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Project Summary

Evaluation of Sample Extract Cleanup Using Solid-Phase Extraction Cartridges

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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.

This Project Summary was developed by EPA's Environmental Monitoring Systems Laboratory, Las Vegas, NV, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

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 (SPE) 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, several extracts of environmental samples were spiked with the target analytes at known concentrations and were fractionated using the solid-phase extraction cartridge procedure.

Experimental

Cartridge Cleanup Procedure

Florisil, alumina, and silica cartridges were conditioned prior to use with 4 mL hexane. Diol cartridges were conditioned with hexane with 10 percent acetone. 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. Details of the cartridge cleanup procedure can be found in the protocol included in Appendix B of the full report.

Gas Chromatographic Analysis

All fractions were analyzed by gas chromatography with ECD using the dual-column approach.

The GC operating conditions for the organochlorine pesticides 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.

GC operating conditions for the phthalate esters 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-inch injection tee (Supelco, Inc.). Temperature program: 250°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.

GC operating conditions for the phenols were as follows: 30-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.

Phenols were derivatized with pentafluorobenzyl bromide (PFBBr) following the procedure by Lee et al. (2).

Results and Discussion

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. We evaluated Method 3620 and found that, although compound recoveries v quantitative, the Florisil fractiona method is not suitable for samples contain both organochlorine pestic and PCBs (3) since the PCBs are el in the same fraction as the bulk of organochlorine pesticides. We under the evaluation of Florisil cartrid specifically for samples that contain the organochlorine pesticides. The s cartridges were considered since Me 8081 describes a procedure in w PCBs can be separated from the bul the organochlorine pesticides using s gel deactivated with 3 percent wa Finally, diol cartridges were evalu since at the time our study conducted, EPA was considering the of diol cartridges for incorporation the Contract Laboratory Progr protocols.

The results of the evaluation study summarized below:

- The use of silica cartridges prove be superior to the use of Flo cartridges because it allov complete separation of the PCBs f all but four organochlorine pesticic quantitative recovery of compounds, and almost comp separation of the Method 8 organochlorine pesticides from Method 8060 phthalate esters. separate the PCBs, the 1-g si cartridges required elution with 3 hexane. To recover quantitatively organochlorine pesticides, the si cartridges were further eluted wit mL hexane with 50 percent die ether (Table 1).
- The use of diol cartridges also all separation of the PCBs from organochlorine pesticides when cartridges are first eluted with hexa and quantitative recoveries for organochlorine pesticides achieved when the cartridges eluted with hexane with 10 perc acetone (Table 2).
- The procedure that uses sil cartridges and hexane with 50 perc diethyl ether was tested w cartridges of 0.5-g, 1-g, and 2-g s each charged with 17 organochlo pesticides at 0.2 µg, 1.0 µg, and 2.0 per cartridge. Two fractions w collected from the 0.5-g and cartridges. An additional 5 mL hexane with 50 percent diethyl et were passed through the 2. cartridges to collect Fraction 3. compounds, except endrin aldehy were recovered quantitativ (recovery >75 percent) in the two three fractions combined. The elu

Table 1. *Percent Recoveries and Elution Patterns for 17 Organochlorine Pesticides from 1-G Silica Cartridges*[a]

Compound	Fraction 1		Fraction 2	
	Average recovery	Percent RSD	Average recovery	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 µg, 1.0 µg, and 2.0 µg 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 µg per cartridge and were eluted with 3 mL hexane. The values given for PCBs are the percent recoveries for single determinations.*

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 cartridges.

- The procedure that uses diol cartridges and hexane with 10 percent acetone was tested with 0.5-g, 1-g, and 2-g size cartridges. Each cartridge was charged with 17 organochlorine pesticides at 0.2 µg, 1.0 µg, and 2.0 µg. Two fractions were collected from the 0.5-g and 1-g cartridges, and up to four fractions were collected from the 2-g cartridges. Overall, all compounds were recovered quantitatively (recovery >75 percent) in the two, three, or four fractions combined. At the 0.2-µg spike level, sixteen compounds were eluted in Fraction 1 from the 0.5-g cartridges, and only two compounds (endrin aldehyde and endosulfan sulfate) were eluted in Fraction 2. Small amounts (<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 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.
- Corn oil or diesel hydrocarbons did not affect the elution patterns of the 17 organochlorine pesticides from either the silica or the diol cartridges (Tables 3 and 4). 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. 4,4'-DDE and 4,4'-DDT also elute in Fraction 1, however, they can be quantified without any difficulty

Table 2. 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 Arochlor 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.

on either the DB-608 or the DB-1701 fused-silica open tubular columns. The remainder of the 17 organochlorine pesticides were retained on the silica cartridge and were 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. It was found that when the cartridge is eluted with hexane with 10 percent acetone, the elemental sulfur elutes together with the organochlorine pesticides and will interfere with the gas chromatographic analysis of six organochlorine pesticides on the DB-1701 column.

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.

We have evaluated both methods with hexane solutions containing 16 phthalate esters. 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, bis(2-methoxyethyl) phthalate (BMEP), bis(2-ethoxyethyl) phthalate (BEEP), and bis(2-n-butoxyethyl) phthalate (BBEP) could not be recovered at all, and dimethyl phthalate (DMP) and diethyl phthalate (DEP) gave recoveries of only 40 and 57 percent, respectively.

We used Florisil and alumina SPE cartridges of 0.5-g, 1.0-g, and 2-g size, charged them the target compounds and interferents, and eluted them with 10 percent acetone (for Florisil) or hexane with 20 percent acetone (for alumina).

The results of the evaluation study are summarized below:

- The procedure that uses alumina cartridges and hexane with 20 percent acetone gave quantitative recoveries for all compounds except BMEP from the 2-g cartridges. BMEP was recovered from the 2-g alum cartridges by eluting the cartrid with two additional 5-mL portions hexane with 20 percent acetone. Ta 5 presents the recovery data for the g alumina cartridges.
- The procedure that uses Flor cartridges and hexane with 10 perc acetone gave good recoveries for 16 phthalate esters except BMEP a BEEP (the 0.5-g and the 1-g Flo cartridge were eluted with 5 hexane with 10 percent acetone, a the 2-g cartridges were eluted with mL of hexane with 10 perce acetone).
- Corn oil and diesel hydrocarbons not affect the elution patterns or recovery of the 16 phthalate est from either type of cartridge (Table except for BMEP and BEEP (s footnotes to Table 6). Elemental sul if present, is eluted from the Flo cartridge with hexane with 10 perc acetone and from the alumi cartridge with hexane with 20 perc acetone. Therefore, extracts that known to contain elemental sul should be subjected to sulfur clear

Table 3. *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.*

(Method 3660) prior to Florisil or alumina cartridge cleanup.

- The organochlorine pesticides, if present, can be separated from the phthalate esters using Florisil cartridges (Table 7). The organochlorine pesticides are first eluted from the 1-g Florisil cartridges with 5 mL hexane with 20 percent methylene chloride. Under these conditions, the phthalate esters are retained on the cartridge and are later eluted with hexane with 10 percent acetone.

Phenols

Silica cartridges were evaluated for cleanup of sample extracts containing phenolic compounds derivatized with pentafluorobenzyl bromide (PFBBr). Quantitative recoveries of the 18 phenolic compounds were obtained using 2-g silica cartridges and hexane with 25 percent toluene as eluant (Table 8).

Matrix interferents such as corn oil, diesel hydrocarbons, and elemental sulfur were added to hexane solutions of the derivatized 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 9). 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.

Evaluation of the ASPEC System

The Gilson ASPEC system (Automatic Sample Preparation with Extraction Columns), with a modified standard program, was used to evaluate the silica and diol cartridges for the cleanup of extracts containing organochlorine pesticides and Aroclor 1260 or organochlorine pesticides and corn oil, diesel hydrocarbons, Aroclor 1260, and elemental sulfur. Furthermore, three environmental sample extracts were processed using the ASPEC system and 0.5-g diol cartridges.

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 10), and there was no crosscontamination when interferents were added such as corn oil, diesel hydrocarbons, and when sample extracts were used.

Conclusions

Currently, there are no EPA-approved sample extract cleanup procedures that specify the use of 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 Capiliary 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

Table 4. *Percent Recoveries and Elution Patterns of 17 Organochlorine Pesticides from 1-g Diol Cartridges in the Presence of Corn Oil ar 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 organochlorin 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 mL hexane with 10 percent acetone in hexane. Vacuum manifold used was the Analytichem SPS24.*

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.

Recommendations

- The protocol for extract cleanup using SPE cartridges which is presented as part of the full report has been evaluated in a single laboratory 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 sillcas 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.

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Table 5. *Percent Recoveries and Elution Patterns for 16 Phthalate Esters from 1-g Alumina Cartridges*[a]

	Fraction 1	
Compound	*Average Recovery*	*Percent RSD*
Dimethyl phthalate (DMP)	*108*	*4.6*
Diethyl phthalate (DEP)	*129*	*6.6*
Diisobutyl phthalate (DIBP)	*92.6*	*7.3*
Di-n-butyl phthalate (DBP)	*107*	*5.6*
Bis(4-methyl-2-pentyl) phthalate (BMPP)	*88.3*	*9.8*
Bis(2-methoxyethyl) phthalate (BMEP)	*92.2*	*5.0*
Diamyl phthalate (DAP)	*100*	*6.4*
Bis(2-ethoxyethyl) phthalate (BEEP)	*101*	*6.3*
Hexyl 2-ethylhexyl phthalate (HEHP)	*93.2*	*13*
Dihexyl phthalate (DHP)	*113*	*5.4*
Benzyl butyl phthalate (BBP)	*104*	*3.9*
Bis(2-n-butoxyethyl) phthalate (BBEP)	*99.5*	*4.7*
Bis (2-ethylhexyl) phthalate (DEHP)	*101*	*6.1*
Dicyclohexyl phthalate (DCP)	*97.2*	*6.2*
Di-n-octyl phthalate (DOP)	*103*	*7.5*
Dinonyl phthalate (DNP)	*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 µg, 80 µg, and 120 µg per compound per cartridge). Fraction 1 was eluted with 5 mL hexane with 20 percent acetone.*

Table 6. *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 cartridges. In Fraction 2 at 81.9 and 95.6 percent when corn oil was present as interferent, and at 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.*

Table 7. *Percent Recoveries and Elution Patterns for 16 Phthalate Esters from 1-g Florisil Cartridges in the Presence of Organochlorine Pesticides*[a]

Compound	Fraction 2	
	Average recovery	Percent RSD
DMP	130	52
DEP	88.2	2.5
DIBP	118	16
DBP	121	13
BMPP	123	5.7
BMEP	31.9	31
DAP	93.7	34
BEEP	82.1	19
HEHP	126	6.4
DHP	62.0	15
BBP	98.2	6.5
BBEP	135	34
DEHP	110	2.7
DCP	106	3.3
DOP	123	7.0
DNP	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 which contained all organochlorine pesticides 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 8. *Percent Recoveries and Elution Patterns for 18 Derivatized Phenols from 2-g Silica Cartridges*[a]

Compound	Fraction 2	
	Average recovery	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 (0.1 µg, 0.2 µg, and 0.4 µg 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*

Table 9. *Percent Recoveries and Elution Patterns of Derivatized Phenols from 1-g Silica Cartridges in the Presence of Corn Oil and Diesel Hydrocarbons*[a]

Compound	Corn oil as interferent				Diesel hydrocarbons as interferents			
	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-Dimethylpehenol	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 10. *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. The number of determinations was 19.

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***Werner F. Beckert** is the EPA Project Officer (see below).*

The complete report, entitled "Evaluation of Sample Extract Cleanup Using Solid-Phase Extraction Cartridges," (Order No. PB 90-162 520/AS; Cost: $23.00, subject to change) will be available only from:

National Technical Information Service
5285 Port Royal Road
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