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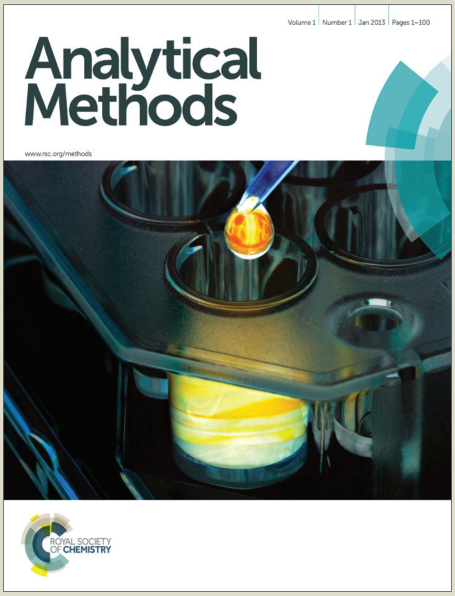

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Metal organic framework MIL-101 coated fiber for headspace solid phase microextraction of volatile aromatic compounds

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The sol-gel coating technique was applied for the preparation of metal organic frameworks (MOFs)-based solid phase microextraction (SPME) fibers by coating MIL-101 onto stainless steel wires. The prepared fiber was explored for the headspace SPME (HS-SPME) of seven volatile aromatic compounds (VACs) from water samples followed by gas chromatography-mass spectrometric analysis. Several important experimental parameters, such as extraction temperature, extraction time, sample volume, salt addition and desorption conditions, were investigated. Under the optimized experimental conditions, the developed HS-SPME method with MIL-101 coated fiber had a good linearity in the range of 0.05-50.0 μg L^{-1} for the analytes with the correlation coefficients (*r*) ranging from 0.9974 to 0.9988. Based on a signal-to-noise ratio (*S/N*) of 3, the limits of detections (LODs) for the seven analytes ranged from 1.0 to 5.0 ng L^{-1}. Compared with two commercial SPME fibers, the laboratory-made MIL-101 coated fiber showed a higher extraction efficiency for the seven VACs. The established method was successfully applied to the determination of the VACs in real local tap and lake water samples. The recoveries of method for the seven VACs at spiking levels of 0.1 and 5.0 μg L^{-1} fell in the range from 76.4% to 116.1%.

Introduction

Solid phase microextraction (SPME), first introduced by Pawliszyn and coworkers in the 1990s,[1] has been widely applied in the analysis of environmental, food, forensic, clinical, pharmaceutical and biological samples[2] due to its advantages such as being solvent-free, simplicity of operation, and easy linkup with chromatographic detection instruments.[3] However, some drawbacks related to SPME, such as the limited variety of the available commercial SPME fibers, the easy breakage of the fiber, the stripping of the fiber coating, and the coating swelling in some organic solvents,[4] have limited its wider applications. It is well known that the coating material of the SPME fiber plays a key role in the SPME process by affecting the partition of the analytes between the coating and sample matrix.[5] Therefore, the exploitation of new coating materials is of great importance to achieve a high extraction efficiency and selectivity. Currently, many home-made adsorbent materials including carbon nanomaterials,[6,7] molecular imprinted polymer,[8,9] mesoporous materials[10,11] and polymeric ionic liquids,[12,13] have received an inceasing attention.

Metal organic frameworks (MOFs) are a recently identified class of porous polymeric materials which consist of metal ions or clusters linked together by organic bridging ligands.[14] Their unique properties, such as permanent nanoscale porosity, high surface area, uniform structured cavities, and the availabe in-pore functionality and outer-surface modifications, have made MOFs a kind of promising materials for the applications in gas storage, catalysis, sensing, adsorption and separations.[15-18] Since the first application of MOF as an efficient adsorption material for SPME in 2009,[19] MOFs-based SPMEs have intrigued more and more attentions from analytical chemists.[20-22] MIL-101 (MIL stands for the Materials of Institute Lavoisier), as one of the typical MOFs, is basically built up from a hybrid supertetrahedral building unit, which is formed by rigid terephthalate ligands and trimeric chromium (III) octahedral clusters.[23] The excellent features of the MIL-101, including mesoporous zeotype architecture with mesoporous cages and microporous windows, high surface area and numerous unsaturated chromium sites,[24] have endowed it with a great application potential as the cartridge packing materials[25] in solid-phase extraction and the fiber coating materials in SPME.

The coating methods for the preparation of MOFs-based SPME fibers in recent literatures included *in situ* hydrothermal growth for MAF-X8,[26] physical agglutination for MIL-53,[27] layer-by-layer deposition for ZIF-8[28] and covalent bonding method for ZIF-90.[29] On the other hand, sol-gel technique, which was established by Malik and coworkers[30] for the preparation of SPME coatings, has been widely used to synthesize porous and dense coatings and organic-inorganic hybrid materials in mild conditions, and the materials prepared by the sol-gel method often exhibited good homogeneity, high thermal and solvent stability and large surface area with porous structures.[31] However, thus far, there have been few reports about the application of the sol-gel technique for the preparation of MOFs-based SPME fibers. Recently, we have reported a successful preparation of the polydimethylsiloxane/metal-organic frameworks (PDMS/MOFs)-based SPME fiber by sol-gel technique and its effective SPME for some polycyclic aromatic hydrocarbons (PAHs) from water samples.[32]

To further explore the potential applications of MOFs-based SPME fibers prepared by sol-gel technique, in this work, MOFs-based SPME fibers were prepared by coating MIL-101 on stainless steel wires by sol-gel technique. The extraction performance of the prepared fibers were examined using seven volatile aromatic compounds (VACs) (chlorobenzene, ethylbenzene, *m*-xylene, *o*-xylene, bromobenzene, mesitylene and *o*-dichlorobenzene) as model analytes, which have shown a serious adverse effect on both human health and environment.[33] As a result, the MIL-101 coated fiber was suitable for the SPME of the VACs from real water samples prior to their gas chromatography-mass spectrometric analysis.

Experimental

Reagents and materials

$Cr(NO_3)_3\cdot 9H_2O$, dichloromethane (CH_2Cl_2), dimethylformamide (DMF), methyltrimethoxysilane (MTMOS), hydrofluoric acid (HF, 40%, w/w), trifluoroacetic acid (TFA, 99%) and hydroxy terminated polydimethylsiloxane (HO-PDMS) were obtained from the Boaixin Chemical Reagents Company (Baoding, China). Terephthalic acid and standards of chlorobenzene, ethylbenzene, *m*-xylene, *o*-xylene, bromobenzene, mesitylene and *o*-dichlorobenzene were purchased from

Aladdin-Reagent (Shanghai, China). A mixture stock solution containing the seven VACs each at 5.0 mg L^{-1} was prepared in acetone and stored at 4 ^{o}C.

The commercial SPME fibers coated with PDMS (100 μm) and PA (85 μm) were supplied by Supelco (Bellefonte, PA, USA). Stainless steel wires (o.d. 304, 310 μm) were purchased from the Anting Micro-Injector Factory (Shanghai, China).

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). Tap water and lake water samples were collected from Baoding (Baoding, China). The samples were directly used for SPME without any pretreatment.

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 injector was operated in the split mode (the ratio was 1:15) and the injection port temperature was maintained at 230 ^{o}C. The column was first maintained at 50 ^{o}C for 1 min and increased to 80 ^{o}C at a rate of 5 ^{o}C min^{-1}, then raised to 260 ^{o}C at 30 ^{o}C min^{-1}. GC-MS interface temperature was maintained at 250 ^{o}C. The electron impact ionization source was operated at 70 eV and 200 ^{o}C. The MS detection was made using full-scan mode at a voltage of 0.7 kV from 50–1000 m/z for qualitative analysis and selected ion monitoring (SIM) mode for quantitative analysis.

The surface morphology of the coating was observed by scanning electron microscope (SEM) on a JSM-7500F (JEOL, Japan). The thermal properties of the fiber coating were measured by thermal gravimetric (TG) analysis with a TG209F1 instrument (NETZSCH, Germany). The infrared (IR) spectra were measured with a WQF-510A spectrometer (Beijing, China). 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).

Preparation of MIL-101 coated fiber

MIL-101 was synthesized according to the reference method.[34] Stainless steel wires were used to fabricate the SPME fibers. One end (2.0 cm in length) of the stainless steel wire was etched by HF (40%, w/w) at room temperature for 30 min[35] to generate a rough surface to increase the contact area between the wire and sol-gel coatings. Then, the treated wire was washed with water and dried in a desiccator.

Sol-gel approach was employed for coating the MIL-101 onto the stainless steel wire. First, 50 mg of MIL-101, 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 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 being dried for about 10 s in an oven at 60 ^{o}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. Then, the fiber was dried in the oven at 60 ^{o}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 μm was obtained. Finally, the coated fiber was assembled in a 5 μL microsyringe and conditioned at 100 ^{o}C for 1 h and 260 ^{o}C for 1 h under a nitrogen flow in the GC injector.

Headspace SPME procedures

To carry out the headspace SPME (HS-SPME) for the analytes, 10.0 mL sample solution containing the seven compounds at each of 10 μg L^{-1} together with 2 g NaCl was put into a 20.0 mL glass vial, which was immediately capped with a PTFE-coated septa to prevent sample evaporation. A Teflon-coated stir bar was used to stir the sample solution at 600 rpm and the MIL-101coated fiber was exposed to the headspace over the sample solution for 20 min for the HS-SPME. After the extraction, the needle was removed from the vial and immediately transferred to the GC injection port for thermal desorption at 230 ^{o}C for 4 min for GC-MS analysis.

Results and discussion

Characterization of the MOFs coating

The surface structure of the etched stainless steel wire and MIL-101 coated fiber were investigated by scanning electron microscope (SEM) under the magnification of 200. As shown in Fig. 1A, a rough structure of the stainless steel wire etched by HF can be obviously observed, which could be beneficial for the formation of a stable coating on the wire. Fig. 1B shows that the surface of the MIL-101 coating was uniform, granulated and rough, which could result in an increase of the surface area and an improvement of the adsorption capacity.

The thermal properties of the MIL-101 coating were analyzed by TG. Fig. 2A shows the TG curve of the MIL-101coating without prior heat treatment. About 10.0% weight loss for the MIL-101 coating was observed at 300.0 ^{o}C, which might be caused by the removal of the adsorbed water and the volatile solvent of CH_2Cl_2 on the material. Fig. 2B shows the TG curve of the coating after its being heat-treated at 100 ^{o}C for 1 h and at 260 ^{o}C for 1 h under nitrogen atmosphere in the GC injector. It shows that no obvious weight loss was observed for the heat-treated MIL-101 coating before 300.0 ^{o}C. Since the desorption temperature for the seven VACs was 230 ^{o}C, the MIL-101 coating could be stable enough for the GC-MS analysis of the analytes. In addition, the experimental results also indicated that under the optimized experimental conditions, the MIL-101 coated fiber can be reused over 120 times without a significant change of the extraction performance, indicating a long life-time of the prepared fiber.

The infrared absorption spectra for the coating are shown in Fig. 3. The PDMS coated fiber was prepared in the same way as for the MIL-101 coated fiber, but without the addition of MIL-101. The wave number at 2966 cm^{-1} for the C-H stretching on methyl groups and the ones at 1018 cm^{-1} and 1101 cm^{-1} for Si-O stretching could be observed[36] in the absorption spectrum for the PDMS coating in Fig. 3A. Compared with the PDMS coating, the infrared absorption spectrum for the MIL-101 coating in Fig. 3B displays remarkable absorptions in the wave numbers ranging from 1300 cm^{-1} to 1800 cm^{-1}, which could be assigned to the asymmetric and symmetric ν(COO) and the ν(C-C).[37] In addition, the strong characteristic absorption peaks for the C=O group stretching at 1684 and 1628 cm^{-1} and the C-O bond stretching at 1404 cm^{-1} for terephthalic acid were also observed. These results could confirm that the MIL-101 framework was successfully coated on the fiber.

Effect of extraction time

HS-SPME is an equilibrium-based extraction procedure and therefore a time-dependent process. The effect of extraction time on the extraction efficiency was examined in the range from 5 to 25 min (Fig. 4A). The peak areas of all the seven VACs were first increased from 5 min to 15 min, and then reached a plateau after 15 min. To ensure the reproducibility for the extraction of the analytes, 20 min of extraction was chosen for further experiments.

Effect of sample volume

For HS-SPME, increasing the volume of headspace would enhance the transfer of the analytes from liquid phase to gas phase so that more VACs could be evaporated to the headspace. However, a large headspace would dilute the analyte concentration and therefore decrease the analytical sensitivity.[38] In this study, the effect of sample volume was investigated by changing the sample volumes from 6.0 to 14.0 mL in a 20.0-mL glass vial. Figure 4B shows that the peak areas of the VACs increased with increased volume of water sample until 10.0 mL, and then remained almost constant. Therefore, 10.0 mL sample solution (the ratio of sample solution to headspace was 1:1) was chosen for the further study.

Effect of salt addition

An addition of NaCl to sample solution could be favorable for HS-SPME since it will enhance the transfer of the analytes from liquid phase to gas phase due to the salting-out effect.[39] In this study, the effect of the NaCl addition to the sample was investigated in the concentration range of NaCl from 0 to 30%. Fig. 4C shows that the peak areas for all the analytes increased with the NaCl concentration being increased from 0 to 20%, and then remain almost unchanged. Therefore, 20%

of NaCl in the sample was selected for subsequent studies.

Effect of extraction temperature

Generally, the increase of extraction temperature can enhance the mass transfer of the analytes from aqueous sample to the headspace and further to the fiber coating. However, the amount of the analytes adsorbed on the fiber could be decreased as the extraction temperature was increased since thermodynamically, adsorption is generally an exothermic process.[40] In this study, different extraction temperatures ranging from 20 to 40 ^{o}C were investigated for the extraction. The experimental results showed that the extraction efficiency was slightly decreased for all the analytes after the temperature was higher than 25 ^{o}C. Thus, 25 ^{o}C was chosen for the extraction.

Desorption temperature and desorption time

The desorption temperature and desorption time were both important in the desorption process. Giving an overall consideration of the thermal stability of the fiber coating and the volatility of the analytes, desorption temperatures between 200 ^{o}C and 260 ^{o}C for 5 min were investigated (Fig. 4D). It could be seen that the peak areas of the seven VACs increased with the desorption temperature being increased from 200 ^{o}C to 220 ^{o}C, and then remain almost unchanged. Based on this result, the desorption temperature at 240 ^{o}C was chosen for the experiments.

A proper desorption time can lead to an achievement of a complete desorption of the analytes from the coated fiber and ensure accurate quantitative analysis. In this work, the effect of desorption time were investigated in the range from 1 to 7 min at 240 ^{o}C. The results showed that 4 min of desorption was sufficient for the desorption of the seven VACs and therefore was selected. After the desorption at 240 oC for 4 min, no carry-over of the analytes was observed.

Comparison with other commercial fibers

The extraction capability of the MIL-101 coated fiber for the seven VACs was compared with that of the two commercial fibers (PDMS and PA). As shown in Fig. 5, the peak areas of all the compounds extracted by the prepared fiber were higher than those by the commercial fibers. The good performance of the MIL-101 coated fiber for VACs may result from the combined effects of the π-π interactions of the aromatic rings of the analytes with the framework 1,4-benzenedicarboxylic acid molecules, the large surface area, as well as the unique porous structures of the MOFs. The MIL-101 coated fiber showed a better extraction efficiency for o-xylene and o-dichlorobenzene than the other five remaining VACs (a similar result was also observed in the literature work[41]). The reason for this could be that the polarity of o-xylene and o-dichlorobenzene is likely more similar to that of the MIL-101-based fiber coatings.

Method evaluation

The MIL-101 coated fiber was used for the HS-SPME of the seven VACs and the analytical data under the optimized experimental conditions are shown in Table 1. A good linearity was observed in the range of 0.05-50.0 μg L^{-1} with the correlation coefficients (*r*) ranging from 0.9974 to 0.9988 for the analytes. Based on a signal-to-noise ratio (*S/N*) of 3, the limits of detections (LODs) for the seven analytes were in the range from 1.0 to 5.0 ng L^{-1}. By using three different fibers prepared in the same way, the relative standard deviation (RSD) for fiber-to-fiber reproducibilities for the extraction of the analyteswas less than 13.9%. When the same fiber was used for five replicate extractions under the same conditions, the RSDs for single-fiber repeatability were below 9.4%. This result indicated that the fiber had a good reproducibility.

Determination of the VACs in real water samples

The established method was applied for the determination of the VACs in tap and lake water samples, respectively. As a result, no VACs were detected in the water samples. The recoveries of the method were determined by expressing the mean concentrations found as a percentage of the concentrations spiked. Five parallel analyses were made at each concentration level. Consequently, the recoveries for the VACs from water samples at spiking levels of 0.1 and 5.0 μg L^{-1} fell in the range from 76.4% to 116.1%, with RSDs between 4.0% and 13.5% (Table 2). Fig. 6 shows the typical GC-MS chromatograms for lake water.

Conclusions

A MIL-101 coated SPME fiber was prepared *via* sol-gel approach. It was successfully applied for the extraction of seven VACs in real water samples prior to their determination by GC-MS. The fiber showed a good thermal stability, high extraction efficiency and good reproducibility compared with commercial fibers (PDMS and PA). The result indicates that the MIL-101 coated SPME fiber can provide an alternative for other commercial fibers in sample pretreatment.

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Table captions

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

Table 2 Recoveries for the determination of the seven VACs in two water samples using the current SPME-GC-MS method.

Figure captions

Fig. 1 Scanning electron micrographs of (A) etched stainless steel wire and (B) MIL-101 coated fiber.

Fig. 2 Thermogravimetric curve of the MIL-101 coating before (A) and after heat-treatment (B).

Fig. 3 FT-IR spectra of the coating material: (A) PDMS coating and (B) MIL-101coating.

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

Fig.5 Comparison of the extraction efficiency of the MIL-101-coated fiber with the commercial fibers for VACs.

Fig.6 Chromatograms of (A) tap water and (B) the tap water spiked at the concentration of 0.1 μg L^{-1} each of the VACs. Peak identification: (1) chlorobenzene, (2) ethylbenzene, (3) *m*-xylene, (4) *o*-xylene, (5) bromobenzene, (6) mesitylene and (7) *o*-dichlorobenzene

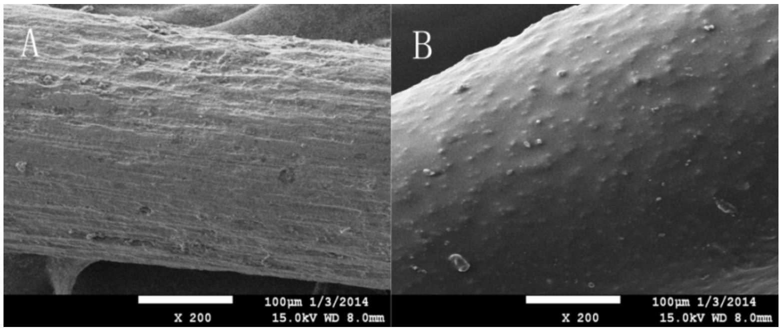
Table 1 Some analytical data obtained for the SPME of the VACs using the MIL-101coated fiber.

Compound	Linear range ($\mu g\ L^{-1}$)	LOD ($ng\ L^{-1}$)	*r*	RSD (%) one fiber (*n*=5)	RSD (%) fiber to fiber (*n*=3)
chlorobenzene	0.05-50.0	5.0	0.9977	5.8	12.7
ethylbenzene	0.05-50.0	1.0	0.9974	6.9	8.4
m-xylene	0.05-50.0	1.0	0.9985	9.1	10.9
o-xylene	0.05-50.0	1.0	0.9988	7.6	8.6
bromobenzene	0.05-50.0	5.0	0.9986	8.3	11.8
mesitylene	0.05-50.0	5.0	0.9975	9.4	13.9
o-dichlorobenzene	0.05-50.0	1.0	0.9987	8.3	9.5

Table 2 Recoveries for the determination of the seven VACs in two water samples using the current SPME-GC-MS method.

Compound	Spiked ($\mu g\ L^{-1}$)	Tap water (n=5)		Lake water (n=5)	
		Detected ($\mu g\ L^{-1}$)	Recovery ± RSD (%)	Detected ($\mu g\ L^{-1}$)	Recovery ± RSD (%)
chlorobenzene	0.1	0.09	90.0 ± 10.9	0.08	86.4 ± 5.5
	5.0	4.3	86.1 ± 7.6	4.9	98.2 ± 7.1
ethylbenzene	0.1	0.11	112.2 ± 7.7	0.10	102.0 ± 4.9
	5.0	5.1	102.0 ± 6.9	5.3	106.3 ± 9.7
m-xylene	0.1	0.08	81.3 ± 5.8	0.07	76.4 ± 13.5
	5.0	4.2	84.4 ±5.4	4.3	86.5 ± 8.3
o-xylene	0.1	0.07	78.0 ± 9.8	0.08	84.7 ± 6.6
	5.0	4.4	88.2 ± 12.2	4.5	90.4 ± 9.5
bromobenzene	0.1	0.08	87.3 ± 7.9	0.09	92.2 ± 4.8
	5.0	5.1	102.3 ± 4.4	4.7	94.0 ± 4.0
mesitylene	0.1	0.09	95.8 ± 8.8	0.10	105.8 ± 10.2
	5.0	5.8	116.1 ± 9.1	4.4	88.2 ± 7.9
o-dichlorobenzene	0.1	0.09	90.8 ± 9.5	0.09	94.4 ± 9.4
	5.0	4.6	95.2 ± 6.7	7.0	78.2 ± 6.3

The sol-gel technique was applied as a novel coating method in the preparation of metal organic frameworks (MOFs)-based solid phase microextraction (SPME) fibers by coating MIL-101 onto a stainless steel wire.



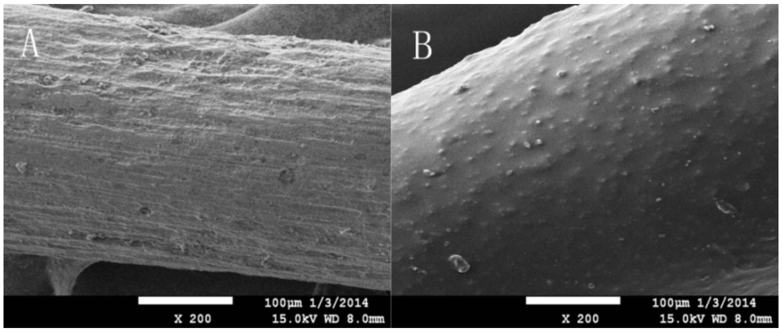


Fig.1 Scanning electron micrographs of (A) etched stainless steel wire and (B) MIL-101 coated fiber.

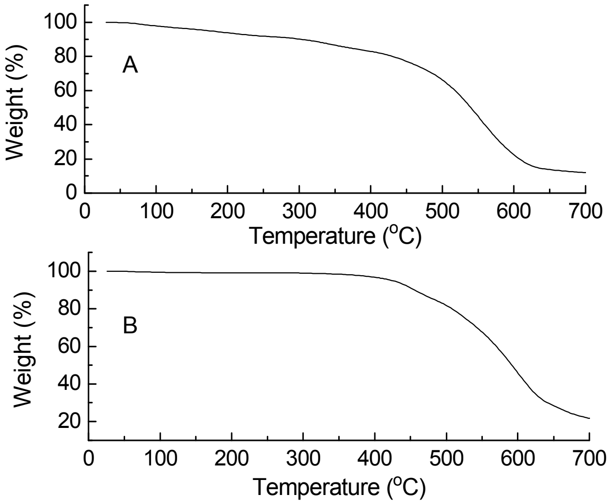


Fig.2 Thermogravimetric curve of the MIL-101 coating before (A) and after heat-treatment (B).

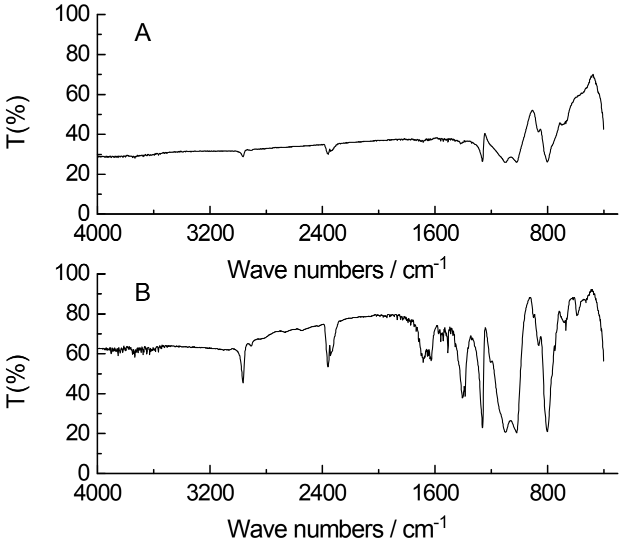


Fig.3 FT-IR spectra of thecoating material: (A) PDMS coating and (B) MIL-101coating.

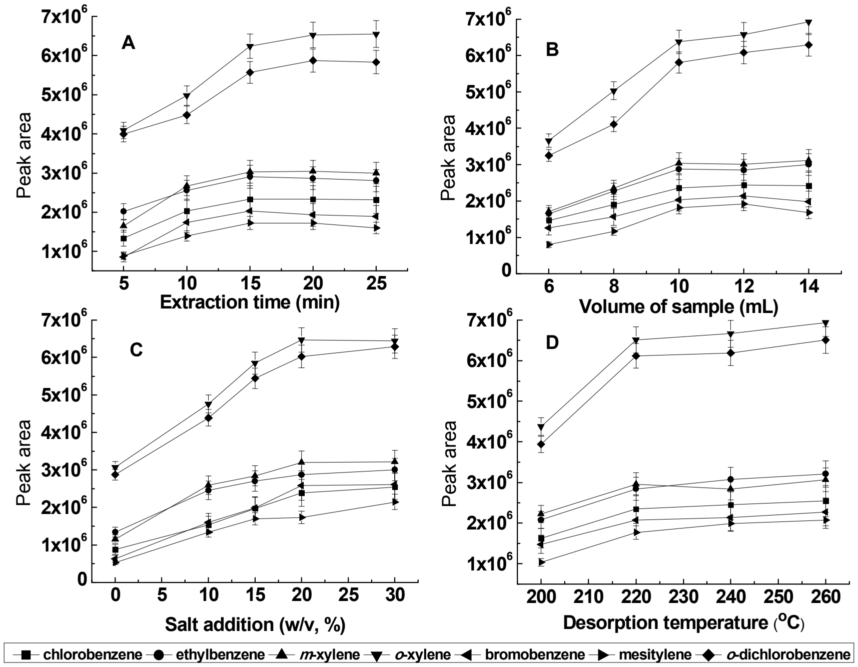


Fig.4 Effect of extraction conditions on the headspace-SPME efficiency: (A) extraction time; (B) sample volume; (C) salt addition; and (D) desorption temperature.

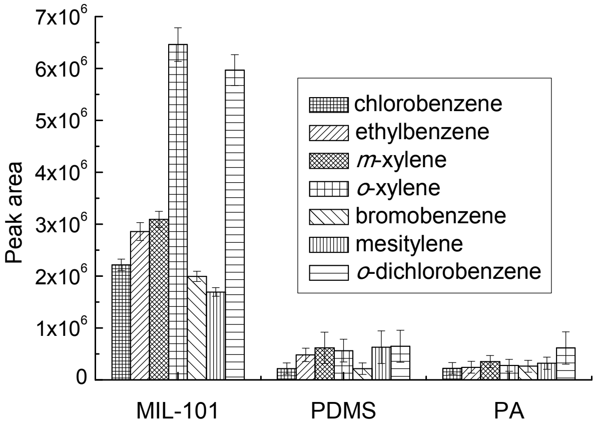


Fig.5 Comparison of the extraction efficiency of the MIL-101-coated fiber with the commercial fibers for VACs.

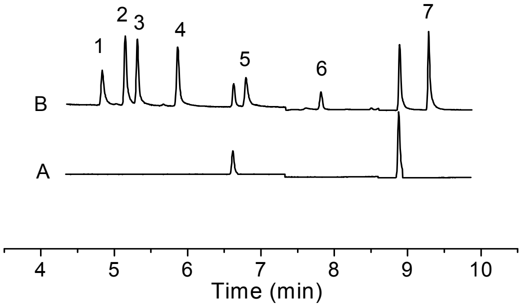


Fig.6 The chromatograms of (A) lake water and (B) the lake water spiked at the concentration of 0.1 μg L^{-1}each of the VACs. Peak identification: (1) chlorobenzene, (2) ethylbenzene, (3) *m*-xylene, (4) *o*-xylene, (5) bromobenzene, (6) mesitylene and (7) *o*-dichlorobenzene