



# A nanoporous carbon material coated onto steel wires for solid-phase microextraction of chlorobenzenes prior to their quantitation by gas chromatography

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## Abstract

A nanoporous carbon material was synthesized by heating potassium citrate without using a template or an activating agent. It is shown to represent a viable coating for use in solid-phase microextraction. The material is thermally stable and mainly consists of amorphous sheets of sp<sup>2</sup>-bonded carbon. It has an extensive pore structure and a surface area as large as 1236 m<sup>2</sup>·g<sup>-1</sup>. The nanoporous carbon was deposited on the surface of steel wires, and the resulting fibers were applied to the extraction of trace levels of chlorobenzenes in water samples. Following extraction by absorbing, the chlorobenzenes were quantified by gas chromatograph in combination with electron capture detection. Extraction temperature and time, and desorption temperature were optimized (80 °C, 10 min and 310 °C). Under optimized conditions, the calibration plots are linear in the following concentration ranges: 2.5 to 100 ng·L<sup>-1</sup> (pentachlorobenzene), 5 to 200 ng·L<sup>-1</sup> (1,2,3,4-tetrachlorobenzene), 10 to 100 ng·L<sup>-1</sup> (hexachlorobenzene) and 10 to 500 ng·L<sup>-1</sup> (1,2,3-trichlorobenzene, 1,2,4-trichlorobenzene, 1,3,5-trichlorobenzene). Other figures of merit include (a) high enrichment factors (8324 to 9920), (b) low limits of detection (0.10–1.03 ng·L<sup>-1</sup>), and (c) good reproducibility (relative standard deviations including intra-day and inter-day with a single fiber and fiber-to-fiber were below 6.4% at a mixed concentration level of 2.5, 5, and 10 ng·L<sup>-1</sup> respectively in ultra-water). This method was successfully applied to the determination of chlorobenzenes in (spiked) lake waters where it gave recoveries between 82.3% and 104.5%.

**Keywords** Separation technology ·  $\pi$  stacking · Adsorption · Potassium citrate · Activation · Coating · Polydimethylsiloxane · Volatile organic compounds · Determination · Water samples

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## Introduction

Solid-phase microextraction (SPME), invented by Pawliszyn's group in the 1990s [1], is a convenient and sustainable separation and extraction technology that combines sampling, purification, and concentration [2]. Typically, compared to solid-phase extraction, accelerated solvent extraction, and liquid-liquid extraction, SPME has the advantages of higher sensitivity, environmental friendliness, lower cost and time consumption, and convenience with smaller sample volumes. Therefore, there have been ever-increasing numbers of studies aimed at improving SPME technology for its optimal application in determining, inspecting, and monitoring trace levels of analytes in the fields of food, medicine, biology, and the environment, both in situ and ex situ [3–6]. In general, the fiber coating used in SPME is an extremely crucial component that plays a key role in extracting analytes from samples

because of the distribution between the matrix and fiber coating [7], and thereby directly determines the sensitivity, accuracy, and repeatability of SPME technology. From a long-term perspective, fabricating new fiber coatings to detect specific analytes with high performance is extremely necessary for the advancement of extraction technology and application in some scientific fields with complex environments, which has hitherto proved to be very challenging [8, 9].

Over the years, many SPME fiber coatings have been commercialized and applied in scientific research institutions globally, such as polyacrylate (PA), polydimethylsiloxane (PDMS), carboxen/polydimethylsiloxane (CAR/PDMS), and polydimethylsiloxane/divinylbenzene (PDMS/DVB). However, these tend to be expensive, show poor thermal stability, and are easily damaged. Therefore, a great deal of researches has been dedicated to devising some new, stable, inexpensive, and high-performance SPME fiber coatings, based on materials such as metal-organic frameworks [10], molecularly imprinted polymers [11], ionic liquids [12], polyethylene glycol [13], and so on.

Various carbon-based materials have been designed as new extraction fiber coatings because of high adsorption capacity (large surface areas and  $\pi$  stacking interactions) [14, 15], great physicochemical stability, and long cycling life of carbon material. When combined with other materials or functional groups, extraction efficiencies can be further improved, such as carbon nanotube-graphene-ionic liquid [16], polyaniline-multiwalled carbon nanotubes [17], carbon nanospheres/polydimethylsiloxane [18], poly(o-phenylenediamine-co-o-toluidine)/modified carbon nanotubes [19]. The extraction efficiencies of these carbon-based materials were proved to be higher than those of commercial coatings, such as PDMS and PA, for determining some volatile organic compounds (VOCs) and semi-volatile organic compounds (SVOCs). Unfortunately, in most cases, the carbon-based SPME fiber coatings have been obtained through complex procedures with multiple steps.

Previously, to obtain large surface areas and  $\pi$  stacking interactions, the carbon materials were derived through methods involving activation with chemical reagents such as potassium hydroxide [20], phosphoric acid [21] or zinc chloride [22] or a templating agent such as KIT-6 [23], MCM-48 [24], or SBA-15 [25]. However, these chemical materials usually accompany incurring high costs and potentially releasing corrosive agents to the environment. Yang et al. [26] reported a template-free synthesis of an ultra-thin porous carbon shell by carbonizing sodium citrate, and the product displayed excellent conductivity for high-rate supercapacitors. Generally, the activation effect of a potassium salt is higher than that of a sodium salt in obtaining a porous structure [27, 28]. Thus, we have now developed a straightforward, solvent-free, template-free, activating agent-free, and low-cost synthetic strategy that involves directly carbonizing potassium citrate to obtain

nano-porous carbon material. Then, we have furthermore assessed the applicability of the product as an SPME fiber coating with good performance.

Chlorobenzenes (CBs), a typical class of VOCs with a chlorinated aromatic ring, have become ubiquitous in the environment because of the synthesis of a multitude of chemicals, particularly in the fields of dyes, degreasers, and pesticides, as well as some release from fireworks [29]. Some studies have already indicated that CBs, have the characteristics of persistence, ease of migration, bio-amplification, and high toxicity to fauna [30]. Indeed, CBs have been classified as priority pollutants by the United States Environmental Protection Agency [31]. Hence, environmental monitoring of CBs concentrations is important and necessary for our health and devising remediation strategies. With this in mind, CBs were selected as model analytes.

Herein, we report the fabrication of a new nanoporous carbon material through one step sustainable method and applied as a novel SPME fiber coating. The SPME fiber coating was homogeneous and evenly distributed and showed high electronegativity, being mainly composed of  $sp^2C$ . Moreover, it showed an extensive pore structure with a large surface area because of the self-templating and self-activating effects of potassium citrate. Subsequently, the SPME fiber coating was successfully applied for the determination of six trace-level CBs in water samples by coupling with a gas chromatograph-electron capture detector.

## Materials and methods

### Materials and reagents

CBs (including 1,2,3-trichlorobenzene, 1,2,4-trichlorobenzene, 1,3,5-trichlorobenzene, 1,2,3,4-tetrachlorobenzene, pentachlorobenzene, and hexachlorobenzene) were purchased from Dr. Ehrenstorfer (Augsburg, Germany, <http://ehrenstorfergmbh.lookchem.com>) with purities >99.5%. Single and mixed stock solutions of the six CBs were prepared in chromatographic grade acetone at a concentration of  $100\text{ mg}\cdot\text{L}^{-1}$  and stored at  $4\text{ }^\circ\text{C}$  prior to use. Potassium citrate was obtained from J&K Scientific Ltd. (Beijing, China, <http://www.jkchemical.com/index.aspx>). Straight stainless steel wires ( $\phi 127\mu\text{m}$ ) were purchased from the Component Supply Company (Fort Meade, MD, USA, <http://www.componentsupplycompany.com>). Chromatographic grade acetone and cyclohexane were obtained from Accustandard Inc. (New Haven, CT, USA, <https://www.accustandard.com>). Sikasil-C silicon sealant was purchased from Sika Ltd. (Beijing, China, <http://chn.sika.com/zh/group.html>). Commercial SPME manual holders and uncoated fibers were purchased from Supelco (Bellefonte, PA, USA, <https://www.laboratoryequipment>).

[com/company-profiles/supelco](http://www.com/company-profiles/supelco)) and XTrust Instruments (Shanghai, China, <http://www.sh-xintuo.com>), respectively.

### Synthesis of nanoporous carbon material

In a typical synthesis procedure, potassium citrate (5 g) was dried in an oven at 120 °C for 24 h and then directly carbonized under a high-purity nitrogen atmosphere at a flow rate of 50 mL·min<sup>-1</sup> in a boat crucible that in a TL1200 tube furnace. The annealing temperature was set at 850 °C, attained at a heating rate of 3 °C·min<sup>-1</sup> and maintained for 1 h. Following carbonization, the black solid residue was washed at 80 °C for 1 h with 100 mL 10% hydrochloric acid (V/V) using magnetic ion stirrer, filtered using 0.45 µm filter membrane, repeated three times, to remove the potassium salt and then washed with ultra-pure water at 60 °C until pH =7. It was then collected by filtration using 0.45 µm filter membrane and dried in an oven at 120 °C for 12 h. In this way, a nanoporous carbon material was obtained.

### Preparation of fibers coated with nanoporous carbon material

The method for preparing the SPME fiber coating was as reported previously, with some modifications [32]. Briefly, straight stainless-steel wires were cut to a length of 2 cm and ultrasonically cleaned with acetone and ultra-pure water. Sikasil-C silicon sealant (0.5 g) was taken up in cyclohexane (1 mL) and treated with sonication for 30 min. Nanoporous carbon material was carefully ground to powder. The cleaned steel wires were immersed in the aforementioned sealant diluent and taken out immediately. By wiping the steel wires with weighing paper, a smooth thin-layer of sealant was left on the surface of the wires. The coated steel wires were then rotated in the powdered nanoporous carbon material and placed in an oven at 105 °C for 10 min. This coating process was repeated three times to obtain fibers coated with three layers of nanoporous carbon for the subsequent experiments.

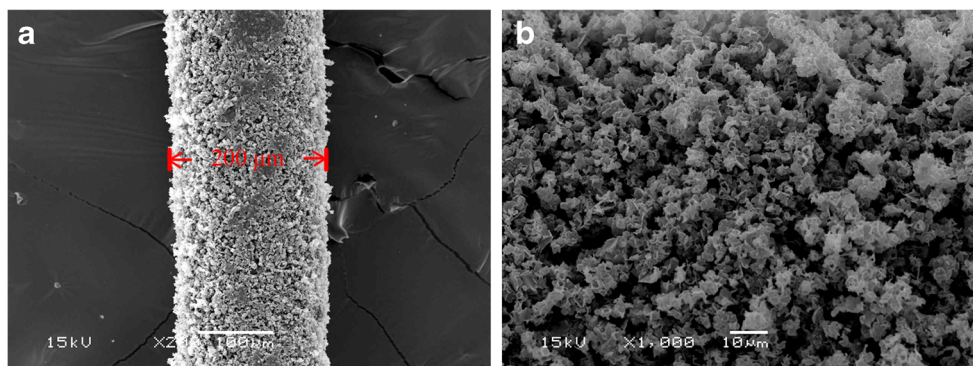
### SPME procedures

Generally, after installing an SPME fiber in the manual holder, it was conditioned by GC injection under nitrogen protection at 250 °C for 1 h. Sample solutions (10 mL) were prepared by diluting stock solutions with ultra-pure water in 20 mL brown glass bottles. Subsequently, the prepared SPME fiber was exposed to the sample through needle puncture. After extracting at 286 rpm at a certain temperature for a specific duration, the SPME fiber was withdrawn and immediately inserted into the GC injector for thermal desorption and analysis (Fig. S1).

### Characterization methods

Scanning electron microscopy (SEM) images were acquired with a JSM-5600LV instrument (Beijing, China, <https://www.jeol.co.jp/en/>). Nitrogen adsorption/desorption isotherms were measured at -195.68 °C by means of a Micromeritics Model ASAP 2020 sorptometer (Shanghai, China, <http://mic.cnpowder.com.cn>). Specific surface area (SSA), pore size distribution (PSD), and cumulative pore volume were calculated using the Barrett-Joyner-Halenda (BJH) method. The total pore volume was measured at P/P<sub>0</sub> = 0.99 and the micropore volume was obtained using t-plot. X-ray diffraction (XRD) was performed with a SmartLab X-ray diffractometer operated at 45 kV and 200 mA, scanning from 10° to 80° with CuKα radiation (Beijing, China, <https://www.rigaku.com/en>). The thermal stability of the prepared carbon material was analyzed using Pyris 1 thermal gravimetric analyzer (TGA) (Shanghai, China, <http://www.perkinelmer.com.cn>) from 100 °C to 800 °C at 10 °C·min<sup>-1</sup> under an air atmosphere (flow rate 100 mL·min<sup>-1</sup>). X-ray photoelectron spectroscopy (XPS) was performed with Escalab 250xi (Shanghai, China, <https://www.thermofisher.com>). Gas chromatography-electron capture detector (GC-ECD) method was shown in Electronic Supplementary Material.

**Fig. 1** Scanning electron microscopy images of the nanoporous carbon coated fiber (**a**) 200 x, (**b**) 1000 x



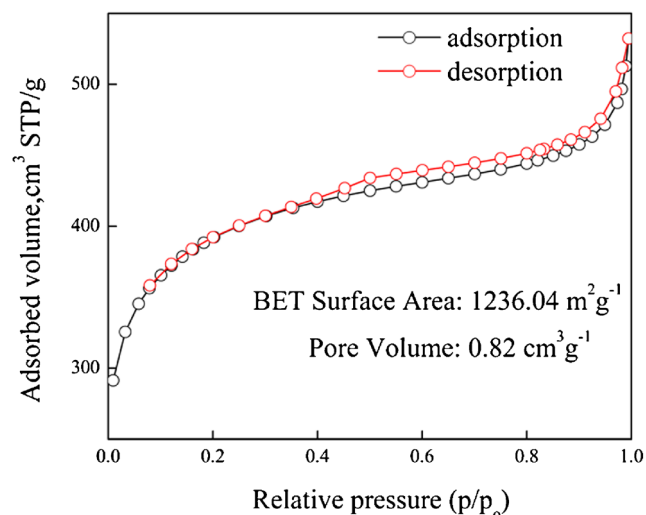


Fig. 2 Nitrogen sorption isotherms of nanoporous carbon

## Results and discussion

### Characteristics of the nanoporous carbon material

The morphological characteristics of synthesized nanoporous carbon derived from potassium citrate were determined by SEM. The prepared carbon material was in sheet form, with size about 1  $\mu\text{m}$  (Fig. S2a and b) and well distributed on the steel wires, which was beneficial for extraction (Fig. 1a and b). The surfaces of the fibers were homogeneous and wrinkled. The fiber diameter was about 200  $\mu\text{m}$ , which indicated that the thickness of the coated material was approximately 36.5  $\mu\text{m}$ .

$\text{N}_2$  adsorption/desorption isotherm analysis of the prepared carbon material was also performed to investigate the SSA and PSD. A typical I/IV-type isotherm with a constant slope was obtained above a relative pressure ( $P/P_0$ ) of 0.1, with a slight hysteresis loop from 0.5 to 0.8 ( $P/P_0$ ), which indicated that the carbon material contained both micropore and mesopore

(Fig. 2). This result was confirmed by the cumulative pore volume curve and pore size distribution (Fig. S3a and b).

The micro-mesopores may have resulted from reaction between the organic part of potassium citrate and species such as  $\text{K}_2\text{CO}_3$ ,  $\text{CO}_2$ , and  $\text{K}_2\text{O}$ , and etched by  $\text{K}_2\text{CO}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{K}_2\text{O}$ ,  $\text{CO}_2$  and K [26, 33]. The BET SSA and total pore volume were evaluated as  $1236.04 \text{ m}^2 \cdot \text{g}^{-1}$  and  $0.82 \text{ cm}^3 \cdot \text{g}^{-1}$ , respectively. This high specific surface area offers abundant adsorption sites and generate strong adsorption energy to bind VOCs. The micropore volume is  $0.35 \text{ cm}^3 \cdot \text{g}^{-1}$  and the meso-macropore/total volume ratio is 57%, which is beneficial for rapid mass transfer of VOCs in SPME.

The XRD pattern (Fig. S4) displayed two characteristic peaks (002, 100) of the nanoporous carbon material, which indicates a disordered amorphous state. The TGA trace (Fig. S5) shown an inconspicuous mass loss below 400  $^\circ\text{C}$ , which indicate great thermal stability for SPME.

The chemical composition and carbon bond forms were analyzed by XPS. Nanoporous carbon material was composed entirely of oxygen and carbon, without any impurities (Fig. 3a). The high-resolution spectrum of C1s in Fig. 3b indicates the presence of  $\text{sp}^2\text{C}$ ,  $\text{sp}^3\text{C}$ , C-OR, and  $\text{C}=\text{O}$ . The  $\text{sp}^2\text{C}$  was the main component, which indicated strong electronegativity that offers a tremendous adsorption force for VOCs. Moreover,  $\text{sp}^2\text{C}$  always displays strong  $\pi$  stacking interactions, further enhancing the adsorption of analytes.

### Optimization of experimental conditions of nanoporous carbon-coated fiber

In this study, fibers coated with nanoporous carbon were prepared with the aim of determining six trace levels of CBs. Main extraction conditions, such as extraction temperature, extraction time, and desorption temperature, were optimized. The relative results and discussions are given in the Electronic Supplementary Material (Fig. S6). At last, extraction

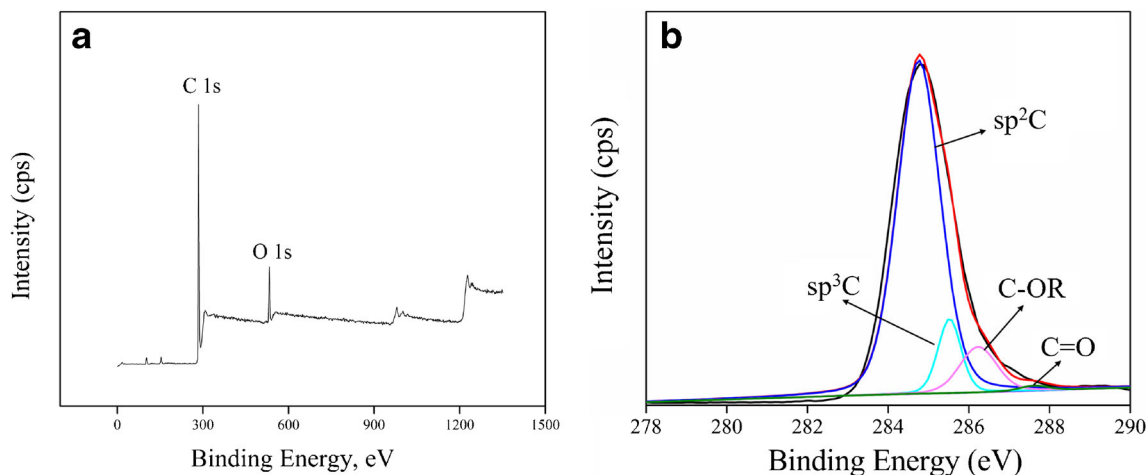
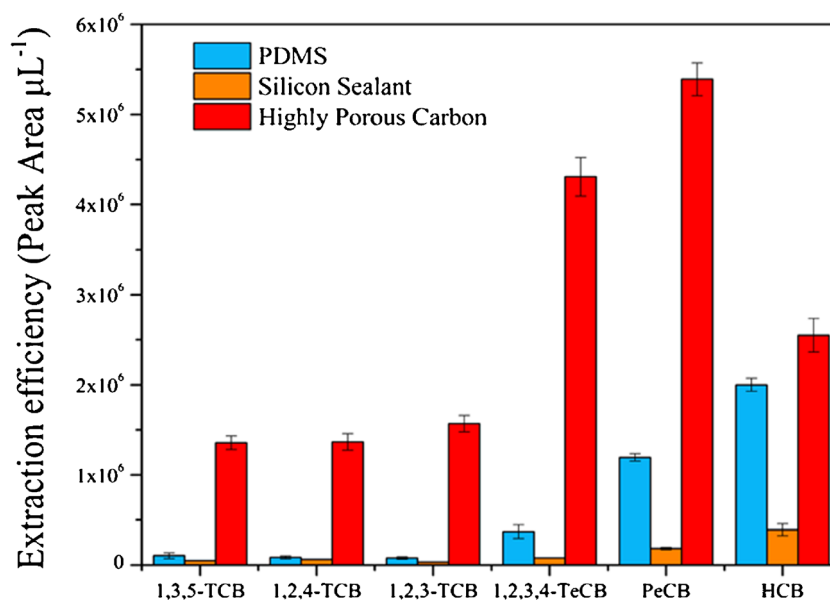


Fig. 3 X-ray photoelectron spectra of the highly porous carbon (a) and C 1s X-ray photoelectron spectra of the nanoporous carbon (b)



**Fig. 4** Comparison of the extraction efficiency of the nanoporous carbon, silicon sealant coated fiber and commercial PDMS fibers for the chlorobenzenes



temperature of 80 °C, extraction time of 10 min and desorption temperature of 310 °C was chosen for this method.

#### Comparison of the nanoporous-carbon-coated fiber with a PDMS coated fiber

To further evaluate the performance of the fibers coated with nanoporous carbon ( $\delta$  36.5  $\mu\text{m}$ , L 1 cm), a commercial and frequently used PDMS-coated fiber ( $\delta$  30  $\mu\text{m}$ , L 1 cm) was selected and compared towards CBs in water samples. Extraction time was 10 min because of the time consuming of GC-ECD. Extraction temperature was at optimum temperature respectively (Fig. S6a and Fig. S7). Desorption temperature was at 280 °C for PDMS-coated fiber according product instruction and 310 °C for nanoporous carbon-coated fiber. Clearly, as shown in Fig. 4, the extraction efficiency on the fibers coated with nanoporous carbon for the six CBs were much higher than PDMS-coated fiber (1.3–20.1 times) and

silicon sealant-coated fiber (6.5–54.6 times) at a concentration of 0.20  $\text{ng}\cdot\text{mL}^{-1}$ .

This result was not surprising in view of the strong surface adsorption energy and abundant sites on the micro/meso/macropore structure with large surface area (1236.04  $\text{m}^2\cdot\text{g}^{-1}$ ). Moreover, the preponderance of  $\text{sp}^2\text{C}$  have motivated the high electronegativity and potential for  $\pi$  stacking interaction.

#### Method evaluation and real sample analysis

##### Method evaluation

The performance of the newly nanoporous carbon coating, including linear range, correlation coefficient ( $R^2$ ), enrichment factors (EFs), limits of detection (LOD), and relative standard deviations (RSDs), was investigated for the six CBs in ultra-pure water under selected conditions.

**Table 1** Performance of the method for determinations of chlorobenzenes

Analytes	Regression line				EFs	LOD ( $\text{ng}\cdot\text{L}^{-1}$ )	RSD (%)		
	Slope	Intercept	$R^2$	Range ( $\text{ng}\cdot\text{L}^{-1}$ )			Intra-day	Inter-day	Fiber-to-fiber
1,3,5-TCB	1415.6	5076.9	0.9996	10–500	8398	1.03	3.0	4.2	6.2
1,2,4-TCB	1077.5	21,359.0	0.9984	10–500	9055	0.97	3.8	3.5	4.7
1,2,3-TCB	1637.6	4953.8	0.9997	10–500	8324	0.74	2.5	4.3	3.8
1,2,3,4-TeCB	4160.6	15,806.0	0.9974	5–200	8953	0.25	3.8	5.1	5.5
PeCB	6045.5	29,540.0	0.9964	2.5–100	9920	0.11	4.0	3.2	6.4
HCB	5182.7	35,277.0	0.9995	10–100	8720	0.10	4.1	2.2	3.0

**Table 2** Comparison of limits of detection and time requirements of the method with those previously reported methods for determining chlorobenzenes in water sample

Analytes	LODs (Extraction time consuming), ng·L <sup>-1</sup> (min)					
	This study	SPME GC/MS [34]	NTME GC/MS [36]	SPME GC/ECD [37]	SPME GC/MS [38]	SDME GC/MS [39]
1,3,5-TCB	1.03 (10)	–	–	–	–	4.00 (37)
1,2,4-TCB	0.97 (10)	–	–	1.50 (10)	–	2.00 (37)
1,2,3-TCB	0.74 (10)	–	0.40 (15)	–	–	2.00 (37)
1,2,3,4-TeCB	0.25 (10)	–	0.80 (15)	0.15 (10)	–	2.00 (37)
PeCB	0.11 (10)	–	–	–	–	1.00 (37)
HCB	0.10 (10)	0.69 (50)	–	–	0.29 (50)	2.00 (37)

All of the analytes exhibited great linearity, with  $R^2$  values ranging from 0.9964 to 0.9997 at concentrations of 2.5–100 ng·L<sup>-1</sup> (PeCB), 5–200 ng·L<sup>-1</sup> (1,2,3,4-TeCB), 10–100 ng·L<sup>-1</sup> (HCB), and 10–500 ng·L<sup>-1</sup> (1,3,5-TCB, 1,2,4-TCB, 1,2,3-TCB) (Table 1). EFs were estimative from the ratio of extraction quantities by SPME using 10 mL sample to directly inject 1  $\mu$ L sample, giving a direct indication of the enrichment capacity of the fiber coating. Excellent EFs ranging from 8324 to 9920 were observed for the prepared fiber coating, which were clearly higher than those reported for an SPME coated fiber for HCB (2436 [34], 1286 [35]). The LODs of the method calculated based on a signal-to-noise ratio (S/N) of 3 ranged from 0.10 ng·L<sup>-1</sup> to 1.03 ng·L<sup>-1</sup>. In Table 2, compared to previously reported methods, this method was highly sensitive with lower LODs and lower extraction time consuming. Moreover, under the selected conditions, RSDs of intra-day and inter-day with a single fiber were in the range of 2.5–4.1% and 2.2–4.3% respectively at a mixed concentration level using ultra-water (10 ng·L<sup>-1</sup> for 1,2,3-TCB, 1,2,4-TCB, 1,3,5-TCB and HCB, 5 ng·L<sup>-1</sup> for 1,2,3,4-TeCB, 2.5 ng·L<sup>-1</sup> for PeCB), thus implying good reproducibility. The fiber-to-fiber reproducibility was evaluated using five SPME fibers, and values of the RSDs were below 6.4% at a mixed concentration level using ultra-water (10 ng·L<sup>-1</sup> for 1,2,3-TCB, 1,2,4-TCB, 1,3,5-TCB and HCB, 5 ng·L<sup>-1</sup> for 1,2,3,4-TeCB, 2.5 ng·L<sup>-1</sup> for PeCB). In summary, these results show that the method using the prepared nanoporous

carbon coating offers excellent linearity, low LODs, low time expenditure, and good reproducibility.

### Real environment sample analysis

To assess the applicability of this method in real samples, Xuan Wu Lake water (Nanjing, Jiangsu, China) was selected as a real model sample. The water sample was collected and filtered using a 0.45  $\mu$ m film to remove particulate matters preliminary. The six CBs were then determined by the method in prepared solution samples. The concentration of 1,2,3-TCB in Xuan Wu Lake was estimated as 7.41 ng·L<sup>-1</sup> with RSD of 10.67%, whereas the other five CBs were not detected (Table 3). To evaluate the recovery of the method, Xuan Wu Lake water samples were spiked with CBs at 50, 20, and 10 ng·L<sup>-1</sup>, respectively. Excellent recoveries in the range 82.28–104.53% were obtained, which indicated that the method in this work was sufficiently accurate and sensitive for the determination of real environmental samples.

### Selectivity

Similar to CBs, phenols, BETX (benzene, toluene, ethylbenzene, xylene), partly PAHs (naphthalene, acenaphthylene and acenaphthene) and drugs (ibuprofen, naproxen, diclofenac) also may be extracted using nanoporous carbon-coated fiber with high performance, because of  $\pi$  stacking interaction with

**Table 3** Real environmental sample analysis of the chlorobenzenes in Xuan Wu Lake

Analytes	Concentration (ng·L <sup>-1</sup> )	RSD (%), $n = 3$	Spiked (ng·L <sup>-1</sup> )	Detected (ng·L <sup>-1</sup> )	Recovery (%)
1,3,5-TCB	nd	–	50	49.51	99.03
1,2,4-TCB	nd	–	50	51.13	102.25
1,2,3-TCB	7.41	10.67	50	53.76	92.70
1,2,3,4-TeCB	nd	–	20	20.49	102.44
PeCB	nd	–	10	8.23	82.28
HCB	nd	–	10	10.45	104.53

benzene, huge surface adsorption energy and proper size of pores. For relatively large molecular structure of analytes, Semi-VOCs or Nicotinamide adenine dinucleotide, this fiber was not inapplicable, because nanoporous carbon material was mainly composed of micropores and mesopores [40]. Mass transfer route would be block, and just a weak adsorption force on the surface. For heavy metal ions, high extraction efficiency would be present due to the huge surface adsorption energy and  $\pi$ -interaction. However, destructive desorption for heavy metal ions limited the application of nanoporous carbon-coated fiber.

## Conclusions

In this study, nanoporous carbon material has been successfully synthesized, characterized, and applied as an SPME fiber coating to simultaneously determine six trace-level CBs with high performance. The nanoporous carbon material was prepared by the carbonization of potassium citrate, which is a convenient and sustainable process. An extensive pore structure with a large surface area ( $1236.04 \text{ m}^2 \cdot \text{g}^{-1}$ ) was obtained after leaching with hydrochloric acid. After coating, a  $36.5 \mu\text{m}$  evenly distributed nanoporous carbon layer was left on the surface of steel wire. Excellent extraction performance of the nanoporous carbon coating has been demonstrated compared with sealant and PDMS coated SPME fibers for six CBs. In addition, this fiber displayed excellent performance with great linearity, high EFs, low LODs, and good reproducibility and recoveries for real water samples. However, for relatively large molecular structure of analytes and heavy metal ions, nanoporous carbon-coated fiber was limited. In conclusion, a novel nanoporous carbon coating for high-performance SPME has been developed through convenient steps, and is considered as a promising alternative to PDMS fiber for the determination of trace-level VOCs in water samples.

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**Compliance with ethical standards** The authors declare no conflict of interest.

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