# Facile fabrication of ionic liquid doped polycarbazole coating for the headspace solid-phase microextraction of some environmental pollutants

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## ARTICLE INFO

## ABSTRACT

A novel polycarbazole (PCz)–ionic liquid (IL, *i.e.* 1-hydroxyethyl-3-methylimidazolium bis[(tri-fluoromethyl)sulfonyl]imide, [HOEMIm][NTf$_2$]) composite coating (PCz-IL) was fabricated by electro-deposition. The IL could facilitate the electrodeposition of poor-conductive PCz and a more porous coating was obtained. The composite coating exhibited enhanced extraction capacity for some en-vironmental pollutants (i.e. o-chlorotoluene, p-bromotoluene, o-nitrotoluene, m-nitrotoluene, p-ni-trotoluene), as they could interact through π-π and hydrophobic interactions. Compared with [HOEMIm][NTf$_2$] coated fiber, some other PCz-IL fibers (here IL=1-hydroxyethyl-3-methylimidazolium hexafluorophosphate and 1-methyl-3-octylimidazolium hexafluorophosphate) and commercial fibers (i.e. polydimethylsiloxane and polyacrylate), the PCz-IL fiber showed better performance. It was used for the determination of the environmental pollutants by coupling with gas chromatography, the limits of detection were 47.8–65.9 ng L$^{-1}$ under the optimized conditions and the linear ranges were 0.1–500 μg L$^{-1}$ with correlation coefficients above 0.9947 for different compounds. The relative standard devia-tions (RSDs) were 3.4–4.6% for five successive extractions with single fiber, and the RSDs for inter-fiber were 6.5–10.4% (*n*=5). The fiber was successfully applied to the detection of real samples and the re-coveries for standards added were 88.6–108.8% with RSDs below 9.7%.

## 1. Introduction

Halogeno-benzenes and nitrobenzenes are important inter-mediates in chemical engineering industry, but they are also dangerous environmental pollutants once they are released into the surroundings. These compounds are difficult to degrade and can be accumulated in living beings, and eventually they will produce irreversible damages towards mankind [1]. As their con-centrations are generally quite low in real samples and the ma-trixes are complex, prior to their determination a pretreatment procedure is usually required [2].

Solid-phase microextraction (SPME) is an advanced sample pretreatment technique for its quick, simple, cost-effective and solvent-free merits [3]. It is also easy to couple with different in-struments, thus it is widely used. SPME is based on the parti-tioning of analytes between sample and the fiber coating [4], so the coating does affect the extraction efficiency and the analysis sensitivity. Recently, various types of coatings were reported,

including conductive polymers, ionic liquid (IL) [5], molecularly imprinted polymer [6], metal-organic framework [7] and carbon materials [8]. They showed advantages of low expense, high temperature resistance and mechanical stability, as well as ex-cellent extraction capability in comparison with commercial coatings [9]. These SPME coatings were prepared by using differ-ent methods, and among them the electrochemical method was considered a more convenient one for preparing metal wires based fibers. By using electrochemical preparation method the coating was easily controlled through changing electrochemical conditions and composition of electrolyte solution [10], and fibers with dif-ferent physicochemical properties could be obtained.

However, electrochemical method just suit the preparation of conductive coatings, such as polyaniline (PANI) coating [11], polypyrrole coating [12], polythiophene coating [13]. Poly-carbazole (PCz) has poor conductivity, so the electropolymeriza-tion of carbazole (Cz) is self-limited [14]. Thus it is difficult to fabricate an adequate thick coating for SPME. But Cz consists of a pyrrole ring and two fused benzene rings, so PCz has large con-jugate range and exhibits some unique properties such as good stability etc [15], which benefits the adsorption/or extraction of some analytes. Recently, research demonstrated that through co-

deposition with proper functional materials the electrodeposition of poor conductive polymers could be promoted. For example, Mirzaei et al. [16] used oxidized multiwalled carbon nanotubes (MWCNTs) as additive in the electrodeposition of poor conductive poly-o-phenylenediamine and obtained a good fiber for the analysis of polycyclic aromatic hydrocarbons. In addition, conductive MWCNT [17], graphene oxide [18], IL [19] and inorganic nanoparticle [20] were also attempted in preparing different coatings.

ILs are organic salt consisting of large organic cation and organic or inorganic anion. By designing their structures they can be immiscible with water or organic solvent, so they act as efficient extraction solvent [21]. Early in 1998, Huddleston et al. thought that ILs were novel extractant because they were characterized for their negligible vapor pressure and non-flammability [22]. After that, ILs gradually became popular in liquid phase extraction, such as single drop microextraction [23] and dispersive liquid–liquid microextraction [24]. As they have high viscosity and can be well immobilized on solid materials, Tian and co-workers [25] exploited ILs-based sorbents for solid phase extraction (SPE). Since then, the application of ILs as stationary phase in SPE and SPME received admirable attention [26–28]. Considering the broad electrochemical window and good stability of ILs, Zhao et al. prepared a PANI-IL composite coating by co-electrodeposition on a platinum wire, and the obtained fiber presented improved extraction performance [19]. Similarly, a nano-structured PANI-IL coating was fabricated on a steel wire for the determination of organochlorine pesticides [29], and a poly(3,4-ethylenedioxythiophene)-IL (PEDOT-IL) coating was reported for the determination of several alcohols [5]. These reports illustrated that ILs were effective dopant in polymers for SPME, however PCz-IL based SPME coatings are not reported so far.

In this work, PCz-IL was electrodeposited on stainless steel wires from acetonitrile solutions containing IL, Cz and tetrabutylammonium percholorate. The conductive IL was used as dopant and it was well retained in the polymer. The resulting fiber was used for the determination of environmental contaminants with headspace (HS) technique coupled with GC, and its performance with respect to sensitivity, linear range and precision was evaluated and discussed.

## 2. Experimental

### 2.1. Apparatus

The GC experiments were performed on a SP-6890 gas chromatograph equipped with a flame ionization detector (Shandong Lunan Ruihong Chemical Instrument, Tengzhou, China), and an SE-54 capillary column (5% phenyl–95% methyl polysilicone, 30 m × 0.25 mm I.D.) with 0.25 μm film thickness (Lanzhou Atech Technologies, Lanzhou, China) was adopted. A N2000 chromatographic workstation program (Zhejiang University of information engineering, Zhejiang, China) was used to process chromatographic data. The column temperature was programmed as follows: initial temperature was set at 50 °C, held for 3 min, and then the temperature was increased to 140 °C at 15 °C min$^{-1}$, to 160 °C at 2 °C min$^{-1}$, to 200 °C at 10 °C and kept at this temperature for 5 min. The inlet was operated under splitless mode; the injector port temperature and detector temperature were set at 260 °C.

Electropolymerization was performed on a CHI 600D electrochemical workstation (CH Instrument Company, Shanghai, China) and cyclic voltammetry mode was adopted. A three electrode system was employed, including a stainless steel wire (2 cm × 0.25 mm O.D.) as working electrode, a Pt wire (2.5 cm × 0.3 mm O.D.) as counter electrode and a Ag/AgCl electrode as reference electrode. The thermogravimetric analysis

(TGA) was conducted with a Setsys instrument (Aetaram, France). The scanning electron microscope (SEM) images and the energy dispersive spectra (EDS) of the coatings were obtained through a Quanta-200 SEM instrument (FEI, The Netherlands). The commercial polydimethylsiloxane (PDMS) and polyacrylate (PA) fibers were purchased from Supelco (Bellefonte, PA, USA).

### 2.2. Chemicals and materials

o-Chlorotoluene (o-CT), p-bromotoluene (p-BT) and tetrabutylammonium perchlorate (TBAP) were purchased from Aladdin Chemistry Company (Shanghai, China); o-nitrotoluene (o-NT), m-nitrotoluene (m-NT), p-nitrotoluene (p-NT), N,N-dimethylformamide (DMF), acetonitrile (ACN) and methanol came from Sinopharm Chemical Reagent Company (Shanghai, China). Carbazole was from Kayon Biological Technology Company (Shanghai, China). 1-Hydroxyethyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide ([HOEMIm][NTf$_2$]), 1-hydroxyethyl-3-methylimidazolium hexafluorophosphate ([HOEMIm][PF$_6$]) and 1-methyl-3-octylimidazolium hexafluorophosphate ([OMIm][PF$_6$]) were from Lanzhou Institute of Chemical Physics (Gansu, China). All the reagents were analytical grade. The stock solutions of analytes (100 mg mL$^{-1}$ for each) were prepared with methanol and stored in a refrigerator, and the working solutions were fresh prepared by diluting the stock solutions with saturated NaCl aqueous solution. Ultrapure water was obtained from a pg water purification system (PingGuan Co., Wuhan, China) and was used in the preparation of all aqueous solutions.

The water samples were lake water (Sample 1, from East Lake, Wuhan) and waste water (Samples 2 and 3, from a local printing-dyeing factory and a local petrochemical factory respectively, Wuhan). These samples were analyzed immediately after sampling without any pretreatment process. For SPME analysis, 10 mL real sample was saturated with sodium chloride.

### 2.3. Preparation of PCz-IL fibers

Prior to electropolymerization the stainless steel wire was etched with a mixture of concentrated acid solutions (i.e. HNO$_3$–HCl, v/v: 1:1) to achieve a rough surface. Then, the wire was washed with distilled water for 15 min with the aid of ultrasonication. The electropolymerization was conducted in 10 mL ACN−DMF (v/v: 9:1) solution containing 0.9% [HOEMIm][NTf$_2$], 0.1 M Cz monomer, 0.1 M TBAP. The potential was cycled for 50 times between 1.0 V and 2.0 V at 50 mV s$^{-1}$. After polymerization, the obtained fiber was washed with water and dried in air. Then it was aged in an electric furnace at 250 °C for 2 h in nitrogen atmosphere. Afterwards, the fiber was adhered to the laboratory-made SPME device with epoxy resin and conditioned in N$_2$ atmosphere in GC injection part for 30 min at 260 °C.

For comparison, other PCz-IL fibers were also prepared through the same method, but the [HOEMIm][NTf2] was replaced by other ILs. PCz fiber was prepared by the similar method but in the absence of IL. The thicknesses of PCz coating and PCz-[HOEMIm][NTf$_2$] coating were measured with an optical microscope and they were 48 μm and 84 μm, respectively.

### 2.4. HS-SPME procedure

A 10 mL saturated NaCl aqueous solution containing proper analytes was transferred into a 15 mL glass vial with silicon rubber septum. The vial was tightly sealed with an aluminum cap and then it was placed on a magnetic agitator with a water bath to control temperature. When the temperature reached the fixed value the fiber was exposed to the headspace over the working solution for a certain time. Then the fiber was withdrawn into the