

Porous carbon derived from aluminum-based metal organic framework as a fiber coating for the solid-phase microextraction of polycyclic aromatic hydrocarbons from water and soil

Xi Zhang¹ · Xiao Huan Zang¹ · Jun Tao Wang¹ · Chun Wang¹ · Qiu Hua Wu¹ · Zhi Wang¹

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Abstract A nanoporous carbon derived from an aluminum-based metal-organic framework was deposited on stainless steel wires in a sol–gel matrix. The resulting fibers were applied to the solid-phase microextraction of the polycyclic aromatic hydrocarbons (PAHs) naphthalene, acenaphthene, fluorene, phenanthrene and anthracene from water and soil samples. The fiber was then directly inserted into the GC injector and the PAHs were quantified by GC-MS. The effects of salt addition, extraction temperature, extraction time, sample volume and desorption conditions on the extraction efficiency were optimized. A linear response to the analytes was observed in the 0.1 to 12 $\mu\text{g L}^{-1}$ range for water samples, and in the 0.6 to 30 $\mu\text{g kg}^{-1}$ for soil samples, with the correlation coefficients ranging from 0.9934 to 0.9985. The limits of detection ranged from 5.0 to 20 ng L^{-1} for water samples, and from 30 to 90 ng kg^{-1} for soil samples. The recoveries of spiked samples were between 72.4 and 108.0 %, and the precision, expressed as the relative standard deviations, is <12.8 %.

Keywords Metal organic framework · Nanoporous carbon · Polycyclic aromatic hydrocarbons · Solid-phase micro-extraction · Gas chromatography–mass spectrometry

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✉ Zhi Wang
zhiwang2013@aliyun.com; zhiwang2000@hotmail.com

¹ Department of Chemistry, College of Science, Agricultural University of Hebei, Baoding 071001, China

Introduction

Solid-phase micro-extraction (SPME), first introduced by Pawliszyn and coworkers in early 1990s [1], has been widely accepted and applied as a sample preparation technique due to its simplicity, being solvent-free and easy linkup with chromatographic instruments [2]. The mechanism of SPME is based on the equilibrium of the target analytes between the sample and the fiber coating [3]. Therefore, the extraction performance of SPME is mainly determined by the properties of the stationary phase coated on the fiber [4–6]. Although several commercial fibers are widely used for routine SPME analysis, several drawbacks, such as the limited variety of the fibers available, high cost, lack of extraction selectivity, and easy breakage of the fiber, still limit their applications. Therefore, the new SPME fiber coating materials with desired properties, such as good adsorption capacity, high thermal, mechanical and chemical stability, and low cost, have been continually explored by scientists.

Nanoporous carbons are known for their high thermal conductivity, high surface area, fast kinetics, and good electron mobility. These features endow nanoporous carbons with potential for the applications for electrochemical capacitation, gas adsorption, catalysis, and sensing [7–9]. Moreover, some of them, such as carbon nanotubes [10, 11], glassy carbon films [12], activated carbon [13], graphene [14] and fullerene [15], have already been used in SPME.

Several methods have been developed to prepare nanoporous carbons, including laser ablation, chemical vapor deposition (CVD), nanocasting, as well as chemical or physical activation methods [16]. Among them, the nanocasting method is an effective way to prepare nanoporous carbon materials. However, this method was somewhat costly and time-consuming since it involved complicated multistep synthetic procedures, which made it unfavorable for large-scale

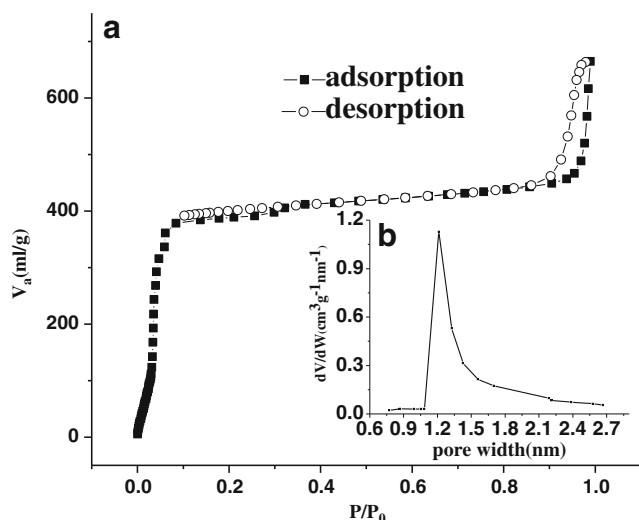
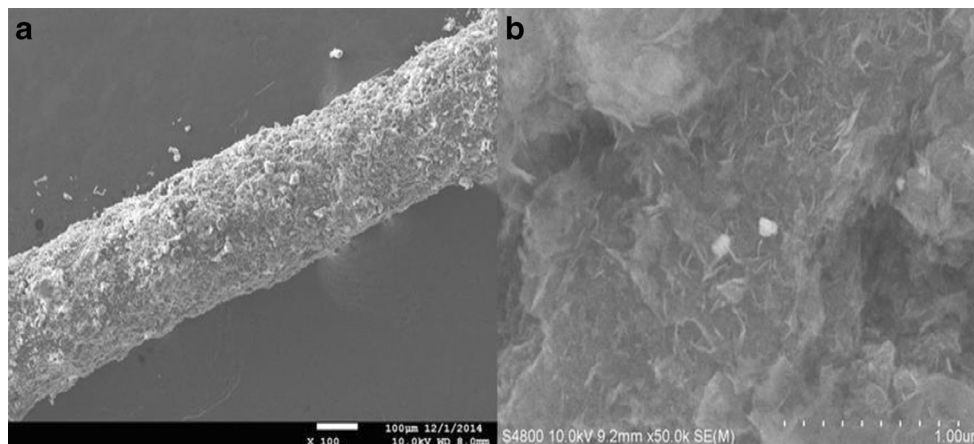


Fig. 1 **a** N_2 adsorption-desorption isotherms and **b** Saito-Foley pore size distribution curve of the C-Al-MOF

preparations. So far, various inorganic porous materials, such as MCM-48, SBA-1 and SBA-15 [17–19], have been successfully used as the hard templates for the preparation of nanoporous carbons by using the nanocasting method. On the other hand, metal organic frameworks (MOFs), with their good porosity, large specific surface area and easy tunability of the pore size from microporous to mesoporous scale [20, 21], have been demonstrated to be ideal templates for fabricating nanoporous carbons. Until now, several MOFs, such as ZIF-8 [22], Al-PCP [23] and MOF-5 [24], have been used as the precursors to yield highly porous carbons with excellent properties for the applications in gas storage [25] and catalysis [26], and as the new materials for super capacitors [27] and carriers for drug deliveries [28, 29]. Moreover, MOF derived nanoporous carbons also showed a great application potential as adsorption material, for instance, the use of a MOF derived carbon- Fe_3O_4 composite for the removal of environmental pollutants [30] and a $CoFe_2O_4$ -carbon composite for phenol degradations [31].

Fig. 2 Scanning electron micrographs of the C-Al-MOF fiber coating: **(a)** 100 \times magnification; **(b)** 50,000 \times magnification



Now we describe a novel aluminum-based metal organic framework derived nanoporous carbon (C-Al-MOF) which was fabricated by one-step direct carbonization of aluminum-based metal organic framework (MOF) without using any additional carbon precursors. The C-Al-MOF was successfully coated onto stainless steel wires through sol-gel technique. To evaluate the performance of the prepared SPME fiber, five polycyclic aromatic hydrocarbons (PAHs) were selected as the model analytes since the vaporized aromatic hydrocarbons in the headspace of the sample can freely diffuse inside the pores with π - π interaction between the porous carbon C-Al-MOF and the benzene-ring molecules. In the end, an effective headspace SPME (HS-SPME) method for the extraction of the PAHs from water and soil samples was established prior to their determination by gas chromatography-mass spectrometric (GC-MS) analysis.

Experimental

Instruments

A Shimadzu (Kyoto, Japan) GCMS-QP2010 SE system equipped with a TG-5MS fused silica capillary column (30 m \times 0.25 mm \times 0.25 μ m) (Scientific, Thermo, www.thermo.com/columns) was used for analysis. The injector was operated first in the splitless mode for 1 min and then changed to split mode at the split ratio of 1:15. The injection port temperature was maintained at 270 $^{\circ}C$. Chromatographic separations were performed with an initial oven temperature of 70 $^{\circ}C$ (held for 1 min), followed by heating at 20 $^{\circ}C$ min $^{-1}$ to 120 $^{\circ}C$, and finally programmed at 30 $^{\circ}C$ min $^{-1}$ to 270 $^{\circ}C$ (held for 2 min). The mass spectrometer was operated in the electron ionization (EI) mode with the temperature of both the transfer line and the ion source being kept at 250 $^{\circ}C$. The MS detection was made using full-scan mode from 50 to 1000 m/z at an electron multiplier voltage of 70 eV. The ions including one for quantification and two for identification (shown in

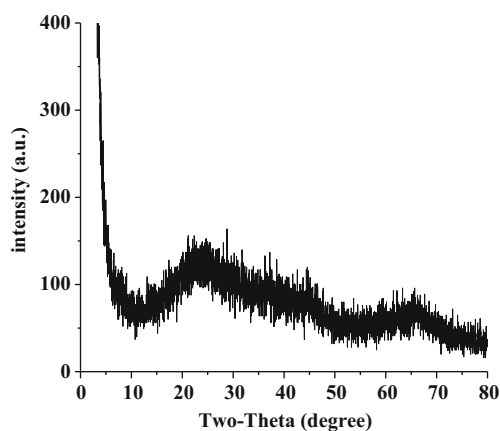


Fig. 3 XRD pattern of the C-Al-MOF

Table S1, Electronic Supplementary Material) were monitored for each PAHs based on the full-scan results.

The WH-861 vortex shaker was from Shanghai Jingong Industrial Limited Company (Shanghai, China, <http://leqing029054.11467.com/>). The DF-101S temperature-controlled magnetic stirrer was purchased from Baoding High-tech Zone Sunshine Science Instrument Company (Baoding, China, <http://www.bdyg117.com/>). The V-sorb 2800 surface area and porosity analyzer was from Beijing Jinaipu Scientific and Technical Corporation (Beijing, China, <http://app-one.cnpowder.com.cn/index.html>). The surface morphology of the coating was observed by scanning electron microscopy (SEM) on a JSM-7500 F (JEOL, Japan).

Reagents and materials

Dichloromethane (CH_2Cl_2), dimethylformamide (DMF), methyltrimethoxysilane (MTMOS), hydrofluoric acid, trifluoroacetic acid (TFA, 99 %), hydroxyl-terminated polydimethylsiloxane (HO-PDMS) and the standards of naphthalene, acenaphthene, fluorene, phenanthrene and anthracene were obtained from Aladdin-Reagent (shanghai, China, <http://www.aladdin-e.com/>). A mixture stock solution containing naphthalene, acenaphthene, fluorene, phenanthrene and anthracene each at 5.0 mg L^{-1} was prepared in acetone and stored at 4°C .

Synthesis of C-Al-MOF

Al-MOF was synthesized according to the literature method [32] as follows. A mixture of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ (92.7 mg, 0.384 mmol) and 2-aminoterephthalic acid (23.3 mg, 0.129 mmol) was suspended in methanol (1.235 mL) and heated at 125°C for 5 h in an autoclave. After the reaction mixture was cooled down to room temperature, the precipitate was filtered and the obtained yellow microcrystalline was washed with water three times and then dried at 80°C under vacuum to get the desired Al-MOF.

C-Al-MOF was synthesized by direct carbonization of the Al-MOF [28]. The above obtained Al-MOF was calcinated directly by being heated first at 150°C for 6 h and then at 800°C overnight in a furnace under the atmosphere of nitrogen gas. After the calcination, the obtained solid was first washed with methanol and then dried at 100°C to get the C-Al-MOF.

Preparation of C-Al-MOF coated SPME fiber

Prior to coating, one end (2.0 cm in length) of the stainless steel wire (18.0 cm long) was first chemically etched with hydrofluoric acid to increase the roughness of the surface and to activate the hydroxyl layer of the stainless steel [33]. After being rinsed with distilled water, the stainless steel wire was dried in a desiccator.

The sol-gel solution of the C-Al-MOF was prepared as follows: 50 mg of C-Al-MOF, 100 μL of CH_2Cl_2 , 100 μL of MTMOS and 100 μL of HO-PDMS were added in a 1.5 mL Eppendorf tube and mixed thoroughly. Then, 50 μL of TFA (95 % water solution) was added. After the mixture was vortexed, the sol-gel solution of the C-Al-MOF coating material was obtained.

The treated stainless steel wire was dipped vertically into the sol-gel solution to a depth of 2.0 cm and held for 1 min with the solution being whirled. Then, it was pulled out and dried at room temperature for 2 min so that the gel coating was automatically formed on the etched surface. This coating process was repeated for appropriate times until the desired thickness of the coating was obtained. Finally, the coated fiber was assembled in a 5 μL microsyringe and conditioned at 100°C for 1 h and 280°C for 2 h under nitrogen in the GC injector.

Sample preparation

Tap and lake water samples were collected from Shijiazhuang (Shijiazhuang, China). 12.0 mL of water sample and 4.4 g of NaCl were added into a glass vial and then, they were mixed until the NaCl was dissolved (nearly saturated). The resultant solution was used for subsequent SPME.

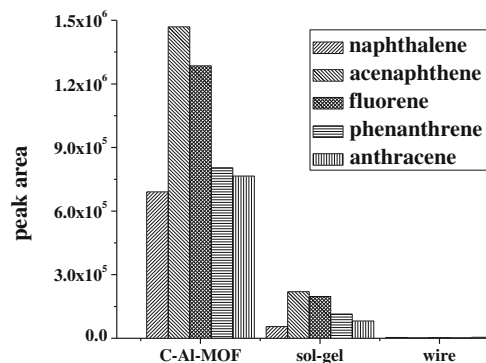


Fig. 4 Comparison with sol-gel materials without C-Al-MOF and etched stainless steel wire

Table 1 Linear range (LR), limits of detections (LODs) and correlation coefficients (*r*) for water and soil samples

Compound	Water samples				Soil samples				RSD%	
	LR μg L ⁻¹	LODs ng L ⁻¹	LOQs ng L ⁻¹	<i>r</i>	LR μg kg ⁻¹	LODs ng kg ⁻¹	LOQs ng kg ⁻¹	<i>r</i>	RSD ^a	RSD ^b
Naphthalene	0.1–10.0	5.0	10.0	0.9966	0.6–30.0	30.0	60.0	0.9934	9.4	11.0
Acenaphthene	0.1–12.0	20.0	40.0	0.9973	0.6–30.0	90.0	180.0	0.9980	8.8	9.8
Fluorene	0.1–12.0	10.0	20.0	0.9976	0.6–30.0	60.0	120.0	0.9985	6.8	8.5
Phenanthrene	0.1–12.0	10.0	20.0	0.9962	0.6–30.0	60.0	120.0	0.9943	9.5	12.3
Anthracene	0.1–12.0	10.0	20.0	0.9962	0.6–30.0	60.0	120.0	0.9982	7.1	8.9

RSD^a, RSD of one fiber (*n* = 5)RSD^b, RSD of fiber-to-fiber (*n* = 3)

Soil samples, collected from a farmland (Baoding, China) and our campus (Baoding, China), respectively, were air-dried at ambient temperature. Then the soil samples were powdered and passed through 450 μm sieves. Then, 4.0 g of the so-prepared soil sample was weighed into a glass vial to which 12.0 mL saturated NaCl solution was added and it was mixed thoroughly for subsequent SPME.

Headspace SPME (HS-SPME) procedures

For HS-SPME, the extraction was carried out with the above obtained water or soil sample solutions in a 20.0 mL glass vial sealed with a Teflon-lined cap. A thermostatic magnetic stirrer

with a Teflon-coated stir bar was used to agitate the solution at 600 rpm. The HS-SPME with the C-Al-MOF fiber was performed at 40 °C for 20 min. After the extraction, the fiber was pulled out and immediately inserted into GC injector at 270 °C for 4 min for GC-MS analysis.

Results and discussion

Characterization of the C-Al-MOF coated fiber

The N₂ adsorption-desorption isotherms and Saito-Foley pore size distribution curve of the resultant nanoporous carbon are

Table 2 Recoveries and precisions (RSDs, *n* = 5) of the five PAHs for water and soil samples by the HS-SPME-GC-MS method

Compound	Spiked/ μg L ⁻¹	Tap water			Lake water			Spiked/ μg kg ⁻¹	Farm soil			Campus soil		
		Found (μg mL ⁻¹)	R ^b (%)	RSD (%)	Found (μg mL ⁻¹)	R ^b (%)	RSD (%)		Found (μg mL ⁻¹)	R ^b (%)	RSD (%)	Found (μg mL ⁻¹)	R ^b (%)	RSD (%)
Naphthalene	0.0	nd ^a			nd ^a			0.0	0.08			nd ^a		
	0.5	0.43	86.0	8.3	0.46	92.0	10.5	1.5	1.39	87.3	8.4	1.35	90.0	9.4
	5.0	4.72	94.4	7.7	4.30	86.1	7.9	15.0	14.6	96.8	9.7	12.9	86.0	6.5
Acenaphthene	0.0	nd ^a			nd ^a			0.0	nd ^a			nd ^a		
	0.5	0.42	84.0	10.2	0.44	88.0	11.1	1.5	1.43	95.0	7.2	1.44	95.8	10.1
	5.0	4.77	95.4	6.4	5.08	101	9.9	15.0	13.1	87.3	4.1	14.9	99.3	9.8
Fluorene	0.0	nd ^a			nd ^a			0.0	nd ^a			nd ^a		
	0.5	0.44	88.2	9.5	0.54	108	9.9	1.5	1.35	89.8	6.7	1.13	75.0	7.8
	5.0	3.62	72.4	12.8	4.34	86.8	3.6	15.0	13.9	92.7	7.7	13.8	92.0	8.2
Phenanthrene	0.0	nd ^a			nd ^a			0.0	nd ^a			nd ^a		
	0.5	0.43	87.0	6.9	0.45	90.0	7.6	1.5	1.23	82.0	6.9	1.35	90.0	4.6
	5.0	4.22	84.4	5.6	4.62	92.4	5.5	15.0	13.4	89.3	7.6	14.6	97.3	5.9
Anthracene	0.0	nd ^a			nd ^a			0.0	nd ^a			nd ^a		
	0.5	0.41	82.0	7.8	0.44	87.3	8.4	1.5	1.15	76.9	9.3	1.25	98.3	5.4
	5.0	4.98	99.6	4.7	4.80	90.6	7.5	15.0	13.6	90.7	8.6	13.5	90.0	7.5

^a nd: not detected^b R: recovery of the method

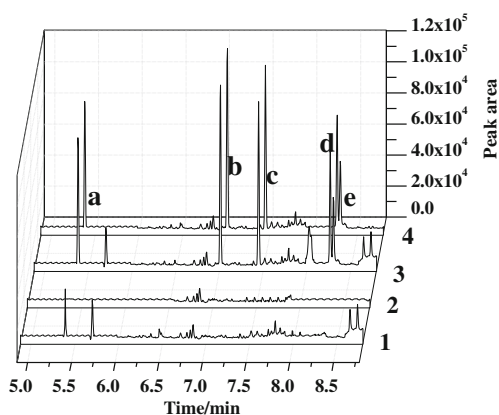


Fig. 5 The total ion current chromatograms obtained under SIM acquisition mode for (1) farmland soil, (2) lake water, (3) the soil sample spiked at $1.5 \mu\text{g kg}^{-1}$ each of the five PAHs, and (4) the lake water spiked at $0.5 \mu\text{g L}^{-1}$ each of the PAHs. Peak identification: (a) naphthalene, (b) acenaphthene, (c) fluorene, (d) phenanthrene, and (e) anthracene

depicted in Fig. 1. The isotherm observed for the C-AI-MOF powder (Fig. 1a) shows a typical type I adsorption–desorption isotherm, which is a characteristic of the microporous material. The pore size distribution shown in Fig. 1b was determined from the desorption isotherm by the SF method. The BET surface area was found to be $1326 \text{ m}^2 \text{ g}^{-1}$ and a SF pore size was 1.13 nm .

Figure 2 presents the scanning electron micrographs (SEM) images of the C-AI-MOF derived nanoporous carbon coating. Figure 2a is a low-magnification SEM image ($100\times$ magnification) of the surface morphological structure of the C-AI-MOF fiber, from which it can be seen that the coating was homogeneous. The SEM image of a high-magnification ($50,000\times$ magnification) (Fig. 2b) shows a porous and corrugated surface structure of the coating, which can increase the surface area of the C-AI-MOF fiber.

Figure 3 displays the XRD pattern of C-AI-MOF composite. The wide diffraction peak at $2\theta=26^\circ$ can be indexed to porous carbon.

The C-AI-MOF fiber was compared with the sol–gel materials without C-AI-MOF and etched stainless steel wire. As shown in Fig. 4, the extraction efficiency of the C-AI-MOF

fiber for the analytes was much higher than those of the other two, indicating that the C-AI-MOF material on the fiber contributed most for the extraction of the compounds.

The mechanical and coating stability of the C-AI-MOF fiber was also examined by investigating the lifetime of the fiber. There was no obvious difference in extraction efficiency after 40, 80, 120 or 160 times extractions of the five PAHs by using the same fiber, suggesting that the C-AI-MOF fiber had a good mechanical and coating stability. Moreover, since the C-AI-MOF fiber was supported by stainless steel wire, it has higher mechanic strength than silica fibers, and also can prevent from being broken during stirring and injection.

Optimization of the HS-SPME method

The HS-SPME mode can minimize the disturbance of sample matrix, provide high sensitivity and lengthen the longevity of the fiber when used for the extraction of semivolatile or volatile compounds [33]. In order to achieve the best extraction efficiency of the new fiber for the five PAHs, the following parameters were optimized: (A) extraction time; (B) extraction temperature; (C) salt addition; (D) desorption temperature; (F) stirring rate.

The respective data are given in Fig. S1 in the Electronic Supporting Material. Based on the experimental results, the following experimental conditions were found to give the best overall results: (A) an extraction time of 20 min; (B) an extraction temperature of 40°C ; (C) a salt addition of 36.6% (w/v); (D) a desorption temperature of 270°C ; (F) a stirring rate of 600 rpm/min.

Method validation

A series of experiments with regard to linear range (LR), the correlation coefficients (r), the limits of detection (LODs), limits of quantification (LOQs) and relative standard deviations (RSDs) were performed to validate the developed HS-SPME-GC-MS method under the optimized conditions. The non-polluted analytes-free water and soil samples were used as blanks for the establishment of matrix-matched standard calibrations. The resulting analytical characteristics are listed

Table 3 Method comparisons for the analysis of PAHs

Methods	Sorbent materials	Extraction time (min)	LODs	RSD (%)	Sample	References
SPME–GC–MS	PDMS	90	70–180 (ng L^{-1})	2.0–8.0	Water	34
			30–220 (ng L^{-1})	3.0–11.0	Water	
SPME–GC–MS	PDMS	50	30–100 (ng L^{-1})	4.0–27.0	Water	35
SPME–GC–MS	PDMS/DVB	60	3–70 (ng L^{-1})	2.0–16.7	Milk	36
SPME–GC–FID	Graphene	50	4–50 (ng L^{-1})	2.8–9.4	Water	37
SPME–GC–MS	C-AI-MOF	20	5–20 (ng L^{-1})	7.5–11.2	Water	This method
			30–90 (ng kg^{-1})	6.8–9.5	Soil	

in Table 1. For water samples, the linear response was observed in the range from 0.1 to 12.0 $\mu\text{g L}^{-1}$ for the PAHs with the correlation coefficients (r) ranging from 0.9962 to 0.9979. For soil samples, the linear range existed from 0.6 to 30 $\mu\text{g kg}^{-1}$ for the compounds with the correlation coefficients (r) ranging from 0.9934 to 0.9985. Based on a signal-to-noise ratio of 3, the LODs were 5.0–20.0 ng L^{-1} for water samples and 30.0–90.0 ng kg^{-1} for soil samples, depending on compounds. The LOQs at a signal-to-noise ratio of 6 were 10.0–40.0 ng L^{-1} for water samples and 60.0–180.0 ng kg^{-1} for soil samples. For repeatability studies, the same fiber was used for five replicate extractions under the same conditions and the RSDs for single fiber repeatability were below 11.2 %. The RSDs for fiber-to-fiber variations were less than 12.3 % using three different fibers prepared in the same way.

Analysis of real samples

The C-Al-MOF fiber-based HS-SPME-GC-MS method was tested for the determination of the five PAHs in water and soil samples. The results are shown in Table 2. As a result, no PAHs were detected in the tested water samples; for farmland soil sample, naphthalene was found to be at 0.08 $\mu\text{g kg}^{-1}$. Then, the water samples were spiked with the standards of each analytes at the concentrations of 0.5 and 5.0 $\mu\text{g L}^{-1}$ and the soil samples were spiked at 1.5 and 15.0 $\mu\text{g kg}^{-1}$, respectively, for the measurements of the recoveries of the compounds for the method. The results listed in Table 2 show that the recoveries of the method for the PAHs from the two environmental samples were in the range from 72.4 % to 108.0 % with the RSDs less than 12.8 %, demonstrating that the accuracy and precision of the present method are acceptable. Figure 5 shows the total ion current chromatograms obtained under SIM acquisition mode for the lake water and soil samples.

Comparison with other SPME coatings

The performance of the current HS-SPME method with the C-Al-MOF fiber for the determination of PAHs was compared with the other reported SPME methods with different fibers including polydimethylsiloxane (PDMS) [34, 35], polyacrylate (PA) [34], polydimethylsiloxane/divinylbenzene (PDMS/DVB) [36] and graphene [37] from the viewpoint of LODs, RSDs and extraction time. As listed in Table 3, the LODs and RSDs for the five PAHs with the current method are comparable with those obtained with the other methods, and the extraction time of the current method is much shorter.

Conclusions

In the present work, a MOF derived nanoporous carbon coated SPME fiber was prepared via sol-gel technology. The fiber

coating had a porous, rough and wrinkled structure, and the fiber showed a high thermal stability, good extraction repeatability and long lifetime. The established HS-SPME-GC-MS method is suitable for the determination of the PAHs from water and soil samples.

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