Journal of Chromatography A, 1217 (2010) 1236–1243

Contents lists available at ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

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

Article history:
Received 11 November 2009
Received in revised form
11 December 2009
Accepted 14 December 2009
Available online 21 December 2009

Keywords:
Ionic liquids
Polymeric ionic liquids
Solid-phase microextraction
Water pollutants
Gas chromatography–mass spectrometry

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.

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].

* Corresponding author. Tel.: +34 922318012; fax: +34 922318090.
** Corresponding author. Tel.: +1 4195301508; fax: +1 4195304033.
E-mail addresses: veropino@ull.es (V. Pino), Jared.Anderson@UToledo.edu (J.L. Anderson).

0021-9673/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.chroma.2009.12.041

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 mΩ 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′-azo-bis(isobutyronitrile) (AIBN), and 1-chlorohexadecane which were purchased from Sigma–Aldrich (St. Louis, MO, USA), lithium bis[(trifluoromethyl)sulfonyl]imide which was obtained from Syn-Quest 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.

Table 1
Analytes studied, average retention times, ions used for their quantification, and segments utilized for the SIS analysis.

Analyte	Retention time ± SD[a] (min)	Quantification ion (m/z)	Analysis segments (SIS)
2-Chlorophenol (2-CP)	5.063 ± 0.023	128	1 (4–6 min)
2-Nitrophenol (2-NP)	6.776 ± 0.028	139	2 (6–7 min)
2,4-Dimethylphenol (2,4-DMP)	6.865 ± 0.009	107, 122	
2,4-Dichlorophenol (2,4-DCP)	7.214 ± 0.018	162	3 (7–8 min)
Naphthalene (N)	7.514 ± 0.004	128	
4-Chloro-3-methylphenol (4-C-3-MP)	8.782 ± 0.008	77, 107, 142	4 (8–9.2 min)
4-*t*-Butylphenol (*t*-BP)	8.800 ± 0.006	135	
2,4,6-Trichlorophenol (2,4,6-TCP)	9.804 ± 0.018	97, 196:200	5 (9.2–11 min)
Acenaphthene (Ace)	11.926 ± 0.004	154	6 (11–13 min)
Fluorene (Fl)	13.485 ± 0.005	165	7 (13–15 min)
4-*t*-Octylphenol (*t*-OP)	13.617 ± 0.051	135	
Pentachlorophenol (PCP)	15.914 ± 0.025	266	8 (15–16.3 min)
4-Octylphenol (OP)	16.103 ± 0.028	107	
Phenanthrene (Phe)	16.509 ± 0.009	178	9 (16.3–17 min)
4-Cumylphenol (4-CP)	17.450 ± 0.034	197	10 (17–19 min)
4-*n*-Nonylphenol (NP)	17.616 ± 0.016	107	
Fluoranthene (Ft)	21.141 ± 0.015	202	11 (19–25 min)
Bisphenol-A (BPA)	21.710 ± 0.047	213	

[a] Standard deviation for $n = 40$.

The IL monomer, 1-vinyl-3-hexadecylimidazolium bromide and its corresponding polymer, poly(ViHDIm-Br), were synthesized following previously reported procedures [30]. Briefly, 1-vinylimidazole was dissolved in 2-propanol and reacted with a 1:1 molar ratio of 1-bromohexadecane under reflux and constant stirring followed by extraction with ethyl acetate. After purification, polymerization was performed in chloroform in the presence of the free radical initiator AIBN to generate poly(1-vinyl-3-hexadecylimidazolium) bromide. The polymerization step was repeated, if necessary, until the peaks belonging to the vinyl group in ^{1}H NMR disappeared. To perform metathesis anion exchange, the PIL was dissolved in chloroform and a 10% excess of $LiNTf_2$ was introduced to the solution. The resulting precipitate was collected, washed with water to remove any residual halide anion, and dried overnight under vacuum to yield poly(1-vinyl-3-hexadecylimidazolium) bis[(trifluoromethyl)sulfonyl]imide [poly(ViHDIm-NTf_2)]. To make the PIL amendable to coating as a thin film on the fused silica fiber support, a solution was prepared by mixing the PIL in acetone at a ratio of 9:1 (v/v). The conditioned bare fused silica fiber was then dipped into the PIL solution, held for 20 s, and removed from the coating solution and allowed to dry in the air for 10 min. Prior to performing extractions, the coated fibers were conditioned at 250 °C in the GC injection port for 10 min to eliminate residual solvents from the fiber support.

All SPME extractions, using either commercial fibers or the PIL fiber, were conducted in direct-immersion mode. The extraction time used for all fibers was 60 min. All SPME extractions using the PIL fiber were performed at constant stirring rate of 500 rpm on a stir plate (big squid IKAMAG® Froggy, Germany). All SPME extractions conducted with the commercial fibers were automatically carried out with the Combi-Pal autosampler.

The glassware and the stir bars used in this study were first washed with detergent and tap water, and then rinsed with methanol (Merck) and deionized water. Finally, the non-graduated glassware and, especially, the sample vials were dried in an oven at 550 °C and wrapped with aluminium foil before use.

3. Results and discussion

3.1. Characterization of the PIL fiber and its utilization in direct-immersion SPME

The PIL SPME fiber was characterized by optical microscopy and the film thickness estimated to be approximately 20 μm. To ensure that the PIL coating was attributed to the extraction of the analytes, experiments were also conducted using a bare fused silica fiber containing no stationary phase. The obtained analyte peak areas were negligible when compared to the peak areas obtained with the 20 μm PIL coating.

A group of eighteen analytes, including polycyclic aromatic hydrocarbons and substituted phenols, were selected in this study to evaluate the extraction behavior of the PIL fiber with these contaminants. The evaluation and monitoring of organic contaminants in environmental samples is an important issue.

The sorption–time profiles for the PIL fiber in water were obtained by direct immersion of the PIL fiber into 20 mL of an aqueous solution containing the studied analytes for different extraction times (from 15 to 100 min) while stirring at room temperature. The profiles were obtained using working solutions containing a constant concentration of the analytes (50 ng mL^{-1}), with the overall content of methanol lower than 0.8% (v/v). For comparative purposes, the profiles for the PDMS 30 μm fiber were also obtained under the same experimental conditions. This fiber has been selected for possessing a similar coating thickness than the PIL fiber (~20 μm), which makes the comparison more adequate. It is well-known the influence of the coating thickness in the extraction efficiency when performing SPME [31,32]: higher coating thicknesses are beneficial for achieving higher extraction efficiencies. Fig. 1 shows an example of the profiles obtained with both fibers for *t*-octylphenol.

With respect to the PIL fiber, the studied analytes generally required extraction times longer than 60 min to reach equilibration. Moreover, analytes such as PCP, Phe, NP, Ft and BPA never reached equilibration under the interval time studied. The behavior of the studied analytes with the PDMS 30 μm fiber, in terms of equilibration time, was similar to the PIL fiber. In order to have acceptable extraction efficiencies to work with, an extraction time of 60 min was selected for further studies. In SPME, it is not necessary for analytes to reach equilibration [33] but to use a relatively short extraction time which ensures acceptable extraction efficiency and limits of detection.

3.2. Calibrations obtained with the PIL fiber in direct-immersion SPME

Calibration curves of each analyte in deionized water were obtained at the selected extraction time (60 min) using the PIL fiber in direct-immersion mode. The figures of merit of the calibration curves for the analytes studied including slope, linearity, calibra-

Table 2
Quality parameters of the SPME calibrations using the PIL fiber (~20 μm coating thickness).

Analyte	Calibration range (ng mL^{-1})	Slope ± SD[a]	Error of the estimate	R	LOD (ng mL^{-1})
2-Chlorophenol	5–20	151 ± 11	179	0.990	4.0
2-Nitrophenol	5–20	546 ± 16	250	0.999	1.9
2,4-Dimethylphenol	5–20	273 ± 16	140	0.992	2.5
2,4-Dichlorophenol	4–20	710 ± 32	479	0.997	1.5
Naphthalene	2–20	53,180 ± 920	17,496	0.999	0.06
4-Chloro-3-methylphenol	6–20	99 ± 5	341	0.999	4.4
t-Butylphenol	2–20	3420 ± 150	2890	0.993	0.6
2,4,6-Trichlorophenol	3–20	35,400 ± 1800	32,783	0.992	0.07
Acenaphthene	0.05–20	110,400 ± 3000	56,874	0.997	0.008
Fluorene	0.05–20	145,900 ± 4700	88,851	0.996	0.009
t-Octylphenol	2–20	22,460 ± 440	8318	0.999	0.08
Pentachlorophenol	2–10	9880 ± 800	5371	0.994	0.4
Octylphenol	0.05–20	372,000 ± 10,000	182,007	0.998	0.006
Phenanthrene	0.05–20	303,000 ± 13,000	241,644	0.994	0.007
4-Cumylphenol	2–20	24,750 ± 790	14,953	0.996	0.09
4-*n*-Nonylphenol	0.05–20	385,000 ± 20,000	376,682	0.991	0.006
Fluoranthene	0.05–15	482,000 ± 38,000	102,089	0.996	0.005
Bisphenol-A	5–20	250 ± 16	300	0.990	2.1

[a] SD: error of the slope for $n = 8$.

tion range, error of the estimate, and limits of detection, are shown in Table 2.

The obtained linearity of the overall method was found to be acceptable, with correlation coefficients (R) ranging from 0.990 to 0.999. The sensitivity, which can be evaluated by the slope, is higher for PAHs like phenanthrene and fluorene, and for endocrine disrupting phenols like octylphenol and 4-*n*-nonylphenol. The limits of detection (LODs) were calculated as three times the signal to noise ratio, and were verified by injection of deionized water samples spiked at such levels and subjected to the overall SPME extraction. LODs oscillate from 0.005 ng mL^{-1} for fluoranthene to 4.4 ng mL^{-1} for 4-chloro-3-methylphenol. For PAHs, literature LODs using SPME-GC–MS oscillate from 0.03 ng mL^{-1} for phenanthrene to 0.12 ng mL^{-1} for fluoranthene when using the PDMS 30 μm fiber (similar coating thickness to compare with the PIL fiber) [34]; and from 0.001 ng mL^{-1} for fluoranthene to 0.017 ng mL^{-1} for phenanthrene when using the PDMS 100 μm fiber [35]. Better detection limits are undoubtedly obtained for PAHs when using SPME-GC–MS–MS detection [36]. For endocrine disrupting phenols, the literature LODs using SPME-GC–MS without performing derivatization reactions oscillate from 0.2 ng mL^{-1} for *t*-nonylphenol to 0.3 ng mL^{-1} for bisphenol-A [37]. Better detection limits are undoubtedly obtained for phenols when using derivatization procedures [38,39]. The LODs obtained with the PIL fiber can therefore be considered acceptable, especially considering that these experiments have been conducted without controlling the pH or the ionic strength of the samples, and using the MS in SIS mode. The ultimate purpose of this work was to evaluate the performance of the PIL fiber in direct-immersion SPME as well as its applicability with analytes of different nature, rather than to establish a method to characterize the selected analytes at ultra trace levels in waters.

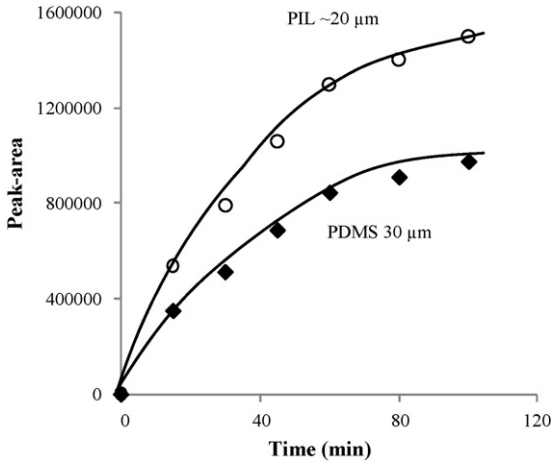

Fig. 1. Profiles obtained for *t*-octylphenol (50 ng mL^{-1}) when using PIL (~20 μm) and PDMS (30 μm) fibers in direct-immersion mode of SPME.

Fig. 2 shows a representative chromatogram obtained with the PIL fiber in direct-immersion SPME for the analytes studied. The retention times of the studied analytes can be observed in Table 1, with relative standard deviations (RSD) oscillating from 0.05% to 0.45%.

3.3. Comparison with commercial SPME fibers

Calibration curves of each analyte in deionized water were also obtained with three commercial SPME fiber coatings: PDMS 30 μm, PDMS 100 μm and PA 85 μm, under the same experimental conditions. The calibrations were obtained using the same calibration range of the PIL fiber. Table 3 includes several analytical figures of merit for the calibrations obtained with the commercial SPME fibers.

The calibrations of the PIL fiber (~20 μm) must be first compared with the ones obtained with the PDMS 30 μm fiber, which has the closest coating thickness to the PIL [6]. Considering the obtained results, it is clear the superior performance of the PIL fiber in terms of sensitivity (slope and LODs) for all analytes studied.

The PIL fiber is even more sensitive than the PDMS 100 μm fiber for analytes such as 2-NP, 2,4,6-TCP, PCP, 4-CP and BPA. The PIL fiber also exhibits comparable sensitivity to the PDMS 100 μm fiber for analytes such as 2,4-DMP, 2,4-DCP, 4-C-3-MP, 4-*n*-NP and Ft. This should be highlighted especially considering the differences in thickness as the PDMS 100 μm fiber is 5 times thicker than the PIL fiber. From Table 3, it can also be observed that PCP and BPA could not be adequately quantified with the PDMS fiber. The PA 85 μm fiber generally exhibits higher sensitivity than the PIL fiber.

The differences in coating thickness among the four studied fibers clearly affect the comparison as the extraction efficiency in SPME is strongly affected by the coating thickness [31,32] and by the surface area of extraction phase [40]. The commercial studied coating fibers and the PIL fiber have an approximate length of 1 cm, and so it can be assumed that they possess similar surface areas. In an attempt to normalize the extraction efficiency with the coating thickness, we studied the influence of the thick-

Table 3
Quality parameters of the SPME calibrations using the commercial fibers: PDMS 30 μm, PDMS 100 μm and PA 85 μm.

Analyte	30 μm PDMS fiber			100 μm PDMS fiber			85 μm PA fiber		
	Slope ± SD[a]	*R*	LOD (ng mL^{-1})	Slope ± SD[a]	*R*	LOD (ng mL^{-1})	Slope ± SD[a]	*R*	LOD (ng mL^{-1})
2-CP	143 ± 6	0.995	5.1	390 ± 24	0.990	2.5	7220 ± 360	0.994	0.5
2-NP	68 ± 4	0.992	3.6	135 ± 26	0.990	3.2	1662 ± 45	0.998	0.7
2,4-DMP	112 ± 7	0.993	4.8	332 ± 25	0.991	2.3	10,510 ± 350	0.996	0.3
2,4-DCP	250 ± 16	0.991	3.3	767 ± 45	0.992	1.4	49,500 ± 2100	0.994	0.07
N	57,100 ± 2300	0.993	0.07	187,000 ± 79,000	0.993	0.008	243,000 ± 14,000	0.990	0.007
4-C-3-MP	30 ± 1	0.999	7.1	118 ± 5	0.999	4.8	8260 ± 400	0.993	0.5
t-BP	1212 ± 19	0.999	0.6	4170 ± 180	0.994	0.4	88,900 ± 2600	0.996	0.01
2,4,6-TCP	251 ± 6	0.999	2.9	373 ± 38	0.990	3.3	29,700 ± 1900	0.990	0.08
Ace	110,000 ± 4400	0.993	0.006	282,000 ± 15,000	0.990	0.003	293,000 ± 6700	0.998	0.007
Fl	123,100 ± 5000	0.994	0.01	360,600 ± 8600	0.998	0.003	390,270 ± 11,000	0.996	0.006
t-OP	14,820 ± 280	0.999	0.2	95,600 ± 4200	0.998	0.01	282,900 ± 5100	0.999	0.007
PCP	–	–	–	–	–	–	7780 ± 830	0.989	0.5
OP	261,600 ± 8000	0.998	0.007	459,000 ± 25,000	0.997	0.003	444,000 ± 8600	0.998	0.005
Phe	250,100 ± 7900	0.998	0.006	544,000 ± 11,000	0.999	0.002	650,000 ± 18,000	0.995	0.001
CP	6310 ± 280	0.993	0.9	23,100 ± 1500	0.990	0.08	387,000 ± 9000	0.998	0.006
NP	285,000 ± 6200	0.999	0.009	462,000 ± 36,000	0.991	0.003	469,900 ± 8900	0.999	0.005
Ft	280,800 ± 16,000	0.995	0.007	491,000 ± 8400	0.999	0.002	427,000 ± 15,000	0.995	0.005
BPA	-	-	-	-	-	-	35,200 ± 1700	0.993	0.07

[a] SD: error of the slope for $n = 8$.

ness for the same coating nature: PDMS. It was first calculated for each analyte the ratio: slope using the PDMS 100 μm fiber/slope using the PDMS 30 μm fiber. The average ratio for all analytes, excluding *t*-octylphenol, possess of confidence interval of 2.6 ± 0.4 ($\alpha = 0.05$). The ratio for the coating thickness (100 μm/30 μm) is 3.3. There is an approximate factor of 3 increase in sensitivity when moving from the 30 μm to 100 μm PDMS fiber. A correlation coefficient (*R*) of 0.971 is obtained when plotting the slopes of the PDMS 100 μm fiber *versus* the slopes of the PDMS 30 μm fiber. If excluding phenanthrene, fluoranthene, octylphenol and 4-*n*-nonylphenol (the heaviest analytes), the relationship among slopes has a *R* value of 0.989 and a slope of 2.8 ± 0.3 (confidence interval with $\alpha = 0.05$), with 0 included in the confidence interval of the intercept ($\alpha = 0.05$).

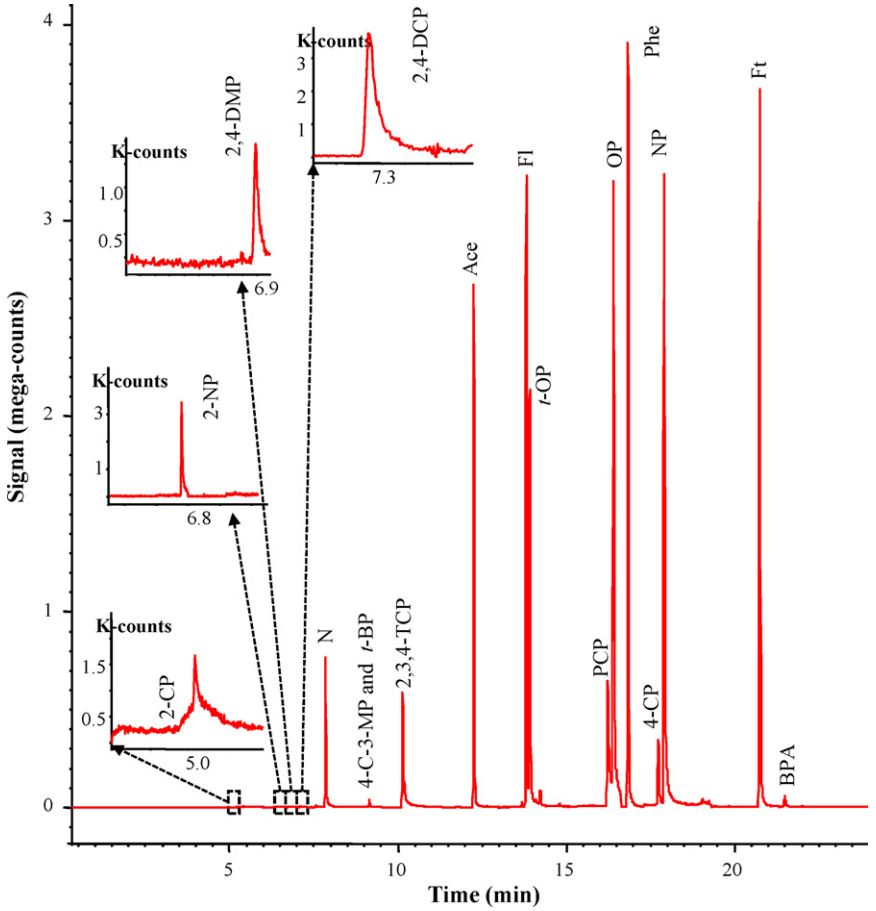

Fig. 2. Chromatogram obtained for the studied analytes (20 ng mL^{-1}) and the PIL (~20 μm) fiber in direct-immersion mode of SPME. The selected ions and segments in the chromatogram (SIS mode) are shown in Table 1.

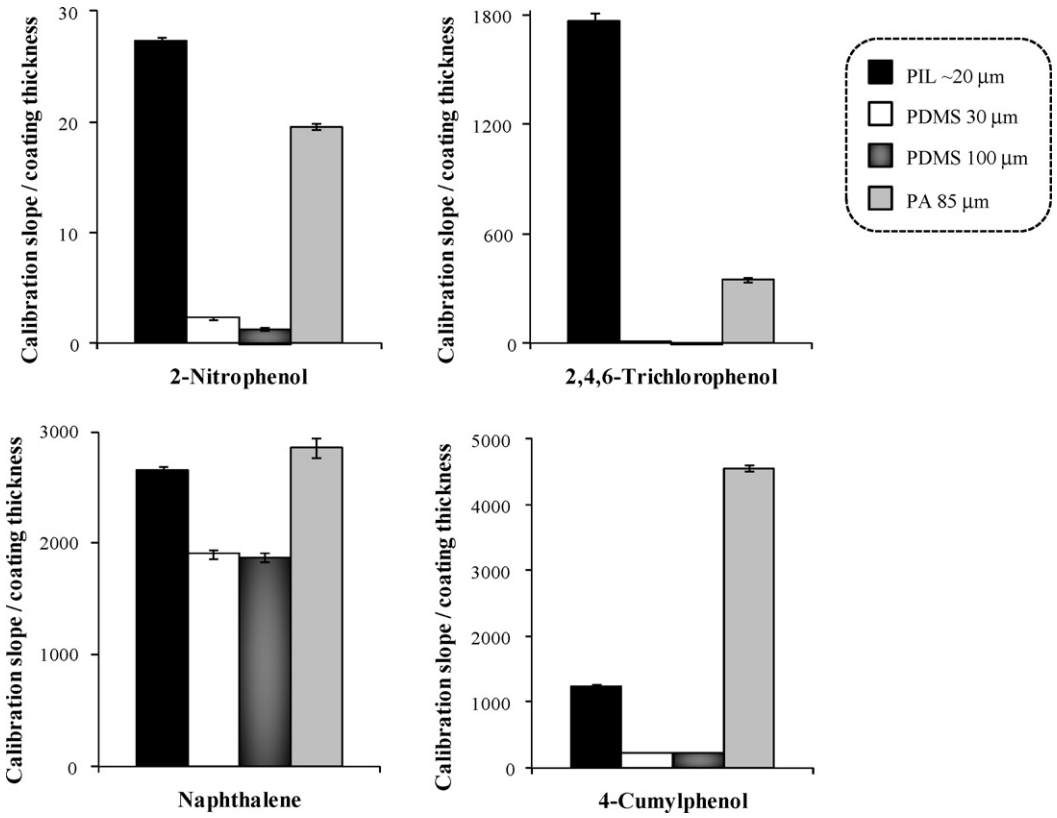

Fig. 3. Comparison among affinities of the studied fibers for several analytes, normalizing the calibration slope by the coating thickness of the SPME fiber used.

In this sense, if dividing the slopes obtained with the PDMS 30 and 100 µm by the coating thicknesses (30 and 100 µm, respectively), the obtained value should be independent of the thickness and only dependent on the coating nature (PDMS). The obtained values can be observed in the Supplementary Material. The agreement between the values is well attained for all analytes, except for Ace, Phe, Ft, OP and 4-*n*-NP. The correlation between both sets of data for the PDMS material (slope/coating thickness) has a *R* value of 0.971 for all analytes. The correlation has a *R* value of 0.990 if excluding the above mentioned exceptions, with a slope of 0.889 ± 0.094 (confidence interval with $\alpha = 0.05$), and the value of 0 included in the confidence interval of the intercept ($\alpha = 0.05$).

Considering the correlations (~1), slope (~1), and intercept (~0) obtained for the PDMS material, it is possible to compare the extraction affinity for specific coating materials by dividing the calibration slope obtained for each analyte by the coating thickness of the fiber. If plotting the slopes normalized by the thickness (calibration slope divided by the coating thickness) of the PIL fiber *versus* the PDMS fiber, the obtained slope is 2.1 ± 0.2 (confidence interval with $\alpha = 0.05$). That is, it seems that the affinity of the PIL material for the studied analytes is twice than the PDMS material. Obtaining a general trend for a comparison of the PIL fiber with the PA is more difficult as the behavior is analyte-dependent. We want to highlight here that the only purpose of this normalization (calibration slope divided by coating thickness) is to qualitatively compare the affinity of specific fiber materials for certain group of analytes. Fig. 3 shows few examples of such comparison. It is clear from Fig. 3 that the affinity for 2-NP and 2,4,6-TCP is higher using the PIL material than using the rest of coating materials. For N, the affinity is similar using PA and PIL, whereas for 4-CP the affinity is higher using PA. Considering all analytes studied, the PIL material presents higher affinity in 50% of the cases, whereas the PA performs better (in terms of affinity) in the remaining 50%. Attending to the nature of the analytes, the PIL material works better for non-polar analytes, whereas PA works better for polar compounds (which is, indeed, its common behavior when compared to PDMS) [37].

In any case, it is reported here an estimated affinity. The sensitivity of each specific fiber is obviously coating-thickness dependent, and the specific performance must be quantitatively taken from Tables 2 and 3.

3.4. Relative recovery and precision obtained with the PIL fiber

The performance of the PIL fiber in direct-immersion SPME was also evaluated by calculating extraction recoveries and precision by spiking a series of deionized water samples and well waters at low levels of concentration (5 ng mL^{-1}). Table 4 includes the results obtained. Extraction recoveries vary from 75.8% for 2-nitrophenol to 119% for 4-*n*-nonylphenol using deionized waters, and from 77.9% for 2,4-dimethylphenol to 110% for acenaphthene using well waters. These relative recoveries, with average values of 92.5% for deionized waters and of 90.8% for well waters, are in agreement with the literature values for new SPME materials when analyzing waters [6,25,41]. The organic matter content of the well waters is not strongly affecting the extraction recoveries of the compounds studied. It should be noted that heavy analytes (like PAHs of more than three rings) have not been analyzed in this study [36], and those are the ones more affected by the presence of organic matter.

The intermediate precision was evaluated by extracting three replicates in two non-consecutive days by the same analyst. The relative standard deviation values oscillate from 5.9% to 19% in deionized waters and from 5.8% to 22% in well waters, with average values of 11% and 12%, respectively. The precision values obtained can be considered acceptable for a SPME application in direct immersion using this non-commercial material, especially considering the low level of concentration spiked. The literature works with new materials for SPME reported precision values lower than 8.9% [5], and lower than 11.8% [25], when used in the headspace

Table 4
Precision and recovery studies carried out with the PIL fiber.

Analyte	Deionized water[a]		Well water[a]	
	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
2-CP	79.8	12	78.9	9.1
2-NP	75.8	17	82.4	17
2,4-DMP	80.1	7.9	77.9	13
2,4-DCP	82.0	5.9	86.0	8.3
N	90.6	7.0	99.2	11
4-C-3-MP	99.8	10	98.1	11
t-BP	93.5	8.2	84.7	10
2,4,6-TCP	81.5	8.1	99.1	20
Ace	85.5	7.4	110	8.8
Fl	104	8.6	87.6	6.0
t-OP	101	16	83.9	21
PCP	83.2	16	96.0	17
OP	116	10	85.1	5.8
Phe	92.9	9.9	94.3	11
CP	97.2	8.8	87.8	5.9
NP	119	11	96.8	8.6
Ft	107	8.7	87.6	13
BPA	76.6	19	99.4	14

[a] $n = 6$ (Spiked level = 5 ng mL^{-1}).

determination of PAHs. Precision values lower around 10% have been obtained in the direct-immersion mode of a novel sol–gel coating for PAHs [6].

Four well water samples (non-spiked) were also extracted using the PIL fiber, and the studied analytes were not detected in any of the samples. This ensures the quality of the well waters analyzed, which will be further used for human consumption (after proper treatment).

It was observed that the PIL sorbent coating begins to discolor (turning dark brown) after 10 extractions, but does not lose its extraction capabilities. The performance of the PIL fiber was still acceptable after 50 extractions in direct-immersion mode, with RSD values lower than 20%. This performance and fiber lifetime was verified by analyzing a standard aqueous solution (10 μg L^{-1}) after every five extractions. The utilization of PIL fibers in headspace extraction has shown a fiber lifetime superior to 150 extractions [27]. A hydroxyfullerene-SPME coating, prepared by sol–gel, resisted 200 extractions when used in headspace mode [5], whereas commercial fibers can be used approximately 50–100 times [42]. New-generation super elastic fiber assemblies have been proposed to increase the lifetime of commercial SPME fibers [43]. While the direct-immersion mode does have an effect on the lifetime of the PIL coating when compared to headspace mode use (as is generally true for commercial SPME coatings), there are several factors that can be controlled to extend the lifetime of the fibers. The desorption temperature and time should be minimized as much as possible to prevent unnecessary bleeding of the stationary phase. In addition, the amount of organic modifier used in the extraction should be kept minimal. As we learn more about how these new materials perform in specific matrices, their properties can be readily controlled by tuning the cationic and anionic components that comprise the PIL.

4. Conclusions

The polymeric ionic liquid poly(1-vinyl-3-hexadecylimidazolium) bis[(trifluoromethyl)sulfonyl]imide has successfully been employed as a coating material in solid-phase microextraction when performing a direct-immersion mode extraction of several pollutants (polycyclic aromatic hydrocarbons and substituted phenols) in water. The optimized PIL-SPME-GC–MS method is characteristic for presenting average recoveries ranging from 75.8% to 119% and from 77.9% to 110% for deionized and well waters, respectively. The precision of the method was also satisfactory, with average relative standard deviations of 11% for deionized waters and 12% for well waters. The limits of detection of the developed method varied from 0.005 ng mL^{-1} for fluoranthene to 4.4 ng mL^{-1} for 4-chloro-3-methylphenol. The PIL fiber shows no obvious decrease in its performance after 50 non-consecutive extractions.

The performance of the PIL material was compared to commercial SPME fibers such as PDMS 30 μm, PDMS 100 μm, and PA 85 μm. The PIL material presented better sensitivity that the PDMS 30 μm for all analytes studied and, for some analytes, its performance was also better than the PDMS 100 μm and PA 85 μm. The different materials: PIL, PDMS, and PA, were qualitatively compared normalizing their sensitivities by their corresponding coating thicknesses. Such comparison reflected that the PIL material was more effective than the PDMS for all analytes studied. The PIL material was also more effective than the PA for non-polar analytes.

The results of this work expand the applicability of these novel materials in SPME to non-volatile analytes, keeping in mind that IL-based SPME materials have not been employed up to date in direct-immersion mode. Moreover, the interesting performance of this polymeric material can be further expanded from SPME to thin film microextraction.

Acknowledgements

A.M.A. acknowledges funding from the Spanish Ministry of Innovation and Science (MICINN) project ref. CTQ2008-06253/BQU and from the Canary Agency for Research and Innovation (ACIISI) project ref. SolSubC20081000171. V.P. thanks the MICINN for the Ramón y Cajal contract with the University of La Laguna. J.L.A. acknowledges funding from the Analytical and Surface Chemistry Program in the Division of Chemistry and the Separation and Purification Process Program in the Chemical, Environmental, Bioengineering, and Transport Systems Division from the National Science Foundation for a CAREER grant (CHE-0748612).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chroma.2009.12.041.

References

[1] S. Risticevic, V.H. Niri, D. Vuckovic, J. Pawliszyn, Anal. Bioanal. Chem. 393 (2009) 781.
[2] C.L. Arthur, J. Pawliszyn, Anal. Chem. 62 (1990) 2145.
[3] C. Dietz, J. Sanz, C. Cámara, J. Chromatogr. A 1103 (2006) 183.
[4] J. Wu, J. Pawliszyn, J. Chromatogr. A 909 (2001) 37.
[5] J. Yu, L. Dong, C. Wu, L. Wu, J. Xing, J. Chromatogr. A 978 (2002) 37.
[6] F. Bianchi, F. Bisceglie, M. Careri, S. Di Berardino, A. Mangia, M. Musci, J. Chromatogr. A 1197 (2008) 15.
[7] E.H.M. Koster, C. Crescenzi, W.D. Hoedt, K. Ensing, G.J. de Jong, Anal. Chem. 73 (2001) 3140.
[8] F. Tang, H. Zhao, X. Li, X. Quan, J. Chen, X. Xiang, X. Zhang, J. Chromatogr. A 1216 (2009) 5647.
[9] H. Bagheri, E. Babanezhad, A. Es-haghi, J. Chromatogr. A 1152 (2007) 168.
[10] Y. Wang, Y. Li, J. Zhang, S. Xu, S. Yang, C. Sun, Anal. Chim. Acta 646 (2009) 78.
[11] J.-F. Liu, J.A. Jönsson, G.-B. Jiang, Trends Anal. Chem. 24 (2005) 20.
[12] R. Liu, J.-F. Liu, Y.-G. Yin, X.-L. Hu, G.-B. Jiang, Anal. Bioanal. Chem. 393 (2009) 871.
[13] J.L. Anderson, D.W. Armstrong, G.-T. Wei, Anal. Chem. 78 (2006) 2892.
[14] J.H. Davis, Chem. Lett. 33 (2004) 1072.
[15] S. Chun, S.V. Dzyuba, R.A. Bartsch, Anal. Chem. 73 (2001) 3737.
[16] F.-Y. Du, X.-H. Xiao, G.-K. Li, J. Chromatogr. A 1140 (2007) 56.
[17] E. Aguilera-Herrador, R. Lucenas, S. Cárdenes, M. Valcárcel, Anal. Chem. 80 (2009) 793.
[18] J.-F. Liu, G.-B. Jiang, Y.-G. Chi, Y.-Q. Cai, J.-T. Hu, Q.-X. Zhou, J.-T. Hu, Anal. Chem. 75 (2003) 5870.
[19] C. Yao, W.R. Pitner, J.L. Anderson, Anal. Chem. 81 (2009) 5054.
[20] Y. Liu, E. Zhao, W. Zhu, H. Gao, Z. Zhou, J. Chromatogr. A 1216 (2009) 885.
[21] C. Yao, J.L. Anderson, Anal. Bioanal. Chem. 395 (2009) 1491.

[22] V. Pino, Q.Q. Baltazar, J.L. Anderson, J. Chromatogr. A 1148 (2007) 92.
[23] L. Guerra-Abreu, V. Pino, J.L. Anderson, A.M. Afonso, J. Chromatogr. A 1214 (2008) 23.
[24] J.-F. Liu, N. Li, G.-B. Jiang, J.-M. Liu, J.A. Jönsson, M.J. Wen, J. Chromatogr. A 1066 (2005) 27.
[25] Y.-N. Hsieh, P.-C. Huang, I.-W. Sun, T.-J. Whang, C.-Y. Hsu, H.-H. Huang, C.-H. Kuei, Anal. Chim. Acta 557 (2006) 321.
[26] Y. He, J. Pohl, R. Engel, L. Rothman, M. Thomas, J. Chromatogr. A 1216 (2009) 4824.
[27] F. Zhao, Y. Meng, J.L. Anderson, J. Chromatogr. A 1208 (2008) 1.
[28] Y. Meng, V. Pino, J.L. Anderson, Anal. Chem. 81 (2009) 7107.
[29] Q. Zhao, J.C. Wajert, J.L. Anderson, Anal. Chem. (2009), in press, doi:10.1021/ac902438k.
[30] R. Marcilla, J.A. Blazquez, J. Rodriguez, J.A. Pomposo, D. Mecerreyes, J. Polym. Sci. A: Polym. Chem. 42 (2004) 208.
[31] H. Prosen, L. Zupančič-Kralj, Trends Anal. Chem. 18 (1999) 272.
[32] I. Bruheim, X. Liu, J. Pawliszyn, Anal. Chem. 75 (2003) 1002.
[33] R. Doong, S. Chang, Y. Sun, J. Chromatogr. A 879 (2000) 177.
[34] E. Cortazar, O. Zuloaga, J. Sanz, J.C. Raposo, N. Etxebarria, L.A. Fernández, J. Chromatogr. A 978 (2002) 165.
[35] A.J. King, J.W. Readman, J.L. Zhou, Anal. Chim. Acta 523 (2004) 259.
[36] V. Fernández-González, E. Concha-Graña, S. Muniategui-Lorenzo, P. López-Mahía, D. Prada-Rodríguez, J. Chromatogr. A 1176 (2007) 48.
[37] P. Braun, M. Moeder, St. Schrader, P. Popp, P. Kuschk, W. Engewald, J. Chromatogr. A 988 (2003) 41.
[38] C. Basheer, A. Parthiban, A. Jayaraman, H.K. Lee, S. Valiyaveettil, J. Chromatogr. A 1087 (2005) 274.
[39] L. Yang, T. Luan, C. Lan, J. Chromatogr. A 1104 (2006) 23.
[40] J. Koziel, M. Jia, J. Pawliszyn, Anal. Chem. 72 (2000) 5178.
[41] A. Mohammadi, Y. Yamini, N. Alizadeh, J. Chromatogr. A 1063 (2005) 1.
[42] Solid-Phase Microextraction: Theory and Optimization of Conditions, Bulletin 923, Supelco, Bellefonte, PA, USA, 1998.
[43] L. Setkova, S. Risticevi, C.M. Linton, G. Ouyang, L.M. Bragg, J. Pawliszyn, Anal. Chim. Acta 581 (2007) 221.