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Electrochemical preparation of polyaniline–polypyrrole solid-phase microextraction coating and its application in the GC determination of several esters

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ABSTRACT

A novel polyaniline–polypyrrole (PANI–PPY) composite film coated stainless steel wire was prepared by cyclic voltammetry. Firstly, PANI was electrodeposited on a stainless steel wire from a solution containing 0.1 M aniline and 1 M HNO_3, after the PANI coating was dried in air PPY was electrodeposited on it from a solution containing 0.1 M pyrrole and 0.1 M *p*-methylbenzene sulfonic acid. The resulting PANI–PPY fiber showed reticulate structure and had large specific surface area. When it was used for the headspace solid-phase microextraction of several esters (i.e. methyl anthranilate, ethyl-o-aminobenzoate, dimethyl phthalate, methyl laurate, and diethyl phthalate), followed by gas chromatographic determination, it presented higher extraction capability in comparison with PPY and PANI coatings. Under the optimized conditions, the linear ranges were 0.07 – 300 μg L^{-1} and the detection limits were 0.05 – 0.38 μg L^{-1} for different esters. The PANI–PPY fiber also showed high durability, after being used for about 160 times its extraction capacity only changed a little. The proposed method was successfully applied to the determination of these esters in real samples and the recoveries were 90–102%.

1. Introduction

Esters are widely used in industrial production and our daily life. They are generally used as solvent, plasticizer or additive in cosmetic, soap, medicine, etc. However, some esters can cause undesirable consequence through interfering endocrine of humans and animals; hence their applications must be controlled [1,2]. The detection of esters is generally performed by using chromatographic methods. Prior to determination esters are accumulated and separated from the samples by various methods such as steam distillation, solvent extraction, etc. [3,4]. Among them solid-phase microextraction (SPME) has attracted increasing attention of researchers in last decade because it has many distinct advantages. SPME is generally performed by using a fiber, thus the property of the fiber is critical. So far many SPME fibers have been reported, including polydimethylsiloxane (PDMS) and polyamide (PA) coated fused-silica fiber. However, these fibers still present some disadvantages such as poor thermal stability, high cost, low extraction capacity and/or short lifetime [5,6]. Therefore, to develop new extraction fibers with high property is still important.

SPME fibers can be prepared through different methods, such as manual coating, the sol–gel method, the electrochemical method, etc. [7–11]. As electrochemical method is simple, rapid and easy to operate it becomes popular now. The electrochemical fabrication of SPME fibers is mainly related to PANI and PPY because they are conductive and easily electrodeposited. In addition, PANI coating is porous and has high extraction capacity. It is suitable for the extraction of a number of polar compounds. However, PANI coating shows poor mechanical strength and is not suitable for the extraction of many nonpolar compounds. PPY is solid and durable and suitable for the extraction of nonpolar compounds, but it has small specific surface and small extraction capacity. In addition, it is not so easy for PPY to electrodeposit on a stainless steel wire. To improve the performance of PANI and PPY, some functional materials are introduced and composite coatings are prepared [12–17]. However, up to now there are no reports on the application of electrochemical polymerization in constructing PANI–PPY composite coating.

In this work, a novel PANI–PPY coating is prepared on a stainless steel wire by cyclic voltammetry. The coating combines the advantages of PANI and PPY, so it shows large extraction capacity, high durability and preparation controllability. The extraction property of the obtained SPME fiber is evaluated by taking several esters as model molecules, and it shows good performance.

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2. Experimental

2.1. Reagents

Methyl anthranilate (MA), dimethyl phthalate (DMP), ethyl-o-aminobenzoate (EOA), methyl Laurate (ML), diethyl phthalate (DEP) were purchased from the Aladdin Chemistry Co. (Shanghai, China). The stock solutions of MA (0.5 mg mL^{-1}), EOA (0.5 mg mL^{-1}), DMP (0.5 mg mL^{-1}), DEP (0.5 mg mL^{-1}) and ML (0.125 mg mL^{-1}) were prepared with methanol and stored in a refrigerator. The working solutions were prepared by diluting the stock solution with saturated NaCl aqueous solution. Aniline (ANI) and pyrrole (PY) came from the Reagent Factory of Shanghai (China). Before use they were purified through vacuum distillation. The samples were obtained from the local cosmetic store and supermarket (Wuhan, China).

2.2. Apparatus

The GC experiments were performed on a Model GC-2010 gas chromatography instrument with a flame ionization detection (FID) system (Shimadzu Corporation, Japan). A GC solution chromatographic workstation program (Shimadzu Corporation, Japan) was used to process chromatographic data. The separation of esters was carried out on an Rtx-1 capillary column (30 m × 0.25 mm I.D.) with 0.25 μm film thickness (RESTEK, USA). The following oven temperature program was used: 50 °C held for 3 min, followed by increasing temperature at 20 °C min^{-1} to 90 °C, and 1.5 °C min^{-1} to 130 °C and kept at this temperature for 5 min. The total runtime was about 35 min. The injection port temperature was set at 250 °C and the extracted analytes were desorbed for 3 min. Its inlet was operated under the splitless mode and the flow rate of carrier gas (i.e. nitrogen gas) was 2.4 mL min^{-1} The FID temperature was set at 250 °C. The SPME device was laboratory-made. Electrochemical polymerization of aniline and pyrrole was performed on a CHI 617A electrochemical workstation (CH Instrument Corp., Shanghai, China) by using cyclic voltammetry. A conventional three-electrode system was adopted, including a stainless steel wire (2 cm × 250 mm O.D.) as working electrode, a Pt wire counter electrode (2.5 cm × 0.1 cm O.D.) and a saturated calomel electrode (SCE) as reference electrode. The scanning electron microscopy images (SEM) were obtained by using a Quanta-200 SEM instrument (FEI, The Netherlands).

2.3. Preparation of PANI–PPY coating

Prior to electrochemical polymerization, the stainless steel wire was pretreated with 1 M nitric acid, 1 M sodium hydroxide and distilled water each for 10 min. Then the electrode system was immersed in 1 M HNO_3+0.10 M aniline solution. The potential was cycled between −0.2 V and 1.5 V for 60 times at 50 mV s^{-1}. After the obtained PANI coating was washed with water and dried in air the electrode system was transferred in 0.1 M pyrrole+0.1 M *p*-methylbenzene sulfonic acid solution, and the potential was cycled between −0.4 V and 1.0 V at 30 mV s^{-1} for 15 times. The resulting fiber was rinsed with methanol and distilled water, and then let the solvent to evaporate in air. Following this, it was conditioned in an electric furnace with nitrogen atmosphere at 100 °C for 30 min, and at 250 °C for 90 min. When the fiber was cool it was fixed on a home-made device for SPME with epoxy resin. The SPME device was assembled in a manner similar to those reported by other researchers [18,19]. The coating thickness was measured with a microscope and it was about 87 μm. For comparison, PANI fiber and PPY fiber were also prepared by the similar method.

2.4. Headspace SPME procedure

An 8 mL saturated NaCl solution and 5 μL stock solution were transferred into a 15 mL glass vial with PTFE–silicon septum. After adding a magnetic stirring bar the vial was tightly sealed with an aluminum cap. The vial was then placed on a magnetism mixer with a water bath and the stirring rate was fixed at 500 rpm. When the temperature reached the fixed value (20–50 °C) the syringe needle was pushed through the vial septum and the SPME fiber was exposed to the headspace over the stirred solution for 10–50 min. Then the fiber was withdrawn into the needle, removed from the vial and immediately introduced into the GC injection port for thermal desorption of 3 min.

3. Results and discussion

3.1. Electrochemical polymerization of aniline and pyrrole at stainless steel wires

Fig. 1 shows the cyclic voltammograms corresponding to the polymerization of aniline and pyrrole at stainless steel wires. As can be seen, for ANI the peak height increases with repeating potential scan, while for PY the peak height decreases. This can be ascribed to the electrochemical activity of PANI and the electro-inactivity of PPY. At the same time, the thickness of polymer films on the steel wires increases. When PPY is electrodeposited on the surface of PANI, the peak height of PANI decreases due to the formation of electroinactive PPY, which hinders the electron/proton transfer. This indicates that PPY is electrodeposited on PANI and a PANI–PPY composite coating is obtained.

3.2. Surface structure of PANI–PPY

Fig. 2 shows the SEM images of PANI, PPY and PANI–PPY coatings. As can be seen, PANI presents netlike structure with large specific surface, while PPY shows cauliflower shape with small surface area. When PPY is electrodeposited on the PANI, the PANI fibers become rough and flossy PPY is observed. Therefore, the PANI–PPY coating not only has large surface area, but also permits rapid mass transfer. The thickness of the PANI–PPY film can be easily controlled by varying the electropolymerization time of aniline. But the electrodeposition time for PPY should not be too long or too short in case the PPY film is so thick to block the pores of PANI or too thin to well cover the PANI surface. In this case, the optimal electrodeposition procedure for PPY is to repeat the potential-scan for 15 cycles at 30 mV s^{-1}.

3.3. Thermal stability

A blank PANI–PPY fiber is introduced into the GC injector port to study its thermal stability. As a result, when the temperature is changed from 250 °C to 280 °C, the obtained chromatograms are a line (see Fig. S1). This indicates that the PANI–PPY coating is stable up to 280 °C. When the temperature is increased to 300 °C, some chromatographic peaks occur due to the thermal decomposition of PANI–PPY film.

3.4. Optimization of extraction conditions

3.4.1. Extraction temperature

For HS-SPME extraction temperature not only affects extraction rate, but also affects adsorption capacity. In this case, the influence of extraction temperature is studied in the range of 20–60 °C (Fig. 3). The peak area increases with temperature rising up to 50 °C and then decreases for MA, EOA, DMP and DEP. As for ML,

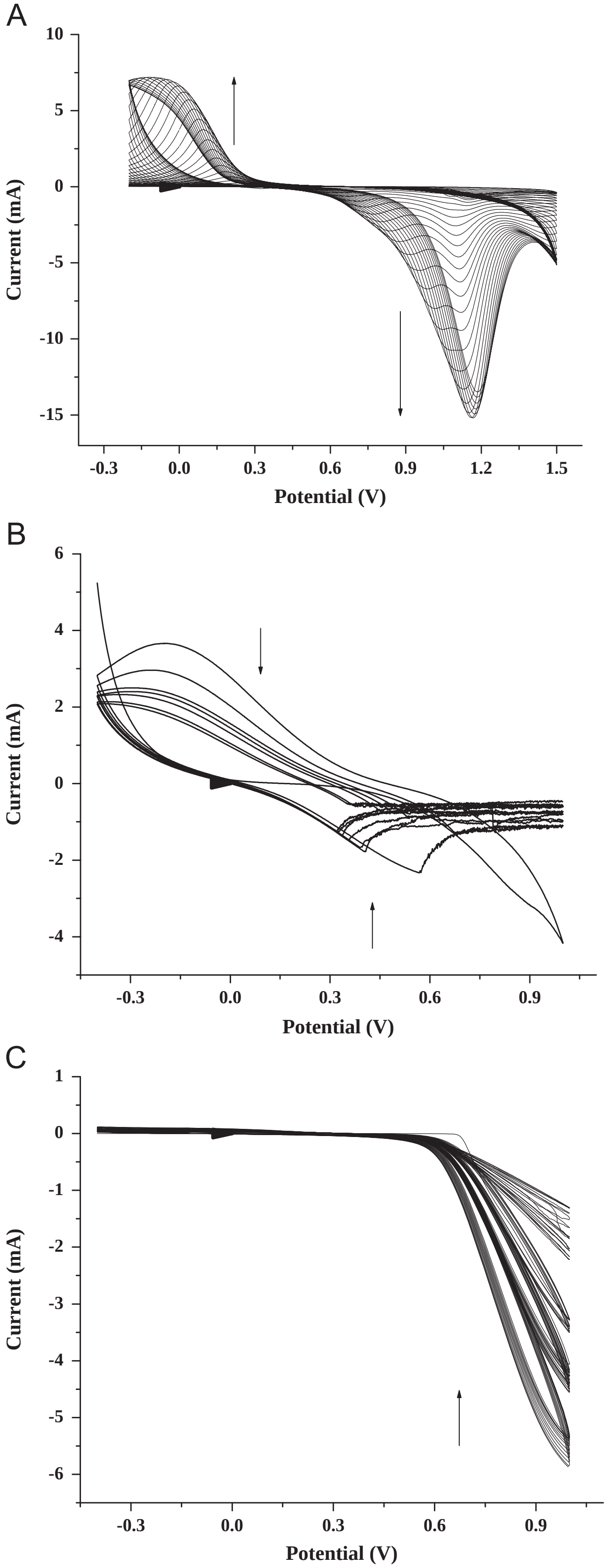

Fig. 1. Cyclic voltammograms corresponding to the polymerization of aniline (A) and pyrrole (C) on stainless steel wires and the polymerization of pyrrole on PANI (B). Solution composition: (A) 0.1 M ANI + 1 M HNO_3, (B) 0.1 M PY + 0.1 M PTSA; and (C) 0.1 M PY + 0.1 M PTSA; scan rate: (A) 50 mV s^{-1}, (B) 30 mV s^{-1}, and (C) 30 mV s^{-1}.

the extraction efficiency reaches a maximum at lower temperature, which is related to its higher volatility. Thus 50 °C is adopted in subsequent experiments.

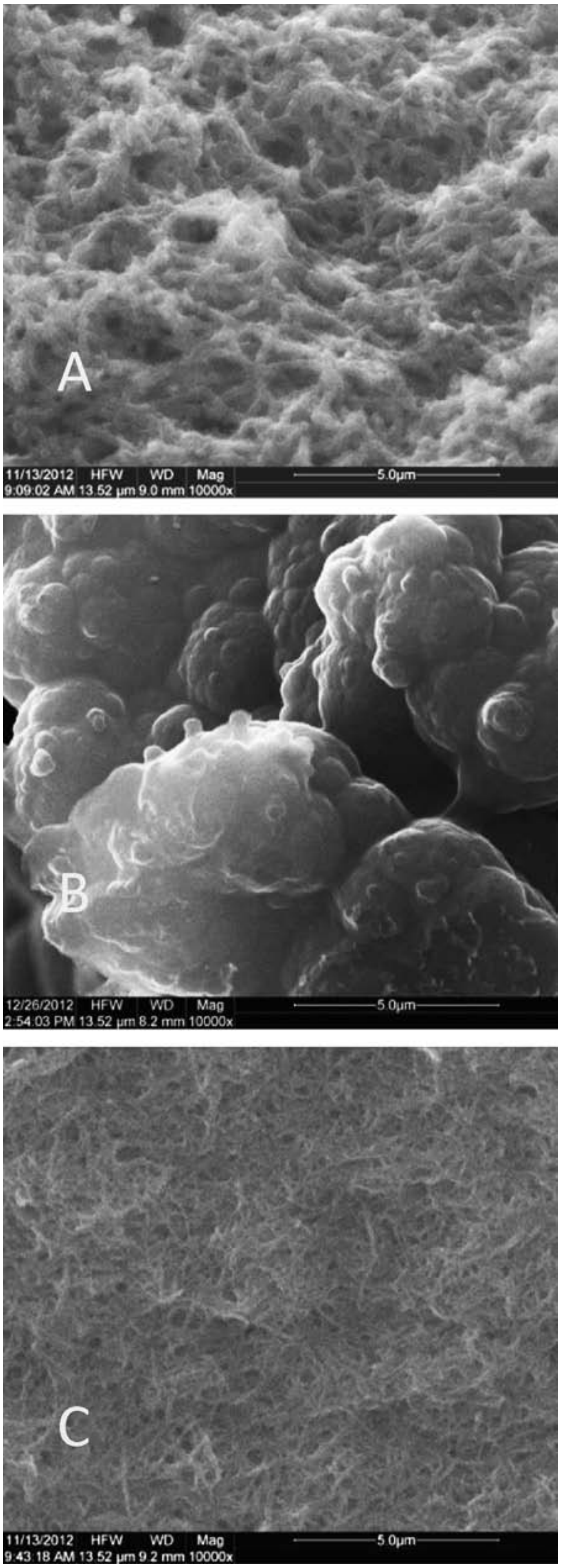

Fig. 2. SEM images of PANI–PPY film (A), PPY film (B) and PANI film (C).

3.4.2. Extraction time

The extraction time is changed from 20 min to 60 min to evaluate its effect. Experimental result shows that the extraction efficiency reaches maximum around 40 min and then it decreases (Fig. S2), meaning that extraction equilibriums are achieved for

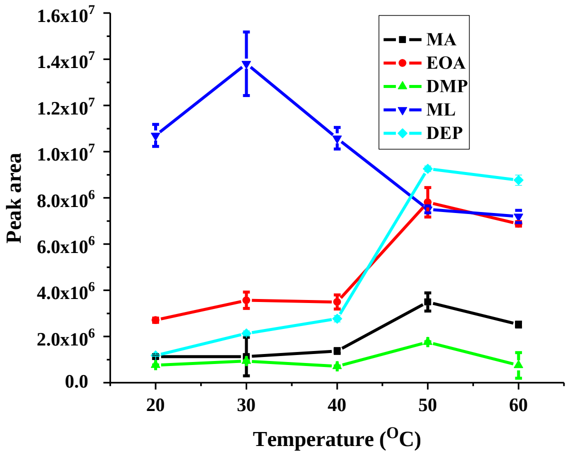

Fig. 3. Influence of temperature on the extraction efficiency of PPY–PAIN fiber. Concentrations of esters: 31.25 ng mL^{-1} (for MA, EOA, DMP, DEP) and 7.81 ng mL^{-1} (for ML); extraction time: 40 min; NaCl concentration: 0.35 g mL^{-1}; stirring rate: 600 rpm; desorption time: 3 min; desorption temperature: 250 °C.

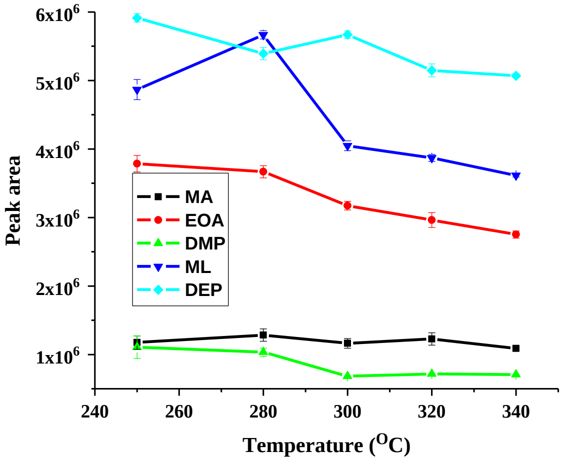

Fig. 4. Influence of conditioned temperature on the extraction efficiency of the resulting PANI–PPY fiber. Extraction temperature: 50 °C; stirring rate: 500 rpm; other conditions as in Fig. 3.

Table 1
Analytical parameters for HS-SPME of esters using the PANI–PPY fiber.

Analytes	LOD (ng mL^{-1})	Linear range (ng mL^{-1})	Correlation coefficient	RSD (%)	
				One fiber (n=5)	Fiber to fiber (n=4)
MA	0.38	0.61–300	0.9971	4.6[a]/6.1[b]	5.2/6.2
EOA	0.15	0.31–300	0.9943	1.7/6.5	3.5/5.7
ML	0.05	0.07–300	0.9960	3.4/3.8	5.4/6.8
DMP	0.31	0.61–300	0.9985	1.8/3.6	9.4/5.8
DEP	0.26	0.61–300	0.9929	3.5/3.9	4.8/3.6

[a] Ester concentration: 31.25 ng mL^{-1} MA, EOA, DMP, DEP and 7.81 ng mL^{-1} ML.
[b] Ester concentration: 3.91 ng mL^{-1} MA, EOA, DMP, DEP and 0.98 ng mL^{-1} ML.

them under this conditions. Hence an extraction time of 40 min is adopted.

3.4.3. Stirring rate

In this case, the extraction efficiency increases slightly with rotating rate changing from 200 to 500 rpm, and then it decreases. Therefore, the rotating rate is fixed at 500 rpm in following experiments.

3.4.4. Ionic strength

Ionic strength usually influences the solubility of organic compounds in water, thus it affects the extraction efficiency of HS-SPME. In this work, NaCl is used to explore the influence of ionic strength. When NaCl concentration is changed from 0.15 g mL^{-1} to 0.35 g mL^{-1} (0.35 g mL^{-1} is the concentration of saturated NaCl solution) the extraction efficiency increases gradually except for ML (Fig. S3). Reasonably, 0.35 g mL^{-1} NaCl is added in the solution for HS-SPME.

3.5. Influence of conditioned temperature, desorption temperature and desorption time

To explore the influence of conditioned temperature the PANI–PPY fiber is held for 30 min at different temperatures and then it is used for HS-SPME (Fig. 4). As can be seen, when the temperature is 250–280 °C the chromatographic peak areas are larger; when it exceeds 280 °C the peak areas decrease. This can be ascribed to the thermal decomposition of PANI–PPY, which makes the adsorption of the coating weak. At the same time, the influence of desorption temperature and desorption time is tested. The results show when desorption temperature is 250–280 °C the extracted analytes are desorbed completely in 3 min and no memory effect is observed for the blank injection. When the temperature is increased further more peaks occur due to the thermal decomposition of PANI–PPY. The peak areas increase with desorption time increasing up to 3 min, then they keep almost unchanged when the desorption temperature is 250 °C.

3.6. Method evaluation

Under the optimized conditions the analytical parameters, including limit of detection (LOD), linear range, repeatability and reproducibility, are tested and the results are listed in Table 1. The LODs are 0.05–0.38 μg L^{-1} (S/N=3) for different esters; the chromatographic peak areas are linear to their concentrations, which can be supported by the ANOVA test results of regression analysis (all “significance F” values are far smaller than selected significance level, α=0.05), illustrating the regressions are significant. The linear ranges are 0.07–300 ng mL^{-1}, with correlation coefficients of 0.9929–0.9985. This indicates that the fiber has high sensitivity and wide quantity range in comparison with those reported [20,21]. The relative standard deviation (RSD) for run-to-run is 1.7–4.6% when the working solutions contain 31.25 ng mL^{-1} MA, EOA, DMP, DEP and 7.81 ng mL^{-1} ML; the fiber-to-fiber RSDs are 3.5–9.4% for different analytes. When the spiked level decreases to one eighth of the concentration, the RSDs for run-to-run and fiber-to-fiber are 3.6–6.5% and 3.6–6.8% respectively. This means that the PPY–PANI fiber has good repeatability and reproducibility [22,23].

3.7. Comparison of different coatings

The extraction efficiency of PANI–PPY, PANI and PPY coatings is compared in Fig. 5. It is clear that the extraction efficiency of PANI–PPY coating is higher than that of PANI and PPY coating. The reason is that the PANI–PPY coating combines the merits of PANI and PPY coating, so it not only has large surface area, but also possesses strong adsorption to hydrophobic molecules. Therefore, it shows high extraction capacity to esters.

3.8. Lifetime of PANI–PPY coating

The lifetime of PANI–PPY fiber is examined by testing its extraction efficiency under the same conditions every week. After being used for about 160 times, its extraction efficiency only changes a little

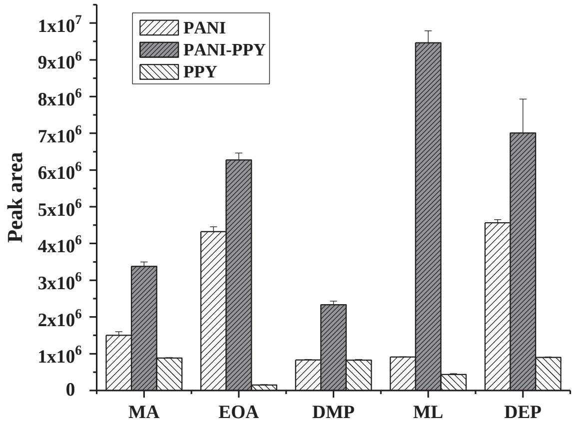

Fig. 5. Comparison of the extraction efficiency of PANI fiber (coating thickness: about 87 μm), PANI–PPY fiber (coating thickness: about 87 μm) and PPY fiber (coating thickness: about 87 μm). Other conditions as in Fig. 4.

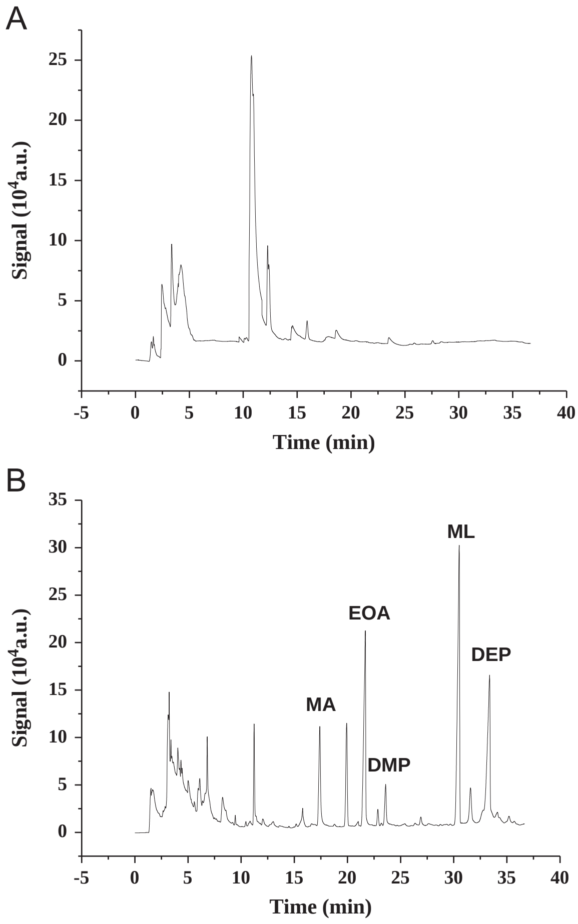

Fig. 6. The chromatograms of lake water after HS-SPME with a PANI–PPY fiber. (A) non-spiked sample and (B) spiked sample.

in comparison with the initial values (Fig. S4). Considering the uncontrollable variation of the GC and extraction conditions, we think that the fiber is quite stable and durable.

3.9. Applications

The PPY–PANI fiber is applied to the determination of esters in lake water, perfume and beer samples. Fig. 6 presents the GC chromatograms of the lake water and spiked solution after extracted with a PANI–PPY fiber. As can be seen, no chromatographic peaks corresponding to these esters occur. After adding standard solution the recoveries are measured and they are 97 – 100% (Table 2).

Table 2
Determination results of lake water using HS-SPME-GC-FID with a PANI–PPY fiber (n=4).

Analytes	Found in water	Added (ng mL^{-1})	Found (ng mL^{-1})	Recovery (%)
MA	nd[a]	189	187 ± 1[b]	99
EOA	nd	189	188 ± 1	99
DMP	nd	189	189 ± 3	100
ML	nd	47	46 ± 1	98
DEP	nd	189	184 ± 4	97

[a] nd: Not detected.
[b] Mean value ± standard deviation.

Table 3
Determination results of perfume and beer samples using HS-SPME-GC-FID with a PANI–PPY fiber (n=4).

Analyte	Sample	Detected (ng mL^{-1})	Added (ng mL^{-1})	Found (ng mL^{-1})	Recovery (%)
MA	Perfume	6.5 ± 0.4[b]	31.25	37 ± 2	98
	Beer	nd[a]		30 ± 1	96
EOA	Perfume	9.0 ± 1.0	31.25	40 ± 2	99
	Beer	4		34 ± 2	97
DMP	Perfume	7.0 ± 0.3	31.25	38 ± 1	99
	Beer	nd		30 ± 2	96
ML	Perfume	98.0 ± 2.0	7.81	105 ± 3	90
	Beer	nd		8 ± 1	102
DEP	Perfume	18.0 ± 1.0	31.25	48 ± 2	97
	Beer	nd		30 ± 1	96

[a] nd: Not detected.
[b] Mean value ± standard deviation.

The measurement results of perfume and beer samples are shown in Table 3. The perfume sample may contain these esters, and their concentrations are ca. 52 ng mL^{-1} for MA, 72 ng mL^{-1} for EOA, 55 ng mL^{-1} for DMP, 784 ng mL^{-1} for ML, 142 ng mL^{-1} for DEP, respectively. After spiking the recoveries are measured and they are 90–99% for different esters. As for the beer sample, it may contain EOA and its concentration is ca. 32 ng mL^{-1}. The recoveries for standard added are 96–102%.

4. Conclusions

A PANI–PPY film coated stainless steel wire is fabricated through electrochemical polymerization for the first time. The coating shows reticulate structure and has large surface area. In comparison with PANI and PPY coatings, the PANI–PPY coating presents higher extraction efficiency for the esters studied. The resulting fiber also shows good durability and reproducibility. In addition, it is cheap and easy to prepare. This work provides a new way for making use of different monomers to prepare SPME fibers with improved property.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2013.08.060.

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