Electrochemical preparation of polyaniline–ionic liquid based solid phase microextraction fiber and its application in the determination of benzene derivatives

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ABSTRACT

A polyaniline–ionic liquid (i.e. 1-butyl-3-methylimidazolium tetrafluoroborate, $[C_4mim][BF_4]$) composite film coated platinum wire (PANI–IL/Pt) was prepared by electrochemical method for the first time. Scanning electron microscopy image showed that the PANI–IL composite film was even and porous. When the PANI–IL/Pt was used as a fiber for the headspace solid-phase microextraction (HS-SPME) of some benzene derivatives (i.e. 1,3-dimethylbenzene, 1,2-dimethylbenzene, 1,4-dichlorobenzene, 1,2-dichlorobenzene, 1,3,5-trimethylbenzene and 1,2,4-trimethylbenzene), followed by gas chromatographic analysis, it presented excellent performance, which was much better than that of PANI/Pt and commercial polydimethylsiloxane fiber. Hence the fiber was coupled with gas chromatography for the determination of these benzene derivatives. It was found that under the optimized conditions the linear ranges were 0.04–400 $\mu g\,L^{-1}$ with correlation coefficients above 0.99, the detection limits were 9.3–48.1 $ng\,L^{-1}$ (S/N = 3), the relative standard deviations (RSDs) were smaller than 5.1% for five successive measurements with single fiber, and the RSDs for fiber-to-fiber were 5.0–11.1% (n = 3) for different benzene derivatives. The proposed method was successfully applied to the extraction and determination of benzene derivatives in waste water and tap water, and the recoveries were 87.1–108.1% for different analytes. Therefore, the PANI–IL/Pt is a promising SPME fiber.

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1. Introduction

Benzene derivatives are important industrial materials, but they are also recognized as pollutants. Early in the seventies of last century, some benzene derivatives such as methylbenzene and ethylbenzene, were included in the list of priority pollutants of the US Environmental Protection Agency (EPA). In the nineties a series of benzene derivatives were included in the list of priority pollutants of Chinese Environmental Protection Agency. Benzene derivatives generally decompose slowly in the environment; hence their danger can last long time.

Benzene derivatives are usually determined by gas chromatography. In order to enhance their concentration and to avoid the interference of other substance, the samples are generally pretreated prior to their determination. Several approaches, including liquid–liquid extraction [1,2], purge-and-trap [3], solid-phase extraction [4,5] and solid phase microextraction (SPME), have been used for this purpose. Among them SPME attracts increasing attention from researchers because it has many distinct advantages,

such as solvent-free, simple, rapid, less sample-consuming and easy to couple with other technologies. At the same time, it is very suitable for the pretreatment of volatile and semivolatile organic compounds. So far, many SPME fibers have been fabricated for the determination of benzene derivatives [6–10]. However, these fibers still show some drawbacks such as high cost and poor durability. Hence, to fabricate new fibers with better performance is significant.

SPME fibers can be fabricated through different methods. Electrochemical method was used firstly by Wu and Pawliszyn for the fabrication of SPME fibers [11]. Afterward, Wang et al. and Li et al. used the method to prepare PANI based fibers for the determination of chlorobenzene, nitrobenzene and substituted benzenes in water [12,13]. In comparison with conventional method (i.e. manual coating), electrochemical method is relatively simple. It can combine surface treatment, coating and modification into one step, and the thickness and structure of the coat can be controlled by changing deposition potential, deposition time and/or solution composition [14–16]. In addition, metal wires are used as substrate in electrochemical coating-approach; hence the resulted fibers have higher mechanical strength.

Ionic liquids (ILs) are novel solvents and they have been widely used in electrochemistry, synthesis, extraction separation, and so

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on. For example, Jiang and Zhao used disposable IL drops and IL-coated fibers in the microextraction of organic compounds and some interesting results were obtained [17–20]. Sekiguchi et al. studied the electrochemical polymerization of pyrrole in 1-butyl-3-methylimidazolium hexafluorophosphate ([Emim]PF$_6$), [Emim]BF$_4$ and [Emim]N(Tf)$_2$, and found that the anion influenced the structure and property of the polymer greatly [21]. Wei et al. declared that they obtained improved PANI film through electrochemical polymerization of aniline in [Bmim]PF$_6$–CF$_3$COOH mixture [22]. However, to the best of our knowledge, there are no reports on the fabrication of PANI–IL based SPME fibers through electrochemical method.

In the present work, a PANI–IL composite film coated platinum wire is fabricated through electrochemical polymerization. The obtained fiber (PANI–IL/Pt) is assessed by SPME-GC technique with benzene derivatives as models. It shows excellent performance and it is a promising SPME probe.

2. Experimental

2.1. 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 m × 0.25 mm I.D.) with 0.25 μm film thickness (Lanzhou Atech Technologies, Lanzhou, China). The following oven temperature program was used: 50 °C hold for 3 min, followed by increasing temperature at 15 °C min^{-1} to 110 °C, and 2 °C min^{-1} to 130 °C, then at 10 °C min^{-1} to 150 °C and kept at this temperature for 2 min. The total run time was about 30 min. The injection port temperature was set at 220 °C and the extracted analytes were desorbed for 3 min. Its inlet was operated under the splitless mode and the on-column flow-rate of nitrogen gas was 16 cm s^{-1}. The FID temperature was kept at 250 °C. The SPME device was laboratory-made. The scanning electron microscopy 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).

Electrochemical polymerization of aniline (ANI) was performed on a CHI 660A electrochemical workstation (CH Instrument Corp., Shanghai, China) using a cyclic voltammetry mode at 25 ± 2 °C. Conventional three-electrode system was adopted, including a Pt wire (2 cm × 280 μm O.D.) as working electrode, a Pt counter electrode (2.5 cm × 0.1 cm O.D.) and a saturated calomel electrode (SCE) as reference electrode.

2.2. Reagents

Aniline was purchased from the Reagent Factory of Shanghai (China) and was purified through vacuum distillation before use. The [C$_4$mim][BF$_4$] (98%) was obtained from Alfa Aesar.

1,3-Dimethylbenzene (1,3-DMB), 1,2-dimethylbenzene (1,2-DMB), 1,4-dichlorobenzene (1,4-DCB), 1,2-dichlorobenzene (1,2-DCB), 1,3,5-trimethylbenzene (1,3,5-TMB) and 1,2,4-trimethylbenzene (1,2,4-TMB) were from Sinopharm Group Chemical Reagent Co. (Shanghai, China). The stock solutions of 1,3-DMB (1.0 mg mL^{-1}), 1,2-DMB (1.0 mg mL^{-1}), 1,4-DCB (1.0 mg mL^{-1}), 1,2-DCB (1.0 mg mL^{-1}), 1,3,5-TMB (2.0 mg mL^{-1}) and 1,2,4-TMB (2.0 mg mL^{-1}) were prepared with methanol and stored in a refrigerator. Working solutions were prepared by
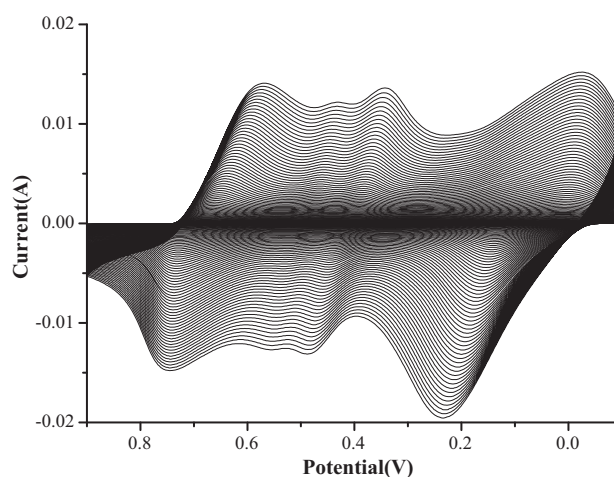
Fig. 1. Cyclic voltammograms for the electrochemical deposition of PANI–IL film on Pt wire. Potential range: −0.1–0.9 V; scan rate: 50 mV s^{-1}; electrolyte solution: 0.1 M ANI + 1 M HNO$_3$ + 0.3% (V/V) IL.

diluting the stock solutions with deionized water. The solution pH was adjusted with 0.10 M sodium hydroxide and 0.10 M nitric acid. The samples were waste water (from a local printing and dyeing factory, Wuhan, China) and tap water.

2.3. Fabrication of PANI–IL coated Pt wire

Prior to coating the Pt wire was treated with 5.0 M HNO$_3$ and acetone each for 15 min, with aid of ultrasonic agitation, and then rinsed with distilled water. The electrode-system was immersed in 0.1 M ANI + 1 M HNO$_3$ + 0.3% (V/V) IL solution, and the potential scan was cycled for 200 times between −0.1 V and 0.9 V at scan rate of 50 mV s^{-1}. During the electrochemical polymerization, the surface of Pt wire gradually became black and the voltammetric peaks increased (Fig. 1), indicating the formation of PANI–IL film. The PANI–IL film coated Pt wire was washed with methanol and deionized water, and subsequently was kept in a desiccator for 24 h at room temperature. Then it was immobilized on the laboratory-made SPME device with high-temperature epoxy resin as mentioned elsewhere [23], followed by conditioned in the GC injection port under nitrogen at 90 °C for 30 min, at 130 °C for about 1 h, at 200 °C for 2 h. Thus a smooth baseline was observed. According to the SEM experimental result, the thickness of the PANI–IL film was estimated to be about 80 μm. For comparison, a PANI coated Pt wire was fabricated under the same conditions except the 0.1 M ANI + 1 M HNO$_3$ + IL solution was replaced by a 0.1 M ANI + 1 M HNO$_3$ solution.

2.4. Headspace SPME procedure

A 10-mL aqueous solution containing proper benzene derivatives (0.1–0.2 μg mL^{-1}) was transferred into a 15 mL glass vial with PTFE–silicon septum. After adding appropriate sodium chloride and magnetic stirring bar, the vial was tightly sealed with an aluminum cap. The sample vial was placed on a magnetism mixer (Ronghua Instrument, Jiangsu, China) with a water bath. When the temperature reached the fixed value, the PANI–IL/Pt was exposed to the headspace over the stirred solution for 10–60 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.
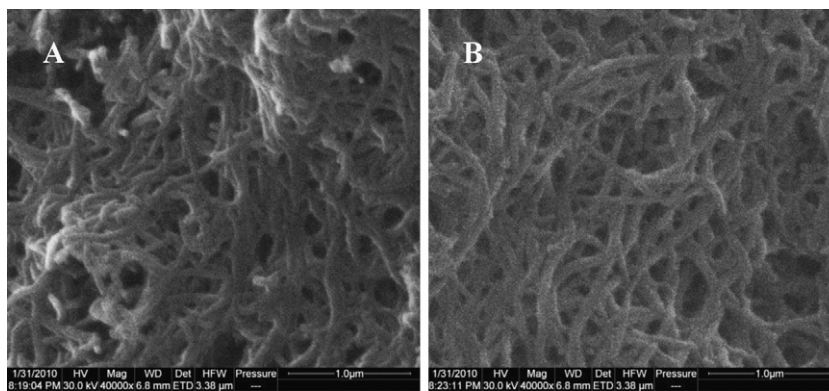
Fig. 2. SEM images of PANI film (A) and PANI–IL film (B).

3. Results and discussion

3.1. Characterization of PANI–IL composite film

Fig. 2 shows the SEM images of PANI and PANI–IL films. As can be seen, they present netty structure, but the PANI–IL film is more even and porous, implying that it possesses larger surface area. This can be ascribed to the influence of IL on the polymerization process of aniline because it can be adsorbed on the surface of Pt wire and may interact with aniline and PANI. FTIR spectrum shows that the components or molecular structures of PANI and PANI–IL films are different to some extent. This indicates that a few IL must be retained in the PANI film in the presence of IL and it may influence the PANI structure.

3.2. Optimization of extraction conditions

The extraction efficiency of fibers is dependent on extraction conditions, such as ionic strength, extraction time, extraction temperature and stirring rate. In order to obtain high extraction efficiency these conditions are optimized, taking 1,3-DMB, 1,2-DMB, 1,4-DCB, 1,2-DCB, 1,3,5-TMB and 1,2,4-TMB as models. All experiments are carried out in triplicate.

3.2.1. Extraction temperature

The headspace-extraction temperature is changed from 20 °C to 60 °C to explore its influence (Fig. 3). It is clear, the extraction efficiency increases with the solution temperature rising up to 40 °C, then it decreases slowly or keeps almost unchanged for different analytes. When the temperature exceeds 50 °C, the extraction efficiency decreases. In general, with temperature rising more analytes enter gas phase, and their adsorption or extraction achieves equilibrium more rapidly. But the adsorption amount may decrease because adsorption is an exothermic process. In this case 40 °C is optimum temperature.

3.2.2. Extraction time

Extraction efficiency usually varies with extraction time. When the extraction equilibrium is not reached yet, the extraction efficiency increases with prolonging extraction time. Therefore, extraction time affect the sensitivity and reproducibility of HS-SPME. Fig. 4 depicts the variation of extraction efficiency with extraction time. When the extraction time exceeds 30 min, the extraction efficiency reaches maximums for 1,3-DMB, 1,2-DMB, 1,3,5-TMB and 1,2,4-TMB, meaning that their extraction achieves equilibrium. As for 1,4-DCB and 1,2-DCB the peak area increases slowly even if extraction time is long to 50 min. This is related to their larger molecular mass [24]. An extraction time of 40 min is adopted in the following experiments.
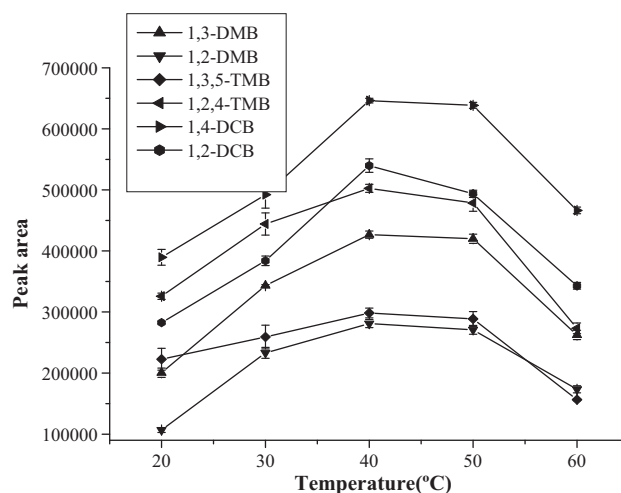

Fig. 3. Dependence of extraction efficiency of PANI/Pt on extraction temperature. Extraction time: 40 min; rotating rate: 600 rpm; NaCl concentration: 0.35 g mL^{-1}; desorption time: 3 min; desorption temperature: 220 °C. The concentrations of benzene derivatives: 0.1 μg mL^{-1} (for 1,3-DMB, 1,2-DMB, 1,4-DCB, 1,2-DCB) and 0.2 μg mL^{-1} (for 1,3,5-TMB, 1,2,4-TMB).
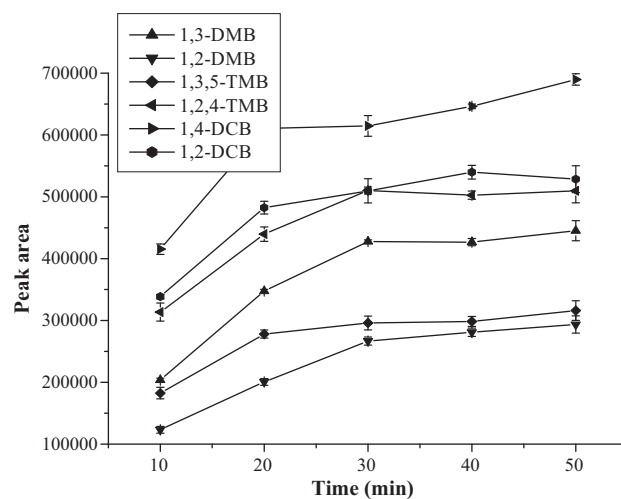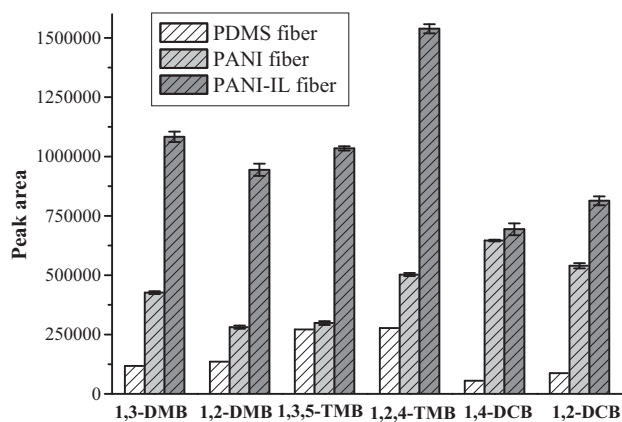

Fig. 4. Influence of extraction time on extraction efficiency. Extraction temperature: 40 °C. Other conditions are the same as in Fig. 3.

Fig. 5. Comparison of the extraction efficiency of PDMS fiber (coating thickness: about 100 μm), PANI/Pt (coating thickness: about 80 μm) and PANI–IL/Pt (coating thickness: about 80 μm). Extraction temperature: 40 °C. Other conditions as in Fig. 3.

Fig. 6. Influence of injection port temperature on the baseline of PANI–IL/Pt fiber. Injection port temperature (from bottom to top): 220 °C, 250 °C, 280 °C, 310 °C, 320 °C, 330 °C, and 350 °C. In order to easily distinguish them the baselines are moved along the ordinate axis to different extent.

3.2.3. Salt concentration

Ionic strength usually influences the solubility of organic compounds in water, thus it affects the extraction efficiency of HS-SPME [25]. In this work, the influence of ionic strength is tested by varying NaCl concentration. As a result, the extraction efficiency increases with NaCl concentration increasing, even if it is up to 0.35 g mL^{-1} (near NaCl saturated solution). Hence 0.35 g mL^{-1} NaCl is added in the solution in the following experiments.
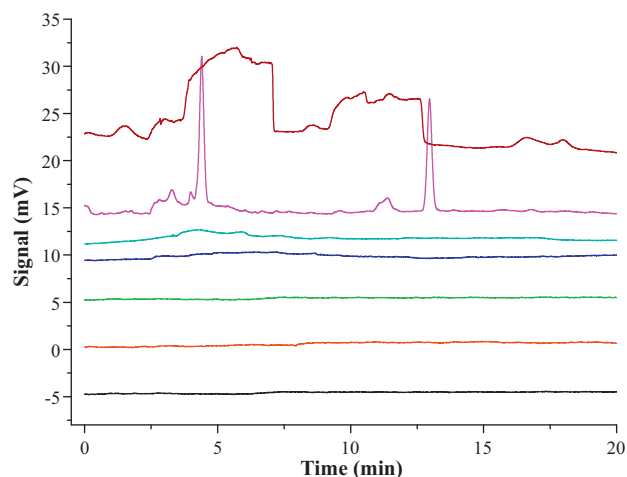
3.2.4. Stirring rate

Stirring the solution can facilitate the equilibrium between the aqueous phase and headspace; hence 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 0 to 600 rpm. However, when it is above 600 rpm the rotating of magnetic stirring bar is not very balanced. Therefore, for all experiments the rotating rate is fixed at 600 rpm.

3.3. Comparison of different fibers

The extraction efficiency of different fibers is compared in Fig. 5. As can be seen, the extraction efficiency of PANI–IL/Pt is much higher than that of PANI/Pt and PDMS fiber. Part of this can be ascribed to the larger surface area of PANI–IL/Pt. In addition, the retained IL must make the extraction efficiency increase, because it is a good extractant. However, when the IL concentration exceeds the value (i.e. 0.3%, in this case), the extraction efficiency of the resulted PANI–IL/Pt will decrease. This may be due to the reduction of its surface area.

3.4. Stability of the fiber

In order to investigate the thermal stability of the novel fiber, the baselines (i.e. blank chromatogram) of the fiber are recorded at different desorption temperatures (Fig. 6). It can be seen that the

PANI–IL coating keeps stable up to 320 °C; it decomposes partly at 330 °C and decomposes more rapidly at higher temperature. Accordingly, the extraction efficiency of PANI–IL/Pt decreases after it is conditioned at temperature above 320 °C.

The influence of solvents is also tested. As a result, after being immersed in CH$_2$Cl$_2$ for 4 h, the PANI–IL/Pt is dried and used for the HS-SPME of benzene derivatives as mentioned above, and its extraction efficiency keeps almost unchanged. Similarly, the influence of acidic/basic aqueous solutions is examined, and only a little change is observed for the extraction efficiency of PANI–IL/Pt. This indicates that the fiber has good chemical stability.

3.5. Method evaluation

Under the optimized conditions, the method is evaluated by testing the analytical parameters of benzene derivatives in artificially prepared water samples. The results are shown in Table 1. For different benzene derivatives the limit of detection (LOD) is 9.3–48.1 ng L^{-1} (S/N = 3). The GC peak areas are linear to their concentration over the ranges of 0.04–400 μg L^{-1}, with correlation coefficients above 0.99. The relative standard deviation (RSD) is below 5.1% for five repetitive extractions of a water sample containing 0.1 μg mL^{-1} 1,3-DMB, 1,2-DMB, 1,4-DCB, 1,2-DCB and 0.2 μg mL^{-1} 1,3,5-TMB and 1,2,4-TMB. The fiber-to-fiber RSD is 5.0–11.1% (n = 3) under the same conditions. After being used for about 120 times, a measure is conducted under the same condition as the initial one, and the extraction efficiency of the PANI–IL/Pt only changes a little, in comparison with the initial one. This indicates that the fiber not only has high sensitivity, but also has good repeatability and reproducibility.

Table 1
Analytical parameters for benzene derivatives measured by using PANI–IL/Pt fiber and HS-SPME-GC-FID method.

Analytes	LOD (ng L^{-1})	Linear range (μg L^{-1})	Correlation coefficient	RSD (%)	
				One fiber (n = 5)	Fiber to fiber (n = 3)
1,3-DMB	13.7	0.05–300	0.9968	2.2	11.1
1,2-DMB	13.0	0.045–300	0.9985	2.0	10.2
1,3,5-TMB	20.8	0.10–400	0.9921	3.1	5.0
1,2,4-TMB	18.0	0.12–400	0.9957	3.7	5.9
1,4-DCB	9.3	0.04–300	0.9981	5.1	5.2
1,2-DCB	48.1	0.06–300	0.9995	4.5	6.3
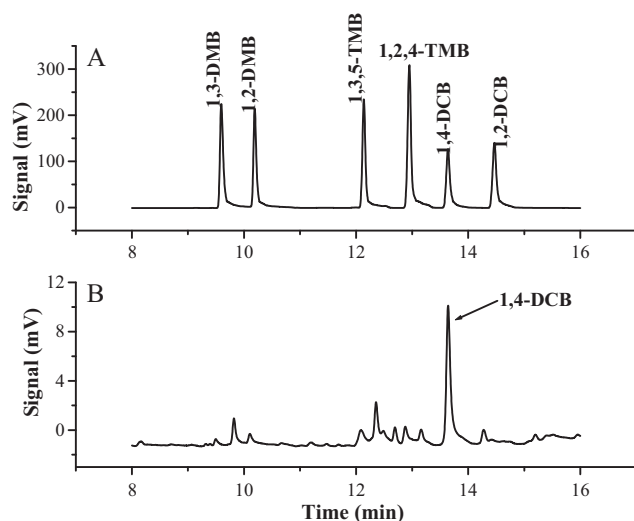
Fig. 7. HS-SPME-GC-FID chromatograms of standard aqueous solution (A) and waste water (B) extracted with PANI–IL/Pt fiber. Other conditions as in Fig. 5.

Table 2
Determination results and recoveries of benzene derivatives in water samples (n = 3).

Analytes	Waste water (ng mL^{-1})	Tap water	Recovery for standard added	
			Waster water	Tap water
1,3-DMB	nd[a]	nd	106.9 ± 17.2[b]	93.0 ± 5.9
1,2-DMB	nd	nd	95.7 ± 3.7	89.0 ± 6.3
1,3,5-TMB	nd	nd	101.6 ± 3.5	87.1 ± 2.1
1,2,4-TMB	nd	nd	101.9 ± 3.1	92.1 ± 1.7
1,4-DCB	10.8 ± 0.3	nd	97.8 ± 2.3	105.4 ± 7.0
1,2-DCB	nd	nd	108.1 ± 2.7	99.2 ± 2.0

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

3.6. Application

The proposed method is applied to the determination of benzene derivatives in water samples. Fig. 7 presents the GC chromatograms of benzene derivatives extracted with the PANI–IL/Pt fiber from the standard solution and waste water. For tap water, no measurable chromatographic peaks for these analytes are observed, while for the waste water potential 1,4-DCB is detected. The concentration of potential 1,4-DCB is calculated and it is 10.8 ng mL^{-1}. Then, standard benzene derivatives (0.1 μg mL^{-1} for 1,3-DMB, 1,2-DMB, 1,4-DCB and 1,2-DCB; 0.2 μg mL^{-1} for 1,3,5-TMB and 1,2,4-TMB) are added in the water samples and determined. The results are listed in Table 2, and their recoveries are 87.1–108.1%.

4. Conclusion

In this work, a PANI–IL/Pt fiber for SPME is fabricated by electrochemical polymerization for the first time. The obtained PANI–IL composite coating is even and porous, and it has large surface area and adsorption capacity. The PANI–IL/Pt fiber presents high extraction efficiency for benzene derivatives. It also shows good stability, repeatability and reproducibility. In addition, it is low cost and easy to prepare. Therefore, this work provides a new way for the preparation of SPME fiber with good property.

References

[1] B.G. Oliver, K.D. Bothen, Anal. Chem. 52 (1980) 2066.
[2] R.G. Melcher, P.L. Morabito, Anal. Chem. 62 (1990) 2183.
[3] F. Bianchi, M. Careri, E. Marengo, M. Musci, J. Chromatogr. A 975 (2002) 113.
[4] Y. Wang, H.K. Lee, J. Chromatogr. A 803 (1998) 219.
[5] G.H. Liu, J.L. Wang, Y.F. Zhu, X.R. Zhang, Anal. Lett. 37 (2004) 3085.
[6] K. Elke, E. Jermann, J. Begerow, L. Dunemann, J. Chromatogr. A 826 (1998) 191.
[7] O. Ezquerro, G. Ortiz, B. Pons, M.T. Tena, J. Chromatogr. A 1035 (2004) 17.
[8] I. Arambarri, M. Lasa, R. Garcia, E. Millan, J. Chromatogr. A 1033 (2004) 193.
[9] B. Tang, U. Isacsson, J. Chromatogr. A 1069 (2005) 235.
[10] K. Farhadi, M. Mamaghanian, R. Maleki, J. Hazard. Mater. 152 (2008) 677.
[11] J.C. Wu, J. Pawliszyn, J. Chromatogr. A 909 (2001) 37.
[12] Y.H. Wang, Y.Q. Li, J.F. Feng, C. Sun, Anal. Chim. Acta 619 (2008) 202.
[13] X. Li, J.M. Chen, L.C. Du, J. Chromatogr. A 1140 (2007) 21.
[14] G. Zotti, S. Cattarin, N. Comisso, J. Electroanal. Chem. 239 (1988) 387.
[15] A. Mohammadi, Y. Yamini, N. Alizadeh, J. Chromatogr. A 1063 (2005) 1.
[16] J.C. Wu, J. Pawliszyn, Anal. Chim. Acta 520 (2004) 257.
[17] J. Liu, G.B. Jiang, Y.G. Chi, Y.Q. Cai, Q.X. Zhou, J.T. Hu, Anal. Chem. 75 (2003) 5870.
[18] J.F. Liu, N. Li, G.B. Jiang, J.M. Li, J.A. Jonsson, M.J. Wen, J. Chromatogr. A 1066 (2005) 27.
[19] F.Q. Zhao, J. Li, B.Z. Zeng, J. Sep. Sci. 31 (2008) 3045.
[20] F.Q. Zhao, S. Lu, W. Du, B.Z. Zeng, Microchim. Acta 165 (2009) 29.
[21] K. Sekiguchi, M. Atobe, T. Fuchigami, Electrochem. Commun. 4 (2002) 881.
[22] D. Wei, C. Kvarnström, T. Lindfors, A. Ivaska, Electrochem. Commun. 8 (2006) 1563.
[23] W. Du, F.Q. Zhao, B.Z. Zeng, J. Chromatogr. A 1216 (2009) 3751.
[24] J.J. Langenfeld, S.B. Hawthorne, D.J. Miller, Anal. Chem. 68 (1996) 144.
[25] K.D. Buchholz, J. Pawliszyn, Environ. Sci. Technol. 27 (1993) 2844.