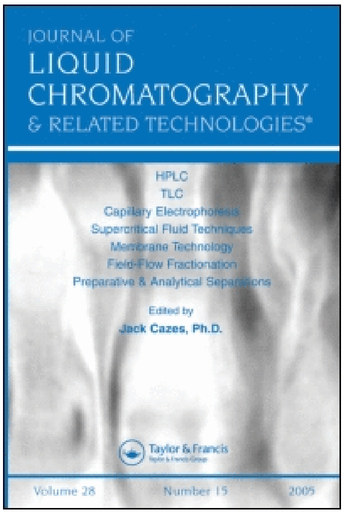

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Z. Hajouj[a]; J. Thomas[a]; A. M. Siouffi[b]
[a] Laboratoire de Chimie Faculté des Sciences et Techniques, Tours, France [b] Laboratoire de Génie Chimique et Chimie Appliquée, Faculté des Sciences et Techniques Saint-Jérôme, Marseille, France

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MIXED MODE S. P. E. OF POLLUTANTS IN WATER ON MECHANICALLY BLENDED SILICA-BASED BONDED PHASES.

I. INFLUENCE OF THE PREPARATION METHOD

Z. Hajouj[1], J. Thomas,*[1] A. M. Siouffi[2]

[1] Laboratoire de Chimie
Faculté des Sciences et Techniques
Parc de Grandmont
37200 Tours - France

[2] Laboratoire de Génie Chimique et Chimie Appliquée
Faculté des Sciences et Techniques Saint-Jérôme
Avenue Escadrille Normandie-Niémen
13397 Marseille - France

ABSTRACT

Cartridges for Solid-Phase Extraction operating in mixed mode were filled with two phases: C_{18} bonded silica and propylsulfonic acid bonded silica, mechanically blended according to two methods: one dry, the other by suspension in acetonitrile. They were compared with cartridges containing the individual phases, and with a mixed phase having two functionalities bonded onto a common silica particle. The percent recoveries of neutral, basic and acidic environmental pollutants and their reproducibilities were determined by HPLC. After evaluation of the optimum eluent volume, the blended phase prepared without solvent and very rapidly, was overall very promising in terms of retention, reproducibility and composition potential.

INTRODUCTION

In Solid-Phase Extraction (S.P.E.) applied to environmental analysis, bonded phases operating with double mechanism have recently been introduced with the aim of maximum retention of the different classes of pollutants on the cartridges. There is a category of mixed phases with two functionalities bonded onto the same particle.[1-3] Variants are represented respectively by a functional group bonded in low concentration onto a resin,[4] and an impurity included in the polymer network.[5]

There is also the category of separate bonded phases whose particles are blended mechanically, and which have only been the subject of very limited and recent work.[3,6] The arrangement of phases in tandem[7-10] could be regarded as a variant.

The potential of this second category rests in its very high flexibility for a given sample. It is, in fact, possible to combine functional groups suitable both in interaction types and proportions. A requirement for this line of research, is to verify that the level of variation of the percent recoveries is acceptable.

Since no information had been published in this area, we have examined two practical methods of cartridge filling. Using an aqueous sample of neutral, acidic and basic environmental pollutants, the results obtained were compared with extraction carried out on individual phases, and on a commercial mixed phase.

MATERIALS

Chemical and Reagents

The solvents (Carlo Erba, Milan, Italy) and the water, purified by the Milli-Q system (Millipore, Bedford, MA, U.S.A.), were all of HPLC quality. The ammonium hydroxide in 28 % solution (Carlo Erba) and diammonium hydrogen phosphate (Merck, Darmstadt, Germany) were of analytical quality.

The p-cresol, anthracene, phenanthrene and fluoranthene (Aldrich, Steinheim, Germany) were 98 % pure. The acridine, phenothiazine, phenazine (Sigma, St. Louis, MO, U.S.A.) and quinoline (Janssen Chimica, Geel, Belgium) were 99 % pure.

A stock solution of a mixture of these compounds was prepared in acetonitrile at a concentration of 1.125 $g.L^{-1}$ total matter, then stored in a refrigerator at 4°C.

Sample solution : a 0.064 mL sample of the stock solution was mixed with acetonitrile up to a volume of 7.5 mL, to which was added 42.5 mL of water. The resulting sample solution was 15 % in acetonitrile, allowing complete dissolution of the P.A.H.

The glass extraction columns (J.T. Baker, Phillipsburg, NJ, U.S.A.) were of 8 mL volume. The polyethylene frits (J.T. Baker) were 12 mm in diameter with 20 μm porosity.

The phases used for the extraction had groups bonded onto silica gel. The Baker Bond octadecyl (C_{18}) phase (J.T. Baker) had the following properties: d_p = 40 μm, pore diameter = 60 Å, bonded carbon = 17 %, specific surface area = 500 $m^2.g^{-1}$.

The Bondesil PRS propylsulfonic acid phase (Analytichem International, Harbor City, CA, U.S.A.) had the following properties: d_p = 40 μm, pore diameter = 60 Å, exchange capacity = 0.18 meq. g^{-1}, specific surface area = 350 $m^2.g^{-1}$.

The characteristics of the commercial mixed phase Bond Elut Certify were not available.

Equipment

The extractions were carried out with a Visiprep Vacuum Manifold (Supelco, Inc., Bellefonte, PA, U.S.A.).

The HPLC system was composed of a model 114 M pump (Beckman, San Ramon, CA, U.S.A.), a model C6W injector (Valco, Houston, TX, U.S.A.), a model 655A variable wavelength U.V. detector (Merck) fitted with an 11 μl cell, and a Chromjet model integrator-calculator (Spectra-Physics, San Jose, CA, U.S.A.).

METHODS

Cartridge Preparation

An equal quantity of each phase, slightly more than 100 mg, was introduced into a test tube containing a magnetic stirrer.

Method A

The homogeneity was achieved, without solvent, by vigorous magnetic stirring for 2 minutes. After inserting a frit, 100 mg of the mixture was introduced into the cartridge where a second frit retained the phase.

Method B

After addition of 2 mL of acetonitrile, the homogeneity was achieved by vigorous magnetic stirring for 5 minutes. The suspension was transferred into a cartridge containing a frit. The phase was dried under vacuum for six hours with a water aspirator pump. After weighing, additions of suspension interspersed with the drying periods enabled the quantity of the mixed phase to be adjusted to the desired level. The mixed phase was retained with a second frit.

Extraction

Only a single cartridge was used for each operation of the Visiprep apparatus. For each operation, the flow rate was 1 mL.min^{-1} considering the slow ion exchange kinetics.

Conditioning was carried out by successive introductions of 2 mL of methanol and 2 mL of water. After attachment of a 50 mL reservoir onto the cartridge, the sample solution was applied to it. The reservoir was washed with 2 mL of water, then the cartridge was connected to a water aspirator pump for drying for 15 minutes.

After elution with 8 mL of acetonitrile, 2 % in NH_4OH, the extract was collected in a graduated flask, neutralized with 3 drops of concentrated HCl, then the level was adjusted to 20 mL with 2 mL of acetonitrile and 10 mL of aqueous buffer (pH = 7.0). The solution was filtered on a Nylon Acrodisc 13 (Gelman Sciences, Ann Arbor, MI, U.S.A.) of porosity 0.2 µm, the only filter not releasing substances interfering with the compounds analyzed.

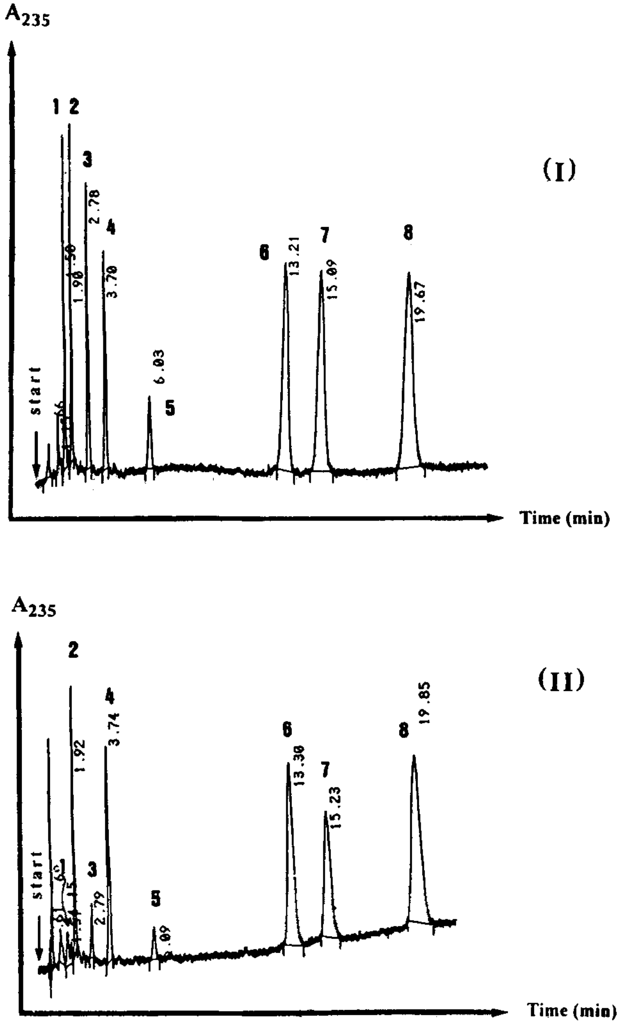

Figure 1. Typical chromatograms of a reference solution (I) and a solution obtained after S.P.E. on a cartridge prepared by mixing the phases without solvent (II). Conditions : column : 125 x 4 mm ; stationary phase : ODS 2 Spherisorb, d_p = 5 μm ; mobile phase : acetonitrile / 0.05 M $(NH_4)_2$ H PO_4 buffer (pH = 7.0) 50/50, flow-rate : 2 mL.min^{-1} ; injection volume : 20 μl ; U.V. detection : 235 nm ; temperature : 20 ± 2°C ; compounds : 1 = p-cresol, 2 = quinoline, 3 = phenazine, 4 = acridine, 5 = phenothiazine, 6 = fluoranthene, 7 = anthracene, 8 = phenanthrene.

Quantitation

Reference solution: a 0.064 mL sample of the stock solution was diluted to 10 mL with acetonitrile, mixed with 10 mL of aqueous buffer (pH = 7.0), then filtered.

Each quantitative determination was performed by comparison with a reference solution, freshly prepared and injected before the extracted sample solution. Two typical chromatograms are shown (Fig. 1).

RESULTS AND DISCUSSION

Although an adsorbent having an organic polymer as base offers better retention of neutral and basic substances than a silica-based adsorbent in mixed mode,[1] we chose to study 50/50 mass percent mechanical mixtures of phases bonded onto silica: an octadecyl phase, C_{18}, and a propylsulfonic phase, PRS. This did not prevent comparison with a commercial mixed phase, Bond Elut Certify,[3] in which these two functions were bonded onto the same silica particle. Above all, this choice could lead in the future to the use of the greatest number of individual functions.

A mixture of neutral compounds: anthracene, phenanthrene, fluoranthene, and basic compounds with one or two nitrogen atoms : quinoline, acridine, phenazine, phenothiazine was suitable for these mixed phases. The acidic compounds were not retained by a cation exchanger. To represent this group, we therefore chose para-cresol which is a very weak acid with hydrophobic properties.

Several parameters affect the percent recovery: the sample solution volume, the type of sample solvent, the amount of matter in the sample, the flow rate during sample application, the quantity of adsorbent, the composition of the phase mixture, the type of elution solvent, the volume of eluent and the flow rate of the eluent.

A preliminary study was carried out on the quantity of adsorbent. This led us to use a mass of 100 mg. With fixed values for the other parameters (Table 1), this mass was sufficient to reach or exceed the cartridge capacity, the breakthrough level, depending on the compounds studies. This allowed better comparison of the differences in retention of these substances.

Table 1

Percentage Recoveries and R.S.D. (%) of Pollutants*, Using Different Elution Volumes, Different Phases and Two Different Mechanical Mixing Preparation Methods, All Other Parameters Being Fixed**

Phase Type	Bond Elut Certify			----PRS/C_{18} Mechanical---- Mixture 50/50 W/W				C_{18}	PRS
Prepration Mode				----------A----------			B		
Compound Elution Volume (mL)	4	6	8	4	6	8	8	8	8
p-cresol	traces	traces	traces	traces	traces	traces	traces	traces	
quinoline	95 ± 6	95 ± 6	98 ± 3	81 ± 8	101 ± 7	98 ± 4	111 ± 4	30 ± 6	101 ± 5
phenazine	65 ± 11	53 ± 7	58 ± 16	14 ± 4	14 ± 5	14 ± 4	16 ± 12	33 ± 9	
acridine	99 ± 7	100 ± 6	97 ± 4	85 ± 6	103 ± 10	101 ± 4	96 ± 2	99 ± 4	109 ± 4
phenothiazine	72 ± 19	73 ± 2	74 ± 13	62 ± 3	63 ± 6	66 ± 8	90 ± 10	101 ± 7	
fluoranthene	98 ± 10	96 ± 2	92 ± 2	90 ± 7	87 ± 15	86 ± 10	90 ± 2	103 ± 1	4 ± 6
anthracene	43 ± 19	79 ± 5	82 ± 1	56 ± 14	83 ± 10	81 ± 4	63 ± 4	76 ± 5	14 ± 5
phenanthrene	94 ± 8	91 ± 4	91 ± 2	76 ± 13	88 ± 15	93 ± 2	98 ± 2	95 ± 7	5 ± 5

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* Each result is the mean of 4 extractions, each extract having been injected 3 times.

**Solid phase: total weight: 100 mg; sample: total weight: 0.072 mg, solution volume: 50 mL of deionized water/acetonitrile (85/15 v/v), flow rate: 1 ml.min^{-1}; elution: solvent: acetonitrile with 2 % ammonium hydroxide, flow rate: 1 mL.min^{-1}.

In addition, it was necessary to verify the complete recovery of the retained matter. We, thus, studied the effect of the variation, from 4 to 8 mL, of the eluent volume on the percent recovery and the relative standard deviations (R.S.D.). This effect was studied on two adsorbents: one double bonded, and the other a mechanical mixture of phases prepared without solvent. It was observed (Table 1) that a volume of 4 mL was not sufficient to desorb the anthracene, whatever the phase type.

The same was the case, to a lesser extent, for quinoline and phenanthrene extracted on the mechanically blended phase . Larger volumes, 6 or 8 mL, led to comparable percent recoveries, whatever the phase. It was also observed that the R.S.D. diminished most frequently with an increase in eluent volume. The volume of 8 mL was, thus, selected for the subsequent studies.

We could now compare a mechanical mixture prepared without solvent (method A), with the same mixture in acetonitrile suspension (method B), these two preparations having potentially very different homogeneities. The comparison was extended to the individual C_{18} and PRS phases (Table 1). As regards percent recoveries, it was the mixture prepared without solvent, which showed the behavior closest to that of the commercial mixed phase, despite a lower ability to extract phenazine. The individual C_{18} and PRS phases showed their weak retention power to the least hydrophobic basic compounds, and the most hydrophobic compounds, respectively. None of the phases retained the acidic compound.

As for the reproducibilities, the range between the smallest and largest R.S.D. values (%) is considered for each phase: 1-9 for the C_{18} phase, 1-16 for the Bond Elut Certify phase, 2-10 for the mechanical mixture prepared by method A and 2-12 for that prepared by method B. The blended phase prepared dry, thus, showed a R.S.D. range very similar to that of an individual homogenous C_{18} phase, and narrower than that obtained with the double-bonded phase.

CONCLUSION

From the performance point of view, and considering its very rapid preparation, the dry-blended phase seems competitive with the double-bonded commercial phase. This justifies further studies considering the great flexibility of composition available.

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