Development of a binary solid-phase extraction cartridge for use in screening water samples for organic pollutants

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Abstract

Two chemically modified resins and a range of commercially available material were evaluated for use as solid-phase sorbents in an analytical procedure designed to screen water samples for trace level organic contamination. A binary cartridge, comprising acetyl-derivatised resin and an anion-exchange phase, was found to perform better for most compounds than conventional liquid–liquid extraction using dichloromethane.

1. Introduction

Liquid–liquid extraction (LLE) using dichloromethane is used in the water industry to extract and concentrate organic compounds from aqueous samples in a process designed to screen for trace level contamination. Dichloromethane is the solvent of choice owing to the tendency of most organic compounds possessing medium or low polarity to partition into the organic phase. The high volatility of the solvent enables its removal at ambient temperature; this is important if volatile analytes are not to be lost.

There are, however, a number of drawbacks associated with LLE in general and the use of dichloromethane in particular. Firstly, LLE is not amenable to automation; this is an important consideration, since automation reduces labour costs and improves turnaround time. The technique also generates a large volume of waste solvent, the disposal of which adds significantly to the cost of analysis. The use of dichloromethane is not favoured owing to its narcotic properties [1], on environmental grounds [2], and the potential for background levels in the laboratory to interfere with volatile organics analysis.

An ideal solution to these problems would be solid-phase extraction (SPE), a technique that is easily automated and requires the use of relatively low volumes of organic solvents. One of the principal characteristics of SPE is its selectivity; by judicious choice of bonded phase, sample pH, ionic strength and elution conditions, the analyst can control the classes of compounds that are isolated from the matrix [3]. In order to replace dichloromethane extraction, however, the SPE sorbent would have to be capable of retaining (and subsequently releasing to the elution solvent) a wide range of different compound types.

Solid-phase sorbents for trace enrichment using bonded silica chemistries have gained popularity owing to their dimensional stability; resin-based sorbents tend to swell or shrink according to the sample matrix and eluting solvent composition. A number of workers have successfully used resin sorbents for the extraction of organic compounds from water [4,5]. Recently, Sun and Fritz [6] reported the synthesis and

use of chemically modified resins for SPE. These modified resins were more hydrophilic than the virgin material, and this was thought to promote extraction of the more polar compounds that might not be retained by non-polar interactions alone. Mills et al. [7] testify to the increasing popularity of mixed-mode SPE sorbents for extracting a greater range of compound classes than previously possible using a single mode of interaction. In the present work, modified resins, along with commercially available sorbents, including mixed-mode material, were evaluated for use in a broadly-based screening method.

2. Experimental

2.1. Reagents

All reagents and standard materials were of analytical-reagent quality or better. Hydroxymethyl and acetyl derivatives of Amberchrom 161M resin (Supelco, Poole, UK) were prepared using the method of Sun and Fritz [6]. The following commercial sorbents were used: 1 g activated carbon (Envi Carb, Supelco); 1 g mixed C_8/anion exchange (Certify II; Varian, Walton-on-Thames, UK); and amino and diamino bonded silicas (J.T. Baker, Reading, UK).

2.2. Equipment

Loading, drying and elution of SPE cartridges was performed on a spe-12G vacuum manifold (J.T. Baker) attached to a filter pump. The extracts were analysed using a Model 3400 GC (Varian) equipped with an on-column injector, open-split coupled to an ion trap detector (Finnigan MAT, Hemel Hempstead, UK) scanning from 49 to 449 u in 1 s. The column used was a J & W 30 m × 0.32 mm DB-1, film thickness 0.25 μm (Jones Chromatography, Hengoed, UK). The column temperature was programmed from 30 to 260°C at 8°C min^{-1}, and held for 10 min. The injector temperature was programmed from 30 to 260°C at 300°C min^{-1}, and held for 3 min.

Helium carrier gas was used at an inlet pressure of 0.90 bar.

2.3. SPE methods

Two SPE procedures were used during the study, details of which are given below. The organic compounds spiked into the water were selected to give a wide range of polarities. They are representative of the types of compound required to show up on screening.

Procedure A

Three 1-l aliquots of an uncontaminated bore water were spiked with the organic compounds listed in Table 1 to a concentration of 1 μg l^{-1}. Methanol (20 ml) was added to each spiked sample and the bottles shaken to mix. Each extraction cartridge was conditioned with 3 × 3 ml methanol and washed with 3 ml HPLC-grade water. The samples were loaded at a flow-rate of approximately 5 ml min^{-1} and the cartridge rinsed with 3 ml HPLC-grade water. The sorbent beds were dried under vacuum for 45 min and the analytes eluted with 3 × 1 ml dichloromethane. The eluate was blown down to approximately 300 μl in a graduated vial, spiked with internal standard (1 μl of a 1 g l^{-1} solution of 1-chloroundecane in dichloromethane) and 1 μl injected for GC–MS analysis.

Procedure B

Sample pretreatment, loading and drying conditions were identical to procedure A, except that five replicate analyses were performed on each cartridge. The elution step was performed with 2 × 1 ml dichloromethane followed by 2 × 1 ml 2% trifluoroacetic acid (TFA) in methanol. The methanolic TFA eluate was collected separately, blown down to dryness and made up with 1 ml dichloromethane. The extracts were combined, blown down to volume and analysed according to the details given for procedure A.

2.4. LLE extraction method

A LLE procedure was adopted to enable a comparison to be made between existing meth-

Table 1
Recoveries of test compounds on the two modified resin types

Compound	Recovery (%)		
	Quantitation mass	Acetyl resin	Hydroxymethyl resin
Ethylbenzene	106	64 (0.4)	34 (27)
Phenol	94	6 (63)	8 (20)
1,4-Dichlorobenzene	146–150	67 (2)	26 (31)
n-Decane	57	38 (1)	33 (44)
2,6-Dimethylphenol	122	29 (25)	15 (28)
Naphthalene	128	59 (9)	75 (21)
2,4,5-Trichlorophenol	196–200	6 (59)	13 (81)
Atrazine	215	75 (16)	14 (86)
Pentachlorophenol	266	11 (115)	30 (75)
Linuron	61	128 (31)	83 (38)
Fluoranthene	202	91 (43)	65 (43)

R.S.D. (%, $n = 3$) in parentheses.

ods and the SPE techniques. Aliquots of 1 l of bore water were spiked at 1 μg l^{-1} and shaken with 80 ml dichloromethane in a separating funnel. The organic layer was collected and the bulk of the solvent removed in a rotary evaporator. The remaining dichloromethane solution was transferred to a graduated vial, blown down and analysed according to the details given for procedure A.

2.5. SPE cartridge preparation

An initial study was conducted to determine which derivatised resin (hydroxymethyl or acetyl) would give the best recoveries of the compounds of interest. Two 6-ml polypropylene syringe barrel cartridges were packed with 600 mg of each resin and evaluated according to procedure A.

As a result of this initial work, the acetyl-modified resin was selected for further evaluation in a binary system with anion exchange phases. Two 6-ml polypropylene syringe barrel cartridges were packed as follows: 300 mg resin with 500 mg diamino-bonded silica; and 300 mg resin with 500 mg amino-bonded silica. The two phases were separated by a porous polyethylene frit. The mass of resin was selected to give a surface area equivalent to 500 mg silica-based material. The Supelco Envi Carb and Varian

Certify II cartridges, also selected for study, were used as received, and all cartridges were processed according to procedure B.

For both trials, an unextracted portion of the spiking solution was used to calculate absolute recoveries.

3. Results

The results of the first study, which compared the two resin types, are given in Table 1 and the data produced by the second trial are given in Table 2.

4. Discussion

The acetyl resin was favoured over the hydroxymethyl-modified material owing to the poor yield of atrazine from the latter under the conditions of the test (Table 1). The reason for this might be strong hydrogen-bonding interactions between the hydroxyl groups on the resin and the secondary amine functionalities of atrazine. Since atrazine and some other triazine herbicides are ubiquitous in surface waters, and also because recoveries for most test compounds were higher from the acetyl phase, it was de-

Table 2
Recoveries of test compounds with SPE and LLE techniques

Compound	Recovery (%)[a]				
	a	b	c	d	e
Ethylbenzene	76 (72)	72 (18)	121 (18)	1 (20)	54 (12)
Phenol	21 (33)	75 (16)	0	0	18 (14)
1,4-Dichlorobenzene	50 (24)	100 (11)	69 (22)	3 (13)	56 (13)
n-Decane	20 (45)	62 (9)	32 (15)	32 (18)	36 (9)
2,6-Dimethylphenol	34 (10)	77 (12)	0	5 (15)	67 (11)
Naphthalene	53 (35)	99 (5)	42 (19)	20 (16)	64 (16)
2,4,5-Trichlorophenol	4 (86)	6 (33)	0	32 (9)	77 (14)
Atrazine	101 (23)	95 (10)	91 (11)	99 (6)	86 (15)
Pentachlorophenol	0	8 (31)	0	0	68 (22)
Linuron	117 (28)	99 (30)	79 (20)	126 (14)	96 (21)
Fluoranthene	69 (16)	87 (12)	0	82 (4)	84 (13)

R.S.D. (%, $n = 5$) in parentheses. For quantitation masses, see Table 1.
[a] a = Diamino/acetyl binary cartridge; b = amino/acetyl binary cartridge; c = Envi Carb cartridge; d = Certify II cartridge; e = dichloromethane extraction.

cided to concentrate development effort on the acetyl material.

The other problem with the derivatised phases used in isolation was poor recovery of more polar, anionic species (see recovery data for phenols in Table 1). Recovery of phenol was significantly lower on both modified resins than the values given by Sun and Fritz [6]. These authors reported phenol recoveries of 94 and 100% on hydroxymethyl- and acetyl-modified resin respectively. This difference can be explained by noting that Sun and Fritz used a sample volume of 20 ml and a sorbent mass of 100 mg compared to a sample volume of 1 l and a sorbent mass of 600 mg in the present work. It is reasonable to assume that breakthrough was responsible for the poor recoveries for phenol reported here. The recoveries of phenol and 2,6-dimethylphenol improved significantly with the incorporation of an anion-exchange phase (Table 2).

The best recoveries for six out of the eleven test compounds were obtained with the acetyl resin/amino-bonded silica combination. This combination of sorbents gave acceptable recoveries and precision for all test compounds with the exception of 2,4,5-trichlorophenol and

pentachlorophenol, for which dichloromethane extraction gave the best recovery data. The recoveries of the chlorinated phenols from the acetyl/aminopropyl cartridge were unexpectedly low considering the relatively good recoveries observed for phenol and 2,6-dimethylphenol and may be caused by a stronger sorbent–analyte interaction, possibly involving both polar and non-polar bonding, than with the non-chlorinated phenols, rendering elution more difficult. Different elution conditions, perhaps using a base-modified solvent, might result in better performance.

The activated carbon cartridge gave low recoveries for most of the trial compounds, particularly for the phenols. The reason for this is unclear, although activated carbon is capable of retaining some organic compounds so strongly that desorption by the elution solvent becomes difficult [8]. The performance of the acetyl resin/diamino cartridge was poorer than that of the resin/amino combination. This cartridge contained a mixture of primary and secondary amine functionalities $[-(CH_2)_3NH(CH_2)_2NH_2]$; the amino phase contained only primary amine (aminopropyl) bonded silica. The primary phase has a more polar character than the mixed

primary/secondary material, which probably promotes a stronger interaction with anionic organic species such as the phenols.

The mixed-mode Certify II material gave very good recovery and precision performance for atrazine; otherwise, the performance of the Certify II sorbent was generally inferior to that of the binary resin phases. Dichloromethane extraction gave better recoveries only for the chlorinated phenols. Since these are environmentally important compounds, the relatively poor performance of the binary resin/ion-exchange cartridges will have to be improved before their routine use is possible.

5. Conclusions

SPE offers a viable alternative to the use of dichloromethane LLE for the screening of water samples for organic micropollutants. The use of SPE resulted in improved recoveries for all but two of the eleven compounds studied compared to dichloromethane extraction. Pressure is being placed upon analytical chemists to replace chlorinated solvents as analytical reagents; this work shows the potential of SPE to replace these chemicals in the analytical laboratory.

Further work needs to be undertaken to improve the reproducibility of the extraction, to assess the use of elution solvents other than dichloromethane, and to improve the performance of the technique with respect to chlorinated phenols. It would also be desirable to extend the range of compounds to which the technique can be applied.

Acknowledgements

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