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Determination of trace PAHs in seawater and sediment pore-water by solid-phase microextraction (SPME) coupled with GC/MS

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Abstract A fast and reliable method for the determination of trace PAHs (polynuclear aromatic hydrocarbons) in seawater by solid-phase microextraction (SPME) followed by gas chromatographic (GC) analysis has been developed. The SPME operational parameters have been optimized, and the effects of salinity and dissolved organic matter (DOM) on PAHs recoveries have been investigated. SPME measures only the portion of PAHs which are water soluble, and can be used to quantify PAH partition coefficient between water and DOM phases. The detection limits of the overall method for the measurement of sixteen PAHs range from 0.1 to 3.5 ng/g, and the precisions of individual PAH measurements range from 4% to 23% RSD. The average recovery for PAHs is 88.2±20.4%. The method has been applied to the determination of PAHs in seawater and sediment porewater samples collected in Jiaozhou Bay and Laizhou Bay in Shandong Peninsula, China. The overall levels of PAHs in these samples reflect moderate pollution compared to seawater samples reported elsewhere. The PAH distribution pattern shows that the soluble PAHs in seawater and porewater samples are dominated by naphthalenes and 3 ring PAHs. This is in direct contrast to those of the sediment samples reported earlier, in which both light and heavy PAHs are present at comparable concentrations. The absence of heavy PAHs in soluble forms (<0.1—3.5 ng/L) is indicative of the strong binding of these PAHs to the dissolved or solid matters and their low seawater solubility.

Keywords: solid-phase microextraction, polycyclic aromatic hydrocarbons, dissolved organic matter, marine sediment porewater, PAH-DOM complex.

1 Introduction

Polynuclear aromatic hydrocarbons (PAHs) are important environmental pollutants because many of them are known or suspect carcinogens. In environmental studies, the extent of PAH contamination as a group is often quantified by the concentrations of 16 of the representative PAH species, which are included in the list of priority pollutants as defined by USEPA[1]. Many analytical techniques have been developed in the past years for the determination of these 16 PAH

species, and among them two of the most widely practiced ones are GC/MS and HPLC-Fluorescence. As is often the case in environmental analysis, effective sample preparation and cleanup holds the key of success for the analysis of trace PAHs. Liquid-liquid extraction (LLE) is a classical method used for PAH extraction but the method is tedious, time-consuming and requires large amounts of solvents. Solid-phase extraction (SPE) consumes less solvent, but reproducibility and recovery are often problematic for complex matrices such as seawater. Recently, a new solvent-free technique, solid-phase microextraction (SPME) is gaining popularity for the extraction of many volatile and semi-volatile samples from water samples. The method is solvent-free, sensitive and requires only very small amounts of samples for analysis. Although the application of SPME has been widely reported in recent years, there is still a lack of systematic data on the performance of the technique in seawater analysis, which is the primary objective of this work.

Upon entering the marine environment, the PAHs can distribute themselves among various phases including water, suspended particles, colloidal matter and sediment solids. It has been shown that PAHs can associate strongly with colloidal matter or DOM (Dissolved Organic Matter) in aquatic environment, enhancing their apparent solubility but making them less available to the soluble and sediment phases[2]. Sediment porewater has been shown to play an important role in PAH speciation. In marine environment, it is believed that only the freely dissolved fraction of PAHs is available for bio-uptake[3]. Thus, the existence of DOM in marine environment can greatly influence the bioavailability and distribution of PAHs[4], and the distribution of PAHs between truly soluble form in pore-water and those associated with dissolved organic matter is of particular importance. SPME, which extracts only the truly dissolved fraction[5,6], is an ideal technique to determine the "truly soluble" PAHs in sediment pore water, and to assess how DOM can affect solubility. The association of PAHs with suspended solid particles has been extensively studied[7,8], but relatively scarce reports are available discussing the interaction between PAHs and DOMs[9]. The topic constitutes the secondary objective of this study.

2 Experimental

2.1 PAH and DOM standards

A standard of 16 PAHs including naphthalene, acenaphthylene, acenaphthene, fluorene, phenathrene, anthracene, fluoranthene, pyrene, benza[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, dibenzo[a,h]anthracene, indeno[1, 2, 3-cd]pyrene, benzo [a]pyrene, and benzo[g, h, i]perylene were purchased from Alfa and Aldrich. Standard solutions of 16 PAHs were prepared in acetone in the concentration range of 84—200 mg/L. The DOM standard (molecular weight rang 532—55556 u) was pursed from Alfa and dissolved in ultra-pure water.

2.2 GC analysis

The SPME device and the polydimethysiloxane (PDMS) fibers (100 μm film thickness) were purchased from Supelco. The fibers were conditioned in GC injection port for 2 h before use. The volume of the headspace vials used for SPME extraction was 15 mL.

An Agilent 6890N GC-5973N MS System equipped with a 7683 series Auto Sampler was used for analysis. Chromatographic separation of 16 PAHs was accomplished on a HP-5MS capillary column (30 m×0.32 mm I.D., 0.25 mm film thickness). Helium was the carrier gas and a flow-rate of 1.0 mL/min was used for column elution. Sample injection was carried out in the splitless mode with an injection volume of 1 μL. The GC oven temperature was programmed first from 70 to 120℃ at a rate of 5℃/min, then to 300℃ at a rate of 10℃/min, and finally held constant for 7 min. The temperatures of the injection port and the interface to the MS system were set at 250℃ and 300℃, respectively. Peak quantification was carried out in Selected Ion Monitoring (SIM) mode.

2.3 Seawater samples

Surface seawater samples were collected from Haibo River, Tianjiayao in Jiaozhou Bay and Dongying Aquaculture Farm in March 2005. Samples were taken using precleaned glass bottles and frozen at 4℃. Aliquots of the sample were filtered under vacuum after returning to the laboratory to remove suspended particulate matter (SPM). Surface sediment samples

were collected with a grab sampler in May 2005, and the top 1 cm surface layer was carefully removed with a stainless steel spoon and stored in precleaned glass bottles. After returning the laboratory, the sediments were centrifuged (3000 r/min) at 4℃ to obtain sediment porewater. Pore-water samples were collected in glass vials with teflon-lined septa. Seawater and sediment pore-water samples were all stored at 4℃ until analyses.

2.4 SPME operation

SPME operations were carried out in 14 mL seawater samples placed in 15 mL amber vials. The vials were capped with PTFE-coated septa. SPME fibers were inserted into the sample vials through the small holes on the caps. The SPME experiments were conducted by immersing the fiber into the aqueous phase (direct SPME) at room temperature for 60 min, during which the analytes reached adsorption equilibrium between the bulk sample and the coatings on the fibers. Magnetic stirring with a PTFE coated stirring bar was used to agitate the samples or standard solutions during SPME extraction at a agitation speed of 1000 r/min. Aqueous standards of PAHs were prepared by proper dilution of the stock solution to the final concentrations of 0.16—0.32 ng/mL. After extraction, the adsorbed analytes were injected into GC by thermal desorption of the fiber in the GC injector port at 280℃.

For PAH-DOM interaction studies, the SPME runs were made in standard PAH solutions (2—5 ng/mL) mixed with known amounts of DOM. The effects of DOM on water PAH were examined by comparing the amounts of PAH adsorbed on SPME fiber with and without the presence of DOM. The differences between the two were assigned to be those PAHs which were bound to DOM, and thus unavailable for fiber adsorption. The DOM concentrations studied were 0, 5, 10, 20, 50, 100 mg/L in short contact-time experiments; and 0, 5, 10, 30 mg/L in long contact-time (adsorption equilibrium) experiments.

3 Results and discussion

3.1 Optimization of experimental conditions

The effects of operational parameters including the pH value, temperature, and extraction time on SPME extraction efficiency have been reported previously[10−12]. The SPME runs made in this study were under conditions where these parameters were optimized, i.e., 60 min extraction time, 25℃ extraction temperature and pH of 8.2. Two additional parameters evaluated in this study were water salinity and the thermal desorption time of the SPME fibers during GC analysis, and these results are summarized as follows.

(1) The effect of salinity on SPME extraction. The salinity of seawater is about 30. The PAH extraction efficiency by SPME fiber was investigated over a wide range of salt content in order to gain better understanding on the effects of seawater salinity. Samples of different salinity were prepared by adding different amounts of NaCl into the water samples to obtain final concentrations of 30, 60, 120, 180 g/L respectively. The extraction efficiency of fresh water samples was also studied for comparison. Figs. 1(a) and (b) show the effect of NaCl concentration on PAH extraction efficiencies. The results show that the effect of salt content on extraction efficiency varies greatly among different PAH species. Compared with fresh water, the efficiencies of light PAHs such as naphthalene, acenaphthylene, acenaphthene and fluorene in seawater are higher, while the opposite is true for the rests of the heavier PAHs. A further increase in salt content reduces the extraction efficiency for all the PAHs except naphathene. The salinity effects on extraction efficiency of solutes are known to correlate with the solubility and polarity of the analytes[13]. According to the solvophobic interaction principle, the solvophobic interaction between solute molecular and the alkyl group of the bonded stationary phase on fiber involves reversible surface adsorptions. Increased salinity enhances fiber extraction efficiency because it enhances the hydrophobic interaction between the solutes and the adsorption layer. On the other hand, the presence of excessive salt in water could lead to a change of the physical configuration of the chemical functionalities on the surface coating, which would then depresses the extraction efficiency. The interplay of the two opposing factors is difficult to sort out from the limited data we have here. But the observation shows clearly that the salt content in normal seawater offers near-optimum salinity level for PAH extractions.

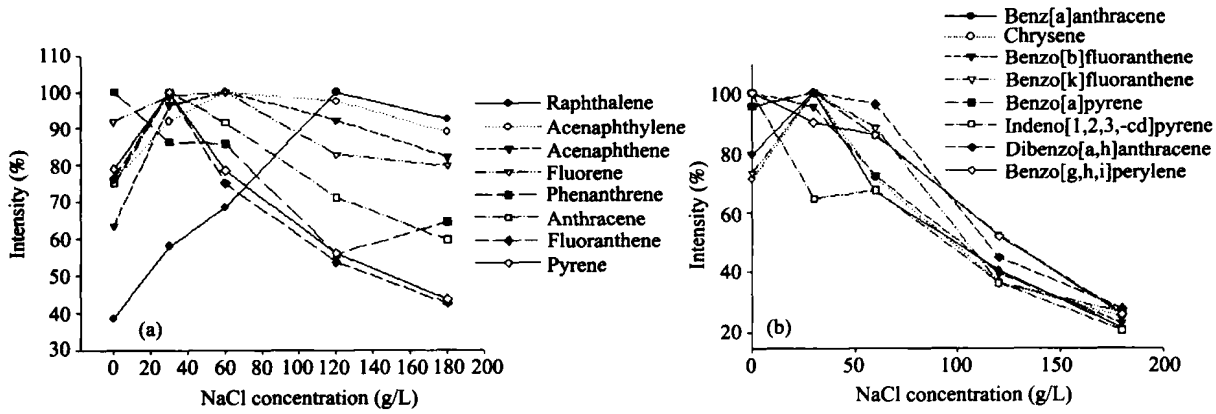

Fig. 1 Effect of salinity on extraction efficiency of PAHs by SPME.

(2) Thermal desorption time of SPME fiber. The SPME fiber was coated with polydimethylsiloxane (PDMS), which has strong adsorption capability towards hydrophobic PAH species. The recovery of adsorbed PAHs during GC analysis by thermal desorption was investigated using samples of standard PAH solutions. After extraction, the adsorbed PAHs on SPME fiber were thermally desorbed in the GC injector in two sequential runs. Data from the first run was used to determine PAH recovery from normal operation. The PAHs observed in the second run provided information on residue PAHs remaining on the fiber which were not desorbed in the first run. Results showed that the residue PAHs remaining on the fiber amounted to only 0.9—9.0 percent and 0—6.7 percent of the total fiber-adsorbed PAHs, respectively, after 5 min and 7 min desorption time. There is no significant difference between the 5 min and 7 min runs. It can be concluded from the experiments that errors caused by incomplete desorption were minor under normal operation. Since the sample and the calibration runs were made under the same conditions, these errors are likely to be further reduced due to error cancellations.

3.2 The effect of DOM on PAH measurement

PAHs dissolved in marine environment are known to associate with DOM in seawater to form PAH-DOM complex. This would affect the total measurable PAHs by SPME. On the average, the concentration of dissolved organic carbon ranges from about 5—10 mg/L in seawater to 40—60 mg/L[3] in sediment or pore-water. The effects of DOM on PAH recovery were investigated by running samples spiked with different concentrations of DOM. The PAHs and DOMs in the samples were allowed to equilibrate for 24 h undisturbed before SPME analysis. In the presence of DOM, a portion of the PAHs is expected to form DOM-PAH complex, and thus unavailable for SPME extraction. Since the adsorption rate of DOM on SPME fiber is much slower than those of PAHs, such competitive adsorption is not expected to affect significantly the PAH measurement. Any reduction in measured PAH by SPME upon DOM addition would therefore be the result of DOM-PAH complexation in bulk water.

As shown in Fig. 2, it is clear that the extractable PAHs decrease significantly with increasing DOM concentration, especially between the 0 to 10 mg/L DOM range. The result agrees very well with those reported in literature studies[3,14]. In natural seawater, the PAH-DOM association processes should be well equilibrated. The SPME measured PAHs thus represent the portion of soluble PAHs which are in equilibrium with the complexes. The situation could be more complicated, however, in waters with multiple pollution source input, and with each having quite different DOM and PAH contents such as those commonly encountered in estuary waters. Here the PAH-DOM reactions in the mixing water have not been fully equilibrated. The PAH measurement in these samples should therefore take this factor into consideration.

3.3 Partition coefficients measured by SPME

The SPME technique provides a convenient way to

determine the partition coefficients of PAHs among different phases. We have investigated the time-dependent association behavior of PAHs-DOM complexation, and the results are shown in Fig. 3. Fig. 3 shows that PAH-DOM association is a slow process, with equilibrium time in the order of 6—8 d. The mechanism of PAH-DOM association has been studied and reported in the literature. The general hypothesis is that the process involves two different types. The first is physical interaction which proceeds with low activation energies and fast rate[9]. The association is loose and mobile. The other is a stronger but slower chemical interaction. The association kinetics of PAH-DOM complex is analogous to those occurring between metal ions and DOM[15]. The factors that can effect the association of PAHs include the configuration of the hydrophobic analytes, the source and the aromaticity of DOM, etc.[16,17]. The processes can be represented by the following reaction:

$$PAH_{free} + DOM \longleftrightarrow PAH_{DOM},$$

where PAH_{free} is PAHs truly dissolved in water, and PAH_{DOM} is PAHs bound to DOM.

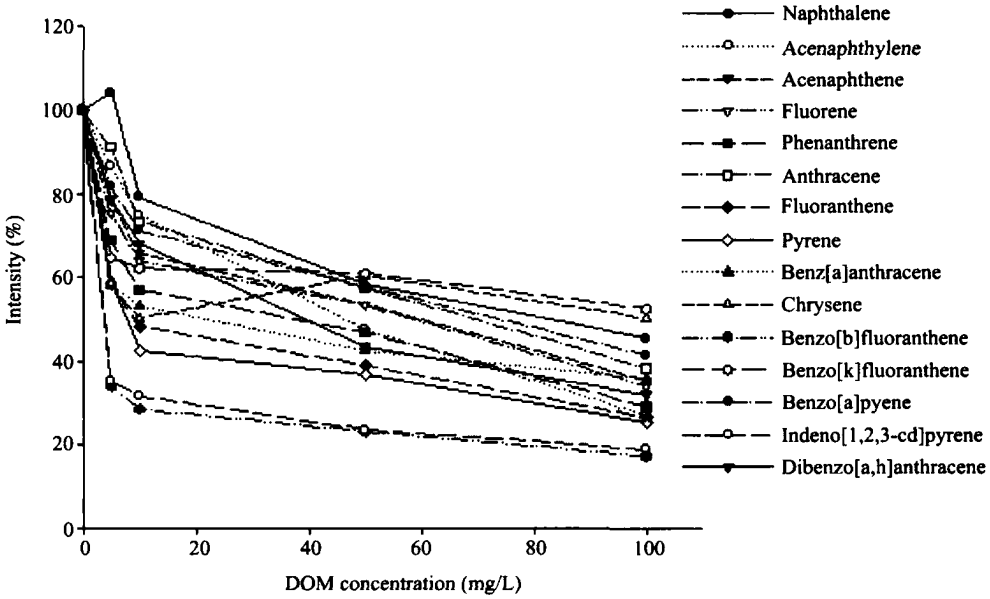

Fig. 2. Effect of DOM concentration on PAH extraction efficiency by SPME.

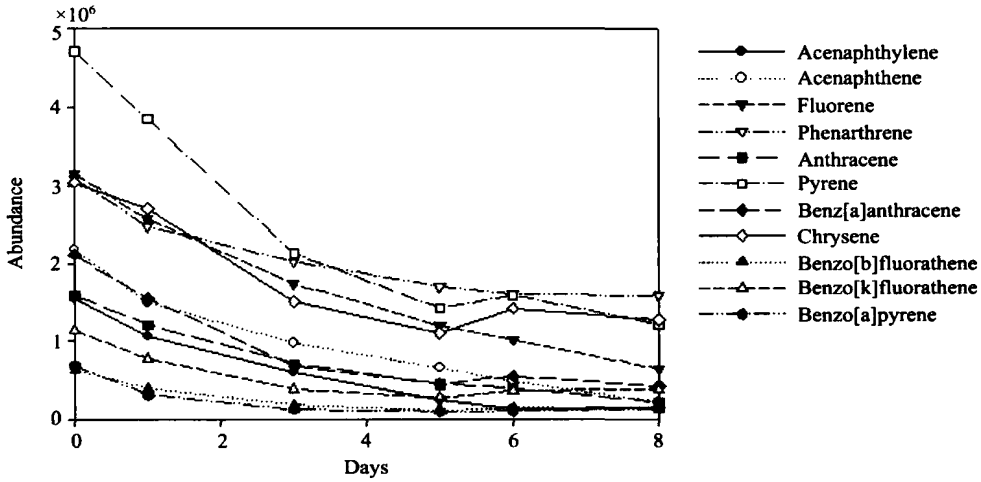

Fig. 3. Time-dependent association between PAHs and DOM (DOM: 10 mg/L, PAHs spiked: 2—5 ng/mL).

The partition coefficient could then be calculated according to eq. (1):

$$K_{\mathrm{DOW},i} = \frac{c_{\mathrm{bound},i}}{c_{\mathrm{free},i}} \times \frac{1}{c_{\mathrm{DOM}}} = \frac{c_{\mathrm{total},i} - c_{\mathrm{free},i}}{c_{\mathrm{free},i}} \times \frac{1}{c_{\mathrm{DOM}}} = \frac{c_{\mathrm{blank},i} - c_{\mathrm{free},i}}{c_{\mathrm{free},i}} \times \frac{1}{c_{\mathrm{DOM}}}. \quad (1)$$

In the above equation, $c_{\mathrm{free},\,i}$, $c_{\mathrm{bound},\,i}$ and $c_{\mathrm{total},\,i}$ are the respective concentrations of the analyte i in the truly dissolved state, bound on the DOM phase and the total amount of analyte i in the water samples; $c_{\mathrm{blank},\,i}$ is the concentration of analyte i in pore-water without the addition of DOM ($c_{\mathrm{total},\,i} = c_{\mathrm{blank},\,i}$); $K_{\mathrm{DOM},\,i}$ is the partition coefficient for analyte i between DOM and water; and c_{DOM} is the concentration of DOM in the water sample.

As was reported in the literature[18], there is a correlation between the DOM-water partition coefficient (K_{DOM}) and octanol-water partition coefficient ($K_{\mathrm{OW},\,i} = c_{i\ \mathrm{in\ 1\text{-}octanol}}/c_{i\ \mathrm{in\ H_2O}}$) represented by eq. (2) below:

$$\log K_{\mathrm{DOM}} = a \log K_{\mathrm{OW}} + b. \quad (2)$$

The regression coefficients a and b are empirical, with no definite physiochemical meaning. The K_{DOM}-K_{OW} correlation is valid when the nonpolar hydrophobic interactions prevail between the solutes and DOM as in the case here involving the PAHs and DOM pairs.

The partition coefficients K_{DOM}'s were calculated for the 13 PAHs using eq. (1). The results are presented in Table 1. The literature data are included in the table for comparison. As shown in Table 1, the overall agreement between our results and the literature data are quite satisfactory for all but a few PAHs. The minor discrepancies existing between the two sets of data are not surprising in view of the differences involved in both DOM materials used and the measurement techniques employed. Table 1 also shows that the PAH partition coefficient decreases slightly with increasing DOM concentration. When the concentration of DOM is increased from 5 mg/L to 30 mg/L, the partition coefficient for the 13 PAHs is lowered by about 4%, i.e., $K_{\mathrm{DOM},\,c_{\mathrm{DOM}}\,=\,5\ \mathrm{mg/L}}/K_{\mathrm{DOM},\,c_{\mathrm{DOM}}\,=\,30\ \mathrm{mg/L}} = 1.04$. This finding is quite similar to the literature results reported for other hydrophobic organic pollutants such as PCB and DDT[19].

Table 1 also listed K_{OW} values for the PAHs reported in the literature[20] by SPME technique. Considering the differences in K_{DOM}'s at different DOM concentrations[21], the correlation between the calculated K_{DOM} and the reported K_{OW} values yields the following relationships:

$c_{\mathrm{DOM}} = 5$ mg/L: $\log K_{\mathrm{DOM}} = 0.7944 \log K_{\mathrm{OW}} + 0.773$ ($R^2 = 0.91$); $c_{\mathrm{DOM}}=10$ mg/L: $\log K_{\mathrm{DOM}}=0.7905 \log K_{\mathrm{OW}} + 0.668$ ($R^2 = 0.97$); $c_{\mathrm{DOM}} = 30$ mg/L: $\log K_{\mathrm{DOM}} = 0.714 \log K_{\mathrm{OW}} + 1.0407$ ($R^2 = 0.91$).

Using the above correlations, one can then calculate the value of K_{DOM}'s for PAHs or other similar hydrophobic organic pollutants from the more widely available K_{OW} values. Results also show that $\log K_{\mathrm{DOM}}$ increases with increasing $\log K_{\mathrm{OW}}$. This indicates that the degree of interaction with DOM is related to the hydrophobicity of the compound, with more hydrophobic compounds interacting more strongly with humic material and therefore being removed to a greater extent from the aqueous phase.

In well equilibrated seawater samples, an equilibrium state is expected between freely dissolved PAHs and PAHs bound to DOM. The freely dissolved and total concentration of PAHs can be calculated through external and internal standard calibration with SPME technique[5]. Using eq. (1), the K_{DOM} values could be calculated and used to estimate the capability of PAHs to bind with DOM in different marine environment.

3.4 Linearity, detection limit and precision of SPME measurement

Under optimized SPME conditions, a series of calibration runs were made and calibration curves were constructed by plotting the observed peak area against concentration for individual PAHs. The samples were prepared in seawater where the DOM concentration is generally less than 5 mg/L. The Detection limits, precision and recovery results for individual PAHs derived from the calibration runs are summarized in Table 2. Overall, the performance of the method is quite satisfactory. Excluding phenanthrene, which suffers from significant GC background interference, the PAH recoveries range from 75.6% to 107% with a mean of 88.2%. Analytical precision of the measurement ranges from 4% to 23% with a mean of 11.9 % (RSD). The detection limits are in the range of few tenths to few ng/L, or ppt range, which are considerably better than those achievable by other conventional techniques.

Table 1 K_{DOM} of PAHs in different concentrations of dissolved organic matter

Compounds	$\log K_{DOM}$				
	$\log K_{OW}$[20]	5 mg/L	10 mg/L	30 mg/L	from literature
Naphthalene	3.3	3.14	3.29	3.85	3.29(a)
Acenaphthylene	4	3.88	3.92	3.82	3.96(b)
Acenaphthene	3.92	3.80	3.77	3.76	3.67(a)
Fluorene	4.18	3.94	3.86	3.86	3.86(a)
Phenanthrene	4.45	4.56	4.14	4.03	4.29(a)
Anthracene	4.46	4.74	4.21	4.13	4.42(a)
Fluoranthene	5.16	5.10	4.83	4.66	4.86(a)
Pyrene	5.18	5.04	4.73	4.58	4.62(b)
Benz[a]anthracene	5.91	5.22	5.14	5.10	5.15(b)
Chrysene	5.86	5.23	5.11	5.09	5.16(b)
Benzo[b]fluoranthene	5.8	5.31	5.41	5.46	5.70(b)
Benzo[k]fluoranthene	6	5.26	5.36	5.42	5.56(b)
Benzo[a]pyrene	6.04	5.86	5.70	5.64	5.68(b)

(a) Data from ref. [22], measured by SPME technique. (b) Data from ref. [23].

Table 2 The detection limits, precision and recoveries of SPME method

PAHs	GC retention time (min)	Correlation coeff. of calib curve	Detection limit (ng/L)	RSD (n = 6, %)	Recovery (%)
Naphthalene	8.96	0.9979	0.2	4	87.5
Acenaphthylene	14.32	0.9981	0.7	4	88.3
Acenaphthene	14.83	0.9999	0.3	10	85.4
Fluorene	16.26	0.9979	0.2	12	75.6
Phenanthrene	18.7	0.9902	0.2	17	52.5
Anthracene	18.83	0.9993	0.4	11	89
Fluoranthene	21.63	0.9973	0.1	9	79.5
Pyrene	22.15	0.9979	0.1	7	78.7
Benz[a]anthracene	25.08	0.9946	0.1	21	89.2
Chrysene	25.16	0.9804	0.3	17	76.8
Benzo[b]fluoranthene	27.49	0.9895	0.8	8	81.3
Benzo[k]fluoranthene	27.55	0.9959	1.7	12	85.7
Benzo[a]pyrene	28.16	0.9915	1.1	6	98.3
Indeno[1, 2, 3-cd]pyrene	30.91	0.9882	1	19	97.1
Dibenz[a,h]anthracene	31.01	0.9002	3.5	23	138.5
Benzo[g, h, i]perylene	31.64	0.9583	1.4	11	107.4
Average value			0.76	11.9	88.2

4 Analysis of PAHs in seawater and sediment porewater samples

Table 3 summarizes PAHs concentrations detected in coastal waters around Jiaozhou Bay and Dongying in Shandong peninsula, China using the developed SPME method. These results are compared with PAHs found in surface seawater in Maluan Bay in Xiamen, China. The latter values were obtained by liquid-liquid extraction followed by GC analysis. Fig. 4 shows the total ion chromatogram (TIC) obtained in the SIM mode for the seawater sample (Haibo River). Table 4 shows the PAH concentrations in the porewater of 10 sediment samples collected in Jiaozhou Bay. Because of its high sensitivity, SPME is ideally suited for the analysis of pore water samples. Table 4 shows that the total PAHs concentrations in sediment pore-water in the 10 samples collected in Jiaozhou Bay varied from 23.8 ng/L to 2989.9 ng/L. The average concentration of total PAH is 305.7 ng/L. The PAH distribution among these stations differs substantially from site to site, reflecting the complexicity in PAH source and the sedimentation processes in the area. PAHs in sediment porewater can be concentrated by fish and seashell in the marine environment. The food safety standards for PAHs in aqueous environment were constituted by international biology organization or country[24]. The

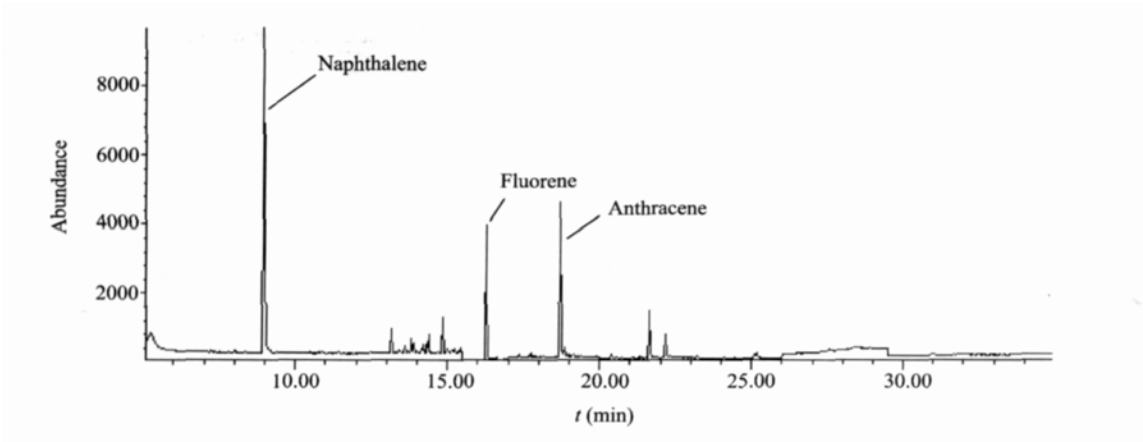

Fig. 4. GC-MS ion chromatogram of seawater sample collected around Haibo River in Jiaozhou Bay.

Table 3 Distribution and concentration levels of PAHs found in seawater samples of different sampling sites

PAHs	Haibo River, Jiaozhou Bay	Tianjiayao, Jiaozhou Bay	Dongying Aquaculture Farm	Maluan Bay, Xiamen[25]
Naphthalene	357.5	473.1	207.14	2
Acenaphthylene	ND	ND	437.26	4
Acenaphthene	ND	ND	ND	ND
Fluorene	97.2	35.4	ND	12.3
Phenathrene	ND	ND	ND	13.6
Anthracene	17.5	16.5	ND	ND
Fluoranthene	ND	62.1	ND	2.8
Pyrene	ND	ND	ND	3
Benz[a]anthracene	ND	ND	ND	ND
Chrysene	ND	ND	ND	17.9
Benzo[b]fluoranthene	ND	ND	30.41	1.1
Benzo[k]fluoranthene	ND	ND	ND	0.4
Benzo[a]pyrene	ND	ND	ND	1
Indeno[1,2,3-cd]pyrene	ND	ND	ND	1.6
Dibenz[a,h]anthracene	ND	ND	ND	2.1
Benzo[g, h, i]perylene	ND	ND	ND	1.7
Total	472.2	587.1	674.8	63.5
2—3 ring PAHs concentration	472.2	525.0	644.4	31.9
2—3 ring PAHs percent (%)	100	89.4	95.5	50.2
Naphthalene percent (%)	75.7	80.6	30.7	31.5

ND: Not detected (Detection limits are shown in Table 2).

concentrations of PAHs in sediment pore-water in Jiaozhou Bay are below these standards, except for anthracene in HP-07, HP-08 and HP-09 stations. The concentrations of 4 or more ring PAHs in HP-03 station are significant higher than those of the other samples and the safety guidelines. The exact sources of these PAHs remain to be identified in our future studies.

As shown in Table 3, total PAHs concentrations in the coastal waters around Jiaozhou Bay, Qingdao, Tianjiayao (Laizhou Bay) and Dongying are 472.2 ng/L, 587.1 ng/L and 674.8 ng/L respectively. Among the PAHs, the dominant one is naphthalene; and 2—3 ring PAHs account for nearly all the PAHs observed. The PAH distribution in these three sites is different from those of Maluan Bay in Xiamen. There the 3 or

Table 4 PAHs concentrations of sediment porewaters in Jiaozhou Bay, Qingdao (ng/L)

PAH	HP-01	HP-02	HP-03	HP-04	HP-05	HP-06	HP-07	HP-08	HP-09	HP-10	Evaluation standard (μg/L)
Naphthalene	16.8	11.7	47.3	11.0	251.1	10.2	33.8	74.7	18.2	213.5	1.0－10*
Acenapthylene	1.6	2.7	2.9	4.5	8.8	1.6	6.6	25.0	3.2	35.6	
Acenaphthene	5.3	2.6	3.8	4.2	18.0	ND	22.1	26.4	9.1	67.1	
Fluorene	14.0	5.9	10.3	21.3	25.0	19.0	78.3	25.7	29.2	94.5	
Phenathrene	6.0	ND	15.0	ND	18.4	ND	79.2	171.0	ND	353.8	2.0**
Anthracene	ND	ND	ND	ND	ND	ND	9.4	16.3	ND	19.2	0.005－0.05*
Fluoranthene	8.0	ND	8.2	20.6	6.8	7.1	24.3	9.4	9.1	18.4	0.5**
Pyrene	1.1	0.9	1.6	1.6	1.3	1.7	5.3	5.4	1.9	9.7	
Benz[a]anthracene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.2**
Chrysene	1.6	ND	81.8	8.2	ND	ND	ND	ND	ND	ND	
Benzo[b]fluoranthene	ND	ND	2.9	ND	ND	ND	ND	ND	ND	ND	0.1**
Benzo[k]fluoranthene	ND	ND	12.5	ND	ND	ND	ND	ND	ND	ND	0.1**
Benzo[a]pyrene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.01－0.1*
Indeno[1, 2, 3-cd]pyrene	ND	ND	440.8	ND	ND	ND	ND	ND	ND	ND	
Dibenz[a,h]anthracene	10.5	ND	220.8	14.8	ND	ND	6.0	2.9	1.3	4.0	
Benzo[g, h, i]perylene	ND	ND	156.1	ND	ND	ND	ND	ND	ND	ND	0.02**
Total	65.0	23.8	1004.0	86.1	329.4	39.6	264.9	356.7	72.0	815.7	
2－3 ring PAH percent (%)	67.3	96.1	7.9	47.5	97.6	77.7	86.6	95.0	83.0	96.1	
Henathrene/Anthracene	ND	ND	ND	ND	ND	ND	8.38	10.50	ND	18.46	
Fluoranthene/Pyrene	7.4	ND	5.00	12.80	5.31	4.15	4.57	1.74	4.93	1.90	

ND: Not detected (detection limits are shown in Table 2).
* Ostro and Paris Committee ecotoxicology estimation standard; ** Ireland maximum allowed concentration.

more ring heavier PAHs are present in significant quantities, while the concentration of naphthalenes is much lower. Our seawater samples were collected in Jiaozhou Bay or Laizhou Bay in Shandong Peninsula, which are both semi-enclosed water body with slow water exchange rate with the open sea. Both bays are surrounded by highly populated areas with many seasonal streams or canals empty into the bay carrying industrial and domestic waste discharges. The high naphthalene concentration observed in these samples is indicative of the extensive industrial pollution problem of the area. The absence of heavier PAHs such as BaP in the water phase, including seawater and porewater, is noted. In a separate study from our laboratory[1)], significant concentrations of PAHs including 4 or 5 ring PAHs were actually found in sediment samples collected in these areas (Our paper on sediment is listed in footnote 1)). The total sediment PAHs (excluding naphthalenes) amounted to few hundreds ng/g, which are comparable to the soluble PAHs observed in this work. The combined results thus indicate that the 3 or more ring PAHs exist primarily in sediment-associated forms. The absence of these PAHs (< 0.1－3.5 ng/L) in the porewater indicates their immobility from the sediment solids due likely to their low water solubility or strong solid-binding strength, or both.

5 Conclusion

SPME sampling coupled with GC-MS analysis has been developed for the quantitative analysis of trace PAHs in marine environment. The SPME oper-

1) Wang L, Lee F S-C, Wang X R, *et al*. Chemical characteristics and source implications of petroleum hydrocarbon contaminants in the sediments near major drainage outfalls along the coastal of Laizhou Bay, Bohai Sea, China. J Environ Monit Assess, 2006 (in press)

ating conditions have been optimized and analytical performance including detection limits, precision and PAHs recoveries has been evaluated: The mean recovery for the 16 PAHs is 88.2%. The mean analytical precision of the technique represented by RSD of repeated samples ($n = 6$) is 11.9 %. The detection limits for individual PAHs range from 0.1－3.5 ng/L, which are considerably better than those achievable by conventional techniques. The effects of salinity and DOM on SPME extraction have been investigated. PAH are found to associate strongly with DOM, leading to the formation of PAH-DOM complex in equilibrium with the two individual partners. SPME can extract only the freely dissolved portion of the total PAHs, and thus provides a convenient way to measure the partition coefficients of PAHs between the bound and the free phases. The developed method has been applied to the determination of PAHs in seawater and porewater samples collected in Jiaozhou Bay and Laizhou Bay in Shandong Peninsula, China. The overall levels of PAHs in these samples show only moderate pollution compared to seawater samples elsewhere. The PAH distribution pattern shows that the soluble PAHs in seawater and porewater samples are dominated by naphthalenes and 3 ring PAHs. This is in direct contrast to what was reported for the sediment samples collected in these sites, in which both light and heavy PAHs are present in comparable concentrations. The absence of heavy PAHs in soluble forms in seawater (<0.1－3.5 ng/L) is indicative of their strong binding to the dissolved or solid matters and low seawater solubility.

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