



## Preparation and characterization of porous carbon material-coated solid-phase microextraction metal fibers

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### ABSTRACT

Two kinds of porous carbon materials, including carbon aerogels (CAs), wormhole-like mesoporous carbons (WMCs), were synthesized and used as the coatings of solid-phase microextraction (SPME) fibers. By using stainless steel wire as the supporting core, six types of fibers were prepared with sol-gel method, direct coating method and direct coating plus sol-gel method. Headspace SPME experiments indicated that the extraction efficiencies of the CA fibers are better than those of the WMC fibers, although the surface area of WMCs is much higher than that of CAs. The sol-gel-CA fiber (CA-A) exhibited excellent extraction properties for non-polar compounds (BTEX, benzene, toluene, ethylbenzene, o-xylene), while direct-coated CA fiber (CA-B) presented the best performance in extracting polar compounds (phenols). The two CA fibers showed wide linear ranges, low detection limits ( $0.008$ – $0.047 \mu\text{g L}^{-1}$  for BTEX,  $0.15$ – $5.7 \mu\text{g L}^{-1}$  for phenols) and good repeatabilities (RSDs less than 4.6% for BTEX, and less than 9.5% for phenols) and satisfying reproducibilities between fibers (RSDs less than 5.2% for BTEX, and less than 9.9% for phenols). These fibers were successfully used for the analysis of water samples from the Pearl River, which demonstrated the applicability of the home-made CA fibers.

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### 1. Introduction

As a new and remarkable sample preparation technique, solid-phase microextraction (SPME) has been widely applied in different fields including the environment, food, natural products, pharmaceuticals, biology, toxicology, and forensics [1–5], due to its high efficiency, non-solvent demanding, and facilitation in automation and coupling techniques [6–8].

SPME is based on the distribution effect of analytes between the samples and the extraction phase, which is typically immobilized on a fused silica fiber or metal wires. SPME fiber coating plays the most important role in the extraction since different kinds of analytes require different coatings [1,6]. Up to now, several kinds of SPME fibers are commercially available. Polymeric materials such as polydimethylsiloxane (PDMS), polyacrylate (PA) which have great affinity for non-polar analytes and polar compounds via absorption, respectively, and mixed-phase coatings such as PDMS/Divinylbenzene (DVB), Carboxen/PDMS, Carbowax/DVB, and Carbowax/Template Resin extract analytes via adsorption [9,10].

Although these commercial fibers have been successfully applied in many fields, some drawbacks such as nonresistance to high temperature, low selectivity, high cost and short lifetime, limit their applications. Therefore, the exploration of SPME fiber coating and the approaches how to combine the coating materials with the fiber in both high selectivity and sensitivity raise huge concern in the chemical and other chemistry-related community [11].

In the past years, several approaches including direct use of uncoated fiber [12], immobilized resin [13,14], sol-gel technology [15–18], molecularly imprinted technology [19–21], electrochemical procedures [22–25] and physical deposition [26,27] have been developed for fiber coating. Among them, immobilized resin and sol-gel technology were widely used. Mesoporous silica particles, silicon particles bounded with C8, C18, phenyl-C18, C15, and  $\beta$ -cyclodextrin were immobilized into the substrate by epoxy resin glue. Sol-gel technology exhibited advantages over commercial fibers because of their porous structure and strong adhesion to the fused-silica fiber. The reports on sol-gel technology to immobilize solid sorbent are increasing in recent years. Fiber coatings, such as carbon nanotubes (CNTs) [28], ceramic/carbon composite [29], low-temperature glassy carbon [30] and activated charcoal [31], were prepared by this method. These studies proved that sol-gel technology as well as immobilized resin is a suitable coating method for solid sorbent.

Porous carbon materials, such as activated carbons, carbon aerogels (CAs), carbon xerogels, nanostructured carbons,

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wormhole-like mesoporous carbons (WMCs), are usually utilized as electrode materials and adsorbent materials, due to their high surface area and porosity. CAs have three-dimensional nano-network, high specific surface area, abundant mesopores and high electric conductivity [32], and have been applied in the fields of mechanics, acoustics, thermotics and optics. They are also considered to be perfect electrode material, insulation material, adsorbent, catalyst and carrier [33,34].

In this work, two types of porous carbon materials, including CAs and WMCs, were synthesized and used as coating materials for preparing SPME fibers, based on three types of coating preparation techniques, including sol-gel, direct-coating and sol-gel plus direct coating. To the best of our knowledge, it is the first time that the CAs and WMCs materials were used as SPME fiber coatings. A series of experiments were performed to evaluate the performance of the porous carbon coating materials, and the effects of the coating preparation methods on the properties of fiber coatings were also discussed.

## 2. Experimental

### 2.1. Chemicals and reagents

The stainless steel wires (100  $\mu\text{m}$  diameter) were purchased from Small Parts Inc. (Miami Lakes, FL, USA). Epoxy glue was from Henkel Inc. (Mississauga, ON, Canada). Methyltrimethoxysilane (MTMOS, 97%), trifluoroacetic acid (TFA, 99%) and poly(methylhydrosiloxane) (PMHS) were purchased from Alfa Aesar (Ward Hill, MA, USA). The standard mixture of four non-polar compounds including benzene (B), toluene (T), ethylbenzene (E), *o*-xylene (X), and five polar compounds which were 2-chlorophenol (2-CP), *p*-cresol (P), 2-nitrophenol (2-NP), 2,4-dichlorophenol (2,4-DCP) and 2,4,6-trichlorophenol (2,4,6-TCP) were purchased from Alfa Aesar and dissolved in methanol (HPLC grade) to make stock solutions at a concentration of 1 mg mL<sup>-1</sup> for each compound. SPME fiber holder and commercial fibers (100  $\mu\text{m}$  PDMS and 85  $\mu\text{m}$  PA) were obtained from Supelco (Bellefonte, PA, USA). A MSH-20D digital magnetic stirrer (Seoul, South Korea) was used for the agitation of the samples.

### 2.2. Synthesis of the porous carbon materials

The synthesis of CA was improved based on the method reported in reference [33]. All reactants, including resorcinol (R), formaldehyde (F), deionized water (W) and cetyltrimethylammonium bromide (CTAB), were mixed by a magnetic stirrer at room temperature. The mole ratio of R/F and R/CTAB were fixed at 1:2 and 500:1, respectively, and the solid content was 40%. Then the mixture was transferred into a glass vial. The vial was sealed and placed inside a water bath at 75 °C. The temperature was increased to 85 °C after 5 h and the reaction was cured for 5 days. After curing, the gel was directly dried in air at room temperature for 1 day, and then dried in an oven at 100 °C at ambient pressure for 8 h. Subsequently, the resultant RF aerogel was heated to 500 °C with a heating rate of 5 °C min<sup>-1</sup> and kept at this carbonization temperature for 3 h in N<sub>2</sub> flow.

The synthesis of WMC was described in reference [34]. Briefly, 2 g sucrose was dissolved in 3 mL sulfuric acid solution (pH 2.0) under stirring, followed by adding 4 mL tetraethyl orthosilicate (TEOS) under intense stirring. The mixture was stirred continuously until complete homogenization. The obtained homogeneous mixture was gelled and aged at 40 °C for 2 days. The resulting colorless, transparent sucrose/silica composite was further reacted for 6 h at 100 °C and subsequently for 6 h at 160 °C. After that, the sample was heated to 900 °C with a heating rate of 5 °C min, and kept at

**Table 1**  
Pore structure parameters of CA and WMC.

Sample	$S_{\text{BET}}^a$ (m <sup>2</sup> g <sup>-1</sup> )	$V_{\text{total}}^b$ (cm <sup>3</sup> g <sup>-1</sup> )	$P_{\text{mic}}^c$ (%)	$P_{\text{meso}}^c$ (%)	$P_{\text{macro}}^c$ (%)
CA	429	0.31	32	53	15
WMC	1372	0.78	25	74	1

<sup>a</sup>  $S_{\text{BET}}$  is the specific surface area calculated by the BET method.

<sup>b</sup>  $V_{\text{total}}$  is the total pore volume obtained from DFT method.

<sup>c</sup>  $P_{\text{mic}}$ ,  $P_{\text{meso}}$ , and  $P_{\text{macro}}$  are micro-, meso- and macropore ratios calculated according to the following equations:  $P_{\text{mic}} = (V_{\text{mic}}/V_{\text{total}}) \times 100\%$ ,  $P_{\text{meso}} = (V_{\text{meso}}/V_{\text{total}}) \times 100\%$ ,  $P_{\text{macro}} = (V_{\text{macro}}/V_{\text{total}}) \times 100\%$ , where  $V_{\text{mic}}$ ,  $V_{\text{meso}}$  and  $V_{\text{macro}}$  are cumulative volume of micro-, meso- and macropores from DFT.

this carbonization temperature for 3 h in N<sub>2</sub> flow. After carbonization, the black carbon/silica composite was washed using 40 wt% HF solution to remove the silica, followed by filtration and drying at 100 °C for 10 h. Then the WMC was obtained.

The pore structure parameters of CA and WMC are shown in Table 1.

### 2.3. Preparation of the SPME fiber

#### 2.3.1. Pretreatment of the stainless steel wire

The stainless steel wire (length 20 cm) was cleaned with deionized water and shaken in acetone for 10 min with an ultrasonicator, and then the wires were put in acetone for 8 h to remove the organic impurity. Afterwards, the steel wire was taken out and cleaned with pure water again and then air dried at room temperature.

#### 2.3.2. Preparation of the sol-gel solution

A 2-mg amount of the porous carbon materials was placed inside a centrifugal tube, and then 50  $\mu\text{L}$  distilled water, 400  $\mu\text{L}$  MTMOS and 20 mg PMHS were added. The mixture was agitated thoroughly by sonication for 20 min. Then 50  $\mu\text{L}$  TFA was added into the resulting solution with ultrasonic agitation for 5 min and a stable sol solution was formed.

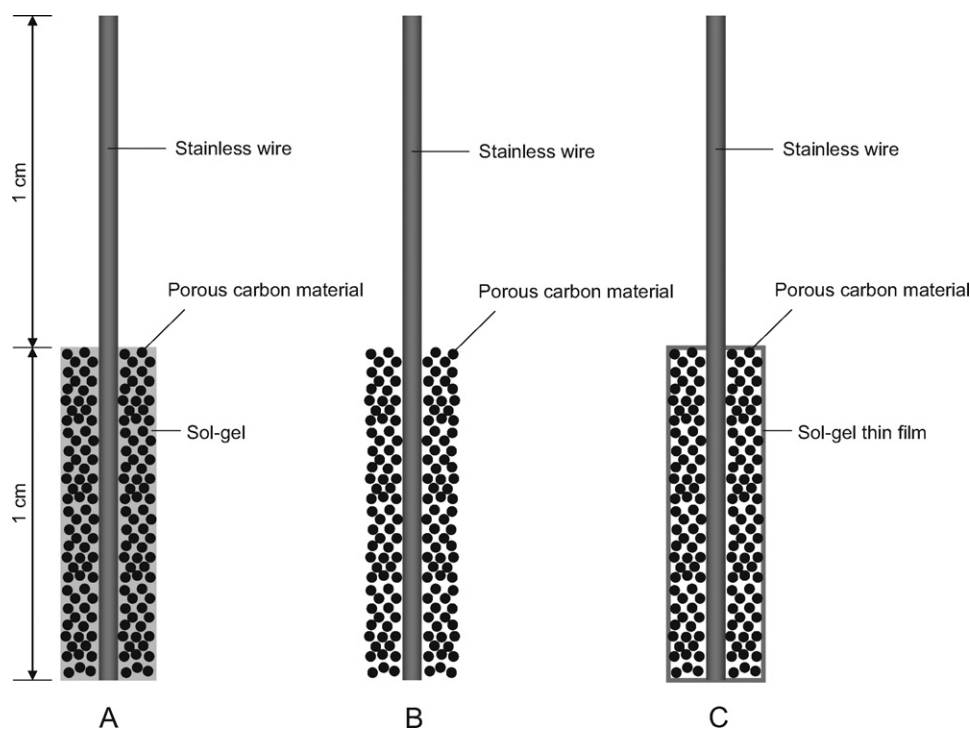
#### 2.3.3. Coating of the fibers

Three approaches were used for the coating of the fibers, including sol-gel, direct coating and direct coating plus sol-gel.

For the fibers prepared with sol-gel method, the prepared sol-gel solution was transferred into a glass tube whose bottom was covered with a Parafilm membrane (Pechiney, Chicago, IL, USA). The treated wire pierced through the membrane and then was drawn at a constant rate. During that time a sol-gel coating layer was formed on the bare outer surface of the wire. After the coating was cured, the process was repeated until the needed thickness was obtained. Two types of fibers (CA-A and WMC-D) were prepared by this method and the thickness of the coating was about 100  $\mu\text{m}$ . Fig. 1(A) shows the schematic diagram of the fiber prepared with sol-gel method.

For the fibers prepared with direct coating method, the treated wire was coated and formed a very thin and homogeneous layer with high temperature resistant epoxy resin, and then the wire was inserted into the porous carbon materials and pulled out. The procedures were repeated until the needed thickness was obtained. Two types of fibers (CA-B and WMC-E) were prepared by this method and the thickness of the coating was about 80  $\mu\text{m}$ . Fig. 1(B) shows the schematic diagram of the fiber prepared with direct coating method.

For the fibers prepared with direct coating plus sol-gel method, the treated wire was first coated with porous carbon material by direct coating method, and then the coated wire was quickly dipped into sol-gel solution, and a very thin gel coating was formed to protect the coated porous carbon material. Two types of fibers (CA-C and WMC-F) were prepared by this method and the thickness of the coating was about 100  $\mu\text{m}$ . Fig. 1(C) shows the schematic



**Fig. 1.** Schematics of three types of fibers. (A) Fiber prepared with sol-gel method; (B) fiber prepared with direct coating method; (C) fiber prepared with direct coating plus sol-gel method.

diagram of the fiber prepared with direct coating plus sol-gel method.

All the prepared fibers were placed in a desiccator overnight at room temperature. Prior to use, the fiber was cut into 2-cm long, and 1 cm coating will be left and the other coating will be scratched off and the exposed metal wire will be coated with a very thin film of Epoxy glue and then inserted into the inside needle of the fiber assembly to fix the fiber coating. The prepared fibers were then conditioned at 50–250 °C under nitrogen for 6 h in a GC injection port with gradually rising temperature program.

#### 2.4. SPME procedures

All of the fibers, including commercial fibers, were conditioned 30 min in the GC injection port at 250 °C under nitrogen flow before use. Twenty five milliliter sample solution of BTEX or phenols was prepared by diluting the stock solution (1 mg mL<sup>-1</sup>) with deionized water in a 40 mL glass vial. The vial contained a magnetic bar inside was placed on a stirring platform and the stirring rate was set to 1500 rpm. The outside needle of the SPME fiber assembly was used to penetrate the septum of the vial and the coated fiber was then exposed in the headspace for a period of time at room temperature (25 ± 1 °C). After extraction, the fiber was withdrawn into the needle and subsequently inserted into the GC injector for desorption and analysis.

#### 2.5. GC-MS analysis

GC analysis was performed on a Hewlett-Packard 6890N gas chromatograph (Agilent Technologies, CA, USA) equipped with a MSD 5975 mass spectrometer (Agilent Technologies) and a split/splitless injector. Chromatographic separation was carried out with a HP-5MS 5% phenyl-/95% methylsiloxane capillary (30 m × 250 μm, 0.25 μm). For BTEX, helium was used as carrier gas at a constant flow rate of 1.0 mL min<sup>-1</sup>. For the optimization experiments, split ratio was set at 10:1; for the other experiments, such as

linear ranges, detection limits and analysis of real samples, splitless mode was applied. The initial oven temperature was 50 °C (held for 2 min), and then increased to 120 °C at a rate of 20 °C min<sup>-1</sup>. The temperature of the injector was kept at 250 °C. The total run time was 5.5 min. For phenols, carrier gas was held at 1.2 mL min<sup>-1</sup>; split/splitless mode was the same as the determination of BTEX; injector temperature was 250 °C; the initial oven temperature was 100 °C (held for 2 min), and then increased to 150 °C at a rate of 8 °C min<sup>-1</sup>, held for 3 min. The total run time was 11.5 min.

The MSD was operated in the electron impact ion (EI) mode with a source temperature of 230 °C. The electron energy was 70 eV and the filament current 200 μA. For qualitative determinations, the MSD was operated in full-scan mode from *m/z* 35 to 450. For quantitative determinations, the MSD was operated in selected ion monitoring (SIM) mode.

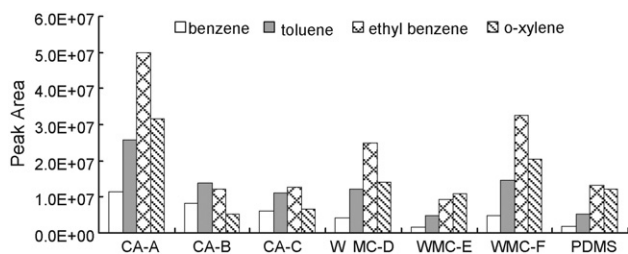
### 3. Results and discussion

#### 3.1. Comparison between the home-made fibers and the commercial fibers

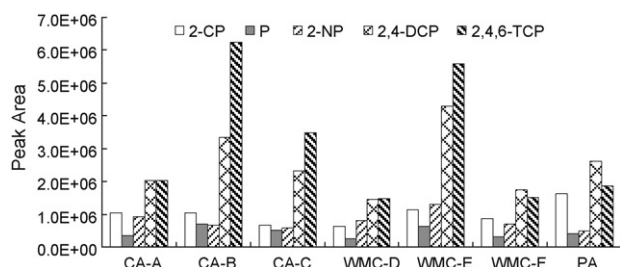
The above six type home-made fibers and the commercial 100 μm PDMS fiber were used for the extraction of four non-polar compounds (BTEX) by headspace-SPME (HS-SPME). From the results shown in Fig. 2, we could see that the fiber of CA-A exhibited the best extraction efficiency for the analytes. The CA-A coating was prepared with sol-gel method which resulted in mixture coating materials, PDMS and CAs. As we know that PDMS has good affinity to non-polar compounds, therefore CA-A coating exhibited best performance for the extraction of BTEX, due to the joint action of PDMS and CAs. Owing to the extraction ability of CAs, the extraction efficiencies of the CA-A fiber for BTEX were much higher than the commercial 100 μm PDMS fiber. Therefore, the CA-A fiber was selected for the subsequent experiments on BTEX.

The above home-made fibers and the commercial 85 μm PA fiber were used for the extraction of five polar compounds (phe-





**Fig. 2.** Comparison of six home-made fibers and commercial 100  $\mu\text{m}$  PDMS fiber for HS-SPME of BTEX (500  $\mu\text{g L}^{-1}$  aqueous solution). Extraction time, 45 min; extraction temperature, 25  $^{\circ}\text{C}$ ; desorption temperature, 250  $^{\circ}\text{C}$ ; desorption time 1.0 min.



**Fig. 3.** Comparison of six home-made fibers and commercial 85  $\mu\text{m}$  PA fiber for HS-SPME of phenols (500  $\mu\text{g L}^{-1}$  aqueous solution). Extraction time, 45 min; extraction temperature, 25  $^{\circ}\text{C}$ ; desorption temperature, 250  $^{\circ}\text{C}$ ; desorption time 1.5 min.

nols) by HS-SPME. From the results shown in Fig. 3, we could see that the fiber of CA-B exhibited the best extraction efficiency for the analytes. CA-B coating was prepared with direct coating method. The extraction efficiency of this coating was determined by the

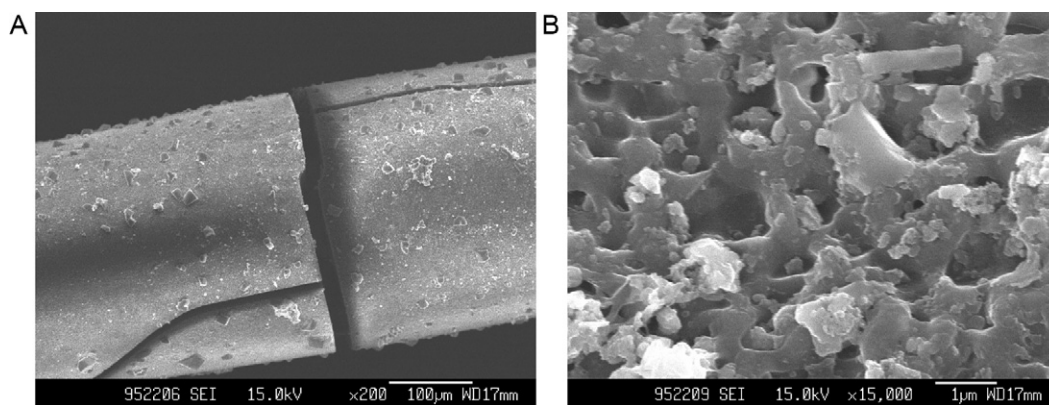
property of CAs. The results illustrated that the prepared CAs are polarity. The extraction efficiencies of the CA-B fiber for most phenols, except 2-CP, were higher than the commercial 85  $\mu\text{m}$  PA fiber. Therefore, the CA-B fiber was selected for the subsequent experiments on phenols.

### 3.2. Surface structure of the fibers

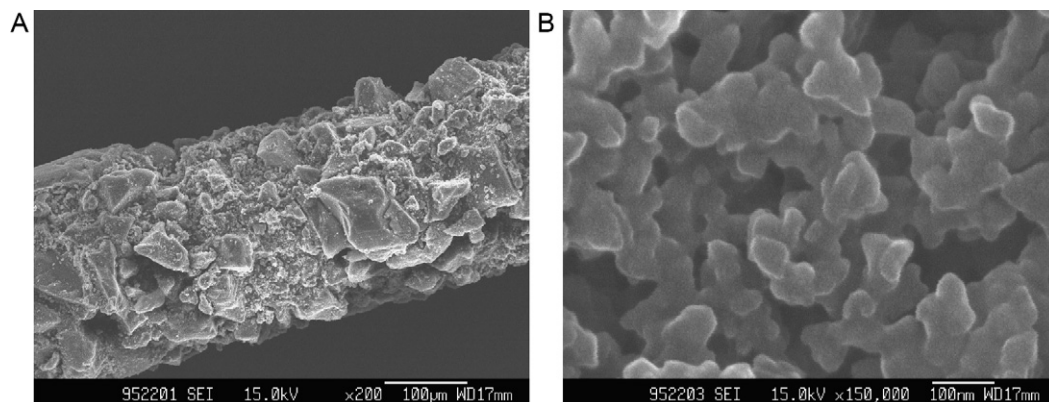
The surface of the selected fibers, including CA-A and CA-B, were characterized by scanning electron microscopy (SEM). Fig. 4A is the surface image of CA-A. No pores and channels appeared on the surface of the coating. Fig. 4B is a picture taken from the crevice of the coating. Lots of pore was observed on the surface of the crevice, which demonstrated well that the CAs were dissolved in the sol-gel solution and homogeneously distributed within the coating. Fig. 5A is the image of CA-B. Comparing to the sol-gel coating, the surface of the direct-coating fiber was very coarse and possesses a lot of pores (Fig. 5B). The images illustrated that both of two types of fibers have their own special surface micro-structure, which possess high extraction capacity for polar and non-polar compounds, respectively.

### 3.3. Thermal stability and lifetime of the fibers

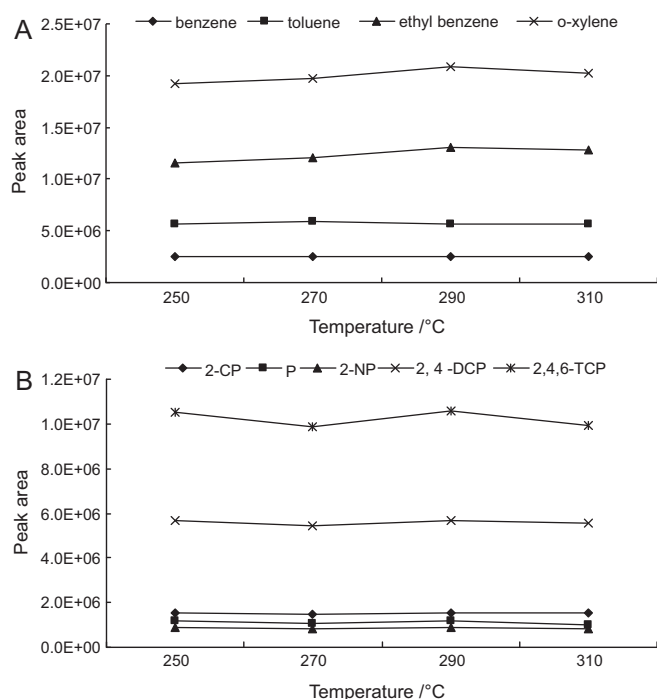
The thermal stabilities of the CA-A and CA-B fibers were studied by HS-SPME of BTEX in aqueous solution and phenols in NaCl saturated solution, respectively. Two types of fibers were conditioned 1 h at different temperatures (ranging from 250  $^{\circ}\text{C}$  to 310  $^{\circ}\text{C}$ ), and then were used to extract the analytes. Fig. 6(A) and (B) illustrated the extraction results of BTEX and phenols, respectively. The extraction efficiencies of two types of fibers were not affected by the



**Fig. 4.** SEM images of the sol-gel-CA-coated fiber (CA-A). (A) The image of the fiber surface ( $\times 200$ ) and (B) the image of the fiber's crack surface ( $\times 15,000$ ).



**Fig. 5.** SEM images of the direct-coated CA fiber (CA-B). (A)  $\times 200$ ; (B)  $\times 150,000$ .



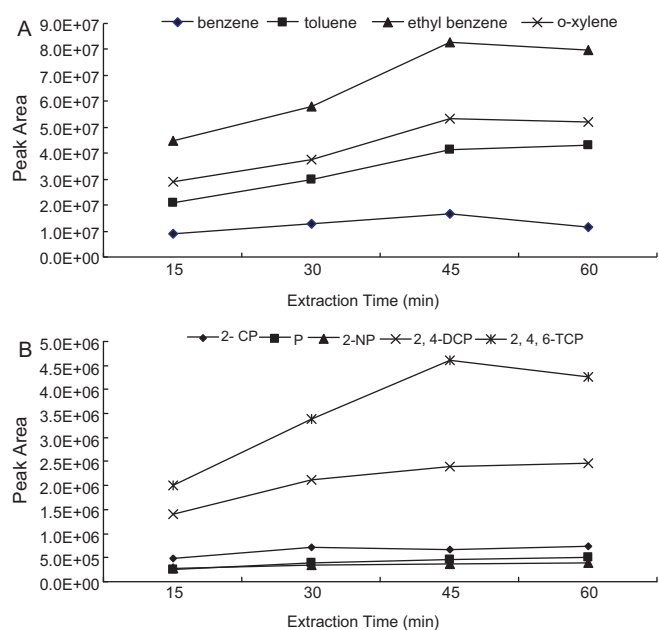
**Fig. 6.** The extraction results of CA-A fiber for headspace sampling of BTEX aqueous solutions (A) and CA-B fiber for headspace sampling of phenols aqueous solutions (B), after the fiber was conditioned at different temperature for 1 h. Other conditions were the same as in Figs. 1 and 2.

conditioning process, which demonstrated the excellent thermal stabilities of the two types of fibers.

The lifetime of a fiber coating is also important for practical application. The lifetime testing of two types of fibers were investigated by extracting BTEX and phenols from spiked samples, respectively. Experiments were carried out with a Multipurpose Autosampler (MPS2) from Gerstel (Munich, Germany). The results indicate that the extraction efficiency of CA-A fiber did not decline even after being extracted 100 times, showing a high durability, whereas the extraction efficiency of CA-B fiber began to decrease after 50 times extractions. The results suggested that the fiber prepared with direct coating method is more easily damaged than that one prepared with sol-gel method.

#### 3.4. Optimization of the extraction and desorption time

To evaluate the properties of the selected two types of fibers, the extraction time profiles of BTEX with CA-A and phenols with CA-B were determined, respectively. The results were shown in Fig. 7(A) and (B). The chromatographic signal increased gradually



**Fig. 7.** Extraction time profiles of BTEX with CA-A fiber (A) and phenols with CA-B fiber (B). Other conditions were the same as in Figs. 1 and 2.

with the extraction time and stabilized at about 45–60 min. Therefore, 45 min was selected as the sampling time.

The desorption time were also optimized. The results showed that there were no significant differences of the peak areas of the analytes, when the desorption time ranged from 1 min to 3 min. Therefore, the exposure time of 1 min in the GC injector port was used for the desorption of BTEX and 1.5 min was applied for phenols.

#### 3.5. Linear ranges, detection limits and repeatabilities

Table 2 summarized the results of method validation for BTEX with CA-A and phenols with CA-B.

The linearity range of BTEX was tested by varying the concentration of the standard solution over a range from 1.0 to 1500  $\mu\text{g L}^{-1}$ , at 1.0, 5.0, 10, 50, 100, 200, 500, 1000, 1500  $\mu\text{g L}^{-1}$  levels, respectively. Regression analysis was used to approximate the linearity of the calibration curves. Four analytes were found to be linear in the tested range, with coefficients ( $R^2$ ) from 0.9927 to 0.9974. The limits of detection (LODs) were based on the lowest detectable peak that had signal/noise = 3, and were 0.008–0.047  $\mu\text{g L}^{-1}$  for BTEX. The LOD values of BTEX were close to the data reported by reference [23,35], but were better than those of commercial and home made fibers [36–43].

**Table 2**  
Linear ranges, limits of detection (LODs) and repeatabilities of BTEX with CA-A and phenols with CA-B.

	Analytes	Linear range ( $\mu\text{g L}^{-1}$ )	$R^2$	LODs ( $\mu\text{g L}^{-1}$ )	RSD % <sup>a</sup> (n=6)	RSD % <sup>b</sup> (n=5)
BTEX	Benzene	1.0–1500	0.9974	0.047	4.6	4.1
	Toluene	1.0–1500	0.9927	0.026	3.9	1.5
	Ethylbenzene	1.0–1500	0.9941	0.008	3.9	5.2
	o-Xylene	1.0–1500	0.9938	0.021	4.0	3.0
Phenols	2-Chlorophenol	20–1000	0.9951	2.6	7.2	8.3
	p-Cresol	50–1500	0.9942	5.7	8.1	9.9
	2-Nitrophenol	50–1500	0.9985	4.9	6.6	8.9
	2,4-Dichlorophenol	10–1500	0.9982	0.35	4.4	5.9
	2,4,6-Trichlorophenol	1.0–1500	0.9949	0.15	9.5	7.5

<sup>a</sup> Repeatability of one fiber.

<sup>b</sup> Reproducibility of fiber-to-fiber.

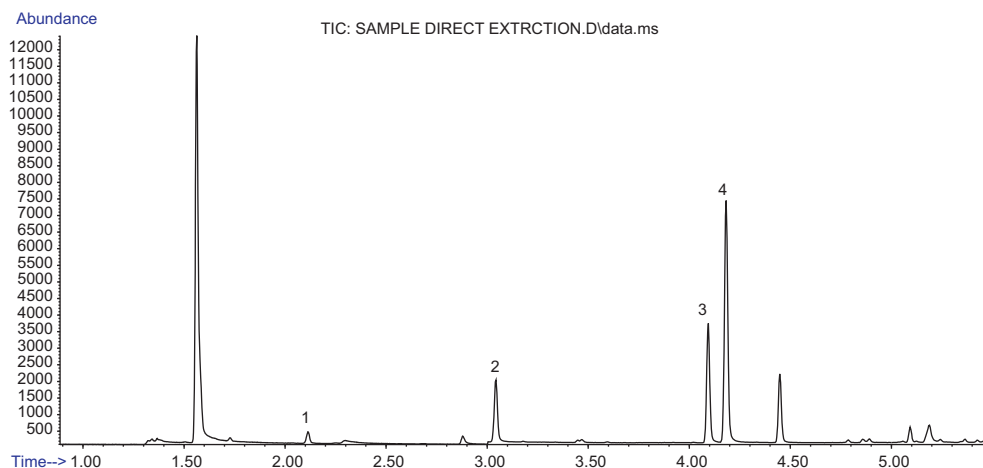


Fig. 8. The chromatogram of the water sample from Pearl River. 1. Benzene, 2. toluene, 3. ethylbenzene and 4. *o*-xylene.

The linearity range of phenols was tested by varying the concentration of the standard solution over a range from 1.0 to 1500  $\mu\text{g L}^{-1}$ . Five analytes were found to be linear in the tested range, 20–1000  $\mu\text{g L}^{-1}$  for 2-chlorophenol, 50–1500  $\mu\text{g L}^{-1}$  for *p*-cresol and 2-nitrophenol, 10–1500  $\mu\text{g L}^{-1}$  for 2,4-dichlorophenol and 1.0–1500  $\mu\text{g L}^{-1}$  for 2,4,6-trichlorophenol, with coefficients ( $R^2$ ) from 0.9942 to 0.9985. The limits of detection (LODs) were 0.15–5.7  $\mu\text{g L}^{-1}$  for the phenols.

Through headspace extraction, the repeatabilities of the selected two types of fibers, were evaluated with BTEX aqueous solutions (100  $\mu\text{g L}^{-1}$ ) and phenols aqueous solutions (500  $\mu\text{g L}^{-1}$ ), respectively. The samplings were performed in 40 mL glass vial containing 25 mL standard solution and the extraction time was 45 min. The RSDs ranged from 3.9% to 4.6% for BTEX, and from 4.4% to 9.5% for phenols.

The acceptable reproducibilities between fibers (RSDs 1.5–4.1% with CA-A fiber for BTEX and 5.9–9.9% with CA-B fiber for phenols) were obtained and listed in Table 2. The results illustrated the feasibility of the fiber preparation methods proposed in this work.

### 3.6. Analysis of the water from the Pearl River

The two type home-made fibers were then applied to analyze BTEX and phenols of the water from the Pearl River (Guangzhou, China). Standard addition method was used for the quantitation. The results showed that the concentrations of BTEX in the water were 10.2, 15.1, 8.5 and 18.9  $\mu\text{g L}^{-1}$ , respectively, and the RSDs were between 5.3% and 8.7%. The chromatogram of the river water sample was illustrated in Fig. 8. Because none of phenols was detected, the water sample was spiked with the standard solution of the phenols to 100  $\mu\text{g L}^{-1}$  to evaluate the CA-B fiber. The results showed that the mean recoveries of phenols ( $n=3$ ) ranged from 80.7% to 112% and the RSDs were between 6.4% and 14.6%. The results demonstrated the applicability of the two home-made fibers prepared in this study.

## 4. Conclusion

In this work, two kinds of home-synthesized porous carbon materials, including CA, WMC, were firstly used as the coatings of SPME fibers. These porous carbon materials are easy to prepare. Although the special surface area of the WMCs (1372  $\text{m}^2 \text{g}^{-1}$ ) is much higher than that of the prepared CAs (429  $\text{m}^2 \text{g}^{-1}$ ), the extraction efficiencies of CAs for both polar and non-polar compounds are better than the WMCs, which might be caused by more uniform pore size of the WMCs (74% mesopore). The results also illustrated

that the specific surface area is not the decisive factor for the extraction efficiency of solid adsorptive materials. Fiber coating prepared with sol-gel techniques exhibited much better extraction efficiencies for BTEX, owing to the presence of PDMS. For the fiber prepared with direct coating method, the extraction efficiency of the coating is determined by the properties of the analytes and the used sorbent. Using a hydrophobic polymer membrane to separate sorbent and sample was proved to be an effective method to protect polar sorbent [44], but our experimental results showed that the extraction efficiency of the sorbent might be decreased.

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