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Electrodeposition of poly(3,4-ethylenedioxythiophene) on a stainless steel wire for solid phase microextraction and GC determination of some esters with high boiling points

Yuyu Ma, Faqiong Zhao*, Baizhao Zeng

Key Laboratory of Analytical Chemistry for Biology and Medicine (Ministry of Education), College of Chemistry and Molecular Sciences, Wuhan University, Wuhan 430072, Hubei Province, PR China

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ABSTRACT

In this work, 3,4-ethylenedioxythiophene (EDOT) emulsion is prepared by ultrasonication agitation and poly(3,4-ethylenedioxythiophene) (PEDOT) coating is fabricated on a stainless steel wire by electrochemical method from a 0.10 M sodium dodecylbenzenesulfonate aqueous solution containing EDOT. The coating is characterized by scanning electron microscopy and Fourier transform infrared spectrophotometry, and it presents cauliflower-like structure. When the resulted PEDOT/steel fiber is used for the headspace solid phase-microextraction of some esters (i.e. methyl anthranilate, dimethyl phthalate, ethyl-o-aminobenzoate, methyl laurate and diethyl phthalate) and their GC detection, the limits of detection (LOD) are ca. 7.8–31 ng L^{-1} ($S/N=3$) and the linear ranges are 0.25–800 $\mu g\ L^{-1}$. The fiber shows high thermal stability (up to 320 °C), good reproducibility and long lifetime (more than 183 times). It also has good chemical stability. After it is immersed in acid, alkali and dichloromethane for 4 h its extraction efficiency remains almost unchanged. Besides esters the fiber also exhibits high extraction efficiency for alcohols and aromatic compounds.

1. Introduction

Solid-phase microextraction (SPME) is a simple, rapid, solvent-free sample preparation technology and it was created by Arhturhe and Pawliszyn in 1990 [1]. Subsequently, commercial device for SPME was developed by Supelco Inc. With it the sampling, extraction, preconcentration and sample introduction can be integrated into one step. Hence the technology is very useful and has been well developed since its inception [2–6]. The key of the technology is the extraction fiber. Its development has undergone a simple to complex and single to diversified process. Initially, fused silica fiber, with good heat resistance and chemical stability, was used for extraction. Then, gas chromatography stationary phase was coated on the surface of quartz fiber to improve extraction efficiency. Currently, there are several commercial coatings available such as polydimethylsiloxane (PDMS) and polyamide (PA), and SPME becomes a mature technology. However, coating fibers still present the disadvantage of poor thermal stability, high cost and/or short lifetime [1,7]. Therefore, to fabricate new extraction fibers with high sensitivity, high stability and long lifetime is still a challenge.

Poly(3,4-ethylenedioxythiophene) (PEDOT), firstly synthesized by Bayer company (Germany) in 1991, has attracted much attention in recent years because it has many excellent properties such as high conductivity, long-term stability, optical transparency, easy to synthesize, simple molecular structure and low band gap [8–12]. The polymer has been widely used as organic thin-film solar cell material, electrochromic material and electrode material [13–15]. PEDOT can be electrodeposited on conductive substrates, and the structure and thickness of the resulting film can be controlled by changing the conditions. However, as 3, 4-ethylenedioxythiophene is insoluble in aqueous solutions, it is difficult to achieve a PEDOT film with enough thickness for SPME.

In this work, 3,4-ethylenedioxythiophene (EDOT) emulsion is prepared by ultrasonication agitation. Then, PEDOT film is fabricated by electrochemical polymerization on a stainless steel wire. The polymer film is used for the extraction and detection of esters with high-boiling points, it shows good performance.

2. Experimental

2.1. Reagents

Methyl anthranilate (MA), dimethyl phthalate (DMP), ethyl-o-aminobenzoate (EOA), methyl Laurate (ML), diethyl phthalate

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* Corresponding author. Tel.: +86 27 68752701; fax: +86 27 68754067.
E-mail address: fqzhao@whu.edu.cn (F. Zhao).

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(DEP), 3,4-ethylenedioxythiophene were purchased from the Aladdin Chemistry Co. (Shanghai, China). The stock solutions of MA (4.0 mg mL^{-1}), EOA (4.0 mg mL^{-1}), DMP (4.0 mg mL^{-1}), DEP (4.0 mg mL^{-1}) and ML (2.0 mg mL^{-1}) were prepared with methanol and stored in a refrigerator. The working solutions were prepared by diluting the standard solutions with deionized water. All other reagents used were analytical grade and purchased from Sinopharm Chemical Reagent Co. (Beijing, China). The samples were obtained from the local supermarket and fruit market (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 ester derivatives 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 10 °C min^{-1} to 140 °C, and 5 °C min^{-1} to 200 °C, then at 20 °C min^{-1} to 220 °C and kept at this temperature for 2 min. The total run time was about 27 min. The injection port temperature was set at 310 °C and the extracted analytes were desorbed for 3 min. Its inlet was operated under the split mode (split ratio: 10:1) and the on-column flow-rate of nitrogen gas was 48.3 cm s^{-1}. The FID temperature was kept at 330 °C. The SPME device was laboratory-made. Electrochemical polymerization of 3,4-ethylenedioxythiophene was performed on a CHI 660A electrochemical workstation (CH Instrument Corp., Shanghai, China) using cyclic voltammetry. A conventional three-electrode system was adopted, including a stainless steel wire (2 cm × 250 μm 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. FTIR spectra were recorded with a Nexus-670 Fourier transform infrared spectrometer (Nicolet, USA). The scanning electron microscopy images (SEM) were obtained using a Quanta-200 SEM instrument (FEI, The Netherlands).

2.3. *Preparation of PEDOT film*

Electrochemical deposition was performed in 10 mL 0.10 M sodium dodecylbenzenesulfonate (SDBS) containing 80 μL 3,4-ethylenedioxythiophene. The scan rate was 50 mV s^{-1}, the potential range was 0.2–1.5 V and the potential scan was cycled for 100 times. The resulting fiber was washed with distilled water to remove monomer and supporting electrolyte. After drying with nitrogen stream the fiber was conditioned in an electric oven at 90 °C for 30 min and then at 310 °C for 1.5 h in nitrogen gas atmosphere. According to the SEM experimental result, the thickness of the PEDOT film was about 70 μm.

2.4. *Headspace SPME procedure*

A 10 mL aqueous solution containing proper esters was transferred into a 15 mL glass vial with PTFE silicon septum. After adding appropriate sodium chloride and a magnetic stirring bar, the vial was tightly sealed with an aluminum cap. The sample vial was placed on an S10-3 magnetism mixer (Siyue Instrument, Shanghai, China) with a water bath. When the temperature reached the fixed value the PEDOT coated stainless steel wire was exposed to the headspace over the stirred solution for 10–50 min. Then the fiber was withdrawn into the needle, removed from the sample vial and immediately introduced into the GC injector port for thermal desorption of 3 min.

3. Results and discussion

3.1. *Characterization of PEDOT*

3.1.1. *Surface structure*

Fig. 1 shows the SEM image of PEDOT coating. As can be seen, it presents cauliflower-like structure. The polymer film thus has large surface area and many binding sites. Such structure also benefits the mass-transport. The thickness of the PEDOT film can be controlled by varying the electropolymerization time, and the size of the cauliflower changes slightly with electropolymerization time.

3.1.2. *FTIR spectra*

Fig. 2 shows the FTIR spectra of PEDOT. The band at 3415^{-1} can be attributed to the stretching vibration of =C–H. The peak at 1616 cm^{-1} is due to the stretching of C=C on the thiophene ring,

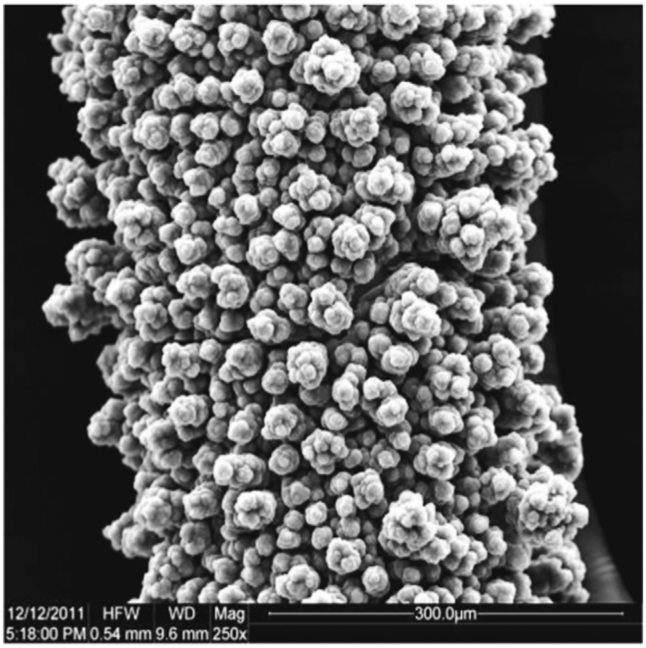

Fig. 1. SEM image of PEDOT prepared by cyclic voltammetry. Electrolyte composition: 10 mL 0.1 M SDBS containing 80 μL EDOT; scan rate: 50 mV s^{-1}; potential range: 0.2–1.5 V.

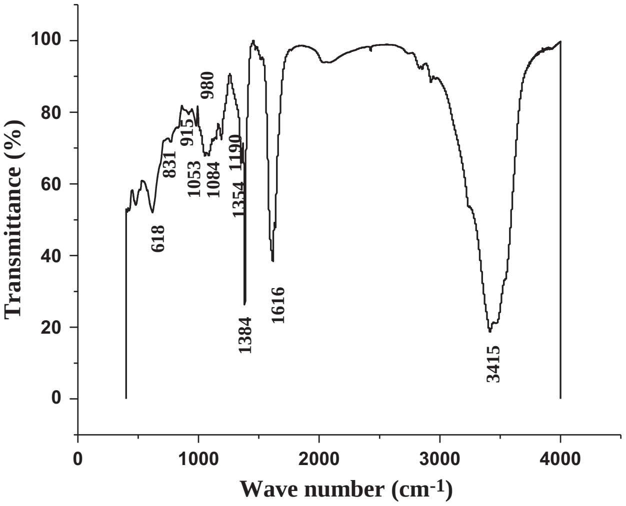

Fig. 2. FTIR spectra of PEDOT film.

and the peaks at 1384 cm^{-1} and 1354 cm^{-1} result from the stretching vibration of C–C. The C–O–C stretching and deformation bands on the thiophene ring produce the peaks at 1084 cm^{-1} and 915 cm^{-1}, and C–S vibration bands are observed at 980 cm^{-1}, 831 cm^{-1} and 618 cm^{-1} [16–18]. In addition, the asymmetric and symmetric stretching of sulfonate of the counter ions (OTs) is reflected at 1190 cm^{-1} and 1053 cm^{-1} [19]. This indicates that the coating is PEDOT and it is almost free of impurity.

3.1.3. *Thermal stability*

A blank PEDOT fiber is introduced into the GC injector port to study its thermal stability. As can be seen in Fig. 3, when the temperature is changed from 270 °C to 320 °C, the obtained chromatograms are a line. This indicates that the film is stable up to 320 °C. Hence it is suitable for the extraction of compounds with higher boiling point. The good thermal stability of the fiber may be due to the formation of long polymer π–π covalent bond [20]. When the temperature increases to 330 °C, some chromatographic peaks occur due to the thermal decomposition of PEDOT film. In the follow experiment, the aging temperature of the fiber is fixed at 310 °C.

3.1.4. *Chemical stability*

An SPME fiber may be damaged by organic solvents, strong acidic and strong basic solutions. Here the influence of several solutions is tested (Fig. 4 and Supplementary Materials, Fig. S1). After being soaked in distilled water, dichloromethane, sulfuric acid or sodium hydroxide for several hours, followed by washing with distilled water and drying, the extraction efficiency of the PEDOT fiber remains almost unchanged. This indicates that the fiber has good chemical stability.

3.1.5. *Lifetime of the coating*

The coating's lifetime is very important for practical application. For most commercial SPME fibers, the extraction efficiency declines with extraction times increasing because the coating is prone to being damaged by organic solvent, high temperature, strong acidic or basic solution [21]. Here the lifetime of PEDOT fiber is examined. As shown in Fig. 5, after the fiber undergoes 183-time adsorption/desorption the extraction efficiency only changes a little. This illustrates that the fiber is quite durable.

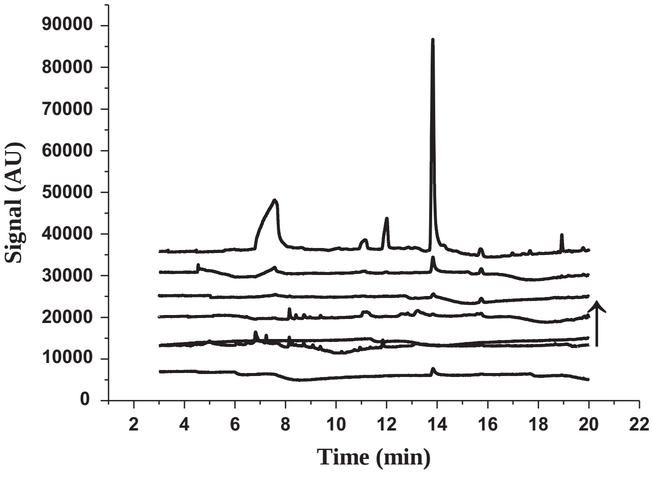

Fig. 3. Influence of injection port temperature on the baseline of PEDOT fiber. Injection port temperature (from bottom to top): 270 °C, 280 °C, 290 °C, 300 °C, 310 °C, 320 °C and 330 °C. In order to easily distinguish them the baselines are moved along the ordinate axis to different extent.

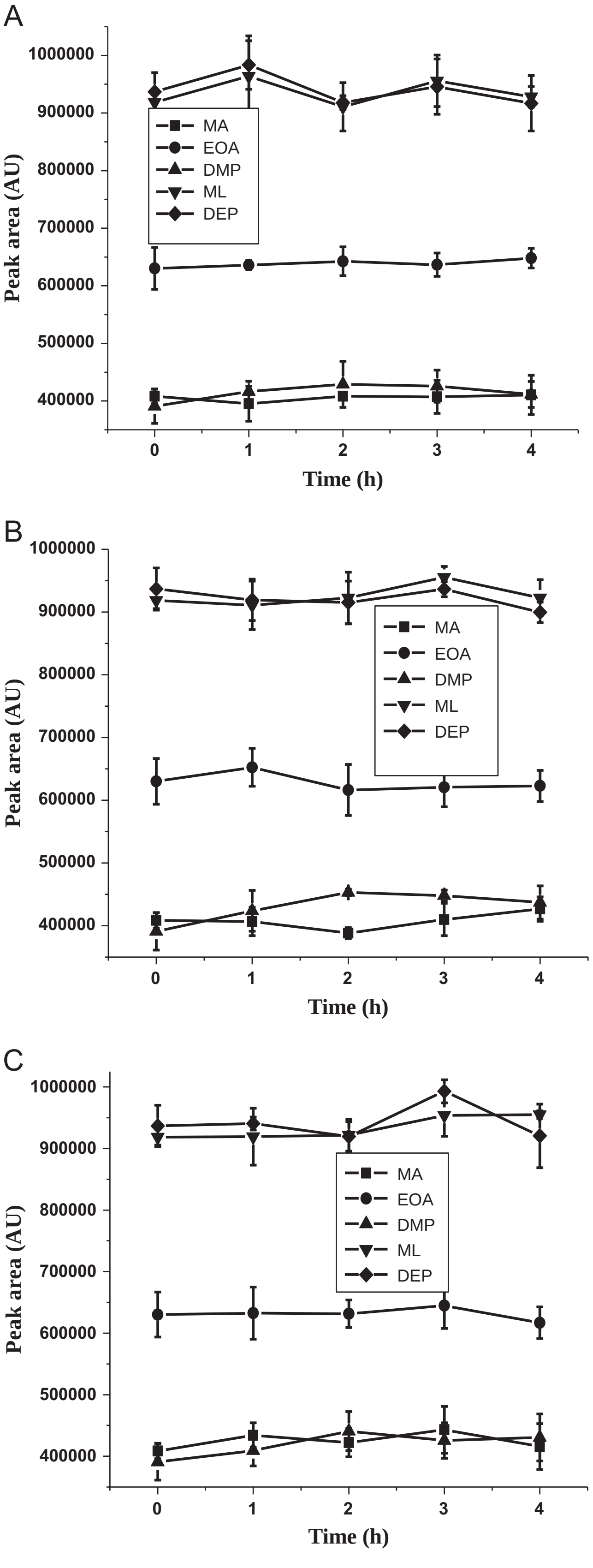

Fig. 4. Influence of soaked time on the extraction efficiency of PEDOT fiber. Soaked solutions: 0.5 M H_2SO_4 (A), dichloromethane (B), 1 M NaOH (C); extraction time: 40 min; NaCl concentration: 0.35 g mL^{-1}; stirring rate: 600 rpm; desorption time: 3 min; extraction temperature: 40 °C; desorption temperature: 310 °C. The concentrations of esters: 0.8 μg mL^{-1} (for MA, EOA, DMP, DEP) and 0.4 μg mL^{-1} (for ML).

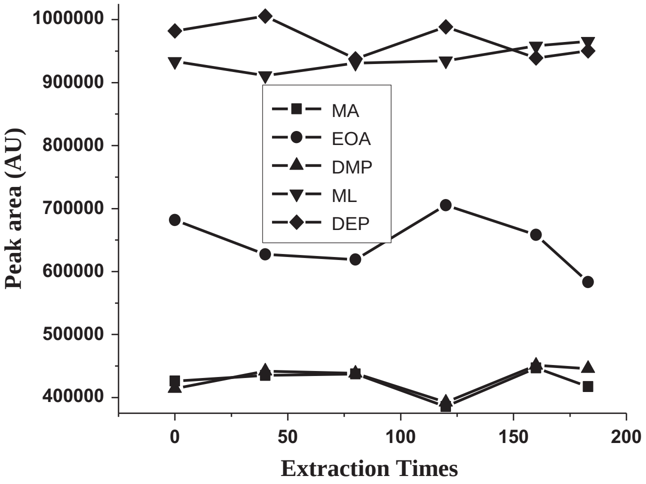

Fig. 5. Variation of extraction efficiency with frequency of use. Other conditions as in Fig. 4.

3.2. *Influence of electrodeposition conditions*

The influence of some electropolymerization conditions is explored. Experimental results show when the scan rate is smaller (e.g. $<25\ \mathrm{mV\,s^{-1}}$), the obtained PEDOT coating is not enough solid and durable though it has higher extraction capacity. When the scan rate is higher (e.g. $>100\ \mathrm{mV\,s^{-1}}$) the resulting PEDOT film becomes solid, but its extraction capacity is smaller. Taking the sensitivity and lifetime of the fiber into account, the scan rate of 50 $\mathrm{mV\,s^{-1}}$ is adopted. As to the potential range, it affects the polymerization rate of EDOT. When the high potential limit increases, the polymerization rate of EDOT increases. However, when it is too high (e.g. >1.6 V) oxygen may occurs. The low potential limit presents less influence. Here the potential range of 0.2–1.5 V is selected. In addition, cyclic voltammetry and potential static electrolysis are compared for the preparation of PEDOT coating. As a result, cyclic voltammetry gives better performance. The coating thickness increases with the number of potential scan increasing. Considering the diameter of the needle of the SPME device the potential scan is cycled for 100 times. In this case, the thickness of the PEDOT film is about 70 μm.

3.3. *Optimization of extraction conditions*

3.3.1. *Extraction time*

Extraction efficiency changes with extraction time until the extraction reaches equilibrium. On the other hand, extraction time affects the sensitivity and reproducibility. Hence extraction time is an important factor. In this case, after extraction of 40 min, the extraction efficiency reaches the maximum for MA, DMP and DEP (Fig. S2), meaning that their extraction achieves equilibrium. As for ML, to the opposite, the peak area reduces with increasing extraction time. The possible reason is that ML volatilizes more easily and it can quickly achieve equilibrium. With increasing extraction time more other compounds compete with it. For EOA the extraction efficiency increases with extraction time going, probably due to its higher boiling point. Taking the time-consuming into account, an extraction time of 40 min is adopted as a compromise between analysis time and sensitivity.

3.3.2. *Salt concentration*

Ionic strength usually affects the solubility of organic compounds in aqueous solution, and then it affects the extraction efficiency [22]. In this work, the influence of ionic strength is examined by varying NaCl concentration. As a result, the peak area increases with NaCl concentration increasing (Fig. S3), even if it is up to 0.35 $\mathrm{g\,mL^{-1}}$ (near NaCl saturated solution). Thus 0.35 $\mathrm{g\,mL^{-1}}$ NaCl is added in the solution in the following experiments.

3.3.3. *Extraction temperature*

For HS-SPME, extraction temperature not only affects extraction rate, but also affects the adsorption capacity of a coating. Here the extraction temperature is changed from 20 °C to 60 °C to test its influence (Fig. S4). At 40 °C the peak area is bigger for most of them for the extraction time used. The temperature is thus adopted.

3.3.4. *Stirring rate*

Stirring the solution can facilitate the equilibrium between the aqueous phase and headspace phase, so the rotating rate of magnetic stirring bar affects the extraction efficiency to some extent. In this case, the extraction efficiency increases with rotating rate changing from 200 to 600 rpm (Fig. S5). However, when it is above 600 rpm the extraction efficiency reduces as the stirring makes the extraction solution splash on the surface of the fiber. Therefore, for all experiments the stirring rate is fixed at 600 rpm.

3.4. *Method evaluation*

Under the optimized conditions, the analytical parameters are measured for ester compounds, and the results are listed in Table 1. For different ester compounds, the limit of detection (LOD) is ca. 7.8–31 ng $\mathrm{L^{-1}}$ ($S/N=3$); the GC peak areas are linear to the concentration of the ester compounds over the range of 0.25–800 $\mathrm{\mu g\,L^{-1}}$, with correlation coefficients above 0.99. The relative standard deviation (RSD) is below 6.9% for five repetitive extractions of water samples containing 0.8 $\mathrm{\mu g\,mL^{-1}}$ MA, EOA, DMP, DEP and 0.4 $\mathrm{\mu g\,mL^{-1}}$ ML, and the fiber-to-fiber RSD is 2.1–9.3% under the same conditions. This indicates that the fiber has good reproducibility and repeatability.

The fiber is also used for the headspace solid-phase microextraction (HS-SPME) of other compounds (i.e. benzenes, phenols, alcohols and aromatic amines). The experimental results show that it presents high extraction efficiency for them too. So, the fiber can be applied to the detection of other small organic molecules.

3.5. *Application*

The established method is applied to the determination of ester compounds in real samples (i.e. orange, apple, banana and tropicana – a fruit juice drink). Prior to determination, the fruit is mashed with a blender, and the juice is transferred to the glass vial

Table 1
Analytical parameters for ester compounds with PEDOT fiber based HS-SPME-GC-FID.

Analytes	LOD ($\mathrm{ng\,L^{-1}}$)	Linear range ($\mathrm{\mu g\,L^{-1}}$)	RSD (%)	
			One fiber($n=5$)	Fiber to fiber($n=5$)
MA	31	0.50–800	3.4	7.8
DMP	16	0.50–800	3.9	4.6
EOA	31	0.25–400	4.5	9.3
ML	7.8	0.25–800	5.1	3.7
DEP	7.8	0.25–800	6.9	2.1

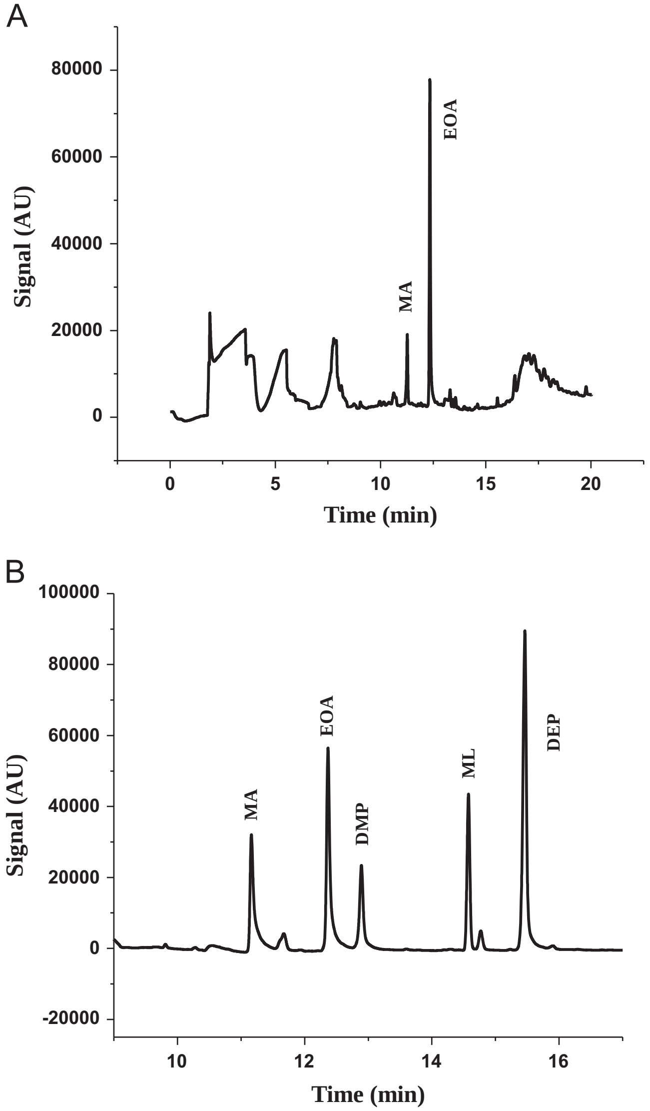

Fig. 6. HS-SPME-GC-FID chromatogram of the orange (A) after extracted with PEDOT fiber. (B) HS-SPME-GC-FID chromatogram of an aqueous solution containing 0.2 μg mL^{-1} MA, EOA, DMP, DEP and 0.1 μg mL^{-1} ML. Extraction conditions: extraction temperature, 40 °C; extraction time, 40 min; saturated with NaCl; stirring rate, 600 rpm; desorption temperature, 310 °C; desorption time, 3 min.

Table 2
Determination results of real samples by HS-SPME-GC-FID using PEDOT fiber (n=3).

Analytes	Orange (μg mL^{-1})	Banana (μg mL^{-1})	Tropicana (μg mL^{-1})	Apple (μg mL^{-1})
MA	0.11 ± 0.01[a]	0.29 ± 0.03	0.10 ± 0.01	nd[b]
DMP	nd	nd	nd	nd
EOA	0.29 ± 0.03	0.63 ± 0.04	0.23 ± 0.01	nd
ML	nd	nd	nd	nd
DEP	nd	nd	nd	nd

[a] mean value ± standard deviation.
[b] nd: not detected.

for extraction. For the samples, measurable chromatographic peaks for MA and EOA occur (Figs. 6and S6). According to the peak area, the contents of MA and EOA are calculated and the results are summarized in Table 2. For the apple sample, standard solution is added and the recoveries for the esters (i.e. MA, DMP, EOA, ML and DEP) are measured. They are 90%, 94%, 106%, 92% and 98%, respectively.

4. Conclusion

In this work, PEDOT coating is fabricated on a stainless steel wire by electrodeposition for the first time. The PEDOT coating presents cauliflower-like structure and large surface area. It shows high extraction efficiency for esters. The resulting fiber has high thermal stability, high chemical stability, good reproducibility and long lifetime. In addition, the fiber also exhibits high extraction efficiency for other compounds such as alcohols and aromatic compounds. Therefore, it has good application potential.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2012.11.011.

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