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Solid-phase extraction of phenols using membranes loaded with modified polymeric resins

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ABSTRACT

Membranes impregnated with polystyrene–divinylbenzene (PS–DVB) or acetyl-PS–DVB resin beads were used for solid-phase extraction of ppm (w/w) concentrations of phenols from aqueous samples. A macro procedure uses 47 × 0.5 mm disks with 200–500 ml sample volumes at *ca.* 200 ml/min flow-rates. A smaller-scale procedure uses a thicker disk (3 mm) packed into a conventional solid-phase extraction column (7 mm I.D.). The retained phenols are eluted from the disk with organic solvent, and the individual phenols are determined quantitatively by GC or HPLC. Recoveries for 16 different phenols, including those included in the US Environmental Protection Agency list of priority pollutants, averaged 98% with a standard deviation of ±2%.

INTRODUCTION

In 1989 a new family of materials for solid-phase extraction (SPE) was introduced [1]. This is a membrane, or disk, of polytetrafluoroethylene (PTFE) fibrils impregnated with small (8 μm) particles of adsorbing material such as C_{18} silica or poly(styrene–divinylbenzene) (PS–DVB). Flow-rates as fast as 200 ml/min are possible, yet uptake of organic solutes is efficient because of fast kinetics. The fast kinetics are a result of the small particles, close and uniform packing, and elimination of channeling.

SPE disks have been used in the sample preparation steps in a number of methods used for water analysis in environmental laboratories [1–3]. While disks containing C_{18} bonded silica sorbents give quantitative recoveries for hydrophobic analytes, such as those found in US Environmental Protection Agency (EPA) Method 525.1 [11], low recoveries are often obtained for the more polar, water soluble analytes such as phenols. When extracting a 1-l water sample for the 11 priority pollutants phenols found in EPA Method 625 [12], for example, quantitative results are only obtained for 2,4,6-trichlorophenol and pentachlorophenol. A number of researchers have investigated ways of increasing SPE recoveries for phenol and substituted phenols, such as pH adjustment to neutralize the phenols, salt (NaCl) addition to "salt out" the phenols, alternative sorbents, ion-pairing, larger sorbent beds, or smaller sample volumes [4–8]. This paper explores an alternative SPE sorbent as a way of increasing recoveries for the phenols.

In a classic paper published in 1974, Junk *et al.* [9] showed that porous PS–DVB particles efficiently extract a wide variety of organic compounds, including phenols, present at very low

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concentrations in aqueous samples. Werkhoven-Goewie *et al.* [4] claim significantly higher breakthrough volumes on PS–DVB than on C_{18} silica for dichlorophenols. Sun and Fritz [10] showed that PS–DVB resins give significantly higher recoveries than C_{18} silica particles for many classes of organic solutes. They also showed that polymeric resins containing a hydrophilic substituent (such as acetyl) often give still higher recoveries than unsubstituted PS–DVB resins.

This paper explores the results obtained when PS–DVB and acetyl-PS–DVB resins are incorporated into SPE membranes and used to extract phenols from water. Also reported is a novel method of packing SPE membranes into standard SPE tubes for the extraction of analytes from smaller volumes of distilled, tap and river water. Good recoveries are obtained for all of the phenols, both from larger volumes (*ca.* 500 ml) through 47-mm disks and from smaller volumes (*ca.* 20 ml) through membrane-packed tubes.

EXPERIMENTAL

Resins and membranes

Spherical, highly cross-linked PS–DVB resins were obtained from Sarasep (Santa Clara, CA, USA). These had a surface area of approximately 400 m^2/g and an average particle size of either 5 or 8 μm. The acetyl derivative was prepared by reaction with acetyl chloride as described previously [10].

The membranes used in this work were of the general type manufactured by 3M (St. Paul, MN, USA) under the trade name Empore. A typical composition is 90% (w/w) resin and 10% (w/w) PTFE fibrils. The PTFE comprises less than 1% of the total surface area, and the open pore volume is approximately 60% (v/v). The disks used in this work were 47 mm in diameter and 0.5 mm thick. An experimental membrane used in part of this work was approximately 3 mm thick. Smaller circles were cut from these membranes with sharpened metal tubing of the appropriate diameter.

Apparatus and equipment

For SPE experiments a 47-mm membrane was placed in a Millipore filtration apparatus attached to a water aspirator. For elution, a 200 × 25 mm test tube was placed in the side-arm flask. A detailed description of the apparatus has been published [3].

Smaller-scale SPE experiments were carried out with a small column obtained from Alltech (Deerfield, IL, USA). A typical column size was 55 × 7 mm. A membrane circle was cut slightly larger in diameter than the column. It was forced into the column with 20 μm polyethylene frits above and below for support. The SPE tube was then connected to a laboratory-made reservoir. Sample solutions were then forced through the membrane at a controlled rate by air pressure applied at the top or by suction from below.

Sample analyses were performed with an HP 5880A gas chromatograph equipped with a flame ionization detector, integrator and auto injector. The column used was a Supelco (Bellefonte, PA, USA) fused-silica capillary SPB-1.

Procedures for SPE

47-mm Disks. Standard samples were prepared by adding several phenols to distilled water so that the concentration of each phenol was approximately 100 μg/l (0.1 ppm). The pH was adjusted to 2 with hydrochloric acid. In some cases sodium chloride was added to a concentration of 10% (w/v).

The disk was placed in the filtration apparatus and washed with acetone to remove any contaminants from storage, handling or manufacture. It was then conditioned with a small amount of methanol to promote wetting and uniform flow through the hydrophobic PTFE matrix. The aqueous sample was then passed through the membrane without allowing it to go dry at any time. At full aspirator vacuum the flow-rate is approximately 200 ml/min. A typical sample volume was 500 ml. Elution of the retained phenols was carried out with three 3-ml portions of tetrahydrofuran. Each portion was allowed to soak into the disk for about 5 min before pulling it through. The combined aliquots of tetrahydrofuran were made up to exactly 10 ml.

To analyze the extracts, HPLC was used with a 150 × 4.6 mm C_{18} column and a water–acetonitrile gradient. The water contained 0.1% acetic

acid to suppress ionization of the phenols. A UV detector was used at 272 nm.

Small disks in SPE column. The sample solution was prepared by adding a standard methanol solution of phenols (50 ppm each) to 20 ml of water so that the final concentration was approximately 0.4 ppm each. The pH was adjusted to approximately 2 with sulfuric acid to repress the ionization of the more acidic phenols.

Prior to each use a small amount of methanol (*ca.* 1 ml) was added to wet the disk. Without allowing the column to go dry, the aqueous sample solution was passed through at a flow-rate of 2 ml/min by applying a pressure of 15 p.s.i. (1 p.s.i. = 6894.76 Pa). The column was then washed with 2 ml of distilled water.

The phenols were eluted with 0.75 ml of methanol. The eluate was then collected in a 1.8-ml GC vial, and 0.1 ml of internal standard (500 ppm toluene in methanol) was added. The vial was then capped and a 2-μl aliquot was injected onto the gas chromatograph. The percentage recovery was calculated by comparing the peak heights (relative to the internal standard) with those of the original standard methanol solution of the phenols. Internal standard was also added to the methanol solution.

RESULTS AND DISCUSSION

SPE with larger disks

Virtually all of the previous work on resin-loaded membranes for SPE has been with disks 25 mm or 47 mm in diameter. Disks containing PS–DVB particles have been shown to be more efficient for the extraction of polar analytes than those containing C_{18} or cyclohexyl-bonded-phase silica particles [3]. However, several phenols gave low recoveries even with membranes loaded with PS–DVB. Somewhat higher recoveries were obtained by adding 10% of salt to the aqueous samples [3].

Membranes containing PS–DVB resins modified by chemical introduction of acetyl groups [10] were evaluated for SPE of phenols from aqueous samples. Two different lots of resin were functionalized separately with acetyl groups and incorporated into membrane disks. The results in Table I show excellent recovery of all eleven phenols with the sole exception of phenol itself with the lot 2 resin. In this particular case addition of salt to the aqueous sample was not necessary. In fact, the recoveries of samples with 10% salt averaged 5% lower than those with no salt.

TABLE I

SOLID-PHASE EXTRACTION OF PHENOLS USING 47-mm MEMBRANE DISKS LOADED WITH ACETYL-PS-DVB RESIN

Results are the average of 3 individual results. Elution with 9 ml of tetrahydrofuran.

Analyte	Lot 1				Lot 2			
	Recovery (%)	R.S.D. (%)	10% Salt: recovery (%)	R.S.D. (%)	Recovery (%)	R.S.D. (%)	10% salt: recovery (%)	R.S.D. (%)
Phenol	86	2	90	1	74	1	85	1
4-Nitrophenol	100	1	94	3	100	1	96	2
2,4-Dinitrophenol	98	2	93	2	98	1	96	3
2-Chlorophenol	93	1	87	1	94	2	90	2
2-Nitrophenol	92	2	88	1	95	2	92	2
2,4-Dimethylphenol	90	3	82	4	90	2	83	4
4-Chloro-3-methylphenol	95	2	90	3	97	2	92	4
2-Methyl-4,6-dinitrophenol	95	2	91	3	96	1	93	4
2,4-Dichlorophenol	94	2	88	2	96	1	91	3
2,4,6-Trichlorophenol	94	1	88	3	95	2	90	5
Pentachlorophenol	85	3	77	4	88	2	83	5
Average	93	2	88	2	93	2	90	3

SPE with 7 × 3 mm disks

The most common mode of SPE in chemical analysis is with small tubes or cartridges filled with loose polymeric resin or bonded-phase silica particles. Usually a bed height of >1 cm is used to ensure good retention of the desired sample compounds. However, this necessitates a relatively large volume of solvent to elute the adsorbed compounds. By packing a tube with disks 5–7 mm in diameter, cut from resin-loaded membranes, it should be possible to obtain efficient extraction with a very short height of resin membrane. The reason for this is that the resin particles are 5 or 8 μm, closely packed, and evenly dispersed throughout the membrane. Since the particles are immobilized, it should be possible to avoid the channeling that would be likely in a tube containing only a short height of a loose resin bed.

Our first experiments were with a small tube packed with 6 layers of membrane circles cut from a larger membrane. The I.D. of the tube was 4.5 mm and the circles were cut to exactly this diameter. These small circles were packed snugly into the tube with frits above and below for support. The recoveries of several test compounds (*ca.* 5 ppm of each) in aqueous samples were quite good, as shown in Table II. Because of probable channeling, somewhat lower results were obtained in one of the runs, so special care was taken to make the disks fit tightly against the walls of the tube. In other experiments an azo dye (pyridylazonaphthol) was passed through a packed tube. This dye formed a tight, even band on the membrane when the disks were packed carefully but the dye was mostly around the outside edges when the disks were not as tightly packed.

A single thick membrane should be easier to pack into a small column than several layers of a thinner disk. A membrane approximately 3 mm thick containing acetyl-PS–DVB resin particles was cut in a circle 7.5 mm in diameter and forced into a small tube 7.0 mm I.D. Frits were placed above and below the membrane to hold it firmly in place. The membrane fit snugly against the inside of the tube without buckling.

Several sample runs were conducted with this tube. Approximately 1 ml of methanol was added first to prewet the membrane. After rinsing with 1–2 ml of water, 20 ml of an aqueous standard was passed through. This standard contained approximately 0.4 ppm each of several phenols and was made up to pH 2 with sulfuric acid to ensure that all phenols were in the molecular form. Three different standard samples were run. One was made up in distilled water, another was in tap water of moderate hardness, and a third was river water to which known amounts of phenols had been added. Two different lots of resin were derivatized separately and tested separately. The results, given in Table III, indicate excellent recoveries for all 16 phenols. The only exception was the somewhat low recovery of 2-methyl-4,6-dinitrophenol from tap water that had been spiked with the test phenols.

TABLE II

RECOVERY OF TEST COMPOUNDS USING ACETYL-PS–DVB RESINS IN EMPORE DISKS

Elution with 0.75 ml of ethyl acetate. Results are the average of 4 individual runs.

Compound	Recovery (%)		
	C_{18} Silica	Underivatized PS–DVB	Acetyl-PS–DVB
Toluene	43	89	96
Phenol	5	36	91
Indene	43	93	94
p-Cresol	19	76	94
2,4-Dimethylphenol	29	93	96
Naphthalene	57	92	91
p-Propylphenol	34	91	96
sec.-Butylphenol	–	93	96
3-Nitrophenol	–	57	73
Dibutylphthalate	60	89	87
Average, R.S.D. (%)	36, ±52	81, ±23	92, ±8

CONCLUSIONS

Phenols in the low ppm concentration range can be effectively concentrated from aqueous samples by SPE with a membrane loaded with acetyl-PS–DVB resin particles. Samples of 500 ml can be passed very rapidly (*ca.* 2.5 min) through a 47 mm membrane disk using conven-

TABLE III

RECOVERY OF PHENOLS USING THICK MEMBRANES LOADED WITH ACETYL-DERIVATIZED RESIN IN A SMALL TUBE

Elution with 0.75 ml of methanol. Results are the average of 3 individual results.

Analyte	Distilled water		Tap water		River water	
	Recovery (%)	R.S.D. (%)	Recovery (%)	R.S.D. (%)	Recovery (%)	R.S.D. (%)
Phenol	99	2	96	2	97	3
3-Methylphenol	95	1	93	2	92	4
2-Nitrophenol	100	4	102	3	98	1
2,4-Dichlorophenol	98	0	97	3	97	2
4-Chloro-3-methylphenol	98	0	85	2	93	4
2,4,6-Trichlorophenol	102	0.5	98	3	101	0
2-Methyl-4,6-dinitrophenol	94	2	75	4	95	2
Pentachlorophenol	100	2	92	1	100	4
2-Chlorophenol	99	2	106	4	103	2
2-Methylphenol	99	4	100	3	100	1
4-Methylphenol	97	5	98	2	98	4
2,4-Dimethylphenol	97	5	94	2	103	5
2,6-Dichlorophenol	100	5	108	8	104	6
2,4,5-Trichlorophenol	96	5	95	5	107	3
2,3,4,6-Tetrachlorophenol	99	3	95	9	101	0.5
2-*sec.*-Butyl-4,6-dinitrophenol	101	4	97	4	101	2

tional filtration under reduced pressure. A total of three 3-ml portions of tetrahydrofuran is recommended for subsequent elution of the adsorbed phenols. On a smaller scale, aqueous analytical samples can be effectively preconcentrated by passing through a 3-mm disk packed into a tube 7 mm in diameter. In this case 0.75 ml of methanol are sufficient for elution of the adsorbed phenols. These membrane methods for SPE of phenols are rugged, quick and efficient.

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