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Polydimethylsiloxane/metal-organic frameworks coated fiber for solid-phase microextraction of polycyclic aromatic hydrocarbons in river and lake water samples

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ABSTRACT

In this study, polydimethylsiloxane/metal-organic frameworks (PDMS/MOFs), including PDMS/MIL-101 and PDMS/MOF-199, were immobilized onto a stainless steel wire through sol–gel technique as solid-phase microextraction (SPME) fiber coating. The prepared fibers were used for the extraction of some polycyclic aromatic hydrocarbons (PAHs) from water samples prior to gas chromatography–mass spectrometry (GC–MS) analysis. Under the optimized experiment conditions, the PDMS/MIL-101 coated fiber exhibited higher extraction efficiency towards PAHs than that of PDMS/MOF-199. Several parameters affecting the extraction of PAHs by SPME with PDMS/MIL-101 fiber, including the extraction temperature, extraction time, sample volume, salt addition and desorption conditions, were investigated. The limits of detection (LODs) were less than 4.0 ng L^{-1} and the linearity was observed in the range from 0.01 to 2.0 μg L^{-1} with the correlation coefficients (r) ranging from 0.9940 to 0.9986. The recoveries of the method for the PAHs from water samples at spiking levels of 0.05 and 0.2 μg L^{-1} ranged from 78.2% to 110.3%. Single fiber repeatability and fiber-to-fiber reproducibility were less than 9.3% and 13.8%, respectively.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs), mainly originated from the incomplete combustion of organic materials, are a large class of ubiquitous and persistent environmental contaminants, which are composed of up to six benzene rings fused together such that the any two adjacent benzene rings share two carbon bonds [1,2]. Due to their adverse effects on human health and environment [3], the PAHs have drawn attention by a number of international environmental protection agencies and scientific communities. Since PAHs are non-polar and very hydrophobic compounds with low water solubilities, they often exist at low concentrations in aquatic environment. Therefore, it is necessary to preconcentrate the analytes from samples before their instrumental analysis.

Solid-phase microextraction (SPME), as a relatively new sample preparation technique developed by Pawliszyn and coworkers in the early 1990s [4], has exhibited the advantages over other conventional sample preparation methods by its ability to integrate sampling, extraction and preconcentration of the analytes into a single one step and being capable of direct desorption of the analytes into the chromatographic systems for analysis [5–7]. In principle, the extraction performance of SPME in terms of sensitivity, selectivity, and reproducibility is determined by the properties of the adsorbent material coated on the fiber and the nature of the analytes. However, currently, the number and the variety of the commercially available SPME coatings are still limited [8]. To solve this problem, various novel home-made SPME coating materials, such as polymeric ionic liquids [9–11], graphene and graphene-based materials [12–14], carbon nanotubes [15,16], and porous materials [17,18], have been synthesized and explored for the use as the SPME fiber coatings.

Metal-organic frameworks (MOFs), constructed from metal ions or clusters and organic ligands, are a class of exotic porous solid material [19]. The outstanding properties of MOFs include their diverse structure topology, tunable pore size, high surface area, the availability of in-pore functionality and outer-surface modification, and good thermal stability [20]. Due to their unique structure and properties, MOFs have been widely applied in gas storage, drug delivery, molecular sensing and catalysis [21]. Moreover, these features endow the MOFs with an application potential in analytical chemistry, especially as the adsorption material in sample pretreatment, such as in micro-solid-phase extraction (μ-SPE) [22], solid-phase extraction (SPE) [23], magnetic solid-

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phase extraction (MSPE) [24,25] and stir bar sorptive extraction (SBSE) [26].

Recently, MOFs-based SPME researches have received an increasing attention from scientists. Generally, the reported MOFs coating methods for the preparation of SPME fibers have mainly involved *in situ* hydrothermal growth [27], layer-by-layer deposition [28] and covalent bonding approach [29]. More recently, Zhao et al. reported an adhesive method for the preparation of MIL-53 (Al, Cr, Fe) fibers for the SPME of 16 PAHs in water samples [30]. On the other hand, the sol–gel technique [31], which has been introduced to prepare SPME fibers in recent years, is a commonly used method for the preparation of inorganic polymer and inorganic–organic hybrid materials in mild conditions. Often, the SPME fibers prepared by the sol–gel technique have the advantages such as low cost, material homogeneity, porous structure, high thermal stability and strong adhesion of the coating to the substrate [32]. However, to the best of our knowledge, the sol–gel technique for the preparation of MOFs fibers has not been reported yet.

In the current work, MOFs were successfully immobilized onto a stainless steel wire through sol–gel technique. The performance of the laboratory-made fibers for the SPME of five PAHs (naphthalene, biphenyl, acenaphthene, fluorene and phenanthrene) from environment water samples was investigated prior to their gas chromatography–mass spectrometry (GC–MS) analysis.

2. Experimental

2.1. Instruments

A Shimadzu (Kyoto, Japan) GCMS-QP2010SE system equipped with a TG-5MS fused silica capillary column (30 m × 0.25 mm × 0.25 μm) (Scientific, Thermo, www.thermo.com/columns) was used for analysis. The column was first maintained at 70 °C for 1 min and increased to 120 °C at a rate of 20 °C min^{-1}, then raised to 270 °C at 30 °C min^{-1} and kept at this temperature for 2 min. The injector was operated in the splitless mode and the injection port temperature was maintained at 250 °C. An electron impact ionization source was operated at 70 eV and 200 °C. The MS detection was made using full-scan mode at a detector voltage of 0.7 kV and GC–MS interface temperature was kept at 250 °C. The ions including one for quantitation and two for qualification (shown in Table 1) were monitored for each PAHs based on the full-scan results.

The DF-101S temperature-controlled magnetic stirrer was purchased from Baoding High-tech Zone Sunshine Science Instrument Company (Baoding, China). The WH-861 vortex shaker was from Shanghai Jinggong Industrial Limited Company (Shanghai, China). The XRD patterns of MOFs were recorded with a Rigaku D/max 2500 X-ray diffractometer (Japan) using Cu Kα radiation (40 kV, 150 mA) in the range of 2θ from 0.5° to 10°. The infrared (IR) spectra were measured with a WQF-510A spectrometer (Beijing, China). The thermal properties of the PDMS/MOF coatings were measured by thermal gravimetric analysis with a TG209F1 instrument (NETZSCH, Germany).

2.2. Reagents and materials

Terephthalic acid and 1,3,5-benzenetricarboxylicacid (H_3BTC) were supplied by Aladdin-Reagent (Shanghai, China). Dichloromethane (CH_2Cl_2), methyltrimethoxysilane (MTMOS), hydrofluoric acid (HF, 40%, w/w), dimethylformamide (DMF), trifluoroacetic acid (TFA, 99%) and hydroxy terminated polydimethylsiloxane (HO-PDMS) were obtained from the Boaixin Chemical Reagents Company (Baoding, China). Standards of naphthalene, biphenyl, acenaphthene, fluorene and phenanthrene were purchased from Aladdin-Reagent (Shanghai, China). A mixture stock solution containing naphthalene, biphenyl, acenaphthene, fluorene and phenanthrene each at 5.0 mg L^{-1} was prepared in acetone and stored at 4 °C.

The water used throughout the work was double-distilled on a SZ-93 automatic double-distiller purchased from Shanghai Yarong Biochemistry Instrumental Factory (Shanghai, China). River water and lake water samples were collected from Baoding (Baoding, China). The samples were directly used for the subsequent SPME without any pretreatment.

Stainless steel wires (o.d. 304, 310 μm) were purchased from the Anting Micro-Injector Factory (Shanghai, China). The commercial SPME fiber coated with PDMS (100 μm) was supplied by Supelco (Bellefonte, PA, USA).

2.3. Synthesis of MIL-101 and MOF-199

MIL-101 was synthesized according to the reference method [21]. Terephthalic acid (166 mg), $Cr(NO_3)_3 \cdot 9H_2O$ (400 mg) and hydrofluoric acid (44.3 μL) were mixed with water (4.8 mL). Then the mixture was transferred to a Teflon-lined bomb. After sealed completely, the Teflon-lined bomb was placed in an oven at 220 °C for 8 h. The as-synthesized MIL-101 was further purified by washing with DMF and hot ethanol to remove the unreacted terephthalic acid. The same purifying procedure was repeated three times. The solid powder was obtained by centrifugation at 4000 rpm for 5 min, and then dried in a vacuum at 150 °C for 12 h.

MOF-199 was synthesized according to the previous report by Zhang et al. [5]. $Cu(OA_C)_2 \cdot H_2O$ (430 mg) was dissolved in 20 mL water and H_3BTC (250 mg) was added to 40 mL of DMF/ethanol solution (v/v, 1:1), respectively. After the two solutions were mixed with stirring, triethylamine (250 μL) was added. The obtained mixture was stirred for 3 h at room temperature. The product was collected via centrifugation at 4000 rpm for 5 min, washed with DMF, and finally dried at 60 °C.

2.4. Preparation of PDMS/MOFs coated SPME fibers

Stainless steel wires with a length of 18.0 cm were used to fabricate the SPME fibers. One end (2.0 cm in length) of the stainless steel wire was etched by hydrofluoric acid [33] to

Table 1
Some analytical data obtained for SPME of PAHs using the PDMS/MIL-101 coated fiber.

Compound	Quantitative icon (m/z)	Qualitative icons (m/z)	Linear range (μg L^{-1})	LOD (ng L^{-1})	*r*	RSD (%)	
						Repeatability	Reproducibility
Naphthalene	128	129,127	0.01–2.0	1.0	0.9986	5.2	10.4
Biphenyl	154	153,115	0.01–1.0	2.0	0.9978	4.9	6.9
Acenaphthene	153	154,152	0.01–2.0	4.0	0.9981	7.1	8.5
Fluorene	166	165,83	0.01–2.0	2.0	0.9959	6.6	9.3
Phenanthrene	178	176,152	0.01–2.0	2.0	0.9940	9.3	13.8

generate a rough surface, which was washed gently with water and dried in a desiccator.

Sol–gel approach was employed for PDMS/MOFs coating. Fifty milligrams of MOFs (MIL-101 or MOF-199), 100 μL of MTMOS, 100 μL of OH-PDMS and 100 μL CH_2Cl_2 were added in a 1.50 mL Eppendorf tube and mixed thoroughly for 5 min. Then, 50 μL of 95% TFA/water solution was added to the mixture and vortexed for 2 min, and the sol solution of the PDMS/MOFs coating material was obtained.

The treated wire was dipped into the sol solution to a depth of 2.0 cm for 1 min with the solution being whirled. After about 10 s drying in an oven at 60 °C, the coated wire was gently rotated into and out of a syringe needle (o.d. 350 μm) of the 5 μL microsyringe served as a sleeve barrel to remove the excessive coating off the surface. The fiber was dried in the oven at 60 °C again for about 2 min to complete the polymerization. This coating process was repeated three times and a desired thickness of the coating of about 70 um was obtained. Finally, the coated fiber was assembled in a 5 μL microsyringe and conditioned at 100 °C for 1 h and 260 °C for 1 h under nitrogen in the GC injector.

2.5. *SPME procedures*

For headspace SPME, 10.0 mL sample solution was introduced to a 20.0 mL glass vial containing 2.0 g of NaCl and immediately capped with PTFE-coated septa. A Teflon-coated stirring bar was used to stir the sample solution at 600 rpm and the PDMS/MOFs coated fiber was exposed to the headspace over the sample solution at 45 °C for 20 min for extraction. After extraction, the fiber was pulled out and immediately inserted into GC inlet at 250 °C for 4 min for GC analysis.

3. Results and discussion

3.1. *Characterization of the MOFs*

An X-ray diffraction (XRD) was employed to characterize the crystalline structure of the MOFs. As can be seen from Fig. 1(A and B), the diffraction peaks are at $2\theta=2.81°$, 3.30°, 5.17°, 8.43° and 9.08° for MIL-101, and at $2\theta=6.74°$ and 9.53° for MOF-199, respectively. These results are in good agreement with the earlier reported data [26,34].

Carboxylic ligands are used in the preparation of MIL-101 and MOF-199. After its complexation with chromium or copper ions, the infrared absorption peaks of carboxyl in the organic ligands are shifted to a lower wave number. Fig. 1(C and D) shows the FT-IR spectra of the MOFs (MIL-101 and MOF-199) and the obtained results are consistent with that reported in the references [5,26]. For MIL-101, the absorption peaks of C=O group stretching at 1689 and 1624 cm^{-1} and the C–O bond at 1386 cm^{-1} in terephthalic acid were observed. For MOF-199, the bands at about 1641 and 1446 cm^{-1} were assigned to the asymmetric stretching of the carboxyl groups in H_3BTC, whereas the band at about 1373 cm^{-1} was assigned to the symmetric stretching of the carboxyl groups in H_3BTC. Both the results of XRD and FT-IR demonstrated that the desired MOFs were formed.

3.2. *Characterization of the PDMS/MOFs coated fibers*

The thermal properties of the PDMS/MOFs coating were evaluated by thermogravimetric (TG) analysis. After heat treatment at 100 °C for 1 h and 260 °C for 1 h, the coating materials were scanned within the investigated temperature range at a rate of 10 °C min^{-1} under N_2 atmosphere protection. Fig. 2 reveals that the materials had about 5.0% weight loss at 425.0 °C for MIL-101 and about 7.5% weight loss at 500.0 °C for MOF-199, which could be caused by the loss of some components from the material under the high temperatures. The TG curves indicate that after the heat treatment, the PDMS/MOFs coatings were stable below the temperature of about 400 °C and could endure the temperature in the GC–MS injector for the determination of the five PAHs at 250 °C.

The extraction performance of the PDMS/MOFs-coated fibers for the five PAHs was compared with that of the commercial PDMS fiber. As shown in Fig. 3, the two laboratory-made fibers exhibited higher extraction efficiency than the commercial PDMS fiber. The

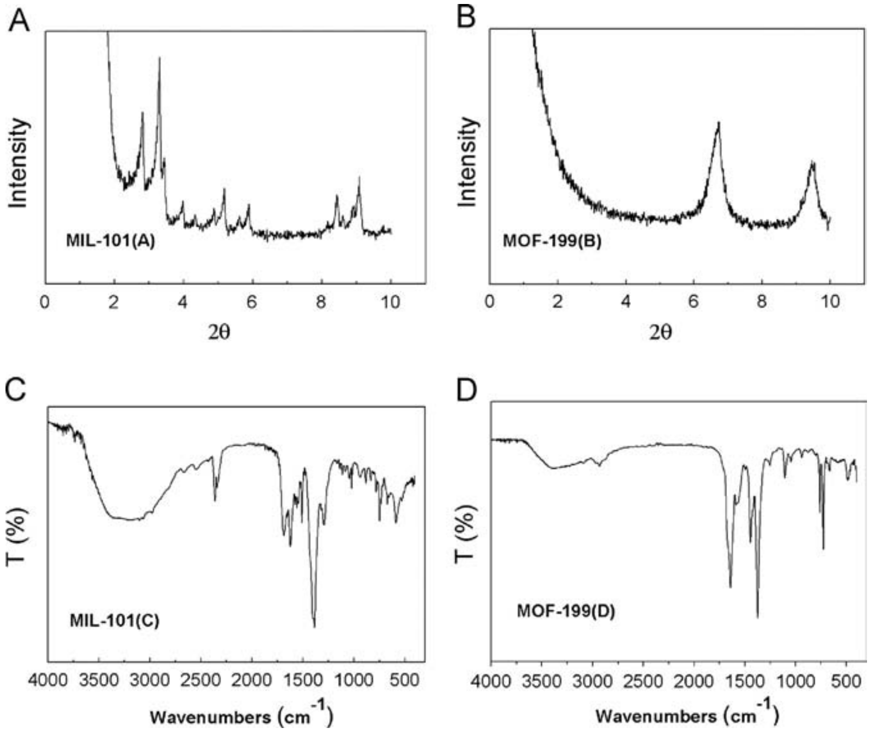

Fig. 1. XRD spectra (A and B) and FT-IR spectra (C and D) of the MOFs.

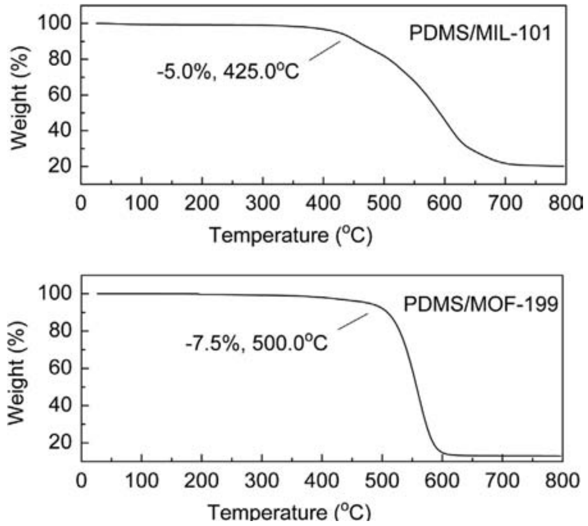

Fig. 2. Thermogravimetric curves of the PDMS/MOFs.

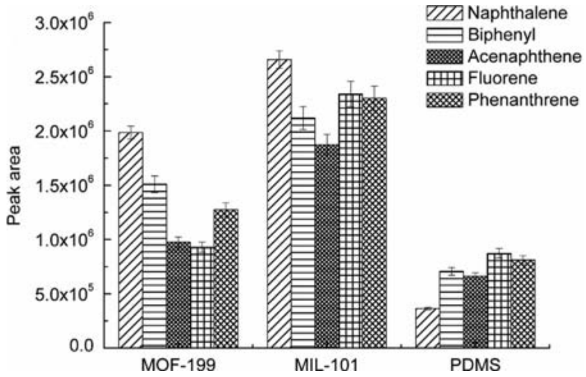

Fig. 3. Comparison of the extraction efficiency of the PDMS/MOFs-coated fibers with the commercial PDMS fiber for the PAHs. Extraction conditions: extraction time, 20 min; extraction temperature, 45 °C; sample volume, 10.0 mL; NaCl concentration, 20%; desorption temperature, 250 °C; desorption time, 4 min.

excellent performance of the newly prepared fibers may result from the combined effects of the large surface area and unique porous structure of the MOFs and the π–π interactions of the aromatic rings of the analytes with the organic ligands molecules. However, due to the competitive occupation of the open metal sites of MOF-199 by H_2O molecules, PDMS/MOF-199 fiber showed a lower extraction performance for the PAHs than that of PDMS/MIL-101 fiber under the experiment conditions (water samples). Therefore, the PDMS/MIL-101 coated fiber was chosen for the extraction of the PAHs in the current work.

The mechanical stability of PDMS/MIL-101 coated fiber was examined by investigating the lifetime of the fiber. The results indicated the fiber allowed more than 120 replicate extractions without measurable loss of performance, which proved that the fiber was quite stable.

3.3. Optimization of extraction conditions

The following factors that mainly influence the SPME efficiency and analysis, including extraction time, extraction temperature, sample volume, salt addition and desorption condition were investigated and optimized to obtain high extraction efficiency for the analytes.

3.3.1. Effect of extraction time and temperature

SPME is an equilibrium-based process and the adsorbed amount of the analytes should increase with increased extraction time before the adsorption equilibrium is reached. As shown in Fig. 4A, the peak areas of the PAHs were increased remarkably from 10 min to 15 min, and then increased slightly from 15 to 25 min. In principle, SPME has the highest sensitivity under equilibrium conditions. However, SPME is applicable for quantitative analysis under non-equilibrium conditions and the absolute extraction equilibrium is unnecessary as long as the experimental conditions are strictly controlled [30]. Making a compromise between the extraction efficiency and extraction time, 20 min of the SPME time was chosen.

Extraction temperature is also a key parameter that can influence the extraction performance of the method. Kinetically, the increase of temperature would facilitate the mass transfer of the analytes from aqueous sample to the headspace. However, thermodynamically, adsorption is generally an exothermic process, and the amount of the analytes adsorbed on the fiber would decrease as the temperature increased [13]. As can be seen in Fig. 4B, when the temperature of the sample solution was increased in the investigated range from 30 °C to 55 °C, the peak area of phenanthrene was increased, while the peak area of naphthalene was decreased. On the other hand, the peak areas of the other three analytes (biphenyl, acenaphthene and fluorene) were first increased when the temperature of the sample solution was increased from 30 °C to 45 °C, and then decreased slightly when the temperature of the sample solution was further increased from 45 °C to 55 °C. On the basis of these experimental observations, the optimum sample temperature was chosen to be 45 °C.

3.3.2. Effect of sample volume

For headspace SPME, the volume ratio of the sample solution to headspace is another important parameter impacting the mass distribution equilibrium [35]. The effect of sample volume was investigated through the experiment by changing the water volumes from 6.0 to 16.0 mL with the extraction being performed in a 20.0 mL glass vials at the same concentrations of the analytes in the water samples. The results showed that the peak areas of the PAHs increased with increased volume of water until 10.0 mL and then decreased slightly. Therefore, 10.0 mL sample solution (the ratio of sample solution to headspace was 1:1) was chosen for the experiment.

3.3.3. Effect of salt addition

The addition of salt can increase the extraction efficiency due to the salting-out effect [36]. For this purpose, the influence of the NaCl concentration on the extraction efficiency was investigated in the range of 0–25% (w/v). The results in Fig. 4C indicate that the peak areas of all the analytes were increased when the NaCl concentration was increased from 0% to 20%, and then remained almost constant. Thus, 20% of NaCl was selected for subsequent studies.

3.3.4. Desorption conditions

For the effective desorption of the adsorbed analytes from the fiber, both desorption temperature and desorption time were optimized.

Generally, desorption temperature must be high enough to effectively release the analytes from the coating. However, too high desorption temperature was unfavorable for the lifetime of the coating [37]. In this study, the desorption temperatures ranging from 230 °C to 280 °C for 5 min were investigated. As can be seen in Fig. 4D, the peak areas of the five PAHs were increased when desorption temperature was elevated from 230 °C to 250 °C and then remained almost unchanged when the desorption temperature was higher than 250 °C. So the desorption temperature for subsequent experiments was set at 250 °C.

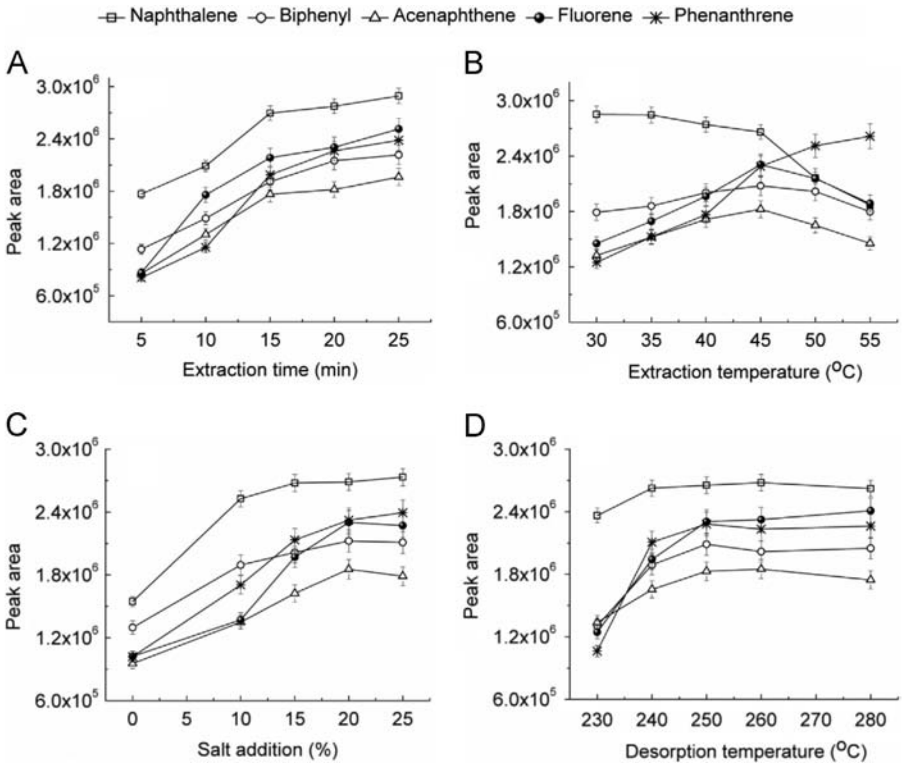

Fig. 4. Effect of the extraction conditions on the headspace-SPME efficiency: (A) effect of extraction time; (B) effect of extraction temperature; (C) effect of salt addition; and (D) effect of desorption temperature.

Table 2
Analytical results for the determination of five PAHs in two water samples using the proposed SPME–GC–MS method.

Compound	Spiked ($\mu g\ L^{-1}$)	River water		Lake water	
		Detected ($\mu g\ L^{-1}$)	Recovery ± RSD (%)	Detected ($\mu g\ L^{-1}$)	Recovery ± RSD (%)
Naphthalene	0.05	0.043	86.0 ± 10.6	0.049	98.1 ± 6.0
	0.2	0.17	85.6 ± 6.3	0.22	110.3 ± 9.5
Biphenyl	0.05	0.051	102.1 ± 9.9	0.053	106.4 ± 8.7
	0.2	0.18	90.4 ± 7.2	0.19	95.7 ± 7.3
Acenaphthene	0.05	0.046	95.3 ± 4.7	0.039	78.2 ± 6.8
	0.2	0.16	80.6 ± 8.1	0.17	85.6 ± 9.3
Fluorene	0.05	0.042	84.3 ± 8.4	0.043	86.2 ± 7.3
	0.2	0.17	85.7 ± 9.0	0.18	90.4 ± 8.6
Phenanthrene	0.05	0.044	88.2 ± 11.2	0.045	90.3 ± 6.3
	0.2	0.21	105.8 ± 5.4	0.17	85.8 ± 12.4

The desorption time was studied in the range from 1 to 8 min at 250 °C. The results showed that 4 min was sufficient for the desorption of the five PAHs and no carry-over effects was observed in this condition.

3.4. Evaluation of method performance

The PDMS/MIL-101 coated fiber was used for the headspace SPME of the five PAHs and the analytical characteristics under optimized conditions are shown in Table 1. A linear response was observed in the range from 0.01 to 2.0 $\mu g\ L^{-1}$ for all the five PAHs with the correlation coefficients (r) ranging from 0.9940 to 0.9986. The limits of detection (LODs), defined as the concentration of the analytes that gave the signal corresponding to three times of the baseline noise were in the range from 1.0 to 4.0 $ng\ L^{-1}$. For the evaluation of the precision, the same fiber was used for four

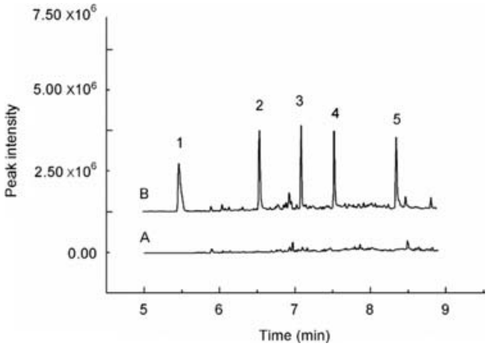

Fig. 5. The chromatograms of (A) river water and (B) the river water spiked at the concentration of 0.2 $\mu g\ L^{-1}$each of the PAHs. Peak identification: (1) naphthalene, (2) biphenyl, (3) acenaphthene, (4) fluorene, and (5) phenanthrene.

Table 3
Method comparisons for the analysis of PAHs.

Methods	Sorbent materials	Extraction time (min)	LOD (ng L^{-1})	Sample	References
μ-SPE–GC–MS	ZIF-8	20	2–12	Water	[22]
SBSE–HPLC–MS/MS	PDMS	180	1–22	Urine	[42]
MSPE–HPLC–PDA	Fe_3O_4@SiO_2–MIL-101	25	2.8–27.2	Water	[24]
SPME–GC–MS	PMO-IL	40	4–9	Water	[38]
SPME–GC–MS	PDMS	45	2–20	Water	[39]
SPME–GC–MS	PDMS/DVB	60	3–70	Milk	[40]
SPME–GC–FID	Graphene	50	4–50	Water	[41]
SPME–GC–MS	PDMS/MIL-101	20	1–4	Water	This method

replicate extractions under the same conditions and the relative standard deviation (RSD) for single-fiber repeatability was below 9.3%. The RSDs for fiber-to-fiber reproducibilities were less than 13.8% using three different fibers prepared in the same way.

3.5. Determination of the PAHs in fortified real river and lake samples

The developed method was applied to the determination of the PAHs in two real water samples from river and lake, respectively. The results showed that they were both free of the contamination from the five PAHs. To test the accuracy of the method, the recoveries of the method for the PAHs from water samples at spiking levels of 0.05 and 0.2 μg L^{-1} were measured. As a result, they fell in the range from 78.2% to 110.3% (Table 2). Fig. 5 shows the GC–MS chromatograms for the river water.

3.6. Comparison with other methods

The performance of the current SPME method with the PDMS/MIL-101 fiber for the determination of PAHs was compared with other literature methods and the results are summarized in Table 3. As can be seen, compared with other SPME coatings, including periodic mesoporous organosilica based on alkylimidazolium ionic liquid (PMO-IL) [38], PDMS [39], PDMS/DVB [40] and graphene [41], the prepared PDMS/MIL-101 coated fiber exhibited faster extraction kinetics for the PAHs. The LODs of the developed method was lower than that obtained by μ-SPE (ZIF-8)–GC–MS [22], SBSE (PDMS)–HPLC–MS/MS [42] and MSPE (Fe_3O_4@SiO_2–MIL-101)–HPLC–PDA [24].

4. Conclusions

In the present work, a PDMS/MIL-101 coated SPME fiber was prepared through sol–gel technology. The new fiber showed to have good thermal stability, good reproducibility and long lifetime. Moreover, the prepared fiber was suitable for the extraction of the five PAHs in real water samples prior to their determination by GC–MS. Compared with other methods, the current method exhibited low LODs and faster extraction kinetics for the PAHs.

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