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EVALUATION OF SAMPLING METHODS FOR THE DETERMINATION OF TRACE ORGANICS IN WATER

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SUMMARY

 The applicability of a closed-loop gas-phase stripping apparatus for the determination of trace organics in water was evaluated. Recoveries were determined for a series of *n*-alkanes. The effects of extraction solvent, stripping temperature, stripping time, pH and salt content on the closed-loop system were investigated. Carbon disulfide was found to be the best extraction solvent, and an extraction temperature of 40°C was found to be optimal. Two water samples spiked with 0.1–0.2 and 1.0–2.0 μg/l of each U.S. Environmental Protection Agency base neutral priority pollutant were investigated. Recoveries for the base neutrals of the more concentrated sample were determined at 25 and 40°C. A direct comparison of the closed-loop gas-phase stripping method and the purge-and-trap method with Tenax GC was performed on a river water sample. Recoveries for the thermal desorption of base neutrals from Tenax were determined at five different desorption temperatures. A new microextraction vessel, which allows the use of solvents heavier than water, was constructed and evaluated. Distribution coefficients and recoveries for compounds of different functionalities were determined at three different water to solvent ratios and at concentration levels of 100 ppb* and 0.5 ppm.

INTRODUCTION

 Over the last decade, concern over the degradation of the environment has led many scientists to focus attention on environmental analysis. Environmental analysis is a difficult subject, as most hazardous compounds are present at very low levels and are often masked by complex patterns of interfering substances. Obtaining representative samples is also a difficult problem in environmental analysis, as concentration procedures usually have to be applied for trace levels of contaminants. Procedures have been reviewed for polynuclear aromatic hydrocarbons[1], pesticides and plant growth regulators[2–4], polychlorinated biphenyls (PCBs)[5], trihalomethanes[6–8] and a variety of organic substances of industrial origin[6,9–11]. Comparisons of different sampling methods have also appeared[11–18].
 Recently, the U.S. Environmental Protection Agency (EPA) proposed test pro-

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* Throughout this article, the American billion (10^9) is meant.

cedures for 113 organic toxic pollutants[19]. These test procedures have been broken down into 15 different analytical methods. Each method utilizes a sample concentration step, based on liquid–liquid partitioning, liquid–gas partitioning or liquid–solid adsorption, followed by extraction. General factors that affect partitioning in water samples are temperature, pH, salt content and the nature of the solvent used. The suggested methods of analysis of the base neutrals fraction of the priority pollutants all involve a solvent extraction and concentration step. Solvent concentration steps have several disadvantages. The solvent must be extremely pure because, on concentration, trace impurities are removed at a much slower rate than the solvent. Also, reproducibility of solvent concentration steps is hard to obtain.

Grob and co-workers have discussed the general requirements for concentration and analysis of trace organics in water[20–22]. A closed-loop gas-phase stripping method[23] has consequently been developed and proposed as a universal sampling method for the determination of organics in water. In this method, a small volume of air, which is equilibrated with both the water and the trace organics from the sample, is continuously passed through a filter containing 1–5 mg of a specially prepared charcoal. The trace organics are trapped in the filter and are then microextracted with approximately 20–30 μl of an appropriate solvent. The major advantage of the method is the avoidance of a solvent concentration step.

The purpose of this study was to determine the effectiveness of this sampling method for the determination of trace organics in water and, in particular, for the determination of the base neutrals fraction of the EPA priority pollutants. A direct comparison of the closed-loop method and the purge-and-trap method[24,25] with Tenax GC was also performed on a river water sample.

The thermal desorption characteristics of the EPA base neutral priority pollutants from Tenax GC were also investigated. Recoveries were determined at five different desorption temperatures, ranging from 200 to 300°C.

A new microextraction vessel that allows the use of solvents heavier than water was constructed and evaluated. Distribution coefficients for compounds of different functionalities were determined at several different ratios of water to extraction solvent. Recoveries for two concentration levels in the parts per billion range were also measured.

EXPERIMENTAL

A closed-loop gas-phase stripping apparatus based on a system described by Grob and co-workers was utilized. Spiked 1-l water samples were stripped with 1.5-mg charcoal filters (Bender-Holbein, Zürich, Switzerland) and then microextracted with 20 μl of an appropriate solvent. The solvents studied were carbon disulfide (MCB Manufacturing Chemists, Cincinnati, OH, U.S.A.), methanol and dichloromethane. Carbon disulfide was used without further purification, but methanol and dichloromethane were distilled in the laboratory in an all-glass system. Solvent blanks were evaluated chromatographically to ensure purity. The stripping time was varied from 1 to 3 h. The temperature of the spiked samples was varied from 25 to 60°C to evaluate the effect of temperature on stripping efficiency for base neutrals. Spiked water samples, containing 0.5 and 1.0 mol of sodium chloride per liter of water, were also evaluated.

The effect of pH on stripping efficiency was also evaluated by adjusting the pH of 1-l water samples, containing base neutrals, with 6 M sodium hydroxide solution. The pH of the samples was varied between 8 and 11. An Orion Model 301 analog pH meter (Orion Research, Cambridge, MA, U.S.A.) was used for measuring the pH of the spiked samples.

Spiked samples were prepared by injecting appropriate amounts of standards in pre-purified water. Purified water was obtained with a Millipore ion-exchange system (Continental Water Systems, Birmingham, AL, U.S.A.) and then stripped for 1 h with a charcoal filter to ensure its purity. System blanks were determined to verify the integrity of the closed-loop system. Spiked water samples were prepared by adding C_8–C_{26} n-alkanes (Polyscience, Miles, IL, U.S.A.), gasoline or EPA base neutrals fractions (Supelco, Bellefonte, PA, U.S.A.) to 1 l of purified water. A set of spiked water samples were prepared by adding between 100 and 200 ng of each base neutral compound to each liter of purified water. A second set of samples were prepared to yield 1–2 μg of each compound per liter of purified water. Samples were stripped within 1 h of spiking. Standards for quantitation were prepared by diluting the appropriate amount of each sample to a total volume of 20 μl with either carbon disulfide, methanol or dichloromethane.

Analysis of the closed-loop extracts was performed by high-resolution glass capillary column gas chromatography. A Hewlett-Packard 5710A gas chromatograph, equipped with a flame-ionization detector and a split/splitless capillary column inlet was used. A 30 m × 0.28 mm I.D. glass capillary column coated with SE-54, prepared by the persilanization method of Grob et al.[26], was utilized. Aliquots of 2 μl of the microextracts were injected in the splitless mode into the system with a 30-sec vent delay. The column temperature was held at 40°C for 4 min, then programmed at 8°C/min to 280°C, and held at 280°C until all compounds were eluted.

River water samples for direct comparison of the closed-loop gas-phase stripping method and the purge-and-trap method with Tenax GC were collected in silanized 1-gal amber bottles equipped with PTFE-lined screw caps. The bottles were filled to overflowing and sealed. Processing proceeded within 1 h of sampling. A 1-l volume of river water was placed in the closed-loop system and stripped for 1 h with a 1.5 mg charcoal filter at 25°C. The filter was subsequently extracted with 20 μl of carbon disulfide and a 2-μl aliquot was analyzed.

A gas-phase stripping apparatus with Tenax GC was used, which has been evaluated previously[8,27]. River water samples of 100 ml were placed in a 250-ml stripping vessel and submerged in a water-bath to prevent interferences from organics in air. Nitrogen, which was used as the purge gas, was purified in a packed trap at dry-ice temperature. Stripping was performed at 25°C, and the trace organics were retained by adsorption on Tenax GC (80–100 mesh) (Applied Science Labs., State College, PA, U.S.A.). Silanized glass tubes containing approximately 500 mg of Tenax GC were used. Samples were purged at 60 ml/min for 1 h. Immediately following the stripping process, approximately 300 ml of dry nitrogen were forced through the adsorbent to displace the majority of the physically retained water. System blanks were determined with distilled water to ensure the integrity of the system.

Analysis of the river water samples was performed on a 25 m × 0.28 mm I.D. OV-101 glass capillary column. A Hewlett-Packard 5830A gas chromatograph, equipped with a single flame-ionization detector and integration capability, was used.

The standard injection port was replaced with an injection port that permits manual splitless injections or heat desorption of the Tenax GC tubes. Tenax GC samples were heat-desorbed at 250°C for 1 h into a liquid nitrogen trap. After sample introduction, the column temperature was held at 25°C for 8 min, then programmed at 3°C/min to 200°C, and held a 200°C until all compounds were eluted. In order to study the effects of heat desorption of base neutrals from Tenax GC, 1 μl of a base neutrals standard, containing 25–50 ng/μl of each compound, was injected directly into a 500-mg Tenax GC tube. The solvent was blown off with 1 l of dry nitrogen at a flow-rate of 100 ml/min. The Tenax GC tube was then placed inside the injection port and heat-desorbed for 1 h into the head of the column by using liquid nitrogen as the trapping coolant. Analysis was performed on a 25 m × 0.28 mm I.D. column coated with OV–1. The desorption temperature was varied from 200 to 300°C in 25°C increments. Desorption results were compared with a splitless injection of 1 μl of the base neutrals standard at 300°C with a 30-sec vent delay. The Hewlett-Packard 5830A apparatus was utilized. After sample introduction, the column temperature was held at 40°C for 4 min, then programmed at 4°C/min to 280°C, and finally held at 280°C until all compounds were eluted.

A new microextraction vessel that allows the use of solvents heavier than water was constructed by modifying a 250-ml separating funnel. Two capillary stopcocks of 2 mm I.D. were placed in series at the bottom of the separatory funnel with a 1-ml reservoir between the stopcocks. Spiked water samples were prepared by adding the appropriate amounts of 1-heptene, toluene, nonane, phenol, nitrobenzene and methyl laurate to distilled water to yield a solution containing 500 ppb of each compound. Anthracene was also added to the spiked water sample to yield a 50 ppb solution. A second set of spiked water samples was prepared to yield 100 ppb of each compound, except anthracene. Anthracene was added to yield a 10 ppb solution. Water samples of 200 ml were extracted with carbon disulfide for 15 min with constant agitation. Appropriate amounts of carbon disulfide were used to give ratios of water to extraction solvent of 200, 100 and 66. Distribution coefficients and recoveries were determined.

A Hewlett-Packard 5710A gas chromatograph equipped with a flame-ionization detector and a split/splitless capillary column inlet was used. A 25 m × 0.33 mm I.D. CP Sil-8 fused-silica capillary column was utilized. Aliquots of 2 μl of the carbon disulfide extracts were injected in the splitless mode with a 30-sec delay. The column temperature was held at 40°C for 4 min, then programmed at 8°C/min to 250°C, and finally held at 250°C for 30 min.

RESULTS AND DISCUSSION

Obtaining representative samples of pollutants is a difficult problem in environmental analysis, as concentration procedures have to be followed for trace levels of contaminants. Methods based on classical extraction techniques and adsorption on charcoal have been found to be unsuitable for trace analysis if large volumes of solvents and large amounts of adsorbents are used. The closed-loop stripping system studied eliminates these problems, as the weight of adsorbent is 1.5 mg and the total extraction volume is only about 20 μl.

Fig. 1 illustrates the recovery of a series of n-alkanes at 25 and 35°C by the closed-loop stripping apparatus. The results are based on an average of three trials at each temperature. n-Decane was used as the internal standard, and all results were
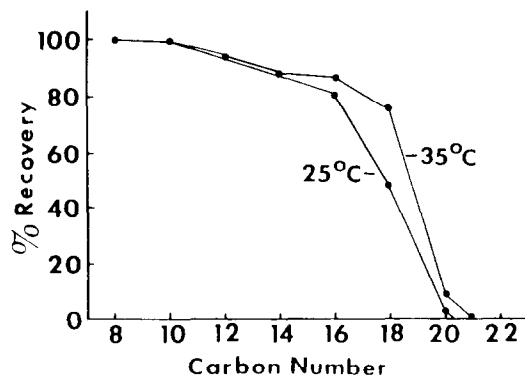
Fig. 1. Recoveries of *n*-alkanes at 25 and 35°C.

normalized to C_{10}. Above C_{21} only trace amounts were recovered and no quantitation was attempted. The reproducibility of recoveries was ± 6% for individual hydrocarbons in the parts per billion range. A gasoline standard was prepared by injecting 1 μl of gasoline directly on to the charcoal filter and extracting it with 20 μl of carbon disulfide. Fig. 2A is a chromatogram of a 2-μl aliquot of this standard. A spiked water sample was prepared by injecting 1 μl of gasoline into 1 l of purified water. The sample was stripped for 1 h at 25°C with a charcoal filter. The filter was then extracted with 20 μl of carbon disulfide, and a 2-μl aliquot was analyzed. Fig. 2B illustrates the results. The recovery of the gasoline is essentially quantitative up to an elution temperature of approximately 170°C.

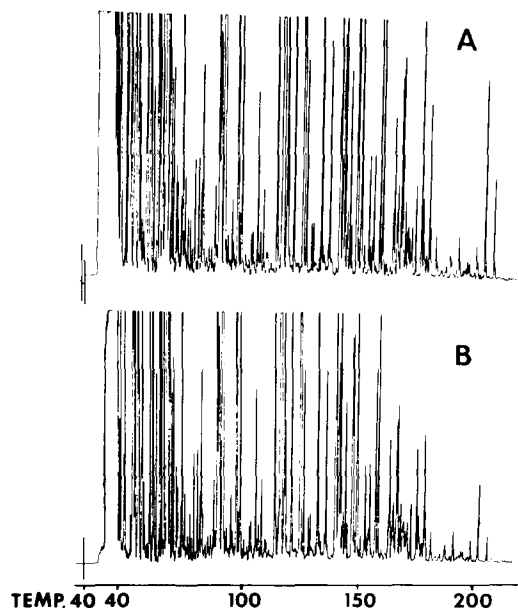The effect of the nature of the solvent on the extraction of base neutrals is il-

Fig. 2. Closed-loop analysis of gasoline. (A) 2-μl aliquot of a gasoline standard; (B) 2-μl aliquot of a 20-μl extract of a closed-loop water sample spiked with gasoline. Temperatures in °C.

TABLE I

CLOSED-LOOP RECOVERIES OF EPA BASE NEUTRAL PRIORITY POLLUTANTS AT 25 AND 40°C.

| Compound	M.W.	B.p. (°C)	Recovery (%) 25°C	Recovery (%) 40°C	Compound	M.W.	B.p. (°C)	Recovery (%) 25°C	Recovery (%) 40°C
Bis(2-chloroethyl) ether	143.0	178	18	56	Flurorene	166.2	293	13	45
1,3-Dichlorobenzene	147.0	173	100	100	1,2-Diphenylhydrazine	184.2	N.A.	N.R.	43
1,4-Dichlorobenzene	147.0	174	101	103	4-Chlorophenyl phenyl ether	204.6	N.A.	N.R.	25
1,2-Dichlorobenzene	147.0	181	88	97	4-Bromophenyl phenyl ether	249.1	N.A.	24	88
Bis(2-chloroisopropyl) ether	171.1	187	34	70	Hexachlorobenzene	284.0	332	44	67
Hexachloroethane	236.7	186	87	103	Anthracene	178.0	340	N.R.	4
Nitrobenzene	123.1	211	6	25	Phenanthrene	178.2	340	N.R.	3
Bis(2-Chloroethoxy)methane	172.0	N.A.*	N.R.**	N.R.	Di-n-butyl phthalate	278.3	340	N.R.	21
1,2,4-Trichlorobenzene	181.4	213	75	103	Fluoranthene	202.3	375	N.R.	19
Naphthalene	128.2	218	56	92	Pyrene	202.3	393	N.R.	36
Hexachlorobutadiene	260.6	215	83	101	Butyl benzyl phthalate	298.2	N.A.	N.R.	21
Hexachlorocyclopentadiene	272.7	239	13	90	Chrysene	228.3	448	N.R.	N.R.
2-Chloronaphthalene	162.6	256	21	56	Benzo(a)anthracene	228.3	N.A.	N.R.	N.R.
Dimethyl phthalate	194.2	284	33	49	Bis(2-ethylhexyl) phthalate	390.2	N.A.	N.R.	10
Acenaphthylene	152.2	270	9	25	Di-n-octyl phthalate	390.2	N.A.	N.R.	N.R.
Acenaphthene	154.2	279	5	52	Benzo(b)fluoranthene	252.3	N.A.	N.R.	N.R.
2,4-Dinitrotoluene	182.1	d300	N.R.	N.R.	Benzo(k)fluoranthene	252.3	N.A.	N.R.	N.R.
Diethyl phthalate	222.2	298	N.R.	15	Benzo(a)pyrene	252.3	495	N.R.	N.R.

* N.A. = Not available.
** N.R. = No recovery.
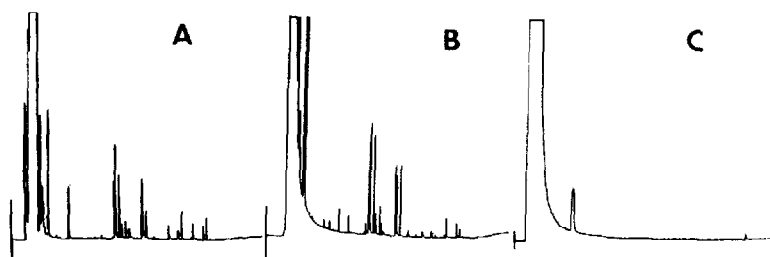
Fig. 3. Effect of solvent on extraction of base neutrals. (A) Carbon disulfide; (B) dichloromethane; (C) methanol.

lustrated in Fig. 3. Three identical spiked water samples were stripped for 1 h at 25°C with a filter and extracted with 20 μl of the appropriate solvent. Equal amounts of each extract were then chromatographed. Carbon disulfide and dichloromethane were found to have comparable extraction efficiencies for base neutrals. As can be seen in Fig. 3C, methanol was found to have a very poor extraction efficiency. No base neutrals were recovered from the charcoal filter. This can be attributed to the fact that the wettability of charcoal with methanol is very low. This result was verified by placing the base neutrals standard directly on the charcoal filter and extracting it with methanol. The analytical results confirmed the previous conclusion. On the basis of these results, carbon disulfide was chosen for the remainder of the study. This is in agreement with the observations by Grob and Zürcher[23] that carbon disulfide is a preferred solvent for volatile compounds.   .

The effect of stripping temperature was also evaluated. Water samples spiked with 1–2 μg of each base neutral were stripped for 1 h at 25, 40 and 60°C. The recovery results are summarized in Table I. Eighteen compounds were partially recovered at 25°C. On raising the stripping temperature to 40°C, increased recoveries were observed for the 18 compounds detected at 25°C, and ten additional base neutral compounds were also detected. On increasing the stripping temperature to 60°C, the expected improvement in the recovery of base neutrals was not seen. Water condensed on the charcoal filter and the recoveries were reduced to zero. Heating of the stripping gas before contact with the filter did not eliminate this problem.

When the stripping time was varied from 1 to 3 h at 25°C, no significant recovery enhancement was observed at the longer times. Repetitive 1-h strippings of the same sample at 25°C also verified this conclusion. The effect of pH on the stripping efficiency was negligible. The pH of water samples spiked with base neutrals was varied between 8 and 11, but no changes in the recoveries for the base neutral compounds were observed in this range. Two spiked water samples, containing 0.5 and 1.0 mol of sodium chloride, were analyzed. No changes in stripping efficiency for the base neutral compounds were observed. Also, attempts to analyze phenols at pH 2 were unsuccessful; no recovery of phenols was seen.

A direct comparison of the closed-loop gas-phase stripping method and the purge-and-trap method with Tenax GC was performed. Appropriate amounts of river water were sampled to allow direct comparison of the chromatograms resulting from the two methods. A direct comparison of the chromatograms is shown in Fig. 4. Fig. 4A is a system blank of the closed-loop apparatus and Fig. 4B is the chromatogram given by a 2-μl aliquot of a 20-μl closed-loop extract of a 1-l river water sample. A
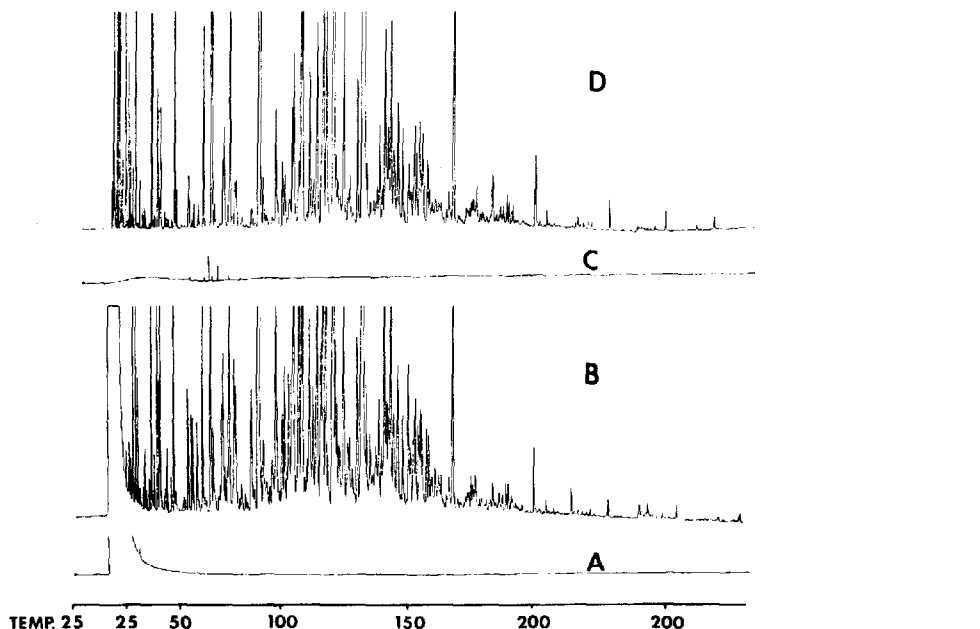
Fig. 4. Direct comparison of the closed-loop and purge-and-trap methods. (A) Closed-loop system blank; (B) 2-μl aliquot of a closed-loop river water extract; (C) purge-and-trap method with Tenax GC system blank; (D) purge-and-trap method with Tenax GC of a river water sample. Temperatures in °C.

system blank for the purge-and-trap system is shown in Fig. 4C. Fig. 4D is the chromatogram produced when 100 ml of river water was purged for 1 h with Tenax GC, heat-desorbed with liquid nitrogen and then chromatographed. The recoveries for the two methods are comparable, except for the early part of the chromatograms. The closed-loop system shows a better recovery for the compounds eluted early. This can be attributed to the breakthrough of these compounds on Tenax GC. Problems with breakthrough are diminished in the closed-loop system, as any compounds which break through are recycled through the entire system. One drawback of the closed-loop system is that several of the most volatile compounds are masked by the solvent peak.

The effect of temperature on the desorption of the EPA base neutral priority pollutants from Tenax GC was studied. Recoveries were determined for 37 priority pollutants at five different temperatures. The desorption temperature was varied from 200 to 300°C at 25°C intervals. The results are summarized in Table II and are based on an average of five trials at each temperature. The reproducibility of the recoveries for each individual compound was ±8% for 25–50 ng of each priority pollutant. Fifteen compounds were partially recovered at 200°C and only six compounds gave recoveries of 90% or better. On increasing the desorption temperature in 25°C increments, the number of compounds recovered increased to a maximum of thirty at 300°C. Nineteen of the thirty compounds detected at 300°C gave recoveries of 90% or better.

A new microextraction vessel that allows the use of solvents heavier than water was constructed and evaluated. Fig. 5 shows a cross-sectional view of the modified separatory funnel. The normal stopcock was replaced by a capillary stopcock of 2 mm I.D. A sample reservoir of approximately 1 ml in volume was added below the capillary stopcock. The dual stopcock design of the extractor allows one to perform multiple

TABLE II

RECOVERY OF BASE NEUTRALS FROM TENAX GC BY THERMAL DESORPTION

Compound	Recovery (%)				
	200°C	225°C	250°C	275°C	300°C
Bis(2-chloroethyl) ether	95	95	99	100	100
1,3-Dichlorobenzene	92	100	100	100	100
1,4-Dichlorobenzene	90	95	99	96	96
1,2-Dichlorobenzene	99	100	102	100	100
Bis(2-chloroisopropyl) ether	97	100	93	97	91
Hexachloroethane	100	100	100	99	100
Bis(2-chloroethoxy)methane	66	77	85	87	103
1,2,4-Trichlorobenzene	72	94	91	98	95
Naphthalene	71	103	101	103	100
Hexachlorobutadiene	69	90	85	87	95
Hexachlorocyclopentadiene	53	94	93	103	104
2-Chloronaphthalene	29	70	100	102	102
Dimethyl phthalate	0	16	32	35	28
Acenaphthylene	19	33	71	85	84
Acenaphthene	0	50	99	96	94
2,4-Dinitrotoluene	78	79	104	87	105
Diethyl phthalate	11	36	83	98	97
4-Chlorophenyl phenyl ether	0	16	34	53	49
4-Bromophenyl phenyl ether	0	34	57	108	103
Hexachlorobenzene	0	43	65	107	101
Phenanthrene	0	21	31	80	93
Anthracene	0	0	16	42	53
Di-n-butyl phthalate	0	20	33	100	110
Fluoranthene	0	0	0	35	66
Pyrene	0	0	24	39	69
Butyl benzyl phthalate	0	0	0	28	65
Benzo(a)anthracene	0	0	0	0	38
Chrysene	0	0	0	25	39
Bis(2-ethylhexyl) phthalate	0	0	19	27	54
Di-n-octyl phthalate	0	0	0	11	27
3,3'-Dichlorobenzidine	0	0	0	0	0
Benzo[b]fluoranthene	0	0	0	0	0
Benzo[k]fluoranthene	0	0	0	0	0
Benzo[a]pyrene	0	0	0	0	0
Indeno[1,2,3-cd]pyrene	0	0	0	0	0
Dibenzo[a,h]anthracene	0	0	0	0	0
Benzo[ghi]perylene	0	0	0	0	0

extractions without removing the sample from the vessel, and the organic layer can be removed from the bottom without passing through the water layer. Contamination problems are thus minimized. The organic layer was forced into the resevoir by applying a pressure of approximately 5 p.s.i. to the top of the extractor. Distribution coefficients and recoveries for seven compounds of different functionalities were determined at two concentration levels and at various volume ratios, R (volume of water divided by the volume of extraction solvent). Table III gives the results for R values of 200, 100 and 66. Carbon disulfide was used as the extraction solvent and the extraction was performed at pH 6.0. Overall, the highest distribution coefficients were obtained for $R = 100$. Percent recoveries were the lowest for $R = 200$. The recoveries

TABLE III

DISTRIBUTION COEFFICIENTS AND RECOVERIES FOR MODEL COMPOUNDS OBTAINED BY USING A MICROEXTRACTION VESSEL

Volume ratio (R) = Volume of water / volume of extraction solvent.

| Compound	Initial concentration (ppb)	Distribution coefficient			Recovery (%)		
		$R=200$	$R=100$	$R=66$	$R=200$	$R=100$	$R=66$
Heptene	500	119	229	198	37	70	75
Toluene	500	278	>9000	>10,000	58	99	100
Nonane	500	39	47	52	16	32	44
Phenol	500	1	1	2	1	1	2
Nitrobenzene	500	102	222	194	34	69	74
Methyl laurate	500	97	68	70	33	41	51
Anthracene	50	138	298	145	41	75	69
Heptene	100	86	342	227	30	77	77
Toluene	100	449	>10,000	>1200	69	101	95
Nonane	100	38	113	56	16	53	46
Phenol	100	4	3	Trace	2	3	Trace
Nitrobenzene	100	136	199	149	41	67	69
Methyl laurate	100	77	185	102	28	65	61
Anthracene	10	108	191	113	35	66	63
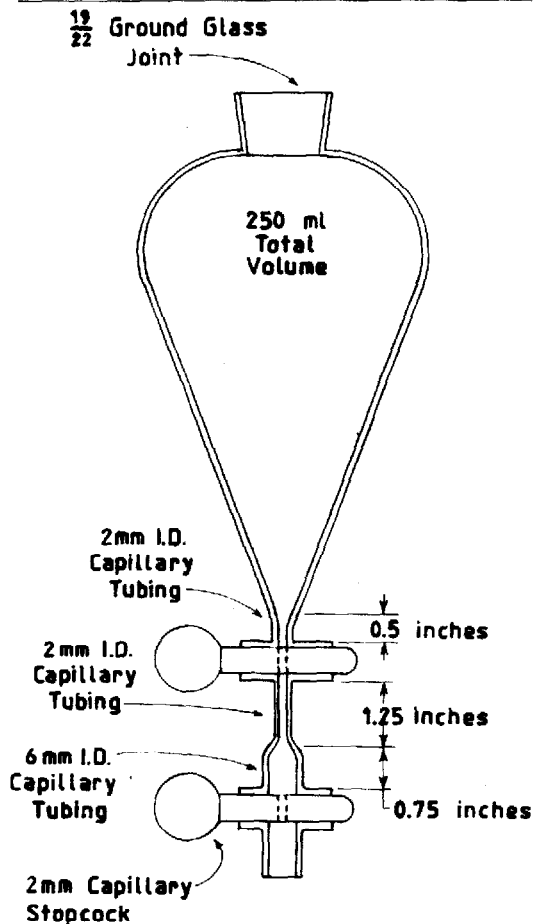
Fig. 5. Cross-sectional view of liquid–liquid microextractor.

for *R* values of 100 and 66 were comparable. All reported results are based on an average of five trials with a reproducibility of ± 7% on recoveries in the ppb range.

ACKNOWLEDGEMENT

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