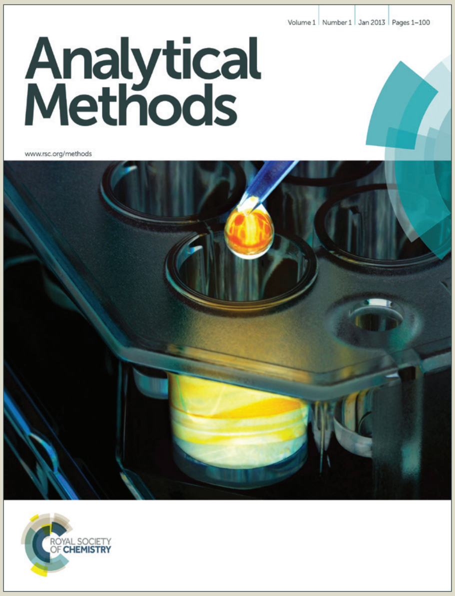
Analytical Methods

Accepted Manuscript



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Electrochemical Preparation of Poly(aniline-co-m-aminobenzoic) – Ionic Liquid Composite Coating for the Head-space Solid Phase Microextraction and Analysis of Aryl halides

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Abstract: In this work, a novel poly(aniline-co- *m*-aminobenzoic acid) - ionic liquid composite coating was presented for the head-space solid phase microextraction (HS-SPME) of aryl halides (i.e. chlorobenzene, brombenzol, 1,4-dichlorobenzene, 4-bromotoluene, 1,2,4-trichlorobenzene). This coating was prepared on a platinum wire by electrochemical deposition in an aqueous solution containing 0.1 mol L^{-1} aniline, 0.1 mol L^{-1} *m*-aminobenzoic acid, 0.02 mol L^{-1} 1- butyl-3-methylimidazolium tetrafluoroborate and 1.0 mol L^{-1} HNO_3. It showed high mechanical stability, thermal stability (up to 320 ºC) and durability (repetitively used for more than 120 times). When it was applied to the HS-SPME and gas chromatographic detection of the aryl halides, it presented high repeatability and sensitivity. Under the optimized conditions (i.e. extraction temperature: 30 ºC; extraction time: 30 min; stirring rate: 600 rpm; NaCl concentration: 0.35 g mL^{-1}), the linear detection ranges were 0.2−100 μg L^{-1}

with correlation coefficients above 0.9922; the detection limits were 0.01−0.05 μg L^{-1} (S/N=3). The relative standard deviations (RSD) of chromatographic peak areas were smaller than 5.3% for five successive measurements with single fiber, and the fiber to fiber RSD was 2.4−9.5% (n=3) for different aryl halides (50 μg L^{-1}). This method was successfully applied to the determination of real samples (i.e. moth ball) and the recoveries for standard added were 85.7 % to 121%.

Keywords: Electrochemical polymerization; Solid-phase microextraction; Ionic liquid; Aminobenzoic acid; Aryl halides; Polyaniline

1. Introduction

Solid-phase microextraction (SPME) was invented by Pawliszyn and co-workers two decades ago [1,2]. It is a fast, solvent free, inexpensive and sensitive sample pretreatment technique. For SPME the choice of suitable fiber is very important [3]. At present commercial SPME fibers generally have some drawbacks such as low thermal and chemical stability, high cost and/or short lifetime. Hence their application is limited to some extent [4]. To overcome these weaknesses, various approaches have been developed for the production of new SPME fibers [5,6]. Electrochemical method has advantages of simpleness and easy control, and is considered a good way for the preparation of SPME fibers [7-8]. This method was attempted by Wu and Pawliszyn et al a decade ago, and polypyrrole and polyaniline (PANI) SPME coatings were constructed by using electrochemical method [9-13]. Afterwards, in order to improve the performance of single polymer-based coatings, composite coatings were fabricated. For example, Kalaee et al. reported a nano-structured coating based on the copolymer of aniline and *m*-amino benzoic acid for the analysis of fatty acids in zooplanktons [14]. It showed higher thermal and mechanical stability compared with common polyaniline coating, resulting from the bonding of some functional groups. Xu et al. fabricated a poly(*p*-phenylenediamine-co-aniline) composite coating on a stainless steel wire for the head-space SPME (HS-SPME) of some derivatives of benzene, it displayed better performance than the polyaniline coated stainless steel wire due to its improved porous structure and adsorption ability [15]. Obviously, compared with the single polymer-based coatings, composite coatings showed higher stability and extraction efficiency.

Ionic liquids (ILs), composed of organic cations and organic or inorganic anions [16], often present high conductivity, negligible vapor pressure, high thermal stability and high solvency. These unique properties make them very useful in sample preparation [17-20]. ILs were also used in SPME [21-23]. Liu et al. [24] reported the preparation of IL-coated fiber for the first time. The performance of the fiber was comparable with the commercial polydimethylsiloxane (PDMS) fiber, but the IL coating was disposable. To resolve this problem Anderson and coworkers replaced IL with polymeric ionic liquids (PILs) in preparing SPME fibers [25-27], thus the coatings could be used for repeated extraction. In addition, Cheng Sun et al. and Wang et al. [28, 29] fabricated nano-structure polyaniline-IL composite coatings by electrochemical method for the HS-SPME of organochlorine pesticides and benzene derivatives. They showed good extraction property and extreme low detection limits. However, no electrochemical copolymer−IL composite coating has been reported hitherto.

In this paper a novel poly(aniline-co-*m*-aminobenzoic acid) ─IL composite coating (PANI-PmAB-IL) was prepared by cyclic voltammetry in a nitric acid aqueous solution containing aniline, *m*-aminobenzoic acid and hydrophilic ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmin]BF_4). The resulting fiber showed the merits of copolymer and IL. When it was used for the HS-SPME of aryl halides, it presented good performance.

2. Experimental

2.1. Reagents

Chlorobenzene (CB), bromobenzene (BB), 1,4-dichlorobenzene (1,4-DCB), 4-bromotoluene (4-BT) and 1,2,4-trichlorobenzene (1,2,4-TCB) were purchased from the Reagent Factory of Shanghai (China), and their stock solutions (1 mg mL^{-1}) were prepared with methanol. Aniline came from Aladdin Chemistry Co. (Shanghai, China) and was distilled before use. Aminobenzoic acids (i.e. *m*-aminobenzoic acid and *p*-aminobenzoic acid) and other chemicals used were of analytical or reagent grade. The samples (i.e. moth ball) were obtained from a local supermarket.

2.2. Apparatus

A CHI 600D electrochemical workstation (Shanghai Chenhua Instruments Co., Ltd) was employed for preparing PANI-PmAB-IL fibers. A conventional three-electrode system was used, 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. A SP-6890 gas chromatography instrument with a flame ionization detection (FID) system (Shandong Lunan Ruihong Chemical Instrument Co., Tengzhou, China) was utilized to separate and detect the analytes extracted. Its inlet was operated under the splitless mode and the flow rate of carrier gas (i.e. nitrogen gas) was 2.4 mL min^{-1}. The Rtx-1 capillary column (30 m × 0.25 mm I.D.) had 0.25 μm film thickness (RESTEK, USA). The instrumental temperature program used for this procedure was as follows: initial oven temperature was 50 ºC (held for 4 min), increased to 110 ºC at rate of 10 ºC min^{-1}, increased to 120 ºC at rate of 2 ºC min^{-1}, then increased to 150 ºC at rate of 10 ºC min^{-1}, and the temperature was held for 3 min. The injector temperature and detector temperature were set at 250 ºC. The scanning electron microscopy images were obtained using a Quanta-200 SEM instrument (FEI, The Netherlands).

2.3. Preparation of PANI-PmAB-IL composite film coated Pt wire

Prior to electrochemical deposition, the platinum wires were cleaned by ultrasonication in nitric acid solution and distilled water each for 15 min. Then the electrode system was immersed in nitric acid electrolyte containing 0.1 mol L^{-1} aniline, 0.1 mol L^{-1} *m*-AB and 0.02 mol L^{-1} [Bmin]BF$_4$. The potential scan was cycled between -0.2 V and 1.0 V for 75 times at 50 mV s^{-1}. After electrodeposition the obtained composite film coated Pt wire was washed with deionized water and subsequently was kept in a desiccator for 24 h at room temperature. Then it was aged in an electric furnace under nitrogen atmosphere for 50 min at 90 ºC and for 120 min at 300 ºC respectively. When the fiber was cool it was fixed on a home-made device for SPME with epoxy resin. According to the microscope measurement result, the thickness of the coating was about 40 μm. For comparison, polyaniline-poly(*p*-aminobenzoic acid)–[Bmin]BF_4 (PANI-PpAB-IL), polyaniline–poly(*m*-aminobenzoic acid) (PANI-PmAB) and PANI coatings were prepared under similar conditions. The thickness of these coatings was about 40 μm.

2.4. HS-SPME procedure

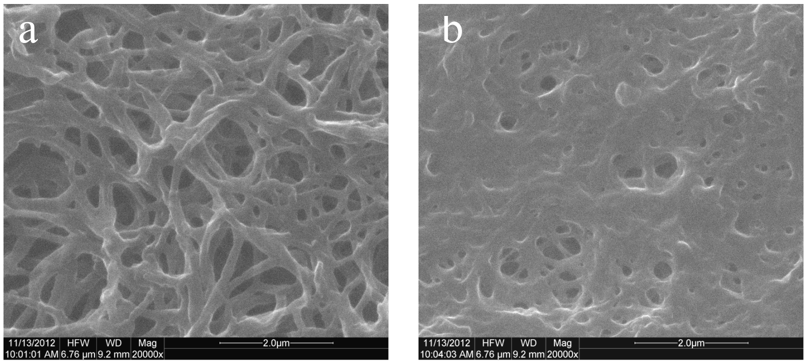
A 10 mL water and proper aryl halides (200 μg L^{-1}) solution were transferred into a 15 mL glass vial with PTFE–silicon septum. After adding appropriate sodium chloride and a magnetic stirring bar, the vial was tightly sealed with an aluminum cap. Then the vial was placed on a magnetism mixer with a water bath. When the water temperature reached the fixed value (i.e. 30 ºC), the PANI-PmAB-IL fiber was exposed to the headspace over the stirred solution for 30 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 PANI-PmAB-IL fiber

3.1.1. Surface structure

The SEM images of PANI-PmAB-IL, PANI-PpAB-IL, PANI-PmAB and PANI coatings were shown in Fig. 1. They all presented netlike structure, but the PANI-PmAB-IL coating presented thicker polymer fiber and larger mesh. This was related to the effect of IL on the polymerization process as it could be adsorbed on the polymer fiber. When IL was absent, the obtained PANI-PmAB coating was more compact and the mesh was smaller. In addition, the PANI-PmAB-IL coating was more smooth than the PANI-PmAB coating, which could be ascribed to the masking action of thin IL film on the fiber. As large mesh benefitted mass transfer and IL could enhance extraction capacity, the PANI-PmAB-IL coating should be suitable for SPME, although its specific surface was likely smaller than that of PANI-PmAB [30]. As could be seen, the structure of PANI and PANI-PpAB-IL coatings was not so good as that of PANI-PmAB-IL and PANI-PmAB. Accordingly, the PANI-PmAB-IL coating was selected.



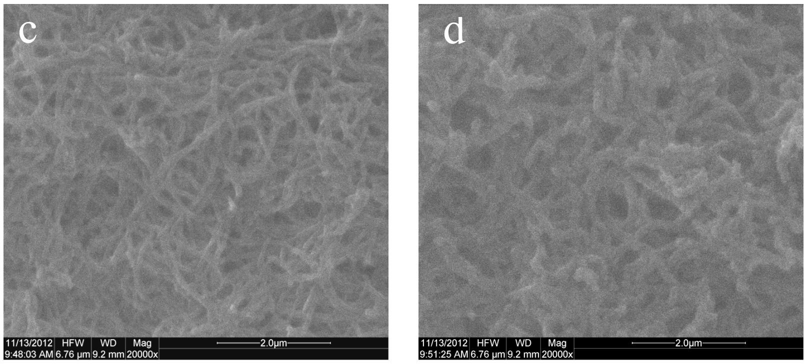


Fig. 1. SEM images of PANI-PmAB-IL coating (a), PANI-PpAB-IL coating (b), PANI-PmAB coating (c) and PANI coating (d).

3.1.2. Thermal stability

In order to investigate the thermal stability of the PANI-PmAB-IL fiber, it was inserted into the injection port of a gas chromatograph and the blank chromatogram was recorded at different desorption temperatures. As a result, when the desorption temperature was lower than 320 ºC the chromatogram was almost a straight line, meaning that the fiber was stable under 320 ºC (Fig. S1). But when the temperature was increased further small peaks appeared due to the partly decomposition of PANI-PmAB-IL. However, the recommended operating temperature for PANI fibers was lower than 250 ºC [13]. This indicated that the PANI-PmAB-IL fiber had wider applied temperature range than PANI fiber.

3.2. Optimization of extraction and desorption conditions

For the analysis of aryl halides, several factors that may influence the extraction efficiency were optimized, including extraction time, stirring speed, extraction temperature and ionic strength. The working solutions contained 0.2 μg mL^{-1} aryl halides and all measurements were replicated for three times.

3.2.1. Extraction temperature

Extraction temperature is an important parameter for HS-SPME. The influence of extraction temperature on the extraction efficiency of PANI-PmAB-IL fiber was shown in Fig. 2. It was clear, the extraction efficiency increased with the solution temperature rising up to 30 ºC, then it decreased slowly for different analytes. In general, temperature can affect the transfer rate of analytes from solution to headspace and the distribution ratio of analytes in coating phase. Here the temperature of 30 ºC was thought to be a balance point between adsorption amount and adsorption rate. Because the extraction temperature was close to the room temperature, it was convenient for the practical application of the fiber.

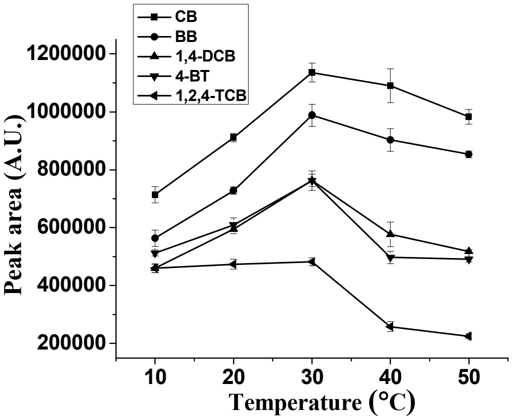


Fig. 2. Effect of extraction temperature on extraction efficiency of the fiber. Extraction time: 30 min; stirring speed: 600 rpm; NaCl concentration: 0.35 g mL^{-1}; desorption temperature: 250 ºC; desorption time: 3 min; concentration of aryl halides: 0.2 μg mL^{-1} (for CB, BB, 1,4-DCB, 4-BT and 1,2,4-TCB).

3.2.2. Extraction time

The influence of extraction time on the extraction efficiency was shown in Fig. 3. In the time range (i.e. 10−50 min) studied, the extraction efficiency increased with extending time until it was up to 30 min, then it kept almost unchanged for different aryl halides, indicating that the five aryl halides reached extraction equilibrium under the condition. Obviously, the extraction was quite quick, probably due to the rapid mass transfer of the analytes in the PANI-PmAB-IL coating.

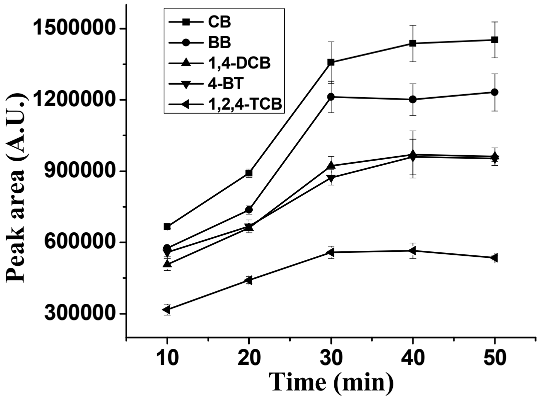


Fig. 3. Effect of extraction time on the extraction efficiency of the PANI-PmAB-IL fiber. Other conditions as in Fig. 2.

3.2.3. Stirring speed

Agitating solution can enhance extraction efficiency and reduce extraction time, thus it is always adopted. In this case, the extraction efficiency increased with stirring speed changing from 0 to 600 rpm (Fig. S2). Although the extraction efficiency probably increased further with stirring speed rising, considering the influence of splashed solution on the fiber at higher stirring speed, the stirring rate was set at 600 rpm in the following experiments.

3.2.4. Ionic strength

To explore the influence of ionic strength，NaCl was added to the solution. As shown in Fig. S3, the addition of NaCl made the extraction efficiency increase for all analytes even if NaCl concentration was up to 0.35 g mL^{-1}. As 0.35g mL^{-1} was the concentration of saturated NaCl solution, in the experiments saturated NaCl solution was used.

3. 3. Method evaluation

Under the optimized conditions, the analytical parameters were determined and the results were listed in Table 1. For different aryl halides, the limit of detection (LOD) was 0.01−0.05 μg L$^{−1}$ based on the signal/noise rate of 3. The GC peak areas were linear to the concentration of aryl halides over two magnitudes, with correlation coefficients above 0.9922. The relative standard deviation (RSD) was below 5.3% for five repetitive extractions of solutions containing 50 μg L$^{−1}$ aryl halides by using a fiber, and the fiber-to-fiber RSD was 2.4% to 9.5% for different aryl halides. This indicated that the novel composite coating not only had high sensitivity, but also had good repeatability and reproducibility. Compared with some fibers reported (e.g. titania sol–gel coated anodizedaluminum fiber) for the HS-SPME of aryl halides [31, 32], it showed more satisfactory analytical parameters.

Table 1

Analytical parameters for aryl halides measured with PANI-PmAB-IL fiber based

HS-SPME-GC-FID method.

Analytes	LOD (μg L^{-1})	Linear range (μg L^{-1})	Correlation coefficient	RSD (%)	
				One fiber （n=5）	Fiber to fiber （n=3）
CB	0.05	0.2 − 50	0.9968	3.2	6.2
BB	0.05	0.2− 100	0.9947	5.3	9.5
1,4-DCB	0.03	0.2 −50	0.9948	2.4	7.1
4-BT	0.03	0.2 −100	0.9922	1.9	2.4
1,2,4-TCB	0.01	0.4 − 100	0.9923	2.7	5.6

3.4. Extraction capability

The extraction capability of the PANI-PmAB-IL fiber was compared with that of PANI fiber, and the result was shown in Fig. 4. The novel fiber had much higher extraction efficiency than PANI fiber. This should be ascribed to the porous nanostructure and strong adsorption of PANI-PmAB-IL coating. Furthermore, the entrapped [Bmin]BF$_4$ was an excellent extractant for aryl halides. Therefore, it must contribute to the enhancement of extraction efficiency.

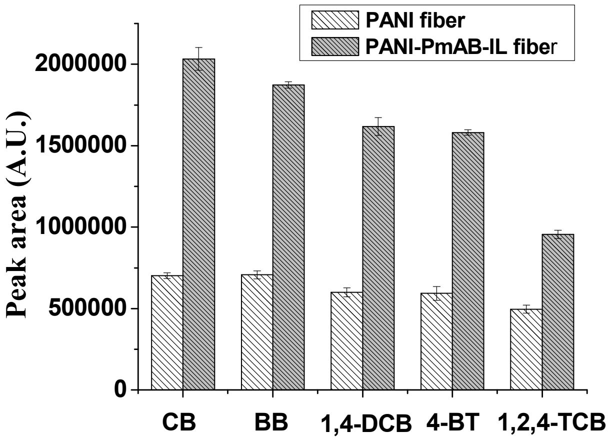


Fig. 4. Comparsion of the extraction efficiency of PANI-PmAB-IL fiber (coating thickness 40 μm) and PANI fiber (coating thickness 40 μm) for aryl halides. Extraction time: 30 min; extraction temperature: 30 ºC; stirring speed: 600 rpm; NaCl

concentration: 0.35 g mL^{-1}; desorption temperature: 250 ºC; desorption time: 3 min; concentration of aryl halides: 0.2 μg mL^{-1} (for CB, BB, 1,4-DCB, 4-BT and 1,2,4-TCB).

The comparison of the extraction efficiency of PANI-PmAB-IL fiber, PANI-PpAB-IL fiber and PANI-PmAB fiber was shown in Fig. S4. They all presented high extraction efficiency, but the PANI-PmAB-IL fiber was better.

3.5. Extraction selectivity

Five phenolic compounds and five ester compounds were extracted with ~~a~~ the PANI-PmAB-IL fiber to test its selectivity (Fig. 5). As a result, the fiber also showed high extraction efficiency for the polar and nonpolar compounds. Therefore, it could be used for the SPME of different volatile compounds.

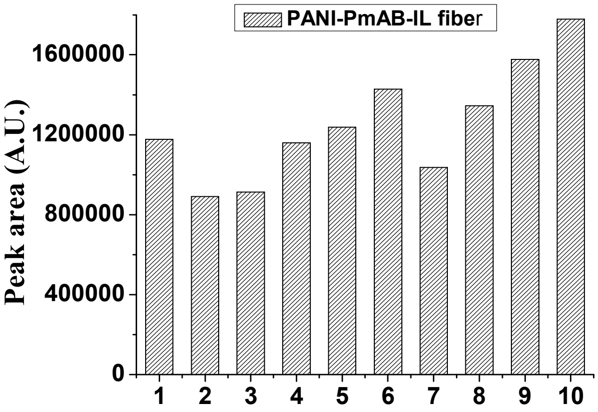


Fig. 5. Extraction efficiency of the PANI-PmAB-IL fiber for different compounds. Phenolic compounds (from 1 to 5): 2-chlorophenol, 2-methylphenol, 3-methylphenol, 2,6-dimethylphenol, 2,4-dimethylphenol; ester compounds（from 6 to 10): dimethyl

phthalate, diethyl phthalate, methyl anthranilate, ethyl-o-aminobenzoate, methyl Laurate. The concentration of analytes: 0.2 μg mL^{-1}; other conditions as in Fig. 4.

3.6. Lifetime of the coating

The lifetime or durability of a fiber is crucial for practical application. For most commercial SPME fibers, the extraction efficiency declined with extraction times increasing because the coating was prone to being damaged by high temperature and organic solvent, etc [33]. Here the lifetime of PANI-PmAB-IL fiber was examined. As a result (Fig. 6), after it undergone 120-time adsorption/desorption, the extraction efficiency almost did not decrease, considering the unavoidable variation of measure conditions. Moreover, ~~it~~ the fiber also had high mechanical strength.

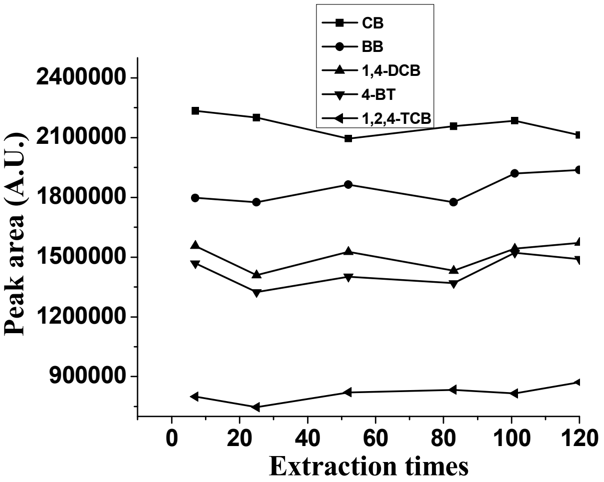


Fig. 6. Variation of extraction efficiency with extraction time of the PANI-PmAB-IL fiber. Other conditions as in Fig. 4.

3.7. Chemical stability

To test the chemical stability of the fiber it was soaked in distilled water, methylene chloride, 1 M H_2SO_4 acid and 1 M NaOH solution for 4 hours, respectively. Then ~~it~~ the fiber was washed with distilled water and dried under a lamp for extraction application. Results showed that the extraction efficiency of the fiber kept almost unchanged (Fig. S5), meaning that the coating had good chemical stability.

3.8. Applications

The proposed method was applied to the determination of aryl halides in three moth ball samples. The moth ball sample (0.01 g) was added into a 10 mL saturated NaCl aqueous solution and then was detected under the optimized conditions. The results were shown in Table 2. In a sample solution 1.4-dichlorobenzene was detected and its concentration was c.a. 29.3 ng mL^{-1}. According to the detected result the content of 1,4-DCB was calculated to be 29 mg/g. The recoveries for standards added varied from 85.7% to 121%.

Table 2

Analytical results of moth ball samples determined with HS-SPME-GC-FID using PANI-mAB-IL fiber (*n*=3).

	Moth ball samples			Recovery for standard added (%)[b]		
Analytes	1 (ng mL^{-1})	2 (ng mL^{-1})	3 (ng mL^{-1})	Sample 1	Sample 2	Sample 3
CB	nd[a]	nd	nd	117.2±3.8[c]	85.7±4.6	97.3±10.5
BB	nd	nd	nd	108.2±3.5	96.5±4.5	100.5±9.3
1,4-DCB	29.3	nd	nd	121.2±8.4	104.2±7.8	100.3±8.1

4-BT	nd	nd	nd	113.8±7.2	107.2±3.	98.1±7.2
1,2,4-TCB	nd	nd	nd	97.4±5.6	119.4±3.2	106.0±3.9

[a] nd: not detected;

[b] the concentration of aryl halides added: 50 ng mL^{-1}.

[c] mean values±standard deviations

4. Conclusion

In this paper, a novel PANI-PmAB-IL SPME fiber was fabricated by electrodeposition method. The composite coating presented porous structure with high adsorption capacity. It also had high thermal stability (up to 320 ºC) and long lifetime. When it was used for the HS-SPME of aryl halides, followed by gas chromatographic detection, satisfactory analytical parameters were obtained. The novel fiber could also be used for the extraction of other compounds.

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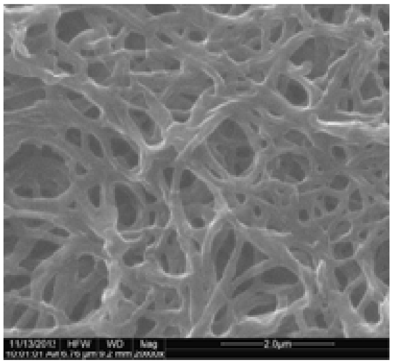
Graphical Abstract



Electrodeposited poly(aniline-co- *m*-aminobenzoic acid) - ionic liquid composite coating presents porous mesh structure, and shows high extraction efficiency for aryl halides.