



# Evaluation of the solid-phase microextraction fiber coated with single walled carbon nanotubes for the determination of benzene, toluene, ethylbenzene, xylenes in aqueous samples

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## ARTICLE INFO

### Article history:

Received 1 December 2009  
Received in revised form 29 January 2010  
Accepted 2 February 2010  
Available online 10 February 2010

### Keywords:

Solid-phase microextraction  
Single walled carbon nanotubes  
BTEX

## ABSTRACT

A solid-phase microextraction (SPME) fiber coated with single walled carbon nanotubes (SWCNTs) was prepared by electrophoretic deposition and treated at 500 °C in H<sub>2</sub> stream. In order to evaluate the characteristics of the obtained fiber, it was applied in the headspace solid-phase microextraction (HS-SPME) of benzene, toluene, ethylbenzene and xylenes (BTEX) from water sample and quantification by gas chromatography with flame ionization detection (GC-FID). The results indicated that the thermal treatment with H<sub>2</sub> enhanced the extraction of the SWCNTs fiber for BTEX significantly. Thermal stability and durability of the fiber were also investigated, showing excellent stability up to 350 °C and life time over 120 times. In the comparison with the commercial CAR-PDMS fiber, the SWCNTs fiber showed similar and higher extraction efficiencies for BTEX. Under the optimized conditions, the linearity, LODs (S/N = 3) and LOQs (S/N = 10) of the method based on the SWCNTs fiber were 0.5–50.0, 0.005–0.026 and 0.017–0.088 µg/L, respectively. Repeatability for one fiber (*n* = 3) was in the range of 1.5–5.6% and fiber-to-fiber reproducibility (*n* = 3) was in the range of 4.2–8.3%. The proposed method was successfully applied in the analysis of BTEX compounds in seawater, tap water and wastewater from a paint plant.

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## 1. Introduction

Benzene, toluene, ethylbenzene, xylene (BTEX) have been widely used in the manufacture of paints, synthetic rubber, agricultural chemicals and chemical intermediates. BTEX compounds are also abundant in petroleum products, such as fuel oil and gasoline. As a result, BTEX are ubiquitously environmental contaminants in air, water and soil. The occurrence of BTEX in water is a great concern because of their toxicity. For this reason, the US Environmental Protection Agency (EPA) established the maximum contaminant level (MCL) for benzene 5 µg/L, for toluene 1000 µg/L, for ethylbenzene 700 µg/L and for xylenes 10,000 µg/L in drinking water [1]. A MCL of 1.0 µg/L for benzene is fixed by European legislation in drinking water [2]. In order to monitor trace BTEX in water, many analytical methods have been developed [3–19]. Sample preparation techniques such as purge and trap (PT) [3,4], headspace (HS) [5–7], solid-phase extraction (SPE) [8,9] and solid-phase microextraction (SPME) [11–19] have been widely applied in these methods to enhance the sensitivity and selectivity.

SPME is a solvent-free sampling and sample preparation technique, which combines sampling, pre-concentration and the direct transfer of the analytes into a GC or HPLC [20]. Typically, a fiber coated with a thin layer of adsorptive material is used to extract analytes from matrix in a SPME procedure. The performance of SPME mainly depends on the properties of the SPME fiber. Several commercial SPME fibers with coatings such as poly dimethylsiloxane (PDMS) [10,11], PDMS-divinylbenzene (DVB) [12], Carboxen (CAR)-PDMS [13] and PDMS-DVB-CAR [14] have been applied in the extraction of BTEX in aqueous samples. In order to overcome some drawbacks with the commercial SPME fibers, a number of home-made SPME fibers with novel coatings have been developed and validated [15–19]. The fibers and the limits of detection (LODs) of BTEX reported in the literatures are listed in Table 1. It shows that the methods based on home-made fibers except PbO<sub>2</sub> have higher LODs of BTEX than those on commercial fibers. It means that the extraction efficiency of BTEX with the recently developed home-made fibers has not been improved significantly, it is still necessary to develop new SPME fibers.

Carbon nanotubes (CNTs) possess some highly desirable characteristics, which make them attractive for a variety of applications including environmental sample preparation. Multi-walled CNTs (MWCNTs) were used by Li et al. to trap volatile organic compounds (VOCs) in gaseous samples and found to have breakthrough vol-

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**Table 1**  
SPME fibers used to extract BTEX in water and the LODs of the established methods.<sup>a</sup>

Fibers	References	Coatings	LODs ( $\mu\text{g/L}$ )				
			Benzene	Toluene	Ethyl benzene	<i>p,m</i> -Xylene	<i>o</i> -Xylene
Commercial fiber	[10]	PDMS	1.0	1.0	2.0	2.0	2.0
	[11]	PDMS	0.28	0.19	0.06	0.05	0.05
	[12]	PDMS–DVB	0.07	0.02	0.02	0.02	0.02
	[13]	CAR–PDMS	0.06	0.14	0.07	0.17	0.09
	[14]	PDMS–DVB–CAR	0.015	0.16	0.032	0.056	0.042
Home-made fiber	[15]	PbO <sub>2</sub>	0.027	0.054	0.012	0.032	0.031
	[16]	Titania sol–gel	7.2	5.4	6.3	14.8	8.1
	[17]	Polypropylene hollow fiber membrane	0.11	0.22	0.26	0.37	0.26
	[18]	Silicone glue	0.17	0.07	0.11	0.10	0.08
	[19]	NiTi–ZrO <sub>2</sub> –PDMS	1.6	1.6	0.6	0.6	0.6

<sup>a</sup> All the methods were based on headspace (HS)–GC–FID, except that in Ref. [11], which was based on HS–GC–MS.

umes two to three orders larger than those of Carboxen B [21]. Cai et al. used MWCNTs as SPE sorbent to extract endocrine disruptors [22] and phthalate esters [23] from aqueous samples. Zhou et al. developed SPE methods based on MWCNTs for the enrichment of atrazine and simazine [24] in water samples. In these studies, CNTs were found to be more effective than, or as effective as, C18 or some other polymer sorbents [22–24]. Our previous work showed that when used as SPE sorbent, oxidized single walled CNTs (SWCNTs) had higher extraction efficiency than Oasis HLB for the extraction of methamidophos and acephate in aqueous sample [25].

The applications of CNTs as SPME coating have been reported. A SPME fiber coated with oxidized MWCNTs was developed by Liu et al. and was found to be effective in the extraction of phenols in water [26]. Lu et al. prepared a SPME fiber coated with SWCNTs and used it to extract organochlorine pesticides in lake water and wastewater [27]. CNTs present in a form of small particle. In order to immobilize CNTs particles to the fiber substrate, adhesives such as epoxy resin [26] and mixture of terpeneol, ethylcellulose, and dibutyl phthalate [27] were usually used in the preparation procedure. The presence of these adhesives would lower the thermal stability, the resistance to organic solvents and even the adsorption capacity of the prepared fibers. A SPME fiber coated with SWCNTs was prepared by electrophoretic deposition (EPD) without the use of adhesive in our previous work [28]. The obtained SWCNTs coating did not swell in organic solvents nor strip off from substrate, and possessed high mechanical strength. The prepared fiber was similar to or superior to commercial PA fiber in extracting phenols in water. It is well known that CNTs are made of graphite, and thus there is the  $\pi$ – $\pi$  interaction between CNTs and aromatic compounds. In addition, CNTs are porous and have high specific surface area. As a result, a high BTEX extraction efficiency of the CNTs coated SPME fiber could be expected. Up to now, the application of CNTs coated SPME fiber in the extraction of BTEX in water sample has not been reported.

In this study, a SPME fiber coated with SWCNTs was prepared by EPD and subsequently treated in a H<sub>2</sub> stream of high temperature. Its properties for the extraction of BTEX in water sample were investigated and compared with those of commercial fiber coated with CAR–PDMS. An analytical method based on this fiber was established and applied in the analysis of BTEX in seawater, tap water and wastewater.

## 2. Experimental

### 2.1. GC analysis

The GC measurements were performed on a gas chromatograph (HP 5890 Series II, Hewlett-Packard, Avondale, PA, USA) equipped with FID and a split–splitless injection port. The separation of BTEX

was carried out on a DB-624 column (75 m  $\times$  0.53 mm, 3  $\mu\text{m}$  in film thickness, J&W Scientific Inc., Folsom, CA, USA). Data acquisition and processing were done using Qianpu chromatography workstation (Qianpu Software Inc., Nanjing, China). The GC oven temperature program was as follows: 50  $^{\circ}\text{C}$  held for 3 min, rate at 5  $^{\circ}\text{C}/\text{min}$  to 130  $^{\circ}\text{C}$  and held for 2 min. The carrier gas was high-purity nitrogen with a pressure of 20 psi in the injection port. The injection port and detector temperatures were set at 300 and 250  $^{\circ}\text{C}$ , respectively. The pressure of the H<sub>2</sub> and air for the detector was 20 and 40 psi, respectively. Splitless mode was adopted.

### 2.2. Chemicals and standard solutions

Benzene (B), toluene (T), ethylbenzene (E), *o*-xylene (*o*-X), *m*-xylene (*m*-X), and *p*-xylene (*p*-X) of analytical grade were supplied by Alfa Aesar China (Tianjin, China). HPLC-grade methanol was purchased from Tedia (Fairfield, OH, USA). Dimethylformamide (DMF), and NaCl of analytical grade were obtained from Sinopharm Chemical Reagent Co. (Shanghai, China). Purified water was obtained from a Milli-Q ultra-pure water system (Millipore, Billerica, USA) and used throughout the experiments. The stock solution of BTEX was prepared by adding 100 mg of each compound in a 10 mL volumetric flask and diluted with methanol. It was then diluted by a factor of 10000 with methanol to obtain a working standard of 1 mg/L which was used to prepare spiked water solutions. All solutions were stored at 4  $^{\circ}\text{C}$  in a refrigerator. A 75  $\mu\text{m}$  CAR/PDMS fiber was purchased from Supelco (Bellefont, CA, USA). Commercially available SWCNTs with a specific surface of 380 m<sup>2</sup>/g were purchased from Chengdu Organic Chemistry Co. (Chengdu, China).

### 2.3. Preparation and thermal treatment of SWCNTs SPME fiber

The procedure to prepare a SPME fiber coated with SWCNTs by EPD has been described in our previous work in detail [28]. In brief, the SWCNTs were oxidized with mixture of concentrated nitric and sulfuric acid and ultrasonically dispersed in DMF to form a stable suspension containing 2 mg/mL of SWCNTs; two Pt wires of 0.1 mm in diameter were immersed into the suspension; when a DC voltage of 40 V was applied between the two Pt wires used as electrodes for 10 s, a SWCNTs deposit was formed on the Pt wire used as anode; then the wire with deposit was taken out from the suspension and dried at 120  $^{\circ}\text{C}$  to remove the solvent, and finally a fiber coated with SWCNTs was prepared. Fibers with different coating thickness could be produced by repeating the EPD procedure for various times. In this study, fibers with a coating thickness about 80  $\mu\text{m}$  were prepared.

The as-prepared SWCNTs fiber was placed in a quartz tube and fixed with quartz wool. The quartz tube was then put into a home-made tube furnace, and H<sub>2</sub> at a flow rate of 40 mL/min was introduced into the tube. The fiber was treated at 500  $^{\circ}\text{C}$  for

30 min, and then a H<sub>2</sub> treated fiber was obtained. A home-made SPME device was built by replacing the fused silica fiber on a used commercial SPME device with the above as-prepared or H<sub>2</sub> treated fiber.

In order to study the change of functional groups on the SWCNTs surface before and after thermal treatment, FTIR (Nexus 470, Thermo Nicolet, USA) was run on KBr pellets containing SWCNTs, which were stripped off from the as-prepared or H<sub>2</sub> treated fiber.

#### 2.4. Solid-phase microextraction procedure

Water sample of 10 mL was transferred into a 15 mL glass vial with PTFE-coated septa (Supelco, Bellefonte, PA, USA), and a magnetic stirring bar was put into the vial. In order to investigate the influence of temperature on extraction, the vial was positioned in a water-jacketed vessel on a magnetic stirrer (Corning Laboratory Stirrer/Hot Plate, Models PC-420, NY, USA) and kept at a selected temperature with a circulating water bath (Chongqing Testing Equipment Factory, Chongqing, China). The fiber was exposed in the headspace of the sample about 1 cm below the septa. NaCl was used to adjust the salt content of the sample. After extraction, the fiber was immediately inserted into the GC injection port for thermal desorption, and the chromatographic peak area of the analyte was used for quantitation and to examine the extraction efficiency of a SPME fiber. Triplicate analyses were performed for each sample.

#### 2.5. Performance and analysis of real sample

The SPME conditions such as extraction time, extraction temperature, salt content added in the sample, stirring rate, and desorption temperature were optimized. Under the optimized conditions, the performance of the established method was investigated. Seawater sample was collected from the beach near Xiamen University. Tap water was sampled from the laboratory. The wastewater was collected from a paint plant. All the samples were extracted without any further pretreatment.

### 3. Results and discussion

#### 3.1. Effect of thermal treatment with hydrogen gas

The SWCNTs are solid sorbent which extracts analytes via adsorption. The extraction occurs on the surface of SWCNTs. When the SWCNTs fiber is used to extract analytes in water sample via HS-SPME, the water molecules in the headspace would compete with the analytes for the surface. The SWCNTs on the as-prepared fiber have been oxidized by the mixture of concentrated nitric and sulfuric acid, therefore polar groups such as carboxylic groups are presented on the tubes [28]. The presence of the polar groups would enhance the affinity of the SWCNTs fiber for water molecules in the headspace and consequently lower the extraction efficiency for analytes. The thermal treatment in a stream of H<sub>2</sub> is an effective way to remove heteroatom bound with carbon [29]. In this study, in order to reduce the polar groups on the surface of SWCNTs, the as-prepared fiber was annealed at 500 °C for 30 min in a H<sub>2</sub> stream.

Fig. 1 is the infrared spectra of the SWCNTs stripped off from the as-prepared and H<sub>2</sub> treated fibers. The band at ~1586 cm<sup>-1</sup> is associated with the stretching vibration of C=C bonds, and assigned to the nanotube phonon modes. The band at ~1715 cm<sup>-1</sup> is resulted from the stretching vibration of carboxylic groups. The band at ~1410 cm<sup>-1</sup> is assigned to the C–O symmetrical stretching vibration of carboxylate ions [30,31]. The broader band at 1109 cm<sup>-1</sup> corresponds to the C–O stretching vibration of hydroxyl and phenol groups. The strength of the bands at ~1715 and ~1410 cm<sup>-1</sup>, which are resulted from carboxylic groups, decreases significantly but the bands does not disappear after the thermal treatment. This

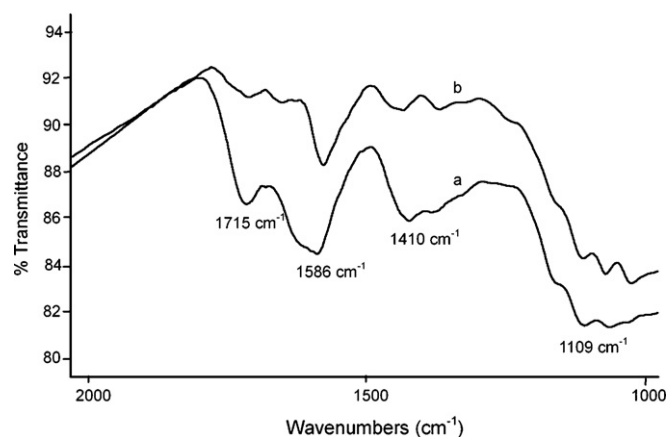


Fig. 1. Infrared spectra of SWCNTs stripped off from: (a) as-prepared fiber; (b) H<sub>2</sub> treated fiber.

result shows that the amount of carboxylic groups on SWCNTs reduced significantly but not completely. If a higher temperature was applied, more carboxylic groups could be removed. However, higher temperature would lead to high loss of SWCNTs on the fiber because of the reaction between SWCNTs and H<sub>2</sub>.

The as-prepared fiber and the same fiber treated with H<sub>2</sub> were used to extract BTEX in the headspace of a standard water sample. The chromatograms of BTEX extracted with the fibers are shown in Fig. 2. The peak area ratios of the extracted BTEX with treated fiber to as-prepared fiber were 6.4, 4.9, 4.6, 4.5, and 5.5 for B, T, E, *m,p*-X, and *o*-X, respectively. The results indicated that after the thermal treatment with H<sub>2</sub> the extraction efficiency of the SWCNTs fiber for BTEX increased significantly. This should be due to the removal of carboxylic groups during the thermal treatment. As a result, the treated fiber was chosen in the following experiments.

#### 3.2. Optimization of desorption conditions and thermal stability of SWCNTs fiber

After extraction, desorption was performed in GC injection port at different temperature with a fixed desorption time of 5 min, and the carryover was measured with one blank injection following initial desorption. Fig. 3 shows the peak areas of BTEX at the desorption temperature of 280, 300, 320 and 350 °C. The peak areas at 280 °C were significantly lower than those at 300 °C; when the temperature was higher than 300 °C, they became almost constant, and no significant carryover was found. These results indicated that all the

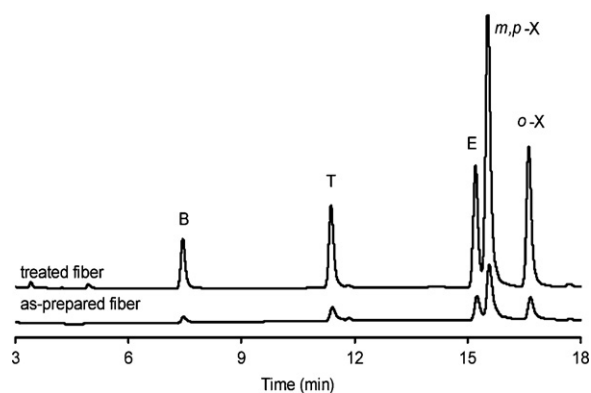


Fig. 2. The chromatograms of BTEX extracted with as-prepared fiber and treated fiber via HS-SPME. Conditions: extraction time, 20 min; extraction temperature, 25 °C; stirring rate, 700 rpm; no salt was added; concentration of BTEX, 50 µg/L; desorption temperature, 300 °C; desorption time, 5 min.

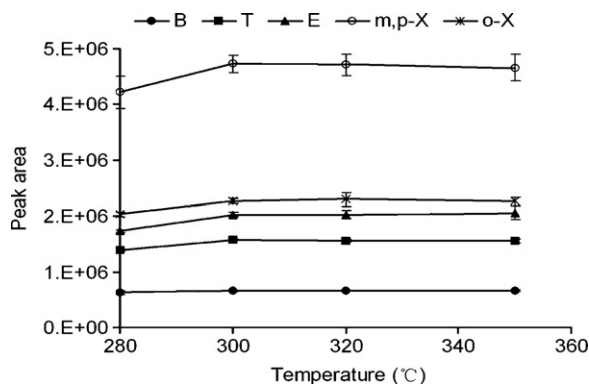


Fig. 3. Effect of desorption temperature on BTEX signals ( $n=3$ ). Conditions: concentration of BTEX, 30  $\mu\text{g/L}$ ; other parameters are the same as described in Fig. 2.

BTEX had been desorbed when the fiber was inserted into the injection port at 300 °C for 5 min. Therefore, the desorption conditions in the following experiments were 300 °C for 5 min.

In order to investigate the thermal stability, the fiber was conditioned at 350 °C for 3 h, and then was used to extract BTEX in water. The extraction efficiency of the fiber was not affected by the conditioning process. It suggested that the fiber was of high thermal stability and had a maximum desorption temperature higher than 350 °C. The high thermal stability of the fiber should be resulted from the graphite structure of the SWCNTs and the thermal treatment at 500 °C, which removed the polar groups on the SWCNTs surface.

### 3.3. Optimization of the extraction conditions

In a HS-SPME procedure, various parameters would affect the extraction efficiency. In this study, the effects of extraction temperature, extraction time, stirring rate and salt content were investigated.

#### 3.3.1. Effect of extraction time

The extraction time is a very important parameter in a HS-SPME procedure because it influences the partition of the target analytes between headspace and fiber coating. Four extraction times, 10, 20, 40 and 60 min, were tested and the obtained results are shown in Fig. 4. When the extraction was longer than 20 min, the signals of B, T, and E almost kept constant and those of xylenes increased slightly with extraction time. Twenty min was chosen as the extraction time based on the consideration of sensitivity and analysis speed.

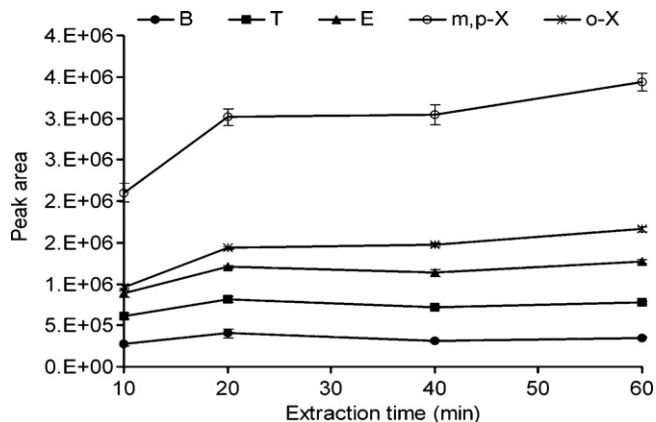


Fig. 4. Effect of extraction time on BTEX signals ( $n=3$ ). Conditions: concentration of BTEX, 20  $\mu\text{g/L}$ ; other parameters are the same as described in Fig. 2.

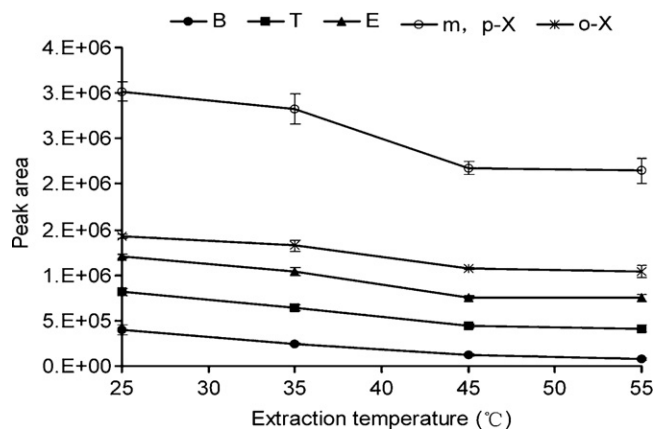


Fig. 5. Effect of extraction temperature on BTEX signals ( $n=3$ ). Conditions: extraction time, 20 min; other parameters are the same as described in Fig. 4.

#### 3.3.2. Effect of extraction temperature

The effect of temperature on the extraction efficiency was studied from 25 to 55 °C. The obtained results are demonstrated in Fig. 5. A significant decrease in sensitivity for BTEX was observed at higher temperatures. This phenomenon was likely to be the overall result of three effects. Firstly, an increase in extraction temperature led to an improvement of the evaporation of BTEX from the sample to the headspace and, consequently, to higher extraction efficiencies; secondly, high temperature could reduce the partition coefficients of BTEX between headspace and fiber, because the adsorption of BTEX on the surface of SWCNTs was generally an exothermic process; thirdly, high temperature increased the vapour pressure and consequently the concentration of water molecules in the headspace. These molecules could not only interfere in the transference of the analytes from sample to headspace but also compete with the analytes for the SWCNTs surface, thus lower the extraction efficiency. The combination of the second and third effects might be much larger than the first, therefore the extraction efficiencies of BTEX decreased with the increase of sampling temperature. 25 °C was chosen as extraction temperature for further studies.

#### 3.3.3. Effect of salt content

The addition of salt to the sample often has a positive influence on the extraction efficiency in HS-SPME procedure because of the salting-out effect. In this study, the influence of salt was studied by adding different amounts of NaCl, ranging from 0 to 30% (w/v), to a spiked water sample. The results are shown in Fig. 6. The extraction efficiency of B increased with the salt content within the studied range. For T, E and X, the highest response appeared when the salt content was 20% (w/v). Therefore, 20% (w/v) of salt content was selected for the subsequent experiments.

#### 3.3.4. Effect of stirring rate during extraction

To evaluate the influence of agitation on the extraction of BTEX, spiked samples were extracted with stirring rate of 100, 400, 700 and 1000 rpm during the adsorption process. The result showed that the signals of BTEX increased continuously with the stirring rate. Because the maximum stirring rate of the magnetic stirrer used in this study was 1000, 1000 rpm was chosen in the further studies.

In short, the optimized conditions for the extraction of BTEX from water sample with treated SWCNTs fiber were: extraction time, 20 min; extraction temperature, 25 °C; salt content, 20% (w/v); stirring rate, 1000 rpm.

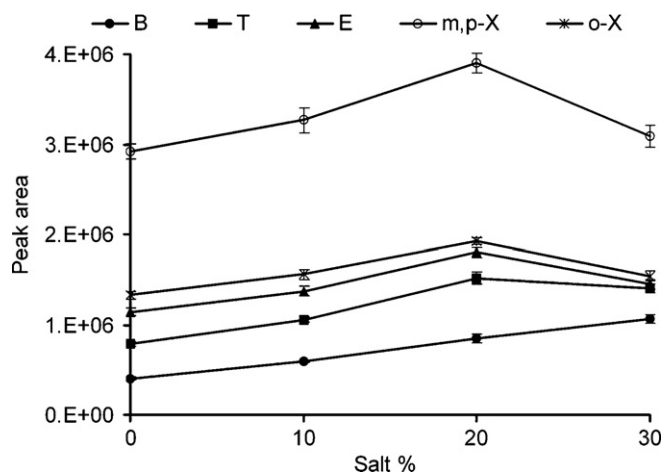


Fig. 6. Effect of salt content on BTEX signals ( $n=3$ ). Conditions: extraction temperature, 25 °C; other parameters are the same as described in Fig. 4.

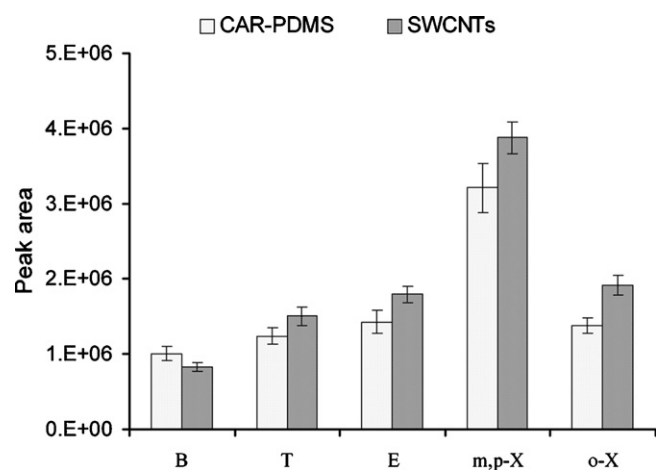


Fig. 7. Peak areas of BTEX extracted with SWCNTs fiber and CAR-PDMS fiber under the optimized conditions ( $n=3$ ).

### 3.4. Comparison with CAR-PDMS fiber

CAR-PDMS fiber is one of the most commonly used fibers in the analysis of BTEX [13]. Under the optimized conditions, both the SWCNTs fiber and CAR-PDMS were applied to extract BTEX from a spiked water sample of 20  $\mu\text{g/L}$  via HS-SPME. The obtained peak areas of BTEX are shown in Fig. 7. The SWCNTs fiber has similar (for B) or higher (for T, E and X) extraction efficiencies than CAR-PDMS fiber. SWCNTs are made of graphite, and thus there is the  $\pi$ - $\pi$  interaction between SWCNTs and BTEX. Furthermore, SWCNTs are porous and have a specific surface area as high as 380  $\text{m}^2/\text{g}$ . As a result, the SWCNTs fiber has high affinity towards BTEX.

Table 2

Characteristic data of the established HS-SPME-GC method for the determination of BTEX.<sup>a</sup>

BTEX	Linear range ( $\mu\text{g/L}$ ) <sup>b</sup>	$r$	LOD ( $\mu\text{g/L}$ ) <sup>b</sup>	LOQ ( $\mu\text{g/L}$ ) <sup>b</sup>	RSD (%) <sup>c</sup>	RSD (%) <sup>d</sup>
B	0.5–50.0	0.999	0.026	0.088	5.6	5.4
T	0.5–50.0	0.999	0.013	0.044	1.5	8.1
E	0.5–50.0	0.999	0.011	0.035	4.5	7.5
<i>m,p</i> -X	0.5–30.0	0.998	0.005	0.017	2.6	8.3
<i>o</i> -X	0.5–50.0	0.999	0.010	0.034	2.3	4.2

<sup>a</sup> The analytical curves were constructed with five concentration levels of each compound. The concentration of the standard solution for the test of reproducibility and repeatability was 20  $\mu\text{g/L}$  for each compound.

<sup>b</sup> LOD and LOQ were calculated based on the 3 and 10 times the average background noise and divided by the detection sensitivity, respectively.

<sup>c</sup> Repeatability of one unique fiber ( $n=3$ ).

<sup>d</sup> Reproducibility between different fibers ( $n=3$ ).

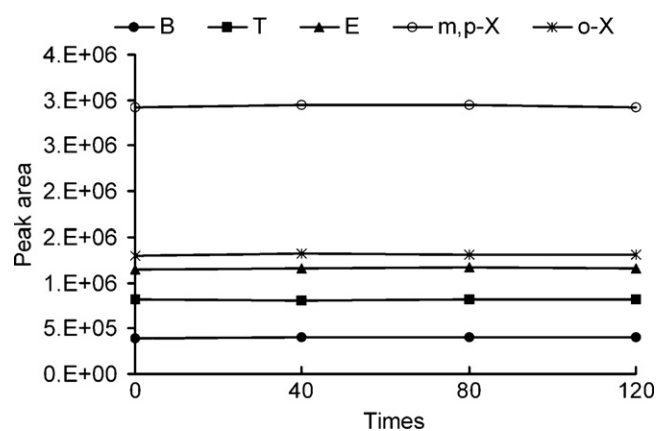


Fig. 8. Durability of SWCNT fiber for the extraction of BTEX in spiked samples. Conditions: concentration of BTEX, 20  $\mu\text{g/L}$ ; other parameters are the same as described in Fig. 1.

### 3.5. Life time of SWCNTs fiber

The life time of the SWCNTs fiber was investigated by extracting BTEX from a spiked sample after the fiber had been used for 0, 40, 80 and 120 times. The results in Fig. 8 indicate that even after being used for 120 times, the extraction efficiency of the SWCNTs did not decline, showing a high durability.

### 3.6. Analytical performance

The linear range, correlation coefficient, limits of detection (LODs), limits of quantification (LOQs), and repeatability of the method for the analysis of BTEX in spiked water with the SWCNTs fiber under the optimized conditions are listed in Table 2. All the compounds exhibited good linearity ( $r > 0.998$ ). The LODs ( $S/N=3$ ) and LOQs ( $S/N=10$ ) of BTEX ranged from 0.005 to 0.026  $\text{ng/L}$  and 0.017 to 0.088  $\text{ng/L}$ , respectively. The lowest LODs were achieved with the SWCNTs fiber in comparison with other fibers as shown in Table 1. A good repeatability (RSD 1.5–5.6%) for one unique fiber was found. An acceptable reproducibility (RSD 4.2–8.3%) between different fibers ( $n=3$ ) was also obtained and listed in Table 2. It shows that SWCNTs fiber can be prepared by EPD followed by thermal treatment in a reproducible manner.

The SWCNTs fiber was applied to extract BTEX in seawater, tap water and wastewater collected from a paint factory. Some BTEX were found in tap water and seawater samples but lower than LOQ. These two samples were spiked at 1  $\mu\text{g/L}$  and extracted with SWCNTs fiber. The recoveries and determination precisions are listed in Table 3. The recoveries were in the range of 75.2–104.7% and the precisions (RSD) were less than 3.2%. High levels of BTEX were detected in the waster from the paint factory. The concentrations and the determination precisions are also listed in Table 3. These

**Table 3**  
Recoveries, precisions and concentrations of BTEX in the analysis of real samples.<sup>a</sup>

BTEX	Seawater		Tap water		Wastewater from a paint factory	
	Recovery (% , n = 3)	RSD (%)	Recovery (% , n = 3)	RSD (%)	Concentration (µg/L, n = 3)	RSD (%)
B	89.0	2.6	82.7	1.8	13.67	1.2
T	75.2	1.4	93.8	1.3	3.35	3.5
E	101.2	3.1	104.7	1.3	7.65	6.2
<i>m,p</i> -X	96.3	0.9	102.7	1.2	8.69	2.8
<i>o</i> -X	82.5	3.2	84.3	2.0	10.18	3.7

<sup>a</sup> Seawater and tap water were spiked at 1 µg/L.

results show that SWCNTs fiber could be used to analyze BTEX in water matrix.

#### 4. Conclusions

In this study, the SWCNTs fiber, prepared by electrophoretic deposition and thermally treated with H<sub>2</sub>, was applied to extract BTEX in water sample via HS–SME–GC–FID. The thermal treatment with H<sub>2</sub> was proved to significantly enhance the extraction of the SWCNTs fiber for BTEX due to the removal of carboxylic groups on SWCNTs. The long durability, high thermal stability and strong affinity for BTEX of the fiber were resulted from the special structure of SWCNTs. With low LODs and good precisions, the proposed fiber could be a reliable alternative to commercial fibers in the analysis of BTEX in aqueous sample.

#### Acknowledgments

The authors acknowledge the financial support of the National Natural Science Foundation of China (No. 20607017), the Natural Science Foundation of Fujian Province of China (No. D0610018) and NCET of Xiamen University.

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