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Ion-exchange preconcentration and group separation of ionic and neutral organic compounds

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ABSTRACT

In many cases sample pretreatment continues to be the most time-consuming and costly step in the analytical process. In the present work it is shown that macroporous ion-exchange resins of low exchange capacity can be used both to preconcentrate organic solutes from aqueous samples and to separate these solutes into groups. Thus, neutral and basic organic compounds are both taken up from aqueous solution by a very short column packed with a special cation-exchange resin. The neutral group of compounds is subsequently eluted with an organic solvent. The bases are then eluted by 2 *M* methylamine in methanol. In a similar manner organic acids are concentrated on a special anion-exchange column. Extensive data are shown to demonstrate the efficiency of the preconcentration and group separation of neutral and basic compounds.

INTRODUCTION

Solid-phase extraction (SPE) is fast becoming the preferred technique for analytical preconcentration [1]. It uses much smaller amounts of organic solvents than liquid–liquid extraction. SPE is easily automated and is capable of obtaining very high concentration factors.

SPE is usually carried out with a very small tube (or column) packed with a spherical solid of small particle size and high surface area. It can be thought of as low-performance liquid chromatography. Maximum retention is desired for the substances of interest with minimum retention of the other sample materials. The adsorbed substance can be subsequently eluted by a very small volume of an organic solvent or other suitable solvent.

The use of a short ion-exchange precolumn is well established to concentrate anions or cations prior to their separation and determination by ion chromatography. In the present work an ion-exchange resin with suitable properties is used to preconcentrate organic substances from aqueous samples and then separate them into two fractions: neutral and basic compounds. The basis for this separation is that neutral organic compounds are readily eluted from the SPE column by an organic solvent while basic compounds remain on the ion-exchange resin as protonated cations. The latter can then be eluted by an organic solvent containing a base to neutralize the protonated solute cations. This same principle has been used previously [2–4], but not to any extent for simultaneous preconcentration and group separation.

EXPERIMENTAL

Reagents and chemicals

The reagents used for the derivatization of the ion-exchange resins were of analytical grade. Reagents used and analytes studied in SPE were >99% pure and used as obtained from Aldrich, Fisher and Kodak. Laboratory distilled water was further purified using a Barnstead Nanopure II system (Sybron Barnstead, Boston, MA, USA).

The resins were prepared using a highly porous, cross-linked polystyrene resin, Amberchrome 161

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(Supelco, Bellefonte, PA, USA). This spherical resin has an average particle size of about 40 μm and a surface area of about 720 m^2/g.

The procedure for the preparation of the sulfonated cation-exchange resin is as follows. In an ice bath, 1 g of resin was wetted with 1 ml of glacial acetic acid and stirred to form a slurry. To this slurry 25 ml of concentrated sulfuric acid was added. After 90 s, the reaction was stopped by adding an excess of ice water. The final product was then rinsed with methanol, water and acetone. The cation-exchange capacity was then determined by first passing 5 ml of 1 *M* HCl through a known mass of resin to assure the resin was all in the protonated form. The resin was then rinsed with deionized water and tested with litmus paper to assure that any excess acid was washed from the reservoir. Then 5 ml of a standardized NaOH solution was passed through the column. This was followed by another rinse with deionized water. The NaOH solution and water rinse was collected and titrated with a standard HCl solution. The capacity of the sulfonated resin was determined to be approx. 1.1 mequiv./g.

The apparatus used for SPE consists of a 30-ml glass reservoir connected by a small adapter to the SPE column itself. The SPE columns were obtained from Varian (Harbor City, CA, USA). Approximately 100 mg of the resin was packed into the 55 × 6.5 mm I.D. columns. The resin was held in place above and below by 20 μm polyethylene frits. The resin bed height was approximately 12–15 mm. The top of the reservoir has a ground glass joint which may be connected to a source of constant adjustable air pressure. The columns were connected to the laboratory-made reservoir by an adapter (Alltech Assoc., Deerfield, IL, USA). The flow-rate was controlled by the air pressure applied to the reservoir.

The concentrated samples collected were analyzed using an HP 5880A gas chromatograph with a flame ionization detector, an HP 5880A Series level 4 integrator, and an HP 7637A automatic sample injector (Hewlett-Packard, Avondale, PA, USA). The capillary column used was a Supelco (Bellefonte, PA, USA) SPB-1.

Procedure for SPE

Prior to initial use, the sulfonated columns were cleaned by passing through *ca.* 2 ml of methanol and acetonitrile. This was followed by approximately 5 ml of a 2-*M* solution of HCl in methanol in order to ensure the sulfonic acid groups on the resin would be protonated. The columns were then "wetted" with approximately 1 ml of methanol. The resin was not allowed to dry before passing the sample solution through the column.

The sample solutions were then prepared by adding a dilute methanol solution of several basic and neutral compounds to 10 ml of deionized water so that the final concentration of each compound was 5 ppm (v/v). In the base-neutral group separation, the pH of this solution was then lowered to *ca.* 2 with HCl. In the separation of strong bases from weak bases and neutrals a 0.1-*M* buffer solution of sodium phosphate was used to adjust the pH to 7. The sample was then added to the reservoir and the air pressure adjusted to give a sample flow-rate of approximately 1 ml/min. The column and reservoir were then rinsed with about 5 ml of water and air dried for several seconds.

The column was then rinsed with 1 ml of methylene chloride to elute the neutral fraction. This was collected in a GC vial. An internal standard of 0.1 ml of 500 ppm quinoxaline in methanol was then added to the vial. The vial was capped, mixed with an orbital stirrer, and then analyzed by GC. A 1-μl aliquot was injected with a split ratio of 1:40. Helium carrier gas was used at a flow-rate of 15 ml/min. The oven temperature was held initially at 65°C for 2 min, then ramped at 15°C/min to a final temperature of 225°C. The basic fraction was then eluted with 1 ml of either 2 *M* methylamine or 2 *M* NH_3 in methanol. Quinoxaline was also added as an internal standard as before. The vial was then capped, mixed, and analyzed by GC under the previously given conditions. Recoveries were calculated by comparing the relative peak heights of collected samples to those not subjected to SPE. All results are an average of multiple trials ($n \geqslant 3$).

RESULTS AND DISCUSSION

Group separation of neutral and basic compounds

Previous work has shown that polystyrene–divinyl benzene (PS–DVB) beads of high surface area (typically *ca.* 400–750 m^2/g) are very efficient for SPE of low concentrations of organic solutes in aqueous samples [5,6]. These resin beads still retain organic solutes when the beads are sulfonated pro-

vided that the degree of sulfonation is rather low. The sulfonated beads are able to retain protonated amine cations by an ion-exchange mechanism. So long as the amines are present as cations, they are not washed off the resin by an organic solvent.

The extent of sulfonation, as indicated by the exchange capacity of the sulfonated resin, can be kept low by sulfonation at 0°C for only a short period of time. To a first approximation over short time periods, the capacity of the resin *vs.* the reaction time is linear. A reaction time of 40 s yielded an exchange capacity of 0.45 mequiv./g, a time of 60 s gave an exchange capacity of 0.8 mequiv./g, and 90 s 1.1 mequiv./g. A sulfonated resin with an exchange capacity of 1.1 mequiv./g was used for SPE.

The scheme for preconcentration of low concentrations of organic solutes and their separation into groups was as follows. The sample was adjusted to an acidic pH with hydrochloric acid. This converted the basic compounds to the protonated cations. Then the sample was passed through a small column containing sulfonated resin in the H^+ form at a flow-rate of approximately 1 ml/min. The neutral organic solutes were eluted as a group with a small volume of metnhylene chloride. Then the basic fraction was eluted with a small volume of methylamine or ammonia in methanol.

TABLE I

RECOVERIES OF NEUTRAL ORGANIC SOLUTES (5 ppm) ELUTED WITH METHYLENE CHLORIDE

Conditions: 10 ml aqueous solution, pH = 1.8, lowered with H_2SO_4, cation-exchange resin (1.1 mequiv./g). All samples 5 ppm.

Compound	Recovery (%)
4-Nitroacetophenone	98
Nitrobenzene	99
Benzothiazole	92
Octyl alcohol	94
o-Hydroxyacetophenone	99
Benzonitrile	95
Toluene	98
trans-2-Hexenylacetate	96
Butyl benzene	95
Anisole	90
Octyl aldehyde	97
Ethyl crotonate	88
Propyl benzene	94
1-Octanol	94
Benzonitrile	95
Nitrobenzene	99

Table I shows excellent recovery of neutral organic solutes in water at 5 ppm. In each case essentially complete elution is obtained with methylene chloride. The recoveries of some basic organic solutes studied are summarized in Table II. None of these compounds was eluted with methylene chloride except 2,3-dimethyl quinoxaline which is an extremely weak base and therefore behaves almost like a neutral compound. Some of the basic compounds were eluted well with methanol containing aqueous ammonia, but stronger bases like butylamine and *n*-octylamine were not eluted. However, methylamine in methanol eluted all of the bases efficiently. Methylamine (pK_b in water = 3.1) is a stronger base than ammonia (pK_b = 4.8). In the gas chromatographic step methylamine is quite volatile and elutes well before any of the sample solutes.

An aqueous mixture containing 5 ppm each of five neutral compounds and six basic compounds was preconcentrated and the groups separated by our scheme. Fig. 1 shows the gas chromatogram obtained for the neutral group. Fig. 2 shows the gas chromatogram of the compounds in the basic group.

The effect of pH on the group separation was investigated. Results were compared for samples buffered at pH 2.0 with 0.1 *M* sodium dihydrogenphosphate and at pH 7.0 using disodium hydrogenphosphate. The results in Table III show that at pH 2.0 neutral compounds were eluted with methylene chloride and basic compounds with methylamine in methanol, as expected. Recoveries averaged lower with the pH 2.0 phosphate buffer than when the sample was acidified with HCl. At pH 7.0 the weaker bases (aniline, quinoline, etc.) were not protonated, and therefore were eluted with the neutral group. The stronger bases (hexylamine, ocytalmine, etc.) remained protonated at this pH, and therefore are not eluted until the methylamine in methanol wash step. Thus an additional group separation of aliphatic amines from aromatic amines and nitrogen heterocyclic compounds appears to be feasible.

Group separation of neutral and acidic compounds

The same principle used to preconcentrate and separate neutral and acidic groups should be appli-

TABLE II

RECOVERIES OF BASIC ORGANIC SOLUTES (5 ppm) ELUTED WITH AMMONIA OR METHYLAMINE IN METHANOL

Conditions 10 ml aqueous solution, pH = 1.8, lowered with H_2SO_4, cation exchange resin (1.1 mequiv./g). All samples 5 ppm.

Compound	Recovery (%)	
	Ammonia in methanol	Methylamine in methanol
Pyridine	91	91
Aniline	95	99
N,N'-dimethyl aniline	61	92
Quinoline	92	96
Butyl amine	0	103
Octyl amine	0	97
Quinaldine	92	95
Ethyl pyridine	–	93
Isopropyl pyridine	–	101
N-methyl aniline	–	92
sym-Collidin	–	95
Phenethyl amine	–	98
2,3-Dimethyl quinoxaline	63[a]	63[a]
Hexyl amine	0	95
Cyclohexyl amine	–	98
2,4-Lutidine	–	101

[a] Eluted with 37% methylene chloride.

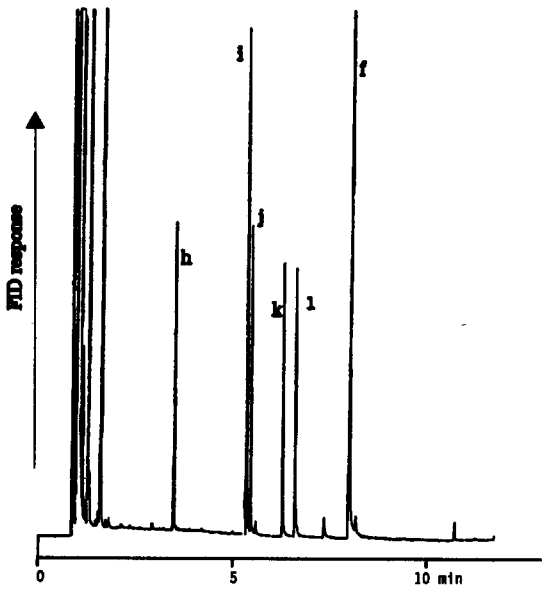

Fig. 1. Gas chromatogram of neutral compounds concentrated from aqueous solution with ion-exchange resin and eluted with methylene chloride. Peaks: h = ethyl crotonate; i = propyl benzene; j = 1-octanol; k = benzonitrile; l = nitrobenzene; and f = quinoxaline (internal standard).

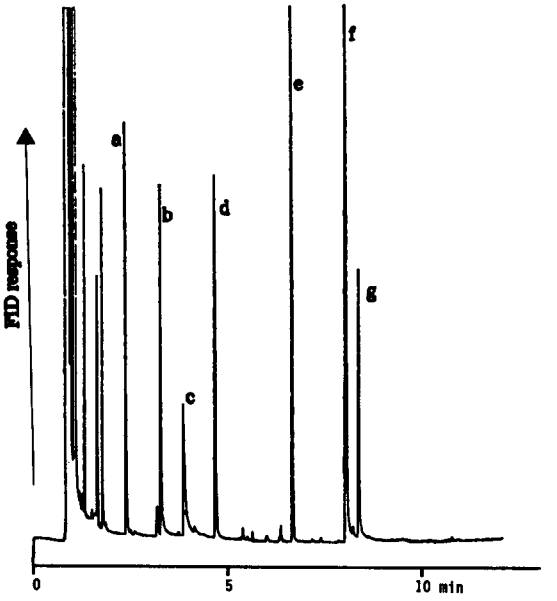

Fig. 2. Gas chromatogram of basic compounds concentrated from aqueous solution with ion-exchange resin from aqueous solution and eluted with methyl amine in methanol. Peaks: a = pyridine; b = hexyl amine; c = cyclohexyl amine; d = 2,4-lutidine; e = N,N'-dimethyl aniline; f = quinoxaline (internal standard); and g = quinoline.

TABLE III

RECOVERIES OF SOLUTES (5 ppm) FROM 10 ml OF AQUEOUS SOLUTION BUFFERED AT pH 2.0 AND pH 7.0

Compound	Recovery (%)			
	pH 2.0		pH 7.0	
	Methylene chloride	Methylamine	Methylene chloride	Methylamine
Pyridine	0	44	43	0
Toluene	95	0	101	0
Cyclohexyl amine	0	76	0	76
Aniline	0	88	81	0
Benzyl alcohol	93	0	98	0
Benzonitrile	98	0	90	0
Octyl alcohol	93	0	99	0
Nitrobenzene	101	0	–	0
N,N'-Dimethyl aniline	0	96	–	0
p-Ethanol	92	0	91	0
o-Hydroxyacetophenone	95	0	94	0
Benzothiazole	94	0	100	0
Quinoline	0	90	93	0
Quinaldine	0	90	88	0
2,3-Dimethyl quinoxaline	85	0	94	0
4-Nitroacetophenone	75	0	86	0
Hexyl amine	0	91	0	90
Octyl amine	0	91	0	90

cable for the separation of neutral and acidic groups of organic solutes. In this case the resin used would be a porous polymeric material functionalized with a quaternary ammonium group. Neutral organic compounds would be eluted from such a resin by an organic solvent, while acidic compounds would be retained as anions (when loaded at an alkaline pH). These organic anions could then be eluted by an organic solvent containing an acid (such as HCl) to convert the solute anions of the molecular organic acid.

Preliminary results indicate that this scheme does indeed work. Research on this project is continuing.

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REFERENCES

1 I. Liska, J. Krupcik and P. A. Leclercq, *J. High Resolut. Chromatogr.*, 12 (1989) 577–590.
2 J. R. Kaczvinsky, Jr., K. Saitoh and J. S. Fritz, *Anal. Chem.*, 55 (1983) 1210–1215.
3 J. J. Richard and G. A. Junk, *Water Qual. Bull.*, No. 2 (1981) 40–42, 54–55.
4 M. Moors and D. L. Massart, *Trends Anal. Chem.*, 9 (1990) 164–169.
5 G. A. Junk, J. J. Richard, M. D. Grieser, D. Witiak, J. L. Witiak, M. D. Arguello, R. Vick, H. J. Svec, J. S. Fritz and C. V. Calder, *J. Chromatogr.*, 99 (1974) 745.
6 J. J. Sun and J. S. Fritz, *J. Chromatogr.*, 590 (1992) 197–202.