 20 percent acetone. A third fraction was collected from the 2-g cartridge by elution with 5 mL hexane with 20 percent acetone.

[b] BMEP was recovered from the 2-g alumina cartridge by eluting the cartridge with two additional 5-mL portions of hexane with 20 percent acetone (Fractions 2 and 3). The recoveries in Fraction 2 were 77.6 and 50.9 percent (40-µg spike), 57.8 and 46.2 percent (80-µg spike), and 26.3 and 61.5 percent (120-µg spike). The recoveries in Fraction 3 were 38.1 percent (40-µg spike), 37.9 and 48.1 (80-µg spike), and 38.1 and 31.9 (120-µg spike).

[c] Additional BEEP was recovered from the 2-g alumina cartridge by eluting the cartridge with an additional 5 mL hexane with 20 percent acetone (Fraction 2). The recoveries in Fraction 2 were 13.3 and 30.9 percent (40-µg spike), 28.6 and 55.9 percent (80-µg spike), and 62.7 and 28.9 percent (120-µg spike).

The data shown in Table 20 indicate that all but two phthalate esters can be recovered from a 0.5-g or a 1-g Florisil cartridge with 5 mL hexane with 10 percent acetone (Fraction 1) and from a 2-g cartridge with 10 mL hexane with 10 percent acetone (no phthalate esters were recovered in Fraction 1, therefore an additional fraction had to be collected). The two phthalate esters that could not be recovered are BMEP and BEEP. When working with the 0.5-g Florisil cartridge, these two phthalate esters were recovered almost quantitatively by eluting the cartridge with an additional 5 mL hexane with 10 percent acetone; however, they could not be recovered from either the 1-g or the 2-g Florisil cartridge under similar conditions.

The alumina cartridge was first eluted with 5 mL hexane with 10 percent acetone (Table 21). Since BMEP was not recovered at all and BEEP had recoveries <20 percent in Fraction 1, the cartridge was eluted with an additional 5 mL hexane with 10 percent acetone. In addition, we also eluted the cartridge with hexane with 20 percent acetone. This allowed quantitative recovery of 15 phthalate esters in Fraction 1. The only compound that had recovery under 70 percent was BMEP (Table 21). The alumina cartridge procedure using hexane with 20 percent acetone was further evaluated with cartridges of 0.5 g, 1 g, and 2 g in size, charged with the 16 phthalate esters at three spiking levels (Table 22). The results indicate that the 16 phthalate esters were recovered quantitatively with the exception of BMEP from the 2-g cartridge.

Matrix interferents such as corn oil, diesel hydrocarbons, elemental sulfur, and the organochlorine pesticides listed in SW-846 Method 8081 were added to hexane solutions containing the 16 phthalate esters at known concentrations, and the hexane solutions were then subjected to the Florisil or alumina cartridge cleanup procedure (Table 23). These interferents were selected because they mimic typical background contamination in certain environmental sample matrices that could also be contaminated with the target compounds. For example, corn oil would be representative of fatty acid triglycerides, diesel hydrocarbons of petroleum hydrocarbons, and organochlorine pesticides of compounds of environmental significance that would be expected to behave in the same way as the target analytes investigated in this study. The data presented in Table 23 indicate that neither the corn oil nor the diesel hydrocarbons affected the elution patterns or the recoveries of the 16 phthalate esters from the Florisil or the alumina cartridge. Corn oil was also removed from the Florisil cartridge with hexane with 10 percent acetone. Fortunately, its presence does not seem to affect the GC determination of the 16 phthalate esters. This statement is true only for corn oil concentrations below 0.2 mg/mL of solvent (or 1 mg per cartridge) because this is the maximum concentration we used. Diesel hydrocarbons do not seem to cause problems with the GC quantification of the phthalate esters because the GC detector is transparent to aliphatic hydrocarbons. Elemental sulfur, if present, is eluted from the Florisil cartridge with hexane with 10 percent acetone (Figure 6) and from the alumina cartridge with hexane with 20 percent acetone (Figure 7). Therefore, extracts that are known to contain elemental sulfur should be subjected to sulfur cleanup (Method 3660) prior to Florisil or alumina cartridge cleanup. Separation of the organochlorine pesticides will be described later in this section.

The effect of interferents when the Florisil cartridges were eluted with hexane/diethyl ether (1:1) is presented in Table 24. Corn oil and the diesel hydrocarbons do not seem to interfere with the determination of the 16 phthalate esters, except for DAP that could not be quantified because of interference and BMEP and BEEP that had low recoveries.

The organochlorine pesticides overlapped with the phthalate esters when the GC analysis was performed on the DB-5 fused-silica capillary column; they have to be separated prior to the GC analysis. Hexane with 50 percent diethyl ether did not give adequate recoveries for 8 of the 16 phthalate esters (Table 24), but use of hexane with 20 percent methylene chloride followed by hexane with 10 percent acetone gave quantitative recoveries for 14 of the 16 phthalate esters (Table 25).

TABLE 23. PERCENT RECOVERIES OF THE PHTHALATE ESTERS FROM FLORISIL AND ALUMINA CARTRIDGES WHEN INTERFERENTS WERE PRESENT[a]

Compound	Florisil cartridge (Fraction 1)				Alumina cartridge (Fraction 1)			
	Corn oil (1000 µg per cartridge)		Diesel hydrocarbons (2000 µg per cartridge)		Corn oil (1000 µg per cartridge)		Diesel hydrocarbons (2000 µg per cartridge)	
DMP	119	123	106	111	105	104	92.5	94.4
DEP	133	133	123	129	120	119	92.5	94.4
DIBP	101	104	111	107	88.8	87.7	82.8	85.8
DBP	111	111	110	114	92.4	91.1	88.7	90.4
BMP	104	104	93.2	95.7	61.2	63.1	69.8	71.0
BMEP[b]	[b]	[b]	[b]	[b]	81.4	81.8	74.1	75.8
DAP	96.6	96.8	98.8	98.8	82.7	83.1	74.9	76.9
BEEP[c]	53.3	64.6	43.7	32.3	70.9	71.8	66.0	67.9
HEHP	89.8	91.2	87.1	86.6	74.3	82.9	71.1	73.1
DHP	108	106	103	104	99.8	98.9	90.3	91.5
BBP	106	107	102	104	93.8	92.6	84.6	87.3
BBEP	104	104	98.8	100	87.8	87.8	88.3	81.6
DEHP	99.9	99.4	92.1	94.6	83.3	83.1	72.6	74.6
DCP	81.4	81.2	68.2	68.2	81.8	81.3	72.0	73.8
DOP	109	108	102	103	93.1	92.7	80.9	82.7
DNP	114	114	107	111	98.5	99.2	86.4	88.3

[a] 1-g cartridges were used for this experiment. Each cartridge was preconditioned with 4 mL hexane. Each experiment was performed in duplicate. The Florisil cartridge was eluted with two 5-mL portions of hexane with 10 percent acetone (Fractions 1 and 2). The alumina cartridge was eluted with two 5-mL portions of hexane with 20 percent acetone (Fractions 1 and 2).

[b] BMEP was recovered from the Florisil cartridge. The recoveries in Fraction 2 were 81.9 and 95.6 percent when corn oil was present as interferent and 71.5 and 62.3 percent when diesel hydrocarbons were the interferents.

[c] Additional BEEP was recovered from the Florisil cartridge in Fraction 2. The recoveries in Fraction 2 were 41.6 and 31.7 percent when corn oil was present as interferent, and 56.8 and 63.4 percent when diesel hydrocarbons were the interferents.

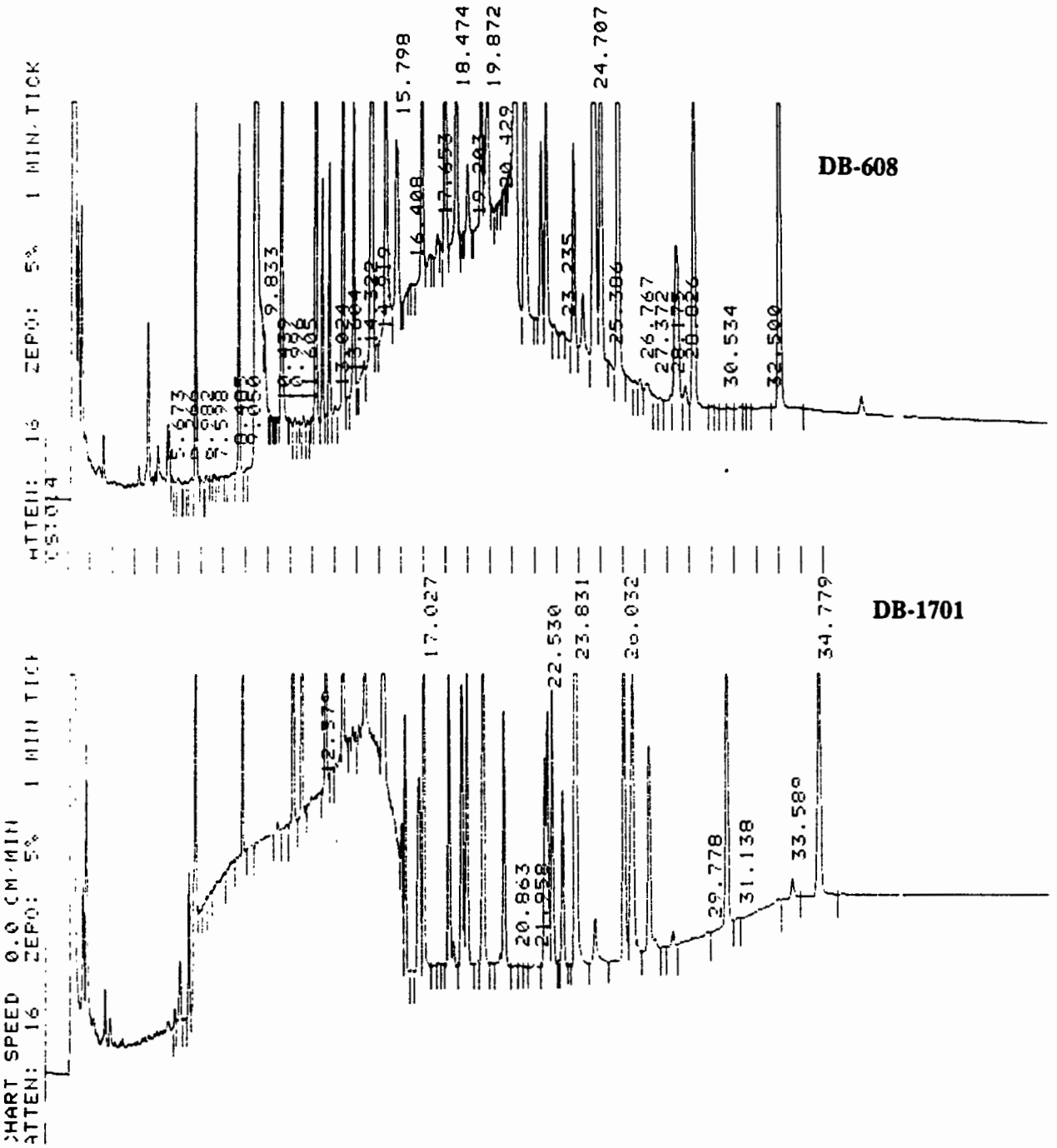

Figure 6. GC/ECD chromatograms of a phthalate esters standard spiked with organochlorine pesticides and elemental sulfur and eluted from the 1-g Florisil cartridge with hexane with 10 percent acetone. GC conditions are presented in Table 2.

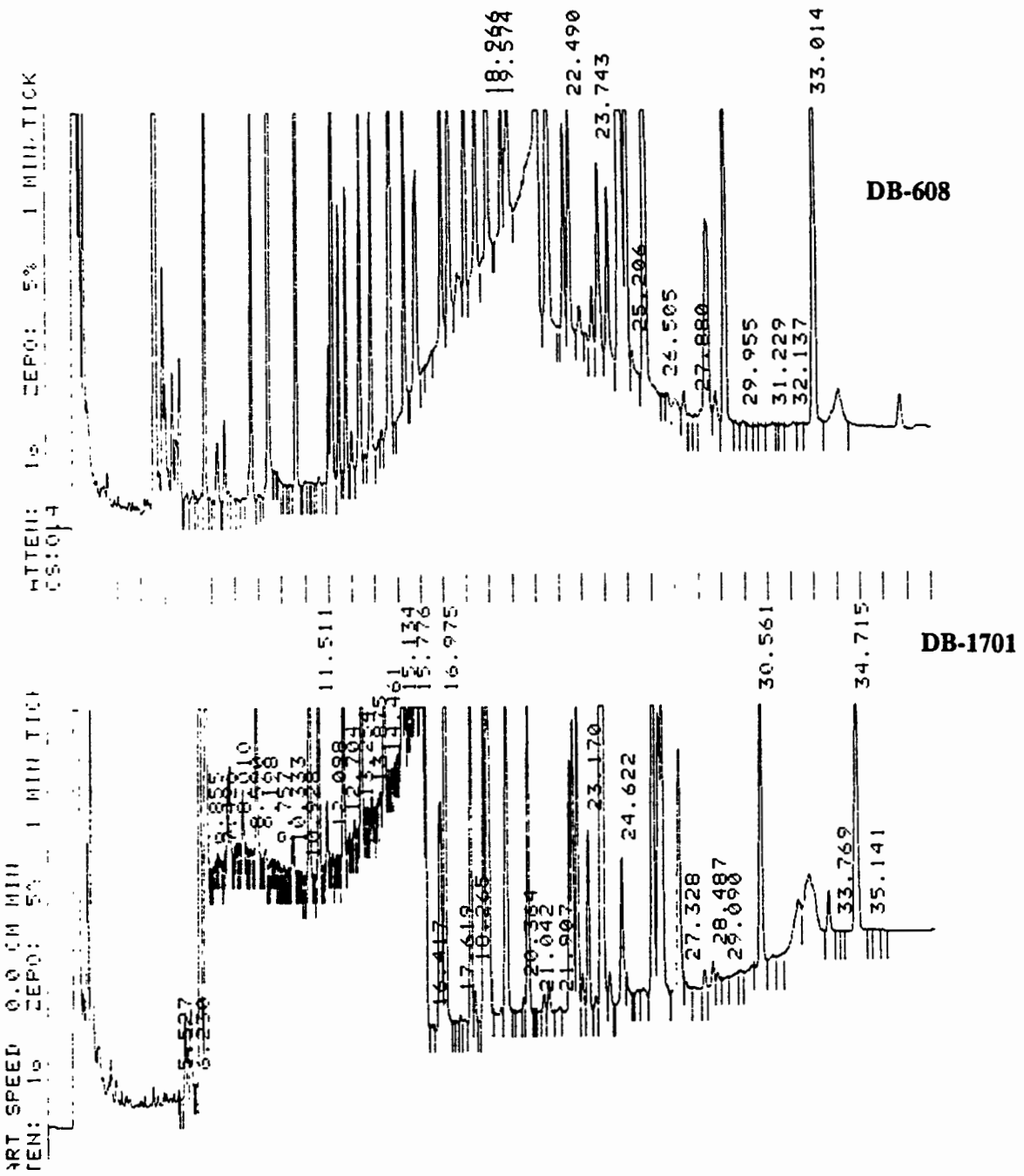

Figure 7. GC/ECD chromatograms of a phthalate esters standard spiked with organochlorine pesticides and elemental sulfur and eluted from the 1-g alumina cartridge with hexane with 20 percent acetone. GC conditions are presented in Table 2.

TABLE 24. ELUTION PATTERNS AND PERCENT RECOVERIES OF PHTHALATE ESTERS FROM FLORISIL CARTRIDGES WITH HEXANE WITH 50 PERCENT DIETHYL ETHER[a]

Compound	Fraction 1								Fraction 2							
	No interferents		With corn oil		With diesel hydrocarbons		With organochlorine pesticides		No interferents		With corn oil		With diesel hydrocarbons		With organochlorine pesticides	
DMP	94	94	78	82	116	108	93	91	<5	<5	<5	<5	<5	<5	<5	<5
DEP	96	95	84	93	74	70	103	98	<5	<5	10	<5	7.6	<5	6.2	6.4
DIBP	122	119	122	115	105	97	118	111	<5	<5	<5	<5	<5	<5	19	22
DBP	116	114	[b]	105	124	113	[b]	[b]	<5	<5	<5	<5	<5	<5	<5	<5
BMPP	108	109	103	87	109	96	[b]	[b]	<5	<5	<5	<5	<5	<5	60	72
BMEP	2.6	96	38	19	128	109	[b]	[b]	32	<5	<5	20	32	22	103	128
DAP	95	101	[b]	103	[b]	[b]	[b]	[b]	<5	<5	<5	<5	6.1	7.2	74	87
BEEP	8.9	99	7.8	44	55	48	14	58	51	<5	66	54	62	58	53	54
HEHP	112	104	127	116	88	81	86	83	<5	<5	11	8.2	8.2	6.0	<5	<5
DHP	98	98	128	106	107	103	[b]	[b]	<5	<5	6.0	<5	<5	<5	17	20
BBP	111	117	122	117	118	112	[b]	[b]	<5	<5	<5	<5	<5	<5	6.8	7.4
BBEP	65	97	78	90	103	112	[b]	[b]	27	<5	25	10	9.6	10	58	69
DEHP	95	103	89	83	85	78	91	86	<5	<5	<5	<5	<5	<5	<5	<5
DCP	98	101	118	86	114	104	100	96	<5	<5	<5	<5	<5	<5	<5	<5
DOP	106	109	114	80	114	107	108	102	<5	<5	<5	<5	<5	<5	<5	<5
DNP	90	91	80	72	104	95	94	90	<5	<5	<5	<5	<5	<5	<5	<5

[a] Florisil cartridges (1 g) were used. Fraction 1 was eluted with 5 mL hexane with 50 percent diethyl ether and Fraction 2 with an additional 5 mL hexane with 50 percent diethyl ether. Final volume of each fraction was 5 mL. The phthalate esters were spiked at 2,500 ng per cartridge.
[b] Not able to determine because of interference.

TABLE 25. RESULTS OF THE FLORISIL CARTRIDGE CLEANUP EVALUATION STUDY (PHTHALATE ESTER STANDARDS ONLY; ELUTION WITH HEXANE/METHYLENE CHLORIDE (4:1) AND HEXANE/ACETONE (9:1))

	Percent recovery					
	8712-013-10 Fraction		8712-013-11 Fraction		8712-013-12 Fraction	
Compound	I	II	I	II	I	II
DMP	0	68.0	0	121	0	201
DEP	0	87.7	0	90.7	0	86.3
DIBP	0	107	0	140	0	108
DBP	0	103	23.5	129	0	131
BMPP	0	116	0	123	0	130
BMEP	0	36.0	0	39.1	0	20.7
DAP	0	75.0	0	130	6.6	76.0
BEEP	0	78.3	0	99.0	0	69.0
HEHP	0	118	0	134	0	127
DHP	0	72.0	0	61.0	0	53.0
BBP	0	91.0	0	102	0	102
BBEP	0	113	0	188	0	103
DEHP	0	107[a]	0	113[a]	0	110[a]
DCP	0	106	0	109	0	102
DOP	0	125	0	131	0	114
DNP	0	100	0	112	0	94.7

[a]Not corrected for method blank; if corrected, recovery would become 0. Study conducted in the presence of OCPs indicated that the OCPs are eluted in Fraction I.

Additional experiments were performed in order to develop a procedure that allowed the determination of the phthalate esters in the presence of the organochlorine pesticides. The experimental design is presented in Table 26. Tables 27 and 28 present the recovery data and elution patterns of the 16 phthalate esters when the cartridges were eluted with hexane/ methylene chloride and then hexane/ethyl acetate. In absence of the organochlorine pesticides, the phthalate esters were recovered from the Florisil cartridge with hexane with 10 percent ethyl acetate. However only BMPP, HEHP, BBP, DCP, DOP, and DNP had satisfactory recoveries (recovery >70 percent). The remainder of the phthalate esters were either not recovered at all (e.g., BBEP) or had very low recoveries. When the organochlorine pesticides were spiked together with the phthalate esters on the Florisil cartridges and the cartridges were eluted with various combinations of hexane/methylene chloride, most of the organochlorine pesticides were eluted from the cartridges with hexane/methylene chloride. Nonetheless, we had difficulties in quantifying the phthalate esters in the hexane/ethyl acetate fraction. High recoveries of some of the 16 phthalate esters were attributed to interferents eluted from the cartridge by hexane with 10 percent ethyl acetate and/or to contaminants in ethyl acetate that interfere with the phthalate ester determination (Table 28).

Interferences in the determination of phthalate esters caused by the organochlorine pesticides are presented in Table 29, and method blank analysis data for Florisil cartridges are presented in Table 30.

The Florisil procedure was further evaluated using extracts of environmental samples spiked with the 16 phthalate esters at known concentrations. The results presented in Table 31 indicate that recoveries were greater than 74 percent except for BEEP phthalate (recovery ranges from 24 to 62 percent) and BMEP phthalate which could not be recovered at all in Fraction 2.

When using these cartridges for the cleanup of extracts with the phthalate esters as the target analytes, method blanks need to be obtained for each batch of cartridges used. The SPE cartridges contain the adsorbent material in a polypropylene housing, and polyethylene frits are used to hold the adsorbent material in place. Junk and co-workers (6) found C_{10} to C_{28} isomeric alkenes, 2,6-di-*tert*-butyl-p-cresol, and alkyl phthalates in procedural blanks obtained by washing the polypropylene housing or the polyethylene frits with ethyl acetate, methanol, and water. We have analyzed Florisil SPE cartridges for the target analytes and found several phthalate esters in procedural blanks (Table 32); however, their levels were not high enough to interfere with the chromatographic determination of the organochlorine pesticides or the phenols, and the preconditioning of cartridges should minimize sample contamination. Furthermore, the volume of solvents needed to elute the interferents or the target analytes from the cartridge is small (5 mL), and the residence time of the solvent in the cartridge is less than 5 min, making it quite desirable for use.

5.3 PHENOLS

Silica cartridges were evaluated for their use in the phenol analysis. These cartridges were chosen because the current SW-846 Method 3630 recommends use of silica gel for cleanup of sample extracts that were derivatized with pentafluorobenzyl bromide (PFBBr). More specifically, a 4-g silica column is preeluted with 6 mL hexane, the derivatized extract is loaded on the column, the column is eluted first with hexane (6 mL), then with 10 mL hexane with 15 percent toluene (Fraction 1), 10 mL hexane with 40 percent toluene (Fraction 2), 10 mL hexane with 75 percent toluene (Fraction 3), and 10 mL toluene with 15 percent 2-propanol (Fraction 4). Under these conditions, 9 derivatized phenols spread over the 4 fractions.

TABLE 26. EXPERIMENTAL DESIGN FOR FLORISIL CARTRIDGE CLEANUP METHOD DEVELOPMENT[a]

Sample identification	Amount spiked (ng) Phthalate esters	Amount spiked (ng) OCPs	Fraction I (5 mL)	Fraction II (5 mL)
8712-013-1	500	500	Hexane	Hexane/diethyl ether (1:1)
8712-013-2	500	500	Hexane	Hexane/diethyl ether (1:1)
8712-013-3	500	500	Hexane	Hexane/diethyl ether (1:1)
8712-013-4	500	500	Hexane	Hexane/acetone (9:1)
8712-013-5	500	500	Hexane	Hexane/acetone (9:1)
8712-013-6	500	500	Hexane	Hexane/acetone (9:1)
8712-013-7	500	500	Hexane/methylene chloride (4:1)	Hexane/methylene chloride (4:1)
8712-013-8	500	500	Hexane/methylene chloride (4:1)	Hexane/methylene chloride (4:1)
8712-013-9	500	500	Hexane/methylene chloride (4:1)	Hexane/methylene chloride (4:1)
8712-013-10	500	0	Hexane/methylene chloride (4:1)	Hexane/acetone (9:1)
8712-013-11	500	0	Hexane/methylene chloride (4:1)	Hexane/acetone (9:1)
8712-013-12	500	0	Hexane/methylene chloride (4:1)	Hexane/acetone (9:1)
8712-013-13	0	500	Hexane/methylene chloride (4:1)	Hexane/acetone (9:1)
8712-013-14	0	500	Hexane/methylene chloride (4:1)	Hexane/acetone (9:1)
8712-013-15	0	500	Hexane/methylene chloride (4:1)	Hexane/acetone (9:1)
8712-013-16	500	500	Hexane/methylene chloride (4:1)	Hexane/acetone (9:1)
8712-013-17	500	500	Hexane/methylene chloride (4:1)	Hexane/acetone (9:1)
8712-013-18	500	500	Hexane/methylene chloride (4:1)	Hexane/acetone (9:1)
8712-013-22	0	0	Hexane/methylene chloride (4:1)	Hexane/acetone (9:1)

(continued)

TABLE 26. (continued)

Sample identification	Amount spiked (ng) Phthalate esters	OCPs	Fraction I (5 mL)	Fraction II (5 mL)
8712-013-23	0	0	Hexane/methylene chloride (85:15)	Hexane/acetone (9:1)
8712-013-24	500	0	Hexane/methylene chloride (85:15)	Hexane/ethyl acetate (9:1)
8712-013-25	500	0	Hexane/methylene chloride (85:15)	Hexane/ethyl acetate (9:1)
8712-013-26	500	0	Hexane/methylene chloride (85:15)	Hexane/ethyl acetate (9:1)
8712-013-27	500	0	Hexane/methylene chloride (75:25)	Hexane/ethyl acetate (9:1)
8712-013-28	500	0	Hexane/methylene chloride (75:25)	Hexane/ethyl acetate (9:1)
8712-013-29	500	0	Hexane/methylene chloride (75:25)	Hexane/ethyl acetate (9:1)
8712-013-30	500	0	Hexane/methylene chloride (70:30)	Hexane/ethyl acetate (9:1)
8712-013-31	500	0	Hexane/methylene chloride (70:30)	Hexane/ethyl acetate (9:1)
8712-013-32	500	0	Hexane/methylene chloride (70:30)	Hexane/ethyl acetate (9:1)
8712-013-33	0	500	Hexane/methylene chloride (85:15)	Hexane/ethyl acetate (9:1)
8712-013-34	0	500	Hexane/methylene chloride (75:25)	Hexane/ethyl acetate (9:1)
8712-013-35	0	500	Hexane/methylene chloride (70:30)	Hexane/ethyl acetate (9:1)
8712-013-36	500	500	Hexane/methylene chloride (85:15)	Hexane/ethyl acetate (9:1)
8712-013-37	500	500	Hexane/methylene chloride (85:15)	Hexane/ethyl acetate (9:1)
8712-013-38	500	500	Hexane/methylene chloride (85:15)	Hexane/ethyl acetate (9:1)
8712-013-39	500	500	Hexane/methylene chloride (75:25)	Hexane/ethyl acetate (9:1)
8712-013-40	500	500	Hexane/methylene chloride (75:25)	Hexane/ethyl acetate (9:1)
8712-013-41	500	500	Hexane/methylene chloride (75:25)	Hexane/ethyl acetate (9:1)
8712-013-42	500	500	Hexane/methylene chloride (70:30)	Hexane/ethyl acetate (9:1)

(continued)

TABLE 26. (concluded)

Sample identification	Amount spiked (ng) Phthalate esters	OCPs	Fraction I (5 mL)	Fraction II (5 mL)
8712-013-43	500	500	Hexane/methylene chloride (70:30)	Hexane/ethyl acetate (9:1)
8712-013-44	500	500	Hexane/methylene chloride (70:30)	Hexane/ethyl acetate (9:1)
8712-013-45	0	0	Hexane/methylene chloride (85:15)	Hexane/ethyl acetate (9:1)
8712-013-46	0	0	Hexane/methylene chloride (75:15)	Hexane/ethyl acetate (9:1)
8712-013-47	0	0	Hexane/methylene chloride (70:30)	Hexane/ethyl acetate (9:1)

(continued)

[a]1-g Florisil cartridges were used. The 16 phthalate esters and the organochlorine pesticides (OCPs) were spiked at 500 ng per component or not at all as indicated.

TABLE 27. RECOVERY OF PHTHALATE ESTERS FROM 1-g FLORISIL CARTRIDGES BY ELUTION WITH HEXANE WITH 15 PERCENT, 25 PERCENT, AND 30 PERCENT METHYLENE CHLORIDE (FRACTION I) AND HEXANE WITH 10 PERCENT ETHYL ACETATE (FRACTION II)[a]

	Percent recovery																	
	8712-013-24 Fraction		8712-013-25 Fraction		8712-013-26 Fraction		8712-013-27 Fraction		8712-013-28 Fraction		8712-013-29 Fraction		8712-013-30 Fraction		8712-013-31 Fraction		8712-013-32 Fraction	
Compound	I	II	I	II	I	II	I	II	I	II	I	II	I	II	I	II	I	II
DMP	7.5	7.0	5.7	6.6	4.1	0	0	13.0	12.3	0	12.6	2.2	4.4	4.3	13.6	13.2	12.8	12.4
DEP	0	34.5	0	37.9	0	40.1	0	65.8	0	27.3	12.9	38.6	0	26.6	0	27.2	0	24.8
DIBP	0	98.0	0	60.4	0	64.2	0	64.6	0	60.7	0	89.8	0	58.6	0	53.6	0	56.1
DBP	13.1	65.0	13.5	80.0	0	85.0	0	112	0	83.7	0	69.8	0	49.8	0	52.4	0	51.9
BMPP	0	101	0	102	0	105	0	102	0	90.7	0	96.6	0	79.4	0	78.7	0	79.4
BMEP	0	0	0	21.0	0	32.8	0	23.4	0	24.2	0	24.2	0	0	0	18.9	0	18.2
DAP	0	156	0	161	0	166	0	143	0	179	0	184	0	159	0	108	0	103
BEEP	0	6.0	0	6.2	0	5.0	0	6.8	0	0	0	17.6	0	0	0	0	0	0
HEHP	13.7	91.0	0	90.0	0	101	0	110	0	120	14.7	89.3	0	115	0	120	0	101
DHP	49.0	40.1	40.2	42.5	43.3	44.3	46.2	50.9	46.2	44.9	80.5	51.3	0	50.7	0	47.2	0	49.2
BBP	4.0	73.0	0	81.0	0	89.0	27.3	95.4	24.7	84.4	29.2	93.4	3.7	101	6.5	106	1.5	103
BBEP	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
DEHP	0	54.0	0	46.0	0	56.0	0	31.3	0	36.2	0	36.0	0	50.0	0	43.9	0	44.9
DCP	0	125	0	97.5	0	110	0	110	0	100	0	108	0	142	0	142	0	148
DOP	0	94.2	0	95.3	0	107	0	108	0	99.8	0	108	0	104	0	100	0	106
DNP	0	80.3	0	75.4	0	82.9	0	93.4	0	81.1	0	78.8	0	105	0	115	0	94.3

[a]The spiking level was 500 ng of each phthalate ester per cartridge.

TABLE 28. RECOVERY OF PHTHALATE ESTERS FROM 1-g FLORISIL CARTRIDGE IN THE PRESENCE OF ORGANOCHLORINE PESTICIDES BY ELUTION WITH HEXANE WITH 15 PERCENT, 20 PERCENT, AND 30 PERCENT METHYLENE CHLORIDE (FRACTION I) AND HEXANE WITH 10 PERCENT ETHYL ACETATE (FRACTION II)[a]

	Percent Recovery								
Compound	8712-013-36 Fraction II	8712-013-37 Fraction II	8712-013-38 Fraction II	8712-013-39 Fraction II	8712-013-40 Fraction II	8712-013-41 Fraction II	8712-013-42 Fraction II	8712-013-43 Fraction II	8712-013-44 Fraction II
DMP	160[b]	172[b]	174[b]	118	112	101	120	113	114
DEP	49.5	57.5	60.0	63.2	56.3	56.7	40.2	51.1	34.9
DIBP	150[b]	105	108	98.2	108	99.0	92.5	95.8	97.6
DBP	123	121	115	118	121	108	109	106	102
BMPP	1560[b]	74.9	72.7	78.8	116	110	109	102	102
BMEP	138[b]	645[b]	224[b]	456[b]	162[b]	185[b]	124	210[b]	367[b]
DAP	5,550[b]	5,620[b]	5,530[b]	1,420[b]	1,410[b]	850[b]	1,640[b]	454[b]	881[b]
BEEP	ND	ND	ND	28.3	26.3	29.2	29.0	24.2	25.7
HEHP	112	102	103	108	113	110	110	88.6	99.7
DHP	137[b]	123	129[b]	146[b]	120	113	126[b]	92.7	110
BBP	123	124	117	127[b]	125	129[b]	117	106	121
BBEP	560[b]	520[b]	530[b]	338[b]	362[b]	274[b]	335[b]	171[b]	227[b]
DEHP	135[b]	119	112	151[b]	128[b]	119	220[b]	181[b]	249[b]
DCP	112	104	97.8	110	110	112	103	94.3	107
DOP	117	118	109	126[b]	123	126[b]	112	90.7	111
DNP	43.0	40.6	38.4	42.0	43.6	43.8	45.2	38.3	44.3

[a] The spiking level was 500 ng per phthalate ester per cartridge. The OCPs were also spiked at 500 ng per component per cartridge.

[b] High recovery due to interferents eluted from the cartridge by hexane with 10 percent ethyl acetate and/or contaminants in ethyl acetate.

TABLE 29. INTERFERENCES IN THE DETERMINATION OF PHTHALATE ESTERS CAUSED BY ORGANOCHLORINE PESTICIDES

	Concentration (ng/mL)[a]											
	8712-013-13 Fraction		8712-013-14 Fraction		8712-014-15 Fraction		8712-013-33 Fraction		8712-013-34 Fraction		8712-013-35 Fraction	
Compound	I	II	I	II	I	II	I	II	I[b]	II	I[b]	II
DMP	ND[c]	260	ND	227	45.2	205	ND	208		137		143
DEP	ND	ND	ND	ND	ND	37.7	ND	ND		ND		ND
DIBP	23.2	24.5	57.3	70.4	50.9	66.6	45.6	20.4		30.3		36.3
DBP	64.1	34.0	26.2	30.0	27.8	26.7	28.6	20.8		ND		ND
BMPP	1,810	660	2,250	386	2,020	19.8	1,260	18.0		130		ND
BMEP	6,160	23.8	6,420	325	6,274	544	7,510	585		313		293
DAP	370	4,220	2,070	2,870	857	3,960	557	6,200		1,110		491
BEEP	ND	ND	ND	32.7	38.2	32.1	60.4	22.1		21.7		22.1
HEHP	3,070	30.9	3,270	69.9	3,120	251	3,540	21.7		19.9		150
DHP	42.2	122	52.6	103	63.8	89.4	65.1	107		87.2		63.0
BBP	33.2	36.3	37.2	31.7	34.5	30.5	35.8	36.5		33.2		28.5
BBEP	ND	586	31.6	583	ND	606	ND	629		346		99.1
DEHP	48.4	70.4	53.0	129	69.3	112	65.9	219		124		76.6
DCP	ND	ND	ND	ND	ND	ND	ND	ND		ND		ND
DOP	ND	ND	ND	ND	ND	ND	ND	ND		ND		ND
DNP	ND	ND	ND	ND	ND	ND	ND	ND		ND		ND

[a] The Florisil cartridges were charged only with OCPs. The various peaks detected in these fractions as phthalate esters are probably not only contaminants in the OCP standards and other materials but also OCPs eluting at the same retention times as the target analytes.
[b] Analysis did not pass QC criteria, results are therefore not reported.
[c] ND -- not detected; detection limit was approximately 10 ng/mL.

TABLE 30. RESULTS OF METHOD BLANK ANALYSES FOR THE FLORISIL CARTRIDGES

	Concentration (ng/mL)[a]									
	8712-013-22 Fraction		8712-013-23 Fraction		8712-013-45 Fraction		8712-013-46 Fraction		8712-013-47 Fraction	
Compound	I	II	I	II	I	II	I	II	I	II
DMP	40.7	151	51.9	200	12.4	55.4	17.0	33.2	24.2	32.4
DEP	ND[b]	ND	ND	ND	ND	ND	ND	ND	ND	ND
DIBP	ND	ND	22.8	22.1	ND	ND	ND	ND	ND	ND
DBP	ND	26.8	ND	30.1	ND	36.8	36.6	13.9	ND	33.1
BMPP	ND	ND	ND	ND	ND	ND	ND	ND	ND	16.4
BMEP	ND	ND	ND	ND	ND	18.5	ND	ND	ND	17.9
DAP	63.9	137	ND	139	ND	ND	46.8	ND	61.8	ND
BEEP	ND	16.3	18.8	18.2	ND	14.9	ND	14.8	ND	20.7
HEHP	33.9	18.6	18.3	ND	ND	16.7	ND	ND	ND	ND
DHP	50.6	49.8	ND	54.4	ND	40.0	ND	38.2	49.0	35.1
BBP	24.9	30.2	35.9	37.5	35.7	35.9	ND	35.6	27.1	24.7
BBEP	ND	ND	ND	ND	ND	ND	59.1	ND	ND	56.7
DEHP	68.8	121	100	114	60.2	56.1	81.1	61.1	58.2	58.1
DCP	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
DOP	52.2	ND	64.1	ND	ND	ND	ND	ND	ND	ND
DNP	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

[a] The Florisil cartridge (1 g) was eluted with 5 mL hexane/methylene chloride (4:1) and 5 mL hexane/acetone (9:1) in the case of samples 8712-013-22, -23, and 5 mL of 85:15, 75:25, and 70:30 hexane/methylene chloride for samples -45, -46, and -47. Fraction 2 for samples -45, -46, -47 was eluted with 5 mL hexane/ethyl acetate (9:1). Final volume of each fraction was 5 mL.

[b] ND -- not detected; detection limit was approximately 10 ng/mL.

TABLE 31. PERCENT RECOVERIES OF PHTHALATE ESTERS IN EXTRACTS FROM VARIOUS MATRICES SUBJECTED TO FLORISIL CARTRIDGE CLEANUP WITH HEXANE/METHYLENE CHLORIDE (4:1) AND HEXANE/ACETONE (9:1) AS ELUANTS[a]

Compound	Sandy loam soil[b]	Sediment of undefined origin	NBS SRM-1572	NBS SRM-1632a	NBS SRM-1633a
DMP	78	75	80	76	82
DEP	79	79	89	79	84
DIBP	79	82	90	108	86
DBP	74	78	84	83	83
BMPP	77	84	102	91	86
BMEP	0	0	0	0	0
DAP	82	86	100	76	89
BEEP	37	24	62	32	33
HEHP	80	88	95	93	81
DHP	78	88	86	92	80
BBP	82	99	114	102	98
BBEP	86	94	98	106	98
DEHP	74	85	108	88	112
DCP	91	96	106	98	95
DOP	80	92	104	95	88
DNP	84	96	106	111	92

[a] The spiking level was 50 ng/mL of extract for each compound. Data shown are for Fraction 2 which was eluted with 5 mL hexane/acetone (9:1).

[b] Sandy loam soil from Puyallup, Washington, with the following characteristics: pH 5.9 to 6.0; 89 percent sand, 7 percent silt, 4 percent clay; cation exchange capacity 7 meg/100 g; total organic carbon content 1,290 ± 185 mg/Kg.

TABLE 32. METHOD DETECTION LIMIT STUDY—FLORISIL CARTRIDGES METHOD BLANKS

	Concentration (ng/cartridge)[a]						
Compound	Rep.1	Rep.2	Rep.3	Rep.4	Rep.5	Average	SD
DMP	412	411	466	495	496	456	42
DEP	192	76.2	155	228	144	159	66
DIBP	94.7	96.6	107	119	107	105	10
DBP	129	116	142	162	132	136	17
BMPP	60.0	73.3	106	152	51.9	88.6	41
BMEP	303	134	302	291	282	262	72
DAP	28.4	40.3	140	33.6	22.0	52.9	49
BEEP	69.2	61.9	65.3	64.2	71.2	66.4	4
HEHP	43.9	16.2	40.3	12.9	4.7	23.6	17
DHP	32.9	29.3	31.6	35.8	33.2	32.6	2
BBP	16.6	16.1	16.6	24.3	18.2	18.4	3
BBEP	30.4	29.8	42.2	59.0	43.1	40.9	12
DEHP	295	267	332	320	243	291	37
DCP	<10	<10	<10	18.2	<10	<10	—
DOP	<10	<10	<10	13.8	<10	<10	—
DNP	<10	<10	<10	<10	<10	<10	—

[a] Each Florisil cartridge (Supelco, Inc.) was eluted with 5 mL hexane with 20 percent methylene chloride (Fraction 1) which was discarded, followed by 5 mL of hexane/acetone (9:1) which was concentrated to 1 mL and analyzed by GC/ECD. The GC/ECD operating conditions were as follows: 30 m x 0.25 mm ID DB-5 fused-silica capillary column (0.25 μm film thickness); 120°C to 260°C (hold 15.7 min) at 15°C/min; carrier gas helium at 21 psi; injector temperature 275°C; detector temperature 320°C; splitless injection.

We have taken 1-g silica cartridges, charged them with the PFB derivatives of 20 phenols, and eluted the cartridges with 4 mL hexane followed by 5 mL hexane with 25 percent toluene. Under these conditions, we got quantitative recoveries of 18 of the 20 compounds. When 0.5-g silica cartridges were evaluated at three spike levels (Table 33), we found that the 18 phenols elute primarily in Fraction 1.

As the cartridge size increases, we see a crossover into Fraction 2 (Table 34), and when the 2-g cartridges were used, 18 compounds were recovered quantitatively in Fraction 2 (Table 35).

Matrix interferents such as corn oil, diesel hydrocarbons, and elemental sulfur were added to hexane solutions of the target phenols at known concentrations, and the solutions were then subjected to the silica cartridge cleanup procedure to establish if any changes occurred in the compound elution pattern and in their recovery when matrix interferents were present (Table 36). No change in compound recovery or elution pattern was observed.

The silica cartridge procedure for the phenols was tested with three extracts of environmental samples spiked with the target compounds at known concentrations. After spiking, the extracts were derivatized with PFBBr using the Lee, et al., procedure (2) and cleaned by the silica cartridge cleanup procedure. The recovery data are presented in Table 37.

5.4 EVALUATION OF THE ASPEC SYSTEM

The Gilson ASPEC system (Automatic Sample Preparation with Extraction Columns) was loaned to us for a period of three weeks by Gilson Medical Electronics, Inc. The ASPEC system is designed to receive either 100-mg cartridges or 500-mg cartridges. The ASPEC software comprises several prestored programs and 8 KB of user memory for free programming. In the standard program, the user enters the parameters via a limited number of easy prompts that indicate the conditioning step, washing step, elution step, and collected fraction mixing step.

We have used the standard program available with the instrument (File 165) and modified it to allow the evaluation of the silica and diol cartridges for the cleanup of samples containing organochlorine pesticides and Aroclor 1260 (Tables 38, 39, and 40) or organochlorine pesticides and corn oil, diesel hydrocarbons, Aroclor 1260, and elemental sulfur (Table 41). Furthermore, sample extracts (identified as SS-2, SS-5, SS-7 and SS-8) were processed using the ASPEC system and 0.5-g diol cartridges (Tables 42 through 45).

Overall, the method reproducibility using the ASPEC system with the 0.5-g diol cartridges is excellent. Thirteen out of 17 organochlorine pesticides had RSDs under 4 percent (Table 40), and there was no crosscontamination when interferents were added such as corn oil, diesel hydrocarbons, and when sample extracts were used.

Slight modifications to the cartridge procedure had to be made when using the ASPEC system. For example, the ASPEC system does not allow collection of more than one fraction per extract. Since the silica cartridge procedure for the organochlorine pesticides calls for elution of the cartridge with 5 mL hexane followed by 5 mL hexane with 50 percent diethyl ether, we first eluted the cartridges with 5 mL hexane which was discarded and followed with 3.5 mL hexane with 50 percent diethyl ether (Table 38). Under those conditions, heptachlor, aldrin, 4,4′-DDE, and 4,4′-DDT were not recovered since they are eluted from the cartridge with hexane. To collect Fraction 1, we had to elute all cartridges on the ASPEC rack with

TABLE 33. ELUTION PATTERNS AND PERCENT RECOVERIES OF THE PFB DERIVATIVES OF PHENOLS FROM 0.5-g SILICA CARTRIDGES[a]

Compound	Spiked at 0.4 μg per cartridge				Spiked at 0.2 μg per cartridge				Spiked at 0.05 μg per cartridge			
	Fraction 1		Fraction 2		Fraction 1		Fraction 2		Fraction 1		Fraction 2	
Phenol	87.3	90.0	0	0	79.0	82.8	9.8	10.8	69.0	70.5	5.0	4.8
2-Methylphenol	103	103	0	0	96.8	99.3	0	0	88.3	88.3	0	0
3-Methylphenol	100	100	0	0	96.8	100	7.5	15.8	86.0	86.8	4.5	4.5
4-Methylphenol	94.9	85.1	5.1	14.9	88.8	93.3	16.3	0	76.5	77.5	10.5	9.8
2,4-Dimethylphenol	100	100	0	0	108	111	0	0	90.8	91.0	0	0
2-Chlorophenol	87.1	73.6	12.9	26.4	87.3	94.3	24.8	18.3	76.5	77.0	13.5	13.5
2,6-Dichlorophenol	113	113	0	0	112	114	0	0	92.3	92.8	0	0
4-Chloro-3-methylphenol	115	112	0	0	113	114	0	0	93.8	94.3	0	0
2,4-Dichlorophenol	88.9	76.6	11.1	23.4	93.3	101	22.8	17.7	81.5	82.8	12.8	13.0
2,4,6-Trichlorophenol	119	121	0	0	116	120	0	0	97.3	96.8	0	0
2,3,6-Trichlorophenol	117	118	0	0	113	115	0	0	98.0	97.8	0	0
2-Nitrophenol	ND[b]	ND	ND	ND	ND	ND	ND	ND	ND	ND	64.0	42.3
2,4,5-Trichlorophenol	69.8	80.5	30.2	29.5	122	126	0	0	90.8	90.5	0	0
2,3,5-Trichlorophenol	69.8	80.5	30.2	29.5	122	126	0	0	90.8	90.5	0	0
2,3,5,6-Tetrachlorophenol	103	100	0	0	107	110	0	0	104	104	0	0
2,3,4,6-Tetrachlorophenol	85.0	76.3	15.0	23.7	106	108	0	0	102	100	0	0
2,3,4-Trichlorophenol	89.5	91.3	19.4	31.5	54.0	68.5	51.3	39.6	64.0	55.8	40.7	48.5
2,3,4,5-Tetrachlorophenol	111	104	0	0	91.3	94.3	12.0	10.5	98.0	95.8	10.3	10.3
Pentachlorophenol	117	119	0	0	104	105	0	0	117	114	0	0
2,4-Dinitrophenol	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

[a] 0.5-g silica cartridges (Supelco lot SP0161) were used in this experiment. Each cartridge was conditioned with 4 mL hexane prior to use. Fraction 1 was eluted with 5 mL hexane. Fraction 2 was eluted with 5 mL hexane with 25 percent toluene. The two values given for each fraction represent data from duplicate experiments.

[b] ND -- not detected.

TABLE 34. ELUTION PATTERNS AND PERCENT RECOVERIES OF THE PFB DERIVATIVES OF PHENOLS FROM 1-g SILICA CARTRIDGES[a]

Compound	Spiked at 0.4 μg per cartridge				Spiked at 0.2 μg per cartridge				Spiked at 0.05 μg per cartridge			
	Fraction 1		Fraction 2		Fraction 1		Fraction 2		Fraction 1		Fraction 2	
Phenol	0	0	95.6	96.5	9.8	10.1	74.0	62.3	26.5	23.5	49.5	52.0
2-Methylphenol	8.8	34.6	101	79.0	0	0	78.1	62.2	81.8	81.5	14.5	13.2
3-Methylphenol	0	0	112	111	0	0	87.7	72.6	28.3	23.8	66.0	70.0
4-Methylphenol	0	0	113	114	0	0	89.0	72.6	15.3	11.0	78.3	81.0
2,4-Dimethylphenol	0	17.6	115	104	0	0	94.5	74.7	71.0	71.0	29.0	28.8
2-Chlorophenol	0	0	119	117	0	0	91.1	76.0	0	0	93.8	94.5
2,6-Dichlorophenol	59.8	89.0	69.8	37.1	41.6	36.7	55.5	47.3	97.3	95.8	5.3	4.5
4-Chloro-3-methylphenol	0	0	119	110	0	0	94.5	78.1	64.0	63.0	37.0	36.8
2,4-Dichlorophenol	0	0	122	123	0	0	96.6	80.8	5.0	0	98.5	100
2,4,6-Trichlorophenol	119	120	7.4	4.9	96.6	94.5	0	0	103	102	0	0
2,3,6-Trichlorophenol	96.8	109	31.3	14.5	73.3	67.5	22.9	25.5	103	101	5.3	5.3
2-Nitrophenol	ND[b]	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
2,4,5-Trichlorophenol	3.3	15.3	109	106	0	0	100	87.0	51.8	49.8	43.3	44.5
2,3,5-Trichlorophenol	3.3	15.3	109	106	0	0	100	87.0	51.8	49.8	43.3	44.5
2,3,5,6-Tetrachlorophenol	122	121	5.6	4.1	89.7	88.4	0	0	110	108	0	0
2,3,4,6-Tetrachlorophenol	122	121	5.6	4.1	87.7	88.4	0	0	112	110	0	0
2,3,4-Trichlorophenol	88.6	42.5	5.1	57.5	0	0	87.7	78.1	0	0	112	109
2,3,4,5-Tetrachlorophenol	0	0	118	119	0	0	89.0	82.9	16.8	12.8	93.3	98.8
Pentachlorophenol	118	116	6.1	6.3	86.3	85.6	0	0	126	122	5.8	5.3
2,4-Dinitrophenol	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

[a] 1-g silica cartridges (Supelco lot SP0161) were used in this experiment. Each cartridge was conditioned with 4 mL hexane prior to use. Fraction 1 was eluted with 5 mL hexane. Fraction 2 was eluted with 5 mL hexane with 25 percent toluene. The two values given for each fraction represent data from duplicate experiments.

[b] ND -- not detected.

TABLE 35. ELUTION PATTERNS AND PERCENT RECOVERIES OF THE PFB DERIVATIVES OF PHENOLS FROM 2-g SILICA CARTRIDGES[a]

Compound	Spiked at 0.4 μg per cartridge				Spiked at 0.2 μg per cartridge				Spiked at 0.05 μg per cartridge			
	Fraction 1		Fraction 2		Fraction 1		Fraction 2		Fraction 1		Fraction 2	
Phenol	0	0	70.8	79.4	14.5	15.0	72.8	72.8	0	0	76.2	72.3
2-Methylphenol	0	0	77.8	87.2	0	0	80.4	80.4	0	0	94.3	88.8
3-Methylphenol	0	0	79.2	87.2	0	0	84.2	82.9	0	0	94.8	90.3
4-Methylphenol	0	0	79.2	87.2	0	0	80.4	81.0	0	0	87.3	81.0
2,4-Dimethylphenol	0	0	84.7	95.2	0	0	89.9	91.1	0	0	98.3	91.5
2-Chlorophenol	0	0	82.6	92.8	0	0	85.4	88.6	0	0	90.3	91.5
2,6-Dichlorophenol	0	0	85.4	83.3	0	0	91.1	91.8	0	0	100	90.5
4-Chloro-3-methylphenol	0	0	87.5	99.2	0	0	91.1	93.7	0	0	103	91.8
2,4-Dichlorophenol	0	0	88.9	100	0	0	93.7	95.6	0	0	100	88.5
2,4,6-Trichlorophenol	0	0	90.3	100	0	0	98.8	100	0	0	105	92.5
2,3,6-Trichlorophenol	0	0	88.2	98.4	0	0	93.0	94.9	0	0	106	93.0
2-Nitrophenol	ND[b]	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
2,4,5-Trichlorophenol	0	0	80.6	92.0	0	0	97.5	99.4	0	0	99.3	84.8
2,3,5-Trichlorophenol	0	0	80.6	92.0	0	0	97.5	99.4	0	0	99.3	84.8
2,3,5,6-Tetrachlorophenol	0	0	100	96.0	0	0	90.5	90.5	0	0	110	98.0
2,3,4,6-Tetrachlorophenol	0	0	100	96.0	0	0	89.9	91.8	0	0	109	95.3
2,3,4-Trichlorophenol	0	0	67.6	74.3	0	0	77.8	85.4	0	0	70.0	58.5
2,3,4,5-Tetrachlorophenol	0	0	87.5	98.4	0	0	85.4	88.4	0	0	111	100
Pentachlorophenol	0	0	85.4	89.6	0	0	87.3	91.1	0	0	122	102
2,4-Dinitrophenol	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

[a] 2-g silica cartridges (Supelco lot SP0161) were used in this experiment. Each cartridge was conditioned with 4 mL hexane prior to use. Fraction 1 was eluted with 5 mL hexane. Fraction 2 was eluted with 5 mL hexane with 25 percent toluene. The two values given for each fraction represent data from duplicate experiments.

[b] ND -- not detected.

TABLE 36. PERCENT RECOVERIES AND ELUTION PATTERNS OF PHENOLS FROM 1-g SILICA CARTRIDGES IN THE PRESENCE OF CORN OIL AND DIESEL HYDROCARBONS

	Corn oil as interferent				Diesel hydrocarbons as interferents			
Compound	Fraction 1		Fraction 2		Fraction 1		Fraction 2	
Phenol	0	0	68.8	69.4	0	0	57.6	61.2
2-Methylphenol	5.0	0	85.9	87.9	0	7.0	77.9	80.6
3-Methylphenol	0	0	82.8	83.8	0	0	75.1	79.6
4-Methylphenol	0	0	71.0	68.6	0	0	62.0	68.2
2,4-Dimethylphenol	0	0	84.2	84.8	0	0	74.6	80.1
2-Chlorophenol	0	0	80.6	80.9	0	0	71.6	77.0
2,6-Dichlorophenol	35.8	18.9	63.1	72.8	9.9	30.6	69.0	64.2
4-Chloro-3-methylphenol	0	0	78.9	78.4	0	0	70.8	75.6
2,4-Dichlorophenol	0	0	80.7	80.3	0	0	71.4	77.6
2,4,6-Trichlorophenol	87.0	81.6	0	8.1	76.4	86.0	6.5	6.6
2,3,6-Trichlorophenol	61.6	45.5	33.2	48.7	34.9	57.1	46.2	37.2
2-Nitrophenol	ND[b]	ND	ND	ND	ND	ND	ND	ND
2,4,5-Trichlorophenol	0	0	126	125	0	0	118	123
2,3,5-Trichlorophenol	0	0	126	125	0	0	118	123
2,3,5,6-Tetrachlorophenol	88.4	83.1	0	5.0	78.4	89.7	0	5.1
2,3,4,6-Tetrachlorophenol	93.6	83.4	4.7	9.9	80.0	93.3	7.9	8.1
2,3,4-Trichlorophenol	0	0	76.5	76.6	0	0	74.5	78.0
2,3,4,5-Tetrachlorophenol	0	0	82.0	81.8	0	0	74.4	81.6
Pentachlorophenol	74.9	70.7	0	0	66.5	76.4	5.3	4.8
2,4-Dinitrophenol	ND	ND	ND	ND	ND	ND	ND	ND

[a] 1-g silica cartridges (J. T. Baker lot B51505) were used in this experiment. Each cartridge was conditioned with 4 mL hexane prior to use. Fraction 1 was eluted with 5 mL hexane. Fraction 2 was eluted with 5 mL hexane with 25 percent toluene. Spiking level was 0.4 μg of derivatized phenols per cartridge.
[b] ND -- not detected.

TABLE 37. PERCENT RECOVERIES AND ELUTION PATTERNS OF PHENOLS FROM 1-g SILICA CARTRIDGES IN THE PRESENCE OF MATRIX INTERFERENTS

Compound	Sample 1				Sample 2				Sample 3			
	Fraction 1		Fraction 2		Fraction 1		Fraction 2		Fraction 1		Fraction 2	
Phenol	0	0	67.6	68.3	0	0	72.8	66.3	0	0	64.8	63.4
2-Methylphenol	4.5	2.6	75.1	76.9	0	0	54.4	49.0	0	0	68.0	66.3
3-Methylphenol	0	0	74.3	74.4	0	0	85.1	48.6	0	0	68.6	66.9
4-Methylphenol	0	0	47.1	44.3	0	0	85.1	30.1	0	0	43.1	42.0
2,4-Dimethylphenol	0	0	64.4	64.9	0	0	35.1	30.6	0	0	51.2	49.3
2-Chlorophenol	0	0	77.5	77.6	0	0	80.1	74.6	0	0	79.2	78.2
2,6-Dichlorophenol	32.4	23.5	61.3	67.9	18.8	10.9	74.0	72.5	20.0	18.9	71.5	70.1
4-Chloro-3-methylphenol	0	0	74.9	75.5	0	0	78.6	72.3	0	0	77.4	76.3
2,4-Dichlorophenol	0	0	78.3	78.4	0	0	80.6	74.6	0	0	79.7	77.9
2,4,6-Trichlorophenol	78.6	77.3	5.6	10.2	77.1	70.8	13.4	10.3	76.3	74.7	11.6	11.0
2,3,6-Trichlorophenol	56.1	47.1	32.4	44.0	43.0	32.3	51.6	50.8	43.3	42.0	48.8	47.8
2-Nitrophenol	ND[b]	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
2,4,5-Trichlorophenol	0	0	68.8	68.5	0	0	133	124	0	0	123	122
2,3,5-Trichlorophenol	0	0	68.8	68.5	0	0	133	124	0	0	123	122
2,3,5,6-Tetrachlorophenol	79.8	79.1	3.9	7.4	77.0	69.9	9.5	6.9	79.0	76.9	7.5	6.9
2,3,4,6-Tetrachlorophenol	83.6	80.5	5.2	10.4	76.6	68.6	}	10.6	87.4	86.9	12.1	11.6
2,3,4-Trichlorophenol	0	0	74.3	77.8	0	0	} 101	71.3	9.6	9.6	78.5	76.1
2,3,4,5-Tetrachlorophenol	0	0	80.1	81.4	0	0	80.6	72.9	0	0	85.1	82.0
Pentachlorophenol	68.4	68.4	3.7	6.2	60.9	56.2	6.8	5.1	77.6	76.9	7.5	3.7
2,4-Dinitrophenol	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

[a] 1-g silica cartridges (J.T. Baker lot 51505) were used in this experiment. Each cartridge was conditioned with 4 mL hexane prior to use. Fraction 1 was eluted with 5 mL hexane. Fraction 2 was eluted with 5 mL hexane with 25 percent toluene. Spiking level was 0.4 µg of derivatized phenols per cartridge.

[b] ND - - Not detected.

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TABLE 38. METHOD REPRODUCIBILITY USING THE ASPEC ROBOTIC SYSTEM[a]

	OCPs only		OCPs and Aroclor 1260	
Compound	Average recovery	Percent RSD	Average recovery	Percent RSD
alpha-BHC	46.8	6.2	89.1	1.6
gamma-BHC	89.8	2.9	91.1	4.4
beta-BHC	88.5	3.6	90.4	4.7
Heptachlor	0	--	0	--
delta-BHC	88.0	3.2	89.5	5.4
Aldrin	0	--	0	--
Heptachlor epoxide	91.6	7.6	89.1	5.0
Endosulfan I	88.8	3.8	88.8	5.3
4,4′-DDE	0	--	0	--
Dieldrin	86.7	3.4	88.6	5.4
Endrin	106	4.5	110	5.8
4,4′-DDD	25.4	8.6	72.7	5.5
Endosulfan II	74.9	3.4	76.6	5.3
4,4′-DDT	0	--	17.2	96
Endrin aldehyde	35.3	5.4	32.7	7.5
Endosulfan sulfate	78.5	4.3	77.4	5.6
4,4′-Methoxychlor	89.2	8.2	86.8	6.3

[a]0.5-g silica cartridges (J. T. Baker) were used for this experiment. Each cartridge was conditioned with 4 mL hexane (speed 5; air volume 100 μL). Standard in hexane (1 mL) was added to the cartridge (height 0, speed 4, air volume 100 μL). The cartridge was washed with 5 mL hexane (speed 5, air volume 100 μL) and eluted with 3.5 mL hexane with 50 percent diethyl ether (speed 4, air volume 200 μL). Finally, to clean the lines, the cartridge was rinsed with 1 mL hexane with 50 percent diethyl ether (speed 8) and the rinse was discarded. Spiking level was 1 μg per cartridge for the OCPs and 10 μg per cartridge for Aroclor 1260. Number of determinations was 4.

TABLE 39. METHOD REPRODUCIBILITY USING THE ASPEC ROBOTIC SYSTEM[a]

	Average recovery (percent RSD)			
	OCPs only		OCPs and Aroclor 1260	
Compound	Fraction 1	Fraction 2	Fraction 1	Fraction 2
alpha-BHC	0	84.7 (2.6)	0	84.0 (1.7)
gamma-BHC	0	87.1 (2.5)	0	85.6 (1.3)
beta-BHC	0	84.4 (1.4)	0	82.2 (1.1)
Heptachlor	83.7 (3.6)	0	71.4 (7.8)	21.4 (49)
delta-BHC	0	81.5 (2.5)	0	79.4 (2.6)
Aldrin	82.6 (4.8)	0	79.9 (1.4)	0
Heptachlor epoxide	0	82.2 (3.0)	0	83.0 (2.5)
Endosulfan I	0	82.0 (3.3)	0	84.1 (2.5)
4,4′-DDE	86.2 (5.7)	0	80.5 (3.3)	8.5 (85)
Dieldrin	0	78.8 (3.2)	[b]	80.8 (2.6)
Endrin	0	88.7 (3.0)	[b]	91.5 (3.2)
4,4′-DDD	0	82.4 (2.8)	0	81.6 (1.3)
Endosulfan II	0	80.5 (2.8)	[b]	79.6 (1.7)
4,4′-DDT	67.8 (12.3)	15.4 (93)	82.9 (2.2)	[b]
Endrin aldehyde	0	21.2 (8.8)	[b]	17.7 (2.9)
Endosulfan sulfate	0	73.2 (4.6)	[b]	43.4 (2.2)
4,4′-Methoxychlor	0	78.5 (3.2)	[b]	80.4 (2.0)

[a]0.5-g silica cartridges (J. T. Baker) were used for this experiment. Each cartridge was conditioned with 4 mL hexane (speed 5; air volume 100 μL). Standard in hexane (1 mL) was added to the cartridge (height 0, speed 4, air volume 100 μL). The cartridge was eluted with 3.5 mL hexane (Fraction 1, speed 4, air volume 200 μL) followed by 3.5 mL hexane with 50 percent diethyl ether (Fraction 2, speed 4, air volume 200 μL). Finally, to clean the lines, the cartridge was rinsed with 1 mL hexane with 50 percent diethyl ether (speed 8) and the rinse was discarded. Spiking level was 1 μg per cartridge for the OCPs and 10 μg per cartridge for Aroclor 1260. Number of determinations was 4.
[b]Interference from Aroclor 1260.

TABLE 40. METHOD REPRODUCIBILITY USING THE ASPEC ROBOTIC SYSTEM[a]

Compound	Average recovery	Percent RSD
alpha-BHC	86.1	3.0
gamma-BHC	87.1	2.9
beta-BHC	81.9	3.3
Heptachlor	86.1	3.2
delta-BHC	83.8	3.2
Aldrin	86.2	3.2
Heptachlor epoxide	86.0	3.3
Endosulfan I	85.3	3.6
4,4′-DDE	85.4	3.4
Dieldrin	86.3	3.3
Endrin	108	4.5
4,4′-DDD	84.0	3.7
Endosulfan II	84.6	3.3
4,4′-DDT	84.7	3.6
Endrin aldehyde	52.9	4.9
Endosulfan sulfate	58.1	10
4,4′-Methoxychlor	79.4	4.6

[a]0.5-g diol cartridges (Supelco, Inc.) were used for this experiment. Each cartridge was conditioned with 4 mL hexane with 10 percent acetone (speed 5, air volume 100 μL). Standard in hexane (1 mL) was added to the cartridge (height 0, speed 4, air volume 100 μL). The cartridge was eluted with 3.5 mL hexane with 10 percent acetone (speed 4, air volume 200 μL). Finally, to clean the lines, the cartridge was rinsed with 1 mL hexane with 10 percent acetone (speed 8) and the rinse was discarded. Spiking level was 1 μg per cartridge. All fractions were adjusted to 5 mL final volume. Number of determinations was 19.

TABLE 41. EVALUATION OF MATRIX INTERFERENTS USING THE ASPEC ROBOTIC SYSTEM[a]

Compound	Percent recovery				
	Corn oil		Diesel hydrocarbons[b]	Aroclor 1260 and sulfur	
alpha-BHC	93.2	98.8	90.0	108	110
gamma-BHC	95.0	100	93.8	112	113
beta-BHC	80.2	85.4	78.4	85.5	87.5
Heptachlor	95.6	101	94.4	110	113
delta-BHC	87.4	92.2	87.0	97.4	99.0
Aldrin	92.8	98.6	92.2	104	107
Heptachlor epoxide	91.6	97.0	92.8	96.7	98.3
Endosulfan I	89.6	94.8	91.8	93.7	95.7
4,4′DDE	89.0	94.4	93.4	106	111
Dieldrin	89.6	94.6	91.0	107	110
Endrin	117	126	132	89.4	91.0
4,4′-DDD	85.6	91.2	89.8	93.4	94.7
Endosulfan II	82.0	86.8	85.2	97.7	99.7
4,4′-DDT	82.6	88.0	86.2	127	130
Endrin aldehyde	42.6	42.8	43.0	54.1	54.1
Endosulfan sulfate	47.4	39.0	44.0	43.7	41.3
4,4′-Methoxychlor	78.4	84.2	80.0	101	102

[a] 0.5-g diol cartridges (Supelco Inc.) were used for this experiment. Each cartridge was conditioned with 4 mL hexane with 10 percent acetone (speed 5, air volume 100 μL). Standards in hexane (1 mL) containing OCPs at 1 μg/mL and corn oil at 500 μg/mL or diesel hydrocarbons at 500 μg/mL or Aroclor 1260 at 0.66 μg/mL or elemental sulfur at 166 μg/mL were added to the cartridge (height 0, speed 4, air volume 100 μL). The cartridge was eluted with 3.5 mL hexane with 10 percent acetone (speed 4, air volume 200 μL). Finally, to clean the lines, the cartridge was rinsed with 1 mL hexane with 10 percent acetone (speed 8) and the rinse was discarded.

[b] Duplicate experiments were also performed in this case but one fraction was lost.

TABLE 42. PERCENT RECOVERIES OF 17 ORGANOCHLORINE PESTICIDES SPIKED INTO SS-2 SOIL EXTRACT[a]

Compound	Unspiked sample (µg/kg)	Percent recovery	
		Fraction 1	Fraction 2
alpha-BHC	<170	82.1	0
gamma-BHC	<170	81.2	0
beta-BHC	<170	76.7	0
Heptachlor	<170	73.8	0
delta-BHC	<170	40.2	52.8
Aldrin	<170	88.7	0
Heptachlor epoxide	<170	79.4	0
Endosulfan I	<170	68.1	0
4,4′-DDE	1,100	[b]	0
Dieldrin	<170	76.7	0
Endrin	<170	92.2	0
4,4′-DDD	2,800	[b]	0
Endosulfan II	<170	80.4	0
4,4′-DDT	2,200	[b]	0
Endrin aldehyde	<170	25.2	38.9
Endosulfan sulfate	<170	64.5	0
4,4′-Methoxychlor	<170	80.0	0
Diazinon	320	[c]	[c]
Ethion	210	[c]	[c]
Ziram	4,100	[c]	[c]
Carbaryl	20	[c]	[c]

[a] Spiking level is equivalent to 330 µg/kg of sample. 0.5-g diol cartridges (Burdick and Jackson) were used for this experiment. Each cartridge was conditioned with 4 mL hexane (speed 5, air volume 100 µL). Sample extract (1 mL) was added to the cartridge (height 0, speed 4, air volume 100 µL). The cartridge was eluted with 3 mL hexane for Fraction 1 and 3.5 mL hexane with 10 percent acetone for Fraction 2 (speed 4, air volume 200 µL). Finally, to clean the lines, the cartridge was rinsed with 1 mL hexane with 10 percent acetone (speed 8) and the rinse was discarded. Single determination.

[b] Not able to determine recovery because the amount spiked is lower than the background level.

[c] Not spiked.

TABLE 43. PERCENT RECOVERIES OF 17 ORGANOCHLORINE PESTICIDES SPIKED INTO SS-5 SOIL EXTRACT[a]

Compound	Unspiked sample (µg/kg)	Percent recovery	
		Fraction 1	Fraction 2
alpha-BHC	<170	85.4	0
gamma-BHC	<170	83.6	0
beta-BHC	<170	80.1	0
Heptachlor	<170	77.6	0
delta-BHC	<170	42.8	53.8
Aldrin	<170	70.4	0
Heptachlor epoxide	<170	84.0	0
Endosulfan I	<170	69.2	0
4,4′-DDE	780	[b]	0
Dieldrin	<170	76.6	0
Endrin	<170	90.3	0
4,4′-DDD	2,200	[b]	0
Endosulfan II	210	65.3	0
4,4′-DDT	1,300	[b]	0
Endrin aldehyde	<170	25.4	42.4
Endosulfan sulfate	260	50.8	14.8
4,4′-Methoxychlor	<170	72.5	0
Benomyl	200	[c]	[c]
Carbophenothion	1,400	[c]	[c]
Ethion	650	[c]	[c]

[a] Spiking level is equivalent to 330 µg/kg of sample. 0.5-g diol cartridges (Burdick and Jackson) were used for this experiment. Each cartridge was conditioned with 4 mL hexane (speed 5, air volume 100 µL). Sample extract (1 mL) was added to the cartridge (height 0, speed 4, air volume 100 µL). The cartridge was eluted with 3 mL hexane for Fraction 1 and 3.5 mL hexane with 10 percent acetone for Fraction 2 (speed 4, air volume 200 µL). Finally, to clean the lines, the cartridge was rinsed with 1 mL hexane with 10 percent acetone (speed 8) and the rinse was discarded. Single determination.

[b] Not able to determine recovery because the amount spiked is lower than the background level.

[c] Not spiked.

TABLE 44. PERCENT RECOVERIES OF 17 ORGANOCHLORINE PESTICIDES SPIKED INTO SS-7 SOIL EXTRACT[a]

Compound	Unspiked sample (µg/kg)	Percent recovery	
		Fraction 1	Fraction 2
alpha-BHC	<170	80.1	0
gamma-BHC	<170	76.4	0
beta-BHC	<170	72.4	0
Heptachlor	<170	72.4	0
delta-BHC	<170	40.1	46.7
Aldrin	<170	65.7	0
Heptachlor epoxide	<170	94.4	0
Endosulfan I	<170	63.8	0
4,4′-DDE	720	[b]	0
Dieldrin	<170	98.2	0
Endrin	<170	110	0
4,4′-DDD	470	[b]	0
Endosulfan II	300	38.3	0
4,4′-DDT	680	[b]	0
Endrin aldehyde	<170	52.1	38.8
Endosulfan sulfate	<170	73.5	18.3
4,4′-Methoxychlor	<170	89.3	12.3
Carbaryl	130	[c]	[c]
Diazinon	260	[c]	[c]
Ethion	130	[c]	[c]
Ziram	2,100	[c]	[c]

[a] Spiking level is equivalent to 330 µg/kg of sample. 0.5-g diol cartridges (Burdick and Jackson) were used for this experiment. Each cartridge was conditioned with 4 mL hexane (speed 5, air volume 100 µL). Sample extract (1 mL) was added to the cartridge (height 0, speed 4, air volume 100 µL). The cartridge was eluted with 3 mL hexane for Fraction 1 and 3.5 mL hexane with 10 percent acetone for Fraction 2 (speed 4, air volume 200 µL). Finally, to clean the lines, the cartridge was rinsed with 1 mL hexane with 10 percent acetone (speed 8) and the rinse was discarded. Single determination.

[b] Not able to determine recovery because the amount spiked is lower than the background level.

[c] Not spiked.

TABLE 45. PERCENT RECOVERIES OF 17 ORGANOCHLORINE PESTICIDES SPIKED INTO SS-8 SOIL EXTRACT

Compound	Unspiked sample (µg/kg)	Percent recovery	
		Fraction 1	Fraction 2
alpha-BHC	<170	83.4	0
gamma-BHC	<170	81.3	0
beta-BHC	<170	75.8	0
Heptachlor	<170	73.5	0
delta-BHC	<170	42.0	48.9
Aldrin	<170	68.1	0
Heptachlor epoxide	<170	101	0
Endosulfan I	<170	110	0
4,4′-DDE	860	[b]	0
Dieldrin	<170	107	0
Endrin	<170	95.7	0
4,4′-DDD	<170	76.0	0
Endosulfan II	<170	77.2	0
4,4′-DDT	1,130	[b]	0
Endrin aldehyde	<170	51.8	0
Endosulfan sulfate	<170	45.8	40.9
4,4′-Methoxychlor	<170	60.6	17.3
Benomyl	200	[c]	[c]
Carbaryl	480	[c]	[c]
Carbophenothion	3,800	[c]	[c]
Diazinon	135,000	[c]	[c]
Malathion	230	[c]	[c]
Ziram	1,200	[c]	[c]

[a] Spiking level is equivalent to 330 µg/kg of sample. 0.5-g diol cartridges (Burdick and Jackson) were used for this experiment. Each cartridge was conditioned with 4 mL hexane (speed 5, air volume 100 µL). Sample extract (1 mL) was added to the cartridge (height 0, speed 4, air volume 100 µL). The cartridge was eluted with 3 mL hexane for Fraction 1 and 3.5 mL hexane with 10 percent acetone for Fraction 2 (speed 4, air volume 200 µL). Finally, to clean the lines, the cartridge was rinsed with 1 mL hexane with 10 percent acetone (speed 8) and the rinse was discarded. Single determination.

[b] Not able to determine recovery because the amount spiked is lower than the background level.

[c] Not spiked.

hexane, then proceeded to the next solvent which was hexane with 50 percent diethyl ether. Another modification made to the cartridge procedure affected the volume of solvent needed to elute the compounds from the cartridge. The ASPEC system cannot handle fractions larger than approximately 3.5 mL because the capacity of the collection vials is 4 mL. Nonetheless, compound recoveries are good for both hexane with 50 percent diethyl ether (Table 39) and hexane with 10 percent acetone (Table 40) and the method reproducibility is acceptable. Additional work is needed to fully evaluate the ASPEC system.

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Appendix A

EVALUATION OF SAMPLE EXTRACT CLEANUP USING SPE CARTRIDGES

LITERATURE REVIEW

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SECTION 1

INTRODUCTION

This literature review report summarizes the relevant literature published recently on the use of solid-phase extraction (SPE) cartridges in environmental analysis. The literature review was performed using the computerized Chemical Abstracts search. Furthermore, issues of Analytical Chemistry, the Journal of Chromatography, the Journal of Chromatographic Science, the Association of Official Analytical Chemists Journal, the Journal of High Resolution Chromatography, the LC•GC Magazine, and the Chromatographia, from 1984 to 1989, were searched to gather references that were not retrieved during the Chemical Abstracts search.

Fourteen articles (References 1 through 14) were judged to be scientifically relevant to the objectives of this study and were retrieved from the literature. Other references (References 15 through 28) were also retrieved, because they were dealing with the use of SPE cartridges in preconcentrating organics from water samples or other applications. However, they were not summarized in this literature review when the information presented in these references did not deal specifically with extract cleanup/fractionation.

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

- The SPE cartridge technology and apparatus needed for sample processing using the SPE cartridge
- The SPE technique
- Applications.

SECTION 2

SPE CARTRIDGE TECHNOLOGY

2.1 SPE CARTRIDGES

A typical SPE cartridge consists of a polypropylene syringe body with a barrel-type cartridge, two polyethylene frits (20-μm pores) or stainless steel frits, and the adsorbent material (Figure A-1). Typical volumes are 1 mL, 3 mL, and 6 mL that accommodate 100 mg to 2000 mg adsorbent material. The average capacity is approximately 5 percent of adsorbent mass, or 5 mg/100 mg of adsorbent. A Luer tip allows easy attachment of the cartridge to adapters, stopcocks, and vacuum manifolds or workstations. Large reservoir capacity (LRC) columns are available for processing larger-volume samples. Figure A-1 shows various types of cartridges that are available commercially.

Silica-gel-filled cartridges and silica-based bonded-phase cartridges seem to dominate the market, but polymeric cartridges are also getting quite popular. Interaction Chemicals of Mountain View, California, has developed a line of polymeric materials known as Polysorb MP-1, MP-2, MP-3 polymers that are spherical, porous, and crosslinked and are based on styrene-divinyl benzene or vinyl pyridine. The MP-1, MP-2, and MP-3 can be used to remove large amounts of fats, waxes, hydrocarbons, and surfactants from complex matrices. MP-2 and MP-3 can be used in either charged or noncharged mode; thus, their capacity depends upon solvent pH. Polysorb packings have 35-μm particles and have a narrow particle size distribution. Their capacity is approximately 100 μg per 100 mg packing. The polymer can be used over a pH range of 0 to 14. Solvents such as methanol, acetonitrile, and tetrahydrofuran can be used in any amount to condition, process, or elute samples. Hydrocarbons and chlorinated solvents can also be used, but these may swell the polymer, causing slightly slower elution times. Finally, one other advantage of these polymeric materials is that they can be reused. These polymers are chemically stable and can be washed with strong acid or base to completely remove any materials left on the cartridge. The number of times the cartridges can be reused depends on the sample matrix and the instrument sensitivity.

A unique SPE phase Cyclobond I was developed by Astec, Whippany, New York. This adsorbent material is prepared by covalent coupling of β-cyclodextrin to 40-μm silica particles. The β-cyclodextrin has a toroid structure with seven glucose units; the primary and secondary hydroxyls are outside the cavity, while the internal void is hydrophobic. The hydrophobic part of the analyte enters this cavity and is held by electrostatic attraction. No preconditioning of the Cyclobond I cartridge is needed because the surface is hydrophilic.

The SPE cartridges are available from various manufacturers (e.g., J. T. Baker Inc., Supelco, Burdick & Jackson, Alltech, Analytichem International, J&W Scientific Inc., etc.). Additional information can be found in Reference 1.

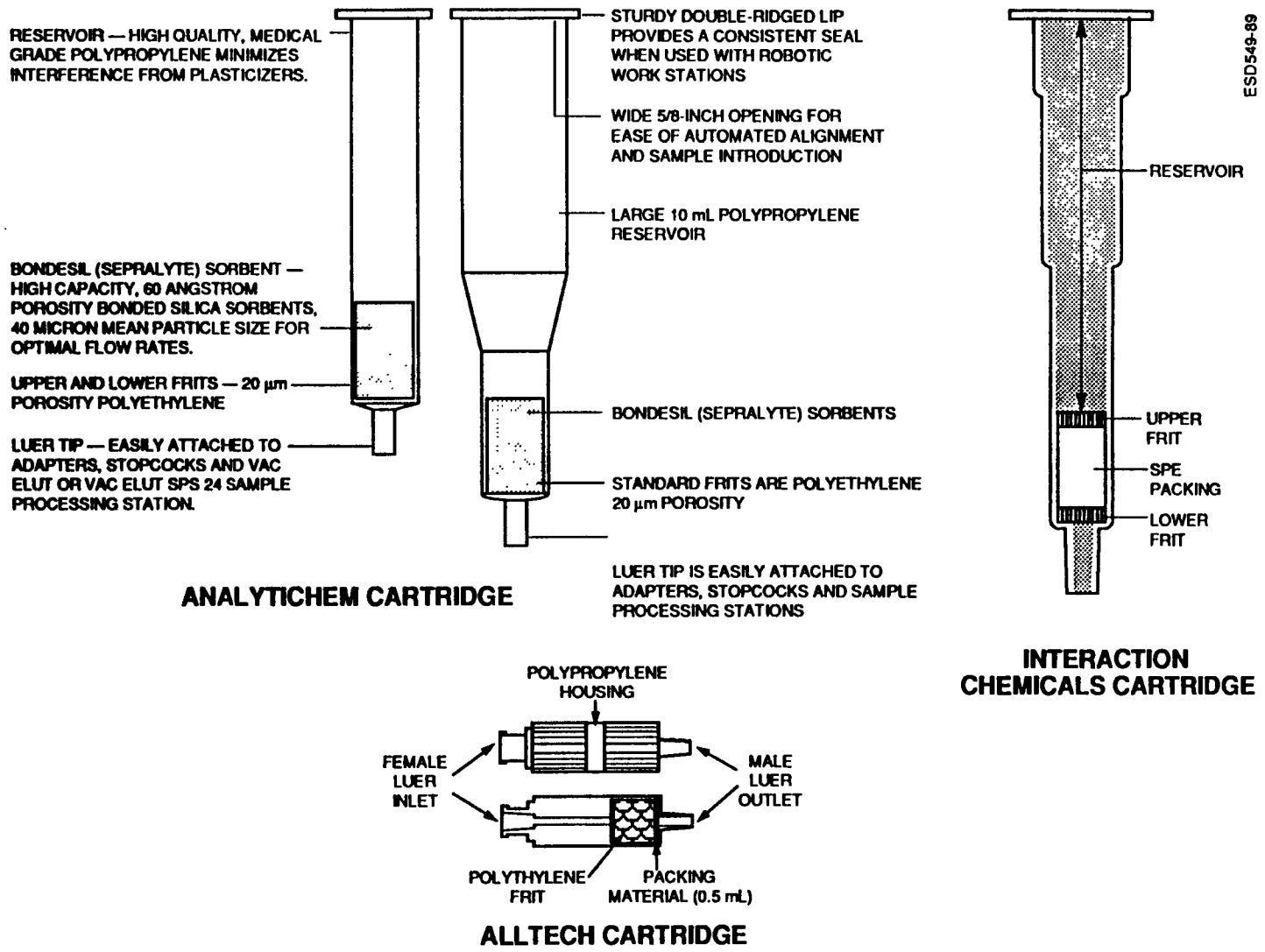


Figure A-1. SPE cartridge.

2.2 APPARATUS FOR HANDLING MULTIPLE SPE CARTRIDGES

Several devices are available for handling multiple cartridges. They include the VacElut SPS24 (Analytichem International) that can handle up to 24 cartridges simultaneously, the original VacElut from Analytichem International that handles up to 10 cartridges (Figure A-2), J&W's SPE Vacuum Manifold for 20 cartridges (Figure A-3), the Visiprep Vacuum Manifold from Supelco Inc. for 12 cartridges (Figure A-4), Alltech's 12-port manifold, Adsorbex SPU 24-port vacuum manifold from EM Science, the Baker-10 SPE and SPE-21 systems (J. T. Baker), and Spe-ed Mate-10 or Spe-ed Mate-30 of Applied Separations.

In general, a vacuum manifold consists of a heavy-duty glass basin that will not discolor, fog, or dissolve when exposed to organic solvents such as tetrahydrofuran. The Analytichem and the EM Science devices have two operating positions that allow a switch to be made between the waste and the collect steps in a matter of seconds. Replaceable stainless steel sample delivery tips provide the cleanest possible extracts, and a series of collection racks allows use of the appropriate collection vials. A built-in vacuum bleed valve and gauge is part of the manifold and a vacuum trap consisting of a 500-mL or larger vacuum flask, 1/4-inch vacuum tubing, and a vacuum source are needed to operate the system. Individual valves on the Visiprep vacuum manifold cover allow precise control of the flow through the cartridges.

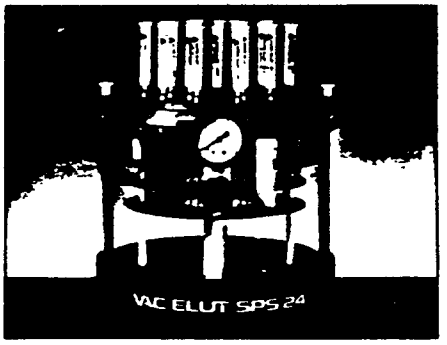
Another interesting device that is available commercially is the Visidry Drying Attachment from Supelco Inc. This device is attached to the vacuum manifold and can dry up to 12 cartridges simultaneously, or it can evaporate solvent from up to 12 fractions at one time in the same containers. Gas flow to each tube can be independently adjusted, preventing sample loss through splashing.

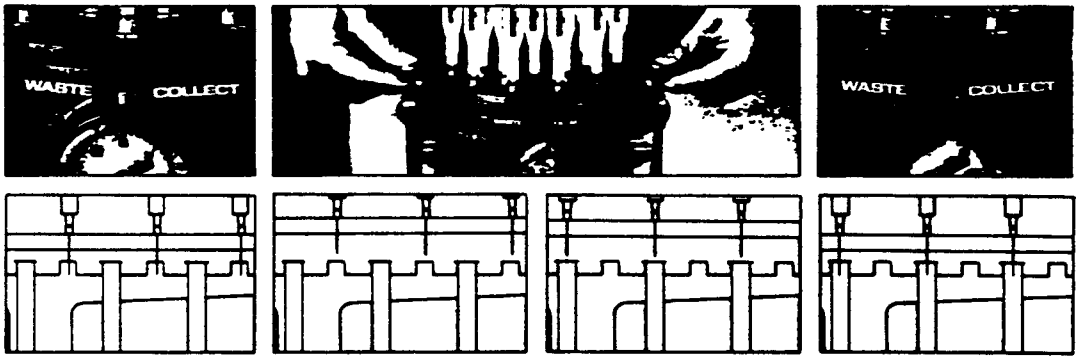
A detailed diagram of a vacuum manifold is shown in Figure A-5.

2.3 AUTOMATED DEVICES

We had the opportunity to see three of the automated devices that are available commercially for processing samples prior to analysis. These devices include: the Millilab Workstation (Waters), the BenchMate (Zymark Corp), and the ASPEC (Gilson Medical Electronics Inc). Each of these devices will be described in detail below. Another system, the Advanced Automated Sample Processor (AASP), was developed by Analytichem International and is currently marketed by Varian Associates. This is the first device for automated SPE; however, the system is considered only semiautomated because the sample is loaded off line. Ten cassettes consisting of 10 sample cartridges each can be processed with this system at a time. When the cartridge is clamped in a compression chamber, it becomes part of the HPLC flowstream and is placed on line with the HPLC column.

The Millilab workstation consists of two modules, a transport system, and a fluidics module (15). The transport module consists of a robotic arm moving in the x, y, and z directions and has a probe with a double-walled tube joined by an inflatable tip. The tip fits into a female Luer fitting on the cartridge, taking hold or releasing the cartridge by inflating or deflating. Cartridges, samples, and receiving tubes are positioned on the work surface of the transport module in racks with preset coordinates that are retained in the memory of the control system. The fluidics module provides the necessary solvents, sensor controls, and the external communication interfaces. Two standard test tube sizes are used with this workstation: 16 mm x 100 mm with a capacity up to 15 mL, and 10 mm x 75 mm with a capacity up to 4 mL. Racks are available that hold 84 of the larger size or 120 of the smaller size tubes.





In the 'WASTE' position, column conditioning and waste solvents flow through a UNIQUE WASTE DIVERSION FUNNEL to an external vacuum trap, keeping the sample collection area clean.

Place thumbs on tabs and lift lid with fingers.

Rotate lid to the 'COLLECT' position.

In the 'COLLECT' position, the sample delivery tips direct the purified eluant into the sample collection tubes with NO CROSS - CONTAMINATION.

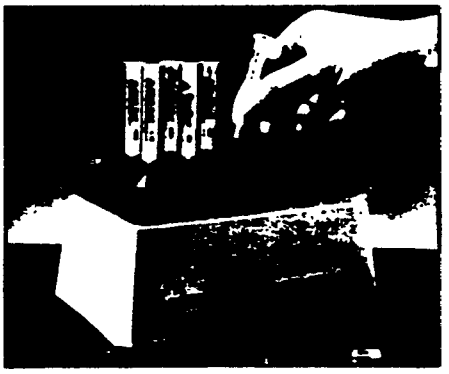


Figure A-2. Analytichem International SPS24 and original VacElut manifold. Figure taken from Analytichem International brochure on SPE cartridges.

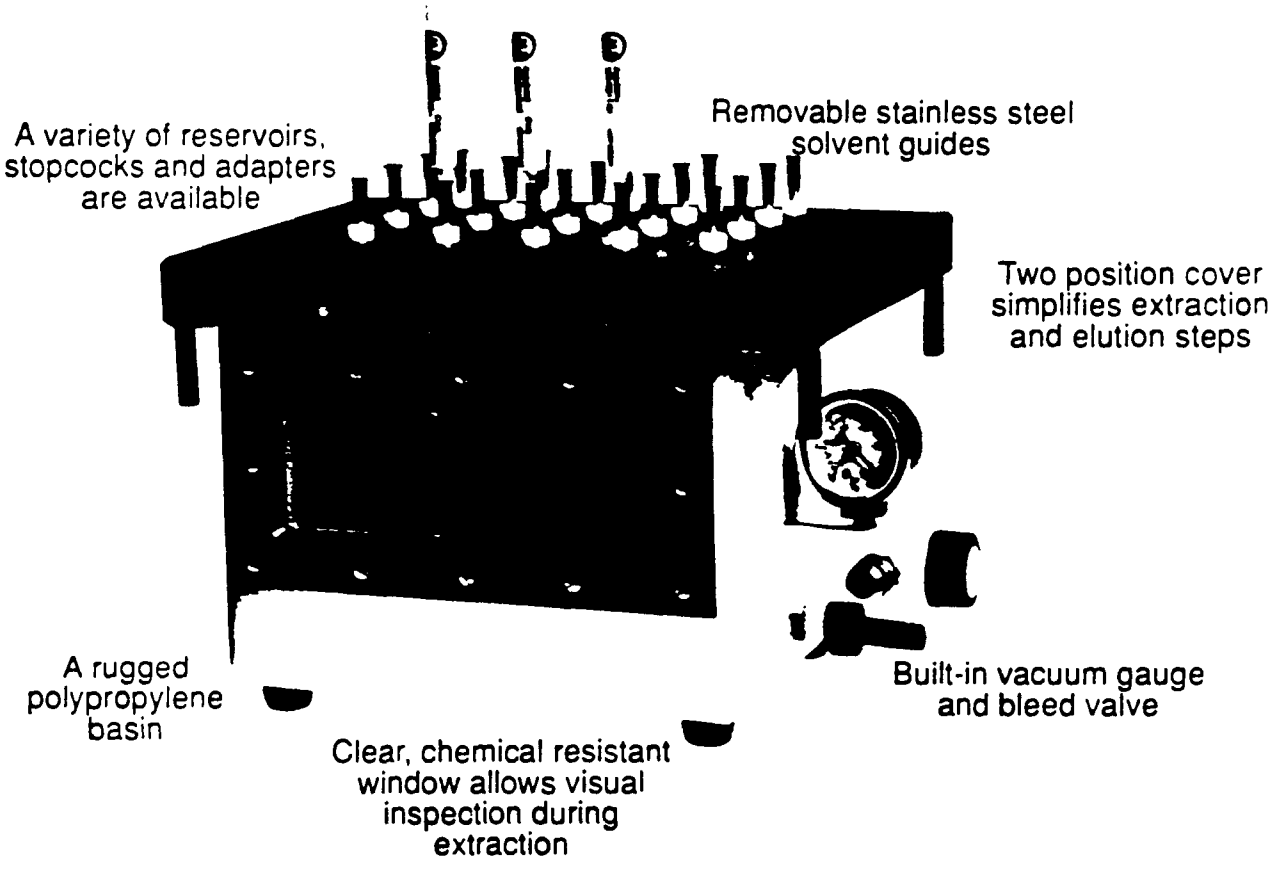
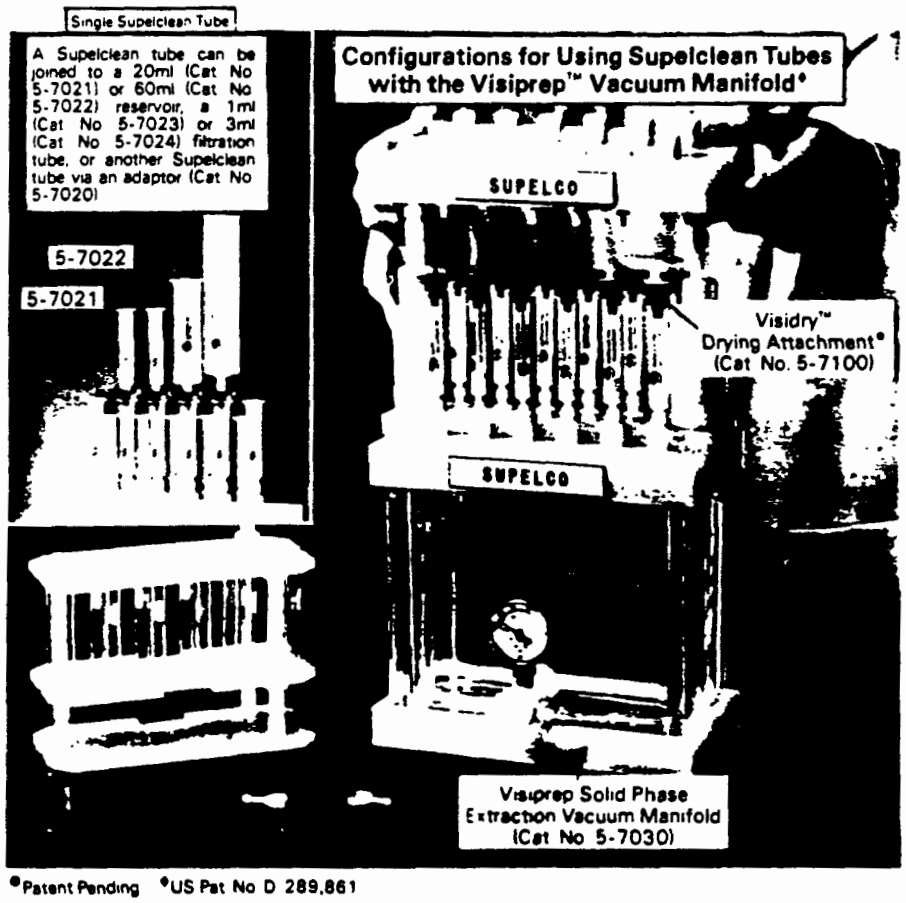


Figure A-3. J&W SPE vacuum manifold. Figure taken from J&W Scientific brochure on SPE cartridges.



*Patent Pending *US Pat No D 289,861

Figure A-4. Visiprep vacuum manifold. Figure taken from 1989 Supelco chromatography catalog 27.

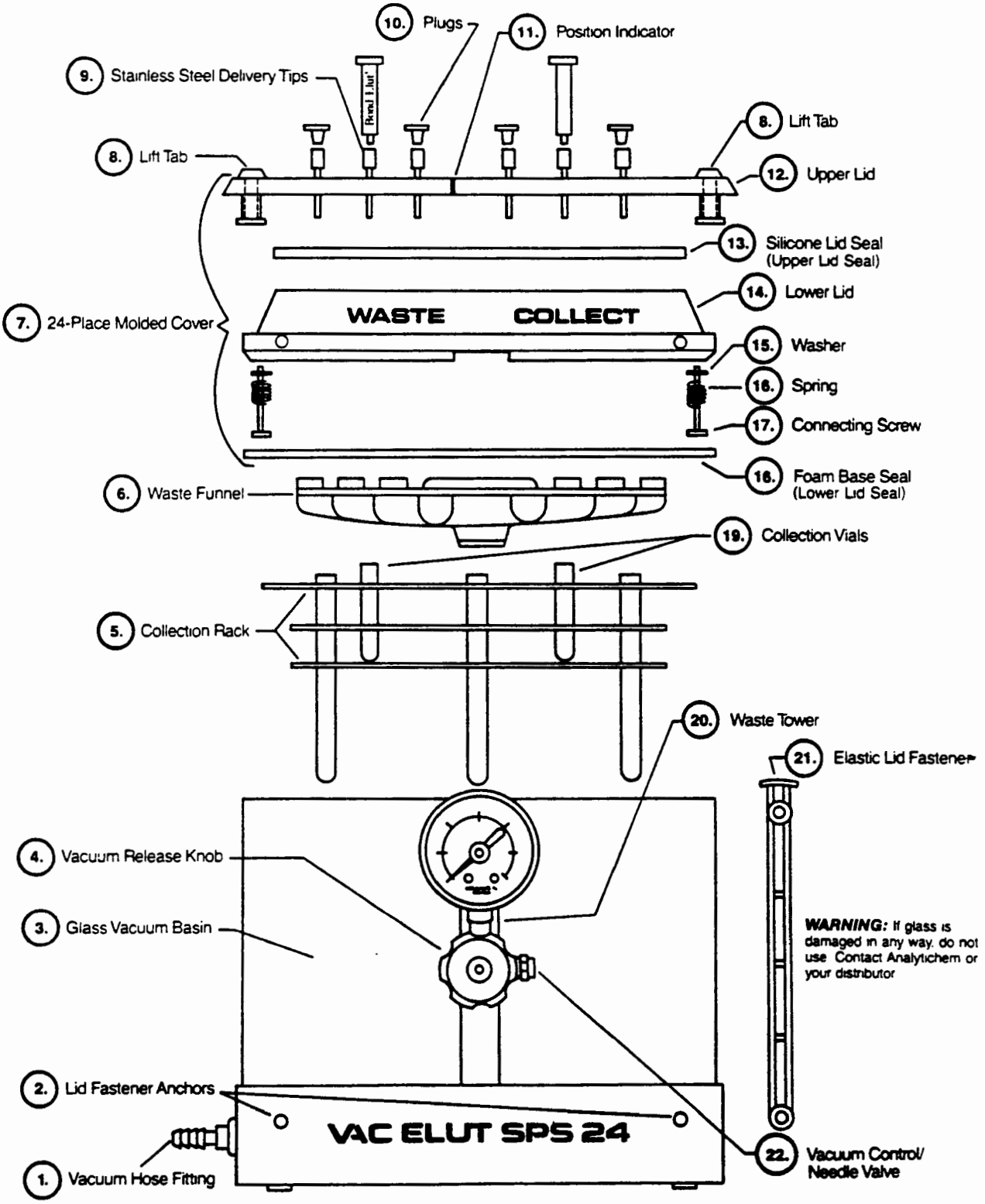


Figure A-5. VacElut SPS24. Figure taken from Analytichem International brochure on SPE cartridges.

The BenchMate Workstation Model B220 with liquid management system, membrane filtration, solid-phase extraction, and HPLC injection is similar to the Millilab Workstation. The system can use up to six solvents and works only with syringe-barrel-type cartridges. Delivery of liquids is achieved by precision syringes through a unique 12-port valving technology. The capacity of the BenchMate is 50 tubes/rack x 4 racks (tube size 16 x 100-mm). It can be used with 200-mg and 500-mg cartridges.

The BenchMate can be operated either in Autostart or Personal Computer (PC) control mode. In the Autostart mode, the method is set up and saved to a disk on an off-line PC; the disk is then loaded into the BenchMate Workstation, and the Autostart button is depressed. In the PC control mode, an IBM-compatible PC is connected to the workstation, and the method is set up on the PC. To set up a method to run on the BenchMate Workstation, a series of menu screens prompt for information such as the type of operations, their sequence, number of samples, transfer volumes, solvent addition volumes, etc. Figure A-6 exemplifies how to build a method with the BenchMate Workstation.

Another workstation, ASPEC from Gilson, also uses an x, y, and z robot-like arm for adding samples, conditioning cartridges (100 mg and 500 mg), and collecting fractions. The system uses positive pressure (2 to 3 psi) to push solvent through the cartridge. The system is compatible with most standard disposable cartridges, can process a maximum of 108 samples without operator intervention, and can accommodate up to 5 different solvents for maximum selectivity. ASPEC software allows the selection of the proper volume and flowrate for each solvent used in cartridge preconditioning, elution, rinsing, etc., and can choose between a sequential and a batch mode of operation.

The complexity of the systems that are available commercially appears to have slowed their acceptance rate. The few laboratories we have talked to indicated that considerable capital investment, setup time, and need for a skilled chemist to operate this type of equipment are required, and that these factors make the use of these systems very expensive. Nonetheless, we feel that automation of the labor-intensive sample preparation step is much needed.

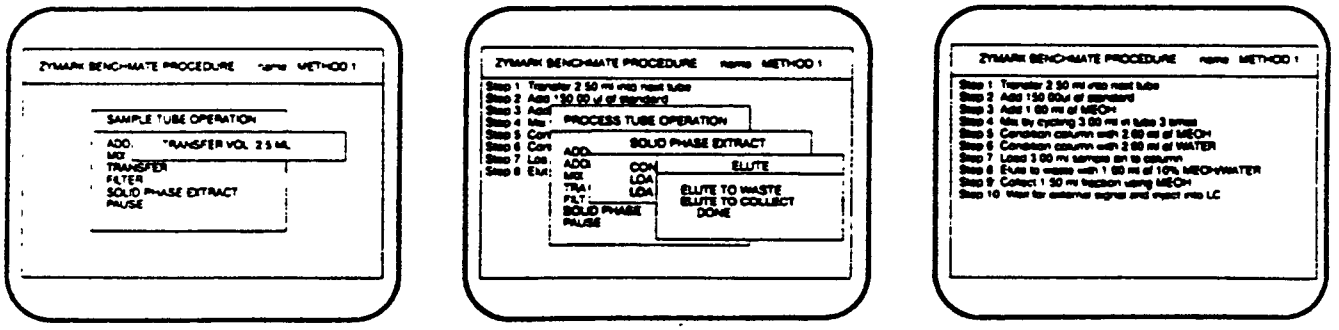


Figure A-6. Building method file and BenchMate Workstation. Figure taken from Zymark brochure on the BenchMate system.

SECTION 3

SPE TECHNIQUE

The SPE technique utilizes the principle of selective retention of compounds from a liquid matrix onto a solid adsorbent. The elution conditions for the SPE cartridges are typically chosen so that the target analytes are retained onto the adsorbent while the coextracted materials are washed off from the cartridge with the eluent. Alternatively, the coextracted materials are retained while the target analytes are eluted from the cartridge. Figure A-7 outlines the steps involved in this process.

The SPE technique is useful in two general areas: in the removal of matrix interferents that might interfere with the determination of the target analytes, and in trace enrichment. The former application which has had very limited evaluation is of interest to this study; the latter application has been dealt with for some time, and there are numerous reports on this subject

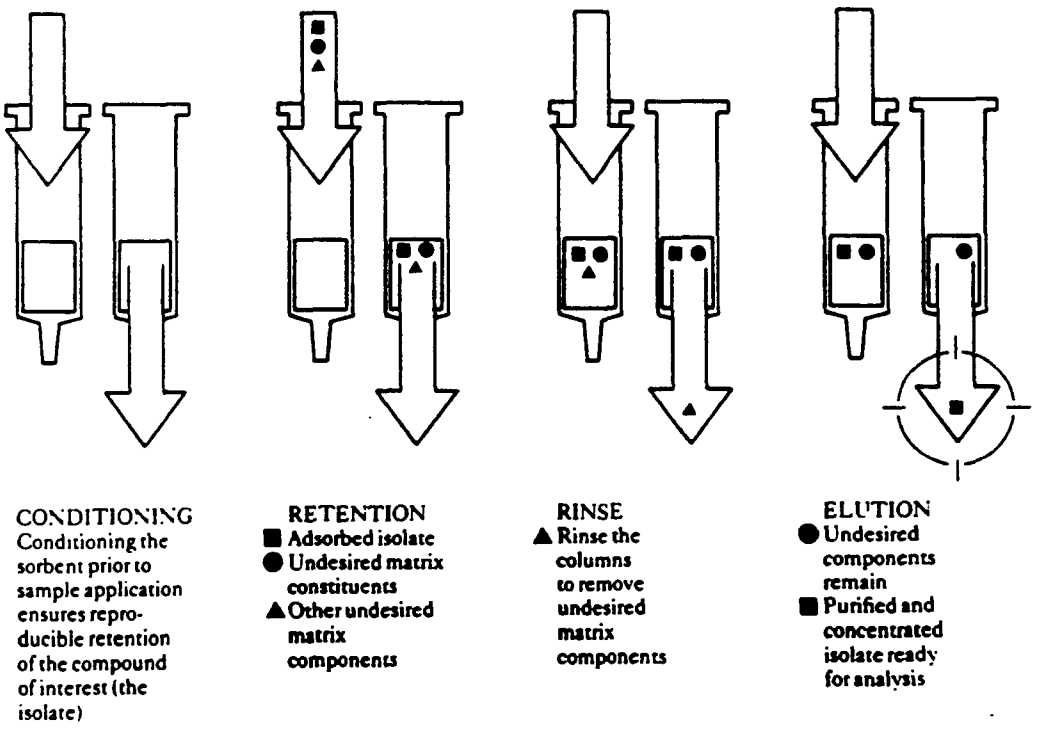


Figure A-7. SPE technique.

matter (16-27). Applications reported for the removal of matrix interferents include those using Florisil, alumina, and silica gel. Applications reported for trace enrichment include mostly bonded-phase silicas, of which C_{18}-bonded silica has had the largest number of applications. Cartridges available commercially for trace enrichment are shown in Table A-1.

Junk et at. (28) performed procedural blanks on the SFE cartridges to establish the background levels of organic contaminants. Experimental data reported by Junk et al. (28) indicated the presence of alkanes, alkenes, various plasticizers and antioxidants; the levels of these contaminants varied from lot to lot. Hence, these cartridges must be checked for background contamination prior to use.

Some of the potential pitfalls with the SPE technique are associated mainly with the adsorbent material, although the eluent cannot be totally ignored. Differences in bonded-phase materials purchased from different manufacturers can cause changes in compound elution patterns and recoveries. If a method is not rugged then conditions should be chosen that may allow some leeway in both solvent and bonded-phase composition (23).

Essentials of the SPE technique are:

- Conditioning of the cartridge prior to the application of the sample is needed to remove contaminants due to packaging and handling processes and to activate the packing. Conditioning will leave the adsorbent material in a state that is compatible with the loading solvent and the analytes of interest. To ensure that the packing does not get dry between conditioning and sample addition, about 1 mm of the conditioning solvent should remain on the upper frit. If the packing gets dry, the conditioning procedure must be repeated.

- In the loading step, the sample is passed through the cartridge, and the analytes of interest are retained by the adsorbent material. For the analytes to be retained by a polar adsorbent, the solvent in which they are dissolved must be relatively nonpolar. For example, in case of alumina, Florisil or silica cartridges, which contain polar materials, the analytes are dissolved in hexane, which is a nonpolar solvent. In the case of C_{18}-bonded silica, which is a nonpolar adsorbent, the analytes must be dissolved in an aqueous solution in order for the C_{18}-bonded silica to retain them.

- In the rinsing step, undesirable sample components are washed off, leaving the target analytes on the cartridge. This step is not always performed, especially for multiresidue analysis, since some target compounds may be washed off with undesirable sample components.

- Cartridge elution is typically performed with 5 to 10 bed volumes of solvent. The bed volume per 100 mg adsorbent of 40-μm particles with 60-Å pores is approximately 120 μL. Therefore, the optimal solvent volume for a 500-mg cartridge is 0.6 to 1.2 mL. The solvent volume should be kept to a minimum to minimize elution of undesirable sample components. This means that solvent polarity should also be taken into consideration. Furthermore, when different solvents are considered for cartridge elution, each solvent that is passed through the cartridge must be miscible with the prior solvent.

TABLE A-1. GUIDE TO SELECTING SPE CARTRIDGES FOR A PARTICULAR APPLICATION

	Bond elut	Analyte functional groups	Matrix	Typical elution solvents	Typical applications
Nonpolar extraction	C18 -- Octadecyl C8 -- Octyl C2 -- Ethyl CH -- Cyclohexyl PH -- Phenyl CN -- Cyanopropyl CN -- Cyanopropyl (endcapped)	Hydrophobic groups Aromatic rings Alkyl chains	Aqueous Water Buffers Biological fluids	Methanol Acetonitrile Ethyl acetate Chloroform Acidic methanol Hexane	Drugs of abuse Peptides Pesticides Therapeutic Drug monitoring
Polar extraction	CN -- Cyanopropyl 20H -- Diol SI -- Silica NH_2 -- Aminopropyl PSA -- Primary/secondary amine	Hydrophilic groups Hydroxyls Amines Heteroatoms (S,O,N)	Nonpolar Hexane Oils Chloroform Lipids	Methanol Isopropanol Acetone	Vitamin D Metabolites Lipid separations Oil additives Carbohydrates Phenols
Cation exchange extraction	SCX -- Benzenesulfonic acid (Strong) PRS -- Propylsulfonic acid (Stong) CBA -- Carboxylic acid (weak)	Cations Amines Pyrimidines	Aqueous Water Acidic buffers Biological fluids	Alkaline buffer High ionic strength buffer	Catecholamines Herbicides Pharmaceuticals
Anion exchange extraction	SAX -- Quaternary amine (Strong) PSA -- Primary/secondary amine NH_2 -- Aminopropyl (weak) DEA -- Diethylaminopropyl (weak)	Anions Carboxylic acids Sulfonic acids Phosphates	Aqueous Water Alkline buffers Biological fluids	Acidic buffer High ionic strength buffer	Organic acids Vitamins Fatty acids Phosphates
Covalent extraction	PBA -- Phenylboronic acid	Vicinal diols	Aqueous Alkaline buffers Biological fluids	Acidic methanol	Nucleotides Nucleosides Carbohydrates Catecholamines

[a]Data taken from Analytichem International brochure on SPE cartridges.

- In developing a method involving the SPE technique, consideration must be given to the properties of the analyte, the adsorbent, and the sample matrix. The analyte could interact with the adsorbent through hydrogen bonding, electrostatic interaction, and van der Waals forces. Hydrogen bonding may occur when functional groups such as carbonyl, amino, and hydroxyl are present. Electrostatic interaction may occur when there are sulfonates, carboxylates, and amines present. van der Waals forces or dispersive interactions occur among alkyl and aromatic groups. Figure A-8 outlines some of these interactions.

- The matrix plays a very important role in the method development. The overall characteristics of the matrix need to be defined (e.g., is it aqueous or organic solvent; major constituents such as lipids, surfactants, pigments, etc. need to be identified.) Once the major constituents are identified, then the particular adsorbent that will differentiate between the interferents and the analyte needs to be selected.

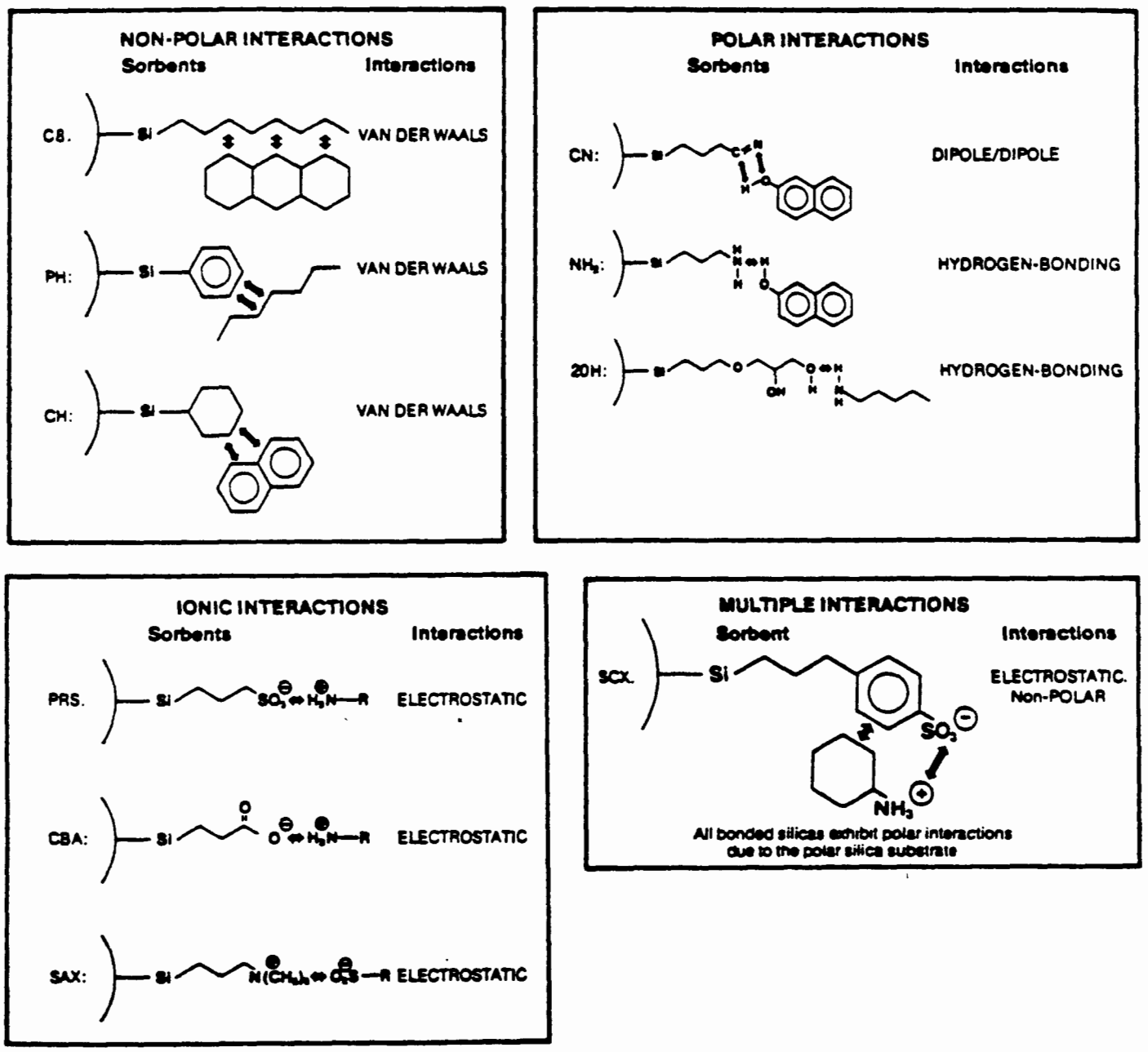


Figure A-8. Types of interactions between the analyte and adsorbent. Figure taken from Reference 18.

SECTION 4

APPLICATIONS

Table A-2 summarizes the various applications of the SPE cartridge technology for extract cleanup as reported in the listed references.

The SPE technique was applied to the cleanup of sediment and fish tissue extracts containing organochlorine pesticides and organophosphorus pesticides (2). Cartridges containing 500 mg Florisil, C_{18}-bonded silica, or silica were employed. Florisil cartridges were used in the cleanup of lake sediment extracts in hexane, and C_{18}-bonded silica cartridges were used in cleanup of lake sediment extracts in acetonitrile. The results shown in Table A-3 indicate that hexane in combination with Florisil cleanup is a poor choice, since recoveries of gamma-BHC, chlorpyrifos, dieldrin, DDE, and DDT are less than 32 percent. Methylene chloride-acetonitrile-hexane (50:3:47) was the solvent of choice in eluting the organochlorine pesticides from the C_{18}-cartridge (Table A-4), and there seemed to be no matrix effects when extracts of loamy fine sand, organic detritus, or very fine sand were processed through the cartridge (Table A-5).

Both silica and C_{18}-bonded silica were used to fractionate petroleum hydrocarbons according to their polarity (3). Very polar oil components, such as asphaltenes, were retained on the silica cartridges when hexane, dichloromethane, and isopropanol were used as the eluting solvents. The separation characteristics of the C_{18}-bonded silica are different from those of the silica. For example, the aromatic compounds are eluted from the silica cartridges in the first fractions, and the aliphatic compounds are eluted later (Figures A-9 and A-10). The C_{18}-phases are sensitive to substituent effects. For example, one to two additional methyl groups have about the same increasing effect on the retention as has an additional ring annellation (3).

Florisil and C_{18}-bonded silica cartridges were used successfully to clean up extracts of plant material containing chlorthalonil, endosulfan I, endosulfan II, and captan (4). Of the two types of cartridges, Florisil gave the higher recoveries under the conditions used.

C_{18}-bonded silica and aminopropyl-bonded silica were used in tandem to clean up extracts obtained from marine sediment and animal tissue (5). The C_{18}-bonded silica retained lipids and long-chain hydrocarbons, while the aminopropyl cartridge retained amines and organic acids. The effect of column order was not evaluated; however, the authors reported that the ion exchange capacity of the aminopropyl-bonded silica was reduced by any nonpolar material in the sample extract if it preceded the C_{18}-cartridge.

A quick cleanup method for waste solvents was reported by Pedersen and Higgins (6). A sample of a waste solvent was diluted with hexane and applied to a 350-mg Florisil column. A major portion of the PCBs and most organochlorine pesticides passed through. Dieldrin, endosulfan, and endrin were retained on the Florisil column and were recovered with hexane/methyl-isobutyl ketone (94:6).

TABLE A-2. SUMMARY OF EXTRACT CLEANUP PROCEDURES THAT EMPLOY SPE CARTRIDGES

Compound	Matrix	Extraction solvent	SPE cartridge	Eluting solvent	Reference
gamma-BHC chloropyrifos Dieldrin DDE DDT	Sediment Fish tissue	Acetonitrile Hexane	C_{18}-bonded silica Florisil	Methylene chloride/ acetonitrile/hexane (50:3:47)	2
Alkanes Alkenes Benzenes 2-Ring aromatics 3-Ring aromatics 4-6 Ring aromatics	Crude oil	Hexane	Silica	Hexane Methylene chloride/hexane Methylene chloride/ isopropanol	3
Asphaltenes Cholesterol Fatty acid esters Phthalate esters		Hexane	C_{18}-bonded silica	Acetonitrile/water (9:1) Isopropanol/acetonitrile Isopropanol/hexane	3
Chlorthalonil Endosulfan I Endosulfan II	Plant material	Acetone	Florisil	Hexane/diethyl ether (1:1)	4
Captan			C_{18}-bonded silica	Acetonitrile	4
PAHs Organochlorine pesticides	Marine sediment Animal tissue	Acetonitrile	C_{18}-bonded silica in series with aminopropyl-bonded silica	Acetonitrile	5
Organochlorine pesticides	Waste solvent	Hexane or hexane/methyl isobutyl ketone (50:50)	Florisil	Hexane/methyl isobutyl ketone (94:6)	6
PCBs	Transformer oil	Isooctane	Florisil	Isooctane	7

(continued)

TABLE A-2. (Concluded)

Compound	Matrix	Extraction solvent	SPE cartridge	Eluting solvent	Reference
Pentachlorophenol	Adipose tissue	Hexane	Silica	Hexane/chloroform	8
Polybrominated biphenyls	Adipose tissue	Hexane	C_{18}-bonded silica Florisil	Acetonitrile/hexane	9
Chlorinated hydrocarbons phthalate esters	Sandy loam sediment NBS standard reference materials (pine needles, river sediment, citrus leaves, coal, coal flyash)	Hexane	Florisil	Hexane/diethyl ether (1:1) Hexane/acetone (9:1) Hexane/methylene chloride (various combinations)	10
Carbofuran Metalaxyl Simazine	Soil	Acetone, HCl-KCl buffer, partitioning with methylene chloride; solvent exchange to benzene	Silica	Hexane/acetone (19:1) Hexane/acetone (1:1)	11
Organophosphorus pesticides	--	--	Diol	Hexane Hexane/acetone (9:1) Hexane/acetone (8:2)	12
Triazines	Soil Muscle tissue Corn oil	See Table A-7	SCX C_{18}-silica Diol	Acetonitrile/0.1 M K_2HPO_4 (50:50)	13
Organochlorine pesticides	Sludge	Methylene chloride/acetone (50:50)	Florisil	Hexane/diethyl ether (50:50)	14

TABLE A-3. RECOVERIES OF PESTICIDES FROM LAKE SEDIMENT USING EXTRACTION SOLVENT AND SPE CARTRIDGE COMBINATIONS[a]

Compound	Extraction solvent	Column	Eluting solvent	Percent recovery
gamma-BHC	Hexane	Florisil	Methylene chloride/	32.3
Chlorpyrifos			acetronitrile/hexane	17.2
Dieldrin			(50:3:47)	20.0
DDE				10.5
DDT				20.8
gamma-BHC	Acetonitrile	C_{18}-bonded silica	Methylene chloride/	87.4
Chlorpyrifos			acetonitrile/hexane	48.6
Dieldrin			(50:3:47)	79.3
DDE				76.7
DDT				90.8

[a]Data taken from Reference 2.

TABLE A-4. PERCENT RECOVERIES OF THE AROCLORS USING FLORISIL AND SILICA CARTRIDGES[a]

Compound	Eluting solvent	Percent recovery
gamma-BHC	Acetonitrile	52.1
Chlorpyrifos		17.1
Dieldrin		21.6
DDE		9.3
DDT		30.2
gamma-BHC	Methylene chloride/ acetonitrile/hexane (50:3:47)	87.4
Chlorpyrifos		48.6
Dieldrin		79.3
DDE		76.7
DDT		90.8
gamma-BHC	Hexane	81.4
Chlorpyrifos		37.3
Dieldrin		5.0
DDE		78.1
DDT		51.3

[a]Data taken from Reference 2.

TABLE A-5. RECOVERIES OF PESTICIDES FROM DIFFERENT SEDIMENT TYPES USING ACETONITRILE AS EXTRACTION SOLVENT AND THE C_{18} SPE CARTRIDGES WITH THE METHYLENE CHLORIDE/ACETONITRILE/ HEXANE (50:3:47) ELUTION MIXTURE[a]

Sediment sample	Compound	Percent recovery
Loamy fine sand	gamma-BHC	87.4
	Chlorpyrifos	48.6
	Dieldrin	79.3
	DDE	76.7
	DDT	90.8
Organic detritus	gamma-BHC	64.5
	Chlorpyrifos	37.9
	Dieldrin	58.6
	DDE	47.3
	DDT	51.8
Very fine sand	gamma-BHC	75.1
	Chlorpyrifos	46.1
	Dieldrin	62.2
	DDE	66.6
	DDT	67.3

[a]Data taken from Reference 2.

ESD T0508

Compound class	F1	F2	F3	F4	F5
Alkanes	xxxxxx				
Alkenes	xxxxxx				
Benzenes		xxxxxx			
2-Ring aromatics		xxxxxx			
3-Ring aromatics			xxxxxx		
4-6-Ring aromatics			xxxxxx		
Asphaltenes				retained	
Cholesterol				xxxxxx	
Fatty acid esters				xxxxxx	
Phthalates				xxxxxx	

[a]Cartridge	F1	F2	F3	F4	F5
3-mL column	2 mL hexane	2 mL 10% methylene chloride	2 mL 20 % methylene chloride	2 mL methylene chloride	2 mL 1:1 methylene chloride/ isopropanol
1-mL column	0.5 mL hexane	0.5 mL hexane	1 mL 10% methylene chloride	1 mL methylene chloride	1 mL 1:1 methylene chloride/ isopropanol

Figure A-9. Separation of standard compounds on silica cartridges (3 mL). Figure taken from Reference 3.

ESD T0509

	I	F1	F2	F2a	F3
Compound class	II	F1	F2		F3
1-2-Ring arom. with alkyl <C_4		xxxxxx			
3-Ring arom. with alkyl <C_3		xxxxxx			
4-Ring arom. with alkyl <C_2		xxxxxx			
5-Ring arom. with alkyl <C_1		xxxxxx			
6-Ring arom.		xxxxxx			
1-6-Ring arom. with alkyl >than above			xxxxx.		
>6-Ring arom.			xxxxxx.		
<n-C_{12}			xxxxx		
n-C_{12} to n-C_{20}				xxxxxx	
>n-C_{20}					xxxxx
Phthalates		depending on sidechain			

[a]Elution system	F1	F2	F2a	F3
I	3.5 mL 9:1 acetonitrile/water	3 mL 1:9 isopropanol/ acetonitrile	3 mL 1:1 isopropanol/ acetonitrile	4 mL 1:1 isopropanol/ hexane
II	3 mL acetonitrile	3 mL 1:4 isopropanol/ acetonitrile		4 mL 1:1 isopropanol/ hexane

Figure A-10. Separation of standard compounds on C_{18}-cartridge (3 mL). Figure taken from Reference 3.

The SPE technique was applied successfully to the determination of PCBs in transformer oil (7). A 0.2-g transformer oil sample was applied to a 500-mg Florisil cartridge prewetted with 500 μL isooctane. Without this prewetting, approximately 20 percent of PCBs present in the sample were found to bind irreversibly to Florisil. PCBs were eluted from the Florisil cartridge with five 2-mL portions of isooctane. Dilution of the transformer oil with isooctane prior to loading it to the Florisil cartridge did not result in improved recoveries. On the contrary, this required additional silanized glassware (7).

Ansari and Hendrix (8) reported that pentachlorophenol can be separated from human adipose tissue using silica gel cartridges (300 to 500 mg) and hexane (17 mL). With an intermediate elution step (hexane/chloroform 1:1, 5 mL), recovery of pentachlorophenol increased to 97 percent; however, more fat was also removed from the cartridge (8). The C_{18}-cartridge was also evaluated for this application; however, pentachlorophenol could not be resolved from fat when methanol/water (9:1) was used to elute the C_{18}-cartridge (8).

A similar application was reported by Hu et al. (9) for the cleanup of adipose tissue extracts containing polybrominated biphenyls. Removal of fat was four times as high with the C_{18}-cartridge than with the Florisil cartridge. Sequential extraction of adipose tissue extracts through both cartridges in either sequence removed 94 to 96 percent of the fat and gave recoveries of 96 to 99 percent for polybrominated biphenyls. In this case, the cartridges were eluted with 40 mL acetonitrile or 10 mL hexane.

Disposable cartridges containing 1 g Florisil were investigated for the cleanup of extracts obtained from various environmental matrices (10). Elution patterns and recoveries were determined for 22 chlorinated hydrocarbons and 16 phthalate esters in the presence of interferents such as corn oil, diesel hydrocarbons, organochlorine pesticides, and chlorinated phenols. Hexane (5 mL) recovered 18 chlorinated hydrocarbons from the 1-g Florisil cartridge. Collection of a second fraction from the Florisil cartridge by elution with hexane/diethyl ether (1:1) helped recover the four BHC isomers that could not be recovered with hexane; however, their elution patterns were difficult to reproduce, especially when interferents were present. When hexane/acetone (9:1) was used as eluent, recoveries of the 22 compounds were >90 percent, except hexachlorobenzene at 78 percent. The cleanup procedure developed by Lopez-Avila et al. (10) was tested for chlorinated hydrocarbons with nine environmental matrices, including relatively clean matrices such as a sandy loam soil and highly contaminated matrices such as Detroit River sediment and Bloody Run Creek sediment. The results indicated that the cleanup procedure works, regardless of the complexity of the matrix, and more than two-thirds of the measurements showed recoveries >75 percent.

Lopez-Avila et al. (10) also reported a Florisil cartridge procedure for the separation of phthalate esters from organochlorine pesticides with hexane containing 26 percent methylene chloride. The phthalate esters were retained on the Florisil cartridge while the organochlorine pesticides were eluted; the phthalate esters were then recovered with hexane/acetone (9:1).

A method for the cleanup of soil extracts containing carbofuran, metalaxyl and simazine was reported by Getzin et al. (11). In this method, pesticide residues were extracted from soil with acetone/aqueous buffer (9:1) at pH 2, and then partitioned into methylene chloride/carbonate buffer (pH 10.7). The solvent was then exchanged to benzene. The benzene extract was passed through a silica cartridge already preconditioned with benzene. Interfering compounds were washed off with hexane/acetone (19:1), and the pesticides were eluted with hexane/acetone (1:1).

Elution patterns and recoveries of 21 organophosphorus pesticides from a diol cartridge were reported by Hatcher et al. (12). Seven organophosphorus pesticides, chlorpyrifos, demeton, disulfoton, fenthion, ethylparathion, phorate, and ronnel were eluted from the diol cartridge with hexane. Hexane/acetone (9:1) was used to recover azinphos methyl, bolstar, coumaphos, ethoprop, EPN, malathion, merphos, methyl parathion, and sulfotepp. Dimethoate and fensulfothion required a more polar solvent (e.g., hexane/acetone 8:2), while monocrotophos and TEPP were not recovered at all from the diol cartridge (Table A-6).

Triazines were selectively eluted from three different types of cartridges (SCX, C_{18}-bonded-silica, and diol), depending on the sample matrix (13). The procedures are outlined in Table A-7. A strong cation exchange cartridge (SCX) was used for the soil matrix because soil contains a large number of charged species that can be selectively retained or eluted by the benzene-sulfonylpropyl packing. To retain the triazines on the SCX cartridge, they were first protonated by the addition of 1 percent acetic acid to the extract. The extract was then transferred to the cartridge. The sulfonyl group of the SCX material is negatively charged and therefore retains the protonated atrazine. After rinsing the cartridge with 1 percent acetic acid, acetonitrile, water, and 0.1 M K_2HPO_4 to eliminate matrix interferents, triazines were eluted with acetonitrile/0.1 M K_2HPO_4 (50:50). In the case of the C_{18}-bonded-silica, the lipids were strongly retained by the C_{18}-chain while the triazines were eluted with methanol. In the case of corn oil cleanup on the diol cartridge, which is very polar, the triazines will be retained by hydrogen bonding and can be later eluted with methanol.

Cleanup of sludge samples spiked with organochlorine pesticides was reported by Supelco researchers (14). The adsorbent material, LC-Florisil, was conditioned with methylene chloride/acetone (50:50) prior to use, and the packing material was allowed to dry under gentle vacuum (15 mm Hg) for 3 min. The sludge extract in acetone (with traces of methylene chloride) was applied to the cartridge and allowed to pass through under gravity only. This was followed by vacuum drying of the cartridge. The organochlorine pesticides were recovered using three 1-mL portions of hexane/diethyl ether (50:50). Compounds were recovered quantitatively (recovery >93 percent), and method precision varied from 4.4 to 12 percent for 12 determinations.

TABLE A-6. PERCENT RECOVERIES OF 21 ORGANOPHOSPHATE PESTICIDES FROM DIOL CARTRIDGES[a]

Compound	Hexane	Hexane/acetone (9:1)	Hexane/acetone (8:2)
Azinphos methyl		100	
Bolstar	4.2	102	
Chlorpyrifos	100		
Coumaphos		105	
Demeton	123		
Dimethoate			55
Disulfoton	95		
Ethoprop	2.5	107	1.9
EPN	12	98	
Fensulfothion		3.0	60
Fenthion	101		
Malathion		116	
Merphos	29	75	
Monocrotophos	ND[b]		
Parathion-ethyl	100		
Parathion-methyl		101	
Phorate	95		
Ronnel	101		
Sulfotep		116	
TEPP	ND		
Tetrachlorvinphos		100	

[a]Data taken from Reference 12. A 500-mg diol cartridge was used for this experiment.
[b]ND -- not detected.

TABLE A-7. EXTRACTION AND CLEANUP OF TRIAZINES FROM SOIL, MUSCLE TISSUE, AND CORN OIL[a]

Soil:	**500 mg SCX cartridge**
Extraction:	100 g soil shaken in 90% acetonitrile
Precondition:	5 mL 1% acetic acid
Load:	5 mL filtered extracted diluted with 25 mL 1% acetic acid
Rinse:	2 mL 1% acetic acid
	1 mL acetonitrile
	1 mL water
	1 mL 0.1M K_2HPO_4
Elution:	2 mL acetonitrile/0.1 M K_2HPO_4(50:50)
Muscle tissue:	**500 mg C_{18} cartridge**
Extraction:	100 g tissue homogenized in 100 mL methanol
Precondition:	5 mL methanol
	5 mL water
Load:	5 mL filtered extracted diluted with 50 mL water
Rinse:	2 mL water
Elution:	2 mL methanol
Corn oil:	**500 mg diol cartridge**
Extraction:	None
Precondition:	5 mL methanol
	5 mL hexane
Load:	5 mL corn oil diluted with 50 mL hexane
Rinse:	2 mL hexane
Elution:	2 mL methanol

[a]Data taken from Reference 13.

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Appendix B

METHOD 3670 -- SAMPLE EXTRACT CLEANUP USING SPE CARTRIDGES

DRAFT PROTOCOL

METHOD 3670

SAMPLE EXTRACT CLEANUP USING SPE CARTRIDGES

1.0 SCOPE AND APPLICATION

1.1 This protocol specifies cleanup procedures using solid-phase extraction cartridges that contain Florisil, alumina, diol or silica. These materials are used for general column chromatography prior to gas chromatographic analysis. Florisil, a registered trade name of the Floridin Co., is a magnesium silicate with acidic properties. Alumina is a highly porous and granular form of aluminum oxide. It is available in three pH ranges (basic, neutral, and acidic). Silica gel is an amorphous silica with weakly acidic properties.

1.2 Specific applications: This method includes guidance for cleanup of sample extracts containing the following analyte groups: Methods 8080/8081 organochlorine pesticides and polychlorinated biphenyls, Method 8060 phthalate esters, Method 8120 chlorinated hydrocarbons, and Method 8040 phenols.

2.0 SUMMARY OF METHOD

2.1 Florisil, alumina, diol or silica solid-phase extraction cartridges containing 40-um particles (60-A pores) are recommended for use. These cartridges consist of serological-grade polypropylene tubes, 6 mL in volume, each packed with 1 g of adsorbent. The material is held between two polyethylene frits (20-um pores). Each cartridge is prewashed with 4 mL hexane or hexane with 10 percent acetone (as specified in this protocol for various type of cartridges) immediately prior to use. Aliquots of 1 to 2 mL of sample extracts in hexane are loaded onto the cartridges which are then eluted with suitable solvent(s). A vacuum manifold is required in order to get reproducible results. The collected fractions are further concentrated prior to gas chromatographic analysis.

3.0 INTERFERENCES

3.1 A reagent blank should be performed for the compounds of interest prior to the use of this method. The level of interferences must generally be below the method detection limit before this procedure is performed on actual samples. However, phthalate esters were detected in Florisil cartridge method blanks at levels ranging from 10 to 406 ng per cartridge, with 5 phthalate esters in the 105 to 460 ng range. Complete removal of the phthalate esters from Florisil and alumina cartridges does not seem possible.

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

4.0 APPARATUS AND MATERIALS

4.1 Vacuum manifold, VacElute Manifold SPS-24 (Analytichem International) or Visiprep (Supelco, Inc.) or equivalent, consisting of glass vacuum basin, collection rack and funnel, collection vials, replaceable stainless steel delivery tips, built-in vacuum bleed valve and gauge. The system is connected to a vacuum pump or water aspirator through a vacuum trap made from a 500-mL sidearm flask fitted with a one-hole stopper and glass tubing.

4.2 Cartridges, Florisil, alumina, diol or silica (40-um particles, 60-A pores), 1 g; cartridges consist of serological-grade polypropylene tubes, 6 mL in volume; the adsorbent is held between two polyethylene or stainless steel frits (20-um pores). Cartridges of 0.5 g and 2.0 g are also available and could be used, however, the compound elution patterns need to be verified when cartridges are used the are different in size from those specified in this method.

4.3 Kuderna-Danish (K-D) apparatus

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

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

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

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

4.4 Muffle furnace.

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

4.6 Boiling chips: Solvent-extracted, approximately 10/40 mesh (silicone carbide or equivalent).

5.0 REAGENTS

5.1 Diethyl ether: Pesticide quality or equivalent.

5.1.1 Must be free of peroxides as indicated by EM Quant test strips (available from EM Laboratories, Elmsford, NY 10523).

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

5.2 Hexane, acetone, methylene chloride, toluene: Pesticide quality or equivalent.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

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

7.0 PROCEDURE

7.1 Cartridge Set-up and Conditioning

7.1.1 Arrange the cartridges on the manifold in the closed-valve position.

7.1.2 Turn vacuum pump on and set pump vacuum to 10 inches of mercury. Do not exceed the manufacturer's recommendation for manifold vacuum. Flow rates can be controlled by opening and closing cartridge valves.

7.1.3 Condition the cartridges by pipetting 4 mL hexane onto each cartridge. Slowly open the cartridge valves to allow hexane to pass through the sorbent beds to the lower frits. Allow a few drops per cartridge to pass through the manifold to remove all air bubbles. Close the valves and allow the solvent to soak the entire sorbent beds for 5 min. Do not turn off the vacuum.

7.1.4 Slowly open cartridge valves to allow the hexane to pass through the cartridges. Close the cartridge valves when there is still at least 1 mm solvent above the sorbent bed. Do not allow cartridges to get dry. If this happens, repeat the conditioning step.

7.2 General extract cleanup procedure

7.2.1 Allow extract to reach room temperature if it was in cold storage.

7.2.2 Inspect the extract visually to ensure that there are no particulates or phase separations and that the volume is as stated in the accompanying documents, and verify that the solvent is compatible with the cleanup procedure. If crystals of sulfur are visible or if the presence of sulfur is suspected, proceed with Method 3660.

7.2.3 Pipet 2 mL of extract onto each cartridge. Open the cartridge valves to allow the extracts to pass through the cartridge beds at approximately 2 mL/min. When the entire extracts have passed through the cartridges, but before the cartridges get dry, rinse the sample vials with additional 0.5 mL solvent portions and add the rinses to the corresponding cartridges. Close the cartridge valves and turn off the vacuum after the solvent has passed through, ensuring that the cartridges never get dry.

7.2.4 Place clean 5-mL vials or volumetric flasks into the sample rack corresponding to the cartridge positions.

7.2.5 Attach solvent-rinsed stainless steel solvent guides to manifold cover and align with collection vials.

7.2.6 Add the first eluting solvent(s) to each cartridge.

7.2.7 Turn vacuum pump on. Adjust pump pressure to 10 inches of mercury. Allow solvent to soak the sorbent beds for 1 min or less. Slowly open the cartridge valves and collect eluates into the collection vials (if the procedure calls for collection of Fraction 1) or discard.

7.2.8 Close cartridge valves, replace collection vials, and add the second eluting solvent(s) to each cartridge to collect Fraction 2. Slowly open cartridge valves and collect eluates.

7.2.9 Bring the total volume of each fraction to 5 mL by adding additional solvent. If this final volume is too dilute for gas chromatographic analysis then the fractions collected have to be concentrated to 1 mL or less, using either nitrogen blowdown or a micro-Snyder column. Measure the final volumes of the fractions collected with a syringe.

7.2.10 Transfer the fractions to autosampler vials for gas chromatographic analysis.

7.3 Organochlorine pesticides

7.3.1 Reduce the sample extract volumes to 2 mL prior to cleanup. The extract solvent must be hexane.

7.3.2 Use 1-g silica cartridges (whenever polychlorinated biphenyls are known to be present) or diol cartridges and perform the steps described in Section 7.1. Hexane is used to condition the silica cartridges, and hexane with 10 percent acetone is used to condition the diol cartridges.

7.3.3 Add the extracts to the cartridges. Follow step by step the instructions given in Section 7.2. Silica cartridges are eluted first with 5 mL hexane to collect Fraction 1 and then with 5 mL hexane with 50 percent diethyl ether to collect Fraction 2. Diol cartridges are eluted with 10 mL hexane with 10 percent acetone. Adjust the volumes of the fractions collected to whatever volume is required (see Method 8081) and analyze. Tables 1 and 2 show compound recoveries for the 1-g silica and the 1-g diol cartridges, respectively.

7.4 Phthalate esters

7.4.1 Reduce the sample extract volumes to 2 mL prior to cleanup. The extract solvent must be hexane.

7.4.2 Use 1-g Florisil or alumina cartridges and perform the steps described in Section 7.1. Hexane is used to condition the cartridges.

7.4.3 Add the extracts to the cartridges. Follow step by step the instructions given in Section 7.2. If organochlorine pesticides are known to be present in the extract, use Florisil cartridges. Elute the Florisil cartridges with hexane with 20 percent methylene chloride to remove the organochlorine pesticides. The phthalate esters are recovered with 10 mL hexane with 10 percent acetone. Alumina cartridges are eluted with 10 mL hexane with 20 percent acetone. Adjust the volumes of the fractions collected to whatever volume is required (see Method 8061) and analyze. Table 3 and 4 show compound recoveries for the 1-g Florisil and the 1-g alumina cartridges, respectively.

7.5 Chlorinated hydrocarbons

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

7.5.2 Use 1-g Florisil cartridges and perform the steps described in Section 7.1. Hexane is used to condition the Florisil cartridges.

7.5.3 Add the extracts to the cartridges. Follow step by step the instructions given in Section 7.2. Florisil cartridges are eluted with 5 mL hexane with 10 percent acetone. Adjust the volumes of the fractions collected to whatever volume is required (see Method 8121) and analyze. Table 5 shows compound recoveries for the 1-g Florisil cartridges.

7.6 Phenols

7.6.1 Reduce the sample extract volumes to 2 mL prior to cleanup. The extract solvent must be hexane.

7.6.2 Use 2-g silica cartridges and perform the steps described in Section 7.1. Hexane is used to condition the silica cartridges.

7.6.3 Add the extracts to the cartridges. Follow step by step the instructions given in Section 7.2. Silica cartridges are eluted first with 5 mL hexane which is discarded (Fraction 1). The phenols are eluted with 5 mL hexane with 25 percent toluene. If smaller cartridges are used, then Fraction 1 cannot be discarded since it contains some of the phenols. Adjust the volumes of the fractions collected to whatever volume is required (see Method

8041) and analyze. Table 6 shows compound recoveries for the 2-g silica cartridges.

8.0 QUALITY CONTROL

8.1 Before any samples are cleaned up using the solid-phase extraction cartridges, the efficiency of the cartridge must be verified. A recovery check must be performed using standards of the target analytes at known concentration. Only lots of cartridges that do meet the recovery criteria for the spiked compounds can be used to process the samples.

8.2 A check should also be performed on each individual lot of cartridges and for every 300 cartridges of a particular lot.

9.0 REFERENCES

1. Lopez-Avila, V., Milanes, J., Dodhiwala, N.S., and Beckert, W.F. "Cleanup of Environmental Sample Extracts Using Florisil Solid-Phase Extraction Cartridges", J. Chrom. Sci. 27, 209-215, 1989.

TABLE 1. PERCENT RECOVERIES AND ELUTION PATTERNS FOR 17 ORGANOCHLORINE PESTICIDES FROM 1-g SILICA CARTRIDGES [a]

Compound	Fraction 1 Average recovery	Fraction 1 Percent RSD	Fraction 2 Average recovery	Fraction 2 Percent RSD
alpha-BHC	0		98.7	2.3
gamma-BHC	0		94.8	1.9
beta-BHC	0		94.3	3.0
Heptachlor	97.3	1.3	0	
delta-BHC	0		90.8	2.5
Aldrin	95.9	1.0	0	
Heptachlor epoxide	0		97.9	2.1
Endosulfan I	0		102	2.3
4,4'-DDE	99.9	1.7	0	
Dieldrin	0		92.3	2.0
Endrin	0		117	2.6
4,4'-DDD	10.7	41	92.4	3.3
Endosulfan II	0		96.0	2.2
4,4'-DDT	94.1	2.0	0	
Endrin aldehyde	0		59.7	2.6
Endosulfan sulfate	0		97.8	2.1
4,4'-Methoxychlor	0		98.0	2.4
Aroclor 1016	124			
Aroclor 1221	93.5			
Aroclor 1232	118			
Aroclor 1242	116			
Aroclor 1248	114			
Aroclor 1254	108			
Aroclor 1264	112			

[a] Silica cartridges (Supelco,Inc. lot SP0161) were used; each cartridge was conditioned with 4 mL hexane prior to use. The organochlorine pesticides were tested separately from PCBs. For organochlorine pesticides, each experiment was performed in duplicate at three spiking levels (0.2 ug, 1.0 ug, and 2.0 ug per compound per cartridge). Fraction 1 was eluted with 5 mL hexane, Fraction 2 with 5 mL hexane with 50 percent diethyl ether. PCBs were spiked at 10 ug per cartridge and were eluted with 3 mL hexane. The value given for PCBs is the percent recovery for single determination.

TABLE 2. PERCENT RECOVERIES AND ELUTION PATTERNS FOR 17 ORGANOCHLORINE PESTICIDES FROM 1-g DIOL CARTRIDGES[a]

Compound	Fraction 1 Average recovery	Fraction 1 Percent RSD	Fraction 2 Average recovery	Fraction 2 Percent RSD
alpha-BHC	101	8.3		
gamma-BHC	95.0	8.4		
beta-BHC	86.7	8.5		
Heptachlor	96.2	8.4		
delta-BHC	75.9	8.2	20.4	45
Aldrin	93.5	8.1		
Heptachlor epoxide	98.1	8.5		
Endosulfan I	100	9.0		
4,4'-DDE	97.3	8.3		
Dieldrin	95.2	8.2		
Endrin	95.9	9.0		
4,4'-DDD	97.8	8.9		
Endosulfan II	86.0	8.2	15.4	30
4,4'-DDT	96.7	8.3		
Endrin aldehyde	19.9	21	58.9	3.7
Endosulfan sulfate	0		80.1	3.9
4,4'-Methoxychlor	90.7	8.2		
Aroclor 1260	90.0		10.0	

[a] Diol cartridges (Supelco, Inc. lot SP0216) were used; each cartridge was conditioned with 4 mL hexane with 10 percent acetone prior to use. The organochlorine pesticides were tested separately from PCBs. For organochlorine pesticides, each experiment was performed in duplicate at three spiking levels (0.2 ug, 1.0 ug, and 2.0 ug per compound per cartridge). Each fraction was eluted with 5 mL hexane with 10 percent acetone. Aroclor 1260 was spiked at 80 ug per cartridge. The value given for Aroclor 1260 is the percent recovery for single determination.

TABLE 3. PERCENT RECOVERIES AND ELUTION PATTERNS FOR 16 PHTHALATE ESTERS FROM 1-g FLORISIL CARTRIDGES[a]

Compound	Fraction 2 Average recovery	Fraction 2 Percent RSD
Dimethyl phthalate	130	52
Diethyl phthalate	88.2	2.5
Diisobutyl phthalate	118	16
Di-n-butyl phthalate	121	13
Bis(4-methyl-2-pentyl) phthalate	123	5.7
Bis(2-methoxyethyl) phthalate	31.9	31
Diamyl phthalate	93.7	34
Bis(2-ethoxyethyl) phthalate	82.1	19
Hexyl 2-ethylhexyl phthalate	126	6.4
Dihexyl phthalate	62.0	15
Benzyl butyl phthalate	98.3	6.5
Bis(2-n-butoxyethyl) phthalate	135	34
Bis(2-ethylhexyl) phthalate	110	2.7
Dicyclohexyl phthalate	106	3.3
Di-n-octyl phthalate	123	7.0
Dinonyl phthalate	102	8.7

[a] Florisil cartridges (Supelco, Inc.) were used; each cartridge was conditioned with 4 mL hexane prior to use. Each experiment was performed in triplicate. The spiking level was 500 ng per compound per cartridge. Fraction 1 was eluted with 5 mL hexane with 20 percent methylene chloride, Fraction 2 with 5 mL hexane with 10 percent acetone. No phthalate esters were detected in Fraction 1.

TABLE 4. PERCENT RECOVERIES AND ELUTION PATTERNS FOR 16 PHTHALATE ESTERS FROM 1-g ALUMINA CARTRIDGES[a]

Compound	Fraction 1 Average recovery	Fraction 1 Percent RSD
Dimethyl phthalate	108	4.6
Diethyl phthalate	129	6.6
Diisobutyl phthalate	92.6	7.3
Di-n-butyl phthalate	107	5.6
Bis(4-methyl-2-pentyl) phthalate	88.3	9.8
Bis(2-methoxyethyl) phthalate	92.2	5.0
Diamyl phthalate	100	6.4
Bis(2-ethoxyethyl) phthalate	101	6.3
Hexyl 2-ethylhexyl phthalate	93.2	13
Dihexyl phthalate	113	5.4
Benzyl butyl phthalate	104	3.9
Bis(2-n-butoxyethyl) phthalate	99.5	4.7
Bis(2-ethylhexyl) phthalate	101	6.1
Dicyclohexyl phthalate	97.2	6.2
Di-n-octyl phthalate	103	7.5
Dinonyl phthalate	110	5.2

[a] Alumina cartridges (J.T.Baker) were used; each cartridge was conditioned with 4 mL hexane prior to use. Each experiment was performed in duplicate at three spiking levels (40 ug, 80 ug, and 120 ug per compound per cartridge). Fraction 1 was eluted with 5 mL hexane with 20 percent acetone.

TABLE 5. PERCENT RECOVERIES AND ELUTION PATTERNS FOR 22 CHLORINATED HYDROCARBONS FROM 1-g FLORISIL CARTRIDGES[a]

Compound	Fraction 1 Average recovery	Fraction 1 Percent RSD
Hexachloroethane	95.4	2.0
1,3-Dichlorobenzene	101	2.3
1,4-Dichlorobenzene	100	2.3
1,2-Dichlorobenzene	102	1.6
Benzyl chloride	101	1.5
1,3,5-Trichlorobenzene	98.4	2.2
Hexachlorobutadiene	94.8	2.0
Benzal chloride	99.2	0.8
1,2,4-Trichlorobenzene	99.2	0.8
Benzotrichloride	90.0	6.5
1,2,3-Trichlorobenzene	97.2	2.0
Hexachlorocyclopentadiene	103	3.3
1,2,4,5-Tetrachlorobenzene	98.0	2.3
1,2,3,5-Tetrachlorobenzene	98.0	2.3
1,2,3,4-Tetrachlorobenzene	99.2	1.3
2-Chloronaphthalene	94.8	1.4
Pentachlorobenzene	104	1.5
Hexachlorobenzene	78.4	1.1
alpha-BHC	100	0.4
gamma-BHC	99.0	0.7
beta-BHC	95.4	1.8
delta-BHC	96.8	2.7

[a]Florisil cartridges (Supelco, Inc.) were used; each cartridge was conditioned with 4 mL hexane prior to use. Five replicate experiments were performed. Spiking level was 1.0 ug per cartridge for hexachloroethane,hexachlorobutadiene,hexachlorocyclopentadiene, penta- and hexachlorobenzene; 10 ug per cartridge for tri- and tetrachlorobenzenes, benzal chloride, benzotrichloride, and the BHC isomers; 100 ug per cartridge for dichlorobenzenes and benzyl chloride; and 200 ug per cartridge for 2-chloronaphthalene. Fraction 1 was eluted with 5 mL hexane with 10 percent acetone.

TABLE 6. PERCENT RECOVERIES AND ELUTION PATTERNS FOR 18 PHENOLS FROM 2-g SILICA CARTRIDGES[a]

Compound	Fraction 2 Average recovery	Fraction 2 Percent RSD
Phenol	74.1	5.2
2-Methylphenol	84.8	5.2
3-Methylphenol	86.4	4.4
4-Methylphenol	82.7	5.0
2,4-Dimethylphenol	91.8	5.6
2-Chlorophenol	88.5	5.0
2,6-Dichlorophenol	90.4	4.4
4-Chloro-3-methylphenol	94.4	7.1
2,4-Dichlorophenol	94.5	7.0
2,4,6-Trichlorophenol	97.8	6.6
2,3,6-Trichlorophenol	95.6	7.1
2,4,5-Trichlorophenol	92.3	8.2
2,3,5-Trichlorophenol	92.3	8.2
2,3,5,6-Tetrachlorophenol	97.5	5.3
2,3,4,6-Tetrachlorophenol	97.0	6.1
2,3,4-Trichlorophenol	72.3	8.7
2,3,4,5-Tetrachlorophenol	95.1	6.8
Pentachlorophenol	96.2	8.8

[a]Silica cartridges (Supelco, Inc.) were used; each cartridge was conditioned with 4 mL hexane prior to use. Each experiment was performed in duplicate at three spiking levels (0.05 ug, 0.2 ug, and 0.4 ug per compound per cartridge). Fraction 1 was eluted with 5 mL hexane and was discarded. Fraction 2 was eluted with 5 mL hexane with 25 percent toluene.