An electrochemically enhanced solid-phase microextraction approach based on a multi-walled carbon nanotubes/Nafion composite coating

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ABSTRACT

In this paper, we proposed an approach using a multi-walled carbon nanotubes (MWCNTs)/Nafion composite coating as a working electrode for the electrochemically enhanced solid-phase microextraction (EE-SPME) of charged compounds. Suitable negative and positive potentials were applied to enhance the extraction of cationic (protonated amines) and anionic compounds (deprotonated carboxylic acids) in aqueous solutions, respectively. Compared to the direct SPME mode (DI-SPME) (without applying potential), the EE-SPME presented more effective and selective extraction of charged analytes primarily via electrophoresis and complementary charge interaction. The experimental parameters relating to extraction efficiency of the EE-SPME such as applied potentials, extraction time, ionic strength, sample pH were studied and optimized. The linear dynamic range of developed EE-SPME-GC for the selected amines spanned three orders of magnitude ($0.005–1\,\mu g\,mL^{-1}$) with R^2 larger than 0.9933, and the limits of detection were in the range of $0.048–0.070\,ng\,mL^{-1}$. All of these characteristics demonstrate that the proposed MWCNTs/Nafion EE-SPME is an efficient, flexible and versatile sampling and extraction tool which is ideally suited for use with chromatographic methods.

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1. Introduction

Organic polar and ionic compounds, e.g., aromatic amines and carboxylic acids, constitute many classes of important chemical compounds, most of which belong to environmental pollutants, illicit drugs, biomolecules and pharmaceuticals [1–5]. However, direct extraction of these analytes from aqueous solution is one of the most challenging tasks in chemistry because of their hydrophilic nature. Accordingly, prior to extraction, a tedious and labor-intensive chemical derivatization step is always required to decrease the polarity and therefore to enhance the extraction phase/water partition coefficient of these compounds [6,7]. Recently, an electrochemically controlled solid-phase microextraction (EC-SPME) device based on a conductive polymer-based film is proposed for the enhanced extraction of ionic species, which eliminates the need of derivatization [8,9]. The extraction mechanism is based on the movement of counterions in and out of the conductive polymer to maintain its electroneutrality. However, this technique suffers from several drawbacks such as low extraction efficiency, incapability of direct coupling to a chromatographic system and need to incorporate different counterions for anionic and cationic extraction, which impede its broad applicability. To date, most of the publications on EC-SPME are limited on the extraction of inorganic ions, such as metal ions and inorganic anions [10–16].

In this paper, we proposed a very simple approach using an MWCNTs/Nafion composite coating as a working electrode (WE) for the enhanced and selective extraction of ionic compounds, termed electrochemically enhanced SPME (EE-SPME). Instead of the electroneutrality in the case of the EC-SPME mentioned above, the extraction of EE-SPME was primarily driven by electrophoresis and complementary charge attraction, in which negative or positive potential can be easily altered to enhance the extraction of cationic or anionic analytes. To the best of our knowledge, this is the first report on the application of an MWCNTs/Nafion composite as a WE, i.e., fiber coating, for EE-SPME of charged compounds.

2. Experimental

2.1. Reagents and solutions

Aniline (A, ≥99.5%), 4-methylaniline (4-MA, >99%), 4-methoxybenzoic acid (4-MOBA, >99%) and benzyl alcohol (BnOH, >99%) were purchased from the National Medicine Corporation

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(Shanghai, China); benzoic acid (BA, 99%) and 3-chlorobenzoic acid (3-CBA) were provided by Alfa Aesar (Tianjin, China). All the standard solutions used for SPME extraction were prepared to the required concentration using double distilled water. Nafion (a 5% by wt. solution in lower aliphatic alcohols and water) was obtained from Sigma–Aldrich (Milwaukee, WI, USA) and used without further dilution. Stainless steel wires (O.D. 0.15 mm) were obtained from the AnTing Micro-Injector factory (Shanghai, China). Each stainless steel wire used in the experiment was cut to a length of 16.5 cm in order to match the laboratory-made SPME holder and the "hot pot" of the GC inlet. MWCNTs of less than 10 nm diameter, 40–300 m^2/g surface area and 1–2 μm in length were obtained from Shenzhen Nanotech Port (Shenzhen, China).

In order to compare results, a commercial manual sampling SPME device with 85 μm polyacrylate (PA), 75 μm Carboxen/polydimethylsiloxane (CAR/PDMS), 65 μm PDMS/divinylbenzene (DVB) and 100 μm PDMS fibers were all obtained from Supelco (Bellefonte, PA, USA).

2.2. Instrument and analytical conditions

An electrochemical analyzer (LabNet VA5021) was used for the EE-SPME experiments. Sample solution pH was measured using a Cyberscan pH 510 (Eutech, Singapore). All SPME-GC experiments were carried out on a Shimadzu GC-2010 GC system equipped with a flame ionization detector (FID). A Hitachi S4800 scanning electron microscope (Tokyo, Japan) was used to obtain the morphologies of the MWCNTs/Nafion fiber coating.

A 30 m × 0.32 mm I.D., 0.25 μm Rtx-Wax capillary was used for the separation of extracted analytes. The column temperature program for the analysis of the mixture containing A, 4-MA and BnOH was as follows: held at 120 °C for 3 min, then ramped to 240 °C at 20 °C min^{-1}, and held for 1 min; the column temperature selected for carboxylic acids and the mixture containing amines, alcohol and carboxylic acids was the same as above-mentioned program except that the 240 °C temperature was held for 4 min; nitrogen (99.999%) was used as the carrier gas and kept at a rate of 2.5 mL min^{-1}; detector flow rates were set to 30 mL min^{-1} for nitrogen (makeup gas), 47 mL min^{-1} for hydrogen and 400 mL min^{-1} for air.

2.3. Preparation of MWCNTs/Nafion composite coatings

The preparation of MWCNTs/Nafion fiber coating was similar to the ceramic/carbon coating developed by our group [17]. MWC-NTs were packed into a Teflon tube (with 6 mm inner diameter and

the length of MWCNTs in the tube was kept as 1.5 cm). An aliquot of 200 μL Nafion solution was placed into a Teflon tube so as to make the depth of Nafion in the tube 1.5 cm. Prior to coating, the stainless steel wire was ultrasonically cleaned with acetone and ethanol for 10 min, then washed with water and finally dried at ambient temperature. The treated stainless steel wire was dipped into the Nafion solution, then immediately drawn out and placed into the MWCNTs. The stainless steel wire coated with MWCNTs was instantly withdrawn and carefully spun to dislodge the loose MWCNTs. Subsequently, the MWCNTs-coated wire was placed into an oven at 180 °C for 30 min. Finally, the coated stainless steel wire was immersed into the Nafion solution again and pulled out immediately. All of the above-mentioned coating steps were repeated again, and the prepared MWCNTs/Nafion fiber coating was at a length of about 1.5 cm with a thickness of about 25 μm. Before use, the MWCNTs/Nafion-coated fiber was conditioned at 200 °C for 1 h to remove contaminants.

2.4. Experimental setup of the MWCNTs/Nafion EE-SPME device

A schematic of the MWCNTs/Nafion EE-SPME device is shown in Fig. 1. The MWCNTs/Nafion-coated fiber was mounted in a laboratory-made SPME holder [17]. A three-electrode system was constructed using the MWCNTs/Nafion composite coating as the WE, a saturated calomel electrode (SCE) as the reference electrode (RE) and a platinum wire as the counter electrode (CE). A 20-mL sample vial was used as the electro-sampling cell. Potentials were provided by an electrochemistry analyzer with a measuring range from −2.0 to +2.0 V. A magnetic stirrer (IKA-Werke, Staufen, Germany) with a speed range of 0–1500 rpm was used to agitate the sample solutions during the EE-SPME.

2.5. SPME procedure

A 10-mL aliquot of standard solution with varying concentrations of analytes was placed in a 20-mL sample vial with a magneton. The sample solution pH was adjusted using 0.1 mol L^{-1} hydrochloric acid (HCl) or 0.1 mol L^{-1} sodium hydroxide (NaOH). Three electrodes were connected to the electrochemistry analyzer, and a potential was provided by the electrochemical analyzer. The EE-SPME and DI-SPME experiments were performed at room temperature for 10 min under stirring at a rate of 750 rpm. After extraction, the fiber was immediately removed from the solution. Finally, the fiber was introduced into the GC injector and the extracted analytes were desorbed at 200 °C for 4 min.
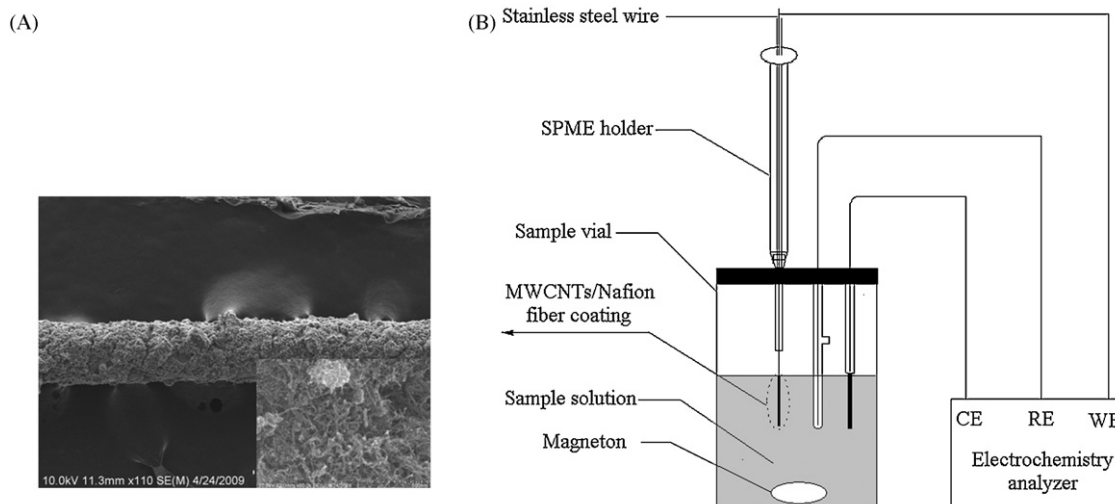

Fig. 1. (A) Scanning electron micrographs of the MWCNTs/Nafion fiber coating and (B) schematic of the proposed MWCNTs/Nafion EE-SPME device.

3. Results and discussion

3.1. Fundamental feature of the MWCNTs/Nafion EE-SPME method

The fundamental feature of the EE-SPME method is similar to that of adsorptive stripping analysis [18,19]: when a suitable negative potential is applied on the WE, the fiber coating is negatively charged and an electrical field is formed. Positively charged analytes are then attracted to the surface of the coating via electrophoresis under electrical field, and subsequently entrapped in the coating via complementary charge attraction. Similarly, a suitable positive potential could also be applied for the enhanced and selective extraction of negatively charged analytes. Thus, using this simple approach, the polarity and magnitude of applied potentials can be readily fine-tuned to enhance the extraction of oppositely charged analytes. To fulfill the hypothesis, the fiber coating, i.e., WE, should possess two characteristics: (1) the coating should be electro-conductive so that it can be charged via control of the potential applied, and (2) the coating should have good adsorptive capabilities and affinity towards the polar analytes, and thus the charged analytes approaching the surface of the coating would be entrapped. Based on these two considerations, we used Nafion as a binder to immobilize MWCNTs on a stainless steel wire base to prepare an MWCNTs/Nafion composite as a fiber coating. MWCNTs have recently attracted great attention due to their unique electronic properties, high surface area-to-volume ratio and good affinity towards aromatic compounds [20–22]. Nafion is a kind of cation exchange polymer well known to be highly conductive and have special affinity towards polar analytes [23,24]. To evaluate the extraction ability of the MWCNTs/Nafion composite coating, several commercial coatings including 85 μm PA, 100 μm PDMS, 65 μm PDMS/DVB and 75 μm CAR/PDMS were selected for comparison. Fig. 2 shows that the MWCNTs/Nafion fiber coating overall presented comparable extraction ability for the selected analytes (A, 4-MA and BnOH) compared to those of the commercial fiber coatings. Since all the compounds selected have a benzene ring and polar groups, the good extraction efficiency obtained for the MWCNTs/Nafion fiber coating was attributed to three aspects: MWCNTs possess a high surface area-to-volume ratio, exhibit a strong π–π conjugated interaction with the benzene ring, and Nafion presents high affinity for the polar groups. In addition,
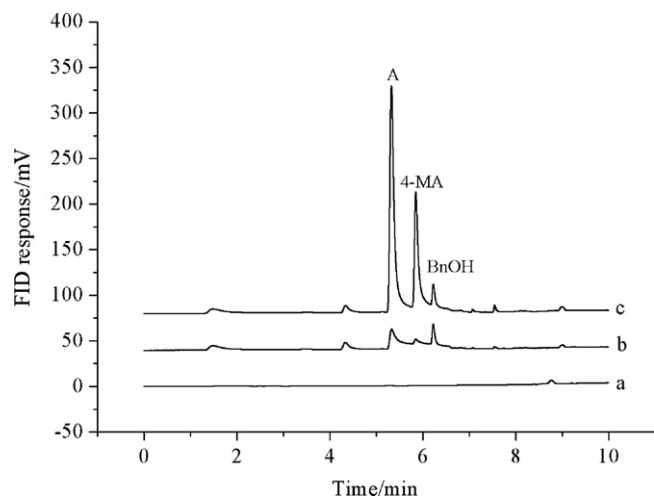
Fig. 3. Comparison of chromatograms between (a) EE-SPME of a standard mixture (1 μg mL^{-1}) at pH 3 using a stainless steel wire; (b) DI-SPME of the same sample solution using an MWCNTs/Nafion fiber coating; and (c) EE-SPME of the same sample solution using the same MWCNTs/Nafion fiber coating.

MWCNTs and Nafion are well known to be electro-conductive [25,26], which was another important factor we considered in the use of EE-SPME.

3.2. EE-SPME procedure for protonated amines

The enhanced and selective extraction of positively charged analytes with EE-SPME using a negatively applied potential was first demonstrated. Two aromatic amines, A and 4-MA, were selected as model compounds. To visualize the enhancement effect and selectivity for the selected amines, an aromatic alcohol, BnOH, was selected as the reference compound, since it is difficult to charge under different pH values. A standard mixture containing each selected amine and alcohol was used for the comparison of direct SPME (DI-SPME) (without applying potentials) and EE-SPME. An aliquot of 50 μL HCl (0.1 mol L^{-1}) was added to the standard mixture to protonate the amines, and the adjusted pH of the sample solution was 3. After that, a negative potential of −0.5 V was applied for the EE-SPME procedure. Fig. 3c shows that enhancement factors of 6.2 and 5.5 for A and 4-MA were obtained for EE-SPME in comparison to those of DI-SPME (Fig. 3b), and no obvious change to the BnOH was found during extraction. This result confirmed that the enhanced extraction mechanism is primarily based on the electrophoresis and complementary charge interaction, and so the extraction of neutral alcohol was inert to the applied potential. Hence, by means of EE-SPME, the extraction efficiency and selectivity (versus BnOH) for amines was both obviously improved. To exclude any possible adsorption ability from the blank fiber, a bare stainless steel wire was used to test EE-SPME under the same conditions. Fig. 3a shows that the blank fiber could not extract any of the analytes, although it was also highly conductive. This result also proved that both conductive and adsorptive properties are compulsory for the application of EE-SPME.

3.3. Optimization of EE-SPME procedure

For the validation of the EE-SPME analytical method, it is obvious that the applied potential is the most important parameter to be optimized. To investigate the effect of applied potentials on the extraction efficiency and selectivity, a potential from −1.2 to 0.5 V, relative to SCE, was applied in the EE-SPME of three analytes. The sample solution pH was adjusted to 3. As depicted in Fig. 4A, the extraction efficiency for the selected amines increased obvi-
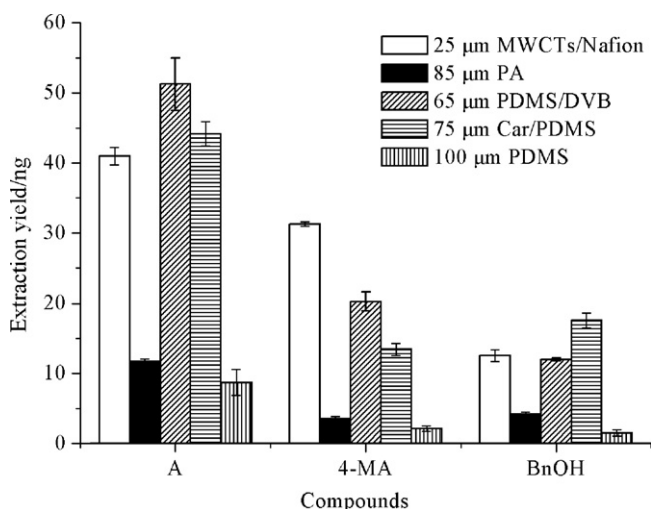
Fig. 2. Comparison of the extraction ability of the selected analytes between a MWCNTs/Nafion-coated fiber and commercial fibers. Concentration of each analyte was 1 μg mL^{-1}. The displayed error bars represent the standard deviation of extraction yields over three extractions.

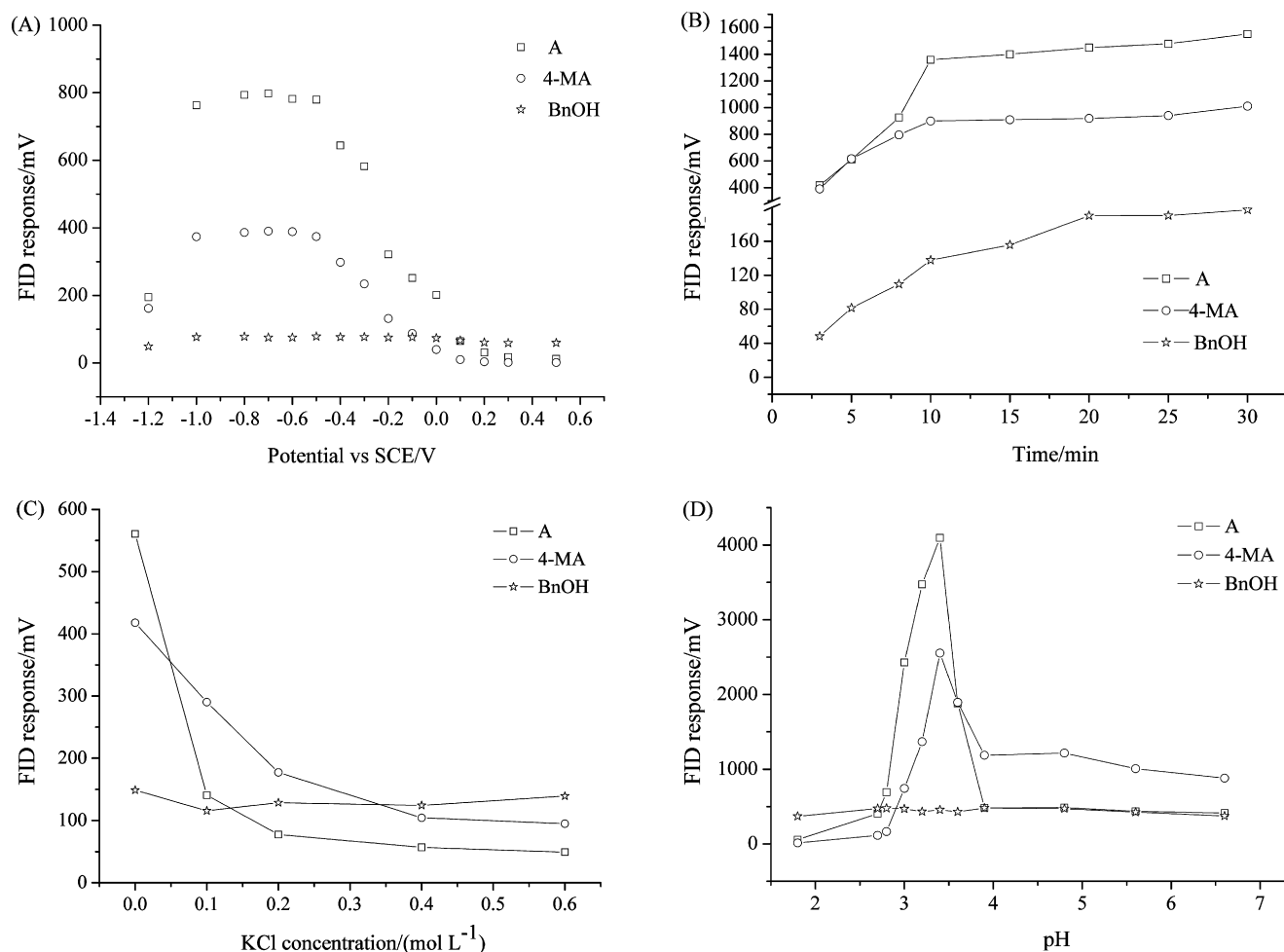**Fig. 4.** Effect of applied potential (A), extraction time (B), ionic strength (C) and sample pH (D) on EE-SPME of the selected analytes in corresponding replicates of the standard mixture. Concentration of each analyte in the standard mixture was 1 μg mL^{-1}.

ously as the potential varied from 0.5 to −0.5 V and tended to reach equilibrium from −0.5 to −0.8 V. With the application of positive potentials, the positively charged fiber coating repelled the protonated amines and thus resulted in lower efficiency. In contrast, the application of negative potentials made the fiber coating negatively charged and therefore enhanced the extraction of protonated amines via electrophoresis and complementary charge interaction. It should be noted that a sharp increase of extraction efficiency was observed from −0.2 to −0.3 V. This result indicates that the potential of zero charge for the electrode may lie in this range, which was similar to that obtained by measuring the differential capacitance as a function of electrode potential (approximately −0.3 V). At a more negative potential, stronger electrophoresis and complementary charge interaction were achieved and resulted in higher extraction efficiency. When the potential was modulated to −1.0 V, a few bubbles slowly escaped from the fiber coating surface due to hydrogen evolution. At a more negative potential up to −1.2 V, a larger number of bubbles occurred and floated on the fiber coating surface, which severely interrupted the extraction of analytes and resulted in much lower extraction efficiency. Furthermore, the bubble generation resulted in the MWCNTs/Nafion coating being cast off the fiber base easily and so shortened its lifetime. Fig. 4A also shows that the extraction efficiency of BnOH was barely affected as the applied potentials ranged from −1.0 to 0.5 V, since the extraction of neutral BnOH was inert to the potential transformation. These results also verified that the extraction mechanism was primarily based on electrophoresis and comple-

mentary charge interaction. Accordingly, an optimum potential of −0.5 V was selected for the following experiments.

The extraction time profile was constructed by plotting the peak areas of the selected analytes versus extraction time. As displayed in Fig. 4B, the peak areas for the amines selected rapidly increased from 3 to 10 min and tended to level off thereafter. A 10-min extraction was calculated to result in extraction amounts of 87, 89 and 68% for A, 4-MA and BnOH as compared with those of a 30-min extraction. The faster extraction rates for the amines were obtained because the electrical field accelerated the movement of protonated amines to the surface of the fiber coating via electrophoresis. The extraction of BnOH was barely affected by the electrical field and was primarily based on passive diffusion, and hence the slower extraction rate. However, it should be pointed out that the equilibration time for the target analytes in this study was longer than that reported in other electro-immigration based extractions [27], probably due to the relatively large volume of the sample vial (20-mL) used in this study. For the electro-immigration based extraction, the electrical field showed a strong impact on the immigration of the ions in a small space, due to the short distance between the electrodes [27]. As the dimension of the sample vial increased, the electrical-field effect decreased because the distance between the electrodes increased. Consequently, it is expected that the equilibration time could possibly be reduced by using a smaller sample vial. Taking both the sensitivity and the analysis speed of the method into account, a 10-min extraction time was employed for the rest of the experiments.

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For EE-SPME, agitation of the sample was also an important parameter to be considered. The results (not shown) reveals that, with stirring at a rate of 750 rpm, the peak areas for A and 4-MA were 3.0 and 2.7 fold higher than those with no stirring. In EE-SPME, electrokinetic migration was the main approach of mass transfer. In a quiescent solution, the electro convection of the charged analytes through a boundary layer of ions at the interfaces was suppressed and resulted in a weak electro migration [28]. The application of agitation significantly affected the boundary layer and thus reduced the electrical resistance and facilitated electro migration. This variation in agitation trend is in accordance with that in the electro membrane isolation method [27–29]. Although a higher stirring rate resulted in higher extraction efficiency for the selected amines, a stirring rate beyond 750 rpm resulted in hopping of the magneton and hence poor reproducibility of the extraction efficiency. As a consequence, a stirring rate of 750 rpm was used for the subsequent experiments.

Typically, the addition of supporting electrolyte increases the electrical conductivity of the sample solution and thus facilitates the movement of target ions. On the other hand, the ions from the supporting electrolyte may interfere in the approach of target ions towards the surface of the fiber coating. To study the effect of the supporting electrolyte, replicates of standard mixture containing different concentration of potassium chloride (KCl) were employed for EE-SPME. Fig. 4C shows that the extraction efficiency of EE-SPME for both amines decreased as the increase of KCl concentration. This result indicated that the concentration of H^+ at pH 3 was sufficient to act as an electrolyte for EE-SPME and that the K^+ and Cl^- from the addition of KCl disturbed the extraction of target ions. Accordingly, in the following experiments, no supporting electrolyte was added into the solution.

As discussed above, the addition of HCl was the key step to the success of EE-EPME, since it not only ensured the complete protonation of the selected amines, but also served as a supporting electrolyte. However, as in the case of KCl mentioned above, H^+ from the excessive amount of HCl may also interfere with the extraction of target ions. Accordingly, the amount of HCl in the sample solution is likely to present a double impact on the extraction efficiency of target analytes. The extraction efficiency of EE-SPME for the selected analytes was investigated in the pH range from 1.8 to 6.6. As can be seen in Fig. 4D, the decrease of pH from 6.6 to 4.8 led to a minor increase of the extraction efficiency for both amines. Theoretically, protonated amines were supposed to be the major forms in the solution in the pH range from 4.8 to 6.6, since the apparent pK_a of A (9.4) and 4-MA (8.7) were both two magnitudes higher than the sample solution pH. However, little difference of extraction efficiency between EE-SPME and DI-SPME was observed in this pH range, which indicated that no obvious enhancement of extraction efficiency was obtained for EE-SPME. This phenomenon was possibly due to the fact that the electrical resistance of the sample solution in this pH range was large, so that the electro-immigration of the target ions was suppressed, so leading to lower extraction efficiency for EE-SPME. During the experiment, we found that the extraction efficiency fluctuated extremely at a pH range from 3 to 4. It is apparent that the optimum pH lies in this range, which caused us to carefully investigate the pH effect in this range. Fig. 4D shows that the extraction efficiency for selected amines reached a maxi-
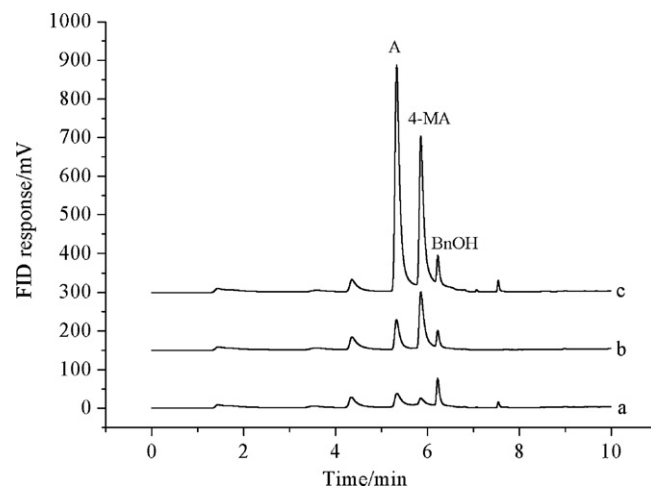

Fig. 5. Comparison of chromatograms between (a) DI-SPME of the standard mixture (1 μg mL^{-1}) at pH 3.4; (b) DI-SPME of the standard mixture (1 μg mL^{-1}) at pH 10.2; and (c) EE-SPME of the same sample solution with (a).

mum at pH 3.4 and declined at a higher or lower pH. As expected, the extraction efficiency of BnOH was hardly influenced over the entire pH range. An optimum pH of 3.4 was therefore adapted for further experiments.

An experiment was performed to evaluate more precisely the improvement of extraction efficiency with EE-SPME under its optimized conditions. A standard mixture, which was used for DI-SPME, was added with an aliquot of 20 μL NaOH (0.1 mol L^{-1}), and the adjusted pH of the sample solution was 10.2. This procedure was carried out to deionize the selected amines and to obtain the optimal extraction efficiency for DI-SPME. Fig. 5b shows that the peak areas of A and 4-MA were obviously improved by a factor of 2.2 and 6.2 at pH 10.2 under the DI-SPME mode. However, compared to the optimal results from DI-SPME, EE-SPME was still more effective in terms of its enrichment capability. It can be observed from Fig. 5c that the peak areas of A and 4-MA with EE-SPME at pH 3.4 were still 6.6 and 3.0 fold larger than those presented in Fig. 5b. These results further demonstrated that EE-SPME appears to be a more efficient preconcentration technique in comparison to DI-SPME.

3.4. Analytical performance of the MWCNTs/Nafion EE-SPME-GC method

The analytical performance of the proposed EE-SPME-GC method was evaluated based on the analytical data obtained in Table 1, including linear dynamic range (LDR), determination coefficient (R^2), limits of detection (LODs) and reproducibility. Analyses of spiked water sample (0.005, 0.01, 0.05, 0.1, 0.2, 0.5, 1, 5 and 10 μg mL^{-1}) were performed to investigate the LDRs of the proposed method. As summarized in Table 1, the LDRs of EE-SPME-GC for selected amines and BnOH spanned three orders of magnitude with R^2 larger than 0.9933. This result indicated that the proposed MWCNTs/Nafion EE-SPME-GC method could be used for the external determination of target analytes in aqueous solution. The slope of the calibration curve and the LODs, which are indicators

Table 1
Analytical data of the proposed EE-SPME-GC-FID method for the determination of selected amines and BnOH.

Compounds	LDR (μg mL^{-1})	R^2	Slope (mV/(ng mL^{-1}))	Intercept (mV/(ng mL^{-1}))	RSD (%, $n = 5$)	LOD^a (ng mL^{-1})
A	0.005–1	0.9933	3.0	55.3	10.9	0.048
4-MA	0.005–1	0.9984	1.3	4.1	9.7	0.070
BnOH	0.05–10	0.9975	0.22	20.8	3.8	0.56

^{a} LODs were calculated as the average amount of analyte yielding a response which was three fold the noise.

of method sensitivity in regard to the same detector, were both approximately one magnitude better for A and 4-MA than those for BnOH due to the enhancement effect via EE-SPME. The LODs obtained for selected amines in this study were lower than those reported in other SPME-based methods using the same detector (FID) [30]. For determination of method precision, five replicates of a sample containing each analyte at a concentration of 0.1 μg mL^{-1} were analyzed. The relative standard deviations (RSDs) of EE-SPME ranged from 3.8% to 10.9%, which were higher than those of DI-SPME (2.9–5.2%). A possible reason was that the application of electric potentials continuously changed the morphology of the fiber coating, and thus caused the lower reproducibility [8]. Based on the experimental results, the MWCNTs/Nafion-coated fiber was durable and could be used more than 100 times without obvious decline of extraction ability.

3.5. EE-SPME procedure for deprotonated carboxylic acids

To further extend the application field of the proposed EE-SPME, an example involving a positive potential on the fiber coating for the extraction of negatively charged compounds was preliminarily demonstrated. Three aromatic carboxylic acids, BA, 3-CBA and 4-MOBA, were selected as model compounds for this series of study. An aliquot of 20 μL NaOH (0.1 mol L^{-1}) was added to the standard mixture (1, 0.05 and 0.02 μg mL^{-1}) to deprotonate the selected carboxylic acids. Subsequently, a positive potential of 1.0 V was applied for the EE-SPME procedure. Fig. 6A shows that, in comparison to the chromatogram of DI-SPME, with the applied potential at 1.0 V, the peak areas greatly increased with an enhancement factor of 11.7, 5.8 and 4.6 for BA, 3-CBA and 4-MOBA, respectively. When the spiked level was down to 0.05 μg mL^{-1}, no integral peak of BA could be obtained in the DI-SPME chromatogram (Fig. 6Ba), but in the EE-SPME mode, the peak of BA appeared and the enhancement factors for 3-CBA and 4-MOBA were 6.8 and 4.2, respectively (Fig. 6Bb). A similar phenomenon was observed at a spiked level of 0.02 μg mL^{-1}. In the chromatograms, the peaks of BA and 4-MOBA could not be detected with DI-SPME (Fig. 6Ca), but they appeared clearly in the chromatogram with EE-SPME (Fig. 6Cb). In addition, an enhancement factor of 6.9 was obtained for 3-CBA. These preliminary results indicate that, by simply switching to a suitable positive potential, EE-SPME could be used for the enhanced extraction of anionic analytes without the need to modify the fiber coating. It should be noted that suitable positive potential should be carefully selected to avoid the oxidation and decomposition of corresponding analytes.

3.6. Selective extraction of anionic and cationic analytes in the same aqueous solution

Another important aspect of this study is to evaluate the availability of proposed EE-SPME for the selective extraction of anionic and cationic analytes in the same aqueous solution, respectively. Two amines (A and 4-MA), one alcohol (BnOH) and two carboxylic acids (BA and 3-CBA) were prepared together as a mixed standard solution. The sample pH was firstly adjusted to 3 and a negative potential (−0.5 V) was applied for the EE-SPME procedure. Fig. 7A shows that the peak areas for A and 4-MA increased with enhancement factors of 3.1 and 8.8, while those for BnOH and two carboxylic acids remain almost unchanged. After that, the sample solution was adjusted to pH 10 and a positive potential of 1.0 V was used for the EE-SPME procedure. As expected, enhancement factors of 5.5 and 3.8 were obtained for BA and 3-CBA, while the extraction efficiency for the amines and alcohol dramatically declined (Fig. 7B). This interesting phenomenon probably arose from the fact that amines and alcohol are oxidized at $E > 0.6$ V [9,31–33]. This result also reminds us another possible means to fine-tune extraction
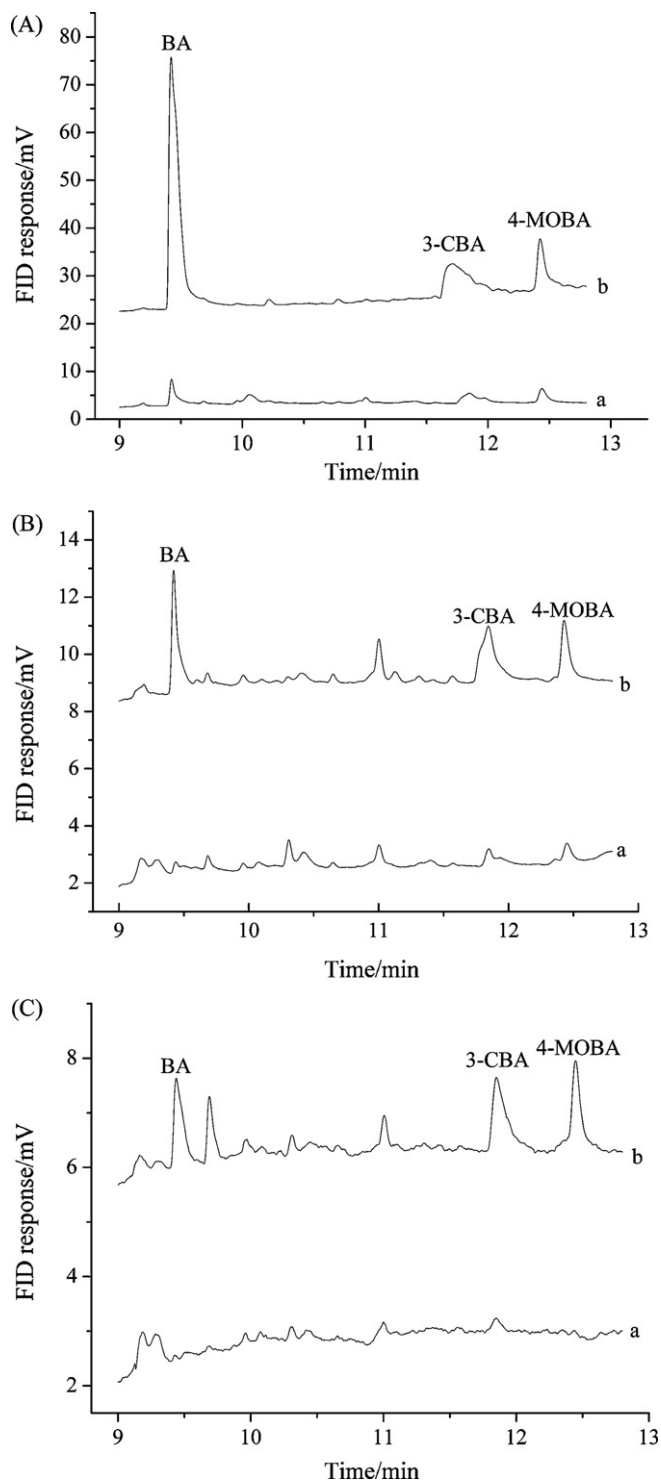

Fig. 6. Chromatograms obtained for standard mixtures containing each carboxylic acid: (A) at 1 μg mL^{-1}, with (a) DI-SPME of the sample solution at pH 10 and (b) EE-SPME of the same sample solution; (B) at 0.05 μg mL^{-1}, with (a) DI-SPME of the sample solution at pH 10 and (b) EE-SPME of the same sample solution; and (C) 0.02 μg mL^{-1}, with (a) DI-SPME of the sample solution at pH 10 and (b) EE-SPME of the same sample solution.

selectivity based on the redox electrochemical properties of different analytes. Although these experiments were somewhat rough, they preliminarily proved that the enhanced and selective extraction of anionic and cationic analytes in the same solution could be separately obtained simply by altering the potential from an electrochemical analyzer. We believe that, after elaborate optimization
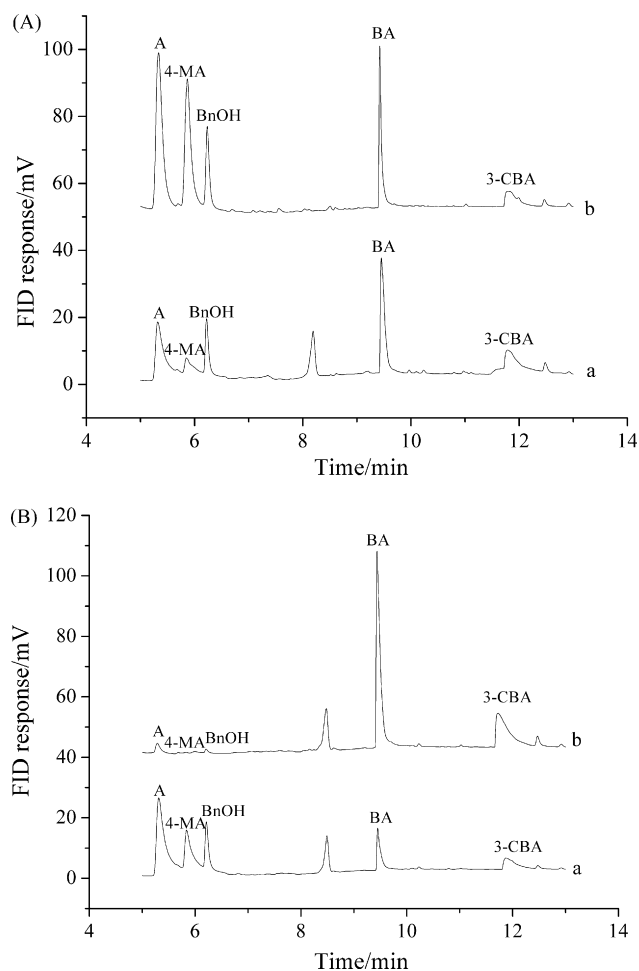
Fig. 7. Chromatograms obtained for the standard mixture: (A) at pH 3 with (a) DI-SPME and (b) EE-SPME with a negative potential of −0.5 V; (B) at pH 10 with (a) DI-SPME and (b) EE-SPME with a positive potential of 1.0 V. Concentration for A, 4-MA and BnOH: 0.1 μg mL^{-1}; for BA and 3-CBA: 1 μg mL^{-1}.

of the conditions, the extraction selectivity is likely to be further improved.

4. Conclusions

In summary, we proposed a very simple and effective approach using an MWCNTs/Nafion fiber coating as a working electrode for the EE-SPME of organic ionic compounds. By simply altering the potential from an electrochemical analyzer, the enhanced and selective extraction of cationic (protonated amines) and anionic compounds (deprotonated carboxylic acids) in the same aqueous solution could be separately obtained without the need to modify fiber coating. Based on the results obtained, it can be predicted that the EE-SPME technique could be used for the enhanced extraction of other ionic species, especially for basic drugs, most of which

are protonated amines in aqueous solution. Work is in progress to develop the EE-SPME technique on the enhanced extraction of basic drugs in aqueous solutions, such as biological fluids. In addition, other electro-conductive materials with good adsorptive characteristics, e.g., metallic nano-materials and graphene, are likely to be specially designed for EE-SPME applications to various charged analytes.

Acknowledgements

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