



# Nano-structured polyaniline-ionic liquid composite film coated steel wire for headspace solid-phase microextraction of organochlorine pesticides in water

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## ABSTRACT

A novel nano-structured polyaniline-ionic liquid (i.e. 1-butyl-3-methylimidazolium hexafluorophosphate, BMIPF<sub>6</sub>) composite (BPAN) film coated steel wire was prepared by electrochemical deposition. Scanning electron microscopy images showed that the obtained porous BPAN coating consisted of nanofibers, whose diameter ranged from 50 to 80 nm. Furthermore, the novel nano-structured composite coating was very stable at relatively high temperatures (up to 350 °C) and it could be used for more 250 times without obvious decrease of the extraction efficiency. The novel BPAN coating was used for the headspace solid-phase microextraction (HS-SPME) of organochlorine pesticides (i.e. hexachlorocyclohexane, dichlorodiphenyldichloroethylene, dichlorodiphenyldichloroethane, dichlorodiphenyltrichloroethane), coupled with gas chromatography-electron capture detection (GC-ECD). The BPAN coating showed better analytical capability on the whole compared with common polyaniline (PANI) and polydimethylsiloxane (PDMS) coatings. The key parameters influencing extraction efficiency were investigated and optimized, including desorption time, stirring speed, extraction temperature, extraction time and ionic strength. The relative standard deviations (RSDs) for single fiber repeatability ranged from 2.3 to 8.7% ( $n=6$ ) and the RSDs for fiber-to-fiber reproducibility ( $n=6$ ) were 4.2–12.1%, respectively. The linear ranges exceeded three magnitudes with correlation coefficients above 0.99. The detection limits were 0.12–0.31 ng L<sup>-1</sup>. The proposed method was successfully applied for the determination of organochlorine pesticides in lake water, waste water and sewage treatment plant effluent with good recoveries from 88.9 to 112.9%.

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## 1. Introduction

Solid phase microextraction (SPME) was introduced by Pawliszyn and co-workers in 1990s [1] and since then it has been widely applied in many areas. Compared with traditional analytical techniques, SPME is a solvent free, easy to handle, and sensitive method. This technique is based on the partitioning of analytes between sample and SPME coating [1]. In order to achieve more extensive applicability for analytes, various approaches have been developed for the production of SPME fibers. Electrochemical method was first attempted by Wu and Pawliszyn to prepare SPME fibers [2,3]. In comparison with conventional coating procedures, electrochemical method offers a simple, low-cost, reproducible and convenient pathway for synthesis of conductive polymers [3–5]. In addition, metal wires are used as substrate in electrochemical coating approach. Consequently, the resulting fibers have higher mechanical strength than commercial fibers which use fused-

silica fibers as substrate. Among numerous conductive polymers, polyaniline (PANI), polypyrrole, polythiophene and their derivatives are widely used as SPME fibers.

SPME is based on the partition/adsorption of analytes to a stationary phase coated on a fused-silica or steel fiber [1], and extraction capacity is low because of limited adsorption sites on the fibers [6]. Using nanomaterials can overcome this problem. Nanomaterials possess unique properties, such as large specific surface area, and multiple active sites for adsorbing analytes. Consequently, nanomaterials offer a significant higher surface area-to-volume ratio that promises much greater extraction capacity and efficiency compared with other materials used for SPME [7]. The applications of nanomaterials in SPME coatings have shown a remarkable growth in recent years. Carbon nanotubes [8], fullerenes [9], nanoporous silica [10], nano-structured metal oxides [11,12] and Au nanoparticles [13] have been successfully used as SPME coatings. The applications of nano-structured polyaniline-based SPME coatings have also been reported [14–16]. Mehdinia [14] first prepared nano-structured PANI coating and the results revealed that it showed higher extraction efficiency for polychlorinated biphenyls (PCBs) than the micro-structured PANI coating due to its nanostructure. Mehdinia et al. [15] also prepared nano-structured self-doped

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polyaniline as a SPME coating to extract 1,4-dioxane and the results showed that the as-prepared fiber could be a good substitute of polyaniline as a SPME coating.

Microemulsions are thermodynamically stable dispersions of two or more immiscible liquids which are stabilized by an adsorbed surfactant film at the liquid–liquid interface. Microemulsions are often used to prepare nanomaterials [17]. Furthermore, it has been demonstrated that ionic liquids (ILs) can substitute water or conventional organic solvent to form novel microemulsion systems in the presence of surfactant. ILs are compounds composed entirely of ions that exist in a liquid state at ambient temperature. With negligible vapor pressure, high thermal stability, high ionic conductivity, wide electrochemical potential window, ionic liquids have been widely applied in electropolymerization. Many anions present in ionic liquids, such as trifluoromethanesulfonate [18,19] and hexafluorophosphate [20,21], are beneficial dopants to the performance and lifetime of polymers [22,23]. Besides these unique properties above, ILs also show good extractability for various organic compounds [24,25] and metals ions [26,27]. Therefore, they are considered as potential absorbents for SPME. For example, He et al. [28] successfully prepared ionic liquid-based SPME coating and found the coating had excellent extraction capability for methamphetamine (MAP) and amphetamine (AP) in human urine samples. Meng and Anderson [29] fabricated polymeric ionic liquid based SPME coating and found it showed impressive selectivity towards polycyclic aromatic hydrocarbons (PAHs) from aqueous samples. However, to the best of our knowledge, there are no reports about the preparation of the nano-structured polyaniline-ionic liquid composite SPME fibers through electrochemical method.

Organochlorine pesticides (OCPs) are known to be one of the most persistent organic pollutants in water. OCPs are phased out because they are persistent, estrogenic, carcinogenic [30], and able to bioaccumulate and biomagnify in higher trophic level animals through the food chain [31]. However, the residual problem is still serious because of their persistence and their huge historical usage. Thus, continuous monitoring of pesticide residues in water is of great importance.

Herein, a novel nano-structured polyaniline-ionic liquid composite (BPAN) film was electrochemically prepared as a SPME coating in microemulsion containing 1-butyl-3-methylimidazolium hexafluorophosphate (BMIPF<sub>6</sub>). Then, the novel BPAN coating was used for the headspace solid-phase microextraction (HS-SPME) of five organochlorine pesticides. The properties of the novel BPAN fiber such as extraction efficiency, thermal stability and lifetime were investigated in detail. The effects of different parameters on the amounts of extracted OCPs from water were investigated. Afterwards, the optimized method was applied to the determination of organochlorine pesticides in real water samples.

## 2. Experimental

### 2.1. Apparatus

A CHI 650A Electrochemical Workstation from CH Instrument (TX, USA) was employed for preparing SPME fibers. The commercial fiber selected in this study was a fused-silica fiber coated with 30  $\mu\text{m}$  polydimethylsiloxane (PDMS) and held in an SPME device supplied from Supelco (Bellefonte, PA, USA). A heating magnetic stirrer was purchased from Jingfeng Instrument Co. Ltd. (Shanghai, China).

A 6890N gas chromatography (Agilent Technologies, USA), equipped with split/splitless injector, a DB-5 capillary column (30 m  $\times$  0.32 mm i.d., 0.25  $\mu\text{m}$  film thickness) and electron-capture detector (ECD), was employed to separate and detect the analytes.

The instrumental temperature program used for this procedure was as follows: initial oven temperature 80 °C (held for 1 min), increased to 140 °C at a rate of 20 °C min<sup>-1</sup> (held for 2 min), and then increased to 280 °C at a rate of 4 °C min<sup>-1</sup> (held for 6 min). The injector temperature and detector were set at 250 °C and 300 °C, respectively. Helium (99.999%) was used as carrier gas at a constant flow of 1.5 mL min<sup>-1</sup> and nitrogen (99.999%) as a make-up gas at a flow rate of 20 mL min<sup>-1</sup>.

### 2.2. Reagents and materials

Aniline ( $\geq 99.8\%$ ) and 1-butyl-3-methylimidazolium hexafluorophosphate (BMIPF<sub>6</sub>) were purchased from Acros (NJ, USA) and Lanzhou Greenchem ILS, LICP, CAS (Lanzhou, China), respectively. The emulsifier nonyphenol ethoxylates (NP-10) was obtained from 3W Industry Co. (Shanghai, China). Hexachlorocyclohexane ( $\alpha$ -HCH), dichlorodiphenyldichloroethylene (p,p'-DDE), dichlorodiphenyldichloroethane (p,p'-DDD, o,p'-DDD) and dichlorodiphenyltrichloroethane (p,p'-DDT) were purchased from Supelco (Bellefonte, PA, USA).

HPLC grade hexane and acetone were purchased from Fisher Chemical (Fairlawn, NJ, USA). A stock solution containing all analytes (20 mg L<sup>-1</sup>) was prepared by dissolving organochlorine pesticides in acetone: hexane (10:90) and stored in dark at 4 °C for use. Fresh working standard solutions of OCPs were prepared by diluting the stock solution with double distilled water before measurements. Sodium chloride was of analytical grade and purchased from the Reagent Factory of Shanghai (Shanghai, China) and calcinated at 450 °C for 4 h before use. Distilled water was produced by the Milli-Q nanopure water system (Milli-Q system, Millipore, Bedford, MA).

The lake water was collected from Hongze Lake (Jiangsu, China) in February, 2011. The waste water was collected from a wine plant (Nanjing, China) and the sewage treatment plant (STP) effluent was collected from Xianlin sewage treatment plant ((Nanjing, China) in May, 2011. No pretreatment procedure was carried out before detection.

### 2.3. Preparation of microemulsion

The microemulsion was prepared as electrolyte according to the previous procedure [32], which contained 0.5 M H<sub>2</sub>SO<sub>4</sub>, 48 wt.% BMIPF<sub>6</sub>, 5.2 wt.% H<sub>2</sub>O and 46.8 wt.% NP-10.

### 2.4. Preparation and characterization of the BPAN coating

Common polyaniline (PANI) fiber was prepared by electrochemical polymerization according to the previous report [33]. The electrochemical polymerization of the novel BPAN fiber was derived from the previous report [34] with some modifications. Briefly, three-electrode system was employed and all potentials were referred to an Ag/AgCl electrode. The tip 10 mm segment of the stainless steel wire (75 mm length and 250  $\mu\text{m}$  diameter) was employed as the working electrode, and Pt was used as counter electrode. Before electrochemical deposition, the steel wires were cleaned by acetone and HPLC grade water in an ultrasonic bath for 30 min and finally air dried at room temperature. The technique of cyclic voltammetry (CV) was employed for the direct electrochemical coating. The CV system was operated in microemulsion at scan rate of 25 mV s<sup>-1</sup> with potential sweep between -0.8 and +1.2 V and the number of cycles was set at 30. After deposition, the as-made fiber was washed with double distilled water in order to remove unwanted chemicals such as monomers and the supporting electrolyte. Then it was aged in the GC inlet under a gentle stream of N<sub>2</sub>. The inlet temperature was initiated at 95 °C for 1 h, and then

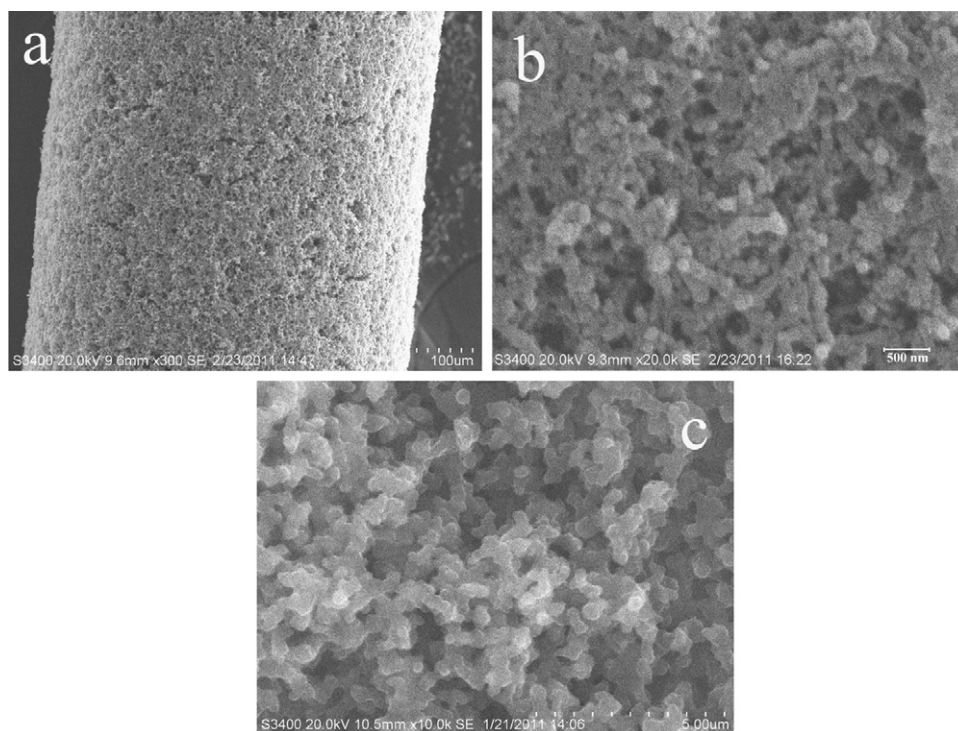


Fig. 1. Scanning electron micrographs of the BPAN fiber (a and b) and PANI fiber (c).

held at 200 °C for 5 h until clean background was obtained for GC analysis.

The micrographs of the fibers were characterized by S-3400N II scanning electron microscopy (SEM) (Hitachi, Japan). The atoms on the polymers surface were analyzed by EX-250 energy dispersive spectrometer (EDS) (HORIBA, Japan).

### 2.5. Headspace SPME procedure

A 15-mL of work solution (spiked with 200 ng L<sup>-1</sup> of each organochlorine pesticide) was placed into a 22-mL brown glass vial with polytetrafluoroethylene-coated septa. A magnetic stirrer was used to accelerate the extraction. After the addition of sodium chloride and magnetic stirring bar, the vial was tightly sealed with an aluminum cap to prevent sample loss due to evaporation. Then, the septum piercing needle of the SPME device was introduced into the glass vial to allow a 10 mm length of the fiber to be exposed to the headspace over the stirred solution for 40 min at 40 °C for extraction. Afterwards, the fiber was withdrawn into the needle, removed from the sample vial and immediately introduced into the GC injector port for thermal desorption.

## 3. Results and discussion

### 3.1. Characterization of the fiber

#### 3.1.1. Surface structure

Scanning electron micrographs (SEM) were used to investigate the surface characteristics of PANI and BPAN coating. As shown in Fig. 1, they both present porous structure, but the BPAN coating is more even and porous. The coating thicknesses of each coating were estimated by SEM and found to be about 27.5 μm for the PANI coating and 15 μm for the BPAN coating, respectively. Furthermore, the morphology of the BPAN film formed on the stainless substrate is nanofibers, whose diameter ranges from 50 to 80 nm. Therefore, the BPAN fiber had high specific surface area owing to

its highly porous network and nano-structure, which is favorable for the adsorption/extraction of analytes. [35,36].

#### 3.1.2. Thermal stability

Since the analytes extracted by the fiber are desorbed at an elevated temperature, the capability of resistance to high temperature is very important in terms of practical application. In order to investigate the thermal stability of the BPAN coating, the baselines (i.e. blank chromatogram) of the fiber were recorded at different desorption temperatures (Fig. 2). It can be seen that the BPAN fiber decomposed slightly at about 350 °C due to the degradation of the polymer backbone. For common polyaniline fiber, the decomposition happened when temperature was higher than 220 °C [37]. It is reported that the polymerization of aniline in the presence of BMIPF<sub>6</sub> can enhance thermal stability of polyaniline film [38], and the enhanced temperature resistance may be due to the introduction of fluorine element in polyaniline [39]. In order to prove the presence of fluorine element, EDS was used to examine the X-ray emissions which were excited by the SEM electron beam (Fig. 3). The spectrum shows the presence of fluorine element in

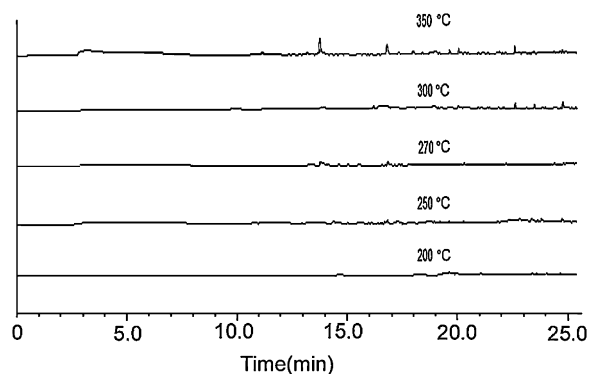


Fig. 2. Blank chromatograms for the BPAN fiber desorbed at different temperatures.

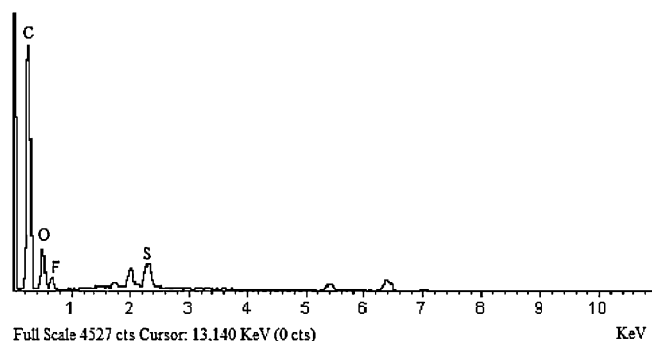


Fig. 3. The EDS spectrum of the BPAN fiber.

the coating. Ionic liquid BMIPF<sub>6</sub> was the only source of fluorine element, indicating that BMIPF<sub>6</sub> was copolymerized with aniline in the preparation of the fiber.

### 3.1.3. Lifetime of the coating

Lifetime is very crucial for practical application of the fiber. For most commercial SPME fibers, the extracting efficiency declines with extraction times increasing because the coating is damaged mainly by its exposure to high temperature, organic solvent, strong acidic or basic solution [40]. In this work, the BPAN coating was used more than 250 times of adsorption/desorption cycle without significant decrement in the extraction efficiencies (Fig. 4). The comparison of lifetimes of the as-prepared coating and other polyaniline-based fibers is shown in Table 1. The BPAN coating had relatively long lifetime compared with commercial fibers (40–100 times) and most other polyaniline coating. The reason for the improved lifetime of the BPAN fiber may relate to the efficient interactions between imidazolium ions of BMIPF<sub>6</sub> and  $\pi$ -electronic compound (polyaniline) [22,23,41].

### 3.1.4. Extraction capability

The extraction capability of the BPAN fiber was compared with the commercial 30  $\mu$ m PDMS, (which is often used to analyze OCPs because of its robustness and reproducibility), and common PANI fiber. The results are shown in Fig. 5 and the differences in extraction efficiencies were analyzed by the analysis of variance (ANOVA) test. The analysis results indicated that the differences in extraction efficiency of the BPAN fiber were very significant from the PANI and PDMS fiber ( $p < 0.01$ ,  $n = 3$  for each group). And it can be seen from

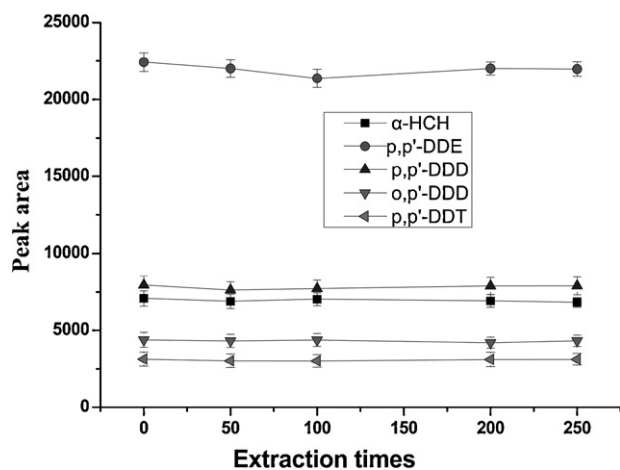


Fig. 4. Variation of extraction efficiency with extraction times. Experimental conditions: concentration of each OCPs, 200 ng L<sup>-1</sup>; desorption time, 3 min; extraction temperature, 40 °C; extraction time, 40 min; stirring speed, 600 rpm; the concentration of salt, 30%(w/v).

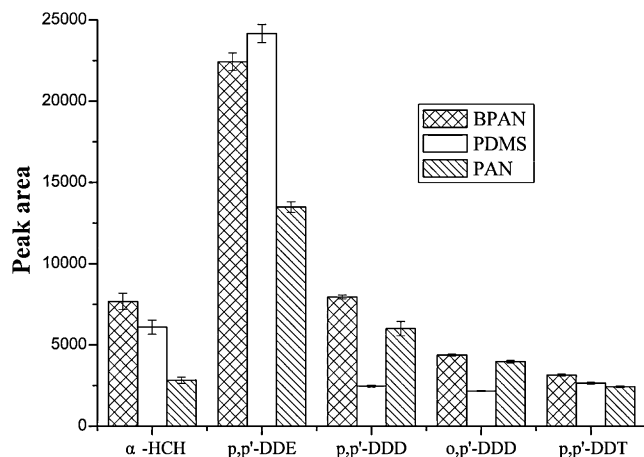


Fig. 5. Comparison of the extraction efficiency of the OCPs by BPAN, 30  $\mu$ m-PDMS and common PANI fibers. Experimental conditions as in Fig. 4.

Fig. 5 that the BPAN fiber demonstrated higher extraction efficiency than common polyaniline and PDMS fiber on the whole. It also was shown in Fig. 5 that the BPAN fiber showed lower extraction efficiency to p,p'-DDE than PDMS fiber. This may be due to the lower coating volume of the BPAN fiber, which has a much thinner coating thickness (15  $\mu$ m) than the PDMS fiber (30  $\mu$ m).

The possible reasons for the excellent extraction efficiency of the BPAN fiber are as follows: (1) for solid porous PANI coating, the extraction of analytes is based on adsorption mechanism [3]. The higher specific surface area will provide more active sites for adsorbing the analytes, thus the adsorption capability of fiber increases with its specific surface area. As discussed in Section 3.1.1, the highly porous nanostructure of the BPANI coating might be one of the reasons for explanation of the improved extraction efficiency. (2) BMIPF<sub>6</sub> is hydrophobic ionic liquid and it is an excellent extractant to non-/less polar compounds, such as OCPs. Therefore, BMIPF<sub>6</sub> retained on the BPAN fiber may be another reason for the improved extraction efficiency. However, when the concentration of BMIPF<sub>6</sub> exceeded 48 wt.%, the extraction efficiency decreased. This may be due to the retained ionic liquid on the coating reduced the surface area of the fiber.

## 3.2. Optimization of SPME conditions

Various factors influencing extraction efficiency were studied, including desorption time, stirring speed, extraction temperature and time, and ionic strength. The working solution in optimization experiment contained 200 ng L<sup>-1</sup> organochlorine pesticides and each measurement was replicated for three times.

### 3.2.1. Desorption time

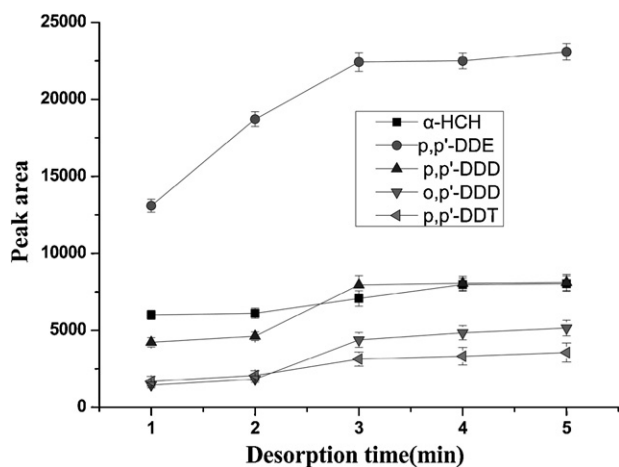
The investigation of desorption time was firstly accomplished. Desorption time has an effect on the amount of analytes desorbed from the fiber. It can be seen from Fig. 6 that the peak areas increased with desorption time increasing, but kept almost unchanged above 3 min. The ANOVA also showed there was significant difference in extraction efficiencies between 3 min and 2 min ( $p < 0.05$ ), but no significant difference between 3 min and 4 min ( $p > 0.05$ ). Consequently, desorption time of 3 min was selected for subsequent studies.

### 3.2.2. Stirring speed

The extraction efficiency is notably affected by stirring speed. The solution agitation can enhance extraction process and reduce extraction time because the equilibrium can be achieved rapidly. The stirring speed ranging from 0 to 600 rpm was investigated. As

**Table 1**  
Comparison of the BPAN coating and other PANI-based coatings.

Ref.	Electropolymerization conditions	Max temp. (°C)	Lifetime	Film thickness (μm)
Proposed coating	CV in microemulsion containing ionic liquid	350	250	15
[42]	CV in H <sub>2</sub> SO <sub>4</sub>	200	No data	0.5
[34]	CV in H <sub>2</sub> SO <sub>4</sub>	350	No data	No data
[37]	CV in H <sub>2</sub> SO <sub>4</sub>	220	No data	20
[43]	CV in H <sub>2</sub> SO <sub>4</sub>	320	216	0.25
[44]	CV in H <sub>2</sub> SO <sub>4</sub>	325	No data	No data
[45]	CV in CF <sub>3</sub> COOH	500	200	No data
[15]	CV in H <sub>2</sub> SO <sub>4</sub> and m-aminobenzoic acid	350	50	80
[16]	CV in H <sub>2</sub> SO <sub>4</sub> and methylbenzene sulphonic acid	350	50	70

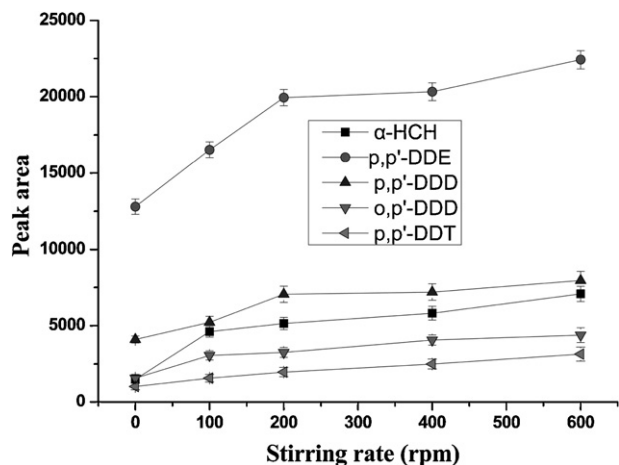


**Fig. 6.** Effect of desorption time on extraction efficiency of the OCPs. Other conditions as in Fig. 4.

can be seen from Fig. 7, when the extraction was performed statically (i.e., without agitation), the extraction efficiency was very low. The extraction efficiency became much higher when the solution was stirred. However, when it was above 600 rpm the rotating of magnetic stirring bar was not very balanced. Thus the stirring speed of 600 rpm was maintained for further studies.

### 3.2.3. Extraction temperature

Extraction temperature is another important parameter in headspace SPME because it can affect two equilibriums, i.e., the distribution of analytes between sample matrix and headspace, and the distribution between headspace and coating. The increasing temperature can enhance mass transfer of analytes from the sam-



**Fig. 7.** Effect of stirring speed on extraction efficiency of the OCPs. Other conditions as in Fig. 4.

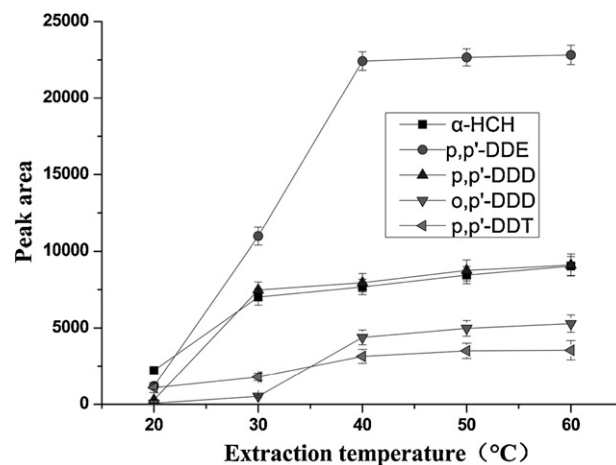
ple solution to headspace. However, it also decreases the amount of analytes that can be retained by the coating. A temperature range of 20–60 °C was used to study the effect of extraction temperature on the extraction efficiency. Results shown in Fig. 8 indicated that for OCPs studied, extraction efficiency improved significantly with extraction temperature increasing to 40 °C. Above 40 °C, extraction efficiency continued to increase but very slightly. Moreover, there was a significant difference in extraction efficiencies between 30 °C and 40 °C ( $p < 0.05$ ), but the extraction efficiencies of 40 °C and 50 °C has no significant difference ( $p > 0.05$ ). According to these results, 40 °C was the optimum temperature chosen for subsequent experiments.

### 3.2.4. Extraction time

SPME is an equilibrium-based technique and there is a direct relationship between the extracted amount and the extraction time. When the extraction equilibrium has not yet reached, the extraction efficiency increases with extraction time prolonging. Therefore, the equilibrium time is selected as extraction time in general. The optimum extraction time was investigated from 20 to 60 min. The profiles for optimum equilibration time were shown in Fig. 9. The analysis of variance showed that there was significant difference in extraction efficiencies between 30 min and 40 min ( $p < 0.05$ ), but the difference in extraction efficiencies between 40 min and 50 min was no significant ( $p > 0.05$ ), indicating that 40 min for the five OCPs was the optimized extraction time, so 40 min was adopted as the optimized extraction time.

### 3.2.5. Ionic strength

NaCl is commonly used to increase the ionic strength to produce a higher partial pressure of volatile analytes in the headspace volume and, consequently, a higher amount of analytes will be extracted by the fiber. The influence of salt on the studied system



**Fig. 8.** Effect of extraction temperature on extraction efficiency of the OCPs. Other conditions as in Fig. 4.

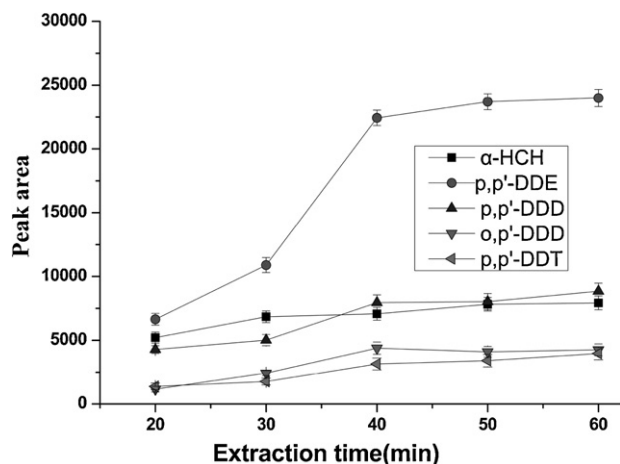


Fig. 9. Effect of extraction time on extraction efficiency of the OCPs. Other conditions as in Fig. 4.

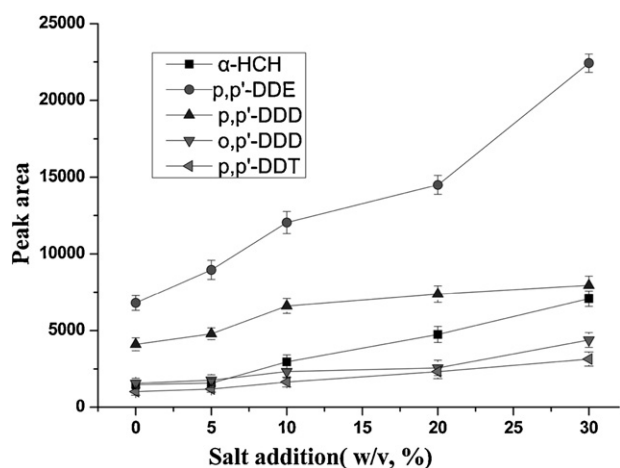


Fig. 10. Effect of the addition of salt on extraction efficiency of the OCPs. Other conditions as in Fig. 4.

was investigated by adding various amounts of NaCl in a series of concentrations varying from 0 to 30% (30% is the saturated solubility of NaCl). The results shown in Fig. 10 illustrated that the addition of NaCl to the sample increased the extraction efficiency for all analytes. Consequently, 30% (w/v) was selected as the suitable content of NaCl in the subsequent studies.

Based on the results above, the following conditions were selected as the optimized analytical conditions: 15 mL sample solution containing  $200 \text{ ng L}^{-1}$  OCPs and 30% (w/v) sodium chloride was placed in a 22-mL vial with stirring speed of 600 rpm. The extraction was carried out at  $40^\circ\text{C}$  for 40 min, and desorption was carried out at  $250^\circ\text{C}$  for 3 min. As shown in Fig. 11, the BPAN fiber exhibited good sensitivity for OCPs determination under the optimized conditions.

Table 2

Analytical parameters for organochlorine pesticides measured with BPAN fiber based HS-SPME-GC method and comparisons of the LODs with commercial PDMS, poly(methylphenylvinylsiloxane)/hydroxy-terminated silicone oil (PMPVS/OH-TSO) and divinylbenzene/carboxen/polydimethylsiloxane (DVB-CAR-PDMS) fibers.

Pesticide	Linear range ( $\text{ng L}^{-1}$ )	R	LOD ( $\text{ng L}^{-1}$ )					RSD(%, $n=6$ )	
			BPAN	PANI	PDMS	PMPVS/OH-TSO[46]	DVB-CAR-PDMS[47]	Single fiber	Fiber-to-fiber
$\alpha$ -HCH	1.5–5000	0.9961	0.20	0.81	0.54	–	–	8.7	12.1
p,p'-DDE	1.5–5000	0.9942	0.12	0.41	0.81	0.835	0.45	4.5	7.2
p,p'-DDD	1.5–5000	0.9941	0.15	0.54	0.23	1.58	0.30	2.3	4.2
o,p'-DDD	1.5–5000	0.9958	0.18	0.73	0.31	–	–	3.1	5.6
p,p'-DDT	5–5000	0.9943	0.31	0.70	1.21	3.09	0.45	3.8	7.8

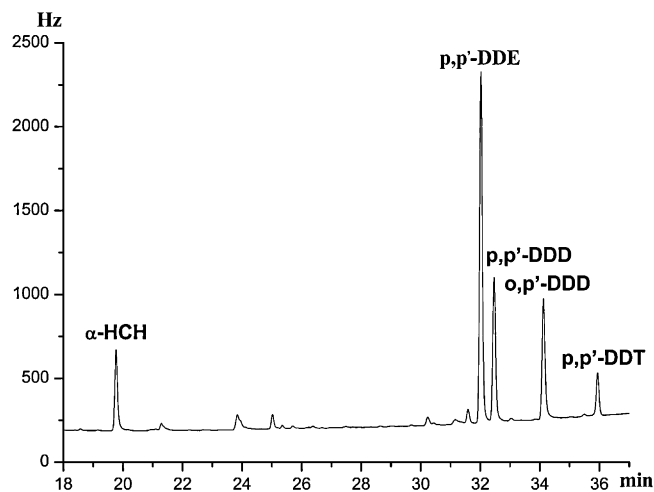


Fig. 11. Gas chromatogram for a mixture of OCPs from a standard aqueous solution ( $200 \text{ ng L}^{-1}$ ) obtained by SPME-GC-ECD with BPAN fiber. Experimental conditions as in Fig. 4.

### 3.3. Method evaluation

The analytical performance and characteristics of the proposed SPME approach were studied at optimized conditions by extracting working standard solution ( $1.5, 5, 100, 500, 1500, 3000, 5000 \text{ ng L}^{-1}$  of each organochlorine pesticides). The results are shown in Table 2. For the studied analytes, good linearity was observed with correlation coefficients ( $R$ ) ranging from 0.9941 to 0.9961. The limits of detection (LOD) of this method were determined using a signal-to-noise ratio of 3 ( $S/N=3$ ) and was found to range from 0.12 to  $0.31 \text{ ng L}^{-1}$ , which are relatively lower than polyaniline and commercial fibers (Table 2). The repeatability (single fiber) were estimated by the relative standard deviations (RSDs,  $n=6$ ) of the peak areas of the analytes. As shown in Table 2, the RSDs for single fiber were from 2.3 to 8.7%. The reproducibility (fiber-to-fiber) was also evaluated by RSDs of the peak areas extracted by six fibers prepared as the same produce and the RSDs varied from 4.2 to 12.1%. It indicates that the novel composite fiber not only has high sensitivity, but also has good repeatability and reproducibility.

### 3.4. Application to real water samples

The analysis of organochlorine pesticide residues has received an increasing attention in the last decades [48]. Many national organizations and government departments have developed laws and regulations to set limits of OCPs to protect public health. The Chinese standard is shown in Table 3. The proposed method was applied to analyze organochlorine pesticides in lake water, waste water and sewage treatment plant (STP) effluent. As listed in Table 2,  $\alpha$ -HCH was detected in all water samples studied. In addition, p,p'-DDD and p,p'-DDT were detected in waste water and STP effluent, respectively. The concentrations of OCPs detected in

**Table 3**  
Measurement results and recoveries of organochlorine pesticides in water sample.

Pesticide	Concentration (ng L <sup>-1</sup> , ±SD)			Chinese standard (ng L <sup>-1</sup> )	Recovery for standard added (% , ±SD)		
	Lake water	Waste water	STP effluent		Lake water	Waster water	STP effluent
α-HCH	4.6 ± 0.2	3.3 ± 0.5	4.0 ± 0.5	5.0	98.8 ± 4.7	93.7 ± 4.6	98.6 ± 5.1
p,p'-DDE	ND	ND	ND	–	101.3 ± 6.8	112.9 ± 3.2	100.8 ± 6.6
p,p'-DDD	ND	1.3 ± 0.7	ND	–	93.4 ± 2.2	88.9 ± 3.2	90.4 ± 1.7
o,p'-DDD	ND	ND	ND	–	89.4 ± 2.8	95.1 ± 12.3	96.9 ± 7.4
p,p'-DDT	ND	ND	1.8 ± 0.2	1.0	91.5 ± 2.6	103.1 ± 8.1	96.0 ± 5.6

water samples were lower than the regulation limits. The recoveries spiked in three samples at 100 ng L<sup>-1</sup> were in the range from 88.9 to 103.1%.

#### 4. Conclusions

A novel nano-structured polyaniline-ionic liquid composite SPME fiber was first prepared by a simple electrodeposition method in microemulsions containing BMIPF<sub>6</sub>. Coupled with GC analysis, the fiber exhibited excellent extraction efficiency for organochlorine pesticides. The proposed method had been used to extract five organochlorine pesticides in water, which achieved a wide linear range and low detection limits. The method was then successfully applied to analyze organochlorine pesticides in three real water samples. The novel nano-structured polyaniline-ionic liquid composite SPME fiber showed high temperature endurance and long life span. In addition, the novel fiber has advantages of easy preparation and low cost (compared with about \$100 each commercial fiber in Chinese market). Both the single fiber repeatability and fiber-to-fiber reproducibility were satisfactory. The novel BPAN fiber has a great potential of widespread use as an effective and useful extraction tool.

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