

Extraction of Hydrophobic Organics from Aqueous Samples with 90-mm C-18 Bonded Disks

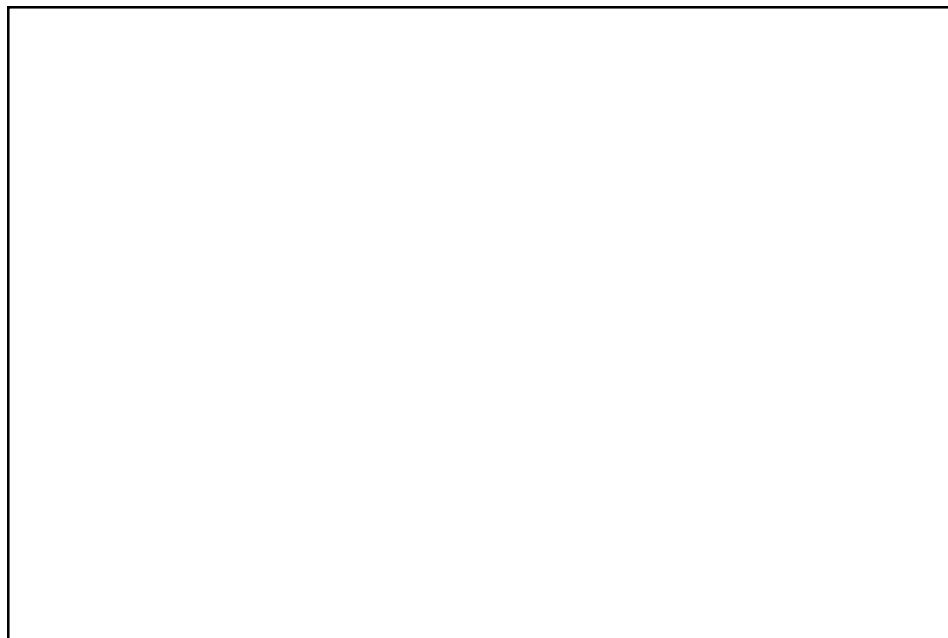
Technological advances in hardware, software, and computing have resulted in sophisticated analytical instruments that are highly automated and reasonably priced. By contrast, sample extraction methods require significant amounts of manpower and time. Sample preparation has become a focus for improving laboratory efficiency compared to instrumental analysis. For instance, the conventional liquid-liquid extraction (LLE) method, which is widely used for extracting semi- and non-volatile organic pollutants from aqueous samples, is labor intensive and requires a large quantity of hazardous organic solvents. The solid phase extraction (SPE) technique is a potential replacement for LLE (Loconto 1991a,b, Markell *et al.* 1992). SPE requires less organic solvent and less labor than LLE, but extraction efficiencies are comparable. SPE also eliminates the emulsification that often occurs with LLE.

SPE can be performed with cartridges (columns) or disks, but cartridges have several disadvantages. Their narrow internal diameter limits the flow rate and the small cross-sectional area is clogged easily by a small amount of suspended solids, which prolongs the extraction of large sample volumes (Markell *et al.* 1992). Interference from SPE cartridges has also been reported (Junk *et al.* 1988). SPE disks have a configuration similar to membrane filters (Markell *et al.* 1992). Because smaller particles are used with the disks relative to cartridges, the large diameter and short length of disks increase the membrane flow rate while matching the effectiveness of cartridges (Hagen *et al.* 1990, Kraut-Vass and Thoma 1991).

We examined the efficiency and precision of the 90-mm EmporeTM C-18 bonded disks (3M Company, St. Paul, MN) for extracting several groups of hydrophobic organic compounds. In some cases, we used LLE simulta-

neously with SPE for comparison. The 90 mm diameter SPE disks are relatively new and have been used primarily in extracting relatively clean samples (purified water, tap water, ground water, etc.). The objective of this study was to extend the application of the SPE method to environmental samples. We analyzed effluent samples from two municipal wastewater treatment plants and we chose polycyclic aromatic hydrocarbons (PAHs), linear alkylbenzenes (LABs), polychlorinated biphenyls (PCBs), and chlorinated pesticides (DDTs) as target compounds.

Chemists examining a chromatogram.



MATERIALS AND METHODS

The 90-mm EmporeTM C-18 bonded disks and Filter Aid 400 (high density glass beads) were obtained from 3M Company. GF/F (0.7 μm pore size) and GF/C (1.2 μm pore size) glass fiber filters were manufactured by Whatman International Ltd. (Maidstone, England). Twelve PAH compounds were custom-made by AccuStandard, Inc. (New Haven, CT) and another sixteen PAHs were purchased from Ultra Scientific, Inc. (North

Kingstown, RI). The LAB mixture (containing 21 resolved LAB peaks) was obtained in neat form from Mr. Robert D. Bowen at SAIC (Narragansett, RI). Aroclors used to prepare the Aroclor mixture were purchased from Supelco, Inc. (Bellefonte, PA). The EPA PCB Congener Calibration Check Solution (20 PCB congeners) and DDTs were purchased from Ultra Scientific, Inc. All standard solutions were prepared in hexane. Ultra resi-analyzed grade hexane, methylene chloride, methanol, and ethyl acetate were obtained from J.T. Baker (Phillipsburg, NJ) and used without further purification. Ultra high purity He and N₂ were supplied by Oxygen Service (Orange, CA).

Sample Collection and Pretreatment

Water was distilled to obtain purified water from Arrowhead Mountain Spring Water Co. (Orange, CA). Sand-filtered seawater was collected from an off-shore intake of Southern California Edison (Redondo Beach, CA). Twenty-four hour composite effluent was obtained from the Point Loma Treatment Plant (PLTP) of the City of San Diego and the County Sanitation Districts of Orange County (CSDOC).

One-liter samples of purified water, seawater, and effluent were used in the spiking experiments. Refrigerated samples were allowed to equilibrate to room temperature prior to extraction. Seawater samples were filtered using a GF/F filter. Since significant amounts of suspended particles were present in the effluent, the samples to be spiked with DDTs were filtered with GF/C and GF/F glass fiber filters consecutively. The spiking amounts of standards in the final extract volume (1 mL) were: PAHs - 5 µg/mL each, LABs - 20 µg/mL total in a mixture, PCBs - 0.08 µg/mL each, and DDTs - 2 µg/mL each.

Ten liters of unspiked PLTP effluent samples were filtered with GF/C and GF/F glass fiber filters consecutively and split equally for SPE and LLE. For the unspiked CSDOC effluent samples, a 4-L sample was filtered with GF/C and GF/F. Another 4-L sample was filtered with GF/C and high density glass beads were placed on the SPE disk before the sample was poured onto it. All the prefiltered samples were spiked with the surrogate standards (and target compounds for spiking experiments) before extraction.

Sample Extraction

Solid Phase Extraction

The extraction assembly with a 3-way valve controlling vacuum was set up on a stainless steel manifold. In a typical experiment, the 90-mm C-18 bonded disk was precleaned by adding 10 mL of a 1:1 mixture of ethyl acetate and methylene chloride. The solvent was allowed to stand for 3 min with vacuum off, and then drawn

through with vacuum. Ten milliliters of methanol were added to the disk for conditioning and allowed to stand for a few minutes. The solvent was drawn slowly through the disk until a thin layer was left on the disk surface. One liter of aqueous sample adjusted to pH 2 with 6N HCl was poured onto the disk. The sample was drawn through with a vacuum pressure of 25 in Hg. After the entire sample had passed through the disk, vacuum was left on for a few minutes to remove any excess water from the disk. Pressure was brought to the atmosphere and a 35-mL test tube was placed below the disk. The sample container and reservoir was rinsed with 10 mL of ethyl acetate. The rinsate was poured into the disk, which was allowed to soak for several minutes and drawn through. This step was repeated once again with 10 mL of ethyl acetate and then with 10 mL methylene chloride. The eluates were combined over anhydrous sodium sulfate for subsequent condensation. Vacuum pressure was adjusted to 25 in Hg, although small variations do not affect recovery efficiencies (Junk and Richard 1988, Hagen *et al.* 1990). The time required for 1 L of sample to pass through a 90-mm disk was typically 10 min.

Liquid-Liquid Extraction

One liter of aqueous sample was transferred to a 2-L separatory funnel and spiked with surrogate standards (and target compounds in spiking experiments). Sixty milliliters of methylene chloride were added to the sample and the separatory funnel was shaken vigorously for 2 min with periodic venting to release excess pressure. The organic layer was separated and collected in a 500-mL flat bottom flask through a long-stemmed glass funnel plugged with glass wool and about 2 g anhydrous sodium sulfate. This extraction step was repeated twice, and the three extracts were combined for further condensation.

Sample Condensation

Purified Water and Seawater

The combined extract from SPE or LLE was concentrated to approximately 3 mL with a rotary evaporator. Five milliliters of hexane were added to the extract, which was further concentrated to approximately 1 mL (solvent-exchanged to hexane). This step was not necessary for the samples extracted by SPE, however, they went through this step to obtain identical treatments. The extract was transferred to a vial and the flask was rinsed with hexane. The rinsate was added to the vial and concentrated to 1 mL under gentle N₂ flow. Internal standards were added to the extract before instrumental analysis.

Spiked and Unspiked Effluent

Because effluents contain complex components, a clean-up procedure was used. The 1 mL extract obtained in hexane was applied to a 1:2 alumina/silica gel glass column for chromatographic separation. The second fraction, which contained PAHs, LABs, PCBs, and DDTs, was collected in a pear-shaped flask by eluting 5 mL of dry hexane and 30 mL of 30/70 methylene chloride-hexane mixture. This fraction was concentrated to about 1 mL, solvent-exchanged to hexane with a rotary evaporator, and transferred to a half dram vial. The pear-shaped flask was rinsed with additional hexane and the rinsate was added to the half-dram vial. The final extract was concentrated to 1 mL under gentle N₂ flow. Internal standards were added to the extract before instrumental analysis.

Chromatographic Conditions

GC/ECD Analysis

An Hewlett Packard (HP) 5890 series II gas chromatograph was equipped with a ⁶³Ni electron capture detector and a 60 m x 0.25 mm ID (0.25 µm film thickness) DB-5 fused silica capillary column (J&W Scientific, Folsom, CA). Ultra high purity helium was used as a carrier gas at 2.0 mL/min at 90°C. Make-up gas used for ECD detector was ultra high purity nitrogen at 30 mL/min. He and N₂ were purified with moisture and hydrocarbon and oxygen filters before use. The oven temperature began at 90°C and immediately increased to 180°C at 6°C/min, followed by a 1°C/min ramp to 290°C. Split/splitless injection of a 2 µL sample was performed by a HP 7673 auto sampler with 1 min solvent split time. Injector and detector temperatures were maintained at 280°C. Data were acquired and reduced with a Perkin Elmer (PE) Nelson Turbochrom 3 data system running on an IBM compatible PC connected to a PE Nelson 900 Series Interface.

GC/MS Analysis

An HP 5890 series II GC with a 5970 Mass Selective Detector (MSD) was used to measure PAHs and LABs. Chromatographic separation was obtained with a 60 m x 0.25 mm ID (0.25 µm film thickness) DB-5 column. The MSD was operated at the electron impact ionization mode with an electron energy of 70 eV. A mass scanning range of m/z 45 to m/z 400 was used at 1.7 scan/s. The electron multiplier voltage was set at 1600 volts and the ion source was maintained at 250°C. The instrument was tuned with decafluorotriphenyl-phosphine (DFTPP) using US EPA criteria before analysis. Data acquisition and processing were controlled by an HP DOS-based ChemStation data system. Data were acquired using identical operating parameters for PAHs and LABs. Chromatographic peaks were identified by matching the relative retention time and

fragmentation profile in the standard solution and the sample. Quantitation was performed with calibration curves stored in the method files. Carrier gas used was ultra high purity helium with a flow of 2 mL/min at 70°C. The initial oven temperature was 70°C, immediately ramped to 200°C at of 6°C/min and to 285°C at 10°C/min where it was held for 42 min.

Calibration Procedure

All the target compounds were analyzed with the internal, multi-level calibration technique. Initial calibration curves were established for individual compounds relative to internal standards. Calibration curves from several concentration levels (typically 5) were stored in a method file. For each batch of samples (typically 10 samples), a calibration check standard solution was run to validate the calibration curves; the difference between initial and subsequent calibrations was typically <20%. Solvent and procedural blanks, spiked samples, and quality control standards were also analyzed with the sample batch.

PAHs

PAHs were measured using GC/MS. Calibration standard solutions were prepared in 0.1, 0.4, 1, 2, 5, and 10 µg/mL for all but 9,10-diphenylanthracene, indeno[1,2,3-cd]pyrene, dibenzo[a,h]anthracene, and benzo[g,h,i]perylene, which had concentrations of 0.4, 1.6, 4, 8, 20, and 40 µg/mL. Internal standards, nitrobenzene-d₅, 2-fluorobiphenyl, and p-terphenyl-d₁₄, and surrogate standards, naphthalene-d₈, acenaphthene-d₁₀, phenanthrene-d₁₀, chrysene-d₁₂, and perylene-d₁₂, were prepared at 2 µg/mL with the target compounds. Continuing calibration was performed with the 2 µg/mL standard solution.

LABs

LABs were measured simultaneously with PAHs. Calibration standard solutions were prepared from the LAB mixture with total LAB concentrations of 2, 5, 20, 50, and 200 µg/mL. P-terphenyl-d₁₄ was used as an internal standard (2 µg/mL) and phenanthrene-d₁₀ as surrogate standard (2 µg/mL). A detailed description of the quantitation method for LABs is given elsewhere (see *Measurements of Linear Alkylbenzenes by GC/MS and GC/FID* in this volume).

PCBs

PCBs were quantified using GC/ECD and an Aroclor mixture that was characterized elsewhere (SCCWRP 1993a). Five calibration standard solutions were prepared from the Aroclor mixture with total PCB concentrations of

10, 20, 40, 80, and 240 ng/mL. The PCB standard used for spiking experiments contained 20 congeners. Congeners 28 and 153 were not present in the Aroclor calibration mixture, therefore only 18 congeners were measured. Internal standard was 2,2',4,4',5,5'-hexabromobiphenyl in 200 µg/mL and surrogate standards were tetrachloro-m-xylene and congener 209 in 800 ng/mL.

DDTs

DDTs were measured simultaneously with PCBs. The standard solutions were prepared in 20, 100, 500, 2000, and 5000 ng/mL to create calibration curves. Continuing

checking was done with the standard solution at 500 ng/mL. Internal standards and surrogate standards used were the same as those for PCBs.

RESULTS

Spiking Experiments

There were no detectable PAHs, LABs, PCBs, and DDTs in the SPE and LLE extracts of purified water and seawater. There were no detectable PCBs and DDTs in the SPE extracts of effluent. Based on these results, we spiked the purified water with PAHs, LABs, PCBs, and DDTs to test the extraction effectiveness of the 90-mm C-18 bonded

TABLE 1. Recoveries of PAHs from spiked purified water and seawater samples by solid phase extraction (SPE) and liquid-liquid extraction (LLE).

PAH Compounds	Recoveries (%)				
	Purified Water		LLE (n=1)	Seawater	
	SPE (n=8)			SPE (n=9)	
	Mean	RSD ^a	Mean	Mean	RSD ^a
Naphthalene	54	21	48	36	17
1-Methylnaphthalene	55	23	58	43	16
2-Methylnaphthalene	55	23	60	44	15
Biphenyl	55	24	70	44	15
2,6-Dimethylnaphthalene	58	26	70	37	17
Acenaphthylene	60	23	73	51	27
Acenaphthene	61	20	78	45	8
2,3,6-Trimethylnaphthalene	57	17	85	44	16
Fluorene	70	9	87	53	19
Phenanthrene	77	10	74	76	18
Anthracene	79	10	74	77	11
2-Methylphenanthrene	86	9	82	93	18
1-Methylphenanthrene	87	10	80	94	12
3,6-Dimethylphenanthrene	88	9	84	95	12
Fluoranthene	93	10	84	99	13
Pyrene	92	9	86	99	14
2,3-Benzofluorene	97	9	88	105	18
Benzo[a]anthracene	96	10	89	105	22
Chrysene	97	9	85	108	24
Benzo[b]fluoranthene	95	11	97	122	27
Benzo[k]fluoranthene	92	8	91	116	26
Benzo[e]pyrene	89	11	93	116	27
Benzo[a]pyrene	84	12	95	109	27
Perylene	80	12	92	107	21
9,10-Diphenylanthracene	82	12	90	108	28
Indeno[1,2,3-cd]pyrene	67	17	78	111	33
Dibenzo[a,h]anthracene	57	15	81	111	36
Benzo[g,h,i]perylene	67	16	86	115	32
<u>Surrogate Standards</u>					
Naphthalene-d ₈	51	32	55	37	15
Acenaphthalene-d ₁₀	59	27	81	47	23
Phenanthrene-d ₁₀	70	35	73	78	23
Chrysene-d ₁₂	93	13	45	94	35
Perylene-d ₁₂	70	45	116	122	21

^aRSD=relative standard deviation of n measurements in percent.

disks. We also spiked seawater with PAHs and LABs, and effluent with DDTs, to examine sample matrix effects.

PAHs

Spiked purified water and seawater samples were extracted by SPE at least eight times. Spiked purified water was also extracted once by LLE for comparison (Table 1). The recoveries of PAHs were similar for SPE and LLE. Recoveries increased with increasing molecular weight (MW) or retention time (RT). For instance, in the purified water samples, a group of PAHs from naphthalene (MW=128) to fluorene (MW=166) had low but consistent recoveries of 54-70% for SPE and 48-87% for LLE. Another group from phenanthrene (MW=178) to 9,10-diphenylanthracene (MW=330) had moderate to excellent recoveries of 77-97% for SPE and 74-97% for LLE. These results were comparable to those obtained by Yoo *et al.* (1992) with 47-mm C-18 disks and a slightly different elution solvent. A similar trend was also observed with the seawater samples. The low recoveries with low molecular weight compounds (e.g., naphthalene, methyl-naphthalene, etc.) were likely due to losses by evaporation

TABLE 2. Recoveries of LABs from spiked purified water and seawater samples by solid phase extraction.

LAB Compounds	Recoveries (%)			
	Purified Water (n=4)		Seawater (n=4)	
	Mean	RSD ^a	Mean	RSD
6-Phenyl undecane	34	16	44	28
5-Phenyl undecane	37	9	38	29
4-Phenyl undecane	38	12	41	25
3-Phenyl undecane	40	11	47	20
2-Phenyl undecane	50	11	54	17
6-Phenyl dodecane	55	14	62	14
5-Phenyl dodecane	59	13	57	17
4-Phenyl dodecane	58	14	62	16
3-Phenyl dodecane	63	15	65	13
2-Phenyl dodecane	69	15	72	18
7&6-Phenyl tridecane	71	16	78	18
5-Phenyl tridecane	75	17	77	16
4-Phenyl tridecane	74	15	80	18
3-Phenyl tridecane	76	17	80	17
2-Phenyl tridecane	80	16	88	22
7-Phenyl tetradecane	79	19	92	21
6-Phenyl tetradecane	88	13	84	22
5-Phenyl tetradecane	83	16	88	21
4-Phenyl tetradecane	83	16	92	20
3-Phenyl tetradecane	88	17	95	20
2-Phenyl tetradecane	87	17	98	24
<u>Surrogate Standard</u>				
Phenanthrene-d ₁₀	75	22	80	13

^aRSD=relative standard deviation of n measurements in percent.

during extraction and concentration. The average relative standard deviations for overall recoveries were 14% for spiked purified water and 20% for seawater samples.

The low recoveries associated with indeno[1,2,3-cd]pyrene, dibenzo[a,h]anthracene, and benzo[g,h,i]perylene in purified water samples were attributed to variations in instrument sensitivity between the times when the calibration curves were established and the samples were analyzed. In this study, quantitation of these compounds (with RT=66.2-70.9 min) was based on p-terphenyl-d₁₄ (RT=34.8 min). The sensitivity of the GC/MS tends to vary unevenly with retention time (or almost equivalently with molecular weight). Hence, if samples were not analyzed immediately after the calibration curves were generated, systematic errors may have occurred. This was verified by the low average recovery (70%) of the surrogate standard perylene-d₁₂ (RT=51.3 min). In fact, recovery peaked at 97% with chrysene (RT=39.8 min) and gradually decreased thereafter. These errors were not associated with the seawater samples, since they were

TABLE 3. Recoveries of PCBs from purified water samples spiked with the EPA PCB Congener Calibration Solution (Ultra Scientific).^a

PCB Congeners	Recoveries (%)		
	SPE (n=4)	RSD ^b	LLE (n=1)
8	100	34	114
18	66	48	90
52	120	35	121
44	82	24	76
66	90	17	86
101	84	11	82
77	71	27	68
118	65	38	61
105	98	38	89
138	56	29	52
126	93	39	91
187	79	34	81
128	90	34	84
180	89	29	87
170	83	47	96
195	115	21	129
<u>Surrogate Recoveries (%)</u>			
Tetrachloro-m-xylene	33	33	108
Decachlorobiphenyl ^c	97	32	66

^aCongeners 28 and 153 were not quantified; congener 206 was interfered by residual peaks possibly derived from the SPE disks.
^bRSD=relative standard deviation of n measurements in percent.
^cBoth the surrogate standard mixture and the EPA PCB Congener Calibration Solution contain decachlorobiphenyl (congener 209); the recovery was corrected for both contributions.

TABLE 4. Recoveries of DDTs from spiked purified water and effluent samples from County Sanitation Districts of Orange County extracted by solid phase extraction.

Compounds	Recoveries (%)			
	Purified Water (n=8)		Effluent (n=3) ^a	
	Mean	RSD ^b	Mean	RSD
Hexachlorobenzene	93	12	87	16
δ-BHC	96	11	77	26
Heptachlor	78	12	64	5
Aldrin	68	15	58	16
Heptachlor epoxide	95	11	74	15
o,p'-DDE	108	9	82	7
α-Chlordane	109	10	74	17
p,p'-DDE	109	16	76	15
Dieldrin	94	27	79	17
o,p'-DDD	93	13	104	7
p,p'-DDD	84	14	96	14
o,p'-DDT	112	11	65	17
p,p'-DDT	110	11	57	12
Mirex	127	8	86	13
Surrogate Standards				
Tetrachloro-m-xylene	82	23	69	33
Decachlorobiphenyl	139	16	142	28

^aEffluent samples were filtered by GF/C and GF/F filters consecutively.
^bRSD=relative standard deviation of n measurements in percent.

analyzed before instrument sensitivity changed significantly.

LABs

Recoveries of LABs from spiked purified water and seawater samples generally increased with molecular weight (Table 2). Phenyl tetradecanes (MW=274) had highest recoveries, while phenyl undecanes (MW=232) had the lowest. Within an isomer group, the recoveries increased slightly with retention time. The recoveries of LABs from seawater samples were slightly better than those from purified water samples, which was consistent with recoveries for PAHs. The average relative standard deviations for all the recoveries were 16% for purified water and 20% for seawater. However, the recoveries varied in a broad range (34-88% for purified water and 38-98% for seawater), although the range of retention times of LABs (24-32 min) were narrower than the retention times of PAHs (16-70 min).

PCBs

Spiked purified water samples were extracted by SPE and LLE with comparable results (Table 3). The recoveries of PCBs were normally better than those of PAHs and LABs from purified water samples. However, the average RSD was 32%, substantially higher than those for PAH and LAB measurements. There was no significant trend of recoveries in terms of retention time or molecular weight. Kraut-Vass and Thoma (1991) extracted PCB congeners 1,

5, 29, 47, 98, 154, 171, and 200 with 47-mm C-8 disks and obtained slightly higher recoveries except for congener 171, which had no significant trend.

DDTs

Analyses of spiked purified water produced excellent recoveries. A set of eight replicates produced an average recovery of 100% with a lowest of 78% for aldrin and highest of 127% for mirex, better than the recoveries of PAHs and LABs. For the surrogate standards, tetrachloro-m-xylene had an average recovery of 82% and congener 209 had an average recovery of 137% (Table 4). There was no correlation between recovery and molecular weight or retention time. The average RSD was 13%. Similar recoveries were reported for DDTs spiked at comparable concentrations and extracted with 47-mm C-8 disks (Kraut-Vass and Thoma 1991) and reverse phase C-18 columns (Vidal *et al.* 1994).

Recoveries of DDTs from spiked CSDOC effluent samples were not as high as those from purified samples, but reasonably good (Table 4). There was no correlation between DDT recoveries and their molecular weights or retention times. The average recovery for the group was 77%; the highest recovery was 104% for o,p'-DDD and the lowest was 58% for aldrin. The average RSD was 14%. Low recoveries of aldrin (51-55%) extracted from ground-water spiked at 1, 10, and 100 µg/L were obtained by Hagen *et al.* (1990).

Unspiked Effluent Samples

Large amounts of suspended solids normally occur in municipal wastewater effluents. To effectively compare the extraction efficiencies of SPE and LLE, only the filtrates were extracted and analyzed while the particulates were discarded. The PLTP effluent filtrates were filtered consecutively with GF/C and GF/F filters before they were split for SPE and LLE. Substantially higher concentrations were obtained by SPE for almost all PAHs and LABs, although recoveries of the surrogate standards were similar (Table 5). The difference between SPE and LLE was greater for LABs than PAHs. Only low molecular weight PAHs were detected; high molecular weight PAHs presumably were bound to the particles. The recoveries of surrogate standards increased with increasing molecular weight with SPE and LLE, which was consistent with the results of the spiking experiments. Concentrations of C₁₄-LABs were below the detection limit (37 ng/L), which suggested strong binding (or partitioning) of high molecular-weight hydrophobic organics to the particular phase. The surrogate standard, phenanthrene-d₁₂, which eluted closely with 7&6-phenyl tridecane, had fairly good recoveries (87% for SPE and 71% for LLE).

TABLE 5. Concentrations of PAHs and LABs in effluent samples from Point Loma Treatment Plant (San Diego) extracted by solid phase extraction (SPE) and liquid-liquid extraction (LLE).^a

PAH Compounds	Concentration		LAB Compounds	Concentration	
	SPE (ng/L)	LLE (ng/L)		SPE (ng/L)	LLE (ng/L)
Naphthalene	674	519	6-Phenyl undecane	74	23
2-Methylnaphthalene	1082	802	5-Phenyl undecane	163	50
1-Methylnaphthalene	893	720	4-Phenyl undecane	123	36
Biphenyl	254	131	3-Phenyl undecane	142	40
2,6-Dimethylnaphthalene	599	351	2-Phenyl undecane	164	44
Acenaphthylene	70	70	6-Phenyl dodecane	219	68
2,3,6-Trimethylnaphthalene	25	73	5-Phenyl dodecane	184	57
Fluorene	<34	127	4-Phenyl dodecane	136	46
Phenanthrene	185	60	3-Phenyl dodecane	130	43
2-Methylphenanthrene	152	60	2-Phenyl dodecane	166	55
1-Methylphenanthrene	159	46	7&6-Phenyl tridecane	237	103
			5-Phenyl tridecane	154	66
<u>Surrogate Recovery (%)</u>			4-Phenyl tridecane	110	44
Naphthalene-d ₈	36	21	3-Phenyl tridecane	95	<41
Acenaphthene-d ₁₀	66	57	2-Phenyl tridecane	102	<41
Phenanthrene-d ₁₀	71	78			
Chrysene-d ₁₂	68	89	<u>Surrogate Recovery (%)</u>		
Perylene-d ₁₂	82	90	Phenanthrene-d ₁₀	87	71

^aEffluent samples were filtered by GF/C and GF/F filters consecutively.

TABLE 6. Concentrations of PAHs in effluent samples from County Sanitation Districts of Orange County filtered by GF/C and GF/F filters (method 1) and GF/C and Filter Aid 400 (method 2) and then extracted by solid phase extraction (SPE).

PAH Compounds	Concentration		Concentration	
	Method-1 (ng/L)	RSD ^a (n=2) (%)	Method-2 (ng/L)	RSD (n=2) (%)
Naphthalene	189	20	153	31
2-Methylnaphthalene	178	15	148	21
1-Methylnaphthalene	130	8	110	18
Biphenyl	51	21	53	9
2,6-Dimethylnaphthalene	76	8	67	11
2,3,6-Trimethylnaphthalene	22	8	27	38
<u>Surrogate Recovery (%)</u>				
Naphthalene-d ₈	56	1.2	36	72
Acenaphthene-d ₁₀	56	38	46	15
Phenanthrene-d ₁₀	94	1.3	89	8
Chrysene-d ₁₂	78	9	86	3
Perylene-d ₁₂	52	2.1	52	5

^aRSD=relative standard deviation of n measurements in percent.

To evaluate the usefulness of glass beads for wastewater, we treated the CSDOC effluent samples by two methods. In the first method, the effluent was filtered consecutively with GF/C and GF/F filters before it was extracted by SPE. In the second method, the effluent was filtered with GF/C filters and then glass beads were used for SPE extraction. The concentrations for four of six detectable PAHs by GF/C and GF/F method were slightly higher compared to GF/C and Filter Aid 400 method, but the differences were within the measurement errors (RSDs; Table 6). Recoveries of the surrogate standards were similar for both methods.

DISCUSSION

The disk SPE experimental parameters (elution solvent, disk preconditioning, sample flow rate, spiking concentration, etc.) were adopted based on either the manufacturer's specifications or data in the literature. Mayer and Poole (1994) extensively evaluated the steps and variables related to the recovery of neutral organic compounds extracted by SPE disks. Their results suggest that our disk SPE experimental parameters were nearly optimal. Therefore, recoveries of the organic compounds (Tables 1-6) were affected by factors other than disk SPE parameters.

Extraction Efficiency

The effectiveness of organic solvent extraction is a function of many factors including the partition efficiency of a compound between organic and aqueous phases, interference of the sample matrix, and losses due to evaporation. Under identical conditions, different extraction techniques can be compared by their effectiveness of extracting agents at retaining a compound.

Retaining Efficiency

The extraction efficiency of LLE depends on equilibrium partitioning of the compound between the organic solvent and the aqueous phase. The magnitude of the

partitioning can be approximated by the octanol-water partition coefficient (K_{ow}). For the PAHs measured here, K_{ow} s range from 10^3 to 10^7 (e.g., Ruepert *et al.* 1985). For LABs from phenyl undecanes to phenyl tetradecanes, K_{ow} s range from 10^7 to 10^9 (Sherblom *et al.* 1992). PCBs and DDTs have K_{ow} values from 10^4 to 10^8 (Hawker and Connell 1988, Sicbaldi and Del Re 1993). Three extractions by LLE should transfer nearly 100% of the PAHs from the aqueous phase into the organic phase (ignoring matrix effects, losses due to evaporation, etc.).

Extraction by SPE disk (membrane-based) depends on the sorption process between hydrophobic particles in the disk and the compound in the aqueous sample, and the desorption process between the organic eluent and adsorbed compound (Hagen *et al.* 1990). The good agreement between SPE and LLE (Tables 1 and 3) for extracting PAHs and PCBs from purified water (minimum matrix interference) suggested that the sorption-desorption processes within an SPE disk were extremely effective in extracting hydrophobic organics. Less solvent and manpower make the SPE technique preferable to LLE for extracting aqueous samples, especially for large volume samples.

Effect of Sample Matrix

Even without quantitative measurement, the color and odor of the effluent samples in this study strongly suggested the presence of humic substance or dissolved organic matter (DOM). DOM enhances the apparent water-solubilities of hydrophobic organic compounds (Kile and Chiou 1989). Consequently, depending on the extraction mechanism, the extraction effectiveness of hydrophobic organic compounds may vary with presence of DOM or humic substance. The recoveries of DDTs from CSDOC effluent by SPE were generally lower than from purified water (Table 4). In addition, SPE obtained higher concentrations of PAHs and LABs from the PLTP effluent than did LLE (Table 5). The extraction efficiencies of both SPE and LLE were affected by DOM, but LLE suffered more losses. In LLE, the partitioning of hydrophobic organics between the organic solvent and aqueous phases may be shifted towards the aqueous phase by DOM, causing losses of the organic compounds. On the other hand, two factors may reduce the effects of DOM with SPE disks. First, the condensed packing of hydrophobic particles in SPE disks may block the passage of large molecular weight organic matter, which is primarily responsible for interacting with PAHs (Whitehouse 1985). The organics adsorbed on the large molecular weight DOM may be partially desorbed by subsequent solvent elution. Second, the sorption process in disk SPE acts as many small extraction processes, which may be more

effective in extracting hydrophobic organics in DOM than three extractions with LLE.

The excellent agreement between the recoveries of PAHs and LABs in the purified water and seawater samples (Table 1 and 2) indicate that inorganic contents in seawater do not constitute interference to the SPE disk extraction.

Losses Due to Evaporation

The increasing recoveries of PAHs and LABs with increasing molecular weight or retention time (Tables 1 and 2) was tentatively attributed to evaporative losses during sample processing. In the spiking experiments with SPE, a standard solution was injected by microsyringe into the sample in a 1-L volumetric flask. The flask was shaken vigorously immediately. After the sample was poured into an SPE disk, the flask was rinsed with ethyl acetate, which was poured into the disk. It was unlikely that losses of PAHs and LABs were significant in this step. Similarly, it was unlikely that the extraction step in LLE caused significant losses of PAHs and LABs. The loss of low molecular weight PAHs and LABs was probably caused by condensation of the sample extract by rotary evaporation or under a stream of N_2 . In rotary evaporation or N_2 blow-out, low boiling-point solvent evaporates, but lighter PAHs and LABs may also be driven out. More investigations are needed to quantify this hypothesis.

Effect of Pretreatment

Suspended solids in wastewater samples create one of the main problems with SPE disks. To prevent particle clogging, the 3M Company manufactured high density glass beads (Filter Aid 400) that can be used with SPE disks. The beads are placed on top of a disk before a sample is poured onto it. In CSDOC wastewater samples, the concentrations and measurement errors of PAHs by GF/C and GF/F method were similar to GF/C and Filter Aid 400 method (Table 6); recoveries of the surrogate standards were also similar. Although glass beads may minimize clogging of SPE disks by particulates, the GF/C and GF/F pretreatment method is preferred if the concentrations of organic compounds in aqueous and particulate phases need to be quantified separately. The filtration by GF/C was necessary before glass beads were used. In a preliminary test with glass beads and unfiltered effluent, the disk was completely clogged by about 100 mL of sample.

Large Volume Samples

The concentrations of most organic contaminants have decreased in point-source discharges as a result of im-

proved and increased treatment and source control (e.g., SCCRWP 1993b). A large volume of sample is required to detect these compounds in the marine environment. SPE disks may be well suited to this purpose. Large dimensional disks can increase the sample flow rate thus shortening extraction time. In experiments with 90-mm disks, it took approximately 10 min to extract 1 L of sample under a vacuum of 25 in Hg. With 47-mm disks under identical conditions, it took 20 min. The 90-mm SPE disks also increase extraction capacity, which we demonstrated by extracting large volumes of wastewater effluent. This technique will find wide application in analyses of a variety of aqueous environmental samples.

Unresolved Chromatographic Peaks

Finally, we point out an unwelcome observation with SPE disks. In the chromatograms of PCB and DDT from GC/ECD, some unresolved peaks appeared at a large retention time. In some cases, they interfered the detection of congener 206. Since we conditioned the disks according to the manufacturer's instructions, and blanks were analyzed simultaneously with samples to eliminate external contamination, these high boiling-point compounds may have come from the disks. We will use GC/MS to identify their composition.

CONCLUSIONS

Extraction of hydrophobic organics (e.g., PAHs and PCBs) by 90-mm EmporeTM C-18 bonded disks was as effective as by liquid-liquid extraction. SPE was superior to LLE because it used less solvent and manpower. In addition, the condensed packing structure in SPE disks allowed better extraction of hydrophobic organic compounds from municipal wastewater effluent enriched with dissolved organic matter. The SPE technique with 90-mm disks will find extensive applications in analyses of low-level hydrophobic organic compounds in aqueous samples.

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