Solid-phase microextraction for determining the distribution of sixteen US Environmental Protection Agency polycyclic aromatic hydrocarbons in water samples

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Abstract

A solid-phase microextraction (SPME) procedure has been developed for the determination of 16 US Environmental Protection Agency promulgated polycyclic aromatic hydrocarbons (PAHs). Five kinds of SPME fibers were used and compared in this study. The extracted sample was analyzed by gas chromatography with flame ionization detection or mass spectrometry. Parameters affecting the sorption of analyte into the fibers, including sampling time, thickness of the fiber coating, and the effect of temperature, have been examined. Moreover, the feasibility of headspace SPME with different working temperatures was evaluated. The method was also applied to real samples. The 85-μm polyacrylate (PA) and 100-μm poly(dimethylsiloxane) (PDMS) fibers were shown to have the highest affinities for the selected PAHs. The PA fiber was more suitable than the PDMS fiber for the determination of low-ring PAHs while high sensitivity of high-ring PAHs was observed when a 100-μm PDMS fiber was used. The method showed good linearity between 0.1 and 100 ng/ml with regression coefficients ranging from 0.94 to 0.999. The reproducibility of the measurements between fibers was found to be very good. The precisions of PA and PDMS fibers were from 3 to 24% and from 3 to 14%, respectively. Headspace SPME is a valid alternative for the determination of two- to five-ring PAHs. A working temperature of 60°C provides significant enhancement in sensitivity of two- to five-ring PAHs having low vapor pressures ($>10^{-6}$ mmHg at 25°C) (1 mmHg=133.3 Pa) and low Henry's constants (>10 atm ml/mol) (1 atm=$1.01 \cdot 10^5$ Pa).   © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Water analysis; Solid-phase microextraction; Environmental analysis; Polynuclear aromatic hydrocarbons

1. Introduction

The preconcentration and extraction of the semivolatile organic compounds from water can be carried out by means of liquid–liquid extraction (LLE) and solid-phase extraction (SPE) techniques [1]. LLE is a very useful technique, which has been used by the US Environmental Protection Agency (EPA). However, it is tedious, time consuming and requires large amounts of solvents. SPE is a less time consuming method, but it still requires toxic solvents for the elution step. Recently, a new solvent-free technique, solid-phase microextraction (SPME) has been introduced for the extraction of many volatile and semivolatile organic compounds [2–8]. Several advantages can be pointed out in relation to this

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technique, such as it is solvent free, uses the whole sample for analysis, requires only small amounts of sample and the fibers are highly reusable [5]. Usually, compounds in the samples are extracted into the polymeric phase according to their affinity towards the coating and then they are thermally desorbed directly in the gas chromatographic injector.

SPME has been successfully used to analyze a wide range of low polarity semivolatile organics, such as polychlorinated biphenyls (PCBs) [2,6], chlorinated pesticides [4,7,8] and some low-molecular-mass polycyclic aromatic hydrocarbons (PAHs) [9–12]. Different fiber coatings were used in these applications. In general, poly(dimethylsiloxane) (PDMS) and polydimethylsiloxane containing divinylbenzene (PDMS–DVB) are considered as less polar coatings so they are useful for non-polar compounds, whereas the polyacrylate (PA) fiber is more polar and is suitable for polar compounds. However, the selection of a fiber according to the physicochemical parameters of the compounds was difficult [13].

PAHs are the ubiquitous contaminants in the environments. These compounds are originally from both natural and anthropogenic sources that involve incomplete combustion, aluminum smelting or from the spillage of fossil fuel. On the basis of properties and molecular mass of PAHs, two classes, the two- and three-ring and four- to six-ring, of PAHs can be distinguished. The low-molecular-mass two- and three-ring PAHs have a significant acute toxicity, whereas some of the high-molecular-mass PAHs show high carcinogenic and mutagenic potentials. Due to their potential or proven carcinogens, the EPA has promulgated 16 unsubstituted PAHs in their list of 129 priority pollutants. For these promulgated PAHs, only some of the PAHs, such as naphthalene, fluoranthene, phenanthrene, anthracene, benz[*a*]anthracene, pyrene and benzo[*a*]pyrene are analyzed by the PDMS fiber. The optimization of other PAHs received less attention. Moreover, due to the different physicochemical properties and toxic characteristics, these promulgated PAHs have different sorption behaviors in the polymeric organic phase as well as in the environmental media. Therefore, the application of SPME to the analysis of 16 PAHs for better understanding the distribution of PAHs is still in demand.

In this work, the optimization and validation of an

SPME procedure for the determination of 16 promulgated PAHs in water samples were carried out. Five kinds of fibers [100-, 30- or 7-μm PDMS, 85-μm PA and 65-μm Carboxen (CAR)–PDMS] were compared for the extraction efficiency of the PAHs. Parameters affecting the sorption of analyte into the fibers, including sampling time, thickness of the fiber coating and the effect of temperature, have been examined. Moreover, the feasibility of headspace SPME (HS-SPME) for the analysis of PAHs under different working temperatures was also evaluated. This method was applied to real environmental samples (river water and groundwater).

2. Experimental

2.1. Reagents and materials

The standard mixtures of 16 PAHs at a concentration of 2000 μg/ml in methylene chloride–benzene (1:1, v/v) were purchased from Supelco (Bellefonte, PA, USA). These standards were stored at 4°C and were used for the preparation of working standard solutions. A working standard (20 μg/ml in acetone) was prepared every week. Deionized water was obtained from a Milli-Q water purification system (Millipore, Bedford, MA, USA). Methanol, dichloromethane, acetone and *n*-hexane were obtained from Mallinckrodt (Phillipsburg, NJ, USA). Toluene was purchased from Riedel-de Haen (Seelze, Germany).

The SPME holders for manual use were obtained from Supelco. Five kinds of different fibers, 100-, 30- or 7-μm PDMS, 85-μm PA and 65-μm CAR–PDMS fibers, were also obtained from Supelco. All fibers were conditioned in the hot injector part of the gas chromatograph for 0.5–3 h and at 250~300°C, according to the instructions provided by the manufacturer.

The glassware used in this study was first washed with detergent and with deionized water followed by placing them in a cleaning solution overnight to remove the trace amounts of organics on the surface of vials. The glassware was then rinsed with deionized water, methanol, acetone and hexane in sequence, dried in the oven at 105°C and wrapped with aluminum foil before use. For SPME, the vials were further silanized by soaking the glassware overnight

in a 10% (v/v) mixture of dichlorodimethylsilane (Supelco) in toluene. Finally, the vials were rinsed with toluene and methanol and oven-dried at 105°C.

2.2. Apparatus and analysis

A Hewlett-Packard 6890 gas chromatograph, with a split–splitless injection port and a flame ionization detection (FID) system, was used for the experiments to determine the optimized SPME conditions. The carrier gas was nitrogen at a flow-rate of 3 ml/min. The detector flow-rates were 350 ml/min for air, 35 ml/min for hydrogen, and 30 ml/min for nitrogen (makeup gas). The gas chromatograph was operated in the splitless mode. The splitless time was 5 min. The injector was maintained between 270°C and 320°C, depending on the fiber used. The temperature of detector was at 350°C. A 30-m Ultra Alloy-5 (5% diphenyl–95% dimethylpolysiloxane) stainless steel capillary column (0.5 mm I.D., 0.5 μm film thickness, Quadrex, New Haven, CT, USA) was used for separating the PAHs. The column was held at 40°C for 5 min, increased to 180°C at a rate of 20°C/min and again ramped at 4°C/min to 250°C, increased the temperature to 270°C at a rate of 2°C/min, held for 2 min, and finally ramped to 320°C at a rate of 10°C/min, and then held for 10 min.

Analysis of PAHs by GC–MS was performed with a Hewlett-Packard 5793 mass-selective detector equipped with a 6890 gas chromatograph and a split–splitless injection port (splitless mode). The column used was a 30-m HP-5 (5% phenyl–95% methylpolysiloxane) (0.25 mm I.D., 0.25 μm film thickness). Helium was used as the carrier gas, and the flow-rate was maintained at 1.3 ml/min (linear velocity 41 cm/s). The ionization was carried out in the electron impact (EI) mode (70 eV). The electron multiplier voltage and automatic gain control target were set automatically. The transfer line and ion trap manifold were set at 280 and 230°C, respectively. The mass range scanned was from 50 to 550 amu under full scan acquisition mode. Selected-ion monitoring (SIM) acquisition was carried out by monitoring the base peak of each compound. The MS system was tuned to m/z 69, 219 and 502 for EI corresponding to perfluorobutylamine (PFTBA). All other chromatographic conditions were identical to those described earlier for GC–FID.

2.3. Solid-phase microextraction procedures

SPMEs were performed by placing 10 ml of deionized water in 15-ml amber vials capped with PTFE-coated septa. Aqueous standards were prepared by spiking an appropriate amount of the working standard to a final concentration of 10 ng/ml. Magnetic stirring with a 1-cm long PTFE coated stir bar was used to agitate the solution at ca. 1000 rpm, 90% of the maximum speed of the stirrer. The SPME equilibrium was conducted by immersing the fiber into the aqueous phase (direct SPME) or in the headspace (HS-SPME) of the sample with stirring at room temperature for an appropriate time period, during which analytes sorb on the stationary phase of the fibers. After extraction, the fiber was thermally desorbed for 5 min into the glass liner of the GC injector port at 270°C (30- and 100-μm PDMS), 300°C (PA and CAR–PDMS) or 320°C (7-μm PDMS). Possible carryover was removed by keeping the fiber in the injector for an additional time with the injector in the splitless mode. Reinserting the SPME fiber after the run did not show obvious carry over. Moreover, blanks were run periodically during the analysis to confirm the absence of contaminants.

The linearity of the method was tested by FID by extracting seven aqueous standards with increasing concentrations over a range between 0.5 and 100 ng/ml. The limit of detection (LOD) is defined as the concentration of an analyte in a sample that gives rise to a peak with a signal-to-noise ratio (S/N) of 3. The FID response was calibrated by injecting liquid standards containing PAHs for calculating the total amounts sorbed by the fiber. The analyte recoveries were determined relative to the ratio of direct injection and the working standards prepared in acetone.

3. Results and discussion

3.1. Fiber selection

Five commercially available SPME fibers (100-, 30- or 7-μm PDMS, 85-μm PA and 65-μm CAR–PDMS) were compared for efficiently determining 16 PAHs from the aqueous phase. The extraction time was 90 min. PAHs with different chemical

characteristics showed different extraction behaviors (Fig. 1). The 65-μm CAR–PDMS fiber provided good extraction efficiencies for two- and three-ring PAHs (naphthalene, acenaphthylene and acenaphthene). However, the extraction efficiency of CAR–PDMS decreased with increasing molecular mass and only eight PAHs ($M_r < 202$) were extracted at levels greater than detection limits of the method within 90 min. When PDMS fibers were used, all 16 PAHs can be extracted from water within a sorption time of 90 min. The extraction efficiencies decreased with the decreasing coating thickness and the 100-μm PDMS fiber extracted the highest amounts of PAHs. Three- and four-ring PAHs, such as phenanthrene, anthracene, fluoranthene and pyrene were the most extensively sorbed compounds.

The application of the PA fiber showed an increase in signal response of two- and three-ring PAHs relative to the PDMS fiber, demonstrating that the PA fiber could improve the extraction efficiency of the low-molecular-mass PAHs. On the contrary, the high-molecular-mass PAHs (higher than four rings) were less effectively extracted by using the PA fiber due to the fact that the PA fiber has a more polar coating and has a low affinity to high-ring PAHs.

The PAHs under investigation fall into the non-polar class with relatively high octanol–water partition coefficients and low water solubility. Therefore, these analytes would be expected to partition readily into a more non-polar fiber coating rather than a polar one. The PDMS polymeric coating with higher film thickness showed a good sorption for PAHs. Also, the extraction efficiency increased with increasing molecular mass from naphthalene to pyrene. Although the PA fiber is designed for the purpose of extracting polar compounds, similar sorption behaviors were also observed in this case. This shows that the PA fiber can successfully extract this class of
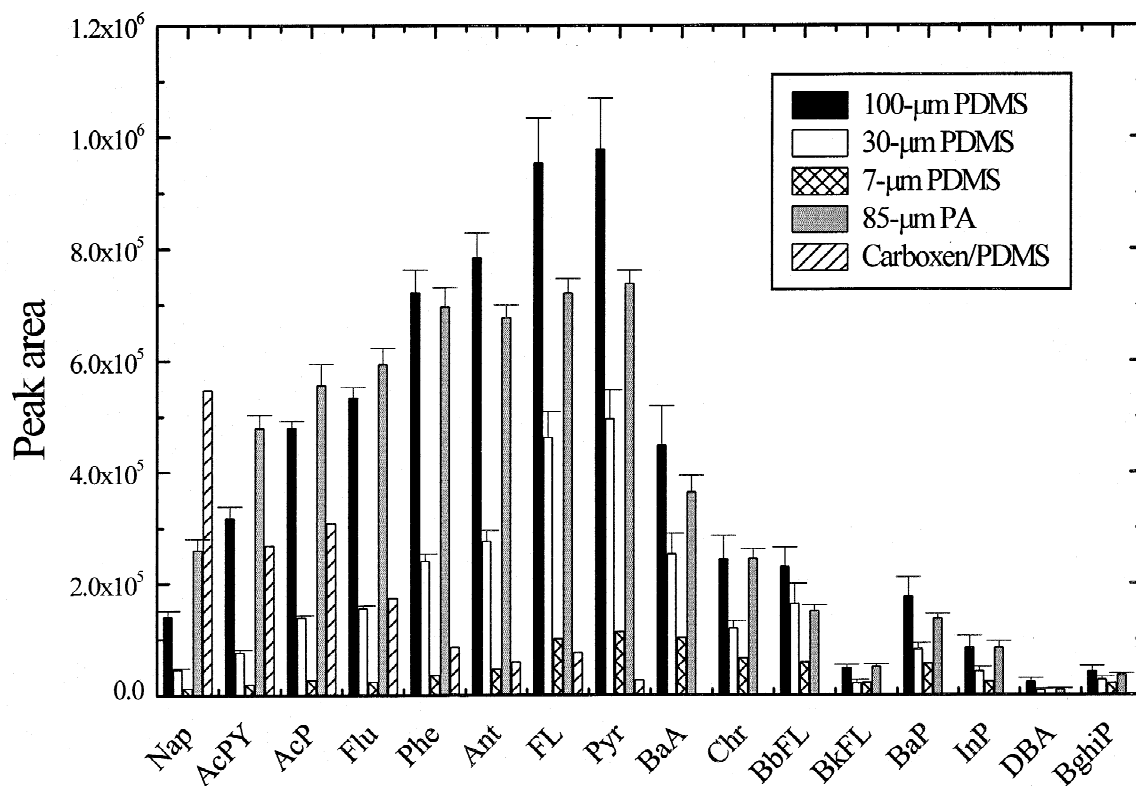

Fig. 1. The comparison of extraction efficiency of 16 PAHs with five different SPME fibers. Aqueous solution (10 ng/ml) was extracted in an extraction time of 90 min at room temperature under magnetic stirring.

compounds. Therefore, these two fibers were selected for further optimization experiments.

3.2. Extraction time profiles

Since SPME is an equilibrium extraction method, the time to equilibrium determines the maximum amount of analyte that can be extracted by the fibers which controls the sensitivity of the method. The sorption time profiles were studied by monitoring the area counting as a function of exposure time, so the fiber was exposed to standard solutions of the PAHs at a concentration of 10 ng/ml for increasing the time intervals from 20 to 1440 min. All the extractions were carried out at room temperature (25±2°C) with continuous stirring at about 1000 rpm in order to ensure that the sample was perfectly agitated. Fig. 2 illustrates the direct SPME equilibrium time profiles for 16 PAHs using the 100-μm PDMS fiber. From the results obtained it can be seen that the equilibrium is compound dependent and can vary significantly among the different compounds. The equilibrium times for the PAHs increased with molecular mass. The equilibrium time was 20 min for naphthalene, 30 min for acenaphthylene, 60 min for acenaphthene, 90 min for fluorene, phenanthrene, anthracene, fluoranthene and pyrene. Longer equilibrium times (720 min) were observed for benz[*a*]anthracene, chrysene and benzo[*b*]fluoranthene. No equilibrium was observed for the five- and six-ring PAHs (benzo[*k*]fluoranthene, benzo[*a*]pyrene, dibenzo[*a,h*]anthracene, benzo[*ghi*]perylene and indeno[1,2,3-*cd*]pyrene). Further SPMEs showed that the six-ring PAHs still did not reach equilibrium at times as long as 60 h.

Different fibers exhibited different extraction profiles. Longer equilibrium time for the PA fiber was needed to extract the same compounds. As depicted in Fig. 3, the time to reach equilibrium was 40 min for naphthalene, 240 min for acenaphthylene and acenaphthene, 12 to 24 h for four-ring PAHs. Also, no equilibrium was reached for six-ring PAHs when the extraction time was prolonged to 60 h. The long equilibration times actually reflect the kinetics of the SPME process, since high-molecular-mass compounds have lower diffusion coefficients. For quantitative analysis, it is not necessary for the analytes to reach equilibrium. Therefore, a 90-min extraction

time was adopted, even though the high-ring PAHs had not reached the equilibrium at this time, but the analytical sensitivity was sufficient. Also, this sampling time was close to the chromatography run which allowed for maximum sample through-put.

3.3. Linearity, precision and detection limits

The linearity of the method was tested by GC–FID by extracting aqueous standards, with increasing concentrations, over a range typically between 5 and 100 ng/ml for low-ring PAHs and 0.1–10 ng/ml for high-ring PAHs. Table 1 illustrates the linearity, precision and detection limits of PAHs with PDMS and PA fibers. The direct SPME procedure showed a good linear behavior in the tested range with correlation coefficients ranging between 0.978 and 0.999 and between 0.945 to 0.999 for the PDMS and PA fibers, respectively. Low correlation of five- and six-ring PAHs may be attribute to the low water solubilities and long equilibrium times of these compounds.

The precision of the method was determined by performing seven consecutive fiber extractions from an aqueous solution with a concentration of 10 ng/ml under the optimal conditions. At room temperature, the reproducibility is expressed as the relative standard deviation (RSD) of the fibers. The RSD obtained using the PDMS fiber ranged from 3 to 24%. In general, the higher RSD values were determined for compounds having higher molecular mass. The RSDs of the high-ring class of PAHs can be improved by using the PA fiber. The RSDs were in the range of 3 to 14%. The precision obtained here is similar or better than other values presented in the literature for the determination of PAHs in water samples at ppb levels using the SPME approach [6,9].

The LODs of the PAHs ranged from 0.08 to 0.53 ng/ml (PDMS fiber) and from 0.03 to 0.59 ng/ml (PA fiber). The detection limits achieved in this study were comparable to the detection limits reported by EPA Method 8270 and published values [9]. Low LOD values for low-ring PAHs were obtained when the PA fiber was used, depicting that the PA fiber is suitable for the determination of two- to four-ring PAHs. However, high detection limits for high-ring PAHs were observed. The use of more sensitive and
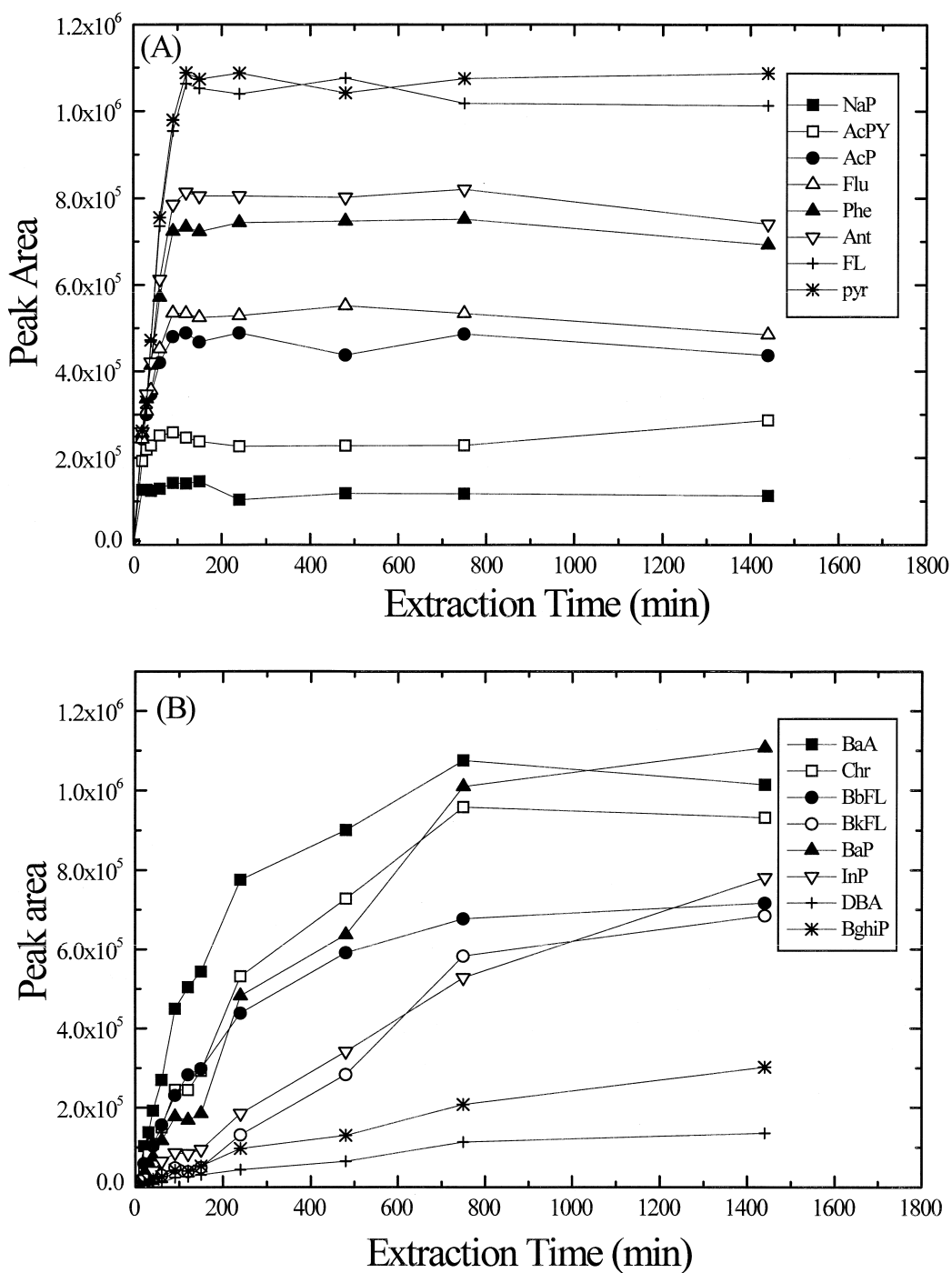
Fig. 2. The SPME sorption time profiles for 16 PAHs with a 100-μm PDMS fiber. Aqueous solution (10 ng/ml) was extracted in an extraction time of 90 min at room temperature under magnetic stirring.
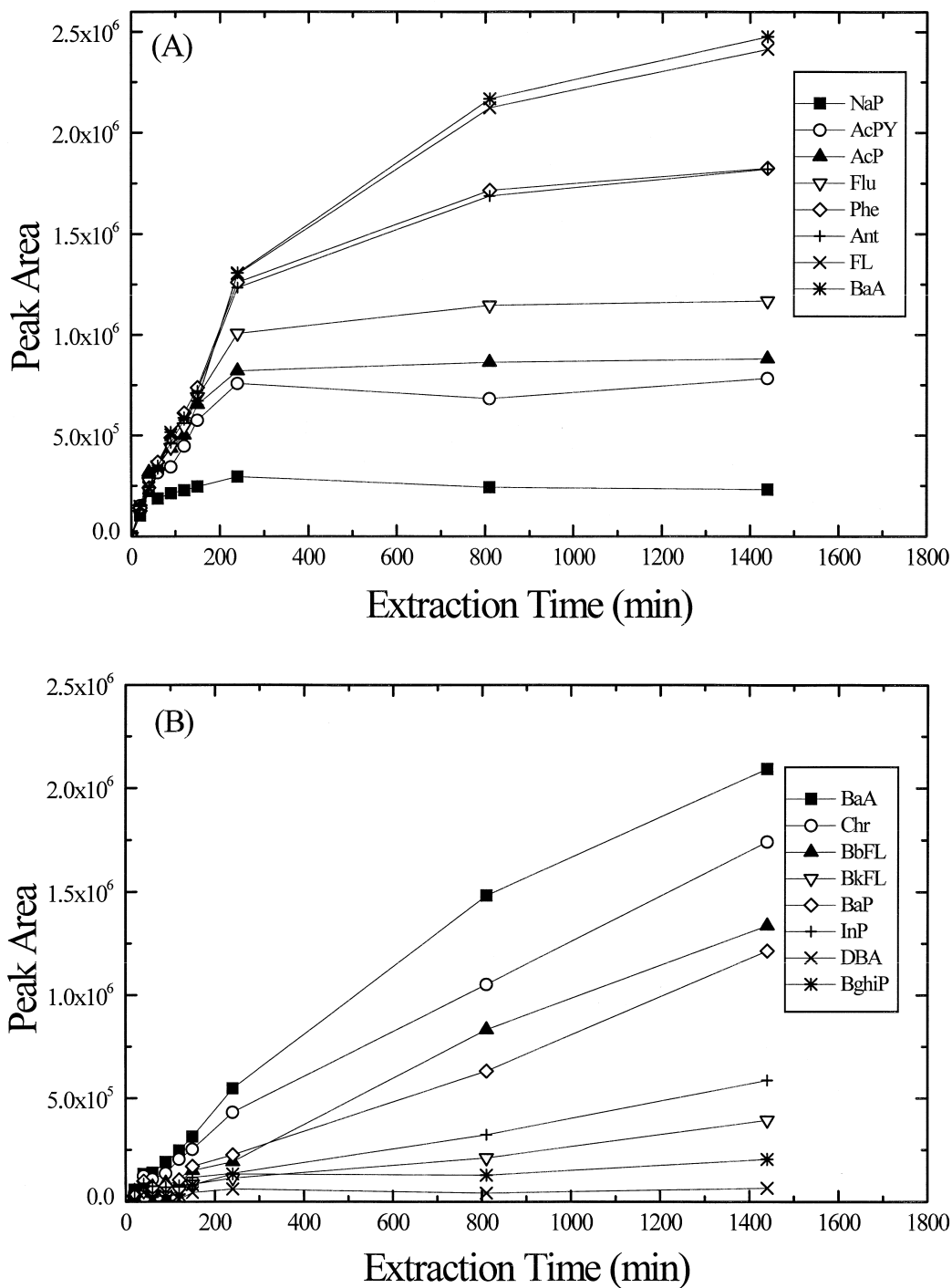
Fig. 3. The SPME sorption time profiles for 16 PAHs with an 85-μm PA fiber. Aqueous solution (10 ng/ml) was extracted in an extraction time of 90 min at room temperature under magnetic stirring.

Table 1
The linearity, precision and LOD of 100-μm PDMS and 85-μm PA fibers for the determination of 16 PAHs

PAH	100-μm PDMS					85-μm PA		
	Precision (n=7)	Linearity		LOD (ng/ml)		Linearity	Precision (n=7)	LOD (ng/ml)
		FID	MS	FID	MS			
Naphthalene	7	0.996	0.997	0.15	0.18	0.996	3	0.22
Acenaphthylene	3	0.996	0.998	0.21	0.27	0.999	10	0.13
Acenaphthene	3	0.995	0.999	0.1	0.1	0.997	4	0.03
Fluorene	2	0.996	0.999	0.08	0.07	0.999	6	0.08
Phenanthrene	3	0.996	0.996	0.12	0.08	0.999	8	0.08
Anthracene	5	0.988	0.999	0.18	0.1	0.999	8	0.11
Fluoranthene	8	0.998	0.999	0.25	0.1	0.999	11	0.17
Pyrene	9	0.997	0.999	0.26	0.11	0.999	12	0.33
Benz[a]anthracene	15	0.994	0.999	0.29	0.15	0.991	12	0.05
Chrysene	17	0.980	0.991	0.24	0.03	0.996	10	0.16
Benzo[b]fluoranthene	15	0.994	0.999	0.52	0.15	0.995	12	0.13
Benzo[k]fluoranthene	10	0.978	0.995	0.4	0.12	0.945	11	0.09
Benzo[a]pyrene	19	0.978	0.985	0.44	0.24	0.995	3	0.16
Dibenzo[a,h]anthracene	24	0.991	0.996	0.14	0.12	0.985	3	0.26
Benzo[ghi]perylene	14	0.993	0.992	0.29	–[a]	0.979	7	0.27
Indeno[1,2,3-cd]pyrene	21	0.998	0.998	0.53	0.09	0.995	14	0.59

[a] –: Not determined.

selective detection methods such as MS can improve the sensitivity of five- and six-ring PAHs. A two- to eight-fold increase in sensitivity relative to GC–FID was obtained when GC–MS under full scan acquisition mode and the 100-μm PDMS fiber was used. This means that SPME is valid for the determination of 16 EPA PAHs.

3.4. Effect of temperature on direct SPME

Since the extracted amount of high-ring PAHs in the SPME fiber is low, an increase in extracting temperature could enhance the final sorbed amounts of PAHs in the fiber [14]. Table 2 illustrates the extraction efficiencies of PAHs under working temperatures of 25°C and 60°C. Different extraction behaviors of PAHs were observed. Increasing temperature can significantly increase the diffusivities and decrease the partition coefficients of PAHs, thereby enhancing the extraction amounts of four- to six-ring PAHs. However, a decrease in sensitivity was also observed for low-ring PAHs. This is attributed to that the elevated temperature significantly increased the mass transfer at the water–gas interface. Therefore, the extraction efficiencies of

PAHs having high Henry's constants, such as naphthalene, acenaphthylene and acenaphthene, decreased when the working temperature increased from 25 to 60°C.

Table 2
The extraction efficiencies of PAHs under different extraction temperatures[a]

PAH	PDMS fiber (%)		PA fiber (%)	
	25°C	60°C	25°C	60°C
Naphthalene	3.1	2.6	8.7	4.2
Acenaphthylene	9.1	4.9	18.0	10.7
Acenaphthene	13.9	8.8	19.2	13.7
Fluorene	16.4	15.7	24.1	22.8
Phenanthrene	25.4	22.2	32.5	42.5
Anthracene	27.9	39.5	32.6	49.4
Fluoranthene	35.6	40.1	31.1	60.5
Pyrene	36.1	53.1	31.4	63.6
Benz[a]anthracene	17.8	56.1	13.5	73.4
Chrysene	11.5	50.1	10.4	70.6
Benzo[b]fluoranthene	13.2	51.5	7.7	63.6
Benzo[k]fluoranthene	8.0	50.2	3.5	61.7
Benzo[a]pyrene	16.6	49.2	4.9	60.6
Indeno[1,2,3-cd]pyrene	17.8	40.3	1.2	47.0
Dibenzo[a,h]anthracene	5.7	14.5	2.1	13.2
Benzo[ghi]perylene	5.0	22.3	3.1	24.0

[a] The extraction time was 90 min.

3.5. Direct SPME and HS-SPME

In this study, the possibility of sampling the headspace over the water sample instead of directly immersing the fiber in the water was also evaluated. In these experiments, the volume of water was 10 ml and the headspace volume was 5 ml. The initial concentration of PAHs in water was 10 ng/ml. Fig. 4 compares the FID responses of PAHs with direct SPME and HS-SPME using a 100-μm PDMS fiber. HS-SPME was shown to be a viable technique for the effective extraction of low-ring PAHs. The responses of two- and three-ring PAHs, such as naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene and anthracene, obtained by HS-SPME were 2–3-times higher than those with direct SPME at room temperature. The four-ring PAHs, benz[a]anthracene and chrysene had low extraction efficiencies with HS-SPME due to their low

vapor pressures $(2.1 \cdot 10^{-7}$ and $6.4 \cdot 10^{-9}$ mmHg) (1 mmHg=133.3 Pa) [15,16]. No five- and six-ring PAHs were detected with HS-SPME within 90 min. Increasing temperature can enhance analyte evaporation rates and mass transfer at the water–gas interface [14]. A temperature of 60°C can increase the sensitivity of the two- to five-ring PAHs by a factor of about 2–4. Owing to the extremely low vapor pressure $(<10^{-9}$ mmHg), however, HS-SPME is not suitable for the determination of indeno[1,2,3-cd]pyrene, dibenzo[a,h]anthracene and benzo[ghi]perylene when the temperature was lower than 60°C. By further increasing the temperature to 80°C, the FID responses of the five- and six-ring PAHs can be significantly enhanced. However, the sensitivity of low-ring PAHs decreased. This can be explained by the exothermic adsorption process. A higher temperature decreases the partition coefficient between the PDMS coating and the headspace,
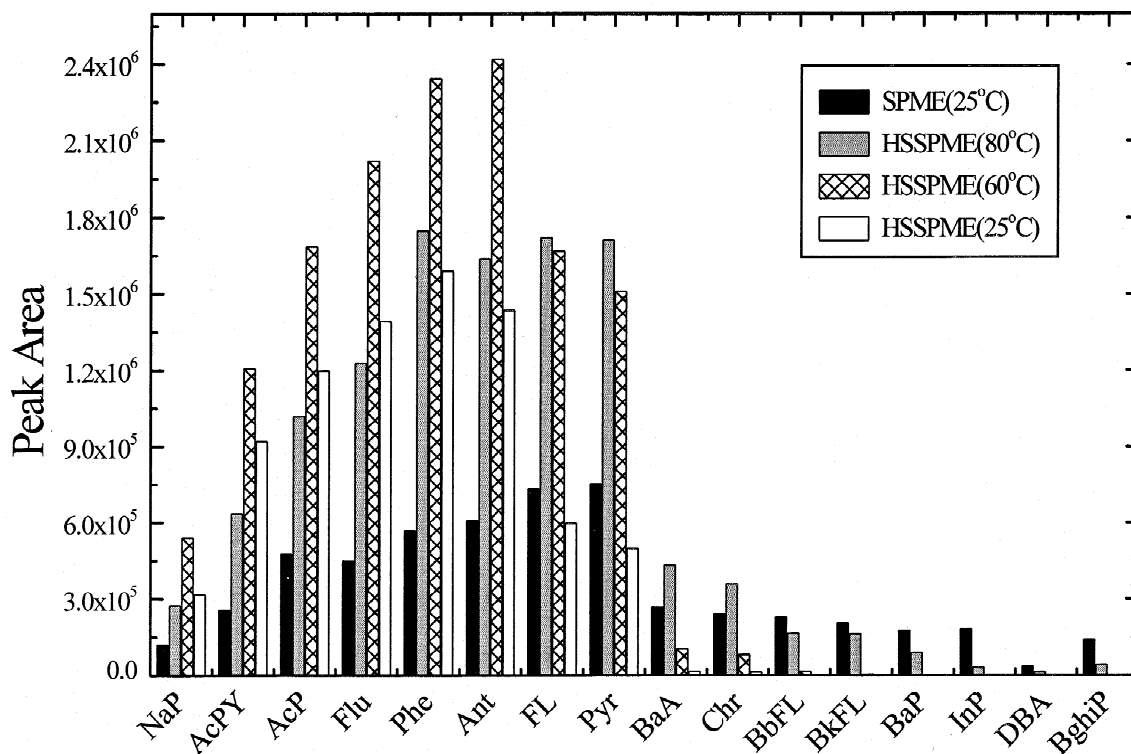

Fig. 4. Temperature effect on the responses of PAHs obtained by SPME and HS-SPME when a 100-μm PDMS fiber was used. The temperatures used were 25, 60 and 80°C. The extraction time was 90 min.

resulting in the decrease of sorbed amounts of low-ring PAHs into the fiber [16,17].

HS-SPME has been reported to be efficient for analytes with high and medium Henry coefficients [18,19]. Zhang and Pawliszyn [18] showed that the HS-SPME technique could be used effectively to extract compounds with Henry's constants higher than 90 atm ml/mol at ambient temperature (1 atm= $1.01 \cdot 10^5$ Pa). Recently, Llompart et al. [19] successfully used HS-SPME for analyzing Aroclor 1260 at a temperature of 100°C. Our results indicated that HS-SPME also could be applied to analyze the semivolatile organic compounds having low vapor pressures ($>10^{-6}$ mmHg at 25°C) and low Henry's constant (>10 atm ml/mol). Fig. 5 illustrates the extraction times of some PAHs at a temperature of 60°C with a 100-μm PDMS fiber. Two- and three-ring PAHs can reach the equilibrium within 120 min, which is consistent with the results obtained by direct SPME technique. Although longer times (360 to 540 min) were needed for four- and five-ring PAHs, the sensitivity is superior to the direct SPME at room temperature. Also, the precision calculated for the PAHs by HS-SPME at 60°C was within in the

range of 4–26% RSD. These results are comparable or better than the direct SPME at 25 and 60°C. Based on these results, we can conclude that HS-SPME should be a potential analytical method for determining the two- to five-ring PAHs.

3.6. Application to real samples

The effectiveness of the SPME method in determining 16 PAHs in real samples was tested on a groundwater sample and a river water sample. The samples were first analyzed by GC–MS under full scan acquisition conditions and then under SIM conditions. No PAHs were found in samples under full scan acquisition mode. Also, no PAHs were identified when LLE was used. The recoveries for river sample obtained by GC–MS under full scan acquisition condition were between 69 and 105%, indicating that the process is not influenced by the matrix for the analysis of the promulgated PAHs. However, 10 PAHs at very low levels were detected in the river sample when the SIM mode was used. The method of standard addition was applied to confirm the results. Fig. 6 illustrates the total ion
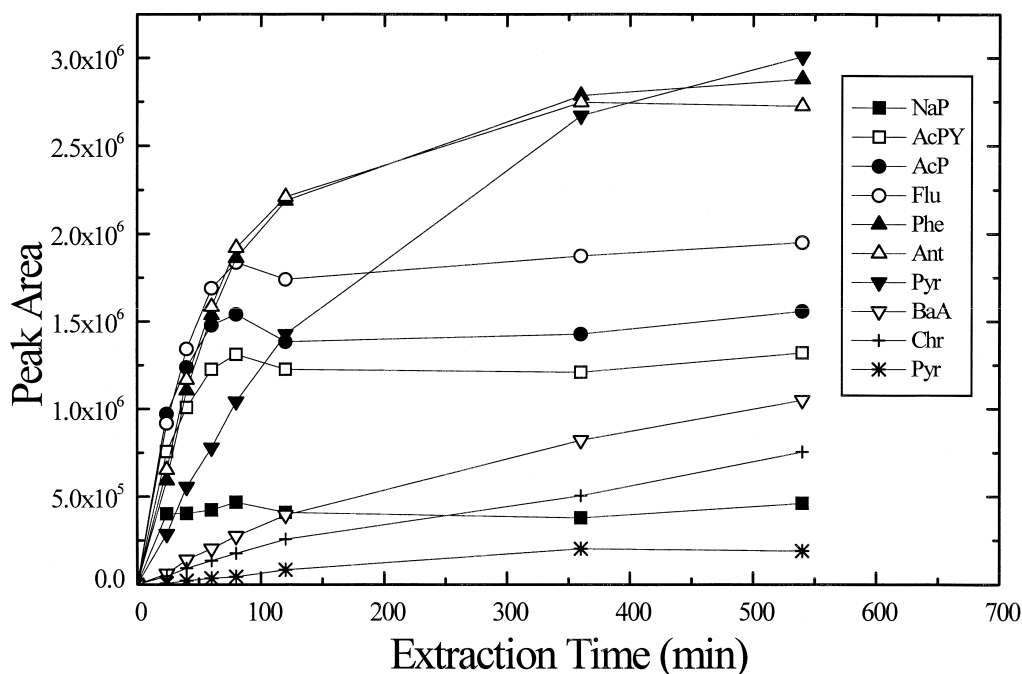

Fig. 5. The extraction time profiles for 10 PAHs at a temperature of 60°C using a 100-μm PDMS fiber. The extraction time was 90 min.
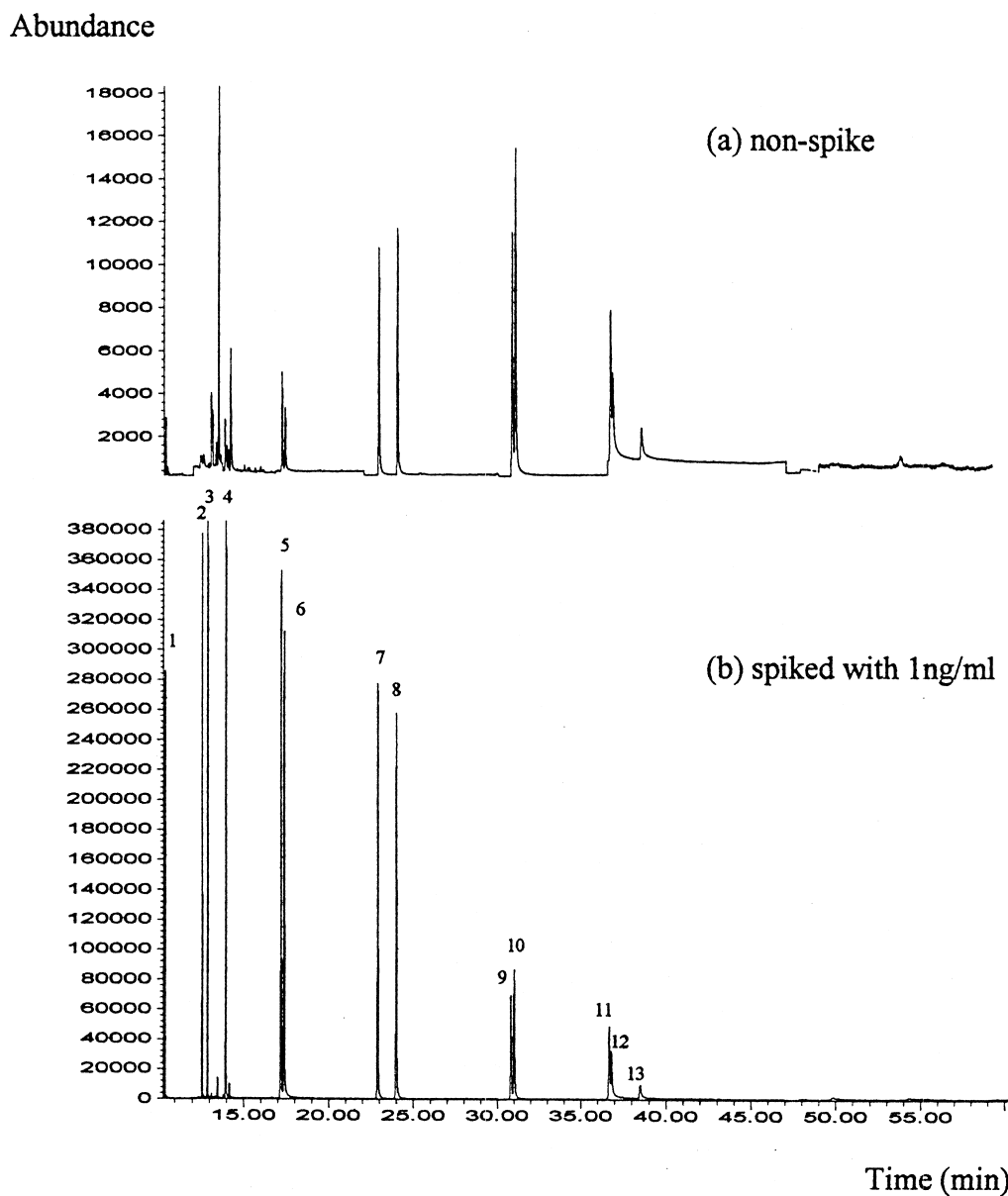
Abundance

Fig. 6. The total ion chromatogram (TIC) obtained by SPME–GC–MS under SIM mode for a river sample in an extraction time of 90 min. (a) Non-spiked and (b) spiked with 1 ng/ml PAHs using a 100-μm PDMS fiber. (1) Naphthalene, (2) acenaphthylene, (3) acenaphthene, (4) fluorene, (5) phenanthrene, (6) anthracene, (7) fluoranthene, (8) pyrene, (9) benz[*a*]anthracene, (10) chrysene, (11) benzo[*b*]fluoranthene, (12) benzo[*k*]fluoranthene, (13) benzo[*a*]pyrene. The peaks corresponding to indeno[1,2,3-*cd*]pyrene, dibenzo[*a,h*]anthracene and indeno[*ghi*]perylene were not shown.

chromatogram (TIC) obtained in the SIM mode for the river sample spiked with 1ng/ml PAHs and non-spiked sample. However, it could not be quantified because the detection concentrations were

found below LOD values obtained under the full scan acquisition mode. The data obtained in this study were considered to be remarkably reasonable and confirmed that the SPME–GC–MS system is

effective in analyzing the 16 EPA promulgated PAHs.

4. Conclusion

In this study, SPME has been successfully applied to the determination of 16 EPA promulgated PAHs using GC–FID and GC–MS. An 85-μm PA fiber or 100-μm PDMS fiber was recommended for the determination of these compounds. The equilibrium time for the PDMS fiber was 20 min to 12 h while for the PA fiber an extraction time of 40 min to 24 h was necessary to reach equilibrium. This solvent-free method shows good precision, linear dynamic range over at least three-orders of magnitude and detection limits in the sub-ng/ml level. HS-SPME at room temperature was successfully applied to the analysis of low-ring PAHs. With a working temperature at 60°C, both direct and headspace SPME provide significant enhancement in sensitivity of high-ring PAHs having low vapor pressures ($>10^{-6}$ mmHg at 25°C) and low Henry's constant (>10 atm ml/mol). The combination of SPME with GC–MS in the full scan and SIM acquisition modes can achieve low LODs and be applied to the determination of PAHs in aqueous phase.

Acknowledgements

References

[1] R.A. Doong, C.Y. Lee, Analyst 124 (1999) 1287.
[2] D.W. Potter, J. Pawliszyn, Environ. Sci. Technol. 28 (1994) 298.
[3] S. Magdic, J. Pawliszyn, J. Chromatogr. A 723 (1996) 111.
[4] T. Gorecki, P. Martos, J. Pawliszyn, Anal. Chem. 70 (1998) 19.
[5] I.J. Barbabas, J.R. Dean, I.A. Fowlis, S.P. Owen, J. Chromatogr. A 705 (1995) 305.
[6] Y. Yang, S.B. Hawrhorne, D.J. Miller, Y. Liu, M.L. Lee, Anal. Chem. 70 (1998) 1866.
[7] S. Magdic, A. Boyd-Boland, K. Jinno, J. Pawliszyn, J. Chromatogr. A 736 (1996) 219.
[8] B.D. Page, G.J. Lacroix, J. Chromatogr. A 757 (1997) 173.
[9] J.J. Langenfeld, S.B. Hawthorne, D.J. Miller, Anal. Chem. 68 (1996) 144.
[10] J. Poerschmann, Z. Zhang, F.D. Kopinke, J. Pawliszyn, Anal. Chem. 69 (1997) 597.
[11] A.L. Nguyen, J.H.T. Luong, Anal. Chem. 69 (1997) 1726.
[12] M.R. Negrao, M.F. Alpendurado, J. Chromatogr. A 823 (1998) 211.
[13] J. Dugay, C. Miege, M.C. Hennion, J. Chromatogr. A 795 (1998) 27.
[14] J. Ai, Anal. Chem. 69 (1997) 3260.
[15] D. Mackay, W.Y. Shiu, K.C. Ma, in: Illustrated Handbook of Physical–Chemical Properties and Environmental Fate of Organic Chemicals, Polynuclear Aromatic Hydrocarbons, Polychlorinated Dioxins and Dibenzofurans, Vol. 2, Lewis, Chelsea, MI, 1992, p. 250.
[16] J. Poerschmann, F.D. Kopinke, J. Pawliszyn, J. Chromatogr. A 816 (1998) 159.
[17] P.G.J. De Maagd, D.E.M. Hulscher, H. Van der Heuvel, A. Opperhuizen, H.M. Sijm, Environ. Toxicol. Chem. 17 (1998) 251.
[18] Z. Zhang, J. Pawliszyn, Anal. Chem. 65 (1993) 1843.
[19] M. Llompart, L. Li, M. Fingas, Anal. Chem. 70 (1998) 2510.