Determination of water pollutants by direct-immersion solid-phase microextraction using polymeric ionic liquid coatings

Jessica López-Darias [a], Verónica Pino [a,*], Jared L. Anderson [b,**], Christa M. Graham [b], Ana M. Afonso [a]

[a] *Departamento de Química Analítica, Nutrición y Bromatología, Universidad de La Laguna (ULL), avda. Astrofisico Fco. Sanchez s/n, La Laguna (Tenerife), 38206, Spain*
[b] *Department of Chemistry, The University of Toledo, Toledo, OH 43606, USA*

ARTICLE INFO

ABSTRACT

The determination of a group of eighteen pollutants in waters, including polycyclic aromatic hydrocarbons and substituted phenols, is conducted in direct-immersion solid-phase microextraction (SPME) using the polymeric ionic liquid (PIL) poly(1-vinyl-3-hexadecylimidazolium) bis[(trifluoromethyl)sulfonyl]imide as a novel coating material. The performance of the PIL fiber coating in the developed IL-SPME-gas chromatography (GC)–mass spectrometry (MS) method is characterized by average relative recoveries of 92.5% for deionized waters and 90.8% for well waters, average precision values (as relative standard deviations, RSD%) of 11% for deionized waters and 12% for well waters, using a spiked level of 5 ng mL^{-1}. The detection limits oscillate from 0.005 ng mL^{-1} for fluoranthene to 4.4 ng mL^{-1} for 4-chloro-3-methylphenol, when using an extraction time of 60 min with 20 mL of aqueous sample. The extraction capabilities of the PIL fiber have been compared with the commercial SPME coatings: polydimethylsyloxane (PDMS) 30 μm, PDMS 100 μm and polyacrylate (PA) 85 μm. The PIL fiber is superior to the PDMS 30 μm for all analytes studied. A qualitative study was also carried out to compare among the nature of the coating materials by normalizing the coating thickness. The PIL material was shown to be more efficient than the PDMS material for all analytes studied. The PIL coating was also adequate for nonpolar analytes whereas the PA material was more sensitive for polar compounds.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

The utilization of microextraction procedures in sample preparation is becoming more popular due to advantages such as minimization (or elimination) of organic solvent consumption in the extraction step and high preconcentration factors [1]. Among microextraction procedures, solid-phase microextraction (SPME) is undoubtedly the most widely technique used nowadays [1,2]. The convenience of the technique is due to the integration of extraction, preconcentration, and sample introduction in one step. The largest disadvantage associated with SPME is arguably the limited number of stationary phases commercially available [3]. The most common coating materials are polydimethylsyloxane (PDMS) and polyacrylate (PA), which are adequate for non-polar and polar analytes, respectively.

There has been an increasing interest in developing new coating materials in SPME in order to achieve better sensitivity and selectivity [3,4]. With respect to fiber coating development, the sol–gel

method is probably the most widely used approach [5,6]. Molecular imprinted polymers (MIPs), which have gained attention for the extraction of analytes from complex samples, are commonly prepared by physical deposition [3,7,8]. Electrochemical deposition is another tool to prepare materials for fiber coatings in SPME [3,9,10].

Ionic liquids (ILs) are non-molecular solvents that have recently gained significant attention as a newer class of designer solvents. These ionic media result from the combination of organic cations and various anions [11,12], with the asymmetrically substituted nitrogen-containing cations being the most common in IL structures. ILs typically possess negligible vapor pressure, high thermal stability, and unique catalytic properties [13] compared to conventional molecular solvents. One of the most interesting characteristics of the ILs is that their physicochemical and solvation properties can be effectively "tuned" by simple tailoring of the substituent groups comprising the cation and/or anion [14].

ILs have been demonstrated in many analytical extraction and microextraction schemes [11,12], such as liquid–liquid extraction [15], microwave-assisted extraction [16], single-drop microextraction [17–19], and dispersive liquid–liquid microextraction [20,21], among others. SPME has also been used with samples dissolved in ionic liquid aggregates [22,23].

The utilization of ILs as coating materials in solid-phase microextraction has also been demonstrated previously. Initially, ILs were used as disposable coatings [24]. They were later supported on nafion membranes [25]. In both cases, the fibers needed to be re-coated after each desorption step. Recently, ILs have been impregnated into a crosslinked silicone elastomer and demonstrated to be reusable IL-SPME coatings [26]. Anderson and co-workers first showed that polymeric ionic liquids (PILs) exhibit unique material properties while largely retaining the solvation properties inherent to ILs [27,28]. The stability of sorbent coatings based on these materials (in terms of stability of the coating layer and thermal stability) have allowed for the development of reusable coatings for headspace SPME. The tuneability of the PIL monomer provides for the incorporation of functional groups within the polymeric structure to produce sorbent coatings capable of selectively extracting target analytes, such as CO_2 [29].

This manuscript describes the utilization of a highly hydrophobic PIL, poly(1-vinyl-3-hexadecylimidazolium) bis[(trifluoromethyl)sulfonyl]imide, as the SPME sorbent coating for the extraction of eighteen contaminants in waters, including polycyclic aromatic hydrocarbons and substituted phenols. This is the first report in which sorbent coatings based on ILs have been utilized in direct-immersion SPME for the extraction of water pollutants and coupled with gas chromatography–mass spectrometry.

2. Experimental

2.1. Reagents and materials

The polycyclic aromatic hydrocarbons (PAHs) studied were naphthalene (N), acenaphthene (Ace), fluorene (Fl), phenanthrene (Phe), and fluoranthene (Ft), all supplied by Sigma–Aldrich Chemie GmBH (Steinheim, Germany), except naphthalene, which was supplied by Merck (Darmstadt, Germany). Individual standard solutions of these PAHs were prepared in methanol of HPLC gradient quality (Scharlau, Barcelona, Spain) with concentrations ranging from 1035 to 1160 $mg\,L^{-1}$. These solutions were used to prepare a standard solution mixture of PAHs of 20 $mg\,L^{-1}$ in methanol.

The alkylphenols used in this study were bisphenol-A (BPA), 4-cumylphenol (4-CP), 4-tert-butylphenol (t-BP), 4-octylphenol (OP), 4-tert-octylphenol (t-OP), and 4-n-nonylphenol (NP). They were all supplied by Sigma–Aldrich Chemie GmBH, except NP, which was supplied by Alfa-Aesar (Karlsruhe, Germany). Individual standard solutions of these analytes were prepared in methanol of HPLC gradient quality (Scharlau) with concentrations ranging from 200 to 850 $mg\,L^{-1}$. These solutions were used to prepare a standard solution mixture of alkylphenols of 20 $mg\,L^{-1}$ in methanol.

The chloro-, methyl- and nitro-phenols used in this study were 2-chlorophenol (2-CP), 2-nitrophenol (2-NP), 2,4-dichlorophenol (2,4-DCP), 2,4,6-trichlorophenol (2,4,6-TCP), pentachlorophenol (PCP), 2,4-dimethylphenol (2,4-DMP), and 4-chloro-3-methylphenol (4-C-3-MP), all supplied by Sigma–Aldrich Chemie GmBH except 2,4-DMP and 4-C-3-MP, which were supplied by Merck. Individual standard solutions of these phenols were prepared in methanol of HPLC gradient quality (Scharlau) with concentrations ranging from 950 to 1100 $mg\,L^{-1}$. These solutions were used to prepare a standard solution mixture of phenols of 20 $mg\,L^{-1}$ in methanol.

SPME working and calibration aqueous standard solutions were prepared by spiking deionized water with the three above mentioned standard solution mixtures of phenols, alkylphenols and PAHs. The total methanol content in the aqueous solutions was always lower than 0.8% (v/v). Another standard solution mixture containing the three above mentioned standard mixtures of phenols, alkylphenols and PAHs, with a concentration of 1 $mg\,L^{-1}$ in methanol, was also prepared to further spike aqueous samples at low levels of concentration.

Deionized water (18.2 $m\Omega\,cm^{-1}$) was obtained from a Milli-Q gradient A10 system (Millipore, Watford, UK). Well waters were kindly supplied by a Water Quality Control Laboratory in Tenerife (Spain). Real water samples were used without any prior treatment.

The synthesis of the 1-vinyl-3-hexadecylimidazolium chloride IL monomer and corresponding polymer involved the use of the following reagents: vinyl imidazole, 2,2′-azobis(isobutyronitrile) (AIBN), and 1-chlorohexadecane which were purchased from Sigma–Aldrich (St. Louis, MO, USA), lithium bis[(trifluoromethyl)sulfonyl]imide which was obtained from SynQuest Labs (Alachua, FL, USA), and ethyl acetate and 2-propanol which were purchased from Fisher Scientific (Fairlawn, NJ, USA). Propane and microflame brazing torches were purchased from Sigma–Aldrich.

All laboratory-made SPME devices were constructed using a 5-μL syringe purchased from Hamilton (Reno, NV, USA) and 0.10 mm I.D. fused silica capillary obtained from Supelco (Bellefonte, PA, USA). Commercial SPME fibers of PDMS (film thicknesses of 30 and 100 μm) and PA (film thickness of 85 μm) were obtained from Supelco.

Glass vials (20 mL) with PTFE/Butyl septa screwcaps supplied by CTC Analytics (Zwingen, Switzerland) were used in the study. PTFE stir bars of 15 mm × 4.5 mm were obtained from VWR International Eurolab S.L. (Barcelona, Spain).

2.2. Instrumentation

The identification and quantification of analytes were achieved using SPME and gas chromatography–mass spectrometry (GC–MS). GC–MS was performed on a Varian model CP-3800 Varian Saturn 2200 GC–MS system, equipped with a 30 m × 0.25 mm I.D. VF-5 ms column (Varian). The equipment also includes a Combi-Pal autosampler (CTC Analytics). The GC column was employed under the following temperature programs: 60 °C, 2 min isothermal, 15 °C min⁻¹ to 120 °C, then 7 °C min⁻¹ to 300 °C, and then 3 min isothermal. The carrier gas was helium, with a flow of 1.2 mL min⁻¹. The temperature of the injector was maintained at 280 °C for all commercial SPME fibers, and 250 °C for the PIL fiber. Desorption time for the fiber in the GC injector was always 6 min, except for the PIL fiber, which was 5 min to increase its lifetime. The temperature of the transfer line was maintained at 280 °C for all SPME fibers. The ionization was performed with a kinetic energy of the impacting electrons of 70 eV. The temperature of the ion trap was 200 °C, and the manifold temperature was 60 °C. MS analysis was carried out in selected ion storage (SIS) mode and therefore, the quantitative determination was carried out using the mass values corresponding to the molecular ions of the different analytes in different analysis segments, as it can be observed in Table 1. The Saturn GC–MS workstation 6.9.1 Software (Varian) was used for data acquisition.

2.3. Procedures

Laboratory-made SPME devices were constructed using a slight modification of the procedure first described by Arthur and Pawliszyn in their early work [2]. The polyimide polymer was subsequently removed from the last 1.0 cm segment of the fiber using a high temperature flame followed by sealing of the end of the capillary using a microflame torch. The fiber was then washed with methanol, hexane, acetone and dichloromethane followed by a 10-min conditioning step in the GC injection port at 250 °C.