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Ionic liquid coated copper wires and tubes for fiber-in-tube solid-phase microextraction[☆]

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ABSTRACT

A fiber-in-tube solid-phase microextraction (SPME) device was developed by filling eleven copper wires into a copper tube, and all of those were functionalized with ionic liquids. Its morphology and surface properties were characterized by scanning electron microscopy. It was connected into high performance liquid chromatography (HPLC) equipment by replacing the sample loop of six-port injection valve, building the online SPME-HPLC system. In the optimization of extraction conditions, sampling rate, sample volume, pH of sample and desorption time were investigated with five estrogens as model analytes. Under the optimum conditions, an online SPME-HPLC analysis method was achieved, showing enrichment efficiency from 611 to 1661 and a good linearity of 0.06–60 $\mu g\,L^{-1}$ with low detection limits of 0.02–0.05 $\mu g\,L^{-1}$. It was applied to detect estrogens analytes in two water samples, with recoveries in the range of 85–114%. Relative standard deviation ($n=3$) of extraction repeatability is in the range of 1.9–3.0%. Relative standard deviation of extraction tubes ($n=3$) is in the range of 12–19%. The extraction mechanism is probably related to hydrophobic, π-π and dipole-dipole interactions between ionic liquids coating and estrogens analytes.

1. Introduction

In-tube SPME introduced by Pawliszyn in 1997 has been developed as an important SPME technique [1]. It presents a convenient format for coupling SPME to HPLC and for automated operation of SPME-HPLC [2], in which extraction and desorption can be exchanged simply. It is especially important for the analysis of a wide range of less volatile or thermally labile compounds [3] that are not amenable to gas chromatography (GC) analysis. GC columns were early used as in-tube SPME materials since they were diverse and available for lab [4,5]. Then fused-silica capillary was widely applied to in-tube SPME because it could be chemically modified with sorbent coating [6–9]. In conventional in-tube SPME, there still exist a number of shortcomings that need to be overcome. These include susceptibility of the tube to mechanical damage, low sample capacity, weak solvent stability of prepared sorbent coatings and large dead volume in tube.

Metal tubes with high strength such as stainless steel tube, copper tube had been introduced in-tube SPME. Chen et al. explored the extraction performance of a stainless steel sample loop toward polycyclic aromatic hydrocarbons (PAHs) [10]. In our previous work, a copper fiber-in-tube was developed as a SPME tube, which exhibited high extraction efficiency for PAHs [11]. The results indicated the application potentiality of metal tubes in-tube SPME. However, extraction performance of metal-based in-tube SPME is limited because metal is chemically inert [12]. Various coating materials including metal-organic nanotubes [13], metal-organic framework [14,15], carboxylated solid carbon spheres [16] and nitrogen-doped ordered mesoporous polymer [17] have been developed recently for fiber SPME. If these coating materials could be chemically modified onto metal tube, the development of in-tube SPME will be greatly promoted. Ionic liquids (ILs) are organic molten salts with a melting point close to or below room temperature [18]. In analytical chemistry, ILs have been widely used in GC [19], capillary electrophoresis [20,21], HPLC [22], liquid-liquid extraction [23], single-drop extraction [24], dispersive liquid-liquid microextraction [25] and so on. In this work, ILs were applied to functionalize copper wires and tube for fiber-in-tube SPME. An ILs functionalized copper fiber-in-tube was connected into HPLC equipment to build online SPME-HPLC system. The SPME-HPLC method was investigated with five estrogens (shown in Fig. 1) as

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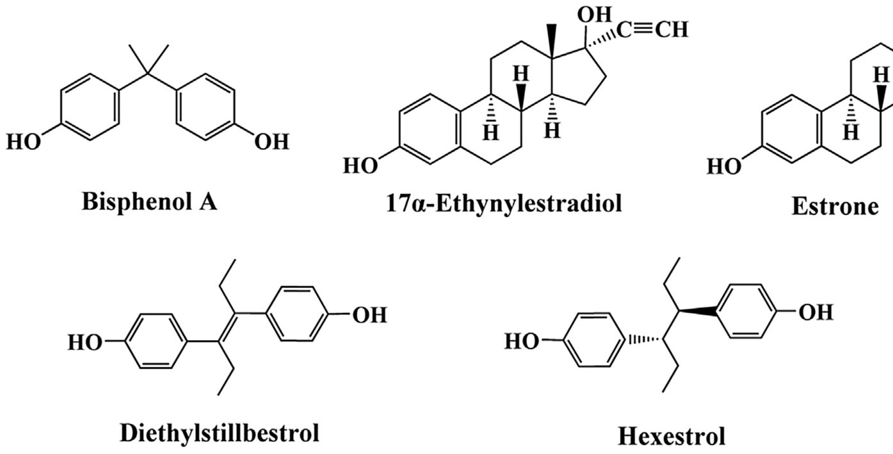

Fig. 1. The chemical structure of five estrogens analytes.

analytes. Analytical parameters including linear range, limits of detection, repeatability and enrichment factors were investigated under the optimized conditions. The analysis method was used to detect these estrogens in water samples.

2. Experimental

2.1. Materials and reagents

Copper tube (0.80 mm i.d., 1.6 mm o.d.) and copper wires (0.14 mm d.) were purchased from Shenzhen Global Copper and Aluminum Co., Ltd. (Shenzhen, China). Bisphenol A, 17α-ethynylestradiol, estrone, diethylstillbestrol and hexestrol were purchased from J&K Chemical Co., Ltd. (Shanghai, China). Acetonitrile was chromatographic grade and obtained from Tedia Company Inc. (USA). 1-Vinylimidazole, 1-bromododecane, 1,6-dibromohexane and 1,8-octanedithiol were purchased from Shanghai Jingchun Industry Co. (Shanghai, China). Azobisisobutyronitrile (AIBN) was obtained from Shanpu Chemical Co. (Shanghai, China) and purified via recrystallization in ethanol. Nitric acid (68%) was of analytical grade quality and obtained from Kangde Chemical Reagent Co. (Laiyang, China). All reagents were analytical grade.

2.2. Apparatus

All chromatographic tests were performed on an Agilent 1260 Infinity series (Santa Clara, CA, USA) equipped with a Zorbax C18 column (250 × 4.6 mm i.d., 5 μm), a 20 μL sample loop and a diode array detector (DAD). Analytes were detected at 202 nm. A P1201 HPLC pump was used to move sample solution for extraction and purchased from Dalian Elite analytical instruments Co., Ltd. (Dalian, China). Mobile phases were filtered with a 0.45 μm nylon membrane filter. Acetonitrile-water (50:50, v/v) was used as the mobile phase at 25 °C and 1 mL min^{-1}.

Ionic liquids monomer and crosslinking agent were characterized by ^{1}H NMR (BRUKER 400 MHz). Extraction tube was characterized by a field-emission scanning electron microscope (SEM, SUPRATM55, Carl Zeiss, AG, Germany).

2.3. Preparation of sample solutions

Stock solution of analytes was prepared at a concentration of 10 mg L^{-1} with acetonitrile solvent. Working solutions were prepared daily by diluting the stock solution with distilled water to 10 μg L^{-1}. Bottled pure water and domestic sewages were collected locally as real samples. Before analysis, water samples were filtered with a 0.45 μm nylon membrane.

2.4. Synthesis of ionic liquids monomer and crosslinking agent

Two kinds of ionic liquids including 1-dodecyl-3-vinylimidazolium bromide and 1,6-di(3-vinylimidazolium) hexane bibromide were synthesized as the monomer and the crosslinking agent, respectively. Synthesis reactions of two ionic liquids are shown in Fig. S1. 1-Dodecyl-3-vinylimidazolium bromide was obtained according to the following procedures: 1-vinylimidazole (0.05 mol) and equimolar 1-bromododecane were dissolved in 30 mL acetone and stirred for 48 h at room temperature. The white product was purified by recrystallization in acetone and then dried at 50 °C under vacuum. 1,6-Di(3-vinylimidazolium) hexane bibromide was synthesized according to the method described in previous reports [26,27]. 1,6-Dibromohexane (0.05 mol) dissolved in 10 mL acetone was slowly added into 1-vinylimidazole (0.10 mol) dissolved in 40 mL acetone. The mixture was stirred for 24 h at room temperature. The precipitate was obtained by filtering the liquid phase. The product was purified by recrystallization in acetone.

The structure was confirmed by ^{1}H NMR. ^{1}H NMR (DMSO-d_6, 400 MHz; δ, ppm, relative to TMS) of 1-dodecyl-3-vinylimidazolium bromide: 9.651 (s, 1H), 8.260–8.269 (t, 1H), 7.990 (s, 1H), 7.306–7.367 (q, 1H), 5.979–6.023 (q, 1H), 5.416–5.444 (q, 1H), 4.199–4.235 (t, 2H), 1.812–1.846 (t, 2H), 1.241 (s, 18H), 0.838–0.872 (t, 3H). ^{1}H NMR (DMSO-d_6, 400 MHz; δ, ppm, relative to TMS) of 1,6-di(3-vinylimidazolium) hexane bibromide: 9.721 (s, 2H), 8.267–8.276 (t, 2H), 8.014–8.022 (t, 2H), 7.318–7.379 (q, 2H), 5.991–6.036 (q, 2H), 5.422–5.449 (q, 2H), 4.222–4.258 (t, 4H), 1.840–1.873 (t, 4H), 1.302–1.336 (t, 4H).

2.5. Preparation of ILs functionalized extraction tube

A copper tube (25 cm) and some copper wires (25 cm) were used as the support. In order to increase surface area, copper tube and wires were etched with a 3.8 mol L^{-1} of nitric acid for 20 min. Then they were washed with water and dried. Copper tube was filled with 20 mmol L^{-1} of 1,8-octanedithiol solution in ethanol. Copper wires were also immersed into this solution for 24 h 1.6 g of 1-dodecyl-3-vinylimidazolium bromide was dissolved into 4 mL dimethyl sulfoxide (DMSO). 0.9 g of 1,6-di(3-vinylimidazolium) hexane bibromide was dissolved into 3 mL methanol. Two solutions were mixed and 40 mg AIBN was dissolved into the solution. The reaction solution was placed into a glass tube (35 cm, 0.5 cm i.d.) sealed at one end, and oxygen was purged by inletting high-