



Electrochemical preparation of poly(*p*-phenylenediamine-co-aniline) composite coating on a stainless steel wire for the headspace solid-phase microextraction and gas chromatographic determination of some derivatives of benzene

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ABSTRACT

A poly(*p*-phenylenediamine-co-aniline) composite coating was prepared on a stainless steel wire through electrochemical method. The coating was characterized by scanning electron microscopy, Fourier transform infrared spectrophotometry and thermogravimetry. It showed thin slice shape and netlike microstructure, and thus it had large surface area and large extraction capacity. When the resulting fiber was used for the headspace solid-phase microextraction of some derivatives of benzene (i.e. chlorobenzene, 1,3-dimethylbenzene, 1,2-dimethylbenzene, 2-chlorotoluene, 1,3,5-trimethylbenzene, 1,2,4-trimethylbenzene), followed by gas chromatographic (GC) analysis, it presented better performance than the polyaniline coated stainless steel wire. Under the optimized conditions, the GC peak areas were linear to their concentration in the ranges of about 0.5–500 $\mu\text{g L}^{-1}$, with correlation coefficients of 0.9911–0.9989; the detection limits were 0.2–0.88 $\mu\text{g L}^{-1}$ ($S/N=3$). The run-to-run RSD was smaller than 5.5% ($n=5$), and the fiber-to-fiber RSD was 3.5%–12.7% ($n=3$). The fiber was quite stable and durable; after it was used for about 140 times, its extraction efficiency kept almost unchanged. The developed method was successfully applied to the determination of the derivatives of benzene in waste water, and the recoveries were 86.9%–107.7%.

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1. Introduction

Solid-phase microextraction (SPME) is a useful sample-pre-treatment technique, which was proposed by Pawliszyn et al. around 1990 [1–2]. It can integrate sampling, extraction, pre-concentration and sample introduction into one step; furthermore, it is simple, solvent-free, reliable and inexpensive. So far the technique has been extensively applied in the analysis of volatile and semi-volatile organic substance. For SPME a fiber is generally used, and its property depends on the coating and substrate material. Nowadays, the commercial SPME fibers are generally made of polymer and fused quartz fiber [3–5]. These fibers show some disadvantages such as small extraction capacity, poor reusability and/or high cost, resulting from the manual coating method and fragile fused quartz fiber [6]. To improve the property of the SPME fibers many new coating methods and substrate materials are developed. Electrochemical method and

metal wire are among them, respectively [7,8]. In comparison with other methods and substrate materials, electrochemical method is more simple and controllable, and metal wire is more flexible and durable [7–9].

As the electrochemical polymerization of aniline (ANI) easily occurs and the resulting polyaniline (PANI) film is porous and conductive, ANI is widely used in the electrochemical preparation of SPME fibers. PANI coating has large extraction capacity and high thermal stability; it is suitable for the extraction of a number of compounds, including phenolic compounds, substituted benzenes, phthalates, n-alkane and aliphatic alcohols [10–15]. However, PANI coating still has some disadvantages. For example, the connection between PANI and stainless steel wire is not very strong, and its extraction capacity is still not large enough. To better its performance, some functional materials are introduced and composite coatings are prepared [11,16]. However, up to now there are few reports on the application of electrochemical copolymerization of ANI with other compounds in constructing SPME fibers [17,18].

Like ANI, some ANI derivatives can be electrodeposited; hence the copolymer of ANI and its derivatives can be prepared by

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electrochemical method [19–22]. Through copolymerization the property of PANI coating can be changed and improved. For example, poly(*p*-phenylenediamine) (PPDA) shows low conductivity and high solubility, so it is difficult to prepare a poly(PPDA) coating by electrochemical method. When it is electrodeposited with ANI, they form copolymer coating. The microstructure and property of the copolymer coating is different from that of PANI coating. In fact, such copolymers have been widely prepared and applied in electrochemistry and electroanalysis, and they present good performance [23,24].

In this work, a poly(PPDA-co-ANI) coating is prepared on the surface of a stainless steel wire by cyclic voltammetry for the first time. The coating is characterized by scanning electron microscopy (SEM), thermogravimetry and electrochemical method. The extraction property of the obtained SPME fiber is evaluated, by taking several derivatives of benzene as model molecules. The fiber shows good performance.

2. Experimental

2.1. Reagents

Chlorobenzene (CB), 1,3-dimethylbenzene (1,3-DMB), 1,2-dimethylbenzene (1,2-DMB), 2-chlorotoluene (2-CT), 1,3,5-trimethylbenzene (1,3,5-TMB), 1,2,4-trimethylbenzene (1,2,4-TMB), 2-chlorophenol (2-CP), 2-methylphenol (2-MP), 3-methylaniline (3-MA) and 2-chloroaniline (2-CA) were purchased from the Reagent Factory of Shanghai (China). The stock solution was prepared with methanol and stored in a refrigerator. It contained 0.1 mg mL^{-1} 1,3-DMB, 1,2-DMB, 1,3,5-TMB, 1,2,4-TMB and 0.2 mg mL^{-1} CB and 2-CT. The working solutions were prepared by diluting the stock solution with water or saturated NaCl aqueous solution. Aniline, *p*-phenylenediamine, *m*-phenylenediamine (MPDA) and *o*-phenylenediamine (OPDA) also came from the Reagent Factory of Shanghai (China). Before use, aniline was purified through vacuum distillation. Other chemicals used were of analytical grade and purchased from the Reagent Factory of Shanghai (China). The water sample was collected from a local printing and dyeing mill (Wuhan, China).

2.2. Apparatus

The GC experiments were performed on a Model SP-6890 gas chromatography instrument with a flame ionization detection (FID) system (Shangdong Lunan Ruihong Chemical Instrument Co., Tengzhou, China). A N2000 chromatographic workstation program (Zhejiang University, Zhejiang, China) was used to process chromatographic data. The separation of benzene derivatives was carried out on a SE-54 capillary column ($30 \text{ m} \times 0.32 \text{ mm I. D.}$) with $0.33 \text{ }\mu\text{m}$ film thickness (Lanzhou Atech Technologies, Lanzhou, China). The stationary phase is polydimethyl phenyl vinyl siloxane (containing 5% phenyl). The following oven temperature program was used: $50 \text{ }^\circ\text{C}$ hold for 3 min, followed by increasing temperature to $110 \text{ }^\circ\text{C}$ at $10 \text{ }^\circ\text{C min}^{-1}$, and to $130 \text{ }^\circ\text{C}$ at $2 \text{ }^\circ\text{C min}^{-1}$ and kept at this temperature for 3 min. The total run time was about 30 min. The injection temperature was $210 \text{ }^\circ\text{C}$ and the desorption of extracted analytes was performed for 3 min. Its inlet was operated under the split mode and the split ratio was 1.78. The flow-rate of carrier gas (i.e. nitrogen gas) was 1.0 mL min^{-1} . The FID temperature was set at $250 \text{ }^\circ\text{C}$.

The SEM images were obtained using a Quanta-200 SEM instrument (FEI, The Netherlands). FTIR spectra were recorded with a Nexus-670 Fourier transform infrared spectrometer (Nicolet, USA). The thermogravimetric analysis (TGA) was carried out with a Setsys instrument (Aetaram, France). Electrochemical experiments were performed on a CHI 660B electrochemical workstation

(CH Instrument Company, Shanghai, China). A conventional three-electrode system was adopted, including a stainless steel wire as working electrode, a platinum wire as counter electrode and a saturated calomel electrode (SCE) as reference electrode.

2.3. Preparation of poly(PPDA-co-ANI) coating

Prior to electrochemical polymerization, the stainless steel wire (diameter: $250 \text{ }\mu\text{m}$) was cut into 2 cm length, and then was ultrasonicated in 1 M nitric acid, 1 M sodium hydroxide and distilled water each for 10 min. Then the electrode system was immersed in an aqueous solution containing 0.10 M ANI, 0.01 M *p*-phenylenediamine and 1 M nitric acid. The potential scan was cycled for 150 times between -0.2 V and 1.5 V at a scan rate of 50 mV s^{-1} . The resulting fiber was rinsed with methanol and distilled water, and then let the solvent evaporate at room temperature in air. Following this, it was conditioned in a electric furnace with nitrogen atmosphere at $90 \text{ }^\circ\text{C}$ for 30 min, at $210 \text{ }^\circ\text{C}$ for 90 min. When the fiber was cool, it was fixed on a home-made device for SPME with epoxy resin. The SPME fiber was denoted as poly(PPDA-co-ANI) fiber and its coating-thickness was about $60 \text{ }\mu\text{m}$. For comparison, other fibers were also prepared by the similar method.

2.4. Headspace SPME procedure

An 8 mL saturated NaCl solution and a $2 \text{ }\mu\text{L}$ 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 600 rpm. When the temperature reached the fixed value ($20\text{--}50 \text{ }^\circ\text{C}$) 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 for 3 min.

3. Results and discussion

3.1. Electrochemical copolymerization of aniline and phenylenediamine at stainless steel wires

Phenylenediamine has three isomerides, i.e. OPDA, MPDA and PPDA. They show different electrochemical behavior and different influence on the polymerization of ANI (Fig. 1). When both ANI and PPDA are present the peak current increases rapidly at first, due to their rapid oxidation at the steel wire. But their copolymer is not so electroactive and conductive as PANI, hence the voltammetric peaks decrease afterwards. Owing to their interaction it is easier to prepare a poly(PPDA-co-ANI) coating on a stainless steel wire than to prepare a PANI coating. However, when PPDA is replaced by OPDA or MPDA the voltammetric peaks keep almost unchanged after two potential-scan circles and the obtained coating is very thin. This indicates that OPDA and MPDA retard the electrochemical polymerization of ANI. This is in agreement with that reported in literature [25]. Without ANI, phenylenediamine cannot form observable polymer coating on the stainless steel wire, meaning that it is difficult for them to polymerize under this condition or their polymers are soluble. In the following experiments, copolymerization of PPDA and ANI is explored.

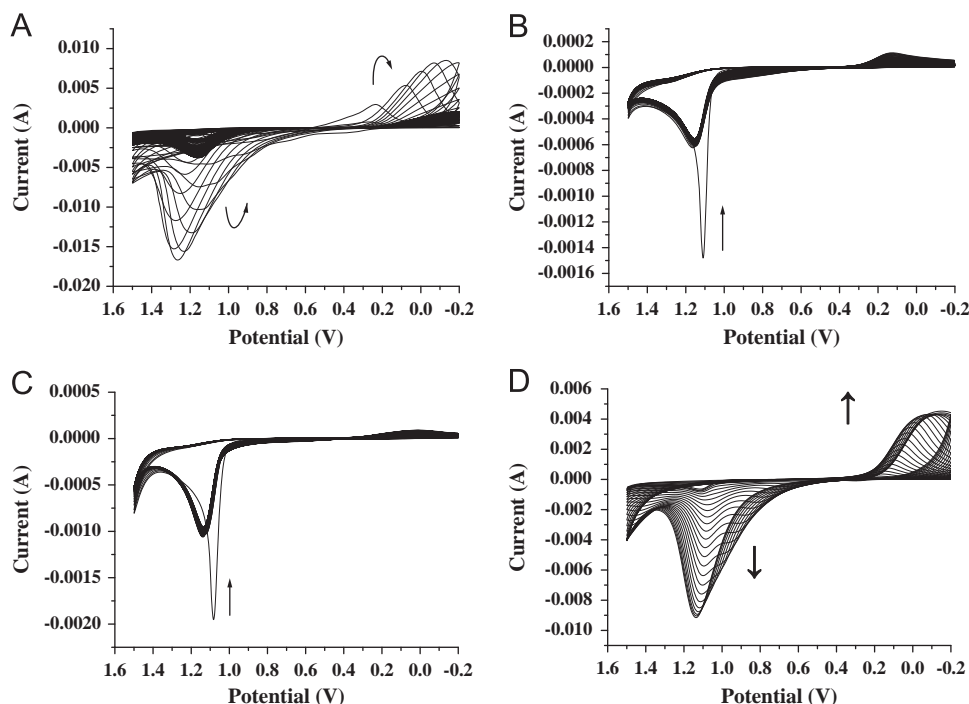


Fig. 1. Cyclic voltammograms corresponding to the copolymerization of ANI and phenylenediamine. Solution composition: (A) 0.1 M ANI+0.01 M PPDA+1 M HNO₃; (B) 0.1 M ANI+0.01 M MPDA+1 M HNO₃; (C) 0.1 M ANI+0.01 M OPDA+1 M HNO₃; (D) 0.11 M ANI+1 M HNO₃. Potential range: -0.2 to 1.5 V; scan rate: 50 mV s⁻¹.

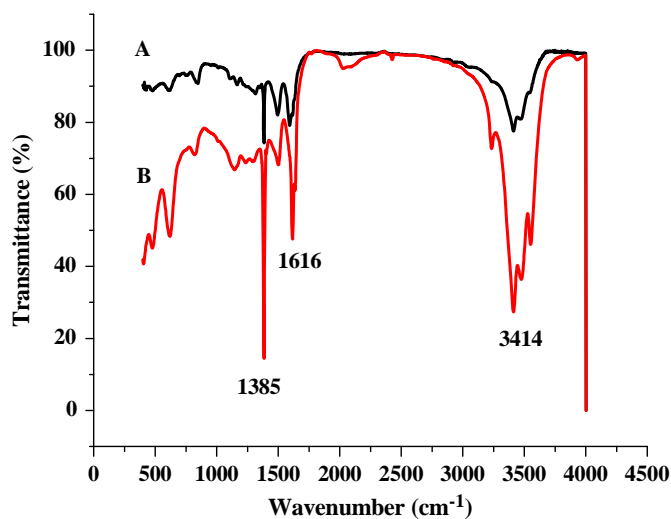


Fig. 2. FTIR spectra of PANI (A) and poly(PPDA-co-ANI) (B) prepared by electrochemical method.

3.2. Characterization of poly(PPDA-co-ANI) composite coating

3.2.1. FTIR spectra

Fig. 2 shows the FTIR spectra of PANI and poly(PPDA-co-ANI). As can be seen, their absorption peaks present some difference. In comparison with those of PANI, the absorption bands corresponding to the N-H and C-N (i.e. the bands at 3414 cm⁻¹ and 1385 cm⁻¹) of poly(PPDA-co-ANI) move slightly toward lower wavenumber. This relates to the formation of bigger conjugated system. In addition, the band at 1616 cm⁻¹, caused by C=N stretching vibration of poly(PPDA-co-ANI), shifts to higher wavenumber. It also should be ascribed to their copolymerization. As it is difficult for us to prepare a poly(PPDA) coating through electrochemical method, further comparison is not carried out.

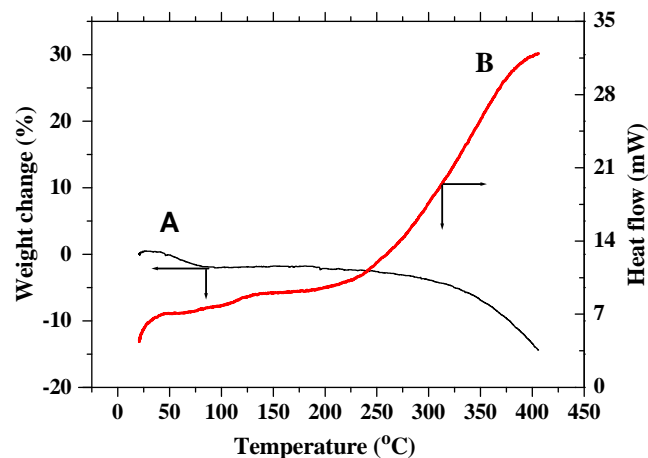


Fig. 3. TGA (A) and DSC (B) curves of poly(PPDA-co-ANI) coating. Conducted in nitrogen gas atmosphere; heating rate: 10 °C min⁻¹.

3.2.2. Thermogravimetric analysis

Fig. 3 displays the thermogravimetric analysis (TGA) and differential scanning calorimetric (DSC) curves of poly(PPDA-co-ANI) coating. The copolymer undergoes two-step weight loss. The first step appears between 25 °C and 100 °C and can be attributed to the loss of moisture and volatile solvents. The second step occurs above 225 °C, which corresponds to the decomposition of copolymer. The DSC curve of the copolymer ascends above 225 °C. This relates to the heat release during the decomposition of copolymer. In comparison with that of PANI, the decomposition temperature of the copolymer is lower.

3.2.3. SEM image of poly(PPDA-co-ANI) coating

The SEM images of poly(PPDA-co-ANI) coating and PANI coating are shown in Fig. 4. The poly(PPDA-co-ANI) coating presents thin slice shape and the “thin slice” displays netlike microstructure,

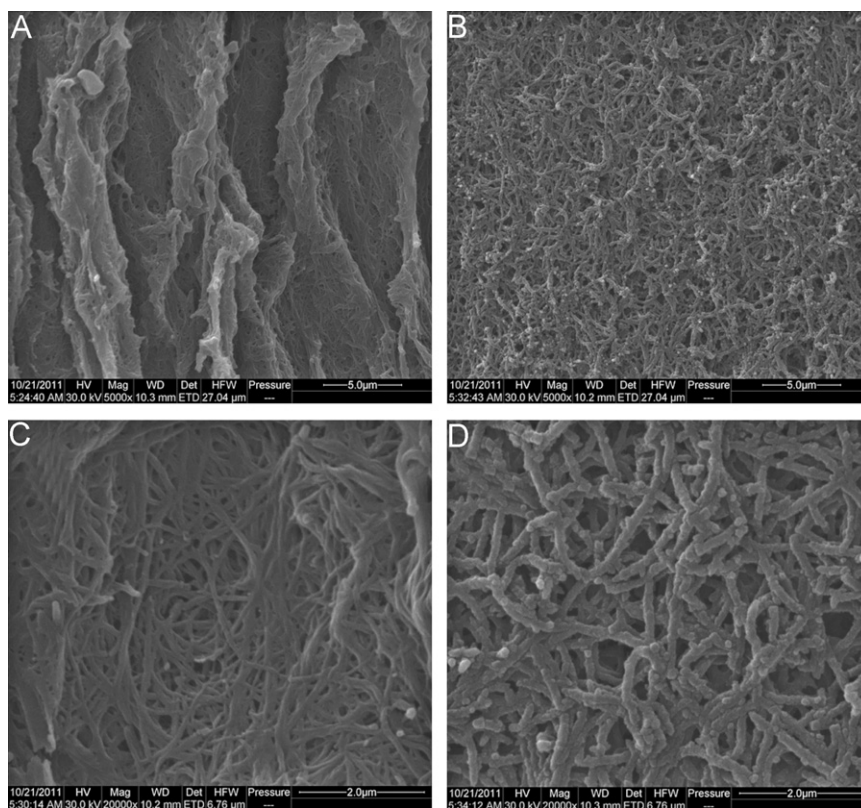


Fig. 4. SEM images of poly(PPDA-co-ANI) coating (A, C) and PANI coating (B, D). Magnified rate: 5000 (for A, B) and 20,000 (for C, D).

unlike PANI coating. Therefore, the poly(PPDA-co-ANI) composite coating not only has large surface area, but also permits rapid mass transfer.

3.3. Optimization of electrochemical copolymerization conditions

3.3.1. The concentration ratio of ANI and PPDA

The structure and property of poly(PPDA-co-ANI) coating depends on the concentration ratio of ANI and PPDA in the electrolyte solution. When the concentration ratio is smaller (e.g. 1:1), the obtained coating does not stick firmly to the steel wire. When it increases, the composite coating becomes more durable and compact. But when it exceeds 15:1, the property of the obtained poly(PPDA-co-ANI) coating is very similar to that of PANI. The microstructures of different poly(PPDA-co-ANI) coatings are similar (see supplementary materials, Fig. S1), but they are different from that of PANI (Fig. 4), due to the change of polymerization process and coating composition. The composite coating is mainly composed of copolymer, but it may still contain some PANI and poly(PPDA) [26]. It should be mentioned that the total concentration of ANI and PPDA influences the polymerization rate, but it shows little impact on the structure and property of the poly(PPDA-co-ANI) coating.

The extraction efficiencies of different poly(PPDA-co-ANI) coatings are compared (see supplementary materials, Fig. S2). When the concentration ratio of ANI and PPDA increases the extraction efficiency of the resulting fiber increases, and when it is 10:1–15:1, the extraction efficiency is higher. Further increasing the ratio, the extraction efficiency decreases. However, the extraction efficiencies of all the poly(PPDA-co-ANI) coatings are higher than that of PANI coating. This should be ascribed to the larger surface area of poly(PPDA-co-ANI) coatings. On the other hand, the composite coating may have stronger adsorption/extraction effect for these analytes. Under the optimized conditions, the extraction capacity of

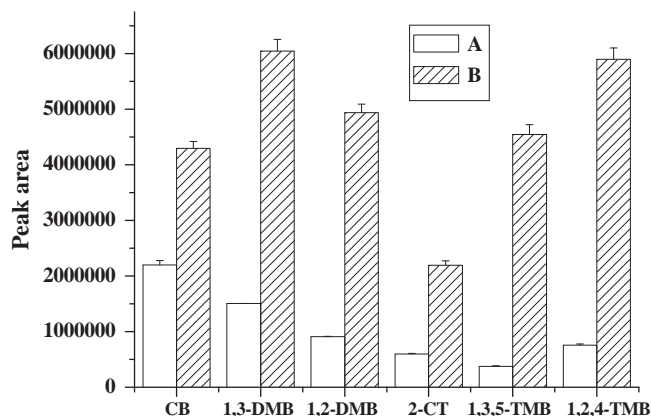


Fig. 5. Comparison of the extraction efficiency of PANI coating and poly(PPDA-co-ANI) coating. The composition of electrolyte solutions: (A) 0.11 M ANI + 1 M HNO₃, (B) 0.01 M PPDA + 0.1 M ANI + 1 M HNO₃; extraction temperature: 30 °C; extraction time: 30 min; stirring rate: 600 rpm; NaCl concentration: 0.35 g mL⁻¹; desorption time: 3 min; desorption temperature: 210 °C. The concentrations of benzene derivatives: 0.25 μg mL⁻¹ (for 1,3-DMB, 1,2-DMB, 1,3,5-TMB, 1,2,4-TMB) and 0.50 μg mL⁻¹ (for CB, 2-CT).

poly(PPDA-co-ANI) coating is 2–12 times as much as that of PANI coating for different benzene derivatives (Fig. 5).

3.3.2. Polymerization time

The effect of polymerization time on coating thickness is explored. It increases with extending polymerization time. At the same time, the coating-resistance rises. As shown in Fig. 6, when the cyclic potential scan is repeated for 40 times, the corresponding resistance is about 450 Ω; when it is repeated for 150 times, the resistance is up to 870 Ω. With the coating-resistance rising, the

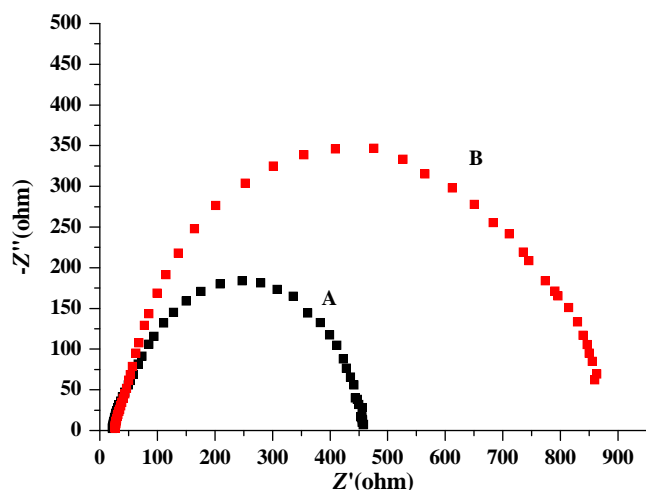


Fig. 6. Electrochemical impedance spectroscopy (EIS) of poly(PPDA-co-ANI) coatings prepared by repeating potential scan for 40 times (A) and for 150 times (B) in the same solution as in Fig. 5. For EIS measurement the solution composition: 5 mM $[\text{Fe}(\text{CN})_6]^{4-/\beta-}$ + 0.2 M KCl; applied potential: 0.23 V (vs SCE); frequency range: 0.1 Hz– 10^5 Hz.

increase of coating-thickness slows down (see supplementary materials, Table S1). Therefore, it is easy to control the coating-thickness by changing the polymerization time. Considering the limit of the diameter of the SPME device, the cyclic potential scan is repeated for 150 times in this case. The coating-thickness is measured by electron microscope and it is about 60 μm .

3.3.3. Supporting electrolyte

The electrochemical polymerization of ANI and its derivatives is generally carried out in acid solutions, thus the obtained polymer coating is conductive and the coating-thickness is controllable. As the anion of acid can be incorporated into the polymer coating and then influences the coating structure [8], different acids are used as supporting electrolyte and the resulting coatings are compared. Experiments show that in H_3PO_4 medium it is difficult to prepare a composite coating with enough thickness for SPME. Hence, the obtained coating reveals weak extraction function for the analytes. In the presence of SO_4^{2-} the obtained coating has flaw and also presents low extraction efficiency. However, in HNO_3 or HClO_4 solution the resulting coating has high extraction efficiency and its surface is smooth. In particular, HNO_3 is suitable for the purpose in this case (see supplementary materials, Fig. S3).

3.4. Optimization of extraction and desorption conditions

3.4.1. Extraction temperature

The effect of temperature on extraction efficiency is studied in the range of 20–50 $^\circ\text{C}$ (see supplementary materials, Fig. S4). The extraction efficiency increases with temperature going up until 30 $^\circ\text{C}$ except for chlorobenzene. Beyond 30 $^\circ\text{C}$ the extraction efficiency decreases. As for chlorobenzene, the extraction efficiency reaches a maximum at lower temperature, which relates to its lower boiling point. Here, 30 $^\circ\text{C}$ is chosen as the extraction temperature in subsequent experiments.

3.4.2. Extraction time

The extraction time is changed from 10 min to 50 min to evaluate its effect, and the results are shown in Fig. 7. As can be seen, at 10 min the extraction amount reaches 70%–85% of the maximum for different analytes; the extraction efficiency reaches

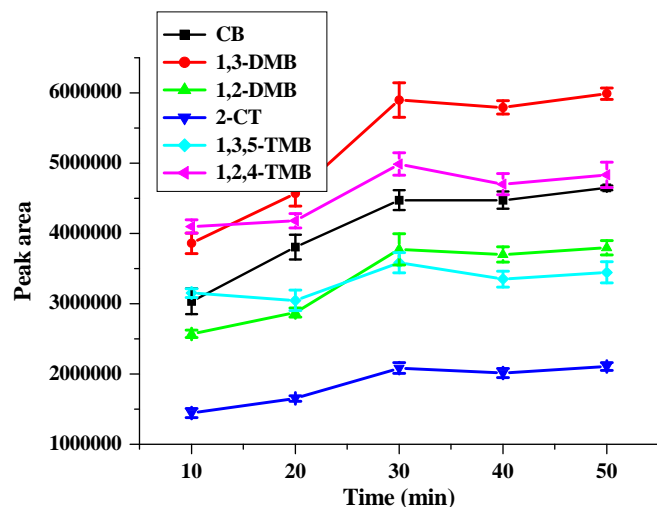


Fig. 7. Variation of extraction efficiency of the poly(PPDA-co-ANI) fiber with extraction time. Extraction temperature: 30 $^\circ\text{C}$. Other conditions as in Fig. 5.

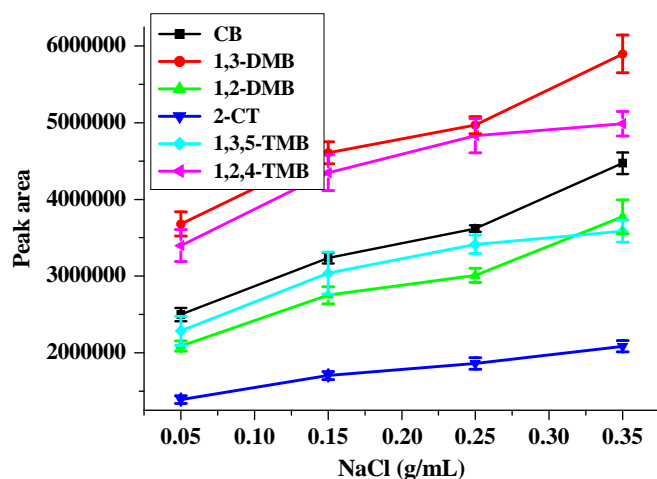


Fig. 8. Influence of NaCl concentration on the extraction efficiency. Other conditions as in Fig. 7.

maximum around 30 min and then it keeps almost unchanged, meaning that extraction equilibriums are achieved for them under this condition.

3.4.3. Stirring rate

With increasing stirring rate, the transfer of analytes from solution to head space is quickened, and the extraction efficiency increases (see supplementary materials, Fig. S5). However, when it exceeds 600 rpm the extraction efficiency decreases. The reason is that the solution is splattered and part of the fiber is covered by salt or/and solution. If this case occurs, the fiber can be renewed by washing with water or/and methanol. Thus, in this work the stirring rate is set at 600 rpm.

3.4.4. Ionic strength

Ionic strength of the solution can affect the extraction efficiency of SPME because the solubility of organic compound varies with it. In this work, NaCl is used to explore the influence of ionic strength. When NaCl concentration is changed from 0.05 g mL^{-1} to 0.35 g mL^{-1} (0.35 g mL^{-1} is the saturated solubility of NaCl) the extraction efficiency increases gradually (Fig. 8). Hence 0.35 g mL^{-1} NaCl is added in the solution for HS-SPME in the following experiments.

3.4.5. Desorption temperature and desorption time

To ensure complete desorption of the extracted analytes and to achieve high sensitivity, the desorption temperature and desorption time are optimized. When the desorption temperature is enhanced the desorption of analytes becomes quick. Considering the decomposition of poly(PPDA-co-ANI) at temperature above 225 °C, here the desorption temperature is fixed at 210 °C. At this temperature the extracted analytes are desorbed completely in 3 min and no memory effect is observed for the blank injection. In addition, the extracted analytes can be well separated under the conditions.

3.5. Linearity, precision and limit of detection

Under the optimized conditions the analytical parameters, including limit of detection (LOD), linear range, repeatability and reproducibility, are tested (Table 1). As can be seen, the LODs calculated are 0.2–0.88 $\mu\text{g L}^{-1}$ ($S/N=3$) for different analytes, which are lower in comparison with those of poly(dimethylsiloxane)-divinylbenzene/quartz and ZrO_2/NiTi fibers [27,28]. The chromatographic peak areas are linear to their concentrations in the ranges of about 0.5 $\mu\text{g L}^{-1}$ to 500 $\mu\text{g L}^{-1}$, with correlation coefficients of 0.9911–0.9989. The run-to-run RSD is 1.8–5.5%, and the fiber-to-fiber RSD is 3.5–12.7% for different analytes. This indicates that the poly(PPDA-co-ANI) fiber has good repeatability and reproducibility. The fiber is also quite stable and durable; after being used for about 140 times, the change of its extraction efficiency (indicated by peak area) is less than 10% except for CB (see supplementary materials, Fig. S6). Part of this change can be ascribed to the fluctuation of experimental conditions.

3.6. Selectivity of poly(PPDA-co-ANI) coating

To evaluate the selectivity of the poly(PPDA-co-ANI) coating, the HS-SPME of other compounds (i.e. 2-chloroaniline, 3-methylaniline, 2-chlorophenol and 2-methylphenol) is performed. The experimental results show that the poly(PPDA-co-ANI) coating presents lower extraction efficiency for the phenol and aniline derivatives than for the benzene derivatives (see supplementary materials, Fig. S7, Table S2). However, when the extraction temperature is enhanced from 30 °C to 50 °C the extraction efficiency increases. This means that the coating is also suitable for the extraction of other compounds.

3.7. Application

The established method is applied to the determination of benzene derivatives in a water sample. The results show that the sample may contain 2-CT and 1,3,5-TMB (Fig. 9), and their concentrations are calculated to be $8.2 \pm 0.9 \text{ ng mL}^{-1}$ and $41 \pm 3.3 \text{ ng mL}^{-1}$, respectively. Afterwards, the water sample is spiked with 1.0 μL

Table 1

Analytical parameters for HS-SPME of benzene derivatives using the poly(PPDA-co-ANI) fiber, followed by GC-FID. Other conditions are the same as in Fig. 5.

Analytes	LOD (ng mL^{-1})	Linear range (ng mL^{-1})	Correlation coefficient	RSD (%)	
				Run to run ($n=5$)	Fiber to fiber ($n=3$)
CB	0.88	0.98–500	0.9989	3.1	7.0
1,3-DMB	0.3	0.5–500	0.9988	3.4	12.0
1,2-DMB	0.225	0.5–500	0.9988	3.4	12.7
2-CT	0.625	0.98–500	0.9932	2.7	12.5
1,3,5-TMB	0.2	0.5–500	0.9911	5.5	7.4
1,2,4-TMB	0.2	1.96–500	0.9986	1.8	3.5

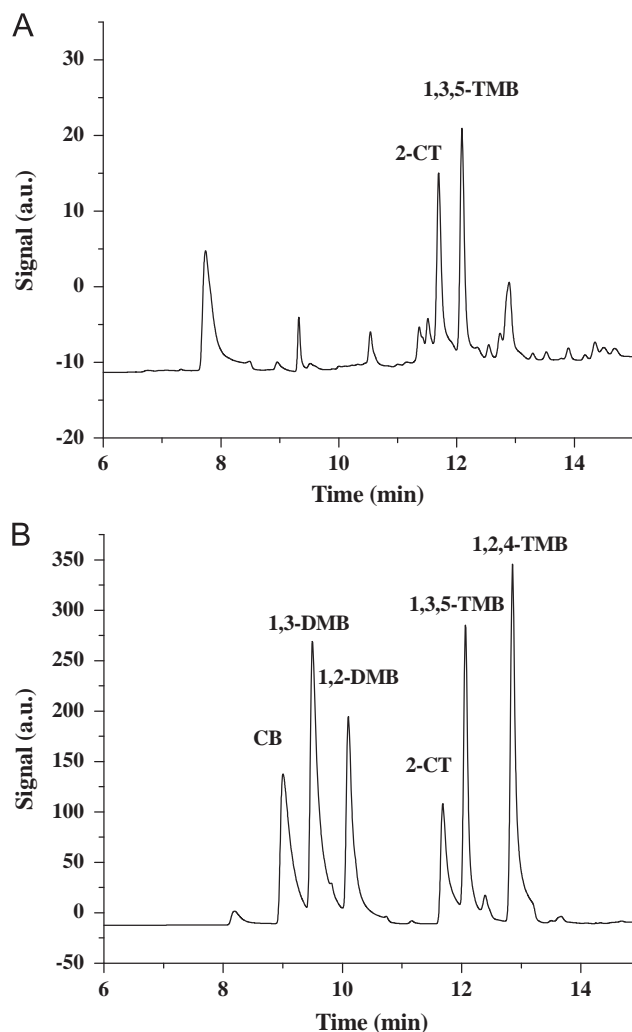


Fig. 9. Chromatograms of water sample after HS-SPME with a poly(PPDA-co-ANI) fiber. (A) Water sample and (B) Spiked sample.

Table 2

Determination results of the water sample using HS-SPME-GC-FID with a poly(PPDA-co-ANI) fiber ($n=3$).

Analytes	Detected in water sample (ng mL^{-1})	Added (ng mL^{-1})	Found (ng mL^{-1})	Recovery (%)
CB	nd ^a	125	121.9 ± 1.9	97.5 ± 1.5^b
1,3-DMB	nd	250	238.5 ± 8.5	95.4 ± 3.4
1,2-DMB	nd	250	246.8 ± 10.8	98.7 ± 4.3
2-CT	8.2 ± 0.9	125	118.9 ± 2.8	89.3 ± 2.1
1,3,5-TMB	41 ± 3.3	250	252.9 ± 7.3	86.9 ± 2.5
1,2,4-TMB	nd	250	269.3 ± 3.8	107.7 ± 1.5

^a Not detected.

^b Mean value \pm standard deviation.

standard solution (containing 2 mg mL^{-1} 1,3-DMB, 1,2-DMB, 1,3,5-TMB, 1,2,4-TMB and 1 mg mL^{-1} CB and 2-CT) and extracted with the poly(PPDA-co-ANI) fiber, followed by GC-FID detection. The recoveries are 86.9%–107.7% for different compounds (Table 2), indicating that the method is credible.

4. Conclusion

A poly(PPDA-co-ANI) coated stainless steel wire is fabricated through electrochemical method. The coating shows thin slice

shape and porous structure, and it has large surface area and large adsorption capacity. In comparison with PANI coating, the poly (PPDA-co-ANI) coating presents much higher extraction efficiency for the benzene derivatives studied. The resulting fiber also shows high mechanical strength, good re-usability and reproducibility. In addition, it is cheap and easy to prepare. Although its thermal stability is not quite satisfactory, the coating is very suitable for the extraction of compounds with lower boiling point. This work provides a new way for making use of different monomers to prepare SPME fibers.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.talanta.2012.07.024](https://doi.org/10.1016/j.talanta.2012.07.024).

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