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Determination of haloethers in water by solid-phase microextraction

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Abstract

A solid-phase microextraction (SPME) technique was used to determine haloethers in water. Three kinds of fibres [100 and 7 μm polydimethylsiloxane (PDMS) and 85 μm polyacrylate fibres] were used and compared. The effects of the structure and physical properties of the analytes, sample volume, duration of absorption and desorption, temperature of absorption, carryover, pH, ionic strength and elutropic strength of samples were investigated. It is concluded that the 100 μm PDMS fibre is the most suitable fibre for the analysis of semi-volatile polar haloethers in water using the SPME technique. This method was applied to environmental samples (tap and lake water) using a simple calibration curve.

Keywords: Water analysis; Environmental analysis; Extraction methods; Haloethers

1. Introduction

The release of haloethers into the environment is of great concern because of their toxicity [1,2], carcinogenicity [2] and widespread usage in industry [1,3]. They have been found in raw water, river water and drinking water in the USA [1,2]. Five haloethers were classified as priority pollutants by the US Environmental Protection Agency (EPA) in 1979. Current standard methods of haloether analysis in water, such as US EPA Methods 611 and 625, are based on liquid–liquid extraction. They require hazardous solvents, and Method 611 recommends a Florisil clean-up. The risk of sample loss increases with each step in the extraction and concentration process [4,5], resulting in recoveries from 46 to 60%, and the precision is poor [6]. The recoveries of chloroethers, using solid-phase extraction (SPE) with a C_8 column, were also low (42–63%) [6]. It is thus of interest to establish whether solid-phase microextraction (SPME), as developed by Pawliszyn and co-workers [7–14], can be used as an analytical technique to determine haloethers in water. It is also important to understand the mechanism of SPME and the factors affecting the SPME in more detail, as this is a relatively new technique. In the present work, we determined the semi-volatile priority pollutant (haloether) using a SPME fibre assembly. The effects of structure and physical properties of analyte, composition of the fibre coating, thickness of the fibre coating, sample volume, duration of absorption and desorption, temperature of absorption,

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carryover, pH, ionic strength (Na_2SO_4) and elutropic strength (methanol) of the sample solution were investigated. This method was applied to environmental samples (tap water and lake water).

2. Experimental

The SPME fibre assembly was purchased from Supelco. The microextraction fibres (from Supelco) are coated (or bonded) with polydimethylsiloxane (PDMS, 100 or 7 μm) or polyacrylate (PARL, 85 μm). The desorption temperature limit of 100 μm PDMS fibre, reported by Supelco [15] when this fibre was put on the market the first time, was 220°C. The desorption temperature limit of this fibre is 280°C for the most recent product. That portion of the work using 100 μm PDMS fibre was done a year ago with the earlier product, so a desorption temperature of 210°C was used. The desorption temperature limits for 7 μm PDMS and 85 μm PARL fibres are 320 and 300°C, respectively. Stock solutions of bis(2-chloroethyl) ether (BCEE, 12 mg/ml), bis(2-chloroethoxy)methane (BCEXM, 12 mg/ml), bis(2-chloroisopropyl) ether (BCIPE, 1 mg/ml), and 4-chlorophenyl phenyl ether (CPPE, 1 mg/ml), and 4-bromophenyl phenyl ether (BPPE, 1 mg/ml) were prepared in acetone (optima grade, Fisher). The haloethers were purchased from Chem. Service (reagent grade, purity>96). Deionized water was prepared using a Millipore Milli-Q SP purification system. Methanol (optima grade, Fisher) and sodium sulfate (Osaka, Japan) were used to prepare the sample solution. Tap water and lake water from National Tsing Hua University served as the environmental samples.

SPME involves a few simple steps [12,13]. The fibre is withdrawn into the needle of the syringe (Hamilton Model 7005) and the needle is used to penetrate the septum of a sample vial (40 or 1.8 ml). The fibre is then inserted into the sample solution by depressing the plunger. The fibre is completely immersed into the sample solution (35 or 1.5 ml). The sample solution in the vial is stirred with a magnetic stirring bar (sized to fit the vial) and controlled by a Digital hotplate/magnetic stirrer (Electrothermal HS 4000/5000). The speed of rotation of the stirring bar was 550±10 rpm and the temperature of the sample solution was 25±2°C, unless otherwise specified. After sample absorption, the plunger is withdrawn to retract the fibre into the needle and the syringe needle is then removed from the vial. For desorption, the needle is inserted into the GC injection port and then the fibre is exposed again.

A gas chromatograph (Hewlett–Packard 5890 series II) with split/splitless injection system, flame ionization detector and a capillary column (HP, Ultra 1, 25 m×0.2 mm I.D., coated with 0.33 μm dimethylpolysiloxane) were used. The temperatures at the injection port and the detector were 210 and 330°C (100 μm PDMS), 320 and 350°C (7 μm PDMS) and 300 and 330°C (85 μm PARL), respectively. For the runs using 100 μm PDMS fibre, as the fibre began its desorption, the column temperature was kept at 40°C for 8 min, then increased at 5°C/min to 118°C, held at 118°C for 3 min, then increased at 10°C/min to 160°C, and held at 160°C for 16 min. For the runs using 7 μm PDMS or 85 μm PARL fibre, in order to shorten the period required for GC analysis, the temperature program was modified as follows: the column temperature was kept at 50°C for 5 min, then increased at 10°C/min to 210°C and held at 210°C for 5 min. The carrier gas was helium of purity 99.99%, further purified by passage through a gas purifier (Alltech) containing molecular sieve 5A and an oxygen-adsorbing gas purifier (OxiClear). The rates of flow of carrier gas and makeup gas were 1 and 30 ml/min, respectively. The splitting ratio was 1:60.

3. Results and discussion

3.1. Chromatogram of the SPME analysis

A chromatogram resulting from the SPME analysis of the mixed haloether standard in water using 100 μm PDMS fibre is shown in Fig. 1. Sharp peaks and good resolution were obtained in spite of the fact that the boiling points [3] of BPPE (310°C) and CPPE (285°C) are substantially higher than the desorption temperature (210°C) at the GC injection port. The first two peaks (BCEE and BCIPE) in the chromatogram are somewhat broader than the following peaks. These peaks could probably be shar-

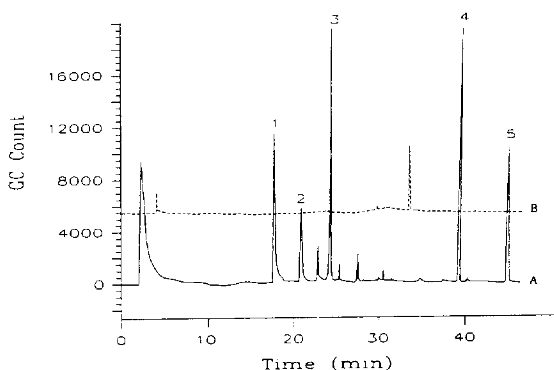

Fig. 1. (A) Chromatogram of haloethers. Extracted from deionized water by SPME for 40 min and desorbed in the GC injection port at 210°C for 8 min. Sample volume 35 ml. (1) bis(2-chloroethyl) ether (BCEE, 60 μg/ml), (2) bis(2-chloroisopropyl) ether (BCIPE, 1 μg/ml), (3) bis(2-chloroethoxy) methane (BCEXM, 60 μg/ml), (4) 4-chlorophenyl phenyl ether (CPPE, 0.1 μg/ml), (5) 4-bromophenyl phenyl ether (BPPE, 0.1 μg/ml). (B) Chromatogram of the SPME analysis of a lake water sample.

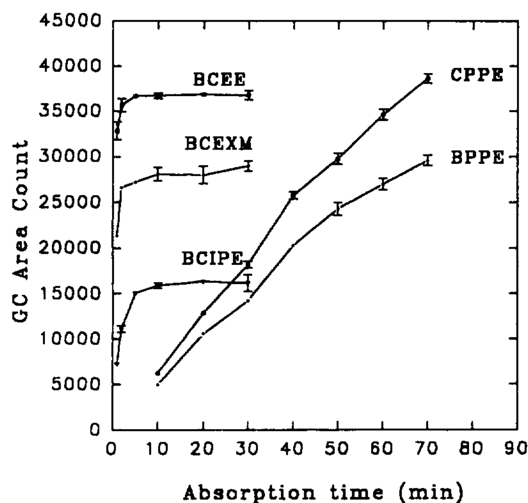

Fig. 2. Absorption–time profile for 100 μm PDMS fibre. BCEE (12 μg/ml), BCIPE (0.2 μg/ml), BCEXM (12 μg/ml),CPPE (0.02 μg/ml), BPPE (0.02 μg/ml). Sample volume 35 ml, desorption time 8 min.

pened by lowering the initial GC oven temperature (40°C) to improve the cold internal trapping. Similar chromatograms were obtained using 7 μm PDMS or 85 μm PARL fibres.

3.2. Absorption–time profile for 100 μm PDMS fibre

The absorption–time profile using 100 μm PDMS fibre is shown in Fig. 2. The concentrations of the haloethers were 12 μg/ml (BCEE and BCEXM), 0.2 μg/ml (BCIPE) and 0.02 μg/ml (CPPE and BPPE). CPPE and BPPE have much stronger affinities for the fibre than do the other haloethers, which could be expected [7–9] by comparing the very high value of the octanol–water partition coefficients (log K_{ow}) [3] of CPPE (4.08) and BPPE (5.12) with those of BCEE (1.58), BCIPE (2.58) and BCEXM (1.28).

The equilibration period was 2 min for BCEE and BCEXM and 5 min for BCIPE. The absorption of CPPE and BPPE on the fibre had not reached equilibrium, even after 70 min. Factors that influence the equilibration period were investigated by Pawliszyn and co-workers [7,8,10]. The equilibration rate is limited by the mass transfer rate of the analytes through a thin static aqueous layer at the fibre–solution interface. The equilibration period increased with increasing distribution constant of the analyte (which could be estimated from the K_{ow} of the analyte) [14] and with increasing thickness of the fibre coating. K_{ow} and the equilibration period of the haloethers follow the same trend, i.e. (BCEE and BCEXM)>>BCIPE>>(CPPE and BPPE). In order to optimize the signal and the speed of analysis, an extraction period of 40 min was chosen for subsequent experiments. It is not essential for equilibrium to be reached; shorter times can be used as long as the extractions are timed carefully and the mixing conditions remain constant [11].

3.3. Absorption–time profile for 7 μm PDMS fibre

The absorption–time profile using the thinner PDMS fibre (7 μm) is shown in Fig. 3. The equilibration periods for the analytes CPPE and BPPE are longer than 60 min. The equilibration period is not significantly reduced using a fibre with a thinner coating. Equilibrium was reached in 3 min for the other haloethers. The amount of CPPE and BPPE absorbed onto the 7 μm PDMS fibre (shown in Fig. 3) is much greater than that absorbed onto the 100 μm PDMS fibre (shown in Fig. 2) since the concentrations of CPPE and BPPE used for these experiments (7 μm) were ten times larger, and the amount of CPPE and BPPE absorbed onto the 100

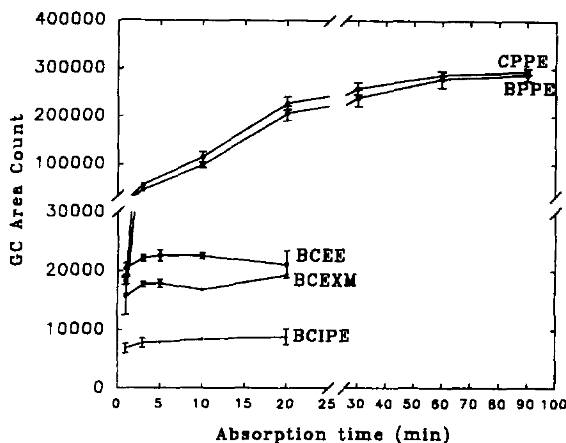

Fig. 3. Absorption–time profile for 7 μm PDMS fibre BCEE (120 μg/ml), BCIPE (2 μg/ml), BCEXM (120 μg/ml), CPPE (0.2 μg/ml) and BPPE (0.2 μg/ml). Sample volume 35 ml, desorption time 8 min.

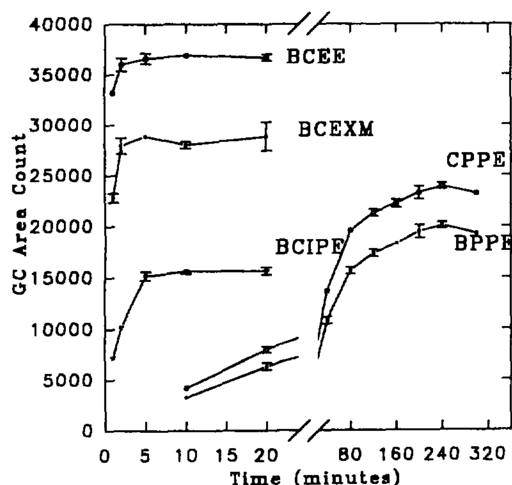

Fig. 4. Absorption–time profile for 100 μm PDMS fibre and reduced sample volume (1.5 ml). Other conditions as in Fig. 2.

μm fibre (shown in Fig. 2) should further increase after the partition of CPPE and BPPE reached equilibration.

3.4. Absorption–time profile for 100 μm PDMS fibre and reduced sample volume (extraction to exhaustion)

As was to be expected, using a smaller volume of sample (1.5 ml) does not noticeably reduce the equilibration period (Fig. 4). The amount of CPPE and BPPE absorbed on the fibre is less than that absorbed using a larger sample volume (35 ml, Fig. 2) due to the concentration of CPPE and BPPE in the solution being decreased as these haloethers with high K_{ow} are absorbed from the smaller volume (1.5 ml) of solution. When a small volume of sample was used, analytes with very large distribution constants could be very quickly exhausted by multiple extraction [8]. The average peak area of CPPE (and its standard deviation for the triplicate runs) generated from the second and third extractions by SPME were 16.8±0.3% and 3.6±0.3% of that generated from the first extraction. The corresponding values of BPPE were 15.0±0.3% and 3.5±0.2%, respectively. The decrease in concentration of the other haloethers with low K_{ow} after double extraction was insignificant.

3.5. Absorption–time profile for 85 μm PARL fibre

The absorption–time profile obtained using 85 μm polyacrylate fibre was studied. The equilibration period required is longer than 120 min for CPPE. It takes at least 90 min before the partitioning of the analytes BCEE, BCIPE and BCEXM reached equilibrium.

3.6. Desorption period

Four minutes were required to desorb BCEE, BCIPE and BCEXM, and 8 min were required to desorb CPPE and BPPE from the 100 μm PDMS fibre (extraction period 40 min, desorption temperature 210°C). A desorption period of 8 min was chosen for subsequent experiments using 100 μm PDMS fibres. The desorption periods required to desorb haloethers from the 7 μm PDMS fibre are 3 to 5 min (extraction period 10 or 30 min, desorption temperature 310°C). A desorption period of 5 min was chosen for further study using 7 μm PDMS fibre. The desorption periods used for PARL fibre

(desorption temperature 280°C) were 5 and 7 min for extraction periods of 10 and 90 min.

3.7. Carryover

To determine whether analyte retention was a significant source of error, the SPME fibre was inserted into the GC injection port a second time after analysis of the aqueous sample was completed. For the runs using 100 μm PDMS fibre (experimental conditions the same as that shown in Fig. 1), no carryover of BCEE, BCIPE and BCEXM was observed in the second GC analysis, and carryover of the less volatile analyte CPPE an BPPE was 0.2–0.6. For the runs using 7 μm PDMS fibre (absorption period 30 min, desorption temperature 320°C, other conditions as shown in Fig. 3) or 85 μm PARL fibre (absorption period 10 min, desorption at 300°C for 5 min, other conditions as shown in Fig. 1), no carryover of any haloether was observed.

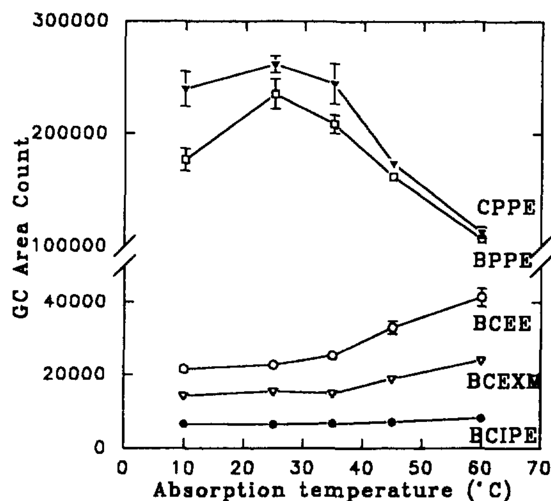

Fig. 5. Absorption–temperature profile for 7 μm PDMS fibre. Absorption time 30 min, desorption time 5 min. Other conditions as in Fig. 3.

3.8. Effect of pH

It was found that the pH of the sample solution in the range 4–9 units does not have a significant effect on the extraction efficiency of the haloethers using either PDMS or PARL fibre.

3.9. Effect of temperature of extraction

The absorption–temperature profile obtained using a 7 μm PDMS fibre is shown in Fig. 5. The amount of BCEE, BCIPE and BCEXM absorbed increased slightly with increasing temperature of extraction. The rate of diffusion of the analyte species through the static aqueous layer at the fibre–solution interface increases with increasing temperature [8], such that more analyte is absorbed at a higher temperature if equilibrium has not been reached. The results shown in Fig. 5 imply that the partitioning of these analytes between water and the fibre has not reached equilibrium during the absorption period (30 min). The amount of CPPE and BPPE absorbed increased with temperature in the range 10–25°C, and then decreased substantially with increasing temperature of extraction. The lower absorption of analytes with decreasing temperature below 25°C was due to the decreased rate of diffusion of the analytes. The decreasing absorption with increasing temperature above 25°C is presumably due to a distribution constant which decreases with increasing temperature.

The absorption–temperature profile using a PARL fibre indicates that the signals increases with temperature for all components (absorption period 10 min, desorption period 5 min, other conditions as in Fig. 2).

3.10. Effect of elutropic strength

The effect of elutropic strength of the sample on absorption was studied by preparing a series of samples that contained methanol at concentrations from 0 to 20%. As methanol concentration increases, less analyte was absorbed onto 100 μm PDMS fibre. The decrease in absorption of CPPE and BPPE was less than 2.5% for solutions containing less than 5% methanol. The decrease in absorption of BCEE, BCIPE and BCEXM in 5% methanol are 9.7, 20 and 8.7%, respectively. An increased proportion of methanol in aqueous solution decreases the polarity of the aqueous sample so that the distribution

constant decreases [8]. Methanol also affected the absorption of haloethers using PARL fibre, the results as expected were similar to those obtained when using PDMS.

3.11. Effect of ionic strength

The effect of ionic strength on the absorption of haloethers by 100 μm PDMS fibre and 85 μm PARL fibre was determined by preparing standards with Na_2SO_4 concentrations ranging from 0 to 20%. The increase in absorption of BCEE, BCIPE and BCEXM, resulting from the "salting-out effect", was highly significant using either fibre. Similar effects were observed for the SPME analysis of many other organic compounds (but not ions) [7,8,13]. Somewhat surprisingly, increasing the ionic strength of the solution has very little effect on the absorption of CPPE and BPPE on either fibre; the absorption of these analytes decreases somewhat when solutions containing a high concentration of Na_2SO_4 are used. The effect of Na_2SO_4 on the absorption of CPPE and BPPE on the fibre is probably due to three factors. The first is the "salting-out effect", which decreases the solubility of analytes and thus increases the absorption. Secondly, salt dissolved in the solution may change the physical properties of the static aqueous layer on the fibre, and thereby reduce the rate of diffusion of the analyte through the static aqueous layer to the fibre. Thirdly, the zwitterions of the resonance forms of CPPE and BPPE molecules are stabilized by high concentrations of salt in the solution, so that CPPE and BPPE become more soluble in water due to the increased contribution of zwitterion form to the resonance structure. These effects compensate each other, so that the absorption of CPPE and BPPE on the fibres is little affected by the salt, or even decreases somewhat from solutions containing a high concentration of Na_2SO_4. A similar effect of ionic strength was observed for 7 μm PDMS fibre and 85 μm PARL fibre.

3.12. Precision, detection limits and linearity

Three runs were used to establish the error bars in Figs. 2–5. Precisions (R.S.D. values) of the method using PDMS fibre (100 μm) are 10–13%; with one exception, 3% for BCEXM [concentrations used for the runs are 120 μg/l (BCEE and BCEXM), 2.0 μg/l (BCIPE) and 0.2 μg/l (CPPE and BPPE)]. Method detection limit (shown in Table 1) is defined as the concentration equivalent of three times the standard deviation of seven replicate measurements of the analyte in reagent water which contain the analyte in a concentration range between 1 and 5 times the estimated detection limit [16]. The detection limits for the analysis of BCEE, BCIPE and BCEXM using 100 μm PDMS fibre do not differ much from those obtained using 1.5-ml samples and extraction for 10 min, or using 35-ml samples and extraction for 40 min. However, the detection limits for the analysis of CPPE and BPPE are improved 7–10 times on using a larger sample volume (35 ml) and a longer extraction period (40 min). The detection limits for the analysis of haloethers increase substantially if fibre with a thinner PDMS coating (7 μm) is used, and the detection limits decrease

Table 1
Dependence of detection limits (μg/l) on fibre coating and extraction period[a]

Compound	Fibre:	PDMS (100 μm)		PARL (85 μm)		PDMS (7 μm)	
	Extraction period (min):	40	10	90	10	30	10
	Sample volume (ml):	35[b]	1.5[c]	35	35	35	35
BCEE		34	37	170	340	18 000	21 000
BCIPE		0.94	0.82	8.5	28	190	200
BCEXM		26	29	330	480	23 000	28 000
CPPE		0.04	0.42	0.33	1.4	10	16
BPPE		0.06	0.43	0.50	1.3	12	17

[a] Seven replicate measurements were used.
[b] Concentrations of haloethers used for the runs are 120 μg/l (BCEE and BCEXM), 2.0 μg/l (BCIPE) and 0.2 μg/l (CPPE and BPPE).
[c] Concentrations of haloethers used for the runs are 120 μg/l (BCEE and BCEXM), 2.0 μg/l (BCIPE) and 1.0 μg/l (CPPE and BPPE).

Table 2
Slope and correlation coefficient of calibration curve for different matrices[a]

Compound	Deionized water		Tap water		Lake water	
	Slope	r	Slope	r	Slope	r
BCEE	2995	0.9999	2981	0.9999	3000	0.9999
BCIPE	76 610	0.9999	76 840	0.9998	76 620	0.9998
BCEXM	2678	0.9999	2697	0.9999	2717	0.9999
CPPE	128 400	0.9991	129 200	0.9990	129 800	0.9984
BPPE	74 980	0.9976	75 140	0.9964	74 890	0.9971

[a] PDMS (100 μm) fibre, absorption period 10 min, sample volume 1.5 ml, concentrations of haloethers used to generate the calibration curve: 0.12, 1.2, 12, 120, 600 mg/l (BCEE and BCEXM), 0.002, 0.02, 0.2, 2, 10 mg/l (BCIPE) and 0.002, 0.02, 0.2, 1.0 mg/l (CPPE and BPPE).

somewhat on using PARL fibre. The linearity of the calibration curves is good for at least 2–3 orders of magnitude with either PDMS or PARL fibres.

3.13. *Test on environmental samples*

The chromatogram resulting from the SPME analysis of a lake water sample is shown in Fig. 1. These haloethers were not found in the lake water sample. Calibration curves of haloethers were compared (Table 2) for deionized water, tap water and lake water using PDMS fibre. The slopes of the calibration curves were almost independent of the matrix of the sample solution, which indicates that the SPME method can be used to analyze for haloethers in natural waters using a simple calibration curve.

4. Conclusions

The SPME technique was successfully applied to the analysis of haloethers in water. Better precision and lower detection limits are achieved with 100 μm PDMS fibre as compared to that with PARL fibre. The lengthy equilibration period is another drawback to the use of PARL fibre to analyse for haloethers. The use of 7 μm PDMS fibre provides results with much higher detection limits. The equilibration period is not significantly reduced by using fibre with a thinner coating (7 μm). The 100 μm PDMS fibre is thus the most suitable fibre (among the fibres tested in this work) for the analysis of semi-volatile polar haloethers in water using the SPME technique. The amount of CPPE and BPPE absorbed onto the fibres and the equilibration period for the partition of these analytes (CPPE and BPPE) are much greater than those of the other haloethers (BCEE, BCIPE and BCEXM) due to the much greater K_{ow} values of CPPE and BPPE. Although the absorption of CPPE and BPPE on the 100 μm fibre has not reached equilibrium after 70 min, a shorter extraction period can be used as long as the extractions are timed carefully and the mixing conditions remain constant. For instance, detection limits of CPPE and BPPE at sub-ppb level can be achieved by extracting for 10 min only. The detection limits for the analysis of CPPE and BPPE can be improved on using a longer extraction period (40 min). An extraction period of 40 min does not increase the analysis time since the chromatographic run is longer than the extraction period (40 min); and the extraction for the next sample can be performed during the chromatographic separation. The addition of salt enhances the absorption of BCEE, BCIPE and BCEXM from water, but does not enhance the absorption of CPPE and BPPE.

In most cases using SPME, only a very small portion of analyte (such as BCEE, BCEXM and BCIPE) is absorbed from the aqueous sample onto the coating, but the procedure facilitates high sensitivity analysis since the total amount of extracted material is transferred onto the GC column, which is different from that for liquid–liquid extraction or conventional off-line SPE. However, the state-of-the-art of SPE–GC is such today that on-line operation [17–19] can easily be achieved. Then, with similar sample volumes and times of analysis, on-line SPE–GC is much more sensitive than the SPME.

Acknowledgments

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