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Determination of endocrine-disrupting compounds in water by carbon nanotubes solid-phase microextraction fiber coupled online with high performance liquid chromatography

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ABSTRACT

The commercial solid phase microextraction (SPME) fibers are not stable enough in organic solvent and tend to swell and strip off from the silica fiber in the high performance liquid chromatography (HPLC) mobile phase, and therefore the application of SPME coupled online with HPLC is limited. In this study, an SPME fiber coated with single walled carbon nanotubes (SWCNTs), prepared by means of electrophoretic deposition, was coupled on line to HPLC for the determination of four endocrine-disrupting compounds, i.e. bisphenol A (BPA), estrone (E_1), 17α-ethynylestradiol (EE_2) and octylphenol (OP), in aqueous samples. The results showed that the SWCNTs coating on the prepared fiber did not swell and strip off from the platinum fiber throughout the experiment, thus indicating a high resistance to the HPLC mobile phase, the mixture of water and acetonitrile. The SWCNTs fiber had similar (for OP) or higher (for BPA, EE_2 and E_1) extraction efficiencies than the commonly used polyacrylate fiber, and had a lifetime of more than 120 operation times. Under the optimized conditions, the linearity of the proposed method was 1.0–30.0 μg/L for BPA and OP and 3.0–90.0 μg/L for E_1 and EE_2. The limits of detection (LODs; S/N = 3) and limits of quantification (LOQs; S/N = 10) of the method were 0.32–0.52 μg/L and 1.06–1.72 μg/L, respectively. Repeatability for one fiber (n = 3) was in the range of 1.3–7.1% and fiber-to-fiber reproducibility (n = 3) was in the range of 1.6–8.4%. The proposed method was successfully applied for the analysis of spiked tap water and seawater samples with recoveries from 81.8 to 97.3%.

1. Introduction

Solid-phase microextraction (SPME) is a relatively new sample pretreatment technique in which sampling, matrix isolation, and enrichment of analyte can be done in one step [1,2]. SPME is traditionally coupled with gas chromatography (SPME-GC) and this combination has proved to be sensitive, accurate, and precise for the quantitative analysis of volatile compounds. In SPME-GC, the SPME fiber is introduced into the injector port and analytes are thermally desorbed from the coating. SPME is also coupled online to high performance liquid chromatography (SPME-HPLC) to widen the application in the analysis of polar or thermally labile compounds, as well as those with poor volatility. In SPME-HPLC, desorption is typically carried out in a manual injection interface, which consists of a six-port injector with a special fiber-desorption chamber filled with desorption solvent or a mobile phase [3–5]. After desorption, the desorbed analytes are delivered to the analytical column for separation. SPME-HPLC is used in the analyses of explosives [6], carcinogenic aromatic amines [7], surfactants [8], phenolic compounds [9,10], estrogenic compounds [11], polycyclic aromatic hydrocarbons [12], organometals [13], heavy metals [14] and triazine [15] in environmental samples, myricetin and quercetin [16], ochratoxin A [17], carbamate and phenylurea [18], trace estrogens [19] and tetracyclines [20] in food; as well as β-blockers [21] and antidepressants [22] in biological fluids.

Even with these reports, practical implementation of SPME-HPLC has lagged far behind that of SPME-GC. One of the major reasons for this is the limited number of commercially available SPME fibers [5]. Moreover, the coatings of the commercially available fibers are unstable and would swell and even strip off from the substrate (silica fiber) when they are immersed in strong organic solvents, thus restricting their use in SPME-HPLC [11–13,16,23]. Swelling of the coating in organic solvents will change its size and it may remain inside the chamber of the SPME-HPLC interface when the fiber is removed. In order to avoid the damage of the fiber, purified water is usually introduced into desorption chamber before the fiber is removed [11,16]. With the increase of interest towards this technique, a few fibers with high organic solvent resistance have been developed and used in SPME-HPLC. Gbatu et al. describe the preparation of SPME fibers that are stable in strong

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organic solvents (xylene and methylene chloride) as well as acidic and basic solutions using the sol–gel process [13]. Several molecular imprinted SPME fibers, which show a high chemical stability when immersed in common solvents, such as *n*-hexane, chloroform, toluene, methylene dichloride and acetonitrile, are prepared and applied in SPME-HPLC [19–21]. However, the type of fibers is still limited and it is necessary to prepare new fibers for the development of the SPME-HPLC technique.

Carbon nanotubes (CNTs) are a kind of new carbonaceous nanomaterials that has received great attention in many fields and applications of CNTs as SPME coating have been reported. SPME fibers coated with oxidized multi-walled carbon nanotubes (MWCNTs) and single-walled carbon nanotubes (SWCNTs) are used in the extraction of phenols [24] and organochlorine pesticides [25] in water samples, respectively. An SPME fiber coated with SWCNTs is prepared using electrophoretic deposition (EPD) without the use of adhesive in our previous works [26,27]. When the obtained SWCNTs fiber is immersed in methanol, acetonitrile (ACN), hexane, acetone or dichloromethane, respectively, for more than 2 h, no swelling or stripping off of the coating is found, showing its good stability in these organic solvents [26] and a potential use in SPME-HPLC. However, this kind of fiber has never been coupled online to HPLC.

Endocrine-disrupting compounds (EDCs), which include both naturally occurring hormones and anthropogenic chemicals, are reported to have adverse effects on humans and other animals [28]. SPME-HPLC is usually an effective method for the analysis of EDCs in various matrixes [8,10,11]. In our study, an SPME fiber coated with SWCNTs was prepared using EPD and evaluated for the online SPME-HPLC applications with EDCs, i.e., bisphenol A (BPA), estrone (E_1), 17α-ethynylestradiol (EE_2) and octylphenol (OP), in aqueous samples as test compounds. The properties for the extraction of EDCs were investigated and compared with those of the commercial polyacrylate (PA) fiber. A SPME-HPLC method based on this fiber was established and applied in the analysis of EDCs in seawater and tap water.

2. Experimental

2.1. Chemicals and materials

BPA, E_1, EE_2 and OP were supplied by Alfa Aesar China (Tianjin, China). HPLC-grade ACN and methanol were purchased from Tedia (Fairfield, OH, USA). Dimethylformamide (DMF), HCl, NaCl and NaOH 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 EDCs was prepared by dissolving certain amount of BPA, OP, E_1 and EE_2 in a 10 mL volumetric flask and diluting with methanol. The working standard of 1 mg/L for each compound was prepared from the stock solution. All solutions were stored at 4 °C in a refrigerator. PA (polyacrylate) fiber (85 μm) was supplied by Supelco (Bellefonte, CA, USA). SWCNTs with a specific surface of 380 m^2/g were purchased from Chengdu Organic Chemistry Co. (Chengdu, China).

2.2. Instrumentation

A liquid chromatography (Shimadzu, Japan) equipped with a binary pump (LC-20AB) and a diode array detector (SPD-M20A) was used in this study. The SPME-HPLC interface was purchased from Supelco (Bellefonte, PA, USA). After extraction, the fiber was desorbed in the desorption chamber of the interface. The separation of EDCs was achieved on a Discovery C_{18} column (Supelco, 5 μm, 250 mm × 4.6 mm i.d.) at room temperature. Water and ACN were used as mobile phases A and B, respectively. The flow-rate of the mobile phase was 1.0 mL/min and the gradient profile was 20% B at 0 min, 70% B at 4 min and held for 3 min, 100% B at 10 min and held for 2 min. The detecting wavelength was set at 280 nm.

2.3. Preparation and hydrogen annealing of SWCNTs SPME fiber

The preparation of SWCNTs SPME fibers using electrophoretic deposition is described in detail in our previous work [26]. In brief, the SWCNTs were treated with a 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 and 2 cm in length were used as electrodes and immersed into the suspension, and when a DC voltage of 40 V was applied between the two Pt electrodes for 10 s, an SWCNTs deposit was formed on the Pt anode. Then the anode with its deposit was removed from the suspension and heated at 120 °C to evaporate the solvent, and finally a fiber coated with SWCNTs was obtained. Fibers with different coating thicknesses could be produced by repeating the EPD procedure for various times. In this study, fibers with a coating thickness of about 40 μm and coating length of about 1.5 cm were prepared. The as-prepared SWCNTs fiber was then annealed at 500 °C in a quartz tube with H_2 as described in our previous work [27]. The surface morphology of the as-prepared and hydrogen annealed fiber was observed with scanning electron microscopy (SEM) (S-4800, Hitachi). The obtained fiber was assembled on a commercial SPME device by inserting the bare end of the fiber into the fiber attachment tubing inside the septum-piercing needle. The SWCNTs fiber in the device could be pushed out and retracted freely without detachment.

2.4. SPME procedure

Each day prior to use, the fibers were conditioned in the interface with the mobile phase until they were free from the contaminants. After conditioning, the fibers were ready to use. Sample of 10 mL was introduced into a 15 mL glass vial with PTFE-coated septa (Supelco, Bellefonte, PA, USA) and a magnetic stirring bar inside. The sample vial was placed in a water-jacketed vessel, which was put on a magnetic stirrer (Corning Laboratory Stirring/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 SPME fiber was positioned at a suitable height so that the coating of the fiber was completely immersed into the sample solution. NaCl and 0.1 M HCl or NaOH were used to adjust the ion strength and pH, respectively. After extraction, the fiber was inserted into the desorption chamber of the interface. The desorbed analytes were delivered into the LC column by the mobile phase when the valve was switched from the load to the inject position. The chromatographic peak area of the analyte was used for quantification and evaluation of the extraction efficiency of the SPME fiber.

2.5. Performance and analysis of real sample

The effects of the parameters, such as desorption mode, desorption time, extraction time, extraction temperature, pH, ionic strength and stirring rate, were studied and optimized, and the performance of the proposed method under these optimized conditions was used for the analyses of real samples. Tap water was collected from the laboratory and sea water from Baicheng beach near Xiamen University. Before analysis, the samples were filtered with 0.45 μm cellulose acetate membrane and stored in brown glass bottles at 4 °C.

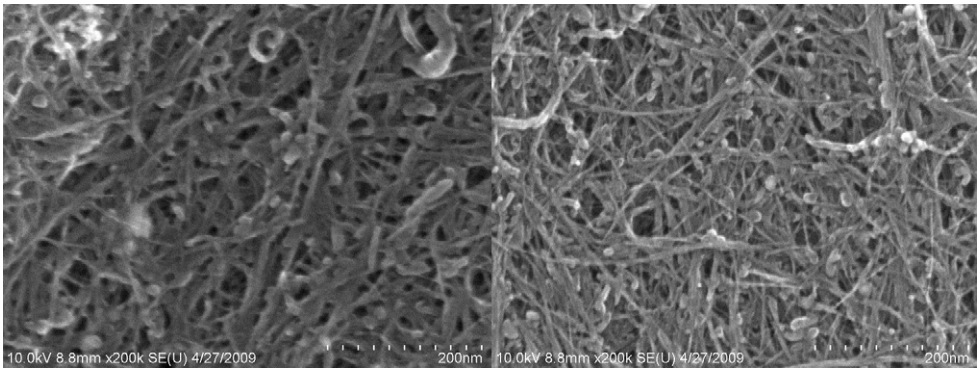

Fig. 1. SEM images of as-prepared (left) and hydrogen annealed (right) SWCNTs fiber.

3. Results and discussion

3.1. Effect of hydrogen annealing

In order to investigate the effect of hydrogen annealing on the properties of the SWCNTs fiber, the as-prepared fiber and the same fiber treated with H_2 were used to extract EDCs in a standard sample spiked with BPA and OP at 10 μg/L and E_1 and EE_2 at 30 μg/L with the same parameters for comparison. The peak area ratios of the extracted EDCs with the treated fiber to those with the as-prepared fiber were 3.52, 2.18, 0.93 and 5.23 for BPA, OP, E_1 and EE_2, respectively. The results indicated that, after hydrogen annealed, the extraction efficiency of the SWCNTs fiber increased significantly for most of the EDCs.

Our previous work shows that polar groups such as carboxylic groups are presented on the SWCNTs surface, and that hydrogen annealing would lead to the reduction of these groups [27]. The occurrence of polar group on an SPME fiber would increase the extraction efficiency for polar compounds. However, BPA, OP, E_1 and EE_2 are low polar compounds and with log octanol–water partition coefficient of 3.40, 4.12, 3.43 and 4.15, respectively [29]. Therefore, the reduction of the polar groups caused by the annealing process would not have a significant effect on the extraction efficiency of the hydrogen annealed SWCNTs fiber for the EDCs studied.

The SEM images of the surface of the as-prepared and hydrogen annealed SWCNTs fibers are shown in Fig. 1. In these images, the nanotubes could be clearly resolved and nanometer-sized pores, formed by the overlaying of SWCNTS, were present on the surface. Powder-liked material was found on the surface of the nanotubes and in some areas between nanotubes in the as-prepared fiber image, but not in the hydrogen annealed one. The powder-liked material was most likely to be the amorphous carbon, which was formed during the preparation of the SWCNTs. These images showed that the hydrogen annealing could remove the amorphous carbon on the SWCNTs. Besides, a weight loss was found after the fiber was annealed, verifying the removal of the amorphous carbon. The removal of the amorphous carbon could expose more SWCNTs to the solution when the SWCNTs fiber was placed in the water sample. Therefore, the extraction efficiency of the annealed fiber was enhanced. As a result, the annealed fiber was considered to be better for the extraction and used in the experiments which followed.

3.2. Optimization of experimental parameters

Both the dynamic and static desorption modes for desorption of EDCs on the SWCNTs fiber were investigated in this study. In the dynamic mode, the fiber was placed in the desorption chamber and the valve was immediately switched from load to inject position. The mobile phase, of which 20% was acetonitrile, delivered the analytes to the chromatographic column. After 5 min, the valve was switched back to the load position and the fiber was removed from the chamber. In the static mode, the fiber was placed in the desorption chamber filled with acetonitrile for 1 min. Then the valve was switched from load to inject position thus the analytes were transferred to the chromatographic column. After 5 min, the valve was back to the load position and the fiber was removed. An experiment was carried out to extract a standard sample spiked with BPA and OP at 10 μg/L and E_1 and EE_2 at 30 μg/L. Fig. 2 shows the chromatograms obtained with the static and dynamic desorption modes. The results indicated that larger amount of analytes were desorbed with the static mode than with the dynamic mode. Thereafter the static mode was adopted in this study. Under these desorption conditions, no significant carry-over of EDCs was found with the SWCNTs fiber.

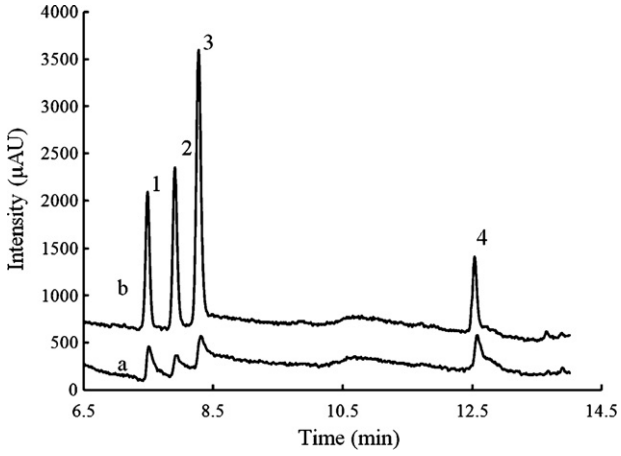

Fig. 2. Chromatograms obtained in the dynamic (a) and static (b) modes. 1, BPA; 2, OP; 3, E_1; 4, EE_2. Conditions: extraction time, 20 min; extraction temperature, 20 °C; stirring rate, 1000 rpm; no salt was added; no pH adjustment; standard water sample spiked with BPA and OP at 10 μg/L and E_1 and EE_2 at 30 μg/L.

Extraction time is a key parameter affecting the method sensitivity in SPME. Six extraction times, i.e., 10, 20, 30, 40, 50 and 60 min, were tested for optimization. The results in Fig. 3 shows that peak areas of the EDCs increased with the extraction time, and the extraction did not reach equilibrium even after 60 min. As shown in Fig. 1, the SWCNTs coating was porous with nanometer-sized pores. The mass transfer rate of the analytes in these pores could be very slow. This might be the reason for the equilibrium time longer than 60 min. Considering the sensitivity and throughput, 30 min was chosen as the extraction time.

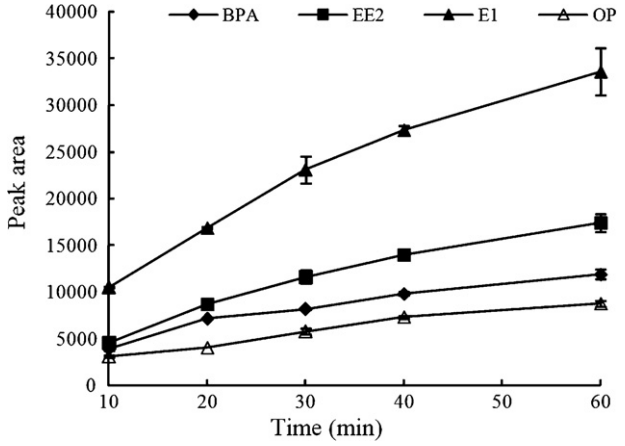

Fig. 3. Effect of extraction time on extraction of EDCs ($n = 3$). Other parameters were the same as those in Fig. 2.

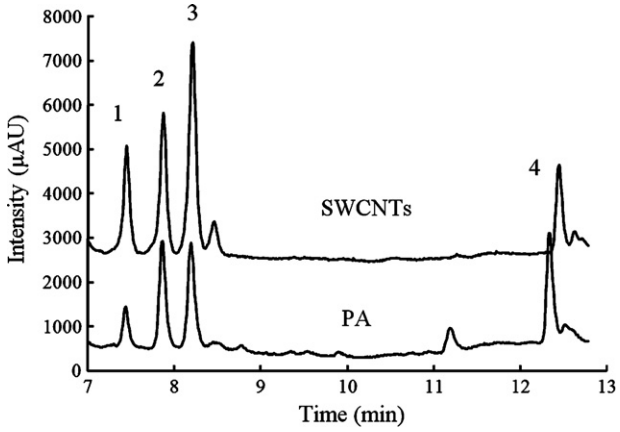

Fig. 4. Chromatograms of EDCs extracted with PA or SWCNTs fibers. Peaks: (1) BPA, (2) EE_2, (3) E_1, and (4) OP. The water sample was spiked with BPA and OP at 10 μg/L and E_1 and EE_2 at 30 μg/L.

The effect of ionic strength on the extraction efficiency was studied with various standard samples spiked with BPA and OP at 10 μg/L and E_1 and EE_2 at 30 μg/L containing different amounts of NaCl ranging from 0 to 30% (w/v). The results show that the extraction efficiency of EDCs decreased with the content of NaCl (data not shown). The salting out effect caused by adding NaCl would lower the solubility of EDCs in water and force more of them adsorbed on the fiber, and therefore increase the efficiency of the extraction. However, SWCNTs coating was a solid porous sorbent, the extraction occurred on the surface of pores. The large amount of NaCl in the sample solution might occupy the surface for adsorption and had a negative effect on the extraction of EDCs. As an overall result, the adding of salt had negative effect on the extraction of EDCs. Therefore, no salt was added in the followed experiments.

The effect of pH in the range of 3–9 on the extraction of EDCs was investigated. The results indicated that the extraction efficiency of EDCs was almost constant within the range (data not shown). The pH usually affects the extraction efficiency of SPME by altering the charges of analytes. The pK_as of BPA, OP, E_1 and EE_2 are 10.3, 10.24, 10.4 and 10.7, respectively [29,30]. Thus these compounds could be in neutral forms at the pH tested. No significant effect of pH on the extraction was found for the SWCNTs fiber. The pH adjustment was unnecessary if the sample pH was within 3–9.

The effect of stirring rate on the extraction efficiency was studied. The results show that the signal increased with the stirring rate (data not shown) because higher stirring rate might result in faster mass transfer of analytes into SWCNTs coating, and consequently more analytes could be extracted. When a stirring rate higher than 1000 rpm was applied, however, the stirring bar could not run smoothly. Therefore 1000 rpm was selected for subsequent studies.

In an SPME procedure, the extraction efficiency is usually affected by the temperature. Different extraction temperatures, i.e., 20, 40, 50 and 60 °C, were investigated. The results show that the sensitivity increased with the temperature from 20 to 40 °C, and then decreased slightly (data not shown). This might have been caused by two facts. Firstly, high temperature could enhance the mass transfer of EDCs into the SWCNTs coating, thus have a positive effect on the extraction. Secondly, the adsorption of EDCs on the surface of SWCNTs is an exothermic process, thus a high temperature could reduce the adsorption of EDCs. For these reasons, 40 °C was chosen in this study.

In short, the optimized conditions for the extraction of EDCs from water samples with the hydrogen annealed SWCNTs fiber were the following: extraction time, 30 min; extraction temperature, 40 °C; stirring rate, 1000 rpm; no salt added; no pH adjustment with pH 3–9.

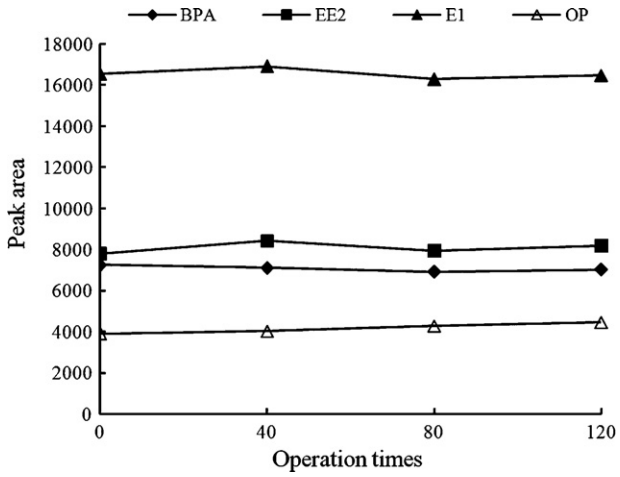

Fig. 5. Durability of SWCNTs fiber to extract EDCs in a spiked sample. Conditions were the same as those in Fig. 2.

3.3. Comparison with PA fiber

For the extraction of EDCs from a water sample, the PA fiber is the most commonly used commercial SPME fiber [10,11]. In this study, the PA fiber was applied to extract EDCs from the standard sample under the optimized conditions described in reference 11, i.e., extraction time, 45 min; extraction temperature, 65 °C; salt content, 18% (w/v); pH, 3; desorption mode, static desorption; desorption time, 2 min; stirring rate, 1000 rpm. At the same time, the SWCNTs fiber was used to extract the same sample under the optimized conditions described in Section 3.2. Fig. 4 shows the chromatograms of the EDCs obtained with both fibers. The results indicated that the SWCNTs fiber had similar (for OP) or higher (for BPA, EE_2 and E_1) extraction efficiencies than the PA fiber. SWCNTs are porous and have a special surface area as high as 380 m^2/g. They are made of graphite, and there is a π–π interaction between the SWCNTs and the analytes. As a result, the SWCNTs fiber has high affinity towards EDCs.

Table 1
Characteristic data of the established SPME-HPLC method for the determination of EDCs.[a]

EDCs	Linear range (μg/L)[a]	*R*	LOD (μg/L)[b]	LOQ (μg/L)[b]	RSD (%)[c]	RSD (%)[d]
BPA	1.0–30.0	0.996	0.32	1.06	2.4	8.4
EE_2	3.0–90.0	0.997	0.52	1.72	1.6	4.0
E_1	3.0–90.0	0.995	0.34	1.12	1.3	1.6
OP	1.0–30.0	0.990	0.34	1.12	7.1	7.8

[a] The analytical curves were constructed with four concentration level of each compound. The concentrations of the standard sample for the test of reproducibility and repeatability were 10 μg/L for BPA and OP and 30 μg/L for E_1 and EE_2.
[b] LOD and LOQ were calculated based on three and 10 times the average background noise and divided by the slope of the calibration curve, respectively.
[c] Repeatability of one unique fiber ($n = 3$).
[d] Fiber-to-fiber reproducibility ($n = 3$).

Table 2
Recovery and precision of the established SPME-HPLC method.[a]

EDCs	Tap water		Seawater	
	Average recovery ($n = 3$)	RSD (%, $n = 3$)	Average recovery ($n = 3$)	RSD (%, $n = 3$)
BPA	89.4	8.1	81.8	8.3
EE_2	90.3	7.0	91.0	7.7
E_1	91.2	7.2	97.3	8.1
OP	88.6	7.7	90.2	3.3

[a] Tap water and seawater were spiked at 3 μg/L for BPA and OP and 9 μg/L for E_1 and EE_2.

3.4. Resistance to mobile phase and lifetime

The coatings of the commercial fibers usually swell in the HPLC mobile phase, and sometimes strip off from the silica fiber when removed from the desorption chamber, resulting in a short lifetime. The SWCNTs fiber could be inserted or removed from the desorption chamber smoothly throughout the experiment. No swelling or stripping off was found. It revealed that the SWCNTs fiber had high resistance to the mobile phase. The lifetime study was carried out to extract EDCs from a spiked sample with a SWCNTs fiber that had been used for 0, 40, 80 and 120 times. The obtained peak areas of EDCs are illustrated in Fig. 5. After 120 times use, no obvious decline of extraction efficiency was found, showing a long lifetime of the SWCNTs fiber.

3.5. Analytical performance

The validation of the established SPME-HPLC method based on the SWCNTs fiber was conducted by analyzing samples spiked at different concentration. The repeatability of the method was obtained by measuring a standard sample for 3 times with one fiber, and the reproducibility of the fiber was carried out by analysing a standard sample with three fibers. The linear range, correlation coefficient, limits of detection (LODs), limits of quantification (LOQs), and the repeatability of the method are listed in Table 1. All the analytes exhibited good linearity ($r > 0.990$). The LODs (S/N = 3) and LOQs (S/N = 10) of the EDCs were 0.32–0.52 μg/L and 1.06–1.72 μg/L, respectively. A good repeatability (RSD 1.3–7.1%) for one unique fiber was achieved. An acceptable fiber-to-fiber reproducibility (RSD 1.6–8.4%) ($n = 3$) was obtained and shown in Table 1, indicating that the SWCNTs fiber could be prepared in a reproducible manner.

The established method was applied to determine EDCs in tap water and seawater, but no target analytes were found in the samples. These samples were spiked at 3 μg/L for BPA and OP, and 9 μg/L for E_1 and EE_2, and analysed again. The recovery and precision are listed in Table 2. The recoveries were in the range of 81.8–97.3% and the precisions (RSD, %, $n = 3$) were better than 8.3%. The salinity of the seawater sample is 33, indicating a salt content less than 3.5%. Although the content of salt has a negative effect on the EDCs extraction efficiency of the fiber, the effect of this low salt content would be insignificant, and satisfied recoveries were obtained with the seawater sample. These results indicated that the potential use of the established method for the determination of EDCs in water samples.

4. Conclusions

The SWCNTs fiber, prepared using electrophoretic deposition and annealed with H_2, was applied to extract EDCs from water samples with on-line SPME-HPLC. The SWCNTs coating on the fiber did not swell and strip off from the substrate throughout the experiment, showing a high resistance to the mobile phase. The SWCNTs fiber had similar (for OP) or higher (for BPA, EE_2 and E_1) extraction efficiencies than the PA fiber, and a long lifetime for more than 120 runs. With low LODs and good precisions, the proposed method based on the SWCNTs fiber had potential use for the analysis of EDCs in environmental samples. In conclusion, the SWCNTs fiber could be a good alternative in the application of on-line SPME-HPLC.

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