

# Chemically modified resins for solid-phase extraction

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(First received May 3rd, 1991; revised manuscript received August 20th, 1991)

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## ABSTRACT

The packings most widely used for solid-phase extraction are hydrophobic and make poor surface contact with aqueous samples unless the resins are first treated with an activating organic solvent such as methanol. Insertion of an acetyl- or hydroxymethyl group into a porous polystyrene–divinylbenzene resin provides a more hydrophilic surface that is easily wetted by water alone. Small columns of the chemically modified resins were found to be very efficient for the solid-phase extraction of many types of organic solutes from aqueous samples. Comparative recovery studies showed that the modified resins are superior to both silica packings and unmodified organic resins for the solid-phase extraction of organic compounds, and especially for polar organics such as phenols.

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## INTRODUCTION

Solid-phase extraction (SPE) is now widely used for the preconcentration and clean-up of analytical samples, for the purification of various chemicals and for applications such as the removal of toxic or valuable substances from a variety of predominantly aqueous solutions. Typical applications include methods for the determination of trace amounts of pesticides [1,2], determination of trace organic contaminants in water [3,4], analysis of industrial waste waters [5], determination of azaarenes in water [6], evaluation of porous polymers [7], isolation of organic compounds from ground water [8], sampling of priority pollutants in waste water [9], collection and concentration of environmental samples [10] and pretreatment of urine samples [11,12].

For analytical purposes, SPE is usually performed using a small column or cartridge containing an appropriate packing. Membranes loaded with appropriate resins have also been used for SPE [13]. Following uptake of extractable solutes from a predominately aqueous sample, it is common practice to elute the adsorbed materials from the resin with a small amount of an organic solvent.

Chemically bonded silica, usually with a C<sub>18</sub> or C<sub>8</sub>

organic group, is by far the most commonly used material for SPE. Use has also been made of porous polystyrene or other polymeric resins in SPE. Graphitized carbon black has been used for the concentration of agricultural chemicals [14] and phenols [15] from water. It was stated that the carbon black appears to function as an anion exchanger and as a non-specified adsorbent.

Chemically bonded silica and porous polystyrene resins have several shortcomings for use in SPE. (1) While silica itself is hydrophilic, the hydrocarbon chains make the surface hydrophobic. The consequence is poor surface contact with predominantly aqueous solutions. Porous polystyrene resins also have a hydrophobic surface. (2) Pretreatment of the SPE materials with an activating solvent (such as methanol, acetone or acetonitrile) must be used to obtain better surface contact with the aqueous solution being extracted. However, the activating solvent can be gradually leached out of the resin, thereby causing the extraction to become ineffective. This is particularly true if the SPE column inadvertently becomes dry, causing air to be sucked into the column. (3) Many types of organic compounds are incompletely extracted from predominantly aqueous solutions. This is especially true with chemically

bonded silica packings [3,7,9]. These drawbacks can be largely overcome by use of a new type of chemically derivatized resin.

In this work, new chemically modified polystyrene-divinylbenzene resins were prepared which are hydrophilic and easily wetted by water while still keeping their extraction ability. Various organic compounds were tested by SPE using these modified resins. The recovery results were compared with those using  $C_{18}$  silica and underivatized polystyrene-divinylbenzene resins. The new resins showed superior recoveries for test compounds in SPE.

## EXPERIMENTAL

### *Reagents and chemicals*

The reagents and solvents used for the derivatization reactions were of analytical-reagent grade and were dried with molecular sieves. Laboratory-distilled water was further purified using a Barnstead Nanopure II System (Sybron Barnstead, Boston, MA, USA).

Several chemically modified resins were prepared from porous, cross-linked polystyrene materials. Amberchrome 161 (Supelco, Bellefonte, PA, USA) is spherical with an average particle size of *ca.* 50  $\mu\text{m}$  and a surface area of *ca.* 720  $\text{m}^2/\text{g}$ . Sarasep resin (Sarasep, Santa Clara, CA, USA) has an average particle size of *ca.* 10  $\mu\text{m}$  and a surface area of *ca.* 415  $\text{m}^2/\text{g}$ .

The acetyl derivative was prepared as follows. To 5.1 g of resin add 30 ml of carbon disulphide, 9.5 g of anhydrous aluminum chloride and 5.5 g of acetyl chloride (added dropwise). Keep at 50°C for 24 h and stir with a magnetic stirrer bar from time to time through the whole reaction. Pour the final product into ice-water. Filter with filter-paper to isolate the resin, wash with acetone, methanol and water until clean, then dry. The presence of a carbonyl group was proved by a strong band at 1690  $\text{cm}^{-1}$  on the spectrum obtained by Fourier transform IR spectrometry with a pellet of powdered potassium bromide and resin. The concentration of  $-\text{COCH}_3$  groups on the resin was found to be 1.2 mmol/g by oxygen elemental analysis.

The hydroxymethyl derivative was prepared as follows. Add 1.2 g of paraformaldehyde, 16 ml of acetic acid and 4 ml of acetic anhydride to 5.2 g of

resin. Stir with a stirrer bar for a few minutes, then add 6.0 g of anhydrous zinc chloride and keep at 60°C overnight with stirring from time to time. Filter the resin, rinse with methanol then heat with methanol-concentrated hydrochloric acid (90:10) for 1 h with stirring from time to time. Wash the final product with methanol and dry with aspiration. The concentration of  $-\text{CH}_2\text{OH}$  groups on the resin was determined as 1.3 mmol/g by oxygen elemental analysis.

### *Apparatus and components*

The apparatus used for solid-phase extraction is shown in Fig. 1. The small columns were packed with *ca.* 100 mg of resin. The  $C_{18}$  silica SPE column was obtained from Alltech (Deerfield, IL, USA). This column was 55  $\times$  6 mm I.D., packed to a bed height of 8–10 mm with resin of 40  $\mu\text{m}$  particle size. Derivatized and underivatized Amberchrome 161 resins were packed dry to a bed height of 12 mm into empty 55  $\times$  6 mm I.D. plastic columns obtained from P. J. Cobert Assoc. (St. Louis, MO, USA). Each column contained polyethylene frits to support and cover the resins. Because of the smaller particle size (10  $\mu\text{m}$ ), the bed height of the Sarasep resin was only about 10 mm, packed in a 55  $\times$  6 mm I.D. plastic column. Each SPE column was connected to a laboratory-made reservoir by an adaptor (P. J. Cobert Assoc.). The flow-rate of the sample solution from the reservoir was controlled by air pressure applied to the top of the reservoir.

The organic compounds eluted from SPE column with ethyl acetate were collected and then analyzed using an HP 5880A gas chromatograph with a flame ionization detector, an HP 5880A Series Level 4 integrator and an HP 7673A automatic sampler (Hewlett-Packard, Avondale, PA, USA). The gas chromatographic columns used were J&W fused-silica capillary megabore DB-5 and minibore DB-1 (Alltech) and Supelco (Bellefonte, PA, USA) fused-silica capillary columns.

A Bruker FT-IR 98 instrument (USA Bruker Instruments, San Jose, CA, USA) was used for structure determination.

### *Procedure for SPE*

Prior to their initial use, columns were cleaned by passing through them small amounts of methanol, ethyl acetate and acetonitrile, then drying. Approxi-

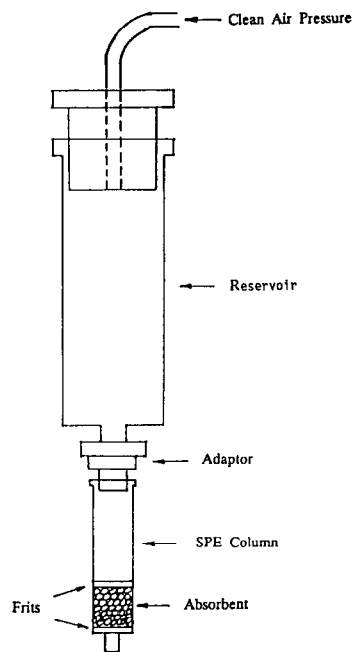


Fig. 1. Solid-phase extraction apparatus.

mately 1 ml of methanol was added to the SPE column just before each sample run to serve as an "activating" solvent.

Samples were prepared by adding a dilute methanol solution of several organic test compounds to 20 ml of water so that the concentration of each test compound would be about 5 ppm. This sample was then added to the reservoir and the air pressure was adjusted to give a sample flow-rate of 5 ml/min through the column. The column was then washed with 1 ml of pure water and air was blown through the column for a few seconds.

The SPE column was disconnected from the reservoir and 1 ml of ethyl acetate was added. The column was again connected to the reservoir and gentle air pressure was applied to make the ethyl acetate pass through the column in *ca.* 1 min. The eluate was collected in a small vessel with a syringe cap. A measured volume of internal standard was added to the vessel, which was capped immediately and agitated to mix well.

The vessel was placed in the automatic sampler of the gas chromatograph. A 1- $\mu$ l aliquot was injected. Nitrogen carrier gas was used at a flow-rate of

15 ml/min, and a splitting ratio of 1:40 was used. Temperature programming was employed. Recoveries were calculated as average values ( $n > 2$ ) by comparing the relative peak heights of collected samples with samples not subjected to SPE.

## RESULTS AND DISCUSSION

### *Selection of resins*

In a previous study, various hydrophilic functional groups were chemically attached to the benzene rings of porous, cross-linked polystyrene resins [16]. When used for high-performance liquid chromatographic separations of typical organic compounds, the derivatized resins gave slightly shorter retention times for relatively non-polar organic solutes, but appreciably longer retention times for more polar test compounds such as phenols. Of the resins studied, the acetyl resin showed the best ability to retain phenols. The resin with a hydroxymethyl group also retained phenols more strongly than the underivatized resin. These results suggest that organic resins containing a hydrophilic group should strongly retain almost all types of test compounds from a predominantly aqueous solution, as in SPE.

Our dry acetyl or hydroxymethyl resin is quickly and easily wetted by water. This can be demonstrated by placing a small amount of the dry resin in a test-tube and adding water. The resins make good surface contact with the water and sink to the bottom. In contrast, dry, underivatized resin or dry  $C_{18}$  silica is not wetted by water and the hydrophobic particles clump together and tend to float on the surface of the water. This suggests that the acetyl or hydroxymethyl resin can be used in SPE from aqueous solutions without any pretreatment with an "activating" organic solvent.

The efficiency of porous resins used in SPE varies with the porosity, those with the largest surface area giving the greatest retention [17]. Amberchrome 161 is a spherical, cross-linked polystyrene resin with an unusually high surface area (720  $m^2/g$ ) and should therefore be well suited for SPE. Another polystyrene resin with a surface area of around 415  $m^2/g$  was also available for testing. Preliminary experiments showed that most organic test compounds are easily eluted from these resins with an organic solvent such as ethyl acetate.

TABLE I

RECOVERIES OF PHENOLS, AROMATIC COMPOUNDS AND POLYHYDROXY AROMATIC COMPOUNDS BY SPE UNDER WET AND DRY LOADING CONDITIONS

Compound	Recovery (%)							
	C <sub>18</sub> Si		Amberchrome		Amberchrome -CH <sub>2</sub> OH		Amberchrome -COCH <sub>3</sub>	
	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry
Phenol	6	<3	91	3	94	75	100	93
<i>p</i> -Cresol	16	4	91	12	98	88	101	94
<i>p</i> -Ethylphenol	66	15	96	37	99	97	101	99
2-Nitrophenol	45	17	93	47	95	96	96	96
3-Nitrophenol	<5	<5	81	<5	85	75	93	73
4-Nitrophenol	<5	<5	87	<5	86	77	87	85
2,4-Dimethylphenol	71	21	95	42	97	96	100	98
4- <i>tert.</i> -Butylphenol	83	49	88	50	96	90	100	95
Anisole	78	58	91	56	94	95	98	96
Aniline	9	<5	94	26	96	90	100	96
Benzyl alcohol	10	<5	92	17	98	85	99	99
Nitrobenzene	54	27	92	51	96	96	100	97
2,4-Dinitrofluorobenzene	44	4	83	23	96	92	98	94
<i>o</i> -Hydroxyacetophenone	88	67	85	54	95	94	96	94
Isopentyl benzoate	84	60	72	73	89	84	96	85
Diethyl phthalate	90	70	87	58	96	84	100	90
Average	47	26	89	35	94	88	98	93
Catechol	0	0	72	0	89	9	75	30
Resorcinol	0	0	61	0	88	0	97	95
<i>o</i> -Methylresorcinol	0	0	83	0	97	16	99	96
Hydroquinone	0	0	26	0	72	0	87	81
Methylhydroquinone	0	0	77	0	98	5	99	94
Phloroglucinol	0	0	0	0	24	0	56	42

*Recovery of test compounds*

Various resins were compared for use in the SPE of different organic compounds from aqueous solution. The apparatus used is shown in Fig. 1. Derivatized and underivatized Amberchrome 161 resins were compared with each other and with a widely used C<sub>18</sub> silica material.

Results for SPE and subsequent elution of the organic test compounds (about 5 ppm in aqueous solution) are summarized in Table I for phenols, aromatic compounds and polyhydroxyphenols. The "wet" designation refers to the usual procedure in which the SPE column is first treated with a 1-2 ml of methanol as an "activating" organic solvent before introduction of the aqueous sample. The recovery of the organic compounds was much higher using Amberchrome 161 than with the C<sub>18</sub>

silica material. However, the recovery of test compounds was still higher for the derivatized Amberchrome 161 resins, with the acetyl derivative giving the highest recovery in every case.

Sometimes a short column (or cartridge) used for SPE inadvertently becomes dry, causing air to be sucked in. This could cause part or all of the activating solvent to be lost from the resin bed. The efficiency of the various resins for SPE was tested after passing air through a column for several minutes to remove the water and activating solvent. Then the sample was added and the recoveries of test compounds were determined as before. These results, denoted as "dry", are also given in Table I. There is a marked decrease in the recoveries for both the C<sub>18</sub> silica and the Amberchrome. However, the recoveries on the hydroxymethyl and acetyl resins

TABLE II

THE RECOVERIES (%) OF ALIPHATIC AND PYRIDINE COMPOUNDS UNDER WET SPE COLUMN LOADING CONDITIONS

Compound	C <sub>18</sub> Si	Amberchrome 161	Amberchrome 161 -COCH <sub>3</sub>
Pentanone	20	91	97
Octanone	91	89	98
Hexyl acetate	85	70	92
Mesityl oxide	58	76	98
Ethyl crotonate	76	74	97
Hexenyl acetate	72	59	85
3-Picoline	41	92	97
3-Ethylpyridine	76	95	97
Average	65	81	95

are only slightly below those obtained under normal conditions where an organic activating solvent is used. These results demonstrate the superior ability of the hydrophilic resins to make intimate contact with aqueous solutions without resorting to the use of an adsorbed organic solvent.

In Table II results are given for several aliphatic compounds and substituted pyridines. Again, the recoveries are much higher on Amberchrome 161 than on C<sub>18</sub> silica, but the recoveries are highest on the acetyl Amberchrome 161 SPE column. When air was passed through each column before addition of the aqueous sample, the average recoveries were as follows: C<sub>18</sub> silica, 50.5%; Amberchrome 161, 50.9%; and acetyl Amberchrome 161, 91.2%.

TABLE III

RECOVERIES (%) OF PHENOLS AND POLYHYDROXY-PHENOLS USING 10- $\mu$ m POLYSTYRENE (PS) RESINS UNDER WET SPE COLUMN LOADING CONDITIONS

Compound	PS	PS-COCH <sub>3</sub>
Phenol	24	98
<i>p</i> -Cresol	91	100
2,4-Dinitrofluorobenzene	100	100
3-Nitrophenol	82	102
Catechol	1	40
Hydroquinone	0	14
2-Methylresorcinol	8	80
Methylhydroquinone	4	59

TABLE IV

COMPARISON OF DIFFERENT ACETYL RESINS FOR SPE

Amberchrome 161: *ca.* 720 m<sup>2</sup>/g surface area and 50  $\mu$ m average particle size. Sarasep: *ca.* 415 m<sup>2</sup>/g surface area and 10  $\mu$ m average particle size.

Compound	Recovery (%)		
	C <sub>18</sub> Si	Amberchrome 161	Sarasep
Benzene	41	86	85
Toluene	75	85	88
Indene	73	84	85
Naphthalene	68	79	79
Anthracene	59	67	71
Phenol	7	98	97
<i>p</i> -Cresol	33	100	99
Dibutyl phthalate	66	84	88
Average	53	85	87

The effect of hydrophilic substituents was further tested by comparing resins from different sources. A highly cross-linked, spherical polystyrene resin was obtained from Sarasep. This resin has an average particle size of 10  $\mu$ m and a surface area of 415 m<sup>2</sup>/g, which is appreciably lower than that of the Amberchrome 161 resins.

The results in Table III show significantly higher recoveries on the acetyl resin than on the underivatized resin for all the compounds tested. The results for the four phenols on the acetyl Sarasep resin are comparable to those obtained on the acetyl Amberchrome resin (Table I). However, recoveries of the polyhydroxyphenols are lower on the acetyl Sarasep than on the acetyl Amberchrome resin. This may be due to the smaller surface area of the Sarasep resin.

Several organic compounds (0.7–7 ppm in water) were selected to compare the recoveries obtained with the acetyl derivatives of the Amberchrome 161 and Sarasep resins. The recoveries were similar, as shown in Table IV. Again, the recoveries with the C<sub>18</sub> silica material were much lower.

## CONCLUSIONS

Incorporation of a hydrophilic group into a porous polymeric resin enables excellent surface contact to be made with an aqueous sample without resorting to any pretreatment of the resin with an

organic solvent. Aromatic and other relatively non-polar organic compounds are taken up from aqueous solutions almost as strongly by the derivatized as by the underivatized resins. More polar compounds (particularly phenols) are retained more strongly by the resins with a hydrophilic group, especially when the resin bears an acetyl group.

The surface area of a porous resin seems to have a major effect on its efficiency for SPE. The better recovery of test compounds by polymeric resins compared with bonded-phase silica resins could be due in part to the significantly higher surface area of the polymeric resins.

#### ACKNOWLEDGEMENTS

We thank John Naples of Rohm and Haas for the Amberchrome 161 resin and Doug Gjerdic of Sarasep for the 10- $\mu\text{m}$  polystyrene resins used in this research. Ames Laboratory is operated for the US Department of Energy under Contract No. W-7405-Eng-82. This work was supported by the Director of Energy Research, Office of Basic Energy Sciences.

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