



# Magnetron sputtering Si interlayer: A protocol to prepare solid phase microextraction coatings on metal-based fiber

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## ABSTRACT

Use of metal fibers in solid phase microextraction (SPME) can overcome the fragility drawback of conventional fused-silica ones. However, the surface modification of metal substrates is rather difficult, which largely prevents many mature traditional techniques, such as sol–gel and chemical bonding, being used in fabrication of SPME coating on metal-based fibers. This study demonstrates a protocol to resolve this problem by magnetron sputtering a firm Si interlayer on stainless steel fiber. The Si interlayer was easily modified active group, and attached with a multiwalled carbon nanotubes (MWCNTs) coating using the reported approach. The as-prepared MWCNTs/Si/stainless steel wire fiber not only preserved the excellent SPME behaviors of MWCNTs coatings, but also exhibited a number of advantages including high rigidity, long service life, and good stability at high temperature, in acid and alkali solutions. This new surface modification technique might provide a versatile approach to prepare sorbent coatings on unconfined substrates using traditional methods.

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## 1. Introduction

During the last decade, SPME, as a new extraction technology, has gained widespread acceptance for analyte matrix separation and preconcentration due to its high sensitivity, rapidity, simplicity and free of solvents. The core part of SPME technique is to design effective SPME fibers, which usually consist of a substrate fiber and a coating as a stationary phase to adsorb the analytes from samples. At present, most commercial SPME fibers have used fused-silica as substrate. Fused-silica substrate is very fragile and must be handled with great care, so the service life is very limited [1]. Hence, recent progress in preparation of SPME fibers is being directed at the development of flexible metal-based fibers [2–4]. However, metal substrates usually have low chemical reactivity and are difficult to adapt to many traditional preparation techniques of SPME fibers, such as sol–gel [5,6] and chemical bonding methods [7]. Although some new techniques including chemical corrosion [8,9], electrodeposition [10] and anodization [11] have emerged as prospect approaches to prepare sorbent coatings on metal-based fibers, the synthesized coatings are mostly metal-based, and cannot be comparable to many other excellent sorbent coatings. So it is of great importance to develop a versatile approach to combine tradi-

tional excellent sorbent coatings and techniques with metal-based fibers. Magnetron sputtering is an outstanding vapor deposition technique for preparing high-quality coatings on various substrates with considerable adhesion strength [12,13]. Therefore, using this technique it is possible to introduce a firm interlayer on metal wires so as to make the surface easy to be functionalized. In this study, a Si interlayer was introduced on stainless steel wire using magnetron sputtering. The Si surface can be easily modified with active groups, and attached with MWCNTs coatings according to the procedure of our previous work [7]. The prepared fiber coupled with gas chromatography (GC) was then used for SPME of seven common phenols from water samples, and was subject to comparisons with the MWCNTs/fused-silica and commercial polyacrylate (PA) fibers.

## 2. Experimental

### 2.1. Preparation of SPME fiber

The Si interlayer was prepared using medium frequency unbalanced magnetron sputtering method in a multifunctional deposition system, as described in detail in Ref. [13]. Stainless steel wire (ASTM304,  $\phi$  150  $\mu$ m) was cleaned with ethanol, distilled water and acetone in ultrasonic bath for 15 min respectively, and then placed in the vacuum chamber. A base pressure of less than  $4.0 \times 10^{-3}$  Pa was attained in the chamber. Prior to the deposition, a

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20 min sputter cleaning in argon plasma was firstly carried out so as to improve the adhesion between the film and substrate. Then, the Si deposition was performed using Ar gas as the sputtering gas, and Si (99.99%) as the target material. The deposition conditions were as follows: (1) deposition pressure: 0.3 Pa; (2) pulse duty cycle: 0.5; (2) Si sputtering current: 12 A; and (3) pulse negative voltage on the substrate: 400 V. The sample holder was kept revolving during deposition process to ensure the uniformity of the Si layer on the stainless steel wire.

The stainless steel wire with Si interlayer was cleaned with the ultrasonic in methanol and acetone, and then was dipped in piranha solution ( $\text{H}_2\text{O}_2$  (30%): $\text{H}_2\text{SO}_4$  (97%)=3:7), and heated to 60 °C for 40 min. After that, the fiber was put in a dry tube and kept at 120 °C for another 30 min in an oven. Thereafter, it was rinsed with ultrapure water until pH 7, and then dried at room temperature. So the hydroxylation of the substrate was completed.

The experimental procedures included oxidation of MWCNTs, silanization of substrate and the followed chemical bonding MWCNTs to the substrate were completed according to Ref. [7].

## 2.2. Characterization of the SPME fiber

The thickness of the Si layer was measured as about 900 nm by a JSM5910 3D non-contact surface profilometer. The surface chemical composition of the Si layer was determined using a PHI-5702 multifunctional X-ray photoelectron spectroscope (XPS, operating with Al-K $\alpha$  radiation and detecting chamber pressure of below  $10^{-8}$  Torr). A Philips X'Pert Pro X-ray diffractometer (XRD, Cu-K $\alpha$  line at 0.15406 nm, with normal mode and grazing incidence at 3° as well) was used to analyze the crystal structure of the Si layer. The adhesion between the Si layer and substrate was investigated by a MFT-4000 tribometer in scratch mode. The diamond stylus (Rockwell C 120°, 0.4 mm in radius) scratched across the surface of films with an increased load, and the critical load, at which the film occurred cracking, was used to evaluate the adhesion strength. SEM micrographs of MWCNTs-covered fibers were obtained on a field emission scanning electron microscope (FESEM, JSM-6701F, Japan).

## 2.3. Chemicals, materials, instrumentation

*o*-Methylphenol (*o*-MP), phenol (P), 2,5-bimethylphenol (2,5-BMP), *p*-methylphenol (*p*-MP), were obtained from the Shanghai Chemical Reagent Corporation (China); *o*-ethylphenol (*o*-EP), *p*-ethylphenol (*p*-EP), 2,3-bimethylphenol (2,3-BMP) were obtained from Sigma–Aldrich; 3-aminopropyltriethoxysilane (APTES) was from the Chemical Industrial Corporation of Gaizhou (China); sodium dodecyl sulfate (SDS), was obtained from Beijing Donghuan Chemical Industrial Corporation (China). All the reagents are of analytical grade except SDS, which is chemical grade.

The standard mixtures of the seven phenols were prepared by dissolving 10.0 mg of each compound in 10.0 mL of ethanol. The stock solution (1 mg mL $^{-1}$ ) was stored at 4 °C and diluted with ultrapure water to give the required concentration. The river water sample was collected from the Yellow River (Lanzhou, China). The wastewater (untreated) was sampled from the sanitary wastewater in Lanzhou. These samples were all filtered through a 0.45  $\mu\text{m}$  filter and stored at 4 °C.

An Agilent 7890A series gas chromatograph (Agilent Technologies, USA) equipped with a flame ionic detector was used. The separation was carried out on a HP-5 capillary column (30 m  $\times$  0.32 mm i.d.  $\times$  0.25  $\mu\text{m}$  film thickness). Separation and detection parameters were optimized. In brief, the column temperature was initially hold at 50 °C, and programmed at 5 °C min $^{-1}$  to 75 °C, then at the rate of 1 °C min $^{-1}$  to 100 °C, finally programmed at 10 °C min $^{-1}$  to 250 °C, which was then held for 30 min. Ultrapure

nitrogen (>99.999%) was used as the carrier gas (1 mL min $^{-1}$ ) and make-up gas (30 mL min $^{-1}$ ). The injector temperature was fixed at 280 °C, and the detector one was fixed at 300 °C. The injection was performed in the splitless mode.

## 2.4. SPME

A home-made SPME device was used for the experiments [14]. A solution with 50  $\mu\text{g L}^{-1}$  analytes was prepared for the following SPME experiments. The sample was extracted through the direct immersion in the solution with a constant depth under the 70 °C for 50 min. KCl was used to adjusted ionic strength to 30%, and HCl and NaOH were used to adjusted pH to 6; a magnetic stirrer was used, and stirring rate was controlled at 600 rpm.

## 2.5. Test stability of coatings in acid and base solutions

The tip of the fiber was placed in two polytetrafluoroethylene (PTFE) sealed vials loaded with hydrochloric acid ( $1 \times 10^{-3}$  M) and sodium hydroxide ( $1 \times 10^{-2}$  M) solution at room temperature, respectively. After 24 h, the fiber was taken out for the extraction experiment. The peak areas of analytes (50  $\mu\text{g L}^{-1}$ ) before and after dipping into different solutions were compared.

# 3. Results and discussion

## 3.1. Preparation of MWCNTs/SPME fibers

Fig. 1 shows the preparation process of MWCNTs/Si/stainless steel wire SPME fiber. Firstly, a firm Si interlayer was deposited on the stainless steel wire using magnetron sputtering. In order to obtain a satisfactory Si interlayer, the effects of sputtering parameters on the chemical composition, crystal structure, and adhesion properties of the Si layer were investigated by means of XPS, XRD, and scratch test (as seen in Supplementary material). The film was composed of Si simple substance, and exhibited the amorphous character. The critical load reached 42 N, illustrating the firmness of the Si interlayer on the stainless steel substrate. Then the stainless steel wire with Si interlayer was treated with piranha solution to form –OH group on the surface. Finally, multilayer-MWCNTs coating was formed on the stainless steel wire according to the method in Ref. [7] by the covalent bond between the active groups on both sides of the substrate and MWCNTs, and the followed van der Waals force-induced spontaneous adsorption of MWCNTs.

## 3.2. Characterization of the SPME fiber

Fig. 2(a) and (b) shows the planar FESEM micrographs of the as-prepared fiber. It can be clearly observed that a coating ( $\sim 20 \mu\text{m}$ ), consisting of cross-linked CNTs, uniformly covered on the fiber surface, implying success of the synthetic strategy. The cross-section FESEM micrograph of the as-prepared fiber (Fig. 2(c)) well characterized the existence of the Si interlayer (about 700 nm) between the MWCNTs coating and stainless steel wire substrate. The intermixed interface between the Si interlayer and stainless steel wire substrate indicated their strong adhesion. Fig. 2(d) shows the 3D surface morphology of the stainless steel substrate after the deposition of Si interlayer, from which it can be seen the Si layer was very smooth and uniform, and without any influences on the surface morphology of the substrate. The height of the preformed step was the thickness of the Si interlayer about 900 nm. It is worth noted that the thickness of the Si interlayer decreased a little after the chemical treatment, which suggested the hydroxylation indeed took place on the Si surface and thus consumed parts of the Si layer. Therefore, by a combi-

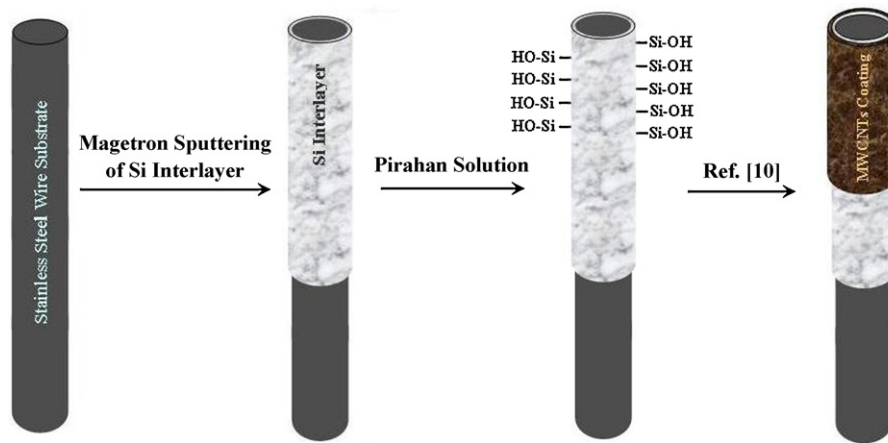


Fig. 1. Schematic illustration of the preparation process of the MWCNTs/Si/stainless steel wire fiber.

nation of above observations, it is concluded that the MWCNTs coating was successfully prepared on the stainless steel wire substrate through introducing a Si interlayer. In other words, the stainless steel wire with Si interlayer is equal to conventional fused-silica substrate because both them can be modified with active groups on the surface. It follows that, many materials, such

as open crown ether [15], polyphenylmethylsiloxane [16], anilinemethyltriethoxysilane/polydimethylsiloxane [17] coatings and so on, which can be coated directly on fused-silica substrate by sol-gel or chemical bonding methods, can also form coatings on stainless steel substrate with Si interlayer according to the procedure of previous works.

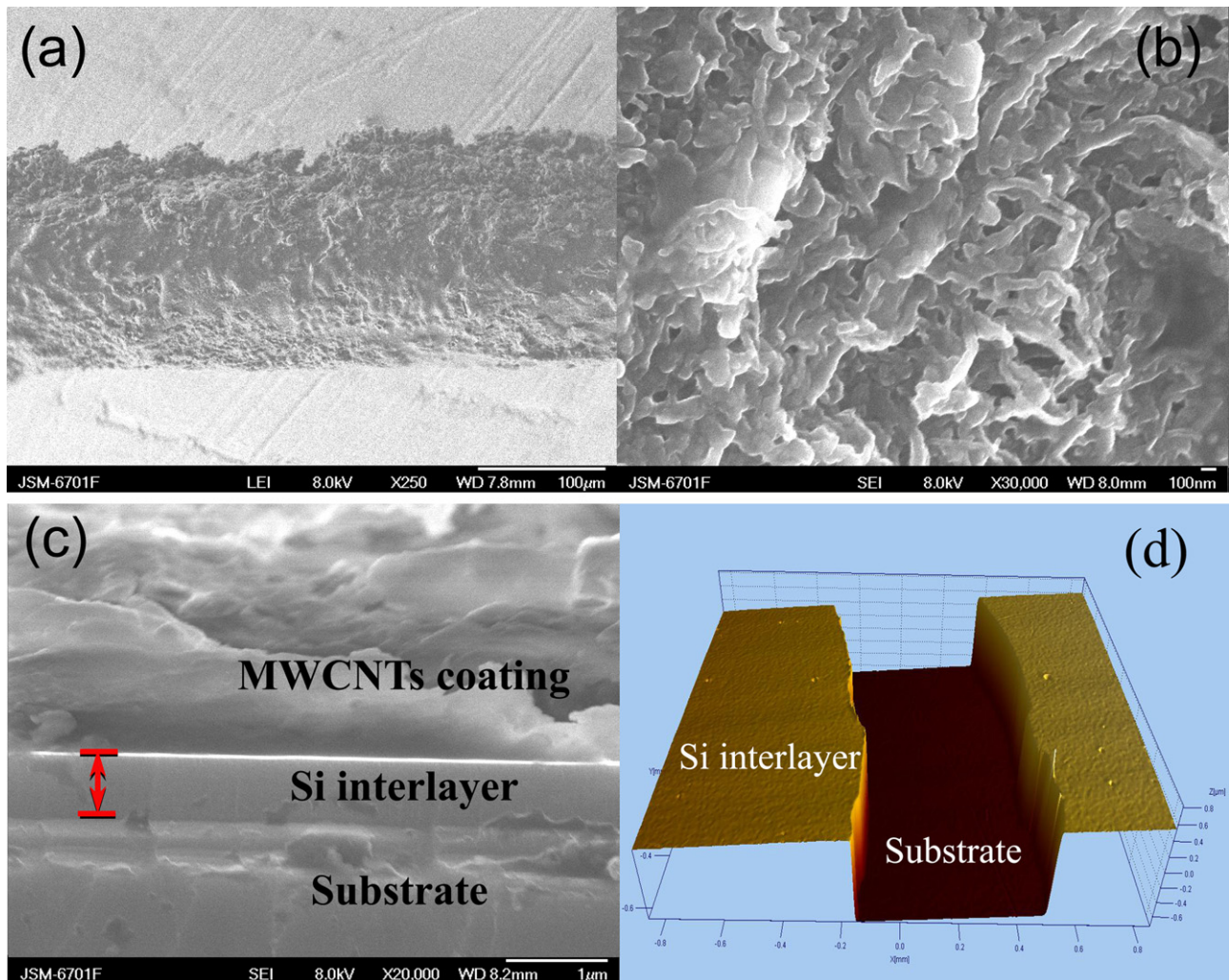


Fig. 2. (a) Planar FESEM micrograph of the as-prepared fiber at a magnification of 500 $\times$ , (b) at a magnification of 20,000 $\times$ , (c) cross-section FESEM micrograph; (d) 3D surface morphology of the stainless steel substrate after the deposition of Si interlayer.

**Table 1**

Analytical characteristic data of seven phenols using the MWCNTs/Si/stainless steel wire SPME fibers coupled with GC.

Compounds	Linear range ( $\mu\text{g L}^{-1}$ )	Linearity	LODs ( $\mu\text{g L}^{-1}$ )	RSD <sup>a</sup> (%)
P	0.5–5000	0.9997	0.05	6.35
<i>o</i> -MP	0.5–5000	0.9985	0.05	5.98
<i>p</i> -MP	0.5–5000	0.9961	0.05	3.47
<i>o</i> -EP	0.05–5000	0.9943	0.005	4.95
2,5-BMP	0.05–5000	0.9941	0.005	2.83
<i>p</i> -EP	0.05–5000	0.9941	0.005	1.98
2,3-BMP	0.05–5000	0.9938	0.005	4.15

<sup>a</sup>  $n = 3$ .

### 3.3. SPME behaviors

The as-prepared MWCNTs/Si/stainless steel wire fiber coupled with GC was used for SPME of seven phenols from water samples. Because the sorbent coating and analytes were the same with that in Ref. [7], the same as desorption and desorption parameters were also adopted in this study, which had been optimized systemically. The analytical parameters including the linearity, accuracy and precision, and detection limits were measured and listed in Table 1. The linearity of the SPME-GC method was investigated with a serial of mixed standard solutions of P, *o*-MP, *p*-MP, *o*-EP, 2,3-BMP, *p*-EP, 2,5-BMP. The results indicated that all of them can be determined quantitatively in wide ranges. As shown in Table 1, good linearities were achieved in the range of 0.05–5000  $\mu\text{g L}^{-1}$  for *o*-EP, 2,3-BMP, *p*-EP, 2,5-BMP, 0.5–5000  $\mu\text{g L}^{-1}$  for P, *o*-MP and *p*-MP with satisfactory correlation coefficients. The detection limits for seven phenols were in the range of 0.005–0.05  $\mu\text{g L}^{-1}$ , which was determined by gradually decreasing the concentrations of analytes until signals could be still discerned at a signal-to-noise ratio of 3 ( $S/N = 3$ ). The precision of the method for three duplicate measurements of mixed standard solution (50  $\mu\text{g L}^{-1}$ ) was investigated, and the relative standard deviation (RSD) varied from 1.98% to 6.35%. It can be found that the analytical parameters of the present MWCNTs/Si/stainless steel wire fiber and the previous MWCNTs/fused-silica fiber coupled with GC [7] are similar, and both exhibit wide linear ranges and low detection limits, which suggested that the introduced Si interlayer does not influence the SPME behaviors of the MWCNTs coatings, and the as-prepared fiber coupled with GC is preponderant to extract and analyze compounds at trace levels in water samples with high sensitivity/efficiency.

### 3.4. Comparison with MWCNTs/fused-silica fiber and commercial PA fiber

Fig. 3 shows the SPME capabilities of the phenols by the MWCNTs/Si/stainless steel wire fiber, MWCNTs/fused-silica fiber and the commercial PA fiber coupled with GC at a trace level of 50  $\mu\text{g L}^{-1}$ . It can be seen that the peak areas of these phenols extracted by the former two fibers are similar, and obviously larger than that by the commercial PA fiber, which indicates that the MWCNTs/Si/stainless steel wire fiber also keeps the excellent SPME behavior of the MWCNTs/fused-silica fiber, and exhibits a superior SPME behavior than the commercial PA fiber. The effectiveness of the present fiber can be ascribed to the high adsorptive ability of MWCNTs and its less compact structure resulting in the larger surface area as compared with agglutinate ones.

At the same time, it is known the sorbent coating of the SPME fiber is usually subjected to high temperature of injection port of a gas chromatograph and/or acidic, alkali solutions or organic solvents in the matrix. The chemical bonding method avoids the usage of agglomerants, and awards the MWCNTs/Si/stainless steel wire fiber good stability at high temperature, in organic solvent (polar and nonpolar) as that for the MWCNTs/fused-silica fiber. Fig. 4

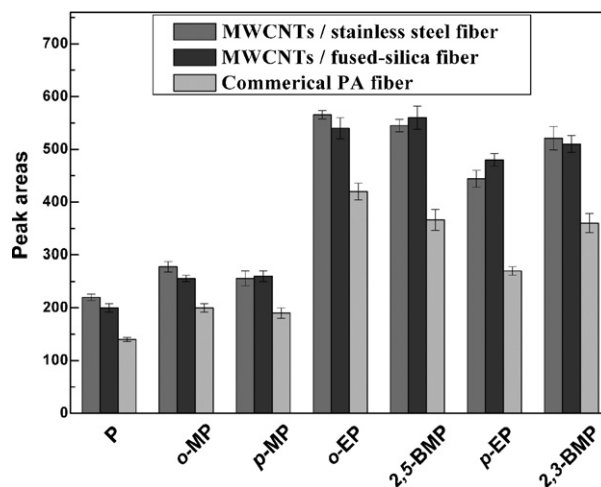


Fig. 3. Comparison of peak areas of the seven phenols (50  $\mu\text{g L}^{-1}$ ) extracted by the MWCNTs/Si/stainless steel wire fiber, MWCNTs/fused-silica fiber and commercial PA fiber.

shows that the extraction abilities of MWCNTs/Si/stainless steel wire fiber have no obvious deduction after the fiber was dipped into hydrochloric acid ( $1 \times 10^{-3}$  M) and sodium hydroxide ( $1 \times 10^{-2}$  M) solution for 24 h, respectively. The relative standard deviations (RSDs) of extraction peak areas determined at concentration of 50  $\mu\text{g L}^{-1}$  are less than 5%, which greatly expands the application range of the present fiber. On the other hand, the magnetron sputtering technique makes it feasible to select the high-strength stainless steel wire instead of the friable fused-silica wire as the substrate by introducing a Si interlayer. The high-strength stainless steel wire is easy to handle in the operation, and greatly prolongs the service life. All these aspects make the MWCNTs/Si/stainless steel wire fiber apparently robust, and exhibits many advantages over the previous and commercial SPME fibers, including high rigidity, long service life and high SPME effectiveness.

### 3.5. Application to real samples

The established SPME-GC method was used to determine the content of the seven phenols in Yellow River and sanitary wastewater samples. Fig. 5(a)–(c) illustrates the chromatograms of the phenols in standard solution (50  $\mu\text{g L}^{-1}$ ), Yellow River and wastewater samples under the previously established conditions,

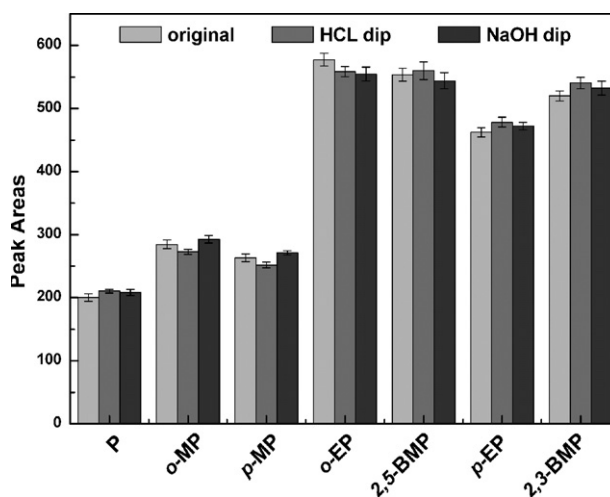


Fig. 4. Comparison of the chromatographic peak area of analytes before and after dipping the tip of the fiber into acid, basic solutions for 24 h.

**Table 2**  
Analytical results for the determination of seven phenols in water samples ( $n=3$ ).

Compounds	Recovery (RSD) %			
	Yellow River		Wastewater	
	No spiking	Spiked with $50 \mu\text{g L}^{-1}$	No spiking	Spiked with $50 \mu\text{g L}^{-1}$
P	Not detected	113.21 ( $\pm 3.22$ )	Not detected	141.70 ( $\pm 6.52$ )
<i>o</i> -MP	Not detected	76.35 ( $\pm 4.75$ )	Not detected	73.25 ( $\pm 3.63$ )
<i>p</i> -MP	Not detected	108.92 ( $\pm 2.49$ )	Not detected	119.71 ( $\pm 5.51$ )
<i>o</i> -EP	Detected but no quantified	123.56 ( $\pm 5.79$ )	$2.75 \mu\text{g L}^{-1}$	119.7 ( $\pm 6.62$ )
2,5-BMP	Detected but no quantified	97.66 ( $\pm 4.85$ )	$1.21 \mu\text{g L}^{-1}$	79.96 ( $\pm 7.47$ )
<i>p</i> -EP	Not detected	89.43 ( $\pm 1.22$ )	$1.94 \mu\text{g L}^{-1}$	97.03 ( $\pm 3.98$ )
2,3-BMP	Detected but no quantified	125.83 ( $\pm 3.18$ )	$3.48 \mu\text{g L}^{-1}$	127.33 ( $\pm 2.22$ )

respectively. Phenols were identified according to corresponding relative retention time calibrated with the standard samples. The analytes of *o*-EP and 2,5-BMP and 2,3-BMP were detected in the two samples, and their concentration can be respectively quantified to 2.75, 1.21,  $3.78 \mu\text{g L}^{-1}$  in the wastewater, while they could

not be quantified in the Yellow River sample. At the same time, *o*-EP can be detected and quantified in wastewater to  $1.94 \mu\text{g L}^{-1}$ , but it could not be detected in Yellow River. In order to demonstrate the applicability and reliability, the recoveries of the target compounds were determined in the two real water samples spiked at a concentration level of  $50 \mu\text{g L}^{-1}$ . The recoveries were 73.25–141.70% for all the analytes in the two water samples, and the recovery in the waste water sample exhibited larger deviations compared with that in Yellow River sample as shown in Table 2. This can be ascribed to the fact that sanitary waste water contained a large number of other pollutants such as cleanser, additive, pesticide and so on, which makes extraction of phenols more complicated.

#### 4. Conclusions

In this study, magnetron sputtering was adopted in fabricating SPME fiber for the first time. By forming a Si interlayer through magnetron sputtering, a MWCNTs coating was successfully chemically bonded on the stainless steel wire. The as-prepared MWCNTs/Si/stainless steel wire fiber not only preserved the excellent SPME behavior of MWCNTs/fused-silica fiber, but also overcome its shortcomings of fragileness and hard to handle. As a result, it exhibits many advantages over commercial SPME fibers, including high rigidity, long service life, good stability at high temperature and in acid and alkali solutions, and high SPME effectiveness. This new surface modification technique might provide a versatile approach to prepare sorbent coatings on unconfined substrates using traditional methods, and represent a key addition to the preparation the family of SPME fibers.

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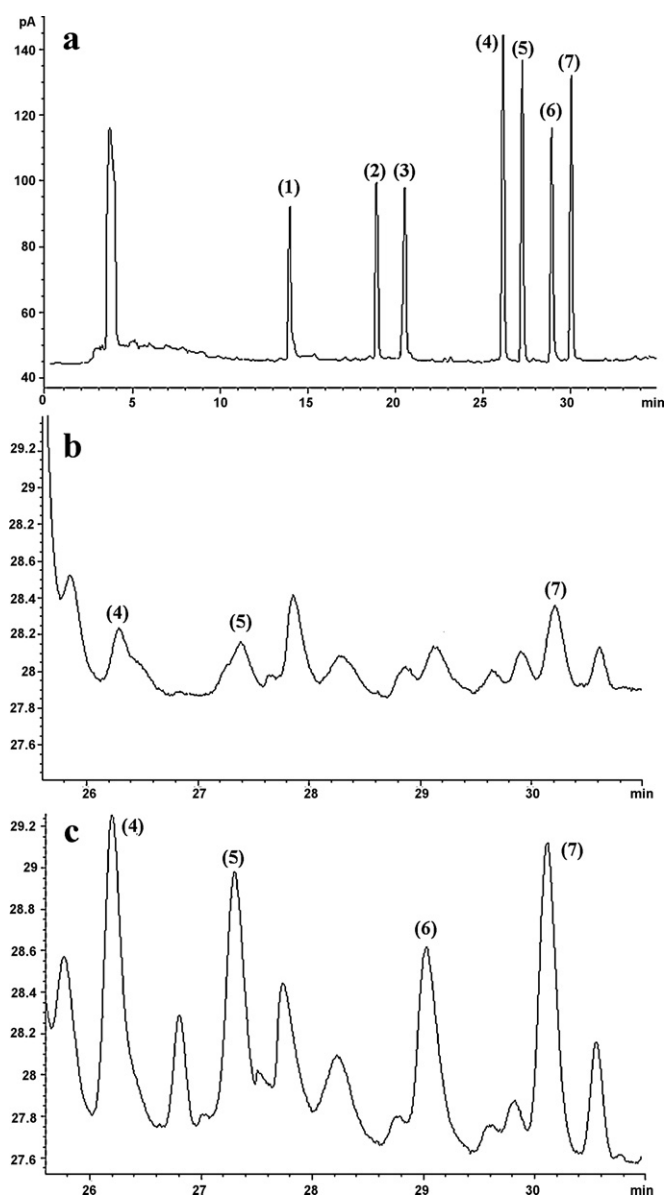
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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.chroma.2011.03.047](https://doi.org/10.1016/j.chroma.2011.03.047).

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**Fig. 5.** Typical chromatogram of phenols in different water samples using MWCNTs/Si/stainless steel wire fiber: (a) standard solution ( $50 \mu\text{g L}^{-1}$ ), (b) Yellow River water, and (c) wastewater samples. Peaks: (1) P, (2) *o*-MP, (3) *p*-MP, (4) *o*-EP, (5) 2,5-BMP, (6) *p*-EP, and (7) 2,3-BMP.

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