ELSEVIER

Journal of Chromatography A, 657 (1999) 247–254

JOURNAL OF CHROMATOGRAPHY A

www.elsevier.com/locate/chroma

Study of applicability of various solid-phase extraction materials for sample handling in screening analysis of organic micropollutants in water

P. Tölgyessy, I. Liška*

Water Research Institute, Nábrežie Svobodu 5, 812 49 Bratislava, Slovak Republic

Received 23 April 1999; received in revised form 6 July 1999; accepted 6 July 1999

Abstract

At present, solid-phase extraction (SPE) has become an often preferred preconcentration technique in the screening for a wide range of organic micropollutants in water. A wide choice of materials available on the market makes SPE a suitable tool to cope with an increasing variability of organic compounds entering the hydrosphere. However, the interactions of various sorbent materials with compounds having different physico-chemical properties leads inevitably to large differences in preconcentration efficiency. The aim of this paper was to investigate the efficiency of preconcentration of selected organic compounds from aqueous solutions on various SPE materials. Simultaneously, the potential of newly emerging SPE procedures was compared to results of traditional liquid–liquid extraction methods. The group of 19 tested analytes was selected so as to represent different classes of organic compounds which may occur in waters. The results obtained showed that most of the tested materials were suitable for sufficient preconcentration of a substantial part of the tested analytes. However, specific differences in recovery of one or more analytes were found for almost each sorbent even in the case when the materials had similar composition. This behaviour clearly indicates the need for a thorough testing of capabilities of any SPE material intended for the use in a wide range screening method for the identification of unknown organic micropollutants in water. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Solid-phase extraction; Extraction methods; Water analysis

1. Introduction

Most of the screening methods used for the identification of organic micropollutants in water include an appropriate sample handling step followed by an instrumental analysis which usually employs a hyphenated technique. While the efficiency of current hyphenated systems is very high, there are still many problems encountered in the isolation and preconcentration of organic compounds present in the investigated water sample. In principle, after an analyte has been successfully transferred from a water sample into the final extract and the successive instrumental analysis has gone wrong, there is still a possibility of using another aliquot of the extract to repeat the chromatographic run under different conditions to confirm the result. However, in the case where the initial sample handling procedure failed the analytes are lost forever. Therefore, great attention has to be given to a careful tuning of the sample handling procedure to assure that the whole range of com-

*Corresponding author. Fax: +421-7-5441-8047.

0021-9673/99/$ – see front matter © 1999 Elsevier Science B.V. All rights reserved.
PII: S0021-9673(99)00787-6

pounds of interest can be efficiently recovered from the original water sample. Moreover, one should realise that a sample handling procedure is usually the most laborious and time-consuming part of the overall analysis and it limits the sample throughput and hence the overall performance of the method [1].

At present, liquid–liquid extraction (LLE) and solid-phase extraction (SPE) are the most frequently applied sample handling techniques in the analysis of organic pollutants in water. The prevalence of the use of LLE in the environmental analysis in the past resulted from the hydrophobic character of compounds listed on the priority pollutant lists at that time as well as from the absence of another equally suitable and efficient technique. At present, LLE is still widely used in routine water analyses primarily due to availability of standardised methods. The increasing popularity of SPE is resulting not only from its obvious advantages over LLE (e.g., minimised consumption of organic solvents, no emulsion formation, reduced contact of analyst with potentially toxic substances) but also from gradual refinements of this procedure which minimise its original drawbacks [2–5]. A wide choice of newly developed materials belonging mostly to one of the three major groups of sorbents (i.e., bonded silicas, polymers and carbon materials) makes SPE a suitable tool to cope with an increasing variability of modern organic contaminants.

The aim of a sample-handling step in a screening method is to recover as many organic compounds as possible. Therefore, the selection of sorption media for SPE preconcentration is focused to more hydrophobic media with a high capacity. The removal of interfering compounds and/or fractionation of preconcentrated analytes can be reached by employing of several different types of sorption media and also by appropriate tuning of operational parameters. For example, DiCorcia et al. [6] presented an off-line approach to monitoring of a large group of pesticides in ground and river water. The method incorporated a fractionation of analytes into basic+neutral and acidic compounds which was based on two different interaction mechanisms of graphitized carbon black. Processing of large volumes of water (0.5–2 l) and evaporation of eluates led to detection limits lower than 0.1 μg/l for most of the pesticides in this case. Nielen et al. [7] used an on-line system with three pre-columns in series (C_{18}, PRP-1 and cation exchanger) for preconcentration and fractionation of organic pollutants in industrial effluents and eluted all pre-columns separately. Brouwer et al. [8] connected two polymer (PLRP-S) pre-columns in series and the outlet of each pre-column was on-line directed to a separate PLRP-S analytical column. The first pre-column was operated in the reversed-phase mode and the second pre-column in ion-pairing mode. This approach enabled preconcentration of acidic and basic compounds within one analysis. The same authors developed a similar system with one high-performance liquid chromatography (HPLC) analytical column [9]. In this system they used specially designed holders packed with membrane extraction discs as pre-columns. A sophisticated on-line system was developed by Slobodník et al. [10] combining on-line SPE with liquid chromatography (LC), separation by gas chromatography (GC) and detection with mass spectrometry (MS). The trace enrichment procedure was automated by a Prospekt cartridge-exchange/solvent-selection/valve-switching unit. After loading of the water sample the pre-column was eluted on-line in two subsequent runs, first onto the GC–MS system and, next, onto the LC–diode array UV detection (DAD-UV)–MS system using a particle beam interface. With this system GC–MS, LC–DAD-UV and LC–MS data of the same water sample could be obtained within 3 h providing a large amount of structural information on unknown organic compounds present in the sample. A combined approach was used during a long-term international programme on river pollution identification that was performed in the Nitra river basin [11]. In this programme two LLE procedures along with the SPE method were applied, simultaneously, to increase the ''isolation range'' as much as possible so that most of the organic pollutants occurring in the river water could be detected.

The aim of the presented work was to investigate the efficiency of preconcentration of different organic compounds from aqueous solutions on various SPE materials. Simultaneously, the potential of newly emerging SPE procedures was compared to results of traditional LLE methods. The group of 19 tested analytes was selected so as it represented different classes of organic compounds occurring in the hydrosphere.

2. Experimental

2.1. Materials and reagents

Isolute ENV+ (200 mg, 6 ml) extraction columns with a hyper cross-linked styrene–divinylbenzene copolymer were a gift from International Sorbent Technology (Hengoed, UK). LiChrolut EN (200 mg, 3 ml) extraction columns with a highly porous poly(styrene–divinylbenzene) polymer were obtained from E. Merck (Darmstadt, Germany). Bakerbond Octadecyl (500 mg, 3 ml) and Baker Phenyl (500 mg, 3 ml) extraction columns were obtained from J.T.Baker (Phillipsburg, NJ, USA). C_{18} and poly(styrene–divinylbenzene) SDB Empore extraction disks (47 mm diameter) (3M, St. Paul, MN, USA) were purchased from Varian (Harbor City, CA, USA). SDB-RPS and Carbon Empore extraction disks (47 mm diameter) produced by 3M were obtained as a gift from 3M (Zwijndrecht, Belgium). SDB-RPS is a poly(styrene–divinylbenzene) copolymer modified with sulphonic acid groups resulting in cation-exchange properties.

Standards of 2-ethyl-1-hexanol, phenol, benzaldehyde, 3-octanone, *n*-octane, *n*-butylbenzene, naphthalene, hexachloro-1,3-butadiene and caffeine were obtained from Avocado (Heysham, UK); dodecanoic acid, propyl decanoate and lindane were from Poly-Science (Niles, IL, USA); 2,4,6-trichlorophenol, bis(2-chloroisopropyl)ether, tetrachloroethylene and 1,4-dichlorobenzene were purchased from Supelco (Bellefonte, PA, USA); cyclohexanol was from Lachema (Brno, Czech Republic), alachlor from AccuStandard (New Haven, CT, USA) and atrazine from Ehrenstorfer (Augsburg, Germany).

SupraSolv grade dichloromethane and ethyl acetate (Merck), analytical-reagent grade diethyl ether (Merck) and methanol (Mikrochem, Bratislava, Slovak Republic) were employed as solvents for elution of sorbed analytes. Sodium sulphate, analytical-reagent grade (Slavus, Bratislava, Slovak Republic) was purified by extraction with acetone in Soxhlet apparatus.

Stock standard solutions (5000 ppm) of individual analytes were prepared by their dissolution in methanol, except of caffeine which was dissolved in ethyl acetate and they were stored at 4°C in a refrigerator. The solution of alachlor was purchased as 1000 ppm solution in methanol. Working solution of a mixture of analytes (250 ppm) was obtained by dilution of the stock standard solutions with methanol. A working solution of alachlor (250 ppm) was prepared separately by dilution of its stock standard solution. Aliquots of these two working solutions were added to tap water to give the test samples with concentrations of analytes of 20 ppb. The test samples were prepared in 2-l glass bottles 24 h before the preconcentration experiment and stored at 4°C.

2.2. Extraction procedures

Preconcentration of test samples on Empore extraction disks was carried out on laboratory-made filtration apparatus for the use of 47 mm diameter filtration membranes. The apparatus was connected with a water vacuum aspirator. Empore extraction disks were first washed with 20 ml of methanol, then with 10 ml of ethyl acetate–dichloromethane (1:1) and conditioned with 5 ml of methanol. The same cleaning and conditioning procedure was also performed with extraction columns, which were attached to a simple holder (for one column) and connected with water vacuum aspirator. The water samples were passed through the extraction disks at a flow-rate of about 25 ml/min and through the extraction columns at a flow-rate of about 8 ml/min. The pH of water was not adjusted before sample handling, during all experiments it was around 7.8. The disks and columns were dried under vacuum (for columns an air stream was also applied), and analytes were eluted either with a tested eluent (in initial experiments) or with 10 ml of ethyl acetate–dichloromethane (1:1, v/v). Finally, the extracts from elution of disks were dried over anhydrous sodium sulphate (for columns this step was not necessary because air-drying was sufficient) and concentrated to a final volume of 200 μl. Extracts were then analysed by GC–MS. The recoveries of the LLE and SPE procedures were evaluated as the concentration of analyte either in the final eluate from the SPE disk (cartridge) or in the final processed combined extract divided by the concentration of the same analyte dissolved in the equivalent volume of eluate or extraction solvent, respectively. The mean recovery was calculated from four to five measurements.

LLE of test water samples (0.5 l) was performed by shaking the sample in a 1-l separatory funnel. Two-step extraction was applied using dichloromethane (20+15 ml) or hexane (10+10 ml). Combined extracts were dried over anhydrous sodium sulphate and after concentration to a final volume of 200 μl and analysed by GC–MS.

2.3. Chromatographic conditions

Analyses were performed using a Hewlett-Packard Model 5890 gas chromatograph (Palo Alto, CA, USA) equipped with a split–splitless injector and a Model 5970 mass-selective detector. A 30 m×0.25 mm I.D. fused-silica DB-1 capillary column with a film thickness of 0.25 μm (J&W Scientific, Folsom, CA, USA) was used for the separation of analytes. Helium (purity 4.6, Linde, Bratislava, Slovak Republic) was used as the carrier gas at an inlet pressure of 80 kPa. Temperatures were as follows: injector port 270°C, transfer line 290°C and the ion source 190°C. The following column temperature programme was employed: initial temperature 40°C (maintained for 5 min), increasing at a rate 8°C/min to 280°C (maintained for 15 min). Extract aliquots of 2 μl were injected manually into the column using a splitless injection mode. Quantitation of analytes was performed calculating with areas of peaks corresponding to characteristic ions of tested compounds (see Table 1).

3. Results and discussion

To select an appropriate eluent composition for SPE procedures a standard polymer material was chosen to trap tested analytes. This approach was preferred because of the relatively non-specific sorption properties of this material which predetermine it as a suitable candidate for sample handling in screening. In the elution experiments 500 ml of test water sample spiked with the analytes was preconcentrated on SDB extraction disks. After the preconcentration the disks were dried and eluted with

Table 1
Relative elution efficiencies of tested compounds from SDB extraction disk using different solvents and their mixtures (experimental conditions are given in the text)

Compound	a/a_{max} [a]							
	2.5 ml EtAc+ 2.5 ml CH_2Cl_2 [b]	5 ml EtAc+ 5 ml CH_2Cl_2	5 ml EtAc– CH_2Cl_2 (1:1)	10 ml EtAc– CH_2Cl_2 (1:1)	2.5 ml ether+ 2.5 ml CH_2Cl_2	5 ml ether+ 5 ml CH_2Cl_2	5 ml ether– CH_2Cl_2 (1:1)	10 ml ether– CH_2Cl_2 (1:1)
2-Ethyl-1-hexanol [ion 83]	0.21	0.55	0.38	1.0	0.27	0.38	0.4	0.68
Cyclohexanol [ion 82]	0.43	0.95	0.48	0.99	0.71	0.96	0.98	1.0
Dodecanoic acid [ion 200]	0.44	0.81	0.51	1.0	0.38	0.61	0.31	0.67
Propyl decanoate [ion 173]	0.32	0.73	0.55	1.0	0.36	0.56	0.42	0.80
Phenol [ion 94]	0.37	1.0	0.72	0.77	0.30	0.47	0.78	0.87
2,4,6-Trichlorophenol [ion 196]	0.36	0.75	0.54	1.0	0.31	0.68	0.44	0.78
Benzaldehyde [ion 106]	0.34	0.84	0.60	1.0	0.32	0.58	0.65	0.80
3-Octanone [ion 99]	0.37	0.81	0.66	1.0	0.39	0.54	0.65	0.92
Bis(2-chloroisopropyl) ether [ion 121]	0.37	0.87	0.71	1.0	0.41	0.52	0.63	0.88
n-Octane [ion 85]	0.05	0.07	0.15	0.16	0.47	0.39	0.67	1.0
Tetrachloroethylene [ion 166]	0.21	0.38	0.58	0.36	0.52	0.28	0.95	1.0
n-Butylbenzene [ion 91]	0.27	0.59	0.55	1.0	0.29	0.38	0.45	0.70
Naphthalene [ion 128]	0.24	0.58	0.48	1.0	0.28	0.39	0.42	0.69
1,4-Dichlorobenzene [ion 146]	0.41	0.88	0.60	1.0	0.42	0.57	0.69	0.95
Hexachloro-1,3-butadiene [ion 225]	0.46	1.0	0.60	0.98	0.41	0.54	0.65	0.90
Lindane [ion 181]	0.55	0.80	0.51	1.0	0.49	0.79	0.55	0.87
Atrazine [ion 200]	0.55	0.84	0.53	1.0	0.47	0.74	0.52	0.86
Alachlor [ion 160]	0.61	0.84	0.57	1.0	0.52	0.67	0.61	0.87
Caffeine [ion 194]	0.86	0.97	0.91	1.0	0.55	0.70	0.61	0.82

[a] a is the peak area of the compound in the chromatogram from the analysis of the final extract and a_{max} is the largest measured peak area of the compound.

[b] EtAc=Ethyl acetate; ether=diethyl ether.

ethyl acetate or diethyl ether in combination with dichloromethane. In each case the elution was done using 5 and 10 ml of a 1:1 mixture of two solvents. In the next experiment the same combination and volume of eluting solvents was used, however, the solvents were applied consecutively and they were combined afterwards. The results are shown in Table 1 as relative peak areas compared to the largest recovery obtained for the particular analyte in all elution experiments. As is clear from this table the best eluent for the recovery of tested compounds was 10 ml of the mixture of ethyl acetate–dichloromethane (1:1). The higher elution efficiency of this mixture in comparison with consecutive use of ethyl acetate and dichloromethane might be attributed to lower flow-rate of the mixture through the disk resulting to increased contact time but also to simultaneous exertion of combined hydrophilic and hydrophobic interactions.

The ethyl acetate–dichloromethane mixture had an unsatisfactory preconcentration efficiency in the case of *n*-octane and tetrachloroethene. For these two analytes the recovery was far better when diethyl ether–dichloromethane was used. This behaviour was explained by higher losses of these analytes in the concentration step during treatment with air stream due to the lower volatility of ethyl acetate compared to diethyl ether. Considering the results from elution experiments, 10 ml of ethyl acetate–dichloromethane (1:1) was used in all following SPE experiments.

Regarding the choice of sorbent materials for the preconcentration of the target group of analytes we tried to test new polymer materials (ENV+ and LiChrolut columns) and membrane extraction disks (SDB, SDB-RPS, carbon and C_{18} disks) as well as classical silica-based sorbents (C_{18} and phenyl columns). For LLE procedures two kinds of solvents were selected – hexane being traditionally used for isolation of nonpolar pollutants and dichloromethane which is often used in screening analyses.

Recoveries of the selected compounds for all the tested extraction procedures are given in Table 2. From comparison of four tested membrane extraction disks with three different types of sorbent material (bonded silica, polymer and carbon) it can be seen that the highest average recovery was achieved with SDB-RPS material. The preconcentration efficiency of C_{18} and SDB disks was somewhat lower while that of carbon material was unsatisfactory for many analytes. The behaviour of the carbon disk was typical for this kind of material, where especially aromatic and heterocyclic compounds (naphthalene, dichlorobenzene, caffeine) and acidic compounds (trichlorophenol, dodecanoic acid) are bound too strongly to be eluted with the tested solvent mixture. Acceptable recoveries with the carbon disk were obtained for oxo compounds, especially for cyclohexanol which was one of the highest. Recoveries obtained with styrene–divinylbenzene and C_{18} disks were in most of the cases similar and, in principle, they differ only for trichlorophenol (better on SDB) and caffeine (better on C_{18}). Sulphonation of SDB material enables preconcentration of hydroxylated analytes and improves the recoveries of other oxo compounds. The SDB-RPS disk was found suitable for preconcentration of practically all the selected analytes. Losses of *n*-octane and tetrachloroethylene on all tested sorbent materials due to the use of a drying step have been described earlier.

Study of recoveries obtained with sorbent cartridges revealed that except for the phenyl silica column that was efficient only for nonpolar analytes all three other tested materials exhibited a certain selectivity to different groups of compounds. C_{18} provided acceptable recoveries of nonpolar analytes and also of ketones, ethers, aliphatic acids and linear alcohols. On the other hand it showed poor recovery of cyclohexanol, phenols and also for caffeine. Polymer cartridges (LiChrolut and ENV+) showed no recovery of trichlorophenol and aliphatic acids, however, they provided by far the best results for phenol, caffeine and cyclohexanol. So, partially complementary efficiencies could be found for silica and polymer materials. It was also interesting to notice that LiChrolut and ENV+ materials exhibited the same pattern of recoveries for particular compounds within the tested group.

Comparison of SPE and LLE procedures confirmed that extraction with dichloromethane was still a powerful isolation tool for a screening method. Dichloromethane was able to satisfactorily extract almost every tested analyte with the exception of phenol. Even though the future perspectives of the use of dichloromethane extraction are not promising due to the health risks, it may be still the preferred

Table 2
Recovery (%) of selected compounds added to tap water (at concentration level of 20 ppb) using various extraction media

Compound	LLE CH_2Cl_2/ 20 ml/15 ml			LLE hexane/ 10 ml/10 ml			C_{18} extraction disk			SDB extraction disk			SDB-RPS extraction disk			Carbon extraction disk			C_{18} extraction column			ENV+ extraction column			LiChrolut extraction column			Phenyl extraction column		
	x[b]	s	s_R (%)	x	s	s_R (%)	x	s	s_R (%)	x	s	s_R (%)	x	s	s_R (%)	x	s	s_R (%)	x	s	s_R (%)	x	s	s_R (%)	x	s	s_R (%)	x	s	s_R (%)
2-Ethyl-1-hexanol	80.6	12.5	15.5	58.2	6.1	10.4	52.0	10.3	19.8	45.4	15.9	35.0	68.4	13.5	19.7	53.4	10.4	19.4	76.6	12.4	16.2	74.4	14.4	19.4	74.6	13.3	17.8	48.0	7.6	15.9
Cyclohexanol	23.8	3.7	15.4	–	–	–	7.0	1.1	15.6	7.6	3.9	51.7	26.2	6.5	24.8	49.8	9.5	19.0	6.4	1.0	15.9	70.4	15.2	21.6	72.0	15.4	21.4	1.2	0.5	43.7
Dodecanoic acid	61.4	8.6	14.1	11.3	8.2	72.5	89.0	19.7	22.1	83.8	28.4	33.9	76.6	8.5	11.0	7.8	3.7	46.9	112	16.4	14.7	–	–	–	–	–	–	26.2	27.0	103.0
Propyl decanoate	82.6	2.4	2.9	76.6	17.1	22.4	50.2	2.5	4.9	42.4	6.7	15.8	59.0	3.9	6.5	46.8	0.8	1.6	36.0	8.2	22.8	29.4	3.3	11.1	29.2	6.3	21.6	39.0	8.6	21.9
Phenol	6.2	5.3	86.2	–	–	–	2.4	1.5	62.4	2.6	2.8	108.0	18.6	14.6	78.3	8.2	5.7	69.6	0.7	0.7	94.2	30.0	24.0	80.0	31.0	29.2	94.2	0.5	0.3	66.9
2,4,6-Trichlorophenol	53.4	16.0	29.9	5.8	2.6	45.5	23.6	4.9	20.7	75.2	11.1	14.7	101.0	27.3	27.1	0.7	0.2	35.0	7.8	0.4	5.1	–	–	–	–	–	–	2.2	0.2	9.1
Benzaldehyde[a]	86.0	9.5	11.0	68.4	5.6	8.2	52.0	5.3	10.2	47.8	14.3	30.0	59.6	6.2	10.3	43.4	7.2	16.7	58.0	11.6	20.0	69.0	6.9	10.0	73.8	15.5	21.0	26.4	7.3	27.8
3-Octanone	90.2	11.3	12.5	79.2	7.4	9.4	53.0	9.3	17.6	47.6	11.6	24.4	73.2	10.0	13.6	56.6	8.1	14.3	83.6	8.8	10.6	69.0	10.5	15.2	64.6	16.8	26.0	42.6	14.3	33.6
Bis(2-chloroisopropyl) ether	89.8	13.6	15.1	87.0	9.5	10.9	54.0	8.0	14.9	53.2	16.7	31.5	69.2	8.5	12.2	56.2	9.2	16.4	88.8	11.5	12.9	67.2	9.3	13.9	70.8	19.4	27.4	25.0	9.0	36.0
n-Octane	14.4	3.1	21.8	21.0	8.8	41.8	1.3	0.3	25.9	4.2	1.5	35.0	5.4	1.0	18.9	4.0	0.9	22.4	0.7	0.4	48.0	0.8	0.2	24.8	1.5	1.2	84.1	–	–	–
Tetrachloroethylene	50.2	9.0	17.9	38.6	7.5	19.3	4.0	3.3	82.7	9.2	0.8	8.1	13.4	2.4	18.0	12.8	4.0	30.9	0.4	0.1	18.2	19.4	5.1	26.2	8.6	4.0	46.9	0.4	0.1	31.6
n-Butylbenzene	70.6	7.3	10.3	68.4	18.0	26.2	39.8	7.0	17.6	38.6	13.4	34.8	51.0	5.1	10.0	29.2	3.5	12.1	38.2	20.7	54.3	42.2	4.7	11.2	29.0	7.1	24.5	19.0	2.3	12.0
Naphthalene	82.4	7.9	9.6	88.0	8.4	9.6	53.8	7.2	13.4	46.0	12.2	26.6	63.6	6.7	10.5	0.1	0.1	63.1	61.4	22.0	35.9	64.2	8.1	12.6	48.6	13.0	26.7	33.0	2.7	8.1
1,4-Dichlorobenzene	80.2	10.2	12.7	75.8	9.9	13.1	38.4	5.0	13.0	41.6	9.7	23.2	60.4	8.2	13.6	4.6	2.0	42.6	34.4	4.3	12.6	57.0	8.5	15.0	40.8	9.3	22.9	4.4	1.4	30.4
Hexachloro-1,3-butadiene	70.0	6.4	9.1	69.8	19.5	27.9	41.8	9.2	21.9	39.8	15.7	39.3	58.2	11.0	18.9	31.0	3.0	9.8	36.0	17.3	48.0	37.4	5.4	14.4	27.8	8.7	31.3	26.4	5.1	19.4
Lindane	96.8	5.1	5.3	92.6	11.8	12.7	68.0	3.8	5.6	67.2	7.2	10.7	73.8	4.5	6.1	45.6	5.6	12.3	90.4	6.9	7.6	98.2	11.8	12.1	83.8	10.8	12.9	92.4	20.9	22.6
Atrazine	101.0	9.7	9.7	12.0	3.6	29.8	74.2	9.4	12.7	71.6	8.1	11.3	43.0	2.9	6.7	55.6	4.1	7.3	100	9.8	9.8	102.0	14.5	14.3	104	13.1	12.6	82.2	20.9	25.4
Alachlor	75.3	14.5	19.3	96.3	17.0	17.7	66.0	9.2	13.9	68.7	10.9	15.8	73.3	13.3	18.1	46.7	8.5	18.2	96.7	17.7	18.4	93.7	24.6	26.3	92.3	9.9	10.7	94.0	40.5	43.1
Caffeine	35.2	4.7	13.3	–	–	–	61.4	9.1	14.7	22.0	2.8	12.9	45.0	11.8	26.3	2.8	1.6	54.8	28.6	4.8	16.8	103.0	13.9	13.5	110	16.1	14.7	25.2	5.2	20.6

[a] The recovery of benzaldehyde is calculated from the sum of peak areas of benzaldehyde and benzaldehyde dimethyl acetal.
[b] x is the mean value from four to five measurements.

way of preconcentration in specific cases in which modern procedures often fail. One example is the handling of water samples from bioremediation technologies with bacterial emulsions leading to clogging of both SPE cartridges and membrane extraction disks. In such a case, when neither pressurised sample flow nor filtering of the colloidal sample can speed up the throughput of samples, the application of LLE may avoid the problems with elevated back pressure.

Examples of chromatograms from GC–MS analyses of extracts of spiked water samples processed by three different extraction methods [LLE with dichloromethane (a), SPE with SDB-RPS Empore extraction disk (b) and with Isolute ENV+ extraction cartridge (c)] are shown in Fig. 1. In these chromatograms an interesting behaviour can be noticed of benzaldehyde (added in methanol solution) and of the product of reaction of benzaldehyde with methanol, i.e., benzaldehyde dimethyl acetal. During preconcentration experiments a different behaviour was observed when water sample was

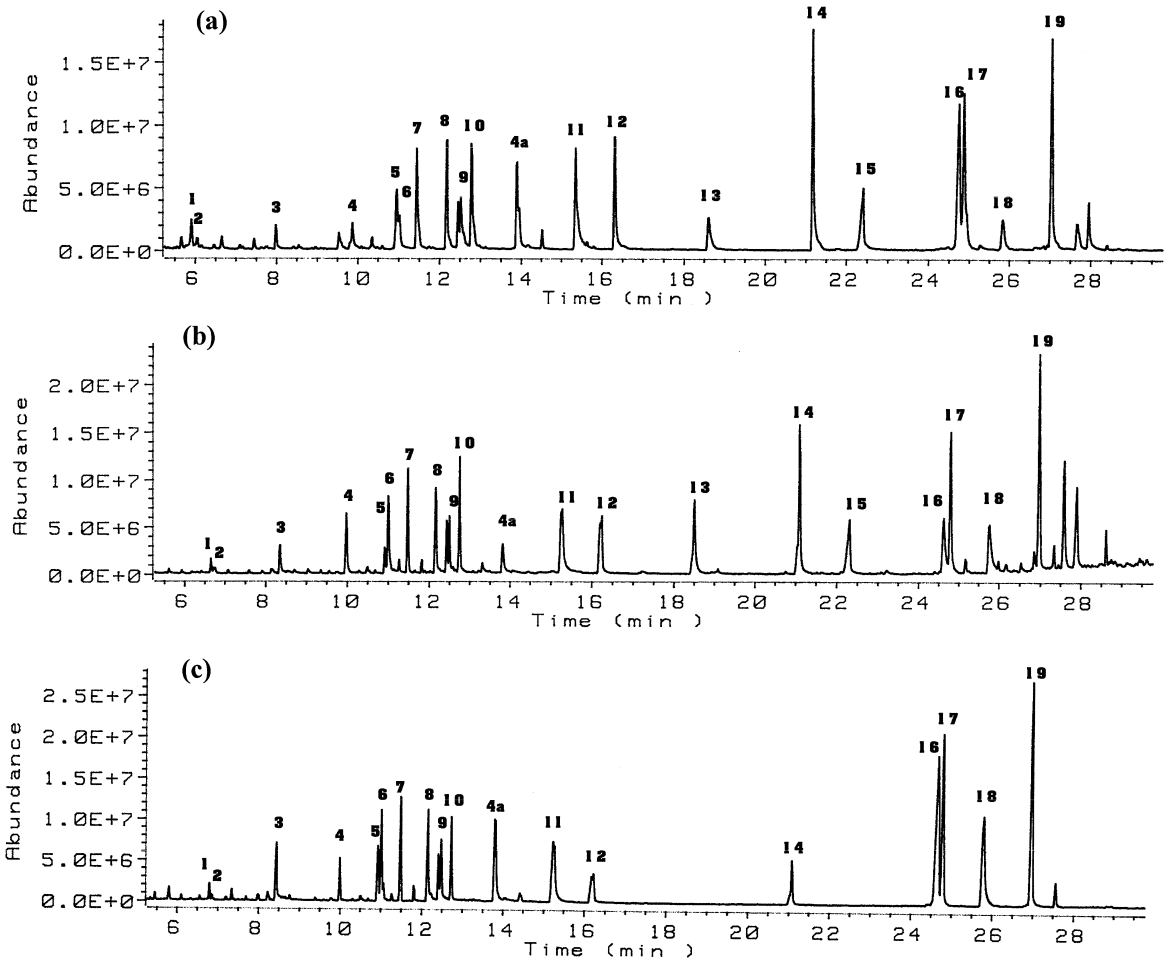

Fig. 1. Total ion chromatograms of: (a) dichloromethane extract of model tap water sample; (b) ethyl acetate–dichloromethane (1:1, v/v) eluate from SDB-RPS Empore extraction disk after SPE of model tap water sample; (c) ethyl acetate–dichloromethane (1:1, v/v) eluate from Isolute ENV+ cartridge after SPE of model tap water sample. Peaks: 1=tetrachloroethylene; 2=*n*-octane; 3=cyclohexanol; 4=benzaldehyde; 4a=benzaldehyde dimethyl acetal; 5=phenol; 6=3-octanone; 7=1,4-dichlorobenzene; 8=2-ethyl-1-hexanol; 9=bis(2-chloroisopropyl)ether; 10=*n*-butylbenzene; 11=naphthalene; 12=hexachloro-1,3-butadiene; 13=2,4,6-trichlorophenol; 14=propyl decanoate; 15=dodecanoic acid; 16=atrazine; 17=lindane; 18=caffeine; 19=alachlor.

extracted or eluted into different extraction media. As can be seen in chromatograms from analyses of dichloromethane extract and of an eluate from Isolute ENV+ SPE column, the balance is shifted towards production of benzaldehyde dimethyl acetal (peak 4a). In case of SPE using the SDB-RPS Empore extraction disk the balance is shifted towards benzaldehyde (peak 4). This phenomenon can be explained by the acidic character of SDB-RPS sorbent (modified with sulphonic acid groups) that has a catalytic effect on the decomposition of benzaldehyde dimethyl acetal to benzaldehyde. To avoid recovery miscalculations resulting from this phenomenon the sum of concentrations of benzaldehyde and benzaldehyde dimethyl acetal was used for recovery evaluation that is given in Table 2.

4. Conclusions

Comparison of the abilities of different SPE materials as well as common LLE solvents to preconcentrate a wide range of various organic compounds showed that most of the tested media were suitable for trace enrichment of a substantial part of analytes for screening purposes. This statement is based on the concept that while for the exact quantitative target method recoveries close to 100% are usually required, a rapid screening method can also utilise recoveries higher than 20–30% provided the relative standard deviations comply with target precision criteria. However, the general suitability of the majority of tested media to preconcentrate a broad range of organic micropollutants does not necessarily mean that no care should be taken as to the selection of an appropriate preconcentration medium. Simple comparison of results obtained using various SPE materials containing styrene–divinylbenzene copolymer reveals that the same is not always the same. While linear alcohol (2-ethyl-1-hexanol) had a relatively satisfactory recovery on all poly(styrene–divinylbenzene) materials, cyclohexanol could be efficiently preconcentrated only on LiChrolut and ENV+ materials. The situation was completely the reverse of that for cyclohexanol in case of dodecanoic acid. Similar remarkable differences were observed also for trichlorophenol and caffeine. It means that using of one of the tested poly(styrene–divinylbenzene) materials for evaluation of, e.g., surface water contamination without the experiments performed in this work might lead to omission of a potentially significant micropollutant. Therefore, any screening for organics in water environment should be based on a thorough evaluation of the sample handling method-of-choice.

Acknowledgements

The authors would like to thank R. Calverley of International Sorbent Technology and B. Dirksen of 3M for providing free samples of SPE materials.

References

[1] R.E. Majors, LC·GC Int. 4 (1991) 10.
[2] I. Liška, J. Krupčík, P.A. Leclercq, J. High Resolut. Chromatogr. Chromatogr. Commun. 12 (1989) 577.
[3] M.C. Hennion, Trends Anal. Chem. 10 (1991) 317.
[4] I. Liška, J. Chromatogr. A 655 (1993) 163.
[5] D. Barceló, M.C. Hennion, Trace Determination of Pesticides and Their Degradation Products in Water, Elsevier, Amsterdam, 1997.
[6] A. DiCorcia, M. Marchetti, R. Samperi, Anal. Chem. 61 (1989) 1363.
[7] M.W.F. Nielen, U.A.Th. Brinkman, R.W. Frei, Anal. Chem. 57 (1985) 806.
[8] E.R. Brouwer, I. Liška, R.B. Geerdink, P.C.M. Frintrop, W.H. Mulder, H. Lingeman, U.A.Th. Brinkman, Chromatographia 32 (1991) 445.
[9] E.R. Brouwer, D.J. van Iperen, I. Liška, H. Lingeman, U.A.Th. Brinkman, Int. J. Environ. Anal. Chem. 47 (1992) 257.
[10] J. Slobodník, A.C. Hogenboom, A.J.H. Louter, U.A.Th. Brinkman, J. Chromatogr. A 730 (1996) 353.
[11] I. Liška, D. Barceló, M. Grasserbauer, Trends Anal. Chem. 15 (1996) 326.