

HEADSPACE SOLID-PHASE MICROEXTRACTION WITH A NOVEL FLUORINATED POLYANILINE-BASED COATING FOR RAPID DETERMINATION OF TRACE POLYBROMINATED DIPHENYL ETHERS (PBDES) IN WATER AND MILK SAMPLES

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Abstract

Novel polyaniline (PANI) electrodeposited in the presence of fluorinated organic acid was applied as a new conductive polymer based solid-phase microextraction (SPME) fiber candidate. A method of headspace solid-space microextraction followed by gas chromatography (HS-SPME-GC) in the assistance of the novel fluorinated polyaniline-based coating was set up for the rapid determination of trace Polybrominated Diphenyl Ethers (PBDEs) in water and milk. The parameters including extraction mode, extraction temperature and time, headspace volume and ionic strength were investigated for optimization of HS-SPME performance. The experimental results under optimized conditions show that the linear ranges were 1-4000 ng/L (BDE-154 and BDE-153 were 1-3000 ng/L and 1-2500 ng/L) with satisfactory correlation coefficient ($R > 0.99$). The detection limit ($S/N=3$) was between 0.10 and 0.30 ng/L. The relative standard deviations for the determination of studied compounds were below 8.5% ($n=7$). Compared to commercial 100 μm -PDMS fiber, the extraction efficiency of self-prepared polyaniline fiber was better. The proposed method has been successfully applied to the determination of PBDEs in river water and milk, and the recoveries ranges were above 90% and 80%, respectively.

Introduction

Polybrominated diphenyl ethers (PBDEs) are bromine-contained persistent organic pollutants (POPs), and widely used as flame retardants in different materials such as varnish, computer and television housings, furniture, building materials, textiles and carpets. As additive. PBDEs are merely blended physically with the polymer and are therefore more likely to leach out and enter the environment during their production, delivery, use, and disposal [1]. Recent reports indicated serious concerns regarding possible developmental neurotoxicity and endocrine disruption, however, little is yet known about their toxic effects on humans [2]. Hence, environmental PBDE analysis has becoming a problem of great social and increasing attention has been paid on the determination of PBDEs.

Selection of suitable fiber is crucial for SPME approach and commercial fibers PDMS is frequently performed for the determination of PBDEs in solid samples [3]. However, large variation of performance, mainly resulting from the carryover effect, was observed, which is not suitable for environment relevant applications. In addition, commercially available SPME fibers have poor thermal, mechanical and chemical stability because they are prepared by physical deposition on the fused silica fiber. Increasing attention was therefore paid on conductive polymers, such as polyaniline, polypyrrole and polythiophene. Electrochemical synthesis method offers a simple, reproducible and convenient pathway for synthesis of conductive polymers on the metal support. The synthesis procedure can be easily controlled by varying different parameters to get desirable conductive polymer based SPME fibers. In spite of this, there are also some problems to restrict their developments. Polypyrrole [4] and

PANI [5,6] were the most popular conductive polymers for SPME fibers. However, their application was limited by low thermal stability, i.e. 200 °C for polypyrrole and 220 °C for common PANI [7]. In addition, due to their low extraction efficiency for non-/less compounds [4,6], several methods were proposed to enhance their performance, such as introducing functional group [8], enhancing surface area [9] etc.. Polythiophene was firstly proposed as SPME fiber by Li et.al [5] but no further report was available.

This present paper reports electrochemical polymerization of novel PANI in the presence of a fluorinated organic molecule which is incorporated into the resulting PANI as a dopant counterion. The prepared novel PANI is expected to improve its thermal stability and enhance extraction efficiency. Then, it is proposed as a superior SPME coating for extraction of PBDEs in the water and milk samples for the first time.

Materials and Methods

Reagents and materials

Six congeners of BDE-28, 47, 99,100, 153 and 154 were purchased from AccuStandard Company (USA). Working solutions were prepared by acetone and then diluted with distilled water for SPME study. Commercial SPME fiber holder, 100- μm polydimethylsiloxane (PDMS) fiber, 22-mL sample vials and PTFE silicone septa were obtained from Supelco (Bellefonte, PA, USA). Spinbar (10 mm \times 3 mm) was purchased from Sigma-Aldrich (St. Louis, MO, USA). Methanol and acetone of HPLC grade were obtained from Tedia (USA). Aniline, CF_3COOH , NaCl and petroleum ether are analytical grade.

Apparatus

A CHI 650A Electrochemical Workstation from CH Instrument (TX, USA) was employed for preparation of SPME fibers. A heating magnetic stirrer (Jingfeng Instrument Co. Ltd, Shanghai, China) was used to heat and stir the samples. The micrographs of the fibers were characterized by S-3400N II scanning electron microscopy (SEM) (Hitachi, Japan). A 6890N gas chromatographer equipped with split/splitless inlet, μECD (Agilent Technologies, USA) and a J&W column (15 m \times 0.25 mm \times 0.25 μm) was used to analyze PDBEs. GC temperature was programmed from 140 °C to 200 °C at the ramping rate of 20 °C min^{-1} , then to 260 °C at the ramping rate of 6 °C min^{-1} , finally to 300 °C at the ramping rate of 12 °C min^{-1} to hold for 7 min. The inlet temperature was set at 290 °C, and fiber desorption was carried out in splitless mode for 5 min. The detector temperature was set at 320 °C. Helium was served as carrier gas at a flow rate of 1.0 mL min^{-1} .

Preparation of SPME coating

For novel PANI, the polymerization method reported in our previous work [10] was modified to prepare this fiber. Briefly, the tip 10 mm segment of the stainless fiber (75 mm length and 350 μm diameter) was employed as the working electrode. Pt was used as counter electrode. Electropolymerization of aniline (0.2 M) was carried out in 0.5 M CF_3COOH by potential sweep between -0.2 and +1.2 V (versus SCE) during first four cycles and then between -0.2 and 1.0 V during the following 76 cycles at a scan rate of 25 mV s^{-1} . Finally it was held at 1V for 10 min in 0.5 M CF_3COOH . After deposition, the new fiber was washed with methanol and double distilled water in order to remove residuals such as aniline and supporting electrolytes. It was then dried in a GC inlet with a gentle stream of N_2 . The inlet temperature was initiated at 125 °C for 1 h, then held at 200 °C for 1 h, and finally held at 320 °C for 5 h until clean background was obtained for GC analysis.

Analytical procedure

10 mL water sample was placed into a 15-mL glass vial with PTFE-coated septa from Supelco

(Bellefonte, PA, USA). Sampling extraction was performed in headspace-SPME (HS-SPME) or direct-SPME (DI-SPME) mode by exposing the fiber over/in the stirred or static samples. 7 μ L of 100 ng L⁻¹ BDEs was spiked to different aqueous solutions to optimize SPME parameters. The extraction time ranged from 20 to 60 min. The extraction temperature ranged from 55 to 95 °C. Salt concentration was from 0 to 20% (w/v). After extraction, the fiber was thermally desorbed for 5 min in GC inlet at 270 (100 μ m-PDMS) or 290 °C (this novel PANI). After the thermal desorption, no carryover was observed for the tested novel PANI.

Results and discussion

3.1. Properties of novel PANI coatings

3.1.1 SEM

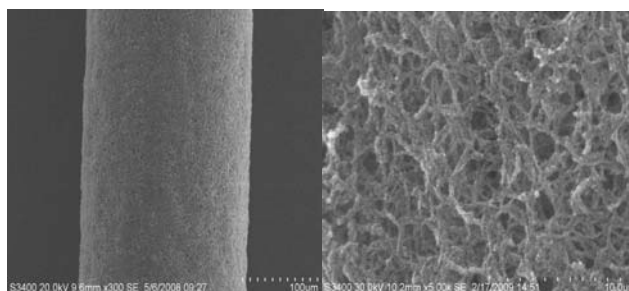


Fig.1 SEM images of novel PANI fiber at 300-fold (left) and 5000-fold (right) magnification

For novel PANI, polymer film grows steadily as the electrolysis proceeds. However, the growth of the novel PANI during the synthesis was much lower and steadier than common PANI does [6, 11], which resulted in long and intact PANI fiber. According to the SEM images in Fig.1, the novel PANI film formed on the stainless substrate possesses integrally fibroid structure and the film is relatively compact. Highly porous network structure suggests higher surface area, which allows for the use of thinner coatings to achieve similar extraction capacities because of enhanced surface area.

3.1.2 Extraction capability

A direct comparison was conducted to evaluate the extraction efficiency of commercial 100 μ m-PDMS and the novel PANI fiber. As shown in Fig.2 (left), the novel PANI demonstrated much higher extraction efficiency than commercial 100 μ m-PDMS. Improved extraction efficiency of the novel fiber may be due to the following reasons: firstly, for PANI with porous structure, extraction of analytes is based on adsorption mechanism [12]. Its adsorption capability increases as the surface area of stationary increases. This is the case especially for neutral molecules, whose surface adsorption ability depends primarily upon van der Waals dispersion forces [13]. As discussed in section 3.1.1, highly porous structure of novel PANI might be one of the reasons for the improved extraction efficiency. Secondly, according to the principle of “like dissolves like”, hydrophobic stationary improved extraction efficiency for non-/less polar compounds. It was reported [14] that high hydrophobic properties were achieved by the introduction of CF₃ groups to the conductive polymers. In this study, CF₃COO⁻ dopant was expected to bring excellent extraction efficiency for PBDEs.

3.1.3 Robustness and reproducibility synthesis of the novel PANI

The extraction efficiency of novel PANI SPME fiber was greatly increased by introducing fluorinated group. In addition, the novel PANI fiber is mechanically, chemically stable and synthesis is reproducible. This new fiber is a promising technique to provide solution for the quantitative analysis of trace PBDEs in water samples.

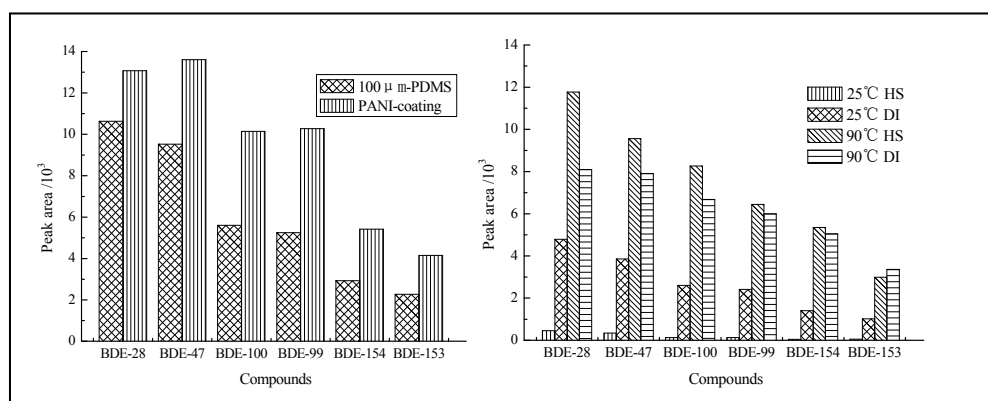


Fig.2 Left: comparison of the extraction efficiency for PBDEs by novel PANI to by 100 μm -PDMS (7 mL sample without agitation; each PBDE, 20 ng/L; extraction temperature, 95 $^{\circ}\text{C}$; extraction time, 40 min; 10% NaCl); Right: comparison of responses for HS-SPME to DI-SPME at 25 $^{\circ}\text{C}$ and 90 $^{\circ}\text{C}$.

3.2. Optimization of experimental parameters

During the SPME process, extraction mode and temperature are the most critical parameters. Some researchers adopted DI-SPME [15], while some others employed HS-SPME as the optimal extraction mode [16]. As shown in Fig.2 (right), HS-SPME showed significant enhancement in sensitivity versus DI-SPME in our study. Lower efficiency in DI mode might be due to the competition between analytes and water molecules. Higher temperature was favored under HS mode, because it increases analytes' vapor pressure which leads to level increase of extracted analytes in the headspace.

The extraction time profile for PBDEs was established by plotting the detector response versus the extraction time. SEM studies showed that the thickness of novel PANI coating on the surface of stainless steel support is about 10 μm , which indicated quick extraction/desorption process. It was validated in the experiment. As shown in Fig.3 (left), all compounds reached equilibrium in 40 min. This confirmed that the kinetic response of the extraction for novel PANI fibers is much faster than that for commercial PDMS based fibers which normally need hours [9], even days of equilibrium time. For a routine analysis, it is not necessary to reach complete equilibrium as long as enough detection limit is acquired. 30min extraction time was chosen to in this study.

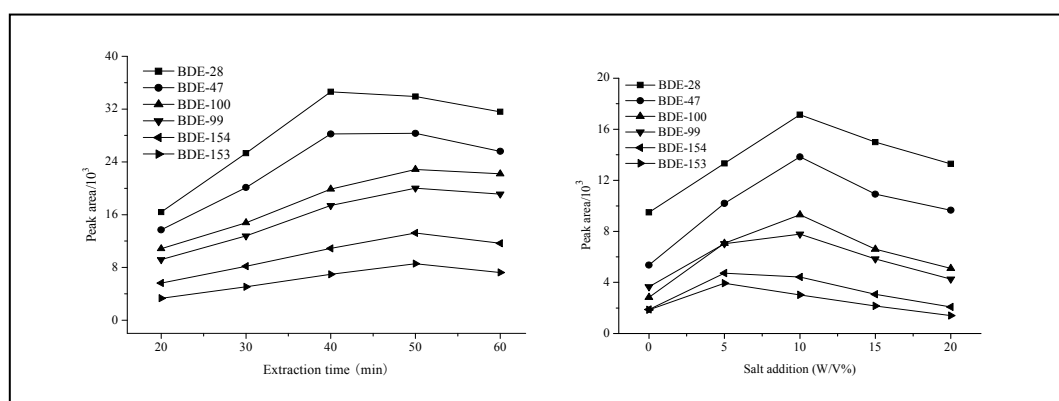


Fig.3 Effect of the extraction time (left) and salt addition (right) on the extraction efficiency of the coating for PBDEs. Concentration of each compound: 40 ng/L; extraction temperature: 95 $^{\circ}\text{C}$.

Commonly, addition of salt decreases the solubility of the compounds in water, and facilitates the

