Talanta 105 (2013) 204–210

Contents lists available at SciVerse ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Application of sol–gel based octyl-functionalized mesoporous materials coated fiber for solid-phase microextraction

Xuemei Wang [a,b], Honghong Rao [a], Xiaoquan Lu [a,b], Xinzhen Du [a,b,*]

[a] College of Chemistry and Chemical Engineering, Northwest Normal University, Lanzhou 730070, China
[b] Key Lab of Bioelectrochemtry Environmental Analysis of Gansu, Lanzhou 730070, China

ARTICLE INFO

Article history:
Received 28 September 2012
Received in revised form
24 November 2012
Accepted 28 November 2012
Available online 5 December 2012

Keywords:
Solid-phase microextraction
Sol–gel technology
High-performance liquid chromatography
Polycyclic aromatic hydrocarbons

ABSTRACT

Octyl-functionalizd mesoporous SBA-15 was first used as precursor and selective stationary phase to prepare solid-phase microextraction (SPME) fiber by using the sol–gel technique. The new SPME coating possessed honeycomb-like porous structure and rough surface and showed excellent chemical stability and longer life span (over 200 cycles of usage). The performance of the octyl-SBA-15-coated fiber was tested through extraction of eight polycyclic aromatic hydrocarbons (PAHs). The results showed that the home-made SPME fiber exhibited higher extraction efficiency compared with the commercial SPME (30 μm and 100 μm PDMS) fibers. For PAHs analysis, the new fiber showed good precision (< 4.8%), low detection limits (0.024–0.050 μg/L), and wide linearity (0.1–200 μg/L) under the optimized conditions. The repeatability of fiber-to-fiber and batch-to-batch was 3.2–8.4% and 4.4–9.5%, respectively. The method was applied to simultaneous analysis of eight PAHs with satisfactory recoveries in different spiking levels, which were 85.7–103.4% (10 μg/L) and 87.0–107.2% (50 μg/L) for water samples and 76.2–89.0% (10 μg/g) and 75.6%–91.2% (50 μg/g) for soil samples, respectively.

1. Introduction

Since solid-phase microextraction (SPME) technique was first introduced in 1989 [1], it has been proven to be a powerful sample preparation technique with simple, fast, and sensitive characteristics. Compared to other conventional techniques such as liquid–liquid extraction (LLE), accelerated solvent extraction (ASE) and solid-phase extraction (SPE), SPME is organic solvent-free and is easily incorporated into chromatographic analyses by integrating sampling, isolation, enrichment, and injection into one step [2–6]. The mechanism of SPME is based on the equilibrium of target analytes between the sample and the fiber coating. Thus, the stationary phase coated onto the fiber is critical in improving the SPME performance [7–9]. At present, several kinds of SPME fibers are commercially available. Many researchers have focused on developing new fibers and coatings by using new preparation methods or new materials. For new preparation methods, electrochemical procedures [10,11], immobilized resin [12,13], sol–gel technology [14,15] and molecular imprinted technology [8,16] have been developed. Among them, sol–gel technology has been widely used. For new materials, carbon nanotubes [17], graphene [18,19] and metal-organic framework [9] has been successfully applied in many fields due to their large specific surface areas and high extraction capacities.

It is well-known that mesoporous materials possess a network of channels and voids of well-defined size in the nanoscale range (2–50 nm). The particular pore architecture makes them have been regarded as attractive candidates for a wide range of applications in adsorption, separation and extraction result from their large surface area, uniform pore structure and huge pore volume [20]. In this work, mesoporous SBA-15 were functionalized with octyltrimethoxysilane in order to enhance the overall hydrophobic nature of the materials and were used as the sorbents of SPME then expected to increase the available surface area of the fiber and the active sites for adsorption, thus enhancing extraction efficiency to analytes. The functionalized product was first used as precursor and selective stationary phase to prepare octyl-SBA-15-coated fiber by sol–gel technology. In order to evaluate the extraction performance and stability of the home-made fiber, eight polycyclic aromatic hydrocarbons (PAHs) were selected as model analytes. The analytical characteristics of the SPME–HPLC method was investigated under optimized conditions. Finally, the proposed method was applied to the analysis of PAHs in real water and soil samples.

2. Experimental

2.1. Reagents and samples

Stainless steel wires (O.D., 0.15 mm) were purchased from AnTing Micro-Injector Factory (Shanghai, China); Commercial manual sampling SPME devices, fiber holder and commercial fibers (30 μm

* Corresponding author at: College of Chemistry and Chemical Engineering, Northwest Normal University, Lanzhou 730070, China.
Tel./fax: +86 931 7970796.
E-mail address: wxm98@163.com (X. Wang).

0039-9140/$ - see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.talanta.2012.11.074

PDMS and 100 μm PDMS) were obtained from Supelco (Bellefonte, PA, USA).

Octyltrimethoxysilane (OTMS) (97%) and poly (ethylene glycol)-block-poly (propylene glycol)-block-poly (ethylene glycol) ($EO_{20}PO_{70}EO_{20}$, Pluronic P123, M_{av}=5800) were obtained from Sigma-Aldrich (Steinheim, Germany). Poly (methylhydrosiloxane) (PMHS) and hydroxylterminated silicone oil (TSO-OH) were purchased from Alfa Aesar (Ward Hill, MA, USA). HPLC-grade acetonitrile, dichloromethane (DCM, 99%), hexane (99%), tetraethyl orthosilicate (TEOS) (98%) and trifluoroacetic acid (TFA) (99.5%) were bought from J. T. Baker (Phillipsburg, NJ, USA). Tetraethyl orthosilicate (TEOS, 98%), hydrochloric acid (HCl, 37%) and ethanol (95%) were purchased from Shanghai Chemical Company (Shanghai, China). All other chemicals were of analytical grade.

The PAHs standards (Acenaphthene (ANE), Anthracene (ANT), Benzo[a]pyrene (BaP), Fluoranthene (FLA), Fluorene (FLU), Naphthalene (NAP), Phenanthrene (PHE), and Pyrene (PYR)) were purchased from Sigma-Aldrich (Steinheim, Germany). A stock standard solution of 50 mg/L of each compound was prepared in methanol. The working standard solution of 1, 10, 50, 100, 200, 500, 1000 μg/ L of PAHs solutions were prepared by diluting the eight stock standard solutions within methanol. They were stored at 4° C. Fresh aqueous solution was prepared daily by diluting the working standard solution with ultrapure water. Ultrapure water was obtained from Aquapro Water Purification System (Chongqing, China).

2.2. Apparatus

The HPLC system consists of Waters 600E pump and Waters 2487 double wavelength UV detector. A N2000 workstation (Zhejiang University, China) was utilized to control the system and acquire of data. All separations are carried out on a Waters Sunfire C_{18} chromatographic column (5 μm, ∅4.6 × 150 mm). The mobile phase is methanol/water (90:10, v/v, flow at 1.0 mL/min) and the wavelength of UV detection is set at 254 nm. The SPME–HPLC interface (Cat. No. 57353) is a commercially available desorption chamber and purchased from Supelco, it is sealed by PEEK (polyether ether ketone) septum which is tight enough to withstand pressure as high as 29.7 MPa.

2.3. Synthesis and characterization of octyl-SBA-15

Octyl-functionalized mesoporous SBA-15 was synthesized according to our previous report [21]. The results of characterization show that octyl-SBA-15 preserve a desirable ordered two-dimensional P6mm hexagonal structure and larger pore diameter (4.6 nm), large surface area (769.4 m^2/g) and pore volume (0.78 m^3/g) [21].

2.4. SPME fiber preparation

Prior to coating, stainless steel wire (SSW, 10 cm) was initially chemically etched for 30 min with hydrochloric acid to increase roughness of the surface and to activate the autoprotective hydroxyl layer of stainless steel. After a copious rinse with deionized water, the wire was dried at 60° C for 30 min.

The sol–gel solution was prepared as follows: 80 mg of octyl-SBA-15 was dissolved in 200 μL of dichloromethane and then 150 μL of TEOS, 50 μL of TSO-OH, 25 μL of PMHS were added and mixed thoroughly for 20 min by ultrasonic bath agitation. A volume of 150 μL of TFA (95% water solution) was sequentially added to the resulting solution with ultrasonic agitation for another 5 min. The mixture was then centrifuged at 5000 rpm for 3 min, and the top clear sol solution was used for fiber coating.

The treated SSW was dipped vertically into this sol–gel solution to a depth of 1.0 cm and held for 10 min for the formation of sol–gel coating. For each fiber, this coating process was repeated two times and each time for 10 min in the same sol solution until the thickness of the coating desired was obtained. The new fiber was dried at 120° C with a gentle N_2 flow for 2 h.

2.5. DE (direct extraction)–SPME procedures

For PAHs analysis, all extraction experiments were carried out in a 10 mL working solution, which was introduced to a 12 mL amber vial capped with PTFE-coated septa. Thermostated magnetic stirrer with a Teflon-coated stir bar was used to agitate the solution at 1000 rpm and at the extraction temperature of 40° C. To perform the extraction, the octyl-SBA-15-coated fiber or the commercial fiber was exposed in aqueous samples for 30 min. After extraction, the fiber was removed from the aqueous sample and was gently inserted into the desorption chamber of SPME-HPLC interface to desorb analytes for 3 min, then the eluent was injected into the HPLC-UV for analysis.

2.6. Sample preparation

Three real water samples were collected from Yellow River (Lanzhou, China), rain water and a pond on our campus. These samples were filtrated through 0.45 μm micropore membrane (Automatic Science, China) and stored in brown flask at 4° C.

One soil sample was collected from the shore of Yellow River. After taken, it was freeze-dried and mixed completely, then sieved through a stainless steel 100-mesh sieve. 1 g soil samples and 2 g anhydrous Na_2SO_4 were added in glass centrifuge tube, and 10 mL DCM/hexane (7:3) was added, then the mixture was sonicated for 1 h and then centrifuged for 5 min at 3000 r/min. The extract was filtered and evaporated to dryness at 50° C using a rotary evaporator. Afterward, the dry residue was redissolved in 1.0 mL of methanol, and 10 μL of this solution was diluted with 10 mL of water for DE-SPME. For the analytical performance assessment, a 10 mL standard methanol solution of 500 μg/L PAH mixture was added to 0.5 g of soil to give a spiked level of 10 μg/g for each of the target compounds. Extractions were performed after 1 h to ensure the solvent had evaporated.

3. Results and discussion

3.1. Morphological structure of octyl-SBA-15 coating.

Fig. 1 presents the SEM images of octyl-SBA-15 coating. Fig. 1a is a low-magnification surface morphology which revealed a rough and loose appearance, the high magnification images are shown in Fig. 1b and Fig. 1c, which had honeycomb-like porous structure. The thickness of the coating was approximately 60 μm (Fig. 1a, the diameter of fiber was about 270 μm) after two coating cycles. The coating material can provide hundreds of hole and channels voids of well-defined size in the microscopic scale, which was beneficial for extraction performance.

3.2. Mechanical and chemical stability of octyl-SBA-15 coating

To evaluate the chemical stability of the octyl-SBA-15 coating, the fiber was immersed into four different solvents including methanol, *n*-hexane, 0.1 mol/L HCl (pH=1) and 0.01 mol/L NaOH (pH=12) for 1 h, respectively. After this, the fiber was washed with deionized water and dried at 100 °C for 1 h. Then, the extraction efficiency for three kinds of PAHs of the treated and untreated fibers was compared (Fig. 2a). The results indicated

that the home-made octyl-SBA-15 coating was stable within a large pH range (1–12) and tolerant to both polar and nonpolar organic solvents. Next, the life span of the octyl-SBA-15-coated fiber was investigated. Fig. 2b showed that the extraction efficiency did not decline even after being used 200 cycles of usage. These results revealed the new SPME fiber possess the remarkable solvent durability and mechanical stability of the fiber.

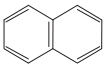
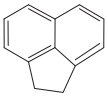
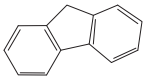
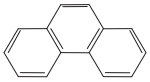
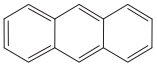
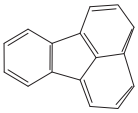
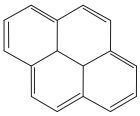
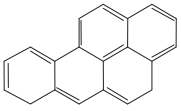
3.3. Optimization of DE-SPME procedures

In order to achieve the best extraction efficiency of the new coating for 8 PAHs (Table 1), several potential factors affecting the efficiency of SPME, such as extraction temperature, extraction time, stirring rate and salt addition were investigated and optimized in standard mixture of PAHs with each target analyte at concentration of 10 μg/L aqueous solution.

3.3.1. Extraction temperature

The extraction temperature is an important factor because of its potential influences on thermodynamics and kinetics of extraction equilibrium of analyte between fiber coating and sample solution. From the thermodynamics, increasing the extraction temperature can enhance mass transfer of analytes from water to the fiber coating, thereby increasing extraction efficiency of DE-SPME. From the kinetics, the extraction process was exothermic, the fiber coating/sample partition coefficient (K) decreased with increased temperature, and the affinity of the analytes for the fiber coating diminished at high temperature, which resulted in lower equilibrium amounts of analytes that the coating was able to extract [22,23]. Therefore, the extraction temperature profiles for PAHs ranging from 20 to 60° C were investigated. As can be seen in Fig. 3a, the extraction efficiency of eight PAHs increased with temperature from 20 to 40° C. However, decrease in the analytical signal were observed for temperatures above 40° C for the four- and five-ring analytes (FLA, PYR, and BaP) with higher thermal instability and larger K_{OW} values [24] (*n*-octanol/water partition coefficients, Table 1), the higher thermal instability indicated that the elevated temperature was adverse to mass transfer of analytes from water to the fiber coating, the larger K_{OW} values showed their strong hydrophobic properties which could accelerate volatilizing of the analyte from

Table 1
Physical–chemical properties of eight PAHs.

PAHs	Abbreviation	Molecular weight	Chemical structure	log K_{ow}[a]
Naphthalene	NAP	128		3.24–3.40
Acenaphthene	ANE	154		4.07
Fluorene	FLU	166		4.18
Phenanthrene	PHE	178		4.46–4.64
Anthracene	ANT	178		4.55–4.79
Fluoranthene	FLA	202		5.12-5.31
Pyrene	PYR	202		5.0–5.18
Benzo[a]pyrene	BaP	252		5.91–6.28

[a] K_{OW}:*n*-octanol/water partition coefficients. Data taken from [24].

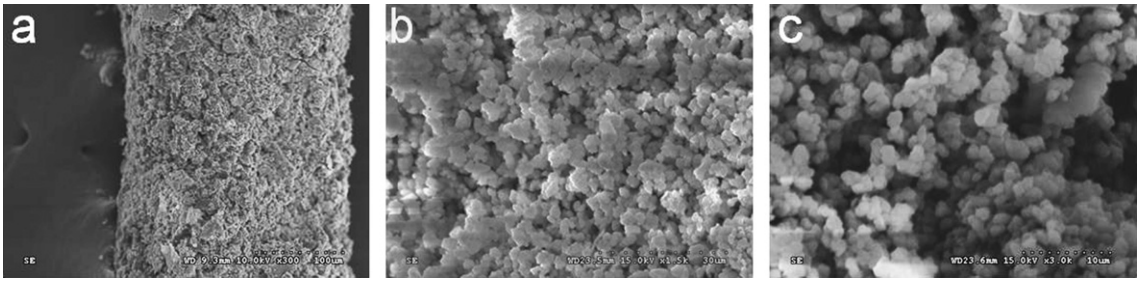


Fig. 1. Scanning electron micrographs of a SPME fiber coated with octyl-SBA-15. The surface images at magnifications of (a) × 300; (b) × 1500; (c) × 3000.

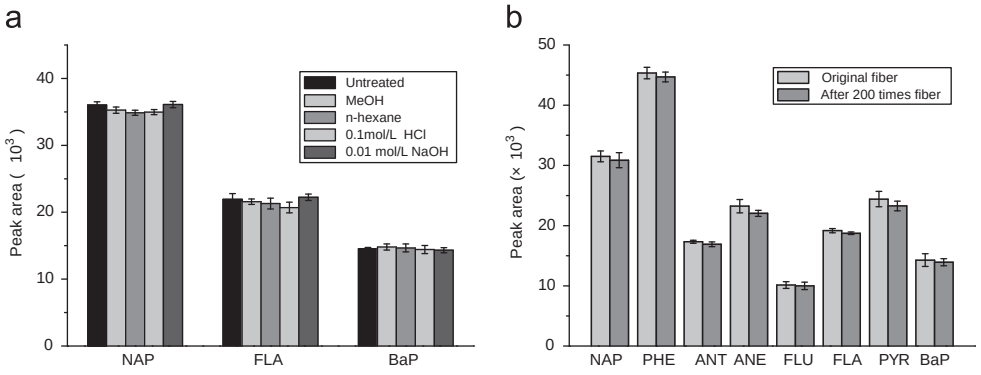


Fig. 2. The chemical stability and life span profile of octyl-SBA-15-coated fiber.

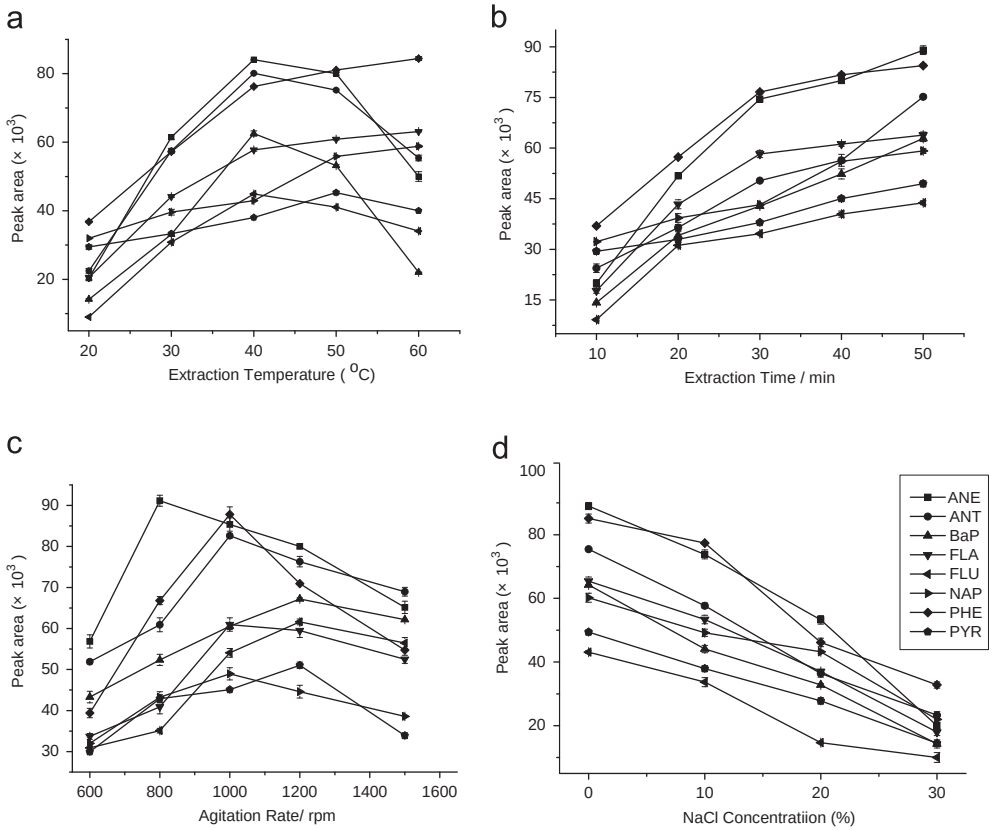


Fig. 3. Effect of the experimental conditions on the extraction efficiency of octyl-SBA-15-coated fiber for 10 μg/L PAHs, including (a) extraction temperature, (b) extraction time, (c) agitation rate, and (d) ionic strength. Errors bars show the standard deviation of the mean ($n=3$).

aqueous phase. Consequently, the extraction temperature of 40° C was chosen for the subsequent experiments.

3.3.2. Extraction time

SPME is an equilibrium-based technique, and there is a direct relationship between the extraction amount and the extraction time. Generally, extraction efficiency increase with the increase of extraction time before equilibrium. The effect of extraction time was investigated ranging from 10 to 60 min. As shown in Fig. 3b, the extraction efficiency of all the eight PAHs increased with the longer extraction time. As SPME is a non-exhaustive approach, it can be designed on the basis of principles of equilibrium, preequilibrium, and permeation [25]. If the achieved analytical sensitivity is sufficient for quantitative analysis, it is not necessary to reach equilibrium. Thus, 30 min was selected for the subsequent experiments based on the sensitivity and time efficiency.

3.3.3. Agitation rate

In general, extraction performance can enhance along with increasing agitation rate, in respect that the agitation can accelerate mass transfer of the analytes between the aqueous sample and the SPME fiber. However, the fast agitation can also promote the analytes vaporize in headspace from the water samples, which was unfavorable to DE-SPME mode used in the present work, especially for more volatile compounds. Fig. 3c exhibited a positive effect of low agitation rate on peak area of eight PAHs. Further increase of agitation speed led to an apparent decrease, and the highest extraction efficiency was achieved at a stirring rate of 1000 rpm for ANT, FLA, NAP, PHE or 1200 rpm for BaP, FLU, PYR, only the highest extraction efficiency of ANE was at 800 rpm, which due likely to the excessive agitation increased mass transfer of the analyte from aqueous phase to headspace of amber vial. Consequently, the stirring rate of 1000 rpm was adopted.

3.3.4. Effect of salt addition

Adding salt to the water sample would decrease the solubility of some analytes in aqueous phase, which was dependent on the polarity of analytes, the type of SPME fiber and the concentration of salt [26,27]. For this reason, the effect of ionic strength for eight nonpolar PAHs was studied by adding different amounts of NaCl (0–30% m/v) as salting-agent. Fig. 3d shows that salt addition had negative effect on extraction performance, which was agreement with the results of other researchers [28–30]. This might be due to the addition of salt could increase the viscosity and density of the aqueous phase and thus negatively affect the kinetics of the process and the extraction efficiency. Based on this, the salt was not added in this study.

3.4. Comparison between commercial and home-made fiber

The eight PAHs are slightly polar and semivolatile compound. Polydimethylsiloxane (PDMS) is proved to be the most efficient for PAH enrichment due to its typically nonpolar polymer phase. Thus, the two commercial PDMS (30 μm and 100 μm thicknesses) were selected for comparing the extraction effect with the octyl-SBA-15 fiber. Because of the different thickness of the commercial coating, the extraction time profiles of two PDMS fiber were investigated to ensure that the comparison was tested under equilibrium. The results indicated that the 30 μm PDMS fiber reached equilibrium in 30 min and the 100 μm PDMS in 40 min for extraction of the eight PAHs. Therefore, extraction time of 30 min and 40 min was the optimum condition for two commercial fibers, respectively. The comparison of

octyl-SBA-15-coated fiber with commercial fiber for DE-SPME of 10 μg/L PAH solution under their own optimum conditions was performed. The results were represented in Fig. 4. It revealed that the octyl-SBA-15 fiber showed superior efficiency than two commercial PDMS fibers. It is possibly due to the rough surface and porous structure of three-dimension sol–gel silica network provided larger surface area and thus improved extraction ability. These results indicated that mesoporous material have a strong physical adsorption ability to hydrophobic PAHs.

3.5. Analytical performance

A serious of experiments with regard to the linearity, limits of detection (LODs) and repeatability were performed to validate the proposed method under the optimized extraction conditions. The analytical characteristics are listed in Table 2. The linear range of eight PAHs compounds was 0.1–200 μg/L for with correlation coefficient (r^2) ranging from 0.9994 to 0.9999. Limits of detection (LODs), calculated on the basis of a ratio of signal-to-noise of 3 (S/N=3), were in the range of 0.024–0.050 μg/L for eight PAHs analytes. For the repeatability study, one fiber was used for five replicate extractions of an aqueous sample containing 10 μg/L PAHs under the same conditions, and the relative standard deviation (RSD) was shown to be 2.2–4.8%. The fiber-to-fiber repeatability for the five fibers prepared in the same batch was in the range 3.2–8.4% (RSD), and the batch-to-batch repeatability for five fibers prepared in different batches was 4.4–9.5%. The fiber life span was studied by monitoring the change of extraction peak areas during its use and no obvious decline was observed after it had been used for about 200 times.

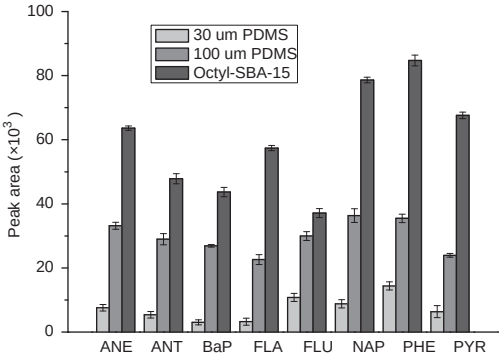


Fig. 4. Comparison of the extraction efficiency of octyl-SBA-15-coated fiber with commercial 30 μm PDMS and 100 μm PDMS fibers for PAHs at 10 μg/L. Errors bars show the standard deviation of the mean (n=3).

To further evaluate the analytical performance of the proposed method, several typical analytical procedures of the method for PAHs from aqueous sample are compared to other methods [31,32], listed in Table 3. It can be seen that use of this method resulted in lower LODs and RSD, wider linear range and more satisfied recovery.

3.6. Analysis of real samples

The optimized octyl-SBA-15-based SPME-HPLC method is validated for the enrichment of PAHs in three real water samples including Yellow River water, rain water and pond water on campus and a soil sample the shore of Yellow River. The results were shown in Table 4, Fig.5 and Fig.6. BaP, NAP, PHE and PYR were detected in river water, ranging from 4.3 to 9.6 μg/L, it was contributed to the industrial wastewater of several large petrochemical enterprises in the Lanzhou Reach of Yellow River. No PAHs were founded in pond water and rain water. The solution was spiked with 10 μg/L and 50 μg/L PAHs to evaluate the accuracy of the method. Good recoveries were obtained by octyl-SBA-15-coated fiber, which ranged from 85.7% to 103.4% (10 μg/L) and 87.0% to 107.2% (50 μg/L) for all the studied analytes.

For the analysis of PAHs in soil sample, the content of BaP, NAP and PHE were in the range of 2.6–7.7 μg/g. Recoveries obtained by spiking at the 10.0 μg/g and 50 μg/g level with PAHs ranged from 76.2% to 89.0% (10 μg/g) and 75.6% to 91.2% (50 μg/g), which were relatively lower than that obtained from the water samples. This could be ascribed to the slight loss of analyte in pretreatment process. On the other hand, the fact is that the complex soil matrix, mainly the natural organic matrix and clay, involved in the absorption of lipophilic compounds might also contribute to the recovery loss [33]. The relative standard deviation (RSD) for the determination of four samples for three replicate analysis of target compounds were less than 7.4%, showing good reproducibility.

Table 2
Linear range, limits of detection (LODs) and repeatability of the proposed method.

PAHs	Linear range (μg/L)	Coefficient of correlation (r^2)	LODs (S/N=3, μg/L)	One fiber (RSD%,n=5)	Repeatability (RSD%, n=5)	
					Fiber-to-fiber	Batch-to-batch
ANE	0.1–200	0.9995	0.035	4.1	4.5	4.9
ANT	0.1–200	0.9994	0.024	3.1	3.9	4.4
BaP	0.1–200	0.9999	0.050	3.3	3.2	5.6
FLA	0.1–200	0.9998	0.044	2.2	5.7	8.5
FLU	0.1–200	0.9999	0.030	4.6	6.5	9.0
NAP	0.1–200	0.9997	0.025	2.5	8.4	6.6
PHE	0.1–200	0.9994	0.048	3.6	7.8	9.5
PYR	0.1–200	0.9994	0.036	4.8	5.4	7.8

Table 3
Typical analytical procedures of the method for PAHs from aqueous sample and comparison with other methods.

Instrumentation	SPME fiber coating	Linear range (μg/L)	LODs (μg/L)	Recovery (%)	RSD (%)	Reference
GC-FID	Hydrofluoric acid Etched stainless steel	2.5–50	0.24–0.63	85.0–103.0	2.9–5.3	[31]
GC-FID	Benzyl functionzlized polymeric ionic liquid	0.1–20	0.25–0.76	83.5–109.0	6.5–12.0	[32]
HPLC-UV	Octyl-functionalized Mesoporous Materials	0.1–200	0.02–0.05	85.7–103.4	2.2–4.8	This paper

Table 4
Analytical results for the determination of PAHs in water and soil samples.

Samples	PAHs	Original	Found[a,b]	Recovery[a,b](%)	RSD[a,b] (%, $n=3$)
Pond water	ANE	n.d[c]	10.3, 51.7	103.0, 103.4	3.3, 3.5
	ANT	n.d	10.1, 51.2	101.0, 102.4	4.3, 3.3
	BaP	n.d	10.2, 51.5	102.0, 103.0	6.5, 4.5
	FLA	n.d	9.5, 51.4	95.0, 102.8	3.4, 4.1
	FLU	n.d	9.8, 48.8	98.0, 97.6	5.6, 6.2
	NAP	n.d	10.1, 48.3	101.0, 96.6	6.4, 6.5
	PHE	n.d	9.6, 47.3	96.0, 94.6	4.5, 5.2
	PYR	n.d	9.7, 52.1	97.0, 104.2	3.4, 3.4
Rain water	ANE	n.d	10.1, 51.3	101.0, 102.6	5.5, 5.2
	ANT	n.d	9.9, 51.5	99.0, 103.0	4.6, 3.9
	BaP	n.d	9.8, 48.5	98.0, 97.0	3.6, 4.5
	FLA	n.d	10.1, 48.6	101.0, 97.2	5.5, 4.9
	FLU	n.d	10.2, 52.3	102.0, 104.6	3.6, 4.1
	NAP	n.d	10.3, 52.5	103.0, 105.0	3.6, 4.3
	PHE	n.d	9.8, 48.1	98.0, 96.2	2.6, 4.1
	PYR	n.d	10.1, 49.2	101.0, 98.4	2.8, 3.6
Yellow River water	ANE	n.d	10.3, 53.6	103.0, 107.2	6.5, 5.6
	ANT	n.d	10.2, 53.3	102.0, 106.6	4.6, 5.1
	BaP	7.2	16.3, 55.5	94.8, 97.0	5.8, 5.5
	FLA	n.d	8.8, 52.5	88.0, 105.0	6.0, 4.8
	FLU	n.d	8.7, 46.5	87.0, 93.0	3.5, 4.1
	NAP	4.3	13.0, 47.6	90.9, 87.7	4.8, 3.8
	PHE	9.6	16.8, 52.8	85.7, 88.6	3.6, 3.5
	PYR	7.5	18.1, 50.0	103.4, 87.0	4.8, 4.5
Soil sample	ANE	n.d	8.8, 45.6	88.0, 91.2	7.0, 7.1
	ANT	n.d	7.9, 43.5	79.0, 87.0	6.8, 6.5
	BaP	4.7	11.3, 43.2	77.1, 79.0	6.1, 6.8
	FLA	n.d	8.5, 44.5	85.0, 89.0	5.6, 5.8
	FLU	n.d	8.9, 42.8	89.0, 85.6	7.0, 6.6
	NAP	2.6	9.8, 41.5	77.8, 78.9	6.4, 5.8
	PHE	7.7	13.5, 43.6	76.2, 75.6	5.9, 7.4
	PYR	n.d	8.6, 40.2	86.0, 80.4	5.7, 5.5

[a] Spiked with 10 μg/L PAHs solution for water samples, spiked at the 10 μg/g level of PAHs for soil sample.
[b] Spiked with 50 μg/L PAHs solution for water samples, spiked at the 50 μg/g level of PAHs for soil sample.
[c] Not detected.

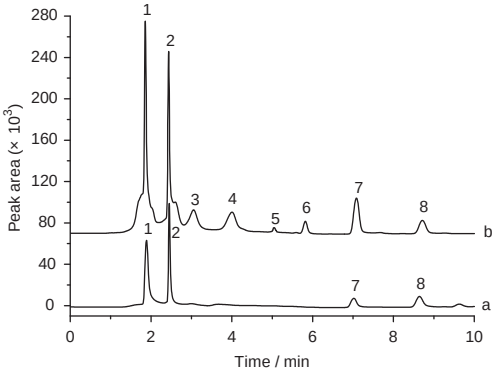


Fig. 5. Chromatograms of extracts of eight PAHs from (a) blank Yellow River water sample and (b) spiked Yellow River water sample (10 μg/L spiked level) using octyl-SBA-15-coated fiber. (1) NAP; (2) PHE; (3) ANT; (4) ANE; (5) FLU; (6) FLA; (7) PYR; (8) BaP.

4. Conclusions

In this study, a novel mesoporous-coated SPME fiber was first prepared by sol–gel technology and successfully applied to the extraction of eight PAHs in real water and soil samples. Compared with the commercial 30 μm and 100 μm PDMS fibers, the novel fiber exhibited higher extraction efficiency for PAHs. Under the optimum conditions, the home-made SPME fiber achieved the satisfactory recoveries, which were 85.7–103.4% (spiking 10 μg/L) and 87.0% to 107.2% (50 μg/L) for water samples and 76.2–89.0% (10 μg/g) and 75.6% to 91.2% (50 μg/g) for soil samples, respectively. The method exhibited good precision, reproducibility and linear response over a wide concentration range and offered a simple, rapid, sensitive, and inexpensive tool for determination of PAHs in real samples. Besides that, mesoporous materials showed great potential for the preconcentration and sample preparation of trace hydrophobic aliphatic analytes, too.

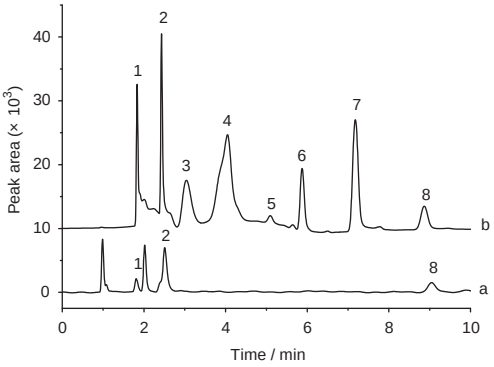


Fig. 6. Chromatograms of extracts of eight PAHs from (a) blank soil sample the shore of Yellow River and (b) spiked soil sample the shore of Yellow River (10 μg/g spiked level) using octyl-SBA-15-coated fiber. (1) NAP; (2) PHE; (3) ANT; (4) ANE; (5) FLU; (6) FLA; (7) PYR; (8) BaP.

Acknowledgments

This work was kindly supported by the Natural Science Foundation of China (Nos. 21107086, 20775060 and 20927004), the Natural Science Foundation of Gansu (No. 3ZS051-A25-011-022), Key Laboratory of Polymer Materials of Gansu Province and the Key Laboratory of Ecological Environment Related Polymer Materials of Ministry of Education.

References

[1] C.L. Arthur, J. Pawliszyn, Anal. Chem. 62 (1990) 2145–2148.
[2] C.L. Arthur, L.M. Killam, K.D. Buchholz, J. Pawliszyn, Anal. Chem. 64 (1992) 1960–1966.
[3] K.D. Buchholz, J. Pawliszyn, Environ. Sci. Technol. 27 (1993) 2844–2848.
[4] K.D. Buchholz, J. Pawliszyn, Anal. Chem. 66 (1994) 160–167.
[5] H. Kataoka, H.L. Lord, J. Pawliszyn, J. Chromatogr. A 880 (2000) 35–62.
[6] H.L. Lord, J. Pawliszyn, J. Chromatogr. A 885 (2000) 153–193.
[7] C.F. Duan, Z Shen, D.P. Wu, Y.F. Guan, TrAC Trends Anal. Chem 30 (2011) 1568–1574.
[8] X. Hu, J. Pan, Y. Hu, Y. Huo, G.K. Li, J. Chromatogr. A 1188 (2008) 97–107.
[9] X. Cui, Z. Gu, D. Jiang, Y. Li, H. Wang, X.P. Yan, Anal. Chem. 81 (2009) 9771–9777.
[10] J.W. Zewe, J.K. Steach, S.V. Olesik, Anal. Chem. 82 (2010) 5341–5348.
[11] I. Minet, L. Hevesi, M. Azenha, J. Delhalle, Z. Mekhalif, J. Chromatogr. A 1217 (2010) 2758–2767.
[12] X.M. Wang, X.Z. Du, H.H. Rao, X.Q. Lu, J. Sep. Sci. 33 (2010) 3239–3244.
[13] J.G. Hou, Q. Ma, X.Z. Du, H.L. Deng, J.Z. Gao, Talanta 62 (2004) 241–246.
[14] H. Bagheri, H. Ghanbarnejad, F. Khalilian, J. Sep. Sci. 32 (2009) 2912–2918.
[15] A. Sarafraz-Yazdi, A. Amiri, G. Rounaghi, H. Eshtiagh-Hosseini, Anal. Chim. Acta 720 (2012) 134–141.
[16] F.G. Tamayo, E. Turiel, A. Martin-Esteban, J. Chromatogr. A 1152 (2007) 32–40.
[17] Q.L. Li, X.F. Wang, D.X. Yuan, J. Chromatogr. A 1216 (2009) 1305–1311.
[18] H. Zhang, H.K. Lee, J. Chromatogr. A 1218 (2011) 4509–4516.
[19] S.L. Zhang, Z. Du, G.K. Li, Anal. Chem. 83 (2011) 7531–7541.
[20] A. Molnar, B. Rac, Curr. Org. Chem. 10 (2006) 1697–1726.
[21] X.M. Wang, X.Z. Du, C.L. Li, X. Cao, Mater. Lett. 62 (2008) 3232–3235.
[22] H.L. Lord, J. Pawliszyn, Anal. Chem. 69 (1997) 3899–3906.
[23] D.L.S. Bruin, P.D. Josephy, J. Pawliszyn, Anal. Chem. 70 (1998) 1986–1992.
[24] R. Doong, S. Chang, Anal. Chem. 72 (2000) 3647–3652.
[25] J. Pawliszyn, Anal. Chem. 75 (2003) 2543–2558.

[26] C. Basheer, J. Akhila, K.K. Meng, S. Valiyaveettil, H.K. Lee, J. Chromatogr. A 1100 (2005) 137–143.
[27] J. Carpinteiro, J.B. Quintana, I. Rodriguez, A.M. Carro, R.A. Lorenzo, R. Cela, J. Chromatogr. A 1056 (2004) 179–185.
[28] J.X. Wang, D.Q. Jiang, Z.Y. Gu, X.P. Yan, J. Chromatogr. A 1137 (2006) 8–14.
[29] J. Zhou, F. Yang, D. Cha, Z. Zeng, Y. Xu, Talanta 73 (2007) 870–877.
[30] M. Polo, G. Gomez-Noya, J.B. Quintana, M. Llompart, C. Garcia-Jares, R. Cela, Anal. Chem. 76 (2004) 1054–1062.
[31] H.L. Xu, Y. Li, D.Q. Jiang, X.P. Yan, Anal. Chem. 81 (2009) 4971–4977.
[32] J. Lopez-Dariasa, V. Pinoa, Y.J. Meng, J.L. Andersonb, A.M. Afonsoa, J. Chromatogr. A 1217 (2010) 7189–7197.
[33] A.J. King, J.W. Readman, J.L. Zhou, Environ. Chem. Health 25 (2003) 69–75.