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Utilization of a benzyl functionalized polymeric ionic liquid for the sensitive determination of polycyclic aromatic hydrocarbons; parabens and alkylphenols in waters using solid-phase microextraction coupled to gas chromatography–flame ionization detection

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ABSTRACT

The functionalized polymeric ionic liquid poly(1-(4-vinylbenzyl)-3-hexadecylimidazolium bis[(trifluoromethyl)sulfonyl]imide (poly(VBHDIm$^+$NTf$_2^-$)) has been used as successful coating in solid-phase microextraction (SPME) to determine a group of fourteen endocrine disrupting chemicals (ECDs), including polycyclic aromatic hydrocarbons (PAHs), alkylphenols, and parabens, in several water samples. The performance of the PIL fiber in direct immersion mode SPME followed by gas chromatography (GC) with flame-ionization detection (FID) is characterized with average relative recoveries higher than 96.1% from deionized waters and higher than 76.7% from drinking bottled waters, with precision values (RSD) lower than 13% for deionized waters and lower than 14% for drinking bottled waters (spiked level of 1 ng mL^{-1}), when using an extraction time of 60 min with 20 mL of aqueous sample. Detection limits varied between 9 ng L^{-1} and 7 ng mL^{-1}. A group of real water samples, including drinking waters, well waters, and swimming pool waters, have been analyzed under the optimized conditions. A comparison has also been carried out with the commercial SPME coatings: polydimethylsyloxane (PDMS) 30 μm, and polyacrylate (PA) 85 μm. The functionalized PIL fiber (~12 μm) demonstrated to be superior to both commercial fibers for the overall group of analytes studied, in spite of its lower coating thickness. A normalized sensitivity parameter is proposed as a qualitative tool to compare among fiber materials, being higher for the poly(VBHDIm$^+$NTf$_2^-$) coating. Furthermore, the partition coefficients of the studied analytes to the coating materials have been determined. A quantitative comparison among the partition coefficients also demonstrates the superior extraction capability of the functionalized PIL sorbent coating.

1. Introduction

The term "endocrine disruptor chemicals" (EDCs) defines a heterogeneous group of chemical compounds which are able to interact with the endocrine system of a living organism [1]. Chemical exposure to EDCs has been linked to neurological and reproductive effects on animals,... [2], and may also affect human fertility [3]. It is not well-known the exact mechanism by which an endocrine disruptor chemical acts. It appears that endocrine disruptors mainly alter the concentration of circulating hormones in the body, the synthesis of hormones, and their hepatic metabolism [4]. The full list of substances catalogued as EDCs includes approximately eight hundred compounds, including synthesized chemical compounds and natural substances. Among them, specific classes include polycyclic aromatic hydrocarbons, pesticides, alkylphenols, dioxins, phthalates, parabens, or polychlorinated biphenyls.

The determination of this wide group of chemicals in environmental samples has been conducted with a high number of analytical methods [5–8]. These extraction schemes are mainly conducted to achieve low detection limits while retaining good analytical quality parameters (efficiency, reproducibility, robustness).

In recent years, the development of new analytical methods must also take into account the necessity of reducing the environmental impact of the wastes generated in the laboratory. Hence, methods should be environmental-friendly. Solid-phase microextraction (SPME) is a successful solvent-free preconcentration technique developed by Arthur and Pawliszyn [9] which fulfils

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such requirements. It has been used as a method to determine a significant number of environmental contaminants [10]. The expense of the fiber coatings as well as the limited number of commercially available coatings, mainly polydimethylsiloxane (PDMS) and polyacrylate (PA), can be cited as important limitations of SPME. For these reasons, an increasing effort has been shifted in developing new materials as SPME sorbent coatings [11–13].

Ionic liquids (ILs) are nonmolecular solvents which are mainly characterized as possessing low melting points, low to negligible vapor pressures, and high thermal stability [14]. They have been used in a number of analytical methods [15,16], with certain classes being recognized as environmentally friendly solvents. These unique materials have also been used as novel disposable coating materials in SPME [17,18]. Polymeric ionic liquids (PILs) constitute a class of re-usable coating materials for SPME and were recently introduced by Anderson et al. [19–21]. They have been used in headspace applications [19,22] and in direct immersion mode [23,24]. The thermal stability of these PIL coatings, their proven reproducibility, as well as their tuneability, make them attractive candidates for successful SPME sorbent coatings. More recently, the functionalized polymeric ionic liquid poly(1-(4-vinylbenzyl)-3-hexadecylimidazolium bis[(trifluoromethyl)sulfonyl]imide (poly(VBHDIm$^+$NTf$_2^-$)) has been synthetically designed to include benzyl groups within its structure in order to increase its aromatic character in addition to enhancing the overall hydrophobic nature of the material [24].

The main aim of this work is to expand the utilization of PIL materials in SPME by testing the utility of the newly designed poly(VBHDIm$^+$NTf$_2^-$) PIL not only with polycyclic aromatic hydrocarbons but also with other endocrine chemical compounds such as parabens and alkylphenols using direct immersion SPME with real water matrices. The analytical quality parameters of the determinations are also obtained with PDMS and PA commercial SPME coatings. To further compare among other fiber coatings, a sensitivity parameter is proposed, and the partition coefficients for the studied analytes are also determined.

2. Experimental

2.1. Reagents and materials

The studied polycyclic aromatic hydrocarbons (PAHs) were naphthalene (N), acenaphthene (Ace), phenanthrene (Phe), anthracene (A), 9-methylanthracene (9-MeA) 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 acetonitrile of HPLC gradient grade (Merck) with concentrations ranging from 970 to 1490 mg L^{-1}, and in cyclohexane (Sigma–Aldrich) with concentrations ranging from 1030 to 1350 mg L^{-1}.

The alkylphenols used in this study were 4-*tert*-butylphenol (*t*-BP), 4-*tert*-octylphenol (*t*-OP), 4-octylphenol (OP), 4-cumylphenol (4-CP), 4-*n*-nonylphenol (NP) and bisphenol-A (BPA). They were all supplied by Sigma–Aldrich, except NP, which was supplied by Alfa-Aesar (Karlsruhe, Germany). Individual standard solutions of these analytes were prepared in acetonitrile of HPLC gradient grade (Merck) with concentrations ranging from 960 to 1300 mg L^{-1}, and in cyclohexane (Sigma–Aldrich) with concentrations ranging from 980 to 1400 mg L^{-1}.

The parabens used in this study were butylparaben (BuP) and benzylparaben (BzP), both supplied by Sigma–Aldrich. Individual standard solutions of these parabens were prepared in acetonitrile of HPLC gradient grade (Merck) with concentrations ranging from 1170 to 1220 mg L^{-1}, and in cyclohexane (Sigma–Aldrich) with concentrations ranging from 1000 to 1760 mg L^{-1}.

A standard solution mixture containing parabens, alkylphenols and PAHs was prepared at a concentration of 100 mg L^{-1} in cyclohexane by dilution of the individual mixtures in cyclohexane. Calibrations solutions in cyclohexane were prepared for the direct liquid injection calibration. Calibration curves of the analyte peak area (from flame-ionization detector (FID) response) versus the mass of analytes injected onto the column were generated by injecting 1 μL of the standard mixture in cyclohexane through the GC autosampler using identical inlet and column conditions as to those carried out during SPME desorption (Table S-1 in the Supplementary Material). The FID response from the direct injection of the standard solutions was also used to estimate the amount of analyte extracted by the three different SPME sorbent coatings examined in this study. The quality parameters of such calibrations are included as Supplementary Material (Table S-2 in the Supplementary Material).

Other standard solutions mixtures containing parabens, alkylphenols and PAHs, with concentrations of 1 and 20 mg L^{-1} in acetonitrile, were also prepared. SPME working and calibration aqueous standard solutions were prepared by spiking deionized water with the two above mentioned standard solution mixtures of parabens, alkylphenols and PAHs in acetonitrile. The total acetonitrile content in the aqueous solutions was always lower than 0.5% (v/v).

Deionized water (18.2 mΩ cm^{-1}) was obtained from a Milli-Q gradient A10 system (Millipore, Watford, UK). Well water samples came from the north area of Tenerife Island (Spain). Well waters characteristically presented a conductivity value of 1825 μS. Swimming pool waters were obtained from a public swimming pool, and characteristically presented a conductivity value of 52.9 mS and a pH value of 7.4. Amber glass bottles of 1 L in volume were used for the sampling of well waters and swimming pool waters, avoiding the formation of air bubbles. Samples were then kept in a portable fridge until they reach the laboratory. The excess of free chlorine in the swimming pool waters was removed by addition of sodium thiosulphate (0.1 mg mL^{-1}). A simulated contaminated swimming pool water sample was also prepared by mixing swimming pool water (20 mL) with 200 μL of a solar cream containing parabens (the common source of parabens in the environment), followed by stirring and centrifugation. 1 mL of the centrifuge was then diluted to 20 mL and further analyzed. Drinking bottled waters of low salty content, for human consumption, were acquired in a market. These bottled waters characteristically presented a conductivity value of 57 μS. Several drinking bottled waters were also left at direct sun exposition for 3 days, to simulate a water bottle left in a car. These drinking waters were kept in two different plastic containers, one belonging to the brand of the drinking bottled water, and the other belonging to another brand, with worse thermal resistance. These waters were analyzed to evaluate the possible presence of alkylphenols in water, by migration from the plastic container exposed to the sun.

The reagents imidazole, 1-bromohexadecane (97%), 4-vinylbenzyl chloride (97%), acrylonitrile (>99%), and 2,2′-azobis(isobutyronitrile) (AIBN), were purchased from Sigma–Aldrich (Milwaukee, WI, USA). Lithium bis[(trifluoromethyl)sulfonyl]imide was purchased from SynQuest labs (Alachua, FL, USA).

Commercial SPME fibers of polydimethylsiloxane (PDMS) with a film thickness of 30 μm, and polyacrylate (PA) with a film thickness of 85 μm, were obtained from Supelco (Bellefonte, PA, USA).

Amber 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 (GC) equipped with flame

ionization detection (FID) system, Varian model CP-3800 Varian 450 (GC–FID) system, equipped with a 30 m × 0.25 mm I.D. VF-5ms column (Varian, Lake Forest, CA, USA). The equipment also includes a Combi-Pal autosampler (CTC Analytics). The GC column was employed under the following temperature program: 60 °C, 2 min isothermal, 15 °C min^{-1} to 130 °C, then 9 °C min^{-1} to 190 °C, then 4 °C min^{-1} to 300 °C, and then 2 min isothermal. The carrier gas was nitrogen, with a flow of 1 mL min^{-1}. The temperature of the injector was maintained at 280 °C when using the PDMS fiber, the PA fiber, and in direct liquid injection mode, and at 250 °C when using the PIL fiber. Desorption time for the fiber in the GC injector was always 5 min. The flame ionization detector (FID) was kept at 280 °C, the make-up flow of nitrogen at 30 mL min^{-1}, the hydrogen flow at 30 mL min^{-1}, and the air flow at 300 mL min^{-1}. The MS workstation 6.9.3 Software (Varian) was used for data acquisition.

Thermal gravimetric analysis (TGA) was performed using a TA instruments SDT 2960 simultaneous DTA-TGA. The poly(VBHDIm$^+$NTf$_2^-$) PIL was subjected to two heating ramps, 5 and 10 °C min^{-1}, using PIL masses of 7.91 and 6.98 mg, respectively. All TGA experiments were conducted under nitrogen using a flow rate of 100 mL min^{-1} and a heating cycle from 22 to 500 °C.

2.3. Procedures

The synthesis and extensive characterization of the poly(1-(4-vinylbenzyl)-3-hexadecylimidazolium bis[(trifluoromethyl)sulfonyl]imide (poly(VBHDIm$^+$NTf$_2^-$)) PIL has been described in a recent publication [24]. Laboratory-made SPME devices were constructed using a slight modification of the procedure first described by Arthur and Pawliszyn in their early work [9]. Briefly, the SPME device was constructed by purchasing a 5 μL syringe from Hamilton (Reno, NV, USA) and the syringe re-assembled by discarding the stainless fiber on the plunger and replacing it with a glued fused silica capillary. The end of the capillary was sealed by a microflame torch and the outer 1 cm of the polyimide coating was removed. The bare fiber segment was washed with methanol, acetone, hexane, and methylene chloride before coating. The coating of the SPME fiber followed the procedures described previously [19]. Briefly, the poly(VBHDIm$^+$NTf$_2^-$) was diluted in chloroform to prepare a coating solution with a ratio of 1:1 (v/v). The bare fiber was then dipped into the solution and slowly removed. After coating, the fiber was dried in the air for 10 min before it was retracted back into the needle. The fiber was conditioned in the GC injection port for 5 min at 250 °C prior to performing extractions.

The obtained PIL SPME fiber was characterized by optical microscopy and the film thickness estimated to be approximately 12 μm [24]. 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 12 μm PIL coating.

All SPME extractions, using either commercial fibers or the PIL fiber, were conducted in direct immersion mode. The optimum extraction time used for all fibers was 60 min. All SPME extractions using the PIL fiber were performed at constant stirring rate of 700 rpm on a stir plate (Agimatic-N JP Selecta, Barcelona, Spain). 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 acetone (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 aluminum foil before use.

3. Results and discussion

The functionalized polymeric ionic liquid poly(1-(4-vinylbenzyl)-3-hexadecylimidazolium bis[(trifluoromethyl)sulfonyl]imide (poly(VBHDIm$^+$NTf$_2^-$)) has been designed to be selective towards polycyclic aromatic hydrocarbons in direct immersion SPME [24], by enhancing π–π interactions. In order to tests its efficiency with real water samples, a group of fourteen endocrine disrupting chemicals, including not only polycyclic aromatic hydrocarbons but also parabens and alkylphenols has been analyzed.

3.1. Sorption–time profiles in direct immersion SPME

The sorption-time profiles for the functionalized poly(VBHDIm$^+$NTf$_2^-$) fiber in deionized 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. Working solutions containing a constant concentration of the analytes (100 ng mL^{-1}) were used for obtaining the profiles, with an overall content of acetonitrile lower than 0.5% (v/v). For comparative purposes, the same experiments were conducted with the commercial fibers PDMS 30 μm and PA 85 μm. The non-functionalized PIL fiber, poly(1-vinyl-3-hexadecylimidazolium) bis[(trifluoromethyl)sulfonyl]imide (poly(HDIm$^+$NTf$_2^-$)) (~12 μm), which has been used in a previous work [23], was also utilized in this comparison. PA is a coating useful for polar compounds, which has proved its efficiency with light PAHs [25,26]. PDMS is more efficient for hydrophobic analytes. PDMS has been selected with a thickness of 30 μm to have a coating thickness closer to that of the new functionalized poly(VBHDIm$^+$NTf$_2^-$) PIL fiber (~12 μm) to make the comparison more adequate. It is well-known the influence of the coating thickness in the extraction efficiency when performing SPME [27,28]: higher coating thicknesses are beneficial for achieving higher extraction efficiencies.

Fig. 1 shows several profiles obtained with the four fibers. Analytes included in the figure are representative for each group: parabens, alkylphenols and polycyclic aromatic hydrocarbons. Considering all profiles obtained for all analytes, the superior performance of the new benzyl functionalized poly(VBHDIm$^+$NTf$_2^-$) PIL fiber is clear compared to the other fibers, in terms of higher peak-areas, except for BPA and *t*-BP when using the PA fiber. The performance of the new PIL fiber is comparable to that of the PA for analytes such as *t*-OP and 4-CP. The comparison here is only qualitative, as only one spiked concentration is used in the profiles (100 ng mL^{-1}), and no correction with the fiber thickness has been conducted.

Considering the functionalized poly(VBHDIm$^+$NTf$_2^-$) PIL fiber, analytes such as naphthalene and *t*-butylphenol reach equilibration at around 45 min; acenaphthene at around 60 min; and butylparaben, benzylparaben and cumylphenol at around 80 min. The rest of analytes did not reach equilibration under the time window studied. An extraction time of 60 min was selected for further experiments in order to have an adequate sensitivity while avoiding long extraction times. It is well-known that in SPME is not necessary for analytes to reach equilibration [26] but to use a relatively short extraction time which ensures acceptable extraction efficiency and limits of detection.

3.2. Sensitivity of the PIL fiber in comparison with commercial SPME coatings

Calibration curves of each analyte in deionized water were obtained with the functionalized poly(VBHDIm$^+$NTf$_2^-$) PIL fiber as

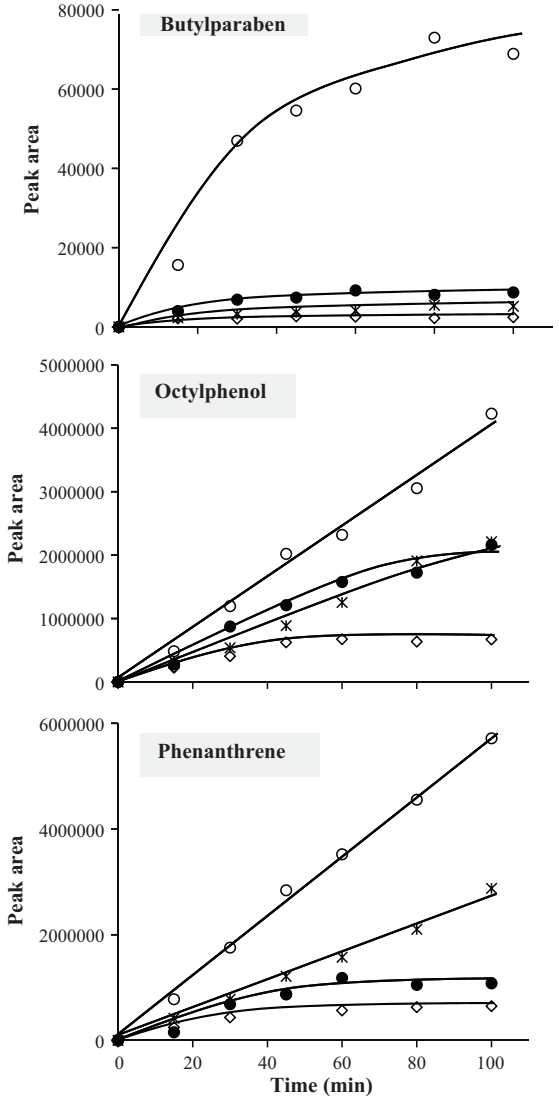

Fig. 1. Sorption-time profiles for butylparaben (as an example of parabens), octylphenol (as an example of alkylphenols), and phenanthrene (as an example of polycyclic aromatic hydrocarbons). The (○) symbol correspond to the benzyl functionalized poly(VBHDIm$^+$NTf$_2^-$) PIL fiber (~12 μm), the (●) is for the non-functionalized poly(HDIm$^+$NTf$_2^-$) PIL fiber (~12 μm), the (*) is for the PA 85 μm fiber, and the (◊) is for the PDMS 30 μm fiber.

well as with the PDMS 30 μm and PA 85 μm commercial coatings using SPME in direct immersion mode with an extraction time of 60 min. Calibration curves were constructed plotting peak area (mVolts) *versus* the concentration of the analytes (in ng mL^{-1}). Table 1 includes several figures of merit of such calibrations including slope, linearity and calibration range. The obtained linearity of the overall method for all fibers was found to be acceptable, with correlation coefficients (R) ranging from 0.988 to 0.999, from 0.987 to 0.999, and from 0.996 to 0.999, for the poly(VBHDIm$^+$NTf$_2^-$) PIL, PDMS and PA fibers respectively.

The sensitivity, which can be evaluated by the calibration slope, was higher for the functionalized poly(VBHDIm$^+$NTf$_2^-$) PIL fiber for all analytes studied when compared to commercial fibers, except for BPA and *t*-BP when using the PA fiber. This aspect should be highlighted, especially considering the low thickness of the PIL fiber (~12 μm) when compared to PA 85 μm and PDMS 30 μm. The ratio of the calibration slopes of PIL *versus* PA is ~1.4 (R value of 0.91), and ~2.3 for PIL *versus* PDMS (R value of 0.84), for the overall group of endocrine chemicals studied.

The PA coating fiber exhibited limited success in the extraction of parabens within the concentration range studied (and with no control of the pH or the ionic strength). Thus, butylparaben could not be extracted by the PA fiber and benzylparaben was barely extracted by the PA fiber. Parabens were extracted by the PA fiber at 100 ng mL^{-1} as can be observed when studying the sorption profiles. The concentration range of the calibrations was selected with the purpose to focus the utilization of the SPME fibers on real water matrices; therefore, low concentrations of the analytes were used. Analytes such as *t*-butylphenol, butylparaben and 4-cumylphenol were also sparingly extracted by the PDMS fiber within the concentration range studied.

Attending to the nature of the analytes, the developed poly(VBHDIm$^+$NTf$_2^-$) PIL fiber exhibited high efficiency in the extraction of polycyclic aromatic hydrocarbons and alkylphenols, and moderate efficiency for parabens. In any case, its extraction efficiency of parabens is much higher than that obtained with commercial fiber coatings.

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. They are shown in Table 2. LODs are much lower for PAHs and parabens when using the functionalized poly(VBHDIm$^+$NTf$_2^-$) PIL fiber than the commercial ones, and also lower for alkylphenols if excluding *t*-BP and BPA. LODs oscillate from 9 ng L^{-1} for fluoranthene to 7 ng mL^{-1} for bisphenol-

Table 1
SPME calibrations obtained for the studied analytes using commercial SPME fibers and the new functionalized PIL fiber.

Analyte	PDMS 30 μm			PA 85 μm			poly(VBHDIm$^+$NTf$_2^-$) PIL ~12 μm		
	Slope ± SD[a]	R	Calibration range (ng mL^{-1})	Slope ± SD[a]	R	Calibration range (ng mL^{-1})	Slope ± SD[a]	R	Calibration range (ng mL^{-1})
N	733 ± 48	0.994	4–45	7930 ± 160	0.999	0.5–20	8950 ± 260	0.999	0.1–20
t-BP	96 ± 13	0.989	25–45	1953 ± 33	0.999	3–20	730 ± 50	0.995	3–20
Ace	4016 ± 61	0.999	2–30	13730 ± 290	0.999	0.5–20	22090 ± 810	0.997	0.1–20
t-OP	2180 ± 29	0.999	2–45	11790 ± 150	0.999	0.5–20	13590 ± 100	0.999	0.5–20
BuP	67 ± 15	0.988	25–45	–	–	–	463 ± 14	0.999	5–20
OP	6340 ± 160	0.998	2–45	11200 ± 210	0.999	0.2–20	15510 ± 400	0.999	0.1–20
Phe	6990 ± 160	0.998	2–45	16530 ± 230	0.999	0.5–20	28910 ± 350	0.999	0.5–20
A	7120 ± 130	0.999	2–45	15920 ± 420	0.999	2–20	20700 ± 560	0.999	2–20
4-CP	204 ± 8	0.999	10–50	4570 ± 240	0.997	1–20	5035 ± 81	0.999	0.5–20
NP	8700 ± 460	0.993	2–40	16930 ± 770	0.996	0.5–20	13650 ± 410	0.998	0.5–20
9-MeA	9690 ± 380	0.995	2–45	14970 ± 200	0.999	0.5–20	26800 ± 4100	0.988	0.5–20
Ft	4960 ± 140	0.998	2–45	7704 ± 65	0.999	0.1–20	11400 ± 360	0.998	0.1–20
BzP	352 ± 58	0.988	25–50	130 ± 5	0.999	15–35	1530 ± 220	0.990	5–20
BPA	464 ± 53	0.987	20–50	3121 ± 88	0.999	5–20	459 ± 28	0.996	20–50

[a] Error of the slope for $N = 7$.

Table 2
Limits of detection (in ng·mL^{-1}) obtained for the studied analytes using commercial SPME fibers and the new functionalized PIL fiber.

Analytes	PDMS 30 μm	PA 85 μm	poly(VBHDIm$^+$NTf$_2^-$) ~12 μm
N	0.60	0.10	0.031
t-BP	8.3	0.50	1.2
Ace	0.35	0.10	0.006
t-OP	0.38	0.092	0.055
BuP	10	–	1.5
OP	0.31	0.083	0.021
Phe	0.25	0.091	0.071
A	0.74	0.20	0.052
4-CP	3.9	0.30	0.10
NP	0.75	0.32	0.11
9-MeA	0.76	0.11	0.083
Ft	0.25	0.034	0.009
BzP	10	9.5	3.4
BPA	12	3.0	7.0

A when using the functionalized poly(VBHDIm$^+$NTf$_2^-$) PIL fiber; from 34 ng L^{-1} for fluoranthene to 9.5 ng mL^{-1} for benzylparaben when using the PA fiber; and from 250 ng L^{-1} for fluroanthene and phenanthrene to 12 ng mL^{-1} for bisphenol-A when using the PDMS fiber. For PAHs, literature LODs using SPME-GC-MS oscillate between 0.03 ng mL^{-1} for phenanthrene and 0.12 ng mL^{-1} for fluoranthene when using the PDMS 30 μm fiber [29]. Better detection limits are obviously obtained for PAHs when using SPME-GC with MS/MS detection [30]. For parabens, literature limits of quantification using SPME (with PA fiber)–GC–MS/MS are 0.4 ng mL^{-1} for butylparaben and 1 ng mL^{-1} for benzylparaben [31], using a derivatization procedure and high ionic strength in the aqueous solution. For alkylphenols, 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 [32]. In a previous work, the non-functionalized poly(HDIm$^+$NTf$_2^-$) fiber generated LODs oscillating from 0.005 ng mL^{-1} for fluoranthene to 2.1 ng mL^{-1} for bisphenol-A using in that case GC–MS in selected ion storage (SIS) mode [23]. Hence, the LODs obtained with the newly functionalized poly(VBHDIm$^+$NTf$_2^-$) PIL fiber must be highlighted, especially if considering the fact that FID detection is used instead of MS and no control of the ionic strength or the pH of the solutions has been carried out. Furthermore, this study did not utilize derivatization procedures and the developed fiber has a coating thickness of only ~12 μm.

It is obvious that the differences in coating thickness among the studied fibers clearly affect the comparison as the extraction efficiency in SPME is strongly affected by the coating thickness [27,28] and by the surface area of extraction phase [33]. The commercial studied coating fibers and the PIL fiber have an approximate length of 1 cm, and so comparisons in extraction performance can be made specifically attending to the coating nature. In a previous work, we proposed to compare the extraction affinity for specific coating materials by dividing the calibration slope obtained for each analyte in SPME by the coating thickness of the fiber [23]. In this work, we suggest another approach to normalize the extraction efficiency with the coating thickness. The amount of analyte extracted by each fiber coating has been estimated by a direct liquid injection calibration obtained with the same liner and with the same conditions as the SPME desorption, as described in the experimental section. Therefore, it is possible to obtain calibrations in which the amount of analyte extracted by the SPME fibers is a function of the initial concentration of analyte in the aqueous solutions (see Tables S-1 and S-2 in Supplementary Material). The slopes of such calibrations divided by the coating thickness is then a much better tool to compare efficiencies among coating materials, having normalized the extraction efficiency by the coating thickness. The utilization of a normalized sensitivity (with mL μm^{-1} units) based on the calibration slope allows one to make a comparison which covers a concentration range, rather than to make a comparison using a single concentration value. Fig. 2 shows the plots of such normalized sensitivity depending on the analyte and on the fiber nature. The affinity of the analytes for the functionalized poly(VBHDIm$^+$NTf$_2^-$) PIL fiber is quite clear from the plots. In fact, BPA is the only analyte in which the affinity for the poly(VBHDIm$^+$NTf$_2^-$) PIL fiber is the same than for the PA fiber. For the rest of endocrine chemicals studied, the affinity for the poly(VBHDIm$^+$NTf$_2^-$) PIL fiber is the highest. In fact, the normalized sensitivity is on average around fifteen times higher for the PIL than for the commercial fibers. The normalized sensitivity also shows lower differences in affinity for the analytes among the commercial fibers. In any case, it is reported here an estimated affinity. The sensitivity of each specific fiber is obviously dependent on the coating thickness and the specific performance of each coating must

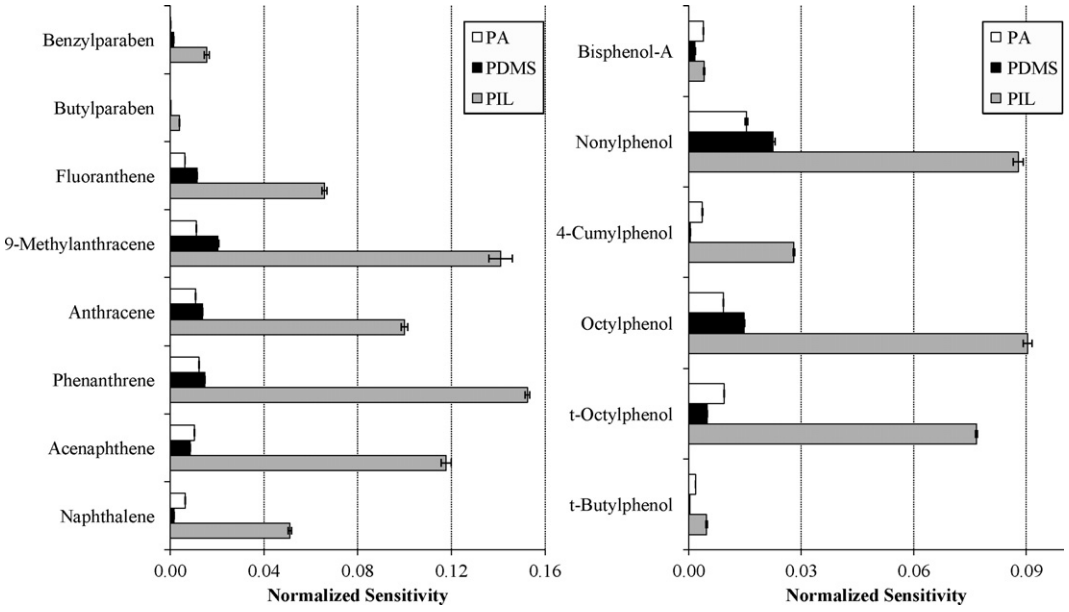

Fig. 2. Normalized sensitivity (calibration slope of the amount extracted by the fibers divided by the coating thickness) for all endocrine chemicals studied with the fibers.

Table 3
Partition coefficients estimated for the studied endocrine chemicals and the fiber coatings, and literature values.

Analyte	Estimated LogK_{fs} values (left value: calculated with n_0 = 100 ng; right value: calculated with n_0 = 400 ng)			Literature log K_{fs} values			
	PDMS 30 μm	PA 85 μm	poly(VBHDIm$^+$NTf$_2^-$) ~12 μm	PDMS 7 μm	PDMS 100 μm	PA 85 μm	Log K_{ow}[f]
N	2.97–2.70	3.00–3.05	3.89–3.84	2.73[d]	3.02[b]; 3.01[c]; 2.85[d]	3.37[b]	3.35
t-BP	nc[a]–nc[a]	2.39–2.48	2.63–2.75				
Ace	3.41–3.34	3.27–3.27	4.23–4.21		3.63[b]	4.09[b]	3.73
t-OP	3.34–3.15	3.32–3.25	4.10–4.03				
BuP	nc[a]–nc[a]	nc[a]–nc[a]	3.47–3.05				3.41
OP	3.74–3.62	3.30–3.24	4.22–4.12				
Phe	3.67–3.58	3.39–3.36	4.47–4.37	4.42[d]; 3.25[e]	3.96[b]; 3.40[d]; 3.45[e]	4.39[b]; 4.47[e]	4.55
A	3.66–3.53	3.31–3.29	4.26–4.17	3.97[d]; 3.20[e]	3.98[b]; 4.10[c]; 3.14[d]; 3.46[e]	4.66[b]; 4.45[e]	4.55
4-CP	nc[a]–2.75	3.06–2.88	3.82–3.64				
NP	3.91–3.81	3.44–3.46	4.24–4.12				
9-MeA	3.83–3.74	3.32–3.31	4.41–4.32				
Ft	3.60–3.48	3.16–3.07	4.18–4.01	4.38[d]; 3.72[e]	4.71[b]; 4.11[d]; 3.79[e]	4.87[b]; 4.84[e]	5.00
BzP	nc[a]–nc[a]	nc[a]–2.55	4.21–3.70				3.57
BPA	nc[a]–3.22	3.21–2.96	nc[a]–3.34				3.64

[a] nc: non-calculated (the amount of n_0 is out of the calibration range).
[b] [36].
[c] [37].
[d] [38].
[e] [39].
[f] Sci Finder data base 2010.

be quantitatively taken from Table 1. It must also be added that the benzyl functionalized poly(VBHDIm$^+$NTf$_2^-$) PIL fiber is much more efficient than a similar PIL developed in a previous work (poly(HDIm$^+$NTf$_2^-$)) which lacks benzyl functionality. In that case, only 50% of the analytes studied showed a higher affinity for the non-benzyl functionalized poly(HDIm$^+$NTf$_2^-$) PIL fiber rather than for the PA fiber [23].

3.3. Estimation of partition coefficients

It has been shown that the developed normalized sensitivity is a qualitative and valuable tool to allow for comparison of various coating materials. However, the best approach to compare the nature of different materials for SPME is by obtaining the partition coefficients for the overall group of studied analytes. The partition coefficient (K_{fs}) values of the studied analytes from deionized water to the different coating materials can be calculated according to Eq. (1) [34]:

$$K_{fs} = \frac{V_s}{V_f(n_0/n_f - 1)} \quad (1)$$

where n_0 is the initial amount of analyte in the sample, n_f the amount of analyte on the fiber after equilibrium, V_s the sample volume, and V_f the fiber coating volume.

In the determination of partition coefficients for this study, the sample volume (V_s) was 20 mL; the initial amount of analytes in the vial (n_0) was considered at two levels: 5 and 20 μg L^{-1} (100 and 400 ng, respectively); and the coating volumes (V_f) were 0.500 μL for the PA 85 μm [35], 0.125 μL for the PDMS 30 μm [35], and estimated to be ~0.094 μL for the benzyl functionalized poly(VBHDIm$^+$NTf$_2^-$) PIL ~12 μm [24]. The n_0 values were selected in an attempt to include the concentration window of the calibrations. The n_f values, corresponding to the n_0 values selected, were directly determined by the calibrations included in Table S-1 in the Supplementary Material. The K_{fs} values were therefore determined in the traditional way of calculating the detector response (FID) of the analytes through on-column injection of standard solutions in cyclohexane followed by comparison with the SPME signal. The obtained partition coefficients are shown in Table 3 together with literature values. We want to emphasize at this point that the partition coefficients obtained in this work are only approximate values as we are not working under equilibration conditions and the n_f values are only estimated by an external calibration method. In addition, the obtained volume of the PIL coating is only an approximation. Accurate methods to determine K_{fs} data should keep the freely dissolved analyte concentration constant during the entire procedure and avoid the introduction of any organic solvent [35]. Nevertheless, the utilized approximation is quite acceptable if comparing the obtained values for PDMS 30 μm with literature values for PDMS 7 and 100 μm (Table 3). The comparison of literature values for the PA fiber is still acceptable but more deviations are observed compared to that of the PDMS coating.

The obtained correlation of log K_{fs} values with the corresponding log octanol–water partition coefficients (see Table 3) presented R values of 0.83 for PDMS 30 μm, 0.45 for PA 85 μm, and 0.60 for for the benzyl functionalized poly(VBHDIm$^+$NTf$_2^-$) PIL ~12 μm. Good correlations coefficients for PDMS and octanol–water partition coefficients have been described if the studied analytes do not have high molecular masses [40]. In fact, there is a general agreement that PDMS fiber distribution coefficients in water depend closely on the analyte hydrophobicity. Given the observed correlations for PA and the functionalized poly(VBHDIm$^+$NTf$_2^-$) PIL, it seems that other extraction mechanisms other than only hydrophobic interactions are taking place with these coating materials. Nevertheless, this is only a mere observation considering the small amount of data included for these correlations.

The log K_{fs} values for alkylphenols and parabens to the functionalized poly(VBHDIm$^+$NTf$_2^-$) PIL are reported for the first time (Table 3). For alkylphenols, they oscillate between 2.69 for *t*-BP to 4.18 for NP. For parabens, log K_{fs} values range from 3.26 for BuP to 3.96 for BzP. The log K_{fs} values reported here for PAHs are also in agreement with previous reported values for the poly(VBHDIm$^+$NTf$_2^-$) PIL [24]. In any case, the partition coefficient values for the studied analytes are always higher for the poly(VBHDIm$^+$NTf$_2^-$) PIL SPME fiber than for PDMS or PA fiber materials, without excluding any analyte. This points out once again the superior performance of this new material for the extraction of the selected group of endocrine disrupting chemicals. The affinity of the PIL material follows, in general, the order: PAHs > alkylphenols > parabens, but the differences are not sig-

Table 4
Relative recovery and precision obtained with the Poly(VBHDIm$^+$NTf$_2^-$) fiber and commercial coatings for deionized waters spiked.

Analyte	PDMS 30 μm		PA 85 μm		Poly(VBHDIm$^+$NTf$_2^-$) ~12 μm			
	Spiked: 5 ng mL^{-1}		Spiked: 5 ng mL^{-1}		Spiked: 5 ng mL^{-1}		Spiked: 1 ng mL^{-1}	
	RR[a] (%)	RSD[b] (%)	RR[a] (%)	RSD[b] (%)	RR[a] (%)	RSD[b] (%)	RR[a] (%)	RSD[b] (%)
N	129	11	88.2	5.2	105	3.4	105	12
t-BP	–	–	89.2	7.3	103	8.2	–	–
Ace	107	1.1	95.9	4.9	98.2	13	109	7.6
t-OP	105	1.6	97.6	7.8	99.9	6.2	104	7.8
BuP	–	–	–	–	89.5	14	–	–
OP	94.4	1.8	98.0	12	101	3.3	90.7	13
Phe	106	3.9	98.4	9.3	95.1	0.9	84.6	13
A	130	4.1	100	18	99.0	3.5	–	–
4-CP	–[c]	–[c]	92.4	14	104	3.3	96.3	10
NP	82.6	3.9	84.8	18	95.9	2.9	98.4	13
9-MeA	101	4.1	93.8	8.6	106	16	93.3	6.8
Ft	107	2.7	97.5	21	95.7	1.0	83.5	6.5
BzP	–	–	–	–	78.3	15	–	–
BPA	–	–	97.4	5.0	–	–	–	–

[a] Average relative recovery for n = 4 determinations.
[b] Precision for *n* = 4 determinations. –: spiked level below the detection limit.
[c] spiked level below the quantification limit.

nificant. This trend is in agreement with that observed when comparing the normalized sensitivity parameters.

3.4. Extraction efficiency and precision

Given the fact that SPME is not an exhaustive extraction method, the utilization of the relative recovery is an appropriate tool to evaluate the extraction performance. The relative recovery (RR) is obtained from the following equation:

$$RR(\%) = 100\frac{C_{found}}{C_{initial}} \quad (2)$$

where C_{found} is obtained from the SPME-GC-FID calibration method and $C_{initial}$ is the spiked concentration. The relative recoveries and precision of the functionalized PIL fiber was calculated by spiking a series of deionized water samples and drinking bottled waters at different levels of concentration, but at low levels in both cases: 1 and 5 ng mL^{-1}. Drinking bottled waters were first analyzed to verify the absence of the studied EDCs. As a comparison, PDMS 30 μm and PA 85 μm were also used with the same waters at the spiked level of 5 ng mL^{-1} (a lower spiked level was not adequate for PA and PDMS for the majority of EDCs studied). The obtained results with deionized waters and drinking bottled waters are shown in Table 4 and in Table 5, respectively.

The obtained relative recoveries using the functionalized PIL fiber with deionized waters varied from 78.3 to 106% for a spiked level of 5 ng mL^{-1}, and from 83.5 to 109% for a spiked level of 1 ng mL^{-1}. For drinking bottled waters, relative recoveries varied from 71.0 to 103% (spiked level of 5 ng mL^{-1}) and from 64.4 to 106% (spiked level of 1 ng mL^{-1}). These relative recoveries, with average values of 96.1 and 97.7% for deionized waters (spiked levels of 1 and 5 ng mL^{-1}, respectively), and of 76.7 and 91.6% for drinking bottled waters (spiked levels of 1 and 5 ng mL^{-1}, respectively), are in agreement with the literature values for new SPME materials when analyzing waters [11,18,41]. As expected, relatively lower recovery values are obtained with drinking waters than with deionized water (slight matrix effect). Average relative recoveries for PDMS oscillate from 107 to 88.0% for deionized and drinking bottled waters, respectively. For the PA fiber, they oscillate between 94.4 and 85.3%. Nevertheless, a higher number of analytes can be extracted from waters when using the functionalized PIL fiber than the commercial coatings.

Intermediate precision of the method with deionized waters presented RSD values ranging from 6.5 to 13% at the spiked level of

Table 5
Relative recovery and precision obtained with the Poly(VBHDIm$^+$NTf$_2^-$) fiber and commercial coatings for drinking bottled waters spiked.

Analyte	PDMS 30 μm		PA 85 μm		Poly(VBHDIm$^+$NTf$_2^-$) ~12 μm			
	Spiked: 5 ng mL^{-1}		Spiked: 5 ng mL^{-1}		Spiked: 5 ng mL^{-1}		Spiked: 1 ng mL^{-1}	
	RR[a] (%)	RSD[b] (%)	RR[a] (%)	RSD[b] (%)	RR[a] (%)	RSD[b] (%)	RR[a] (%)	RSD[b] (%)
N	90.6	14	85.5	4.6	95.1	4.2	64.4	6.7
t-BP	–	–	84.6	1.9	87.0	3.7	–	–
Ace	86.6	11	94.1	6.9	80.4	20	106	14
t-OP	89.4	8.7	93.4	7.7	97.8	22	96.3	13
BuP	–	–	–	–	84.7	4.4	–	–
OP	78.1	11	80.7	8.3	97.0	14	69.6	15
Phe	85.2	6.4	94.4	4.8	94.9	14	67.8	5.1
A	96.5	6.3	88.1	4.1	93.4	16	–	–
4-CP	–[c]	–[c]	85.9	13	103	5.8	69.6	9.2
NP	67.7	9.3	68.8	14	95.0	20	66.5	8.9
9-MeA	79.4	4.2	83.7	1.9	94.9	12	73.3	14
Ft	119	3.7	73.2	7.2	96.6	14	76.4	7.6
BzP	–	–	–	–	71.0	20	–	–
BPA	–	–	91	7.2	–	–	–	–

[a] Average relative recovery for *n* = 4 determinations.
[b] Precision for *n* = 4 determinations. –: spiked level below the detection limit.
[c] Spiked level below the quantification limit.

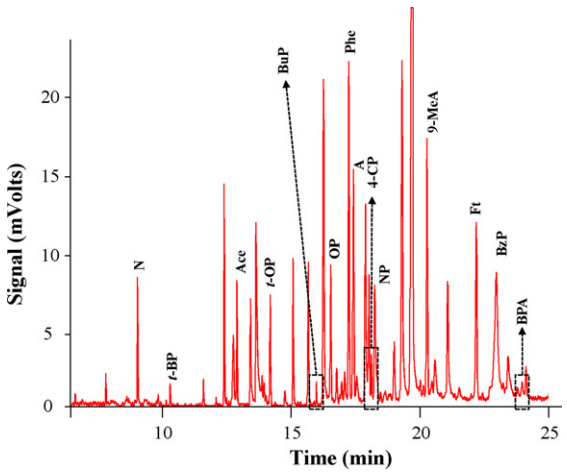

Fig. 3. Chromatogram obtained using the functionalized poly(VBHDIm$^+$NTf$_2^-$) PIL fiber with a drinking bottled water spiked at 10 ng mL^{-1} for BPA and BzP, 5 ng mL^{-1} for *t*-BP and BuP, and 2 ng mL^{-1} for the rest of EDCs studied.

1 ng mL^{-1}, and between 0.9 and 16% at the spiked level of 5 ng mL^{-1}. With drinking bottled waters, RSD values range from 5.1 to 14% at the spiked level of 1 ng mL^{-1}, and from 3.7 to 22% at the spiked level of 5 ng mL^{-1}. The precision values achieved with the functionalized PIL fiber must be highlighted, particularly considering the coating thickness of the fiber. Similar precision values are obtained with the commercial SPME coatings.

Fig. 3 shows a representative chromatogram obtained with the functionalized PIL fiber in direct-immersion SPME for the analytes studied using a drinking bottled water spiked at a level of 10 ng mL^{-1} for BPA and BzP, 5 ng mL^{-1} for *t*-BP and BuP, and 2 ng mL^{-1} for the rest of EDCs. The studied analytes presented retention times with relative standard deviations (RSD) oscillating from 0.05% for anthracene to 1.88% for 4-cumylphenol.

The functionalized PIL fiber was finally used for the analysis of EDCs with non-spiked real water samples. Drinking bottled waters of low salty content were free of the studied EDCs as aforementioned. Drinking bottled waters, which were artificially exposed to the sun as described in the experimental section, were analyzed in order to test the possible presence of alkylphenols. Drinking water samples exposed to the sun in plastic containers of higher thermal resistance were free of alkylphenols. However, several analytes (A, NP and 9-MeA) were extracted by the functionalized PIL fiber when analyzing drinking water samples exposed to the sun in a plastic container of poor thermal resistance. In these samples, A and 9-MeA were detected but not quantified due to the fact that the estimated concentrations were close to their respective the limits of quantification. NP was quantified at 1.5 ± 0.1 ng mL^{-1} (average value ± standard deviation). The same water sample was analyzed using the PA and PDMS fibers, and 9-MeA and NP were also detected but they could not be quantified.

Well water samples were also analyzed with the functionalized PIL fiber and were shown to be practically free of the studied EDCs, except for 4-CP which was detected but not quantified.

Swimming pool waters were analyzed as described in the experimental section and were found to be free of parabens. Simulated contaminated swimming pool water was prepared according to the experimental section conditions and analyzed with the studied fibers. The PIL fiber determined BuP, NP and BzP in the diluted swimming pool sample at concentrations (average value ± standard deviation) of 29.1 ± 1.3, 16.0 ± 3.2, and 42.9 ± 6.4, respectively. The same diluted swimming pool water sample was analyzed with PA and PDMS coatings. The PA fiber determined NP and BzP at concentrations of 19.3 ± 3.5 and 61.5 ± 3.1 ng mL^{-1}, respectively. The concentration of BuP was below the detection limit for the PA fiber. The PDMS fiber determined BuP, NP and BzP at concentrations of 25.7 ± 1.8, 21.1 ± 0.8, and 49.8 ± 3.5 ng mL^{-1}, respectively. It can be observed that the PIL fiber is adequate to determine these contaminants in water, with adequate analytical performance as the commercial fibers. It must be noted that the concentration of these contaminants in the simulated swimming pool water sample (non-diluted) was twenty times higher.

During the development of this study, it was observed that the functionalized PIL sorbent coating begins to discolor (turning clear brown) after ~5 extractions, but does not lose its extraction capabilities as observed with a non-functionalized PIL coating [23]. The performance of the PIL fiber was still acceptable after 70 extractions in direct-immersion mode, with RSD values lower than 22%. On-going experiments are being conducted to further characterize this benzyl-functionalized poly(VBHDIm$^+$NTf$_2^-$) PIL coating. As a preliminary study, the thermal gravimetric analysis (TGA) of the poly(VBHDIm$^+$NTf$_2^-$) PIL has been carried out to determine its thermal stability. The obtained results at two different heating ramps are included as Figure S-1 in the Supplementary Material. In any case, it can be observed that this coating is very stable up to about 350–365 °C. At the working temperature of the present study, 250 °C, the poly(VBHDIm$^+$NTf$_2^-$) PIL coating is quite stable. Nevertheless, higher temperatures are also adequate and even recommendable for future works with this coating.

4. Conclusions

The newly developed benzyl-functionalized poly(VBHDIm$^+$NTf$_2^-$) PIL coating has proved to be a successful material to perform direct immersion SPME extractions from real waters for polycyclic aromatic hydrocarbons, alkylphenols and parabens. The functionalized PIL material demonstrated superior performance compared to the PA 85 μm and PDMS 30 μm commercial fibers, in spite of its lower coating thickness (~12 μm). The utilization of the poly(VBHDIm$^+$NTf$_2^-$) PIL coating with real water samples is characterized with average relative recoveries between 96.1 and 97.7% for deionized waters (spiked levels of 1 and 5 ng·mL^{-1}, respectively), and between 76.7 and 91.6% for drinking bottled waters (spiked levels of 1 and 5 ng·mL^{-1}), The precision (%RSD) was found to be lower than 16% for deionized waters and lower than 22% for drinking bottled waters. The PIL material was stable after 70 extractions in direct immersion mode with real samples.

The proposed normalized sensitivity parameter has also shown to be a useful tool to perform a qualitative comparison among diffrent fiber materials, independent of their coating thicknesses. Furthermore, the partition coefficients values obtained for the group of EDCs and the fiber materials (PA, PDMS and PIL) have also highlighted superior extraction capability of the functionalized poly(VBHDIm$^+$NTf$_2^-$) PIL coating for the group of fourteen EDCs studied.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chroma.2010.09.016.

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