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CNT–TiO_2 coating bonded onto stainless steel wire as a novel solid-phase microextraction fiber

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ABSTRACT

A novel solid-phase microextraction (SPME) fiber based on carbon nanotubes–titanium oxide (CNT–TiO_2) composite coating bonded onto stainless steel wire was prepared via electroless plating and sol–gel techniques. The SPME coating was characterized by scanning electron microscopy and Raman microscopy. Coupled to gas chromatography (GC), the fiber was investigated with seven polycyclic aromatic hydrocarbons (PAHs) in direct-immersion mode. The SPME-GC analytical method was evaluated under optimized extraction conditions. Compared with other reports, higher sensitivity (LODs, 0.002–0.004 $\mu g\ L^{-1}$) and better linear range (0.01–100 and 0.01–200 $\mu g\ L^{-1}$) were obtained by the proposed method. The fiber exhibited high thermal stability to 300 °C and excellent durability in HCl and NaOH solutions. The as-established SPME-GC method was used to analyze the real water samples and satisfactory results were obtained.

1. Introduction

Solid-phase microextraction (SPME), introduced two decades ago by Belardi and Pawliszyn [1], is a combination of sampling, concentration, matrix removal and sample introduction steps [2,3]. Due to its simple, fast, solventless, inexpensive, easily automated and reliable profile, SPME has become a very important sampling technique and has gained a widespread acceptance in many areas such as environmental, food, pharmaceutical, clinical and forensic analyses [4,5]. The core part of the SPME technique is the SPME fiber. Commercially available SPME fibers are fused silica fibers coated with organic polymers, ranging from polydimethylsiloxane (PDMS) for nonpolar analytes to polyacrylate (PA) for polar analytes. Fused silica support is fragile and must be carefully handled, so the life is limited [6]. Recently, metallic supporting substrates have attracted more and more attentions in the preparation of novel SPME fibers. Some new methods including chemical corrosion [7,8], electrodeposition [9], anodization [10], hydrothermal method [11], electrospinning [12] and magnetron sputtering [13] have been used to prepare metal-based SPME fibers. However, the obtained coatings were limited and the lack of chemical bonding between coating and metal support often resulted to low stability. Metallic supporting substrates are chemically inert and are difficult to adapt to many traditional preparation techniques; e.g., sol–gel technique [14,15] and chemical bonding method [16]. So, it is very important to develop a versatile approach to improve the chemical activity of metal wires.

Silver wire was applied to prepare a SPME fiber [17]. It was self-assembled by a monolayer of 3-mercaptopropyltrimethoxysilane, and processed through vinyl functionalization and *in situ* polymerization. A molecularly imprinted coating was bonded with silver wire. Compared with silver wire, the stainless steel wire is less expensive and possesses a higher hardness, and it is more economical to be used as the support of SPME fibers. The electroless plating is one of the most frequently adopted industrial processes for metallization to pattern 2D and 3D structures [18,19]. Uniform metallic thin films can be fabricated on either conductive or nonconductive substrates [20–22]. Feng et al. prepared a silver-coated SPME fiber with stainless steel wire as support via electroless plating [23]. The fiber with porous and micrometer silver coating exhibited excellent stability and extraction performance. The silver coating was also easily modified by 3-mercaptopropyltrimethoxysilane, and then functionalized to obtain novel SPME fiber [24,25]. So, electroless silver plating is a potential solution to activate stainless steel wire.

The extraction performance of SPME fiber mostly depends on the property of the coating. Carbon nanomaterials (fullerenes, carbon nanotubes and graphene) which possess excellent physical

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and chemical properties have attracted great attention in the field of separation science [26–29]. Carbon nanotubes (CNTs) exhibit excellent adsorbent and thermal properties due to their particular tubular structure. For example, the highly hydrophobic surface of CNTs showed strong sorption property toward various compounds such as phenols [26,27], phthalate esters [30], chlorobenzenes [31] and dioxin [32]. CNTs coated SPME fiber exhibited high extraction efficiencies for both polar (phenols) and non-polar (benzene, toluene, ethylbenzene and o-xylene) compounds, good thermal stability to resist 350 °C and excellent solvent durability in methanol and acetonitrile [5]. CNTs were excellent SPME coating materials for their strong physical adsorption ability to various analytes [5,16,33].

Sol–gel technique is a popular chemical method that offers a simple route for synthesizing new material systems and surface coating. It can efficiently incorporate inorganic materials into organic compounds structure under mild conditions [34]. The application of sol–gel technique in SPME fiber preparation has some advantages, e.g., high stability due to chemical binding between coating and support, creating hybrid organic–inorganic coating, and possibility to control the coating thickness [35]. Because the strong chemical binding is easily formed between sol–gel coating and silanol groups on substrate, sol–gel method is usually used to prepare SPME fibers with fused silica fiber as support. However, fused silica support is fragile and silica-based coating is not resistant to basic solution, limiting its applications greatly. It is well known that titanium oxide is more resistant to basic condition than silica.

In this work, a novel SPME fiber based on carbon nanotubes–titanium oxide (CNT–TiO_2) composite coating was prepared by electroless plating and sol–gel techniques on stainless steel wire. The stainless steel wire was activated with silver layer via electroless plating, and then was functionalized by self-assembled 3-mercaptopropyltrimethoxysilane monolayer to derive silanol groups. The CNT–TiO_2 composite coating was bonded with reactive stainless steel wire through sol–gel method. Seven polycyclic aromatic hydrocarbons (PAHs) were used as model analytes to investigate the extraction performance of the fiber, coupled with gas chromatography. The fiber exhibited strong mechanical strength, excellent extraction efficiency and stability. The proposed SPME-GC method was used to analyze real water samples.

2. Experimental

2.1. Materials and reagents

The stainless steel wire (Φ 180 μm) was purchased from the Yixing Shenglong Metal wire Net. Co. (Jiangsu, China). Fluorine (Flu), anthracene (Ant), *o*-terphenyl (*o*-TP), fluoranthene (FlA), *p*-terphenyl (*p*-TP), chrysene (Chr) and benzo(a)pyrene (BaP) were of analytical grade quality and purchased from Shanghai Jingchun Industry Co. (Shanghai, China). $AgNO_3$, glucose, titanium butoxide and KCl were of analytical grade quality and obtained from Sinopharm Chemical Reagent Co. (Shanghai, China). Short hydroxy purified multi-walled carbon nanotubes (MWCNTs–OH) (length, 0.5–2 μm; outside diameter, 0.8 nm; OH content, 5.58 wt%; purity, 95 wt%) were obtained from Chengdu Organic Chemicals Co., Chinese Academy of Sciences (Chengdu, China). 3-Mercaptopropyltrimethoxysilane (98%) was obtained from Qufu Chenguang Fine Chemical Co. (Qufu, China) and purified by vacuum distillation before use. Toluene was dried by refluxing with sodium for 24 h, and then distilled before use. All the other chemicals were of analytical grade quality. Real water samples were collected locally in rainwater and Yellow River.

2.2. Apparatus

Analysis of the model compounds was performed with an Agilent 7890A GC system (Agilent Technologies, USA) equipped with a flame ionization detector (FID) and a split/splitless inlet. HP-5 capillary GC column (30 m × 0.32 mm id. × 0.25 μm film thickness) was used for separation.

Ultrapure nitrogen ($>$99.999%) was used as the carrier and make-up gas at 3 mL min^{-1} and 25 mL min^{-1}, respectively. The inlet was used in splitless mode at 300 °C. The detector temperature was fixed at 300 °C. For the chromatographic separation, the column temperature was programmed as follows: initial temperature was held at 100 °C and programmed at 15 °C min^{-1} to 300 °C.

Surface properties of the SPME fiber were characterized by a scanning electron microscope (Hitachi S-4800, Hitachi High-Technologies Co., Japan). Raman spectra of the SPME coating were performed with a Raman microscope (633 nm laser excitation, Renishaw inVia Raman microscope, UK).

2.3. Preparation of the CNT–TiO_2 coated fiber

CNT–TiO_2 coated SPME fiber was prepared via electroless plating and sol–gel technique. As shown in Fig. 1, the preparation process contains four main steps. One end of stainless steel wire was immersed into the reaction solution containing 0.10 mol L^{-1} $[Ag(NH_3)_2]^+$ and 0.50 mol L^{-1} glucose at room temperature for 2 h. Silver activated wire was obtained. It was immersed into 20 mmol L^{-1} 3-mercaptopropyltrimethoxysilane in toluene for 24 h to form self-assembled molecule film. The self-assembled molecule film was derived to the silanol in 0.1 mol L^{-1} HCl for 2 h. The silanol functionalized wire was immersed into toluene solution of titanium butoxide (1:1, v/v) for 0.5 min, and then it was coated with MWCNTs–OH. After that, the processed wire was heated under nitrogen at 150 °C for 30 min. This step was repeated to increase layer number until satisfactory thickness was obtained. A black coating on the wire was obviously apparent.

2.4. Preparation of sample solutions

Stock solution of PAHs was prepared in ethanol at a concentration of 100 mg L^{-1} and stored at 4 °C for use. Working solutions were prepared daily by diluting the stock solution with distilled water to 100 μg L^{-1}. Water from Yellow River and rainwater was used as real samples. KCl was added into working solutions and real samples to increase ionic strength.

2.5. Solid-phase microextraction

The prepared fiber was equipped into a homemade SPME device which was a modification of a 5 μL syringe. Before the extraction, the fiber was aged in the GC inlet at 300 °C for 20 min. All the extractions were performed in direct-immersion mode with 10 mL aqueous solution in a 15 mL vial. A magnetic bar at 800 rpm rate was inside the vial to accelerate the extraction. After the extraction, the fiber was withdrawn into the needle and thermally desorbed for 5 min in GC inlet at 300 °C. Possible carryover effect was minimized by keeping the fiber in the inlet for an additional time. The times of repetition of each data point were three.

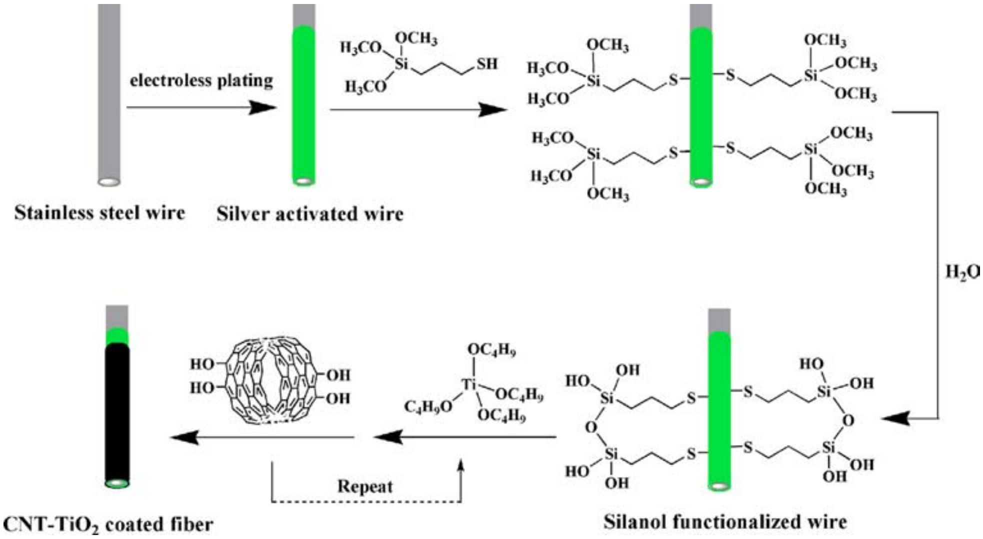

Fig. 1. Preparation process of the CNT–TiO_2 coated SPME fiber.

3. Results and discussion

3.1. Preparation of the CNT–TiO_2 coated fiber

Stainless steel wire possesses high hardness and thermal resistance, both of which can improve the lifespan of SPME fiber. However, stainless steel wire is chemically inert. So electroless plating was used to activate it with silver layer. Then 3-mercaptopropyltrimethoxysilane molecule was self-assembled to silver and the silanol was produced through hydrolysis. Sol–gel technique was applied to prepare CNT–TiO_2 coating. Titanium butoxide not only bonded with Si–OH of the support but also bonded with C–OH of MWCNTs–OH in heating process. The thickness of coating can be regulated by layer number in sol–gel process.

3.2. Characterization of the CNT–TiO_2 coated fiber

Surface structure of the SPME fiber was investigated by SEM. As shown in Fig. 2, the micro-structured coating is rough, porous and uniformity. Thickness of the coating is about 10 μm.

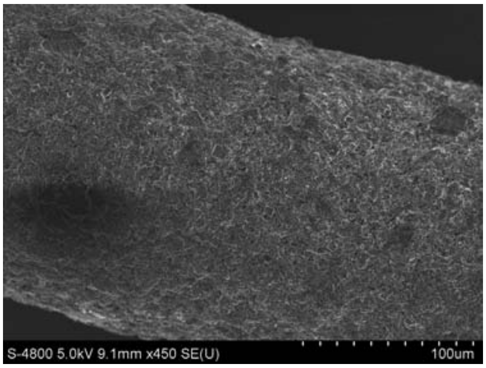

Fig. 2. SEM image of the CNT–TiO_2 coated SPME fiber.

The SPME coating and stainless steel wire were characterized by Raman spectroscopy. Raman spectroscopy yields information about the purity, defects and tube alignment, and assists in the distinction of the presence of MWCNTs relative to other carbon allotropes [36,37]. As shown in Fig. 3, no obvious Raman shifts are seen in Raman spectrum of stainless steel wire. In the spectrum of the SPME coating, a group of peaks around 1330 cm^{-1} (D-band), 1580 cm^{-1} (G-band), 2630 cm^{-1} (G′-band) and 261 cm^{-1} (RBM-band) are assigned to the presence of MWCNTs. In addition, another group of Raman shifts around 153 cm^{-1}, 415 cm^{-1} and 605 cm^{-1} are attributed to the presence of TiO_2.

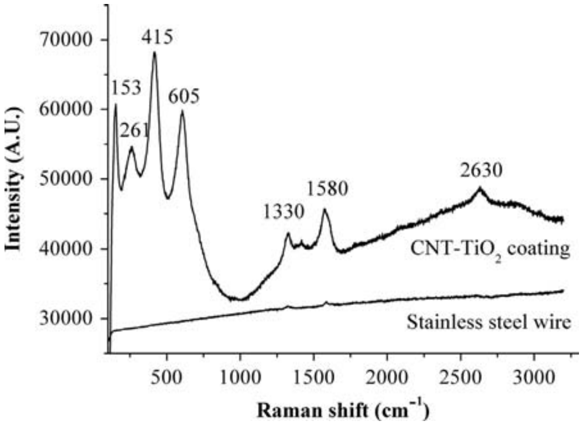

Fig. 3. Raman spectra of the CNT–TiO_2 coating and the stainless steel wire.

Extraction efficiency is mainly determined by coating thickness and extraction equilibrium. Thick coating has high extraction capacity, but more time is needed to reach extraction equilibrium. So, coating thickness has dual effect on extraction efficiency. The thickness of CNT–TiO_2 coating depended on the layer number in sol–gel process. As shown in Fig. 4, the effect of layer number from one to four on extraction efficiency is investigated. For Chr and BaP, highest extraction efficiency is obtained at one layer. For other five PAHs, highest extraction efficiency is obtained at two layers. Large molecules (Chr and BaP), which have slow mass transfer rate, were of higher extraction efficiency on thin coating. In consideration of most analytes, the layer number of CNT–TiO_2 coating was determined as two in the preparation of SPME fiber.

3.3. Optimization of SPME conditions

The extraction efficiency of SPME fiber is significantly influenced by extraction conditions. In order to get highest extraction efficiency, extraction conditions including extraction time,

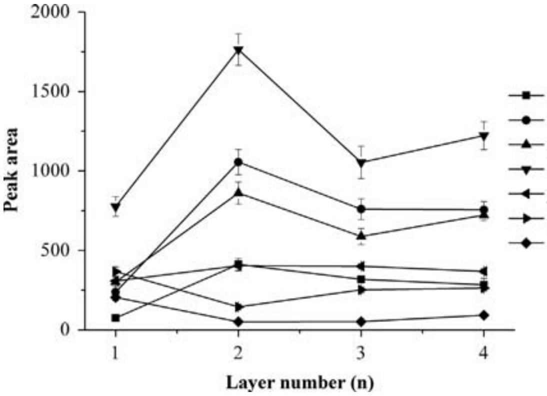

Fig. 4. The effect of the layer number of CNT–TiO_2 coating on extraction efficiency. Conditions: extraction temperature, 50 °C; extraction time, 40 min; content of KCl, 30% (w/v); analytes concentration, 100 μg L^{-1}; the times of repetition of each data point were three.

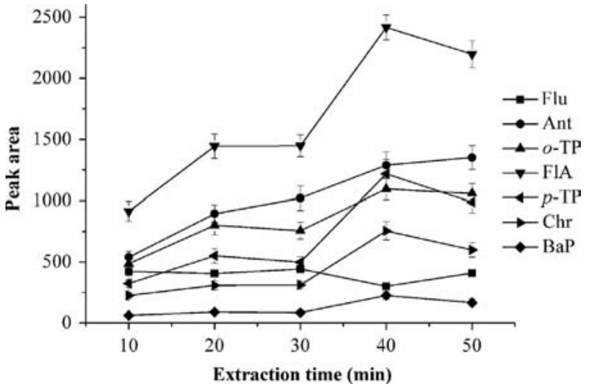

Fig. 5. The effect of extraction time on extraction efficiency. Other conditions are the same as in Fig. 4.

extraction temperature and ionic strength of sample solutions were optimized by a factor-by-factor optimization.

3.3.1. *Extraction time*

SPME is an equilibrium-based technique, and the equilibrium time should be the best extraction time. The effect of extraction time on extraction efficiency was investigated from 10 to 50 min. As shown in Fig. 5, the highest extraction efficiency was obtained at 40 min for analytes except for Flu. Considering most analytes, the optimal extraction time was selected as 40 min.

3.3.2. *Extraction temperature*

Temperature has a twofold impact on the extraction. In general, increasing the extraction temperature can enhance the mass transfer, but partition coefficients of analytes between the fiber coating and the sample solution decrease. Extraction efficiency of seven PAHs was tested in the range of 30–60 °C. As can be seen from Fig. 6, with the increase of extraction temperature, extraction efficiency of *p*-TP, Chr and BaP was increased, but extraction efficiency of Flu was decreased. It seems that the increase of the mass transfer is dominant than reduce of partition coefficients of *p*-TP, Chr and BaP from 30 to 60 °C. For Ant, *o*-TP and FlA, extraction efficiency is highest at 50 °C. According to the results in Fig. 6, 50 °C was chosen as the extraction temperature for the experiment.

3.3.3. *Ionic strength*

Addition of salt into sample solution can reduce the solubility of analytes in water due to the formation of hydration spheres around the ionic salt molecules [38]. The effect of ionic strength on extraction efficiency was investigated from 0 to 30% (w/v) KCl in working solution. And 30% (w/v) KCl of solution is near to saturated solution. As shown in Fig. 7, extraction efficiencies of all analytes are increased with the increase of content of KCl. So, content of KCl in working solution and samples was fixed at 30% (w/v) in all extraction processes.

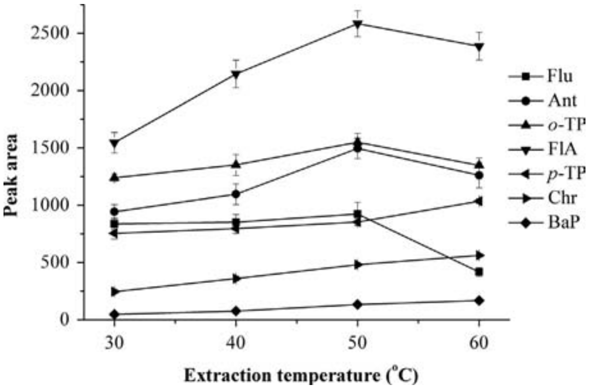

Fig. 6. The effect of extraction temperature on extraction efficiency. Other conditions are the same as in Fig. 4.

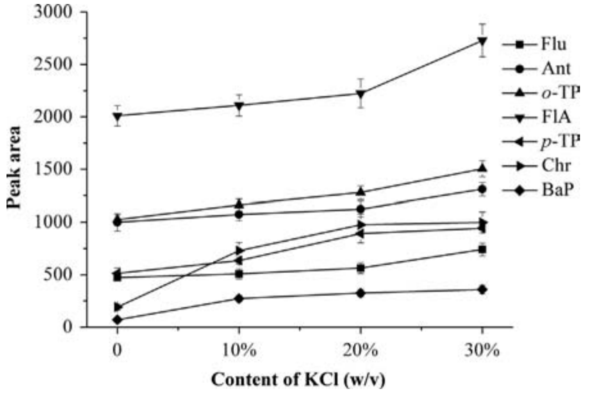

Fig. 7. The effect of ionic strength on extraction efficiency. Other conditions are the same as in Fig. 4.

3.4. *Method evaluation*

The proposed SPME-GC analytical method including linear range, correlation coefficient of calibration, limits of detection, single fiber and fiber-to-fiber repeatability was investigated at optimal conditions by extracting a series of standard working solutions. All the results are listed in Table 1. For the seven PAHs, good linearity was obtained ranged 0.01–100 μg L^{-1} or 0.01–200 μg L^{-1}, with correlation coefficient (R) from 0.993 to 0.999. LODs were calculated as three time of the signal to noise ratio ($S/N=3$), and were investigated by extraction of distilled water samples spiked at different levels to meet such signal. LODs were 0.002–0.004 μg L^{-1} for seven PAHs. The precision of the method was tested by performing five consecutive extractions, and the RSDs ($n=5$) were at the range of 6.61–17.9%. Fiber-to-fiber repeatability was also tested with five different fibers. The RSDs ($n=5$) ranged from 14.9 to 23.7%. So the proposed CNT–TiO_2 coated fiber not only has high extraction efficiency but also has good repeatability. The performance of the proposed analytical method was also compared with other reports with the same

Table 1
Analytical performances of the CNT–TiO_2 coated fiber and some other fibers for PAHs.

Analytes	Linear range (μg L^{-1})	[a] Correlation coefficient (R)	LODs (μg L^{-1})	[b] Repeatability ($n=5$, RSD%) (single fiber)	[b] Repeatability ($n=5$, RSD%) (fiber-to-fiber)	Etched stainless steel fiber [7]		NHAP/SPME fiber [39]		Commercial PDMS fiber [40]	
						Linear range (μg L^{-1})	LODs (μg L^{-1})	Linear range (μg L^{-1})	LODs (μg L^{-1})	Linear range (μg L^{-1})	LODs (μg L^{-1})
Flu	0.01–200	0.998	0.004	9.77	22.4	2.5–50	0.30	0.5–200	0.04	0.5–100	0.08
Ant	0.01–200	0.999	0.003	6.92	19.3	–	–	0.2–200	0.04	0.5–100	0.18
o-TP	0.01–100	0.993	0.003	9.30	21.9	–	–	–	–	–	–
FlA	0.01–200	0.994	0.003	6.61	23.7	2.5–50	0.58	0.2–200	0.04	0.5–100	0.25
p-TP	0.01–200	0.999	0.003	14.2	19.2	–	–	–	–	–	–
Chr	0.01–200	0.997	0.002	12.7	14.9	–	–	0.1–200	0.02	0.5–100	0.24
BaP	0.01–100	0.998	0.002	17.9	20.5	–	–	0.1–200	0.02	0.5–100	0.44

[a] Calibration level: $n=9$.
[b] Spiked level: 100 μg L^{-1}.

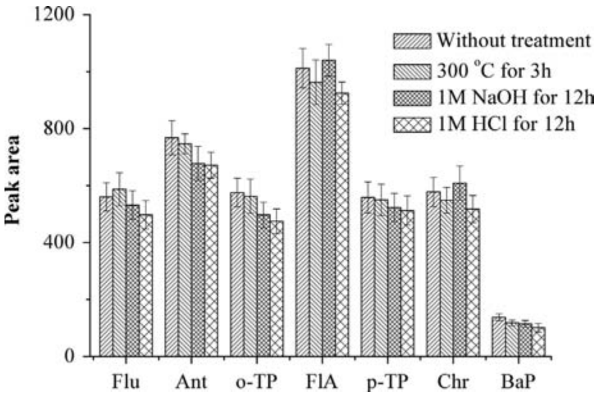

Fig. 8. The stability of the CNT–TiO_2 coated SPME fiber. Conditions: analytes concentration, 20 μg L^{-1}; other conditions are the same as in Fig. 4.

Table 2
Detected results and recoveries for PAHs in two real samples.

Analytes	Concentration (μg L^{-1}) in rainwater	[c] Recovery for standard addition ($n=3$, RSD%)	Concentration (μg L^{-1}) in yellow river water	[c] Recovery for standard addition ($n=3$, RSD%)
Flu	[a]N. D.	93.5 ± 4.9	[b]N. Q.	91.1 ± 6.5
Ant	0.84	115 ± 8.1	[b]N. Q.	105 ± 9.8
o-TP	[a]N. D.	121 ± 5.3	[a]N. D.	114 ± 7.1
FlA	[a]N. D.	98.9 ± 11.5	[a]N. D.	120 ± 7.5
p-TP	[b]N. Q.	117 ± 8.2	[a]N. D.	98.6 ± 10.2
Chr	[a]N. D.	92.8 ± 6.7	[a]N. D.	104 ± 7.1
BaP	[a]N. D.	93.5 ± 4.9	[a]N. D.	102 ± 4.3

[a] Not detected.
[b] Detected but not quantified.
[c] Spiked level: 10 μg L^{-1}.

analytes. We can see from Table 1 that, LODs of the proposed method are much lower than that of the other methods. The linear range is comparable or better. These indicate the high extraction efficiency of the proposed SPME fiber.

3.5. Stability of the CNT–TiO_2 coated fiber

Stability is crucial for practical application of the SPME fiber. Damage of the coating was mainly caused by its exposure to high temperature, acidic or basic solution, and strong mechanical stirring during extraction processes. In order to investigate the stability, a CNT–TiO_2 coated fiber was heated at 300 °C for 3 h, immersed in 1 mol L^{-1} NaOH for 12 h and immersed in 1 mol L^{-1} HCl for 12 h in turn. As shown in Fig. 8, the extraction capacity of the fiber is reduced slightly. The resistance of the fiber to basic condition was further examined. The loss of extraction efficiency was less than 10% after immersing the fiber in 0.1 mol L^{-1} NaOH solution for 120 h. It is clear that the CNT–TiO_2 coated fiber is very stable. Exactly, hundreds of extraction processes used to investigate the performances of the fiber were accomplished with a single fiber. The fiber can withstand so many times extraction tests without large lose of extraction efficiency, which further indicates the excellent stability.

3.6. Application to real samples

Two real samples including rainwater and Yellow River water were analyzed with the proposed SPME-GC method. The results are shown in Table 2. Ant was quantified at 0.84 μg L^{-1} in rainwater. *p*-TP in rainwater was detected but not quantified. Flu and Ant were also detected but not quantified in Yellow River water. Relative recoveries with standard addition level at 10 μg L^{-1} were ranged from 92.8 to 121% and 91.1 to 120% in two real samples, respectively. According to the analysis results of two real samples, it is obvious that the as-established SPME-GC method is an effective analytical method.

4. Conclusions

A stainless steel wire was applied to prepare an unbreakable SPME fiber. The electroless plating was used to activate stainless steel wire with silver layer. The silver layer was functionalized by self-assembled 3-mercaptopropyltrimethoxysilane monolayer and then derived to silanol groups by hydrolysis. MWCNTs–OH and titanium oxide were bonded with silanol groups on stainless steel wire via sol–gel technique. Coupled to GC, the prepared fiber was investigated using seven PAHs. The results indicated that the fiber had good mechanical strength, high extraction efficiency, excellent thermal and chemical stability. SPME-GC analytical method provided higher sensitivity (LODs, 0.002–0.004 μg L^{-1}) and better linear range (0.01–100 and 0.01–200 μg L^{-1}) than other reports. The as-established SPME-GC method was used to analyze the real water samples and several kinds of analytes were detected or quantified. Relative recoveries were also in acceptable ranges. The novel fiber can be efficiently applied in SPME analysis. The further work will research on other novel coating bonded stainless steel wire as SPME fibers, which will be prepared via electroless plating and chemical bonding method.

Acknowledgments

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